Hot-Gas Desulfurization with Sulfur Recovery

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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.
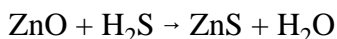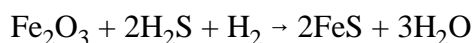
Objective

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.
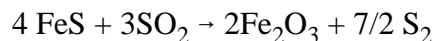
Approach

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:
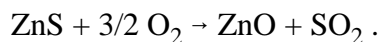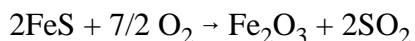
1. Sulfidation

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

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

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
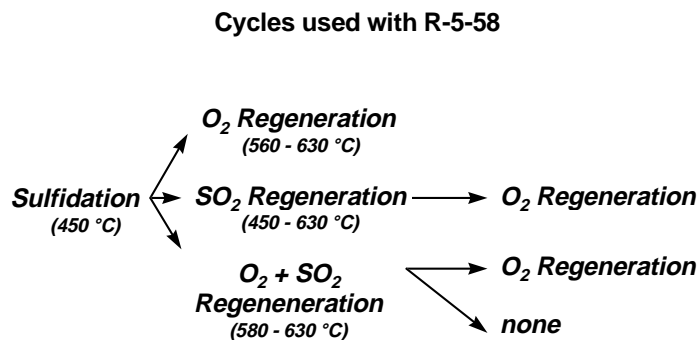
Cycles used with R-5-58

Figure 1. 50-cycle bench-scale test.

Table 1. 50-Cycle Test Conditions

		Coal gas composition (vol%)	
Pressure:	20 atm		
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

by integrating the metered gas flows of H_2S into the reactor, minus the outlet concentration as determined by gas 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.
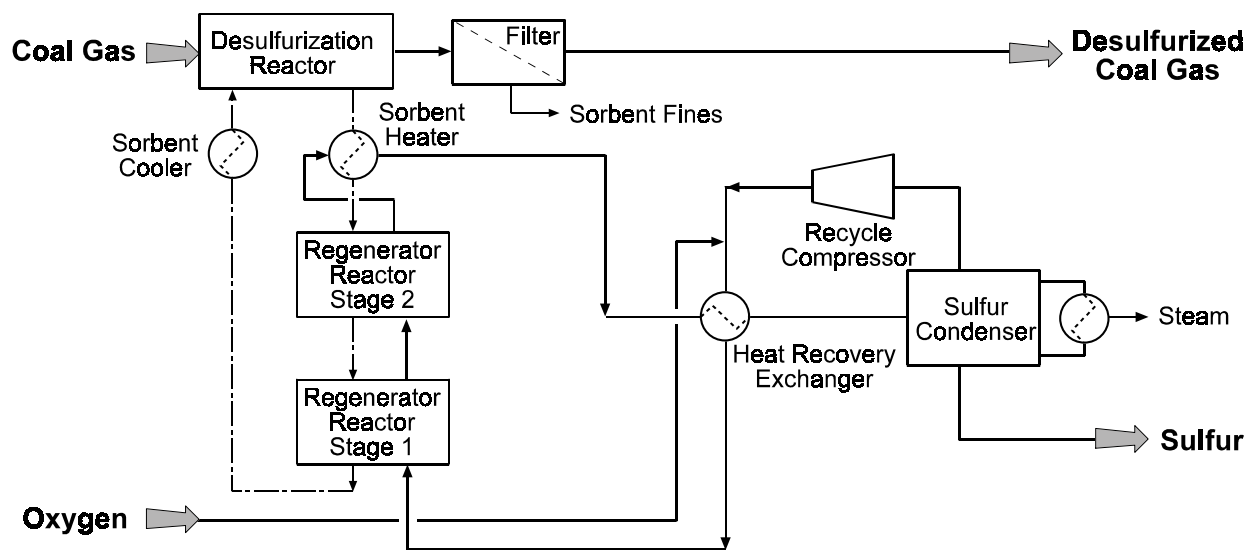
Figure 2. Advanced hot gas desulfurization.

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
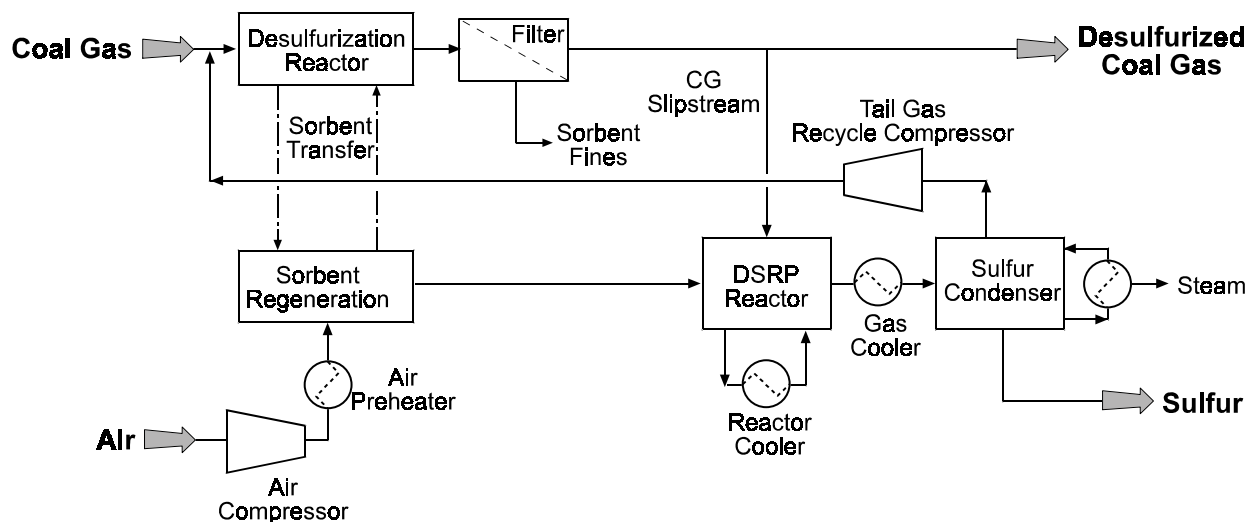
Figure 3. Hot-gas desulfurization with DSRP.

reactor 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 break-through 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 concentra-tion 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.
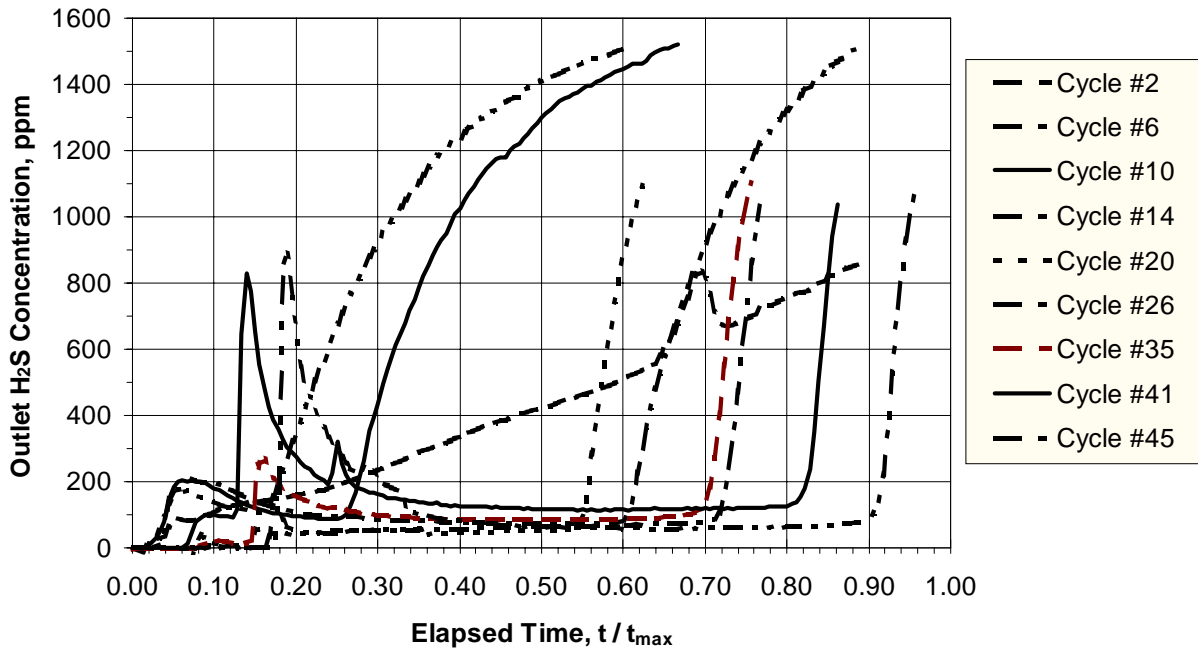
Figure 4. Sulfidation breakthrough curves.

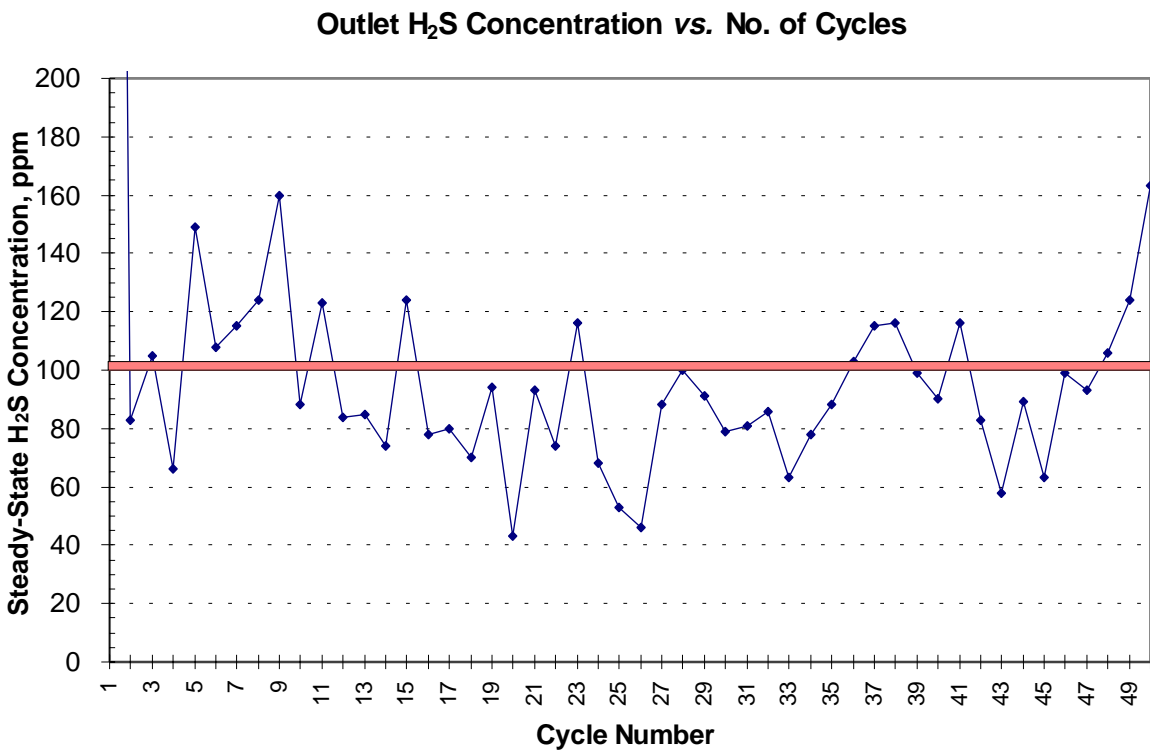**Outlet H$_2$S Concentration *vs.* No. of Cycles**

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.
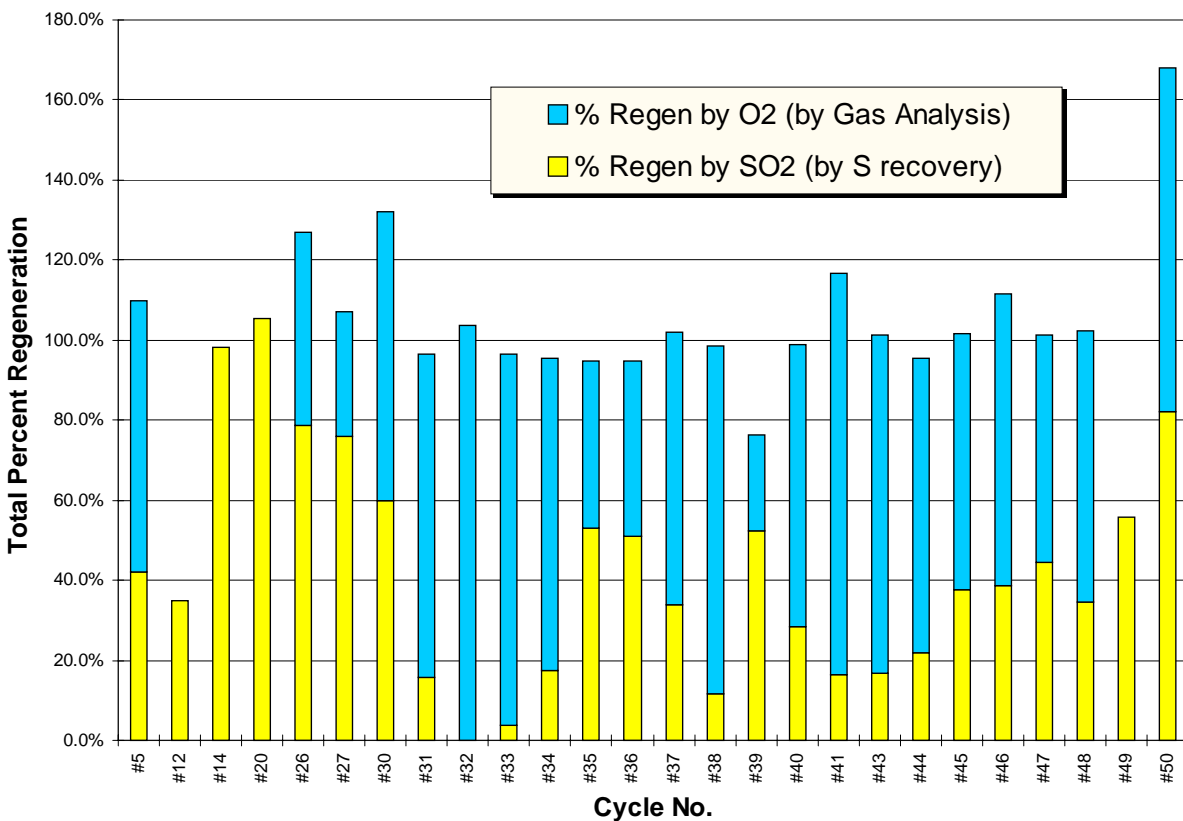

Figure 6. Sulfur balance.
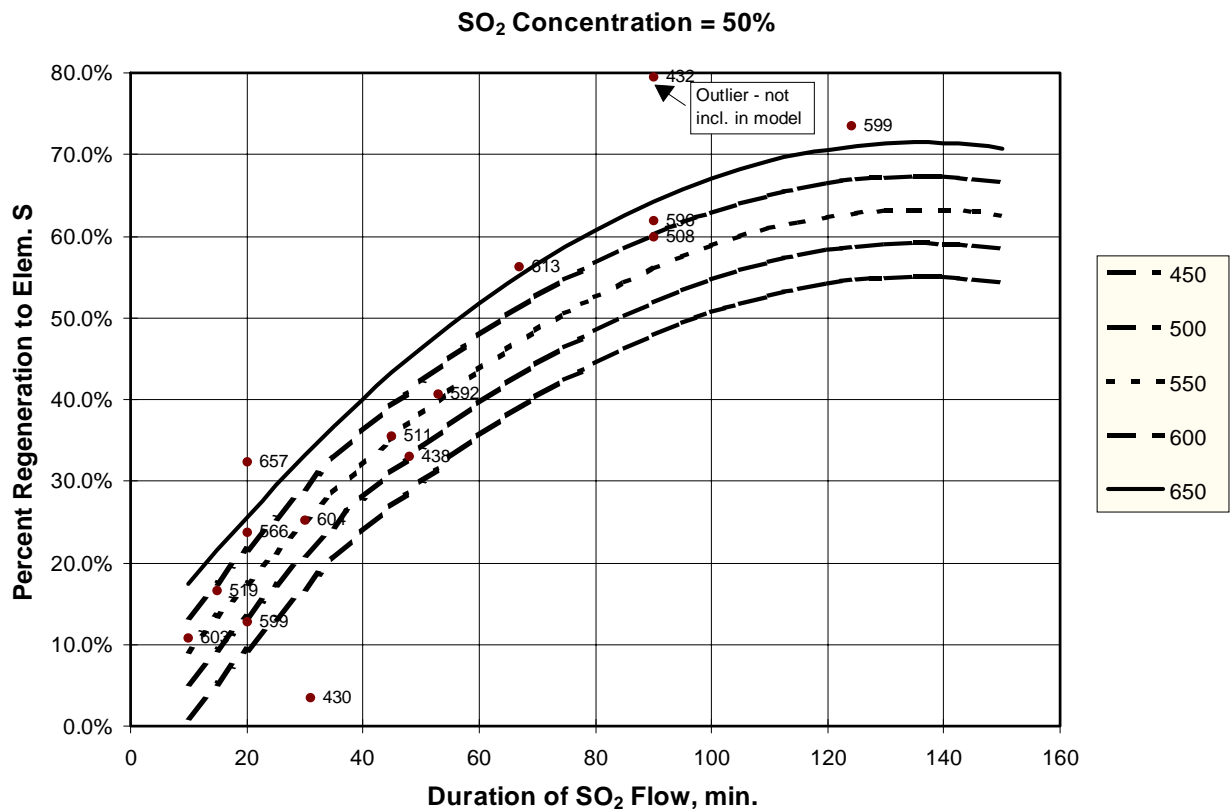
SO₂ Concentration = 50%

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.

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.

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 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

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