APPENDIX C Hot Gas Desulfurization with Sulfur Recovery: Proceedings of the Advanced Coal-Based Power and Environmental Systems '97 Conference

Hot-Gas Desulfurization with Sulfur Recovery

Jeffrey W. Portzer (jwp@rti.org; 919-541-8025)
Ashok S. Damle (adamle@rti.org; 919-541-6146)
Santosh K. Gangwal (skg@rti.org; 919-541-8033)
Research Triangle Institute
3040 Cornwallis Road
Research Triangle Park, NC 27709

Introduction

Advanced integrated gasification combined cycle (IGCC) power plants require advanced particle filters and hot-gas desulfurization (HGD) following gasification in order to achieve high thermal efficiency. The Federal Energy Technology Center's (FETC's) research program is focusing on the development of regenerable metal oxide sorbents, such as zinc titanate, for efficient removal of hydrogen sulfide (H_2S) from coal gas. During regeneration of these sorbents, there is the opportunity to produce elemental sulfur (S_x) as a valuable byproduct. Currently, the leading technologies use air or dilute-air regeneration of the sorbents to produce a tail gas containing mostly nitrogen plus 2 to 14 vol% sulfur dioxide (SO_2). This tail gas must be treated further to avoid release of SO_2. One option is the catalytic reduction of SO_2 with a coal gas slipstream using the Direct Sulfur Recovery Process (DSRP), a leading first- generation technology to produce elemental sulfur.

The FETC is sponsoring the development of the DSRP (Dorchak et al., 1991; Portzer and Gangwal, 1995), a single-step catalytic process that uses the reducing components (H_2 and CO) of coal gas to directly and efficiently reduce the SO_2 to elemental sulfur:

$$SO_2 + 2H_2 \text{ (or } 2CO) \rightarrow 2H_2O \text{ (or } 2CO_2) + 1/nS_n \, .$$

In the DSRP, for every mole of SO_2, two moles of reducing gas are used, leading to a small but noticeable consumption of coal gas. Although the DSRP continues to show promise and has undergone field testing at gasifier sites (Portzer et al., 1996), alternative or improved processing is still possible.

Objective

The objective of this study is to develop a second generation HGD process that regenerates the sulfided sorbent directly to elemental sulfur using SO_2, with minimal consumption of coal gas. The goal is to have better overall economics than DSRP when integrated with the overall IGCC system.

Approach

Direct production of elemental sulfur during sorbent regeneration, using SO_2 as an oxidizing agent, was chosen as the approach for development of the second-generation HGD process

(Gangwal et al., 1995, 1996). SO_2 regeneration involves the reaction of nearly pure SO_2 with sulfided sorbent at elevated temperature and pressure. Under these conditions, elemental sulfur is the only product predicted from thermodynamics. Based on a theoretical evaluation of a number of potential sorbent candidates, iron- and zinc-based regenerable sorbents were chosen for experimental evaluation in this study (Gangwal et al., 1995). Iron is considered the most promising candidate based on a combination of factors—desulfurization efficiency, SO_2 regenerability, cost, and knowledge base. Zinc is a leading candidate, primarily in combination with iron, due to its excellent desulfurization efficiency, its extensive knowledge base, and its low cost. Although zinc sulfide (ZnS) shows essentially no SO_2 regenerability at temperatures of interest, zinc can act as a polishing agent when combined with iron to remove H_2S down to very low levels. Advantageously the ZnS can be regenerated using air to produce the SO_2 needed for regeneration of the iron sulfide (FeS). The key chemical reactions of interest are as follows:

1. Sulfidation

$$Fe_2O_3 + 2H_2S + H_2 \rightarrow 2FeS + 3H_2O$$

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

2. SO_2 regeneration

$$4\ FeS + 3SO_2 \rightarrow 2Fe_2O_3 + 7/2\ S_2$$

3. O_2 regeneration

$$2FeS + 7/2\ O_2 \rightarrow Fe_2O_3 + 2SO_2$$

$$ZnS + 3/2\ O_2 \rightarrow ZnO + SO_2\ .$$

The feasibility of SO_2 regeneration of iron- and zinc-based sorbents was demonstrated using high-pressure thermogravimetric analysis (TGA) and high-pressure, small-scale lab reactors. A number of sorbents were prepared and tested at the bench scale over multiple cycles. Attrition-resistant zinc and iron formulations were developed, and the most promising material was tested for 50 cycles of alternating sorption and regeneration. Computer flowsheet simulation of a conceptual process design is proceeding in preparation for a preliminary economic evaluation of a commercial embodiment (nominal 250 MWe [net] scale plant).

Project Description

Summary of Previous Experiments

In previously reported work, microreactor-scale experiments were conducted at elevated pressure (10 atm) and temperatures up to 750 °C to test the concept of SO_2 regeneration. Concentrations up to 15 vol% SO_2 were used (Gangwal et al., 1995). An iron-zinc sorbent designated R-5 showed promising results, with solid sulfur being recovered from the lab-scale system or condenser. Following this initial success, four different iron- and zinc-based fluidizable sorbents,

manufactured by two different methods, were chosen for scale-up, These were prepared in larger batches (350 g) suitable for fluidized-bed testing.

An existing 3-in. diameter, high-temperature, high-pressure (HTHP), bench-scale, fluidized-bed reactor system was modified to enable SO_2 regeneration as well as air regeneration, plus elemental sulfur recovery. The reactor system is described by Gangwal et al. (1996) and was operated for the multicycle HTHP testing of the iron-zinc sorbents. For each test cycle (conducted at 20 atm), sulfidation of the sorbent at 450 °C was accomplished using a synthetic coal-gas mixture containing 3,000 ppm of H_2S. Figure 1 shows the several combinations of conditions that were used for regeneration of each cycle. The SO_2 regeneration was accomplished by vaporizing liquid SO_2 into a heated nitrogen stream (at 450 to 630 °C). Concentrations up to 75 vol% were used. Oxygen regeneration was typically conducted following the SO_2 regeneration step. The procedure was convenient from the experimental standpoint, as the instrumentation for the evolved SO_2 of the O_2 regeneration step gave an independent measure of the amount of sulfur still in the sorbent following SO_2 regeneration. In addition, some O_2 regeneration half-cycles were run with the air mixed with the N_2-SO_2 stream to simulate the O_2 + SO_2 regeneration. These conditions are present in the conceptualized three-reactor process described later in which SO_2 regeneration of the iron component of the sorbent **is** followed by O_2 regeneration of the zinc component using a single recirculation loop of regeneration gas consisting mainly of SO_2.

50-Cycle Bench-Scale Testing

One highly attrition-resistant formulation was selected for a long-duration, 50-cycle test. Table 1 shows the conditions used for that test.

In the HTHP testing, the candidate sorbent demonstrated H_2S removal down to the 50 to 100 ppm levels with stable desulfurization activity over the duration. Attrition resistance of the sorbent is excellent. Other characterizations show a small loss of surface area and pore volume after 50 cycles of testing.

In the 50-cycle test campaign, considerable effort was expended to verify the degree of SO_2 regeneration to elemental sulfur that actually occurred. The amount of sorbent regeneration occurring during the SO_2 regeneration portion of the cycles was typically determined by mass in balance based on gas analyses during the sulfidation step and the air-regeneration step. The amount of sulfur loaded on the sorbent in each cycle was calculated by integrating the metered gas flows of H_2S into the reactor, minus the outlet concentration as determined by gas

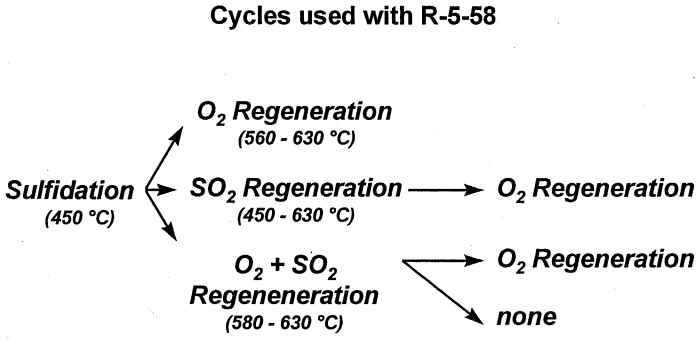

Figure 1. 50-cycle bench-scale test.

Table 1. 50-Cycle Test Conditions

Pressure:	20 atm	Coal gas composition (vol%)	
Flow rate:	36 slpm	CO:	15
Sorbent amount:	250 g	H_2:	10
Temperature (°C)		N_2:	55
Sulfidation:	450	CO_2:	10
SO_2 regeneration:	450–630	H_2O:	10
Dilute air regeneration:	560–630	H_2S	3,000 ppm
SO_2 regeneration gas (vol%)		Oxidizing gas (vol%)	
SO_2	25–75	O_2	2
N_2	balance	N_2	98

chromatography and continuous H_2S analyzer. During SO_2 regeneration, no reliable gas analysis was possible, due to the high concentration of SO_2. During O_2 (dilute air) regeneration, the evolved SO_2 was metered using a continuous analyzer, giving a measure of the amount of absorbed sulfur from the sulfidation step that was not regenerated by the SO_2. The difference (after discounting any obvious experimental error) represents the production of elemental sulfur.

The weight of elemental sulfur recovered in a downstream trap confirmed the degree of SO_2 regeneration. In the earlier experiments, elemental sulfur was produced, but no material balance was obtained probably because of poor collection efficiency. With some redesign of the outlet piping and a sulfur trap design, more reliable sulfur recovery was obtained for the later runs in the 50-cycle test.

Process Conceptualization and Simulation

A three-reactor, fluidized-bed HGD process involving sulfidation (absorption), SO_2 regeneration, and O_2/SO_2 regeneration was conceptualized for direct elemental sulfur production (see Figure 2). In this Advanced Hot Gas Desulfurization (AdvHGD) process, the two stages of regeneration could likely be contained in a single reactor vessel. The desulfurization of the coal gas (sulfidation of the sorbent) takes place at about 450 °C at the pressure of the coal gas (typically 20 atm). The sulfided sorbent is heated to 600 °C using waste heat from the regenerated sorbent and enters Stage 2 of the regenerator to contact the recirculating SO_2 gas stream. The elemental sulfur formed exits in the gaseous state. The partially regenerated sorbent then passes into Stage 1 of the regenerator where oxygen will be added to the regeneration gas. In a fully heat-integrated process, the energy from the exothermic O_2 regeneration will be used to drive the endothermic SO_2 regeneration. The regenerated sorbent is then cooled and recirculated to the desulfurization reactor.

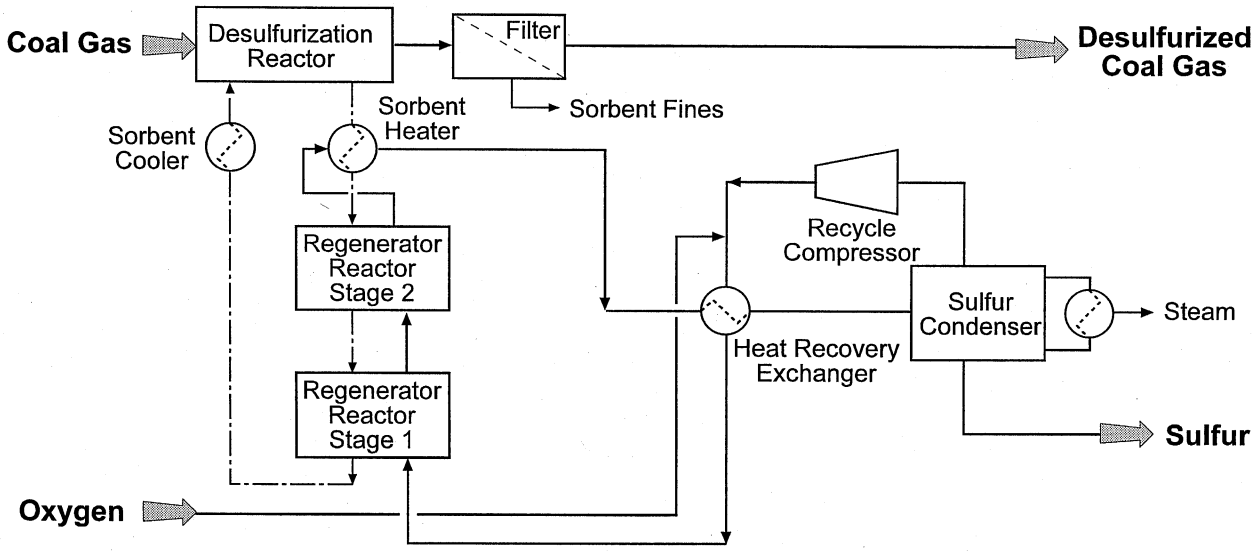

Figure 2. Advanced hot gas desulfurization.

The recirculation loop for the regeneration gas functions as follows: the regeneration off-gas exiting from Stage 2 is cooled to condense out the sulfur, which is removed as a molten product. The exit gas from the sulfur condenser is then compressed slightly (to recover the pressure drop losses from recirculation) and is reheated by countercurrent exchange with the hot regeneration off-gas. With control of the ratio of iron and zinc in the sorbent, and by balancing the amount of oxygen supplied to Stage 1 with the amount of elemental sulfur that is actually being produced, the SO_2 material balance of the recirculation loop can be maintained. For startup purposes, an external supply of liquid SO_2 is required to charge the recirculation loop.

Because of the need for transfer of sorbent from the sulfidation reactor to the multistage regenerator, fluidized-bed reactors are envisioned. However, a detailed configuration has not been proposed. Heat transfer from fluidized-bed reactors is also expected to be more straightforward than with fixed beds. The recirculation rate of the SO_2 stream is fixed by the gas velocity needed in the regeneration reactors for proper fluidization of the sorbent. However, the production of sulfur is a function of the sorbent circulation rate and is thus somewhat independent of the regeneration gas flow rate. It should be noted that the concentration of the elemental sulfur in the regeneration loop is dependent on the engineering design of the system; it is not inherent to the chemistry of the regeneration process.

For comparison, Figure 3 presents an HGD process based on using the DSRP to produce elemental sulfur. The sulfidation takes place at about 600 °C and at the pressure of the coal gas (20 atm). The sulfided sorbent passes to the regenerator where it is contacted with preheated, compressed air. The off-gas from the regenerator (ROG), containing approximately 14 vol% SO_2, is the feed to the DSRP reactor. In this reactor, the ROG is contacted with a slipstream of the coal gas to produce a gas stream containing mostly nitrogen plus elemental sulfur. The DSRP reactor

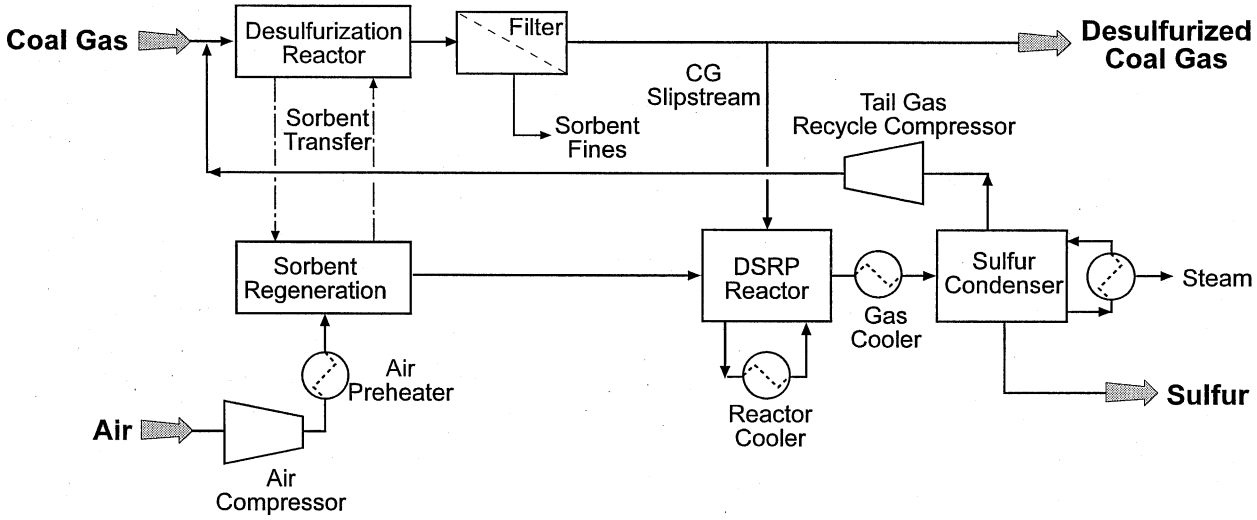

Figure 3. Hot-gas desulfurization with DSRP.

effluent is then cooled to recover the sensible heat, and the sulfur is condensed while producing low-pressure steam. The gas stream from the condenser, DSRP tail gas, contains some sulfur compounds (H_2S and SO_2). Most likely it cannot be discharged, so in this process conceptualization, the tail gas is recompressed slightly and recycled to the desulfurizer. An economic analysis comparing the conceptualized AdvHGD process with this conceptualized DSRP-based scheme is under way.

Results/Accomplishments

Experimental

In the HTHP testing, sorbent R-5-58 demonstrated H_2S removal down to the 50 to 100 ppm levels with stable desulfurization activity over the duration. Figure 4 shows the sulfidation breakthrough curves for selected cycles covering the full test period. Interestingly, the sulfidation performance, as measured by time to breakthrough, improved considerably after the first few cycles. Figure 5 plots the steady-state concentration of H_2S in the sulfidation reactor outlet. One can see that in several cycles the concentration was <50 ppm and that, in general, the concentration was 100 ppm or better. However, a successful commercial embodiment would require consistent removal of H_2S to 20 ppm or less. Additional sorbent development is required to achieve this level of performance while maintaining the ability to be regenerated with SO_2.

Based on the gas analysis "difference" methodology described above, the SO_2 regeneration step accounted for as much as 55 to 70 percent of the total regeneration of the sorbent. This compares to a theoretical limit of approximately 80 percent, assuming complete regeneration by SO_2 of the iron component. Many of the cycles had lower percent regeneration because the test conditions were intentionally set at nonoptimal levels.

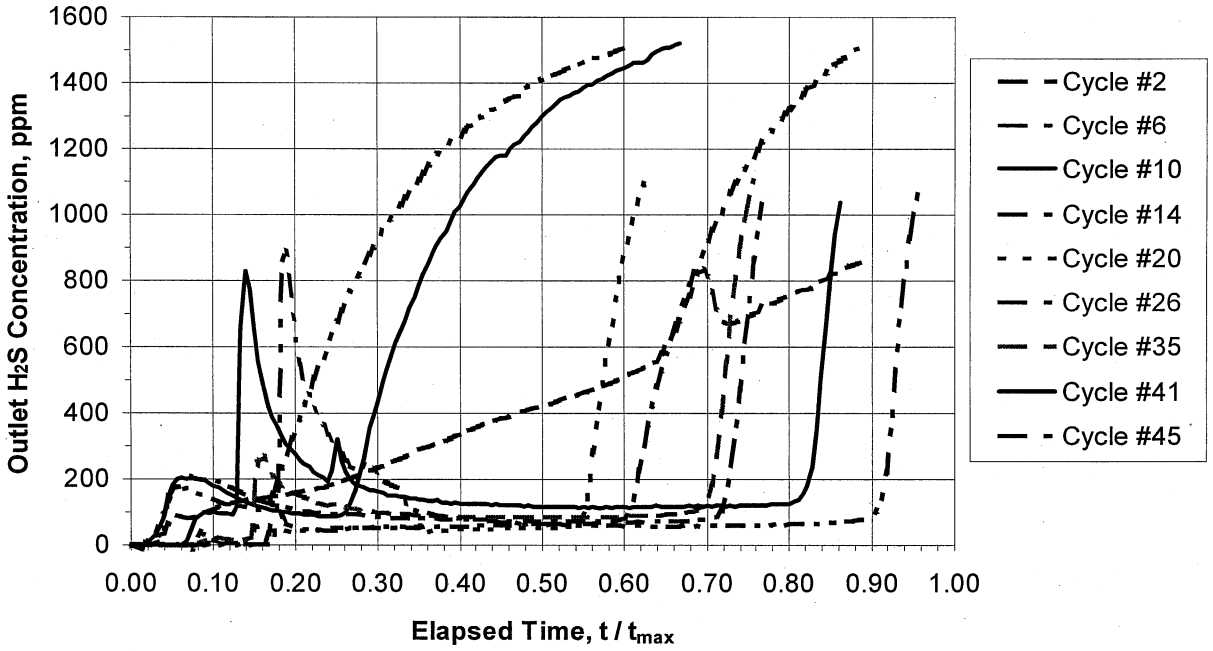

Figure 4. Sulfidation breakthrough curves.

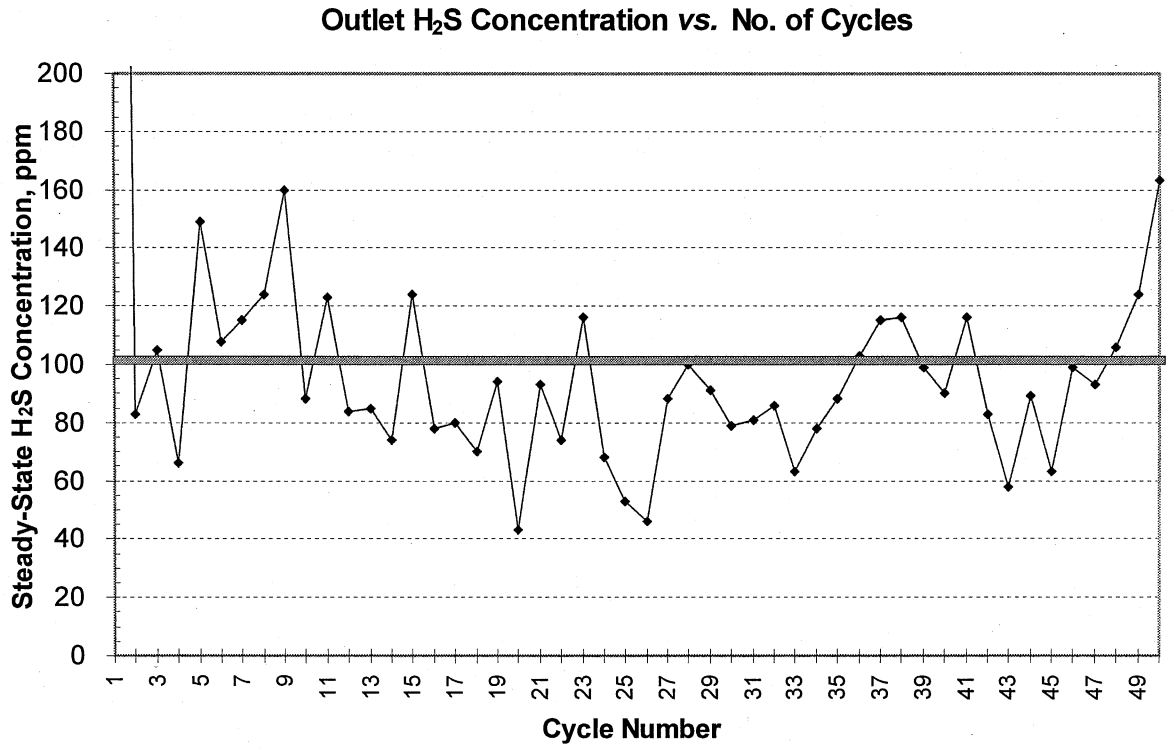

Figure 5. Sulfidation activity—sorbent R-5-58.

Reasonable sulfur balances were obtained by comparing the gas compositions and flow rates with the solid sulfur recovered. Figure 6 shows the total regeneration of the sorbent (SO_2 regeneration calculated by sulfur recovery, and O_2 regeneration calculated by gas analysis) for those cycles for which complete data are available. In most cases, the resulting value is approximately 100 percent of the sulfur that was loaded, confirming that the experimental protocol is yielding a sulfur balance.

In addition to durability testing of the sorbent, one main objective of the 50-cycle test program was to determine the effects of three primary variables: SO_2 concentration in the regeneration gas, temperature of the regeneration gas, and duration of the SO_2-regeneration half-cycle. Statistical analysis was applied to the results to generate an empirical second-order polynomial fit. The statistical model shows that duration of regeneration is the most important variable, percent regeneration is directly proportional to temperature, and SO_2 concentration has a small effect. Figure 7 shows a plot of the calculated percent regeneration (model values) as a function of duration for one SO_2 concentration value. The actual data points are also shown for comparison. Because an empirical model based on a small data set was used, there are obvious limitations to its application. However, the model is useful for guiding thinking on the process simulation and economic analysis.

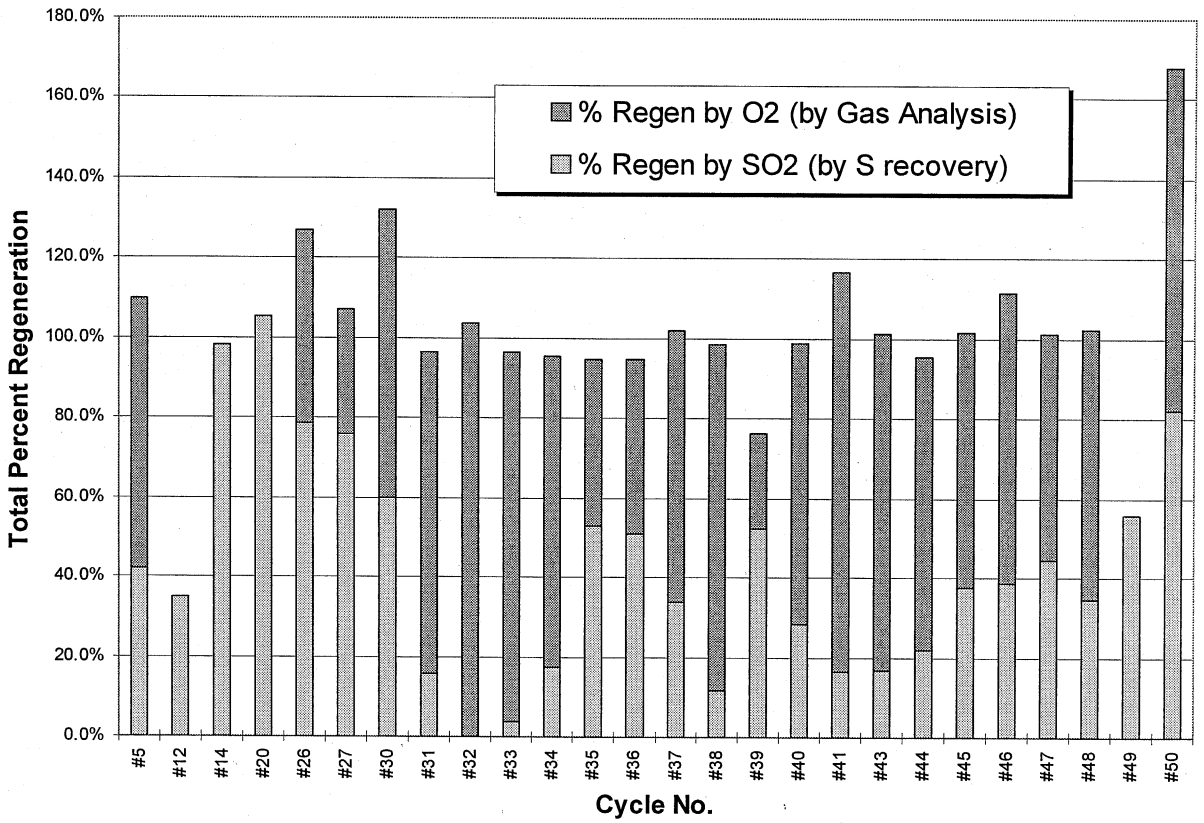

Figure 6. Sulfur balance.

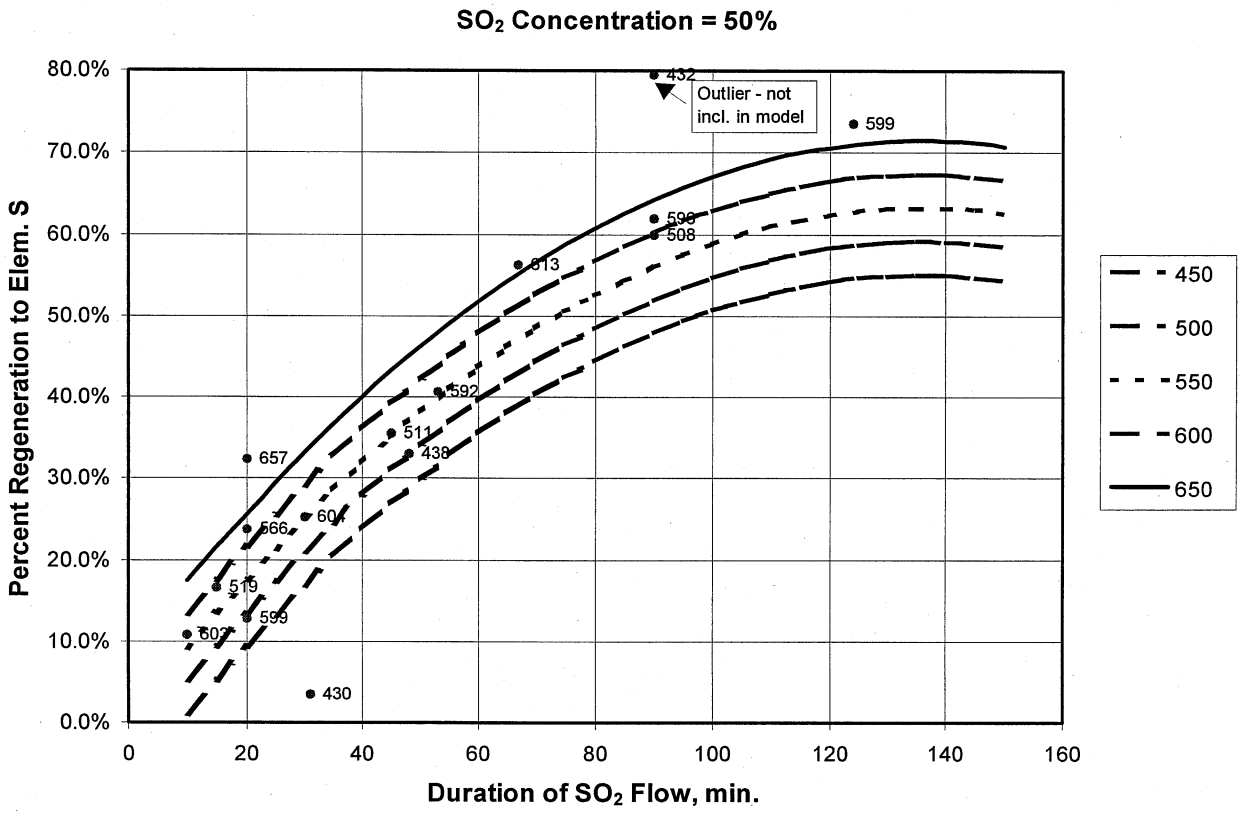

Figure 7. Statistical model of R-5-58 regeneration.

Characterization tests were run on the sorbent before and after the 50-cycle test run; Table 2 reports the results. The attrition losses were very low, as expected for this highly attrition-resistant formulation; the values are comparable to those for fluid catalytic cracking (FCC) catalysts. There was little change in the BET surface area and mercury pore volume measurements, attesting to the relative ruggedness of the candidate sorbent.

Table 2. Characterization of Sorbent R-5-58

	Fresh (%)	50-Cycle used (%)
BET surface area (m^2/g)	100	94
Hg pore volume (mL/g)	100	89
Attrition test:		
5-h loss	3.6	1.2
20-h loss	6.8	5.0

Process Simulation/Economic Analysis

The nominal plant size of 250 MW_e (net) was chosen as the design basis for the process simulations (material and energy balances) that are being conducted using the ASPEN PLUS software. Table 3 lists the flow rate, composition, and conditions of the clean coal gas exiting the simulations of both processes; the basis is an O_2-blown gasifier. One advantage of the ASPEN PLUS simulation software is the large built-in physical property database. The heat capacities, heats of reaction, reaction equilibrium based on Gibbs free energy minimization, and vapor-liquid equilibrium data based on Peng-Robinson

equation-of-state allowed for accurate accounting of the heat effects and phase changes. Selection of appropriate tear streams and convergence criteria resulted in consistently converged material and energy balances for a given set of conditions.

Table 3. Clean Coal Gas

Composition (vol %)	
H_2	27
CO	35.5
CO_2	12.5
H_2O	19
N_2	6
H_2S	20 ppm
Flow rate (lb/h)	450,000
Pressure (psia)	275
Temperature (°C)	460

The AdvHGD process scheme schematically shown in Figure 2 was modeled by the flow sheet simulator using appropriate fluidized-bed reactors, gas/solid phase separators, sulfur condenser, and heat exchanger blocks. The assumptions involved in the AdvHGD simulation have been described above. Pure O_2 is assumed to be available for adding to the recycle SO_2 stream to balance the sulfur being removed continuously as a liquid product. The simulation used the reactions presented above in the Approach section. The simulation further assumed that the consumption of SO_2 in Stage 2 was balanced by that produced in the air regeneration stage with no net generation of SO_2 within the system. As Figure 2 indicates, heat is released during desulfurization, cooling of the hot regenerated sorbent, and sulfur condensation. This available heat is assumed to produce high pressure (850 psig) steam from the high-temperature sources, and low-pressure steam from the sulfur condenser. In addition, the heat content of the regenerator off-gas is used to preheat the sulfided sorbent and the SO_2 recycle stream for in-plant heat integration.

The DSRP-based HGD simulated by ASPEN PLUS is shown schematically in Figure 3. The simulation assumed a fluidized-bed desulfurizer with zinc-based sorbent, fluidized-bed/transport reactor for air regeneration, and a fluidized-bed/transport reactor for DSRP reaction. A small slipstream of clean coal gas is used in the DSRP reactor for direct conversion of SO_2 to sulfur. This slipstream can essentially be viewed as a penalty experienced by the DSRP approach when compared with the AdvHGD scheme. Consequently, the DSRP releases considerably more heat in the air regenerator, DSRP reactor, and condenser units. The ASPEN simulation again assumed that this heat would be used to produce high-pressure stream (and low-pressure steam from the sulfur condenser). In addition, gas-gas heat exchangers are employed for in-plant heat integration similar to the AdvHGD simulation.

A preliminary comparison of the two process schemes, based on the ASPEN PLUS simulations, suggests the following: The DSRP uses approximately 2.2 percent more raw coal gas (about 10,000 lb/h) to produce an equivalent amount of clean fuel gas. As a consequence, the DSRP route releases about 27 million Btu/h more heat (potentially as high-pressure steam) than the AdvHGD route. The clean fuel gas from the AdvHGD route is more concentrated because it is not diluted with nitrogen from the air regeneration, but the process heat integration is more complicated with the AdvHGD route.

Application/Benefits

An AdvHGD process, such as that conceptualized in Figure 2, that results in the direct production of elemental sulfur during regeneration has potential advantages over existing process options if it can be economically integrated with IGCC. The existing process options are production of undesirable calcium waste, production of sulfuric acid, or production of elemental sulfur using DSRP. Production of sulfuric acid is attractive if a market is readily available nearby. It may be difficult to find several such sites for IGCC plants. Elemental sulfur is the preferred option, and DSRP is a highly efficient process but, as discussed earlier, requires the use of a small portion of the coal gas that results in an energy penalty to the power plant. Application of a reactive and attrition-resistant sorbent such as R-5-58 to an IGCC with the capability to undergo direct SO_2 regeneration to elemental sulfur is a process option that needs to be developed further.

Future Activities

The simulation work will continue; the converged heat and mass balances by ASPEN PLUS will provide the input to the planned economic analysis: preliminary equipment sizing, preliminary capital costs, and operating cost comparisons.

Additional sorbent modification and testing to demonstrate H_2S control to under 20 ppmv in the AdvHGD process is planned for FY97-98. Bench-scale testing with actual coal gas using the RTI/FETC Mobile Laboratory at the Power Systems Development Facility (PSDF) is planned for FY98-99.

Acknowledgments

This research is sponsored by the U.S. Department of Energy's Federal Energy Technology Center, under Contract No. DE-AC21-94MC31258 with Research Triangle Institute (fax: 919-541-8000). The authors gratefully acknowledge the guidance of the FETC Contracting Officer's Representative, Mr. Thomas P. Dorchak. United Catalysts, Inc. assisted with preparation of iron- and zinc-based sorbents. Mr. Steven C. Kozup, a graduate student at North Carolina State University working under the supervision of Dr. George Roberts on a subcontract with RTI, prepared the ASPEN PLUS process simulations. Texaco is following this project's progress and will review the simulation and economic evaluation. The contract period of performance is from March 21, 1994, to September 30, 1999.

References

Dorchak, T.P., S.K. Gangwal, and W.J. McMichael. 1991. "The Direct Sulfur Recovery Process." *Environmental Progress* 10(2):68.

Gangwal, S.K., B.S. Turk, and R.Gupta. 1995. "Advanced Sulfur Control Concepts." In *Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting*, pp. 622-630, DOE/METC-95/1018, Vol. 2, NTIS/DE 95009733. Springfield, VA.

Gangwal, S.K., J.W. Portzer, B.S. Turk, and R.Gupta. 1996. "Advanced Sulfur Control Processing." In *Proceedings of the Advanced Coal-Fired Systems Review Meeting July 16–19, 1996.* (CD-ROM). U.S. Department of Energy, Morgantown, WV.

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.

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 16–18, 1996*. (CD-ROM). U.S. Department of Energy. Morgantown, WV.

APPENDIX D Advanced Hot Gas Desulfurization Process with Sulfur Recovery: Proceedings of the International Symposium on "Gas Cleaning at High Temperatures", University of Karlsruhe, 1999

Advanced Hot Gas Desulfurization Process with Sulfur Recovery

S.K. Gangwal[1], J.W. Portzer[1], T.P. Dorchak[2], and K. Jothimurugesan[3]

[1]Research Triangle Institute, Research Triangle Park, NC 27709, USA
[2]Department of Energy, Federal Energy Technology Center,
Morgantown, WV 26505, USA
[3]Department of Chemical Engineering, Hampton University,
Hampton, VA 23668, USA

Abstract

Advanced integrated gasification combined cycle (IGCC) power plants employ a hot-gas desulfurization (HGD) process, typically involving a zinc oxide-based sorbent that efficiently removes H_2S from coal gas down to less than 20 ppmv and that can be regenerated using air for multicycle operation. However, an inherent complication in this air-regeneration-based HGD process is the disposal of the problematic dilute SO_2 containing regeneration tail gas. Some H_2S sorbents based on metal oxides other than zinc oxide, such as iron oxide, can be regenerated using SO_2 to produce a desirable elemental sulfur byproduct via the direct reaction of FeS and SO_2 ($2FeS + SO_2 - 2FeO + 3/2\ S_2$). The objective of this study is to develop an advanced hot-gas process (AHGP) that can eliminate the problematic SO_2 tail gas and yield elemental sulfur directly using a sorbent containing a combination of zinc and iron oxides. AHGP uses a two-stage regeneration reactor in which the sulfided sorbent flows down countercurrent to a regenerating gas containing a dilute mixture of O_2 in SO_2. The iron sulfide portion of the sorbent is regenerated by SO_2 in the upper stage whereas the zinc sulfide portion of the sorbent is regenerated using O_2 in the lower stage. The effluent SO_2 and S_2 mixture is cooled to condense elemental sulfur, and the SO_2 is recycled. Following lab-scale feasibility studies of AHGP, a 50-cycle bench-scale test was conducted at high-temperature, high-pressure conditions to demonstrate quantitative elemental sulfur recovery. A field test of the process is currently planned to take place in late 1999. Further work that will be described focuses on sorbent improvements using metallic additives to the zinc-iron sorbent to produce advanced attrition-resistant sorbents that can consistently reduce the H_2S during sulfidation to less than 20 ppmv.

Key words: IGCC, desulfurization, zinc oxide, iron oxide, sorbent, regeneration, sulfur

1. Introduction

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

The HGD process typically uses a regenerable zinc-oxide-based sorbent and is carried out in a two-reactor system consisting of a desulfurizer and an air regenerator:

$$ZnO + H_2S \rightarrow ZnS + H_2O \qquad \text{(desulfurizer)}$$
$$ZnS + (3/2)\, O_2 \rightarrow ZnO + SO_2\,. \qquad \text{(regenerator)}$$

Early developments emphasized fixed bed reactors for HGD. 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). 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.

Air regeneration leads to a problematic SO_2 tail gas that must be disposed. Converting to a salable product—sulfuric acid or elemental sulfur—is an attractive option. Elemental sulfur is particularly attractive because it is the smallest volume sulfur product and because it can be stored easily, transported over long distances, readily disposed, or sold. DSRP, a promising process, is currently in an advanced development stage to treat the SO_2 tail gas (Portzer et al., 1996, 1997). In this process the SO_2 is catalytically reduced to elemental sulfur at the pressure and temperature condition of the tail gas using a slipstream of the fuel gas

$$SO_2 + 2\, H_2 \text{ (or CO)} \rightarrow 1/2\, S_2 + 2\, H_2O \text{ (or } 2\, CO_2)$$

The process has undergone testing with actual coal gas from a gasifier and is being scaled up to a small pilot-scale stage.

The problematic SO_2 tail gas produced by air regeneration not only needs disposal but also consumes 2 mol of valuable reducing components in fuel gas for every mole of sulfur dioxide treated if elemental sulfur is to be produced using DSRP. Novel regeneration processes that could lead to elemental sulfur with limited use of fuel 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 that can remove H_2S to below 20 ppmv and can be regenerated using SO_2, O_2 mixtures to directly produce elemental sulfur. Along similar lines as above, RTI is developing an advanced HGD process (AHGP) that uses a zinc-iron sorbent (Portzer et al., 1997).

2. AHGP Process Concept

AHGP is a second-generation HGD process that regenerates the sulfided sorbent directly to elemental sulfur using SO_2. SO_2 regeneration involves the reaction of nearly pure SO_2 with sulfided sorbent at elevated temperature and pressure. Under these conditions, elemental sulfur is the only product predicted from thermodynamics. Some H_2S sorbents based on metal oxides other than zinc oxide—iron oxide, for example—can be regenerated following sulfidation using SO_2 to directly produce the desirable elemental sulfur byproduct according to the following sulfidation and regeneration reactions:

$$FeO + H_2S \rightarrow FeS + H_2O$$
$$2FeS + SO_2 \rightarrow 2FeO + 3/2\ S_2$$

Based on a theoretical evaluation of a number of potential sorbent candidates, iron- and zinc-based regenerable sorbents were chosen for experimental evaluation (Gangwal et al., 1995). Iron oxide was considered the most promising candidate based on a combination of factors—desulfurization efficiency, SO_2 regenerability, cost, and knowledge base. Zinc oxide is a leading candidate due to its excellent desulfurization efficiency, its extensive knowledge base, and its low cost. Although zinc sulfide (ZnS) shows essentially no SO_2 regenerability at temperatures of interest, zinc oxide can act as a polishing agent when combined with iron oxide to remove H_2S down to very low levels. Advantageously, the ZnS can be regenerated using air to produce the SO_2 needed for regeneration of the iron sulfide (FeS).

3. AHGP Process Description

Based on a feasibility study, initial laboratory testing, and successful bench-scale testing of several sorbent formulations, AHGP was conceptualized as shown in Figure 1. The primary elements of the process are a single

desulfurization reaction stage, but two stages of regeneration: an SO_2 regeneration stage, and an oxygen regeneration stage. The sulfided sorbent flows countercurrently to an internally recirculating regeneration gas (high concentration SO_2). The desulfurization of the coal gas (sulfidation of the sorbent) takes place at about 450°C at the pressure of the coal gas (typically 2.0 MPa) in the desulfurization reactor. This would most likely be a "transport" type fluidized-bed reactor, resulting in a research focus on attrition-resistant sorbents.

The sulfided sorbent enters a multistage reaction vessel to be heated to 600°C using waste heat from the regenerated sorbent. This reactor is envisioned to be a bubbling-type fluidized bed. The heated sorbent passes to Stage 2 of the regenerator to contact the recirculating SO_2 gas stream. The elemental sulfur formed exits in the gaseous state. The partially regenerated sorbent then passes into Stage 1 (the lowest stage) of the regenerator, where oxygen is added to the regeneration gas. In this heat-integrated process, the energy from the exothermic O_2 regeneration is used to drive the endothermic SO_2 regeneration. The regenerated sorbent is then cooled and recirculated to the desulfurization reactor.

The regeneration off-gas exiting from Stage 2 is cooled to condense out the sulfur, which is removed as a molten product. The exit gas from the sulfur condenser is then compressed slightly (to recover the pressure drop losses from recirculation) and is reheated by countercurrent exchange with the hot regeneration off-gas. With control of the ratio of iron and zinc in the sorbent, and by balancing the amount of oxygen supplied to Stage 1 with the amount of elemental sulfur that is actually being produced, the SO_2 material balance of the recirculation loop can be maintained. For startup purposes, an external supply of liquid SO_2 could be used to charge the recirculation loop.

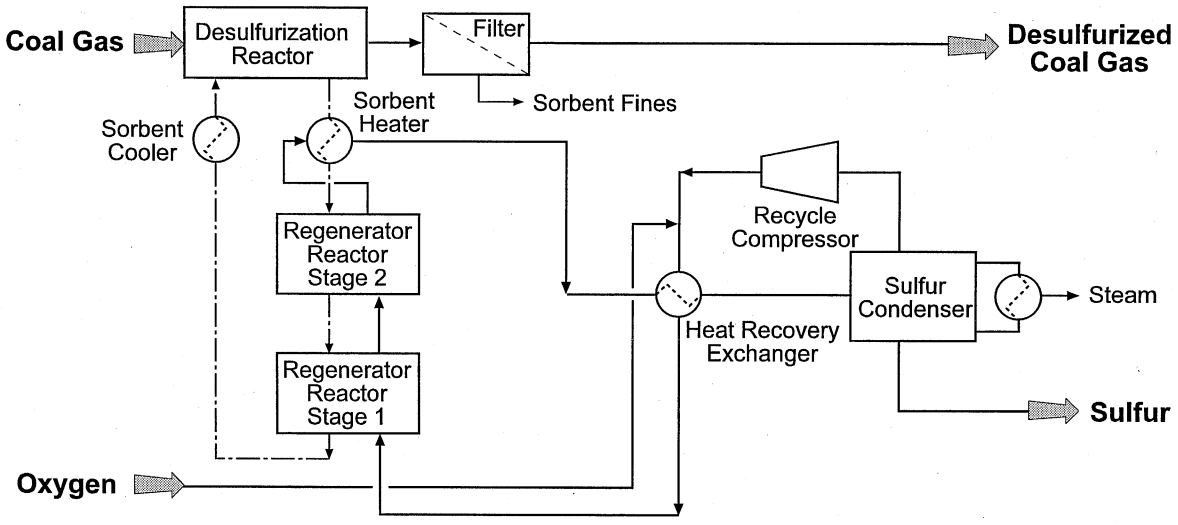

Figure 1. Conceptualized advanced hot-gas process (AHGP).

4. Experimental

a. Lab-scale feasibility studies

Laboratory experiments to test the SO_2 regeneration concept were carried out using a high-pressure thermogravimetric analyzer (TGA) and a high-pressure lab-scale reactor (Gangwal, et al., 1995). The reactor was made of a 1.25-cm stainless steel tube capable of operation at 750°C and 1.5 MPa. Provision was made for sulfiding up to 10 g of sorbent with simulated coal gas and regenerating the sulfided sorbent with up to 15 vol% SO_2. The gas exiting the reactor passed through heated tubing into a 130°C convective oven where a 0.1-m filter was used to collect sulfur. The gas vented through a back pressure regulator.

b. Bench-scale testing (50-cycle test)

An existing 10-cm diameter, high-temperature, high-pressure (HTHP), bench-scale sorbent test reactor system was modified to enable SO_2 regeneration plus elemental sulfur recovery (Figure 2). The reactor could operate in either the fluidized-bed or fixed-bed mode using an internal sorbent cage of up to 7.5 cm inside diameter. The reactor vessel was rated for operation at temperatures up to 800°C and pressures up to 3.0 MPa.

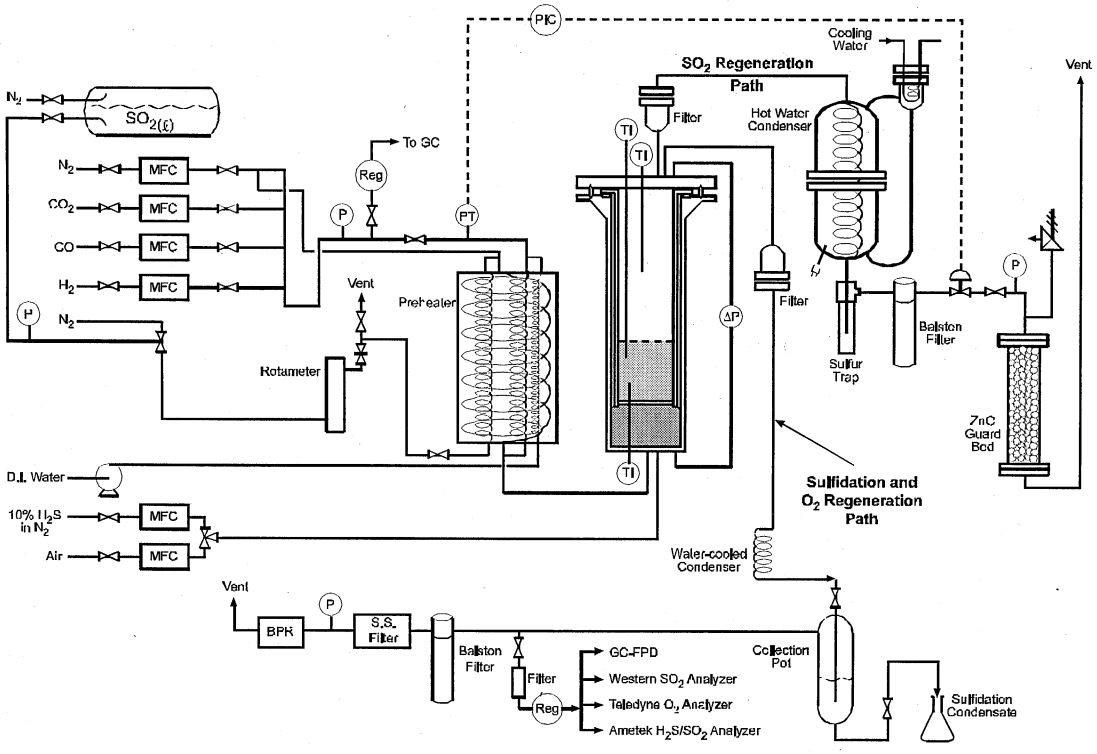

Figure 2. Bench-scale sorbent test facility.

Reactor throughput up to 24 Nm^3/h can be processed, and sorbent volumes up to 1,000 cm^3 could be tested.

The bench-scale test unit was used for screening tests (10 cycles or less) of several fluidized-bed sorbents (Gangwal et al.,1996) and for a long duration test (50 cycles; Portzer et al., 1997) of one highly attrition-resistant formulation. For each test cycle (of the 50-cycle test series conducted at 2.0 MPa), sulfidation of the sorbent at 450°C was accomplished using a synthetic coal-gas mixture containing 3,000 ppm of H_2S. For SO_2 regeneration, a metered flow of liquid SO_2 under pressure was fed to the reactor system by displacement of liquid SO_2 from a pressurized supply tank. The liquid SO_2 was vaporized into a heated nitrogen stream (at 450°C to 630°C); concentrations up to 75 vol% were achieved. What is designated as the "oxygen regeneration" step was in actuality dilute-air regeneration, and was accomplished by introducing a small air stream into the hot reactor through which was flowing a preheated nitrogen stream.

The SO_2 regeneration was conducted through a hot exit line with a sulfur condenser, catch pot, and a heated back pressure control valve. Sulfidation and air regeneration were conducted through a separate exit line. Reactor outlet gas samples were analyzed continuously for H_2S during sulfidation and for SO_2 during air regeneration using continuous analyzers. Oxygen concentration during the O_2 regeneration was measured continuously. H_2S, COS, and SO_2 were measured intermittently during sulfidation using a gas chromatograph with a flame photometric detector.

A major goal of the bench-scale experiments, in which gram quantities of elemental sulfur could be recovered, was to achieve a sulfur mass balance. With the instrumentation described above, it was possible to compare the amount of physically recovered elemental sulfur with a value calculated on the basis of the gas analyses.

c. Sorbent improvement studies

Sorbent improvement studies were undertaken to enable consistent reduction of H_2S to less than 20 ppmv during sulfidation. These studies followed two avenues: the replacement of zinc with molybdenum, and the use of other proprietary metals and stabilizers as an addition to the iron-zinc formulation. Other researchers have reported success with SO_2 regeneration using sorbents containing molybdenum (deWild et al., 1996). Therefore, several small batches of sorbent containing iron and molybdenum on γ-alumina were prepared and tested (one cycle each of sulfidation) in a fixed-bed lab-scale reactor at 450°C and 0.1 MPa. A large batch of the most active of the three

was prepared and tested in the bubbling fluid-bed bench-scale unit for eight cycles.

The second avenue of sorbent improvement research involved preparing small batches of the attrition-resistant zinc-iron formulation with the addition of other metal species, with stabilizer additives, and at varying calcination temperatures. The details of this experimental program are proprietary, at this time, pending potential patent activity. Multiple cycle screening tests were conducted in a 1-cm diameter microreactor at 0.1 MPa pressure and 480°C for sulfidation, and 630°C for dilute-air regeneration.

Two variations of the best-performing material from this second line of research were prepared in larger quantities and were tested in a 1-cm diameter lab-scale reactor at 0.1 MPa for six cycles (sulfidation at 480°C and dilute-air regeneration at 630°C). The better of the two was selected for multicycle testing including SO_2 regeneration at 0.1 MPa with 10% SO_2 in nitrogen.

d. Field test plans

Associated with a related process development project, RTI (with DOE support) outfitted a modified office trailer as a Mobile Laboratory (Portzer and Gangwal, 1998). The 3.65 m by 15.25 m trailer is divided into a control room/analytical lab and an equipment room that houses a bench-scale AHGP test unit that is essentially a duplicate of the one described above. The concept is to conduct long duration testing of candidate sorbents using a slip stream of actual coal gas by moving the Mobile Laboratory to the site of an operating gasifier. The immediate plan is to relocate the lab trailer to Wilsonville, Alabama, the site of DOE/FETC's Power Systems Development Facility (PSDF) for testing to be conducted in the late 1999, early 2000 time frame.

5. Results and Discussion

a. Feasibility studies

A number of proprietary sorbents based on iron and zinc oxides were prepared and tested for SO_2 regeneration. They were compared with benchmark zinc titanate and zinc ferrite sorbents developed for fluidized-bed desulfurization with air regeneration as part of a previous project with the DOE. The sulfided sorbent that was based purely on ZnO as the active sorbent showed essentially no rengeration with 3.3% SO_2 in N_2 at up to 800°C and 1.0 MPa. However, sulfided iron- and zinc-based sorbents showed good regeneration with SO_2. TGA rates of SO_2 regeneration ranged

from 1.3 x 10^{-2} to 3.6 x 10^{-2} g sulfur/g sorbent/h with 3.3 vol% SO_2 at 700°C and 1.0 MPa.

A zinc-iron sorbent designated R-5 showed promising results and was tested further using the high-pressure lab-scale reactor. Atmospheric TGA analysis showed that the zinc portion of the sorbent was not regenerated, but the iron portion of the sorbent regenerated at a rate of 1.2 x 10^{-2} g sulfur/g sorbent/h, similar to the rates achieved with the high-pressure TGA. Solid yellow sulfur was recovered from the experimental apparatus, giving a visual, qualitative confirmation of direct regeneration to elemental sulfur.

The R-5 sorbent was also tested for SO_2 regeneration as a function of SO_2 concentration and for O_2 (dilute air) regeneration. The SO_2 regeneration rate, as measured by the high pressure TGA increased from 1.3 x 10^{-3} to 2.2 x 10^{-2} g sulfur/g sorbent/h at 650°C and 1.0 MPa when SO_2 concentration was increased from 3.3 to 15 vol%. The O_2 regeneration rate at 700°C and 1.0 MPa was about 3 x 10^{-2} g sulfur/g sorbent/h with 2 vol% O_2 in N_2.

The R-5 sorbent recipe was scaled up to kilogram quantities of a fluidizable form. Two different scale-up procedures were tried. One formulation had poor attrition resistance and was immediately rejected. Four others were tested with the HTHP bench-scale apparatus for varying numbers of cycles. Generally, each of the sorbents was able to reduce the outlet H_2S to below 100 ppmv and was regenerable over multiple cycles. Also, measureable (several grams) quantities of elemental sulfur were produced during SO_2 regeneration of each of the sorbents. As much as 60 to 80% of the sulfur absorbed during sulfidation was recovered as elemental sulfur.

However, the materials produced by the first scale-up procedure experienced excessive loss in reactivity with multiple cycles. As well, their attrition, as measured by a three-hole attrition tester (similar to ASTM test method 5757), increased significantly following cyclic testing. On the other hand, the sorbents prepared by the second procedure showed no loss in reactivity over the cyclic operation, and in fact, the reactivity improved with cycling. These sorbents also had very low attrition, comparable to that of fluid catalytic cracking (FCC) catalysts, as measured both before and after cyclic testing. The best material prepared by the second procedure, R-5-58, was selected for a 50-cycle, long duration test.

b. 50-cycle test

In the 50-cycle, HTHP testing, sorbent R-5-58 demonstrated H_2S removal down to the 50 to 100 ppm level with stable desulfurization activity over the

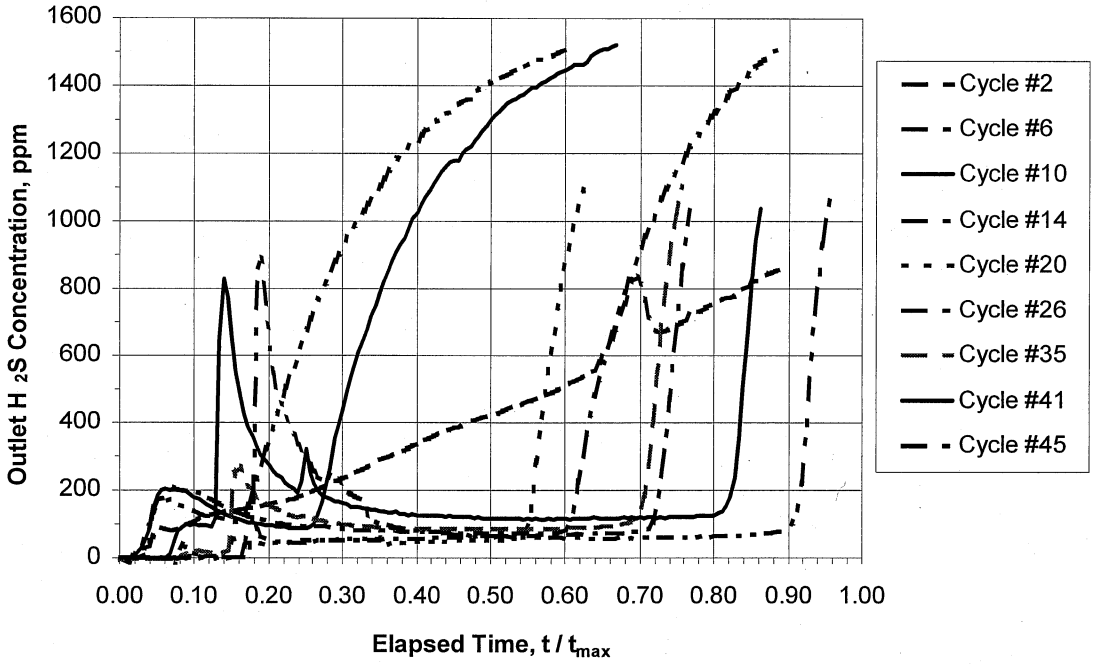

Figure 3. Sulfidation breakthrough curves from 50-cycle test of promising Zn-Fe sorbent.

duration. Figure 3 shows the sulfidation breakthrough curves for selected cycles covering the full test period. Interestingly, the sulfidation performance, as measured by time to breakthrough, improved considerably after the first few cycles.

In several cycles the concentration was less than 50 ppm and in general, the concentration was 100 ppm or lower. However, a successful commercial embodiment would require consistent removal of H_2S to 20 ppm or less. Sorbent improvement studies as described in the next section are being carried out to achieve this level of performance while maintaining the ability to be regenerated with SO_2.

Based on the "gas analysis difference" methodology described in the Experimental section above, the SO_2 regeneration step accounted for as much as 55 to 70% of the total regeneration of the sorbent. This compares to a theoretical limit of approximately 80%, assuming complete regeneration by SO_2 of the iron component. Many of the cycles had lower% regeneration because the test conditions were intentionally set at nonoptimal levels.

The observed rates of SO_2 regeneration in the 50-cycle bench-scale testing ranged from approximately 1.2×10^{-2} to 4.2×10^{-2} g S/g sorbent/h, consistent with the earlier TGA and microreactor studies. There is significant scatter in these data, but it appears that there is only a modest temperture dependency

for this process step. More precise data will be required for optimization of the regeneration reactor design.

The observed rates of the O_2 regeneration cannot be analyzed in detail, since there was an unexpected correlation of rate with cycle number; the later cycles had generally higher rates, apparently independent of operating conditions. The values fell in the range of 1.2×10^{-2} to 1.8×10^{-1} g S/g sorbent/h, much higher than was observed in the small-scale testing.

Figure 4 presents sulfur balance data in the form of a stacked-bar chart for those cycles for which complete data are available. In this chart, the total regeneration is the sum of SO_2 regeneration calculated by sulfur recovery, and O_2 regeneration calculated by gas analysis. In most cases, the resulting value is approximately 100% of the sulfur that was loaded, confirming that the experimental protocol yielded a sulfur balance.

In addition to durability (*i.e.,* multicycle regenerability) testing of the sorbent, another objective of the 50-cycle test program was to determine the effects of three primary variables: SO_2 concentration in the regeneration gas,

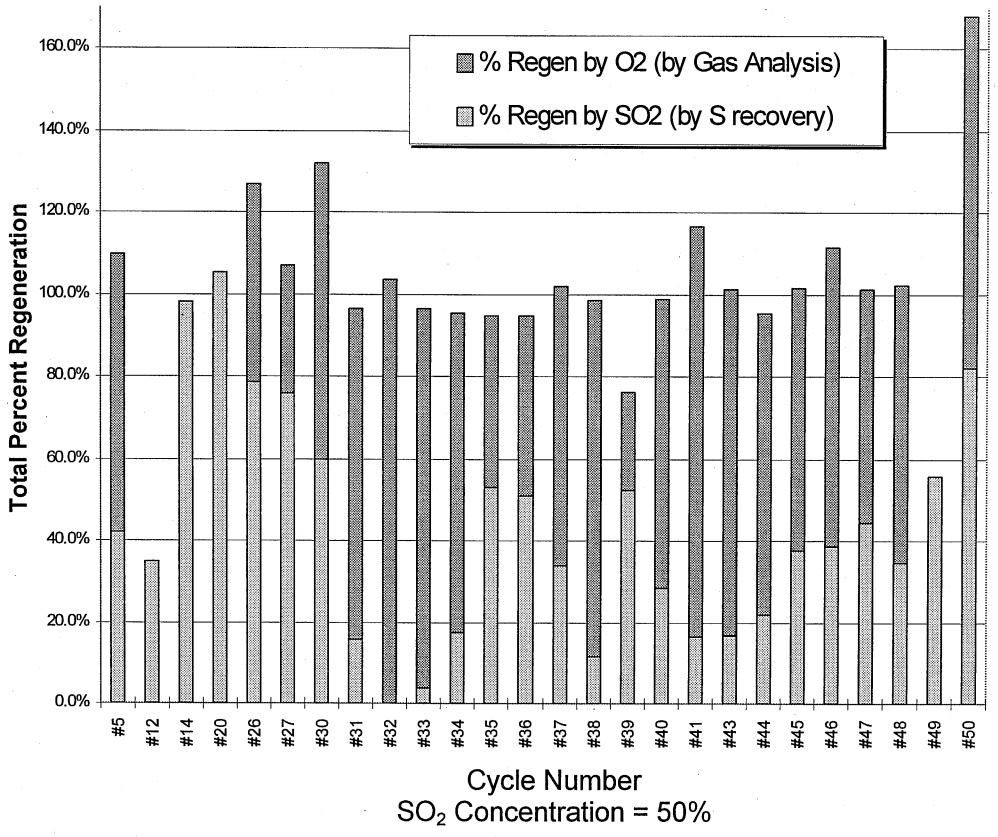

Figure 4. Sulfur balance of the combination of SO_2 and O_2 regeneration.

temperature of the regeneration gas, and duration of the SO_2-regeneration half-cycle. Statistical analysis was applied to the results to generate an empirical second-order polynomial fit. The statistical model shows that duration of regeneration is the most important variable,% regeneration is directly proportional to temperature, and SO_2 concentration has a small effect. Figure 5 shows a plot of the calculated % regeneration (model

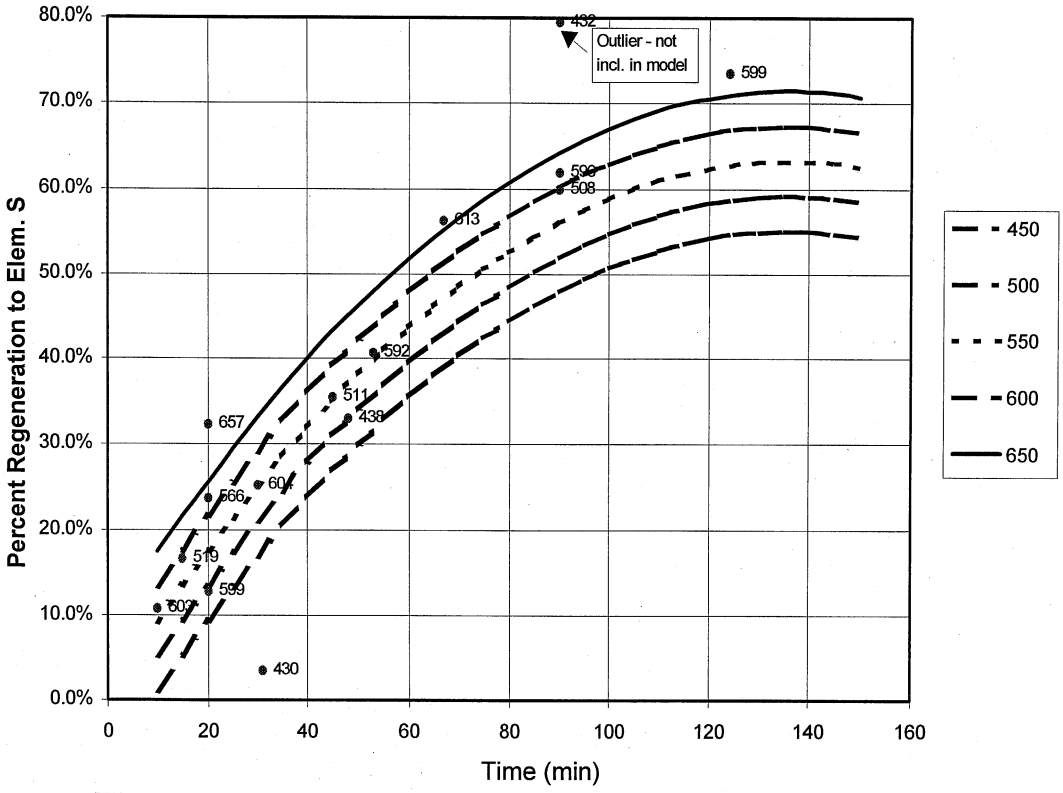

Figure 5. Empirical model of SO_2 regeneration operating parameters.

values) as a function of duration for one SO_2 concentration value. The actual data points are also shown for comparison. Because an empirical model based on a small data set was used, there are obvious limitations to its application. However, the model is useful for guiding thinking on the process simulation and economic analysis.

c. Sorbent improvement studies

The attempts to produce an iron-moly-based sorbent were disappointing. Although the initial activity of the materials, as tested in the microreactor, was promising—the outlet H_2S concentration was well below 20 ppmv—the multicycle performance of a larger sorbent batch (FHR-4) during the multicycle test was poor, as shown in Figure 6.

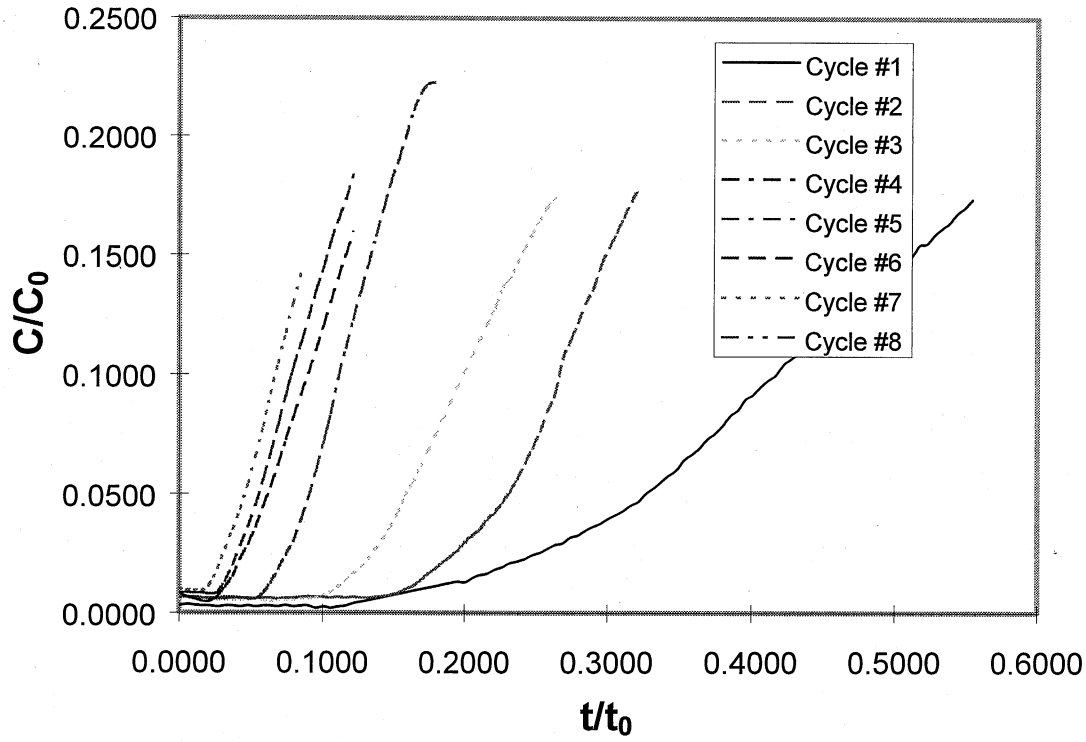

Figure 6. Dimensionless breakthrough curves for sorbent FHR-4.

By monitoring of the SO_2 evolved during the air-regeneration half cycles, it appeared that the reason for the capacity decline was that a significant portion of the absorbed sulfur was not released during regeneration; the formation of sulfate was suspected. This idea was at least partially confirmed when reductive regeneration conditions at the start of subsequent sulfidation half cycles resulted in H_2S evolution. The capacity of the sorbent could not be fully restored, however. No further work with the iron-moly combination was attempted.

The next phase of sorbent material development work was aimed at determining the conditions that result in sulfate formation (sulfation), and to determine the effect of multiple cycles of sulfidation and regeneration. The sorbent calcination temperature, additives, and additive content were evaluated using the atmospheric pressure microreactor. In particular, runs with sorbents FHR-6 and FHR-8 showed that using a higher calcination temperature resulted in stable capacity from cycle to cycle after the third cycle. However, sulfation continued to occur on the sorbent as evidenced by the evolution of SO_2 during sulfidation. Sorbent FHR-8 had superior performance in terms of reduced outlet H_2S concentration—less than 10 ppmv—and was selected for subsequent testing. A sample of R-5-58 (the sorbent used for the 50-cycle test) was tested with the same1-atm test protocol; FHR-8 showed superior H_2S removal activity.

The formulation for FHR-8 was used as the basis for preparation of two attrition-resistant candidate materials in larger batches, designated AHI-1 and AHI-2. Both samples were tested in the atmospheric TGA using a combination of gases and temperatures that simulated the complete AHGP: sulfidation, SO_2 regeneration, and O_2 regeneration. Variations in specific conditions and multiple cycles with constant conditions were run in the TGA in order to determine the preferred conditions to use for further testing. The microreactor setup was modified to include SO_2 regeneration, as well as sulfidation and air regeneration.

The initial testing did not include SO_2 regeneration. Promising reductions of H_2S concentration in the outlet gas were obtained, with AHI-2 performing slightly better and achieving approximately 10 ppmv. AHI-1 generally achieved better than 20 ppm H_2S outlet concentration, and always less than 40 ppm. A longer test program, 27 cycles, was conducted with the addition of the SO_2 regeneration step on the more promising sorbent formulation – AHI-2.

The protocol for the sulfidation at 480°C using simulated coal gas consisted of a 20-minute initial reductive regeneration, with no H_2S present, followed by the introduction of 4000 ppm of H_2S into the feed gas. Excellent activity in terms of low outlet H_2S concentration was observed; concentrations below 20 ppmv were consistently obtained, with many runs below 10 ppmv. Interestingly, the later runs showed higher activity than the initial runs; starting at cycle 19, the initial concentrations were undetectable (below 1 ppmv). No H_2S or SO_2 was detected during reductive regeneration indicating the absence of sulfation.

The SO_2 regeneration consisted of 3.5 hours of 10% SO_2 in nitrogen at 630°C. There are no analytic data from this step, nor was elemental sulfur recovered from the small-scale apparatus involved. The amount of regeneration accomplished with the SO_2 was estimated by difference from the O_2 regeneration data. Integration of the values for outlet SO_2 concentration (obtained by GC) gave an estimate of the amount of residual sulfur in the sorbent that was regenerated by the dilute air stream. By these calculations, the SO_2 regeneration resulted in up to 50% regeneration to elemental sulfur.

The AHI series of sorbents was designed to be highly attrition-resistant. The attrition indices for AHI-1 and -2 were 0.5 and 1.2, respectively—similar to the values for the benchmark FCC catalysts. These sorbents have been scaled up to 500 g quantity and are due to be tested at bench-scale at elevated pressure. Eventually one of these sorbents will be selected for the field test of the AHGP to be conducted in early 2000.

6. Conclusions

Conceptual and process development of AHGP, an advanced HGD process, has been carried out. AHGP uses a proprietary Zn-Fe sorbent. It requires two regeneration stages (SO_2 and O_2) but uses significantly less coal gas compared to DSRP for elemental sulfur recovery. The feasibility of AHGP as a promising alternative to DSRP has been demonstrated at bench-scale. Attrition-resistant Zn-Fe sorbent formulations have been prepared that can remove H_2S to below 20 ppmv from coal gas and can be regenerated using SO_2 to produce elemental sulfur.

7. Acknowledgments

The research is sponsored by the DOE/FETC, under Contract No. DE-AC21-94MC31258, with Research Triangle Institute and Contract No. DE-FG26-97FT97276 with Hampton University.

8. 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.

deWild, P.J., J.H.A. Kiel, and E. Schenk. "Iron Oxide/Molybdenum Oxide Sorbents for High Temperature Fuel Gas Desulfurization." In *Procedings of the Thirteenth Annual International Pittsburgh Coal Conference (1996).*

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., J.W. Portzer, B.S. Turk, and R.Gupta. 1996. "Advanced Sulfur Control Processing." In *Proceedings of the Advanced Coal-Fired*

Systems Review Meeting July 16-19, 1996. (CD-ROM). U.S. Department of Energy, Morgantown, WV.

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.

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.

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.

Portzer, J.W., and S.K. Gangwal. 1998. "Bench-Scale Demonstration of Hot-Gas Desulfurization Technology." In *Proceedings of the Advanced Coal-Based Power and Environmental Systems '98 Conference*. July 21-23, 1998. Available on the U.S. Department of Energy, Federal Energy Technology Center Web site. (http://apis.fetc.doe.gov/publications/proceedings/98/98ps/pspb-1.pdf)

Portzer, J.W., A.S. Damle, and S.K. Gangwal. 1997. "Hot-Gas Desulfurization with Sulfur Recovery." In *Proceedings of Advanced Coal-Based Power and Environmental Systems '97 Conference*, Federal Energy Technology Center, Pittsburgh, PA, July.

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 16-18, 1996.* (CD-ROM). U.S. Department of Energy. Morgantown, WV.

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