5. CONCLUSIONS AND RECOMMENDATIONS

The major conclusions from the **fixed-bed micro-reactor catalyst screening** for SSRP are:

- A total sulfur conversion of 99% with only 35ppm COS formation was achieved at 300psig and 154°C (309°F) on a commercial alumina catalyst (E-alumina).
- Sulfur conversion is limited only by thermodynamic equilibrium from reaching 100%.
- Higher reaction pressures shift the thermodynamic equilibrium toward higher conversion, thus sulfur removal activity increases with increasing pressure.
- Catalyst activation and feed procedure are critical for enhanced selectivity of sulfur removal (minimized COS formation).
- SO_2 is more selective than O_2 for the catalytic oxidation of H_2S in the presence of excess reducing gases (H_2, CO) on two different catalysts (alumina and silica gel) under the examined reaction conditions.

The major conclusions from the **micro-bubbler concept evaluation study** for SSRP are:

- The selective catalytic oxidation of H_2S by SO_2 in the presence of excess reducing gases (CO, H_2) is feasible in a molten sulfur medium.
- Higher pressures and an intermediate SO_2 concentration enhance sulfur removal.
- Reaction of CO with an active form of sulfur is the major pathway for COS formation.
- Molten sulfur appears to be inactive for direct reaction with CO.

The major conclusions from the **bench-scale process evaluation study** for SSRP are:

- A 97.5% sulfur conversion with 365 ppm COS formation was achieved at 400 psig and 135°C (275°F) on E-alumina suspended in molten sulfur.
- Conversions under comparable residence times, as expected, are lower in a CSTR compared to a fixed-bed reactor. The data trends, however, were identical. The SBCR commercial embodiment is expected to achieve conversions of fixed-bed reactor levels with proper design.
- COS formation was reduced to 75ppm without affecting the sulfur removal activity, by increasing the steam feed content to 18% at 125°C.
- Reaction temperature, inlet steam concentration, and total feed flow, appear to be important parameters in limiting the formation of COS, without significantly impeding the sulfur removal efficiency of SSRP.
- The overall sulfur removal efficiency of SSRP (minimization of outlet S concentration) is enhanced by higher residence times, and by higher reaction pressures; higher reaction pressures are favored in industrial applications involving gasifier-syngas.
- The beneficial effect of higher reaction pressure on sulfur removal activity appears to be more prominent at lower reaction temperatures.
- The overall sulfur removal efficiency is favored at lower reaction temperatures in the presence of the E-alumina catalyst, but at higher reaction temperatures in Molten Sulfur only (no catalyst). The presence of catalyst changes the relative progress of the H_2S+SO_2 reaction vs. COS formation, making lower temperatures more favorable for SSRP.

- Addition of SO_2 suppresses the formation of COS in the presence of the E-alumina catalyst, in contrast to the blank reactor and Molten Sulfur only (no catalyst) systems. In the presence of the catalyst, addition of SO_2 apparently shifts the pathway for COS formation from the (inevitable for H_2S-containing syngas feed) $CO + H_2S$ reaction to that of CO with active sulfur formed by the Claus reaction, at least to a major extent.
- No catalyst deactivation was observed after running for more than 100 hours, indicating that the formed sulfur was recovered by the molten sulfur medium. In other words, a self-regenerable catalyst system was established. This is a major accomplishment since in fixed-bed reactors conversion will drop due to pore plugging.
- Molten sulfur is inactive for direct reaction with reducing gases (H_2 and CO), but is itself shown to be an active catalyst (or medium) for the Claus reaction.
- Addition of catalyst to molten sulfur enhances its catalytic activity for SSRP, while decreasing the undesirable formation of COS.

The major conclusions from the **economic evaluation of SSRP** are:

- Even with highly conservative assumptions, SSRP gives significant reductions in the total capital requirements, operating costs, and COE, over conventional amine systems.
- The COS hydrolysis reactor may not be needed for SSRP as opposed to amine systems. Also, gas-cooling requirements for SSRP are lower than amine systems.

Based on the **experimental results on SSRP** described in Section 3, it is recommended to focus the future work on SSRP in the following:

- The formation of COS as the main undesirable reaction during SSRP should be prevented or minimized. The effect of various reaction parameters (temperature, pressure, total flow, steam concentration, catalyst to Molten Sulfur ratio) in minimizing the formation of COS (as opposed to maximizing the Claus reaction) has to be examined.
- The role of steam as an active participant in the Claus and COS formation reactions (in both the presence and absence of SO_2, and in both the presence and absence of catalyst) must be elucidated.
- The COS hydrolysis or hydrogenation during SSRP should be promoted through use of suitable catalysts. Evaluation of various catalysts in terms of their activity for these reactions in relation to the Claus reaction needs to be performed.
- Evaluation of SSRP as a process for the potential removal of COS in the absence of H_2S (using an active COS hydrolysis or hydrogenation catalyst) should be conducted.
- Evaluation of SSRP and optimization of reaction parameters for a combined H_2S and COS removal from coal-derived synthesis gas must be performed.

Based on the **economic calculations** and the discussion of the various Texaco-IGCC alternatives the following recommendations are made:

- More precise engineering data needs to be collected, concerning the solubility and diffusivity of H_2S and SO_2 in liquid elemental sulfur.
- The kinetics of the formation of elemental sulfur and COS in liquid sulfur and for the liquid sulfur/SSRP catalyst system should be elucidated in more detail.

- A more detailed analysis of the Gas Cooling Section should be carried out using ASPEN.
- The fate of COS entering the SSRP SBCR should be investigated. Experiments should be carried out to determine if COS can be controlled in the SSRP by imparting COS hydrolysis functionality to the SSRP catalyst or by simply mixing COS hydrolysis catalyst into the SSRP sulfur/catalyst slurry.

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APPENDIX A   Advanced Sulfur Control Concepts: Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting

7A.5   Advanced Sulfur Control Concentration

CONTRACT INFORMATION

Contract Number	DE-AC21-94MC31258
Contractor	Research Triangle Institute P.O. Box 12194 Research Triangle Park, NC 27709-2194 Telephone: (919) 541-8033 Facsimile: (919) 541-8000
Other Funding Sources	None
Contractor Project Manager	Santosh K. Gangwal
Principal Investigators	Brian S. Turk Raghubir P. Gupta
METC Project Manager	Thomas P. Dorchak
Period of Performance	March 21, 1994 to March 20, 1997

Schedule and Milestones

FY94-96 Program Schedule

	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D
Concept Assessment	─	─	─															
Laboratory Development				─	─	─	─	─	─	─	─	─	─	─				
Feasibility Demonstration																─	─	─

OBJECTIVES

Regenerable metal oxide sorbents, such as zinc titanate, are being developed to efficiently remove hydrogen sulfide (H_2S) from coal gas in advanced power systems. Dilute air regeneration of the sorbents produces a tailgas containing a few percent sulfur dioxide (SO_2). Catalytic reduction of the SO_2 to elemental sulfur with a coal gas slipstream using the Direct Sulfur Recovery Process (DSRP) is a leading first-generation technology. Currently the DSRP is undergoing field testing at gasifier sites. The objective of this study is to develop

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second-generation processes that produce elemental sulfur without coal gas or with limited use.

Novel approaches that were evaluated to produce elemental sulfur from sulfided sorbents include (1) sulfur dioxide (SO_2) regeneration, (2) substoichiometric (partial) oxidation, (3) steam regeneration followed by H_2S oxidation, and (4) steam-air regeneration. Preliminary assessment of these approaches indicated that developing SO_2 regeneration faced the fewest technical and economic problems among the four process options. Elemental sulfur is the only likely product of SO_2 regeneration and the SO_2 required for the regeneration can be obtained by burning a portion of the sulfur produced. Experimental efforts have thus been concentrated on SO_2-based regeneration processes.

BACKGROUND INFORMATION

### Leading Hot-Gas Desulfurization Technologies

Hot-gas desulfurization research has focused on air-regenerable mixed-metal oxide sorbents such as zinc titanate and zinc ferrite that can reduce the sulfur in coal gas, present primarily as H_2S, to <20 ppmv and that can be regenerated in a cyclic manner with air for multicycle operation.

The sulfidation/regeneration cycle can be carried out in fixed-, moving-, and fluidized-bed reactor configurations. The regeneration reaction is highly exothermic, requiring the use of large volumes of diluent to control the temperature and results in a dilute SO_2-containing tailgas that must be further treated. Under contracts with the U.S. Department of Energy/ Morgantown Energy Technology Center (DOE/METC), many approaches have been evaluated for treatment of the tailgas. These include adsorption of SO_2 using calcium-based sorbents followed by landfilling of calcium

sulfate as well as conventional methods such as Wellman-Lord coupled with high-temperature syngas reduction and augmented Claus for converting the SO_2 to elemental sulfur. There are two leading advanced approaches that DOE/METC is currently sponsoring to convert the SO_2 tailgas to useful byproducts. These include the General Electric (GE) moving-bed process and the DSRP.

In the GE moving-bed process (Cook et al., 1992), the H_2S in coal gas is removed by moving a bed of sorbent countercurrent to the upward gas flow. The sulfided sorbent is transferred to a moving-bed regenerator below the moving-bed absorber using a lock-hopper arrangement. In the regenerator, SO_2 recycle and limited air are used to control the temperature of the exothermic reactions, producing a tailgas containing 10- to 13-vol% SO_2. The regenerated sorbent is lifted back to the absorber using a bucket elevator arrangement. The 10- to 13-vol% SO_2 is a suitable feed for a sulfuric acid plant. The GE moving-bed process has undergone a series of pilot-scale tests and has been selected for demonstration in a Clean Coal Technology project.

In the DSRP (Dorchak et al., 1991; Gangwal et al., 1993), the SO_2 tailgas is reacted with a slipstream of coal gas over a fixed bed of a selective catalyst to directly produce elemental sulfur at the high-temperature, high-pressure (HTHP) conditions of the tailgas and coal gas. Major reactions involved are shown below:

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

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

$$H_2 + (1/n) S_n \rightarrow 4 H_2S.$$
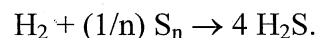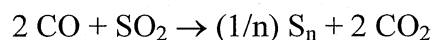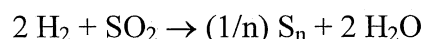
The DSRP was originally envisioned as a two-stage process. Recent results, however, indicate that sufficient selectivity (>99 percent or better) to elemental sulfur can be achieved in a single stage

by careful control of the inlet stoichiometry to maintain a reducing gas (H_2 + CO) to SO_2 mole ratio of 2.0. The DSRP integrates well with zinc titanate fluidized-bed desulfurization (ZTFBD) (Gupta et al., 1992), as opposed to fixed- or moving-bed desulfurization because of the relative ease of achieving a constant concentration of SO_2 in the tailgas using the fluidized-bed desulfurization-regeneration system. Both ZTFBD and DSRP have been demonstrated at bench scale using simulated gases and are being demonstrated in an integrated manner using a slipstream of actual coal gasifier gas under another contract awarded to the Research Triangle Institute (RTI) by DOE/ METC.

Economic evaluations of the GE moving-bed process coupled to a sulfuric acid plant and fluidized-bed desulfurization coupled to DSRP have been conducted by Gilbert Commonwealth for DOE. These evaluations show that the two approaches are closely competitive, with costs within 1 percent of each other, cost of electricity basis.

Need for Simpler Processing

Production of a sulfuric acid byproduct, e.g., using the GE moving-bed process, is site specific, requiring a nearby sulfuric acid plant and a ready market because sulfuric acid cannot be stored in bulk for long periods of time and cannot be transported over long distances. Another inherent problem with the GE moving-bed process has been that, in spite of several attempts, a steady (constant) level of SO_2 has not been achieved in the tailgas, which could present operation problems for converting to sulfuric acid in the downstream sulfuric acid plant. A number of other problems have been encountered in the operation of the GE moving-bed process, e.g., control of temperature in the regenerator and corrosion in the SO_2 recycle system.

Elemental sulfur is the desired sulfur byproduct because it is easily stored, transported, or sold. It is also the preferred choice of utilities. DSRP has the advantage that it produces elemental sulfur and is also significantly cheaper than conventional processes to reduce SO_2 to elemental sulfur.

Nevertheless, simpler processes that can be more fully and economically integrated with regenerable sorbents are needed because the DSRP requires a small portion of the fuel gas (i.e., coal gas) to reduce SO_2 to elemental sulfur and, thus, imposes an inherent efficiency and economic penalty on the overall system. For every mole of SO_2 converted to elemental sulfur in DSRP, approximately 2 mols of reducing gas (H_2 + CO) are consumed. As the sulfur content of the coal fed to the gasifier increases, obviously the proportion of the reducing gas required in the DSRP will increase as will the cost associated with it. A greater incentive thus exists for developing alternative processing schemes for higher sulfur coals that eliminate or minimize the use of coal gas.

PROJECT DESCRIPTION

This project seeks to recover sulfur (as elemental sulfur) from sulfided sorbents using alternative regeneration reactions/process schemes that do not result in the production of a dilute SO_2-containing tailgas requiring coal gas for reduction to sulfur (as in DSRP). The project is divided into three tasks shown in the Schedule and Milestones. Task 1, Concept Assessment, is complete; Task 2, Laboratory Development, is currently ongoing; and Task 3, Feasibility Demonstration, will not begin until 1996.

Based on a concept assessment, the alternative regeneration techniques listed in order of increasing potential are partial oxidation, simultaneous steam and air regeneration, steam regeneration with direct oxidation of H_2S, and SO_2 regeneration.

Partial oxidation is attractive due to lack of thermodynamic limitations, thereby allowing the choice of sorbent purely on its ability to remove H_2S. The challenge, however, is to inhibit subsequent oxidation of elemental sulfur to SO_2 which is rapidly catalyzed by the sorbent as the sulfur attempts to escape its pores. Possible remedies include reducing reaction rates by reducing temperature, limiting the oxygen supply, and reducing sorbent and sulfur contact. However, none of these are complete solutions or achievable in practice without a great deal of difficulty. Lower temperatures would reduce the rate of sulfur vapor diffusions out of the sorbent. Oxygen concentrations at all points in the reactor must be at a level to control the sequential reaction, sorbent $\rightarrow$ sulfur $\rightarrow$ SO_2, to make sulfur but prevent SO_2 formation. This would require highly complex reactor designs. Reducing contact between sorbent and sulfur will require modifying sorbents to have a wide pore structure without altering attrition resistance. Thus, significant barriers exist to development of partial oxidation for direct sulfur production during regeneration.

The use of steam for regeneration involves the reaction that is simply the reverse of the sulfidation reaction. Thus, an immediate barrier to steam regeneration is that any sorbent capable of removing H_2S down to ppm levels will only release ppm levels of H_2S during steam regeneration. The ppm H_2S release will increase with steam concentration but only weakly (e.g., linearly, depending on sorbent stoichiometry). Higher steam concentrations and temperatures assist the regeneration but could result in severe sorbent sintering. Both steam regeneration followed by H_2S oxidation to sulfur and simultaneous steam and air regeneration followed by Claus reaction face additional technical problems. Mixtures of steam and SO_2 are corrosive. Effective condensation of sulfur occurs at a lower temperature than steam at HTHP conditions. A large heat duty is required to generate steam from condensed process steam or fresh water.

Based on detailed thermodynamic calculations and the barriers presented above, all alternative regeneration concepts, other than dry-SO_2 regeneration, were eliminated from further immediate consideration. Assessment and laboratory results of SO_2 regeneration are described in the Results section. Laboratory experiments to test the SO_2 regeneration concept were carried out using an atmospheric pressure thermogravimetric analyzer (TGA), a high-pressure TGA, and a high-pressure lab-scale reactor. The high-pressure lab-scale reactor system is shown in Figure 1. The reactor is made of a ½-in. stainless steel tube capable of operation at 750 °C and 200 psig. Provision is made for sulfiding the sorbent with simulated coal gas, or regenerating the sorbent with up to 15 vol% SO_2. The gas exiting the reactor passes through heated tubing into a 130 °C convective oven where a 0.1-micron filter is used to collect sulfur. A sample of the exit gas is analyzed by gas chromotography (GC) to measure H_2S breakthrough. The gas finally vents through a back-pressure regulator.

Zinc and iron containing sorbents have been the primary candidates that have been tested. The atmospheric pressure and high-pressure TGA experiments have involved cyclic tests using simulated coal gas for sulfidation and up to 15 vol% SO_2 for regeneration. The concept of SO_2 regeneration followed by air regeneration has also been evaluated.

RESULTS

Assessment of SO_2 Regeneration

Like steam regeneration, SO_2 regeneration has thermodynamic constraints as the thermodynamic calculations presented later show. However, high-pressure conditions are anticipated to enhance
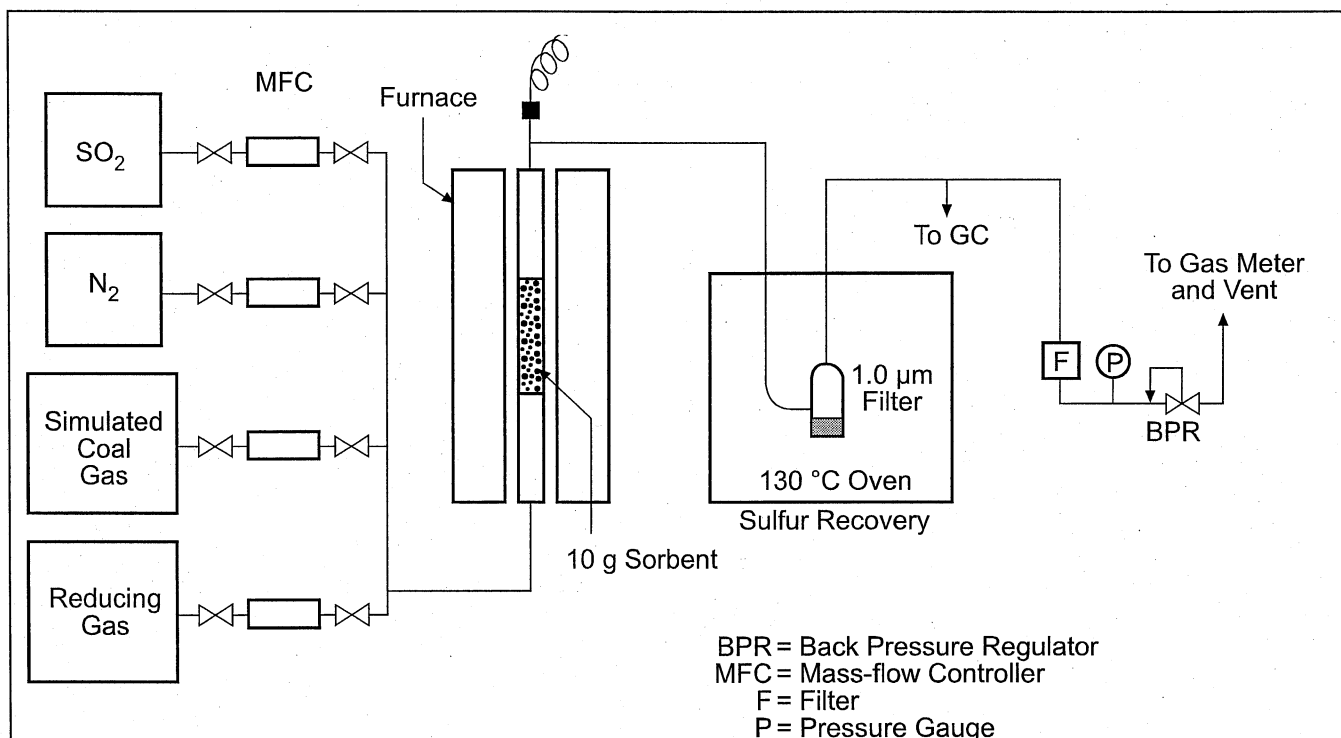
Figure 1. Laboratory-Scale SO$_2$ Regeneration Test System

elemental sulfur formation. Based on Le Chatalier's principle, high pressure favors formation of fewer gaseous products. Since formation of sulfur oligomers larger than S$_3$ result in few moles of gaseous products, high pressure should favor formation of higher oligomers. Also, nonideal behavior of sulfur oligomers could lead to increased yield at higher pressures.

Unlike thermodynamic limitations for steam regeneration, development of sorbents for SO$_2$ regeneration may benefit from the thermodynamic limitations. Regeneration with SO$_2$ will require SO$_2$ and heat because SO$_2$ regeneration is endothermic. Oxygen regeneration, which is rapid and extremely exothermic, produces SO$_2$ and heat. By balancing the amounts of SO$_2$ and O$_2$ regeneration, it may be possible to achieve complete regeneration, convert all sulfur species into elemental sulfur, and balance heat

requirements. Since SO$_2$ regeneration is slow, achieving this balance requires increasing SO$_2$ regeneration rates. Increasing temperature will increase reaction rates, but the maximum temperature is limited by sorbent sintering and materials of construction available for reactor and process heat integration. Any temperature effects on the thermodynamic equilibrium constant will be further augmented by the increase in reaction rate. Although pressure effects on reaction rate constants are generally assumed insignificant, research with DSRP found rate constants, specifically for the H$_2$-SO$_2$ reaction, increased with pressure while all other conditions were kept constant. Thus HTHP conditions offer considerable potential for effective SO$_2$ regeneration.

With SO$_2$ regeneration, sulfate formation, a major cause of sorbent decrepitation, does not occur. Absence of sulfate formation during SO$_2$ regeneration should increase mechanical stability and extend life expectancy for sorbents. Sulfur

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dioxide regeneration allows simple separation of SO_2 and elemental sulfur and dry SO_2 is much less corrosive than a SO_2 and steam mixture. The endothermic nature of SO_2 regeneration may require additional heat in spite of extensive heat recovery from the sulfidation unit and O_2 regenerator. Although a certain amount of sorbent optimization will be needed, SO_2 regeneration has a much greater potential for rapid process development than any of the other alternative regeneration techniques.

Sorbent Metal-Oxide Selection

A number of sorbent metal-oxide formulations were assessed on the basis of literature information and thermodynamic calculations. A review of the literature indicated regenerable sorbents based on oxides of cerium, copper, cobalt, iron, manganese, molybdenum, tin, and zinc individually and in combinations. These metal or mixed metal oxides have been investigated both without as well as combined with a secondary oxide, typically silica, alumina, titania, and chromia. The roles of these secondary oxides include support for strengthening mechanical structure, as stabilizers against reduction of the metal oxide to metal in a reducing environment, and/or as modifiers of thermodynamic properties of the metal oxide to enhance elemental sulfur formation during regeneration.

Based on the evaluations, sorbents based on cerium, cobalt, cobalt, molybdenum and tin were found to be poor desulfurizing agents, costly, or not easily regenerated with SO_2. Some had a combination of these deficiencies. Thus, they were eliminated from further consideration. Of the remaining metal oxides, namely oxides of manganese, iron, and zinc, due to the similarity of reduction and desulfurizing properties of manganese and iron, iron was chosen for further consideration because more is known about iron.

Also zinc remained a candidate for further consideration due to its very high desulfurization efficiency even though it showed very poor thermodynamics for SO_2 regeneration. In combination with iron, zinc could act as a polishing agent for H_2S which could be regenerated using air to produce SO_2 needed for SO_2 regeneration. Thus, the laboratory work concentrated on iron and zinc-based sorbents.

Thermodynamic and Process Evaluation of SO_2 Regeneration

As stated earlier, SO_2 regeneration also shows thermodynamic constraints as seen from thermodynamic calculations shown in Table 1. Results are relevant only for zinc- and iron-based sorbents and thus Table 1 is limited to these sorbents. It is noted that, as the sorbent becomes less effective for H_2S removal, it becomes thermodynamically more easily regenerated by SO_2. This suggests that a sorbent combination from the top and bottom parts of the table may be necessary for an effective SO_2 regeneration process.

The SO_2 regeneration could be followed by air or O_2 regeneration to complete the regeneration before returning the sorbent to the sulfider as shown conceptually in Figure 2. Of course, alternative process schemes employing various combinations of SO_2 and O_2 regeneration are also possible but are not discussed here in the interest of space.

Test Results

A number of sorbents based on iron and zinc oxides were prepared and tested for SO_2 regeneration using the TGAs and the laboratory reactor system. The benchmark zinc titanate and zinc ferrite sorbents were ZT-4 and L-7. These sorbents have been developed for fluidized-bed desulfurization incorporating air regeneration under a previous DOE contract. The ZT-4 sorbent (based purely on ZnO as the active sorbent) and other ZnO-only-based sorbents showed essentially no

Table 1. Thermodynamic Calculations for Sulfidation and SO$_2$ Regeneration

Sorbent	Sulfidation Equilibrium H$_2$S Concentration with 20% Steam at 800 K (ppm)	Equilibrium Constants for SO$_2$ Regeneration			
		800 K		1,000 K	
		S$_2$ (x10^{-4})	S$_8$ (x10^{-4})	S$_2$ (x10^{-4})	S$_8$ (x10^{-4})
ZnO	3	0.17	0.51	3.3	1.1
ZnO-TiO$_2$	3	0.19	0.56	3.7	1.2
FeO	107	6.2	19.0	55.0	18.0
ZnO-Al$_2$O$_3$	1,055	61.0	183.0	316.0	100.0
FeO-Al$_2$O$_3$	3,484	202.0	605.0	717.0	227.0
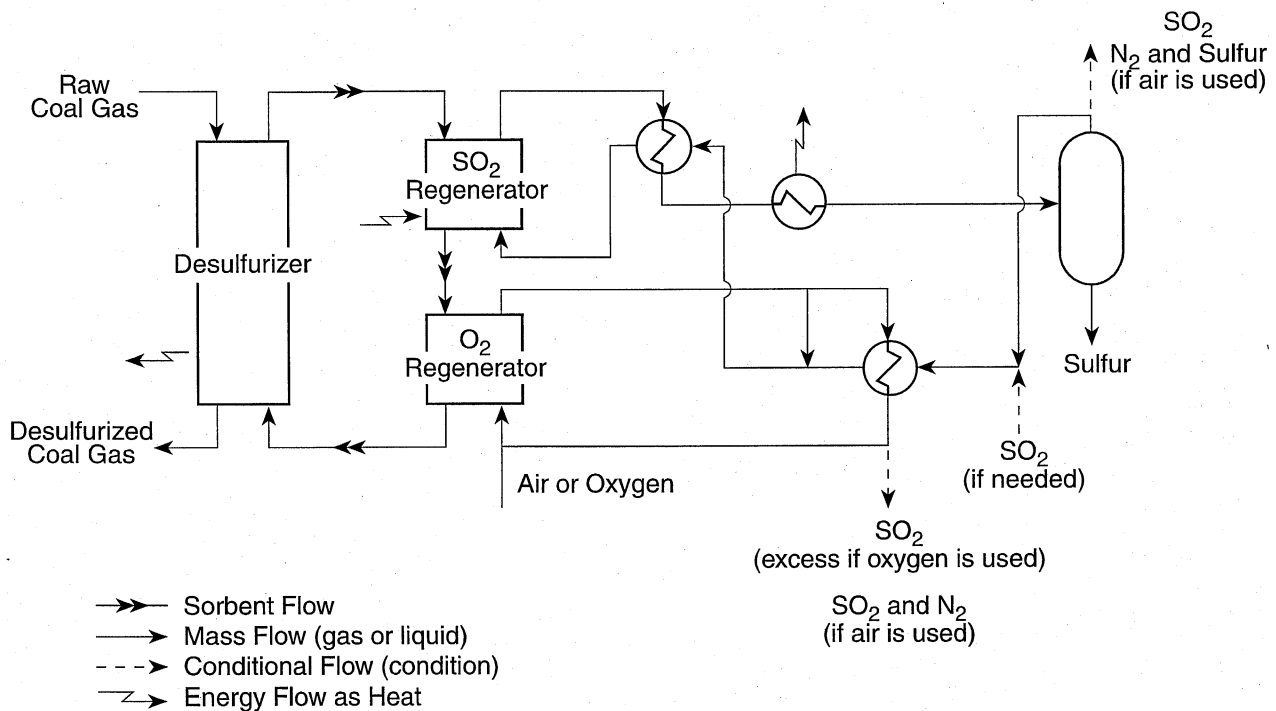
Figure 2. Three Reactor Systems for SO$_2$ Regeneration Followed by O$_2$ Regeneration

regeneration with 3.3 percent SO$_2$ in N$_2$ at up to 800 °C and 10 atm. However, iron- and zinc-iron-based sorbents showed good regeneration with SO$_2$. The rates of regeneration of the various sorbents depended on how they were prepared. Due to the proprietary nature of the preparations, no data related to the sorbent's preparation or pore structure are presented. Average regeneration rates (expressed in terms of sulfur production rate) are presented in Table 2 along with average sulfidation rates and conditions. The sulfidations were conducted using a 0.5 vol% H$_2$S containing simulated coal gas. The results suggest that SO$_2$ regeneration is a feasible approach for iron-based sorbents. Significant potential for increased SO$_2$-regeneration rates is possible by increasing the SO$_2$ concentration and pressure and by modifying sorbent properties.

Table 2. Comparison of Sulfidation and SO₂ Regeneration for Several Sorbents
(3.3 percent SO₂, 10 atm)

Sorbent Designation	Sorbent Type (P = proprietary additive)	Sulfidation Temperature (°C)	Regeneration Temperature (°C)	Sulfidation Rate ($\times10^{-4}$) (g sulfur/g sorbent/min)	Regeneration Rate ($\times10^{-4}$) (g sulfur/g sorbent/min)
L-7	Zn+Fe	550	800	10.8	2.0
RTI-3	Fe+P	450	800	19.2	18.2
FE-90	Fe	400	800	34.0	4.6
R-2	Zn+Fe	550	700	24.0	2.2
R-3	Re+P	500	700	3.8	5.8
R-4	Fe+P	500	700	2.0	4.4
R-5	Zn+Fe+P	460	00	13.4	4.4

The L-7, R-2, and R-5 sorbents did not show complete regeneration in SO₂ because the zinc portion of the sorbent did not regenerate. The iron-only-based sorbents completely regenerated in SO₂. To test the potential of SO₂ regeneration (with higher SO₂ concentrations) followed by air regeneration for zinc-iron-based sorbents, the R-5 sorbent was subjected to three cycles at 10 atm, each consisting of a sulfidation at 460 °C, a SO₂ regeneration with 3.3 to 15 percent SO₂ at 650 to 700 °C, and finally an air regeneration with 2 percent O₂ at 700 °C.

The sorbent showed consistent behavior over the three cycles of operation. The rates of sulfidation, SO₂ regeneration, and air regeneration are compared in Table 3. Results show that as SO₂ concentration is increased, regeneration can be carried out effectively at lower temperatures. Also, the various rates are not widely different and thus system design difficulty would not be very formidable.

Table 3. Comparison of Sulfidation, SO₂-Regeneration and Air-Regeneration Rates for R-5 Sorbent (Pressure = 10 atm)

Reactant	Temperature (°C)	Rate g sulfur/ (g sorbent/min)
Simulated Coal Gas (0.5% H₂S)	460	13.4
SO₂		
3.3%	700	4.4
3.3%	650	0.22
15%	650	3.7
2% O₂ in N₂	700	5[a]

[a] Result probably limited by mass transfer

Laboratory-scale tests of SO₂ regeneration were carried out with the R-5 sorbent. About 5 g of the sorbent was loaded in the reactor and fully sulfided using simulated coal gas. SO₂ regeneration was then started at 7.8 atm and 700 °C with 15 percent SO₂ in N2. Samples were withdrawn after 5.5 h and 10 h of regeneration for TGA analysis. The TGA analysis showed, as expected, that the zinc portion of the sorbent was not regenerated.

However, the iron portion of the sorbent regenerated at a rate of 2.1×10^{-4} g sulfur/ (g sorbent/min). This result is the same order of magnitude as most TGA results presented in Table 3 at 10 atm. After 10 h of operation, sulfur plugging downstream of the reactor occurred. The sulfur was removed and examined. It was found to be yellow without any kind of odor.

Based on the results, the concept of SO_2 regeneration processes shows significant promise for development as an effective hot-gas desulfurization system with sulfur recovery.

FUTURE WORK

Laboratory scale tests and TGA experiments will continue to narrow the choices for sorbents for the SO_2 regeneration concept. Feasibility demonstration with a larger reactor system will begin in the next fiscal year. Process evaluations will be carried out using the lab-scale and larger-scale data.

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APPENDIX B Advanced Sulfur Control Processing: Proceedings of the Advanced
Coal-Fired Power Systems '96 Review Meeting

Advanced Sulfur Control Processing

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Introduction

Advanced integrated gasification combined cycle (IGCC) power plants call for hot particulate removal and hot-gas desulfurization (HGD) following gasification in order to achieve high thermal efficiency. The Morgantown Energy Technology Center's (METC's) HGD research program has focused on the development of regenerable metal oxide sorbents to remove hydrogen sulfide (H_2S) from coal gas. Leading sorbents such as zinc titanate can reduce the H_2S in coal gas to low parts-per-million levels and can be regenerated using air for multicycle operation. The sulfidation-regeneration cycle for a generic metal oxide (MO) is as follows:

$$MO + H_2S \rightarrow MS + H_2O \qquad \text{(sulfidation)}$$
$$MS + {}^3/_2O_2 \rightarrow MO + SO_2 \ . \qquad \text{(regeneration)}$$

Because the regeneration reaction is highly exothermic, temperature control is required to prevent overheating and sorbent sintering. One way to control the temperature is to use a highly dilute air stream, typically containing up to 3 vol% oxygen. This would result in a tail gas containing up to 2 vol% sulfur dioxide (SO_2). More elegant methods to control exothermicity of air regeneration that could potentially produce up to 14 vol% SO_2 are being developed (Cook et al., 1992; Campbell et al. 1995). In any event, a problematic tail gas containing 2 to 14 vol% SO_2 is produced that must be disposed of. The most desirable treatment option for the tail gas is to convert the SO_2 to elemental sulfur. METC is sponsoring the development of the Direct Sulfur Recovery Process (DSRP) (Gangwal and Portzer, 1995) that uses the reducing components (H_2, CO) of coal gas to directly and efficiently reduce the SO_2 to elemental sulfur in the presence of a catalyst in one step:

$$SO_2 + 2H_2 \text{ (or 2CO)} \rightarrow 2H_2O \text{ (or } 2CO_2) + \tfrac{1}{2}S_2 \ .$$
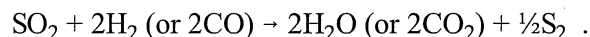
In the DSRP, for every mole of SO_2, 2 mol of reducing components are used. DSRP is a leading first generation technology and is undergoing field testing at gasifier sites. This study seeks to develop more advanced HGD approaches leading to elemental sulfur recovery in IGCC systems.


Objectives

The objective of this study is to develop a second generation HGD process that produces elemental sulfur without or with minimal use of coal gas and has better overall economics than DSRP when integrated with the overall IGCC system.
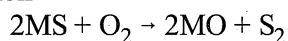
Approach

Direct production of elemental sulfur during sorbent regeneration was chosen as the approach for development of the required second generation HGD process. Concepts that were evaluated to produce elemental sulfur from sulfided sorbent included:
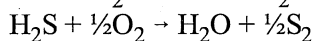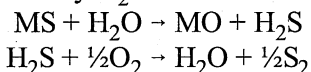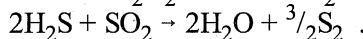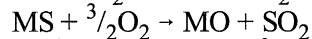
1. SO_2 regeneration

$$2MS + SO_2 \rightarrow 2MO + {}^3/_2S_2$$
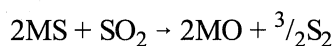
2. Substoichiometric oxidation

$$2MS + O_2 \rightarrow 2MO + S_2$$

3. Steam regeneration followed by H_2S oxidation

$$MS + H_2O \rightarrow MO + H_2S$$
$$H_2S + \tfrac{1}{2}O_2 \rightarrow H_2O + \tfrac{1}{2}S_2$$

4. Steam-air regeneration followed by Claus reaction

$$MS + H_2O \rightarrow MO + H_2S$$
$$MS + {}^3/_2O_2 \rightarrow MO + SO_2$$
$$2H_2S + SO_2 \rightarrow 2H_2O + {}^3/_2S_2 \ .$$
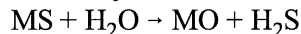
Preliminary assessment of these concepts indicated that Concept 1, SO_2 regeneration faced the fewest technical and economic problems among the four options (Gangwal et al., 1995). Elemental sulfur is the only likely product of SO_2 regeneration and the SO_2 required for the regeneration can be obtained by burning a portion of the sulfur produced. With SO_2 regeneration, sulfate formation, a major cause of sorbent decrepitation, does not occur. This should result in longer sorbent life. At high pressure, dry SO_2 is also simpler to separate from elemental sulfur than steam. Thus, recycle of unused SO_2 to the regenerator would be possible and this would be much less energy intensive than the use of steam. Efforts have thus concentrated on SO_2 regeneration.

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). The selection criteria included desulfurization efficiency, SO_2 regenerability, cost, and knowledge base. Iron was considered to be the most promising candidate among numerous metals based on the above selection criteria. Also zinc remained a candidate for consideration (primarily in combination with iron) due to its excellent desulfurization efficiency, its extensive knowledge base, and its low cost, even though ZnS showed essentially no SO_2 regenerability at temperatures of interest. In combination with iron, zinc can act as a polishing agent to remove

H_2S down to very low levels and can be regenerated using air to produce SO_2 needed for regeneration of the iron sulfide. Thermogravimetric analyzer (TGA) and lab-scale reactor testing of a number of iron-zinc sorbents demonstrated the feasibility of direct regeneration of these sorbents using SO_2 to produce elemental sulfur (Gangwal et al., 1995). This year the experimental work has progressed to the bench-scale. A number of sorbents were prepared and tested at the bench-scale over multiple cycles. Work on development and multicycle testing of attrition-resistant zinc and iron sorbents is continuing. Based on results of bench-scale testing of promising sorbents, an economic evaluation for a 300 MWe plant is to be conducted next year.

Project Description

Summary of Previous Experiments

Laboratory experiments to test the SO_2 regeneration concept were carried out using a high-pressure TGA and a high-pressure lab-scale reactor (Gangwal et al., 1995). The reactor was made of a ½-in. stainless steel tube capable of operation at 750 °C and 200 psig. 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-μm filter was used to collect sulfur. The gas finally vented through a back pressure regulator.

A number of proprietary sorbents based on iron and zinc oxides were prepared and tested for SO_2 regeneration. The benchmark zinc titanate and zinc ferrite sorbents were ZT-4 and L-7. These sorbents have been developed for fluidized-bed desulfurization incorporating air regeneration under a previous DOE contract. The sulfided ZT-4 sorbent which was based purely on ZnO as the active sorbent showed essentially no regeneration with 3.3 percent SO_2 in N_2 at up to 800 °C and 10 atm. However, sulfided iron- and zinc-iron-based sorbents showed good regeneration with SO_2. TGA rates of SO_2 regeneration ranged from 2.2×10^{-4} to 5.8×10^{-4} g sulfur/g sorbent/min with 3.3 vol% SO_2 at 700 °C and 10 atm.

A zinc-iron sorbent designated R-5 showed promising results and was tested further using the high-pressure lab-scale reactor. About 5 g of the sorbent was loaded in the reactor and fully sulfided using simulated coal gas. SO_2 regeneration was then started at 7.8 atm and 700 °C with 15 vol% SO_2 in N_2. Samples were withdrawn after 5.5 h and 10 h of regeneration for TGA analysis. As expected, the 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 2.1×10^{-4} g sulfur/g sorbent/min. This result is similar to rates with the high-pressure TGA. At the end of 10-h, sulfur plugging occurred and solid yellow sulfur was recovered downstream of the reactor.

The R-5 sorbent was also tested for SO_2 regeneration as a function of SO_2 concentration and for air regeneration. The SO_2 regeneration rate, as measured by the high pressure TGA, increased from 2.2×10^{-5} to 3.7×10^{-4} g sulfur/g sorbent/min at 650 °C and 10 atm when SO_2 concentration was increased from 3.3 to 15 vol%. The air regeneration rate at 10 atm and 700 °C was around 5×10^{-4} g sulfur/g sorbent/min with 2 vol% O_2 in N_2.

Process Concept

Based on the results presented above, the concept of SO_2 regeneration with iron- and zinc-based sorbents showed significant promise for development as an effective HGD system resulting in sulfur recovery with limited use of coal gas. A number of HGD processes could be conceptualized using alternative combinations of SO_2 and air regeneration. The similarity of air and SO_2 regeneration rates and the significant increase in SO_2 regeneration rate with SO_2 concentration were highly encouraging. It suggested that, with further increase in SO_2 concentration to 90 to 100 vol%, rates could be increased sufficiently to allow the use of even lower regeneration temperatures around 600 °C. This temperature is closer to the expected sulfidation temperature of iron sorbents which is around 450 °C. A conceptual three-reactor process based on sulfidation of iron-zinc sorbents followed by SO_2 regeneration followed by air regeneration is shown is Figure 1. The SO_2 regeneration produces sulfur from the iron portion of the sorbent and the air regeneration regenerates the zinc portion of the sorbent.

In this process concept, the sorbent from the sulfider at around 450 °C would have to be heated to around 600 °C for SO_2 regeneration. The required heat could be obtained using indirect heat exchange with coal gas which is being cooled to 450 °C, by injecting a small amount of O_2 along with SO_2 in the SO_2 regenerator, by indirect heat exchange with the sorbent being returned from the air regenerator to the sulfider, or using a convenient combination of these approaches. An alternative process concept with partial air (or O_2) regeneration of the sorbent to effect the required temperature increase and some zinc regeneration prior to SO_2 regeneration can also be visualized. A number of other process combinations are also possible but are not presented here in the interest of space.
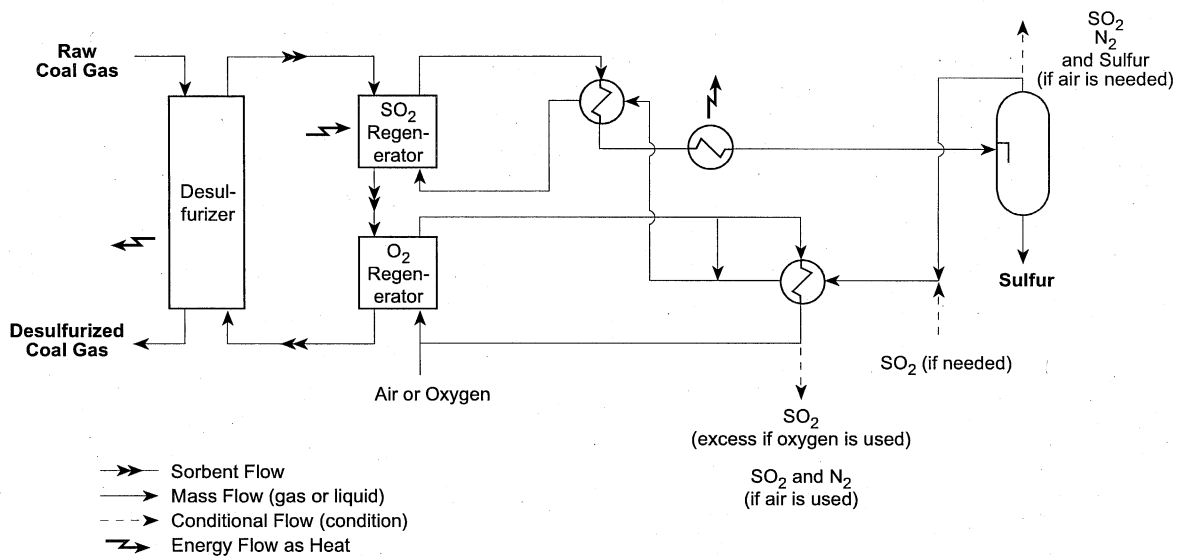
Bench-Scale Testing

Figure 1.   **Three-Reactor System for SO$_2$ Regeneration Followed by O$_2$ Regeneration**

Efforts this year have concentrated on scale-up of the R-5 sorbent preparation to

attrition-resistant fluidizable form, construction and commissioning of a high-temperature, high-pressure (HTHP) bench-scale unit and multicycle HTHP testing of the iron-zinc sorbents simulating the conceptualized three-reactor process of Figure 1.

The bench-scale reactor system which was built by modifying an existing unit is shown in Figure 2. The system has the capability of simulating a complex coal gas mixture using a set of mass flow controllers for gaseous components and a positive displacement pump for water to generate steam. The reactor can operate either as a fluidized-bed or as a fixed-bed with up to a 3-in. inside diameter sorbent cage. The pressure and temperature rating of the reactor is 400 psig at 750 °C and it is Alon-processed to reduce corrosion of the stainless steel. Reactor throughput up to 400 slpm of gas can be processed and sorbent up to 1.0 liter can be tested.

For SO_2 regeneration, pure SO_2 or SO_2 mixed with N_2 can be fed to the reactor by displacement of liquid SO_2 from a tank using a head pressure of nitrogen. Air regeneration (air line not shown in the figure) can also be carried out. Two separate reactor exits and downstream vent systems are utilized. SO_2 regeneration is conducted through a hot exit line with a sulfur condenser, catch pot, and a hot pressure control valve. This line is maintained hot to prevent sulfur plugging. Sulfidation and air regeneration are conducted through the other exit line. Gas samples are analyzed continuously for H_2S during sulfidation and SO_2 during air regeneration using Ametek continuous analyzers. Oxygen during air regeneration is measured continuously using a fuel cell-based analyzer and H_2S, COS, and SO_2 are measured intermittently during
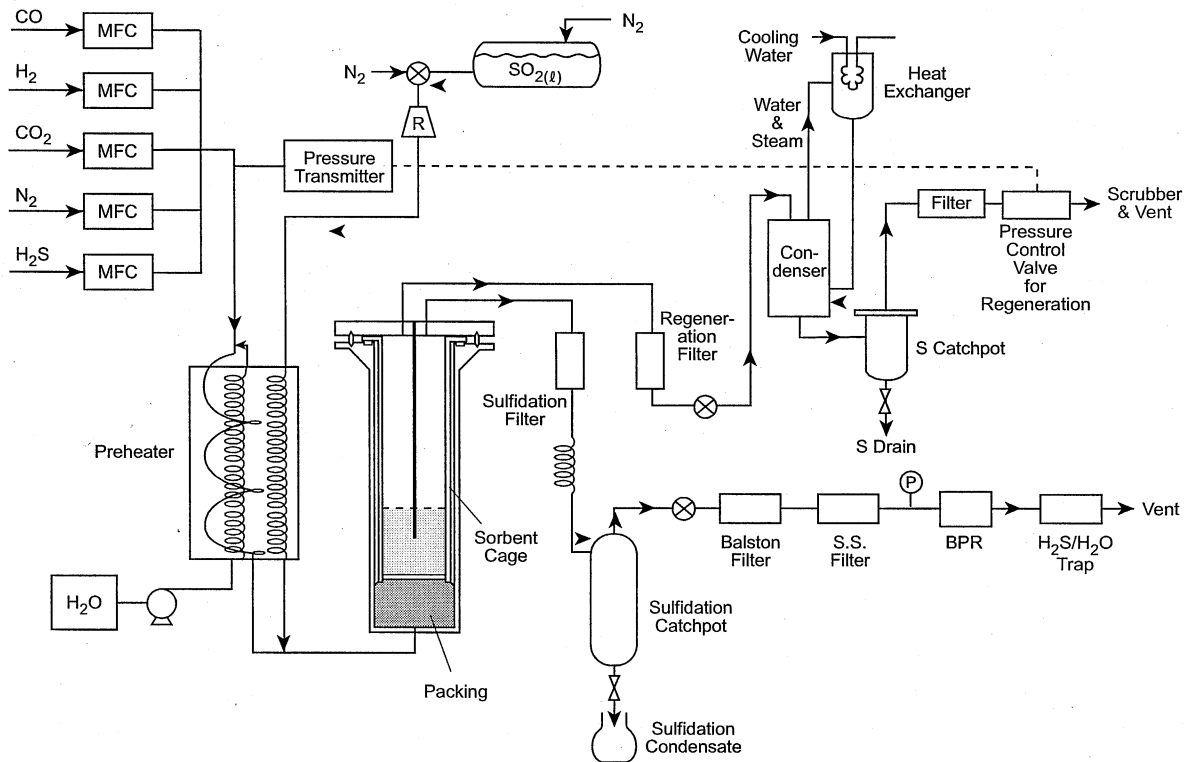

Figure 2. Bench-Scale Reactor System

sulfidation using a gas chromatograph with a flame photometric detector.

Results

Iron- and zinc-based sorbents were tested at HTHP conditions for multiple cycles. The sorbent preparation is proprietary and a patent application is pending, thus any information that could result in revealing the chemical composition and structure of the sorbents such as breakthrough curves and physical properties will not be presented. The R-5 sorbent recipe was scaled up to kilogram quantities of fluidizable attrition-resistant form with the help of a catalyst manufacturer. Two separate scale-up procedures were attempted. Using the first procedure, sorbents R-5-AWB, R-5-B, and R-5-C were produced in kilogram quantities. Using the second procedure, sorbents R-5-52, R-5-57, and R-5-58 were prepared in kilogram quantities.

R-5-B had poor attrition resistance and was immediately rejected. R-5-AWB, R-5-C, R-5-52, and R-5-58 were tested over multicycles simulating the three-reactor process of Figure 1 (R-5-57 is yet to be tested). The nominal test conditions for these multicycle tests are shown in Table 1.

The cycles typically consisted of sulfidation until breakthrough, followed by two types of regeneration. The first type of regeneration was a full air regeneration (up to 60 min) whereas the second type consisted of SO_2 regeneration (for 30 to 120 min followed by air regeneration for up to 60 min. Since a procedure for directly measuring elemental sulfur in a gas stream containing large amounts of SO_2 is yet to be developed, the amount of elemental sulfur produced during SO_2 regeneration was determined by actual measurement of the elemental sulfur that was collected or by the difference between the SO_2 produced by the two types of regeneration.

A total of 40 cycles have been run. The number of cycles completed with the various sorbents is shown in Table 2.

Table 1. Bench-Scale Test Conditions

Pressure:	275 psig	Coal gas composition (vol%)	
Flow rate:	18-75 slpm	CO:	15
Sorbent amount:	270-350 g	H_2:	10
Temperature (°C)		N_2:	Balance
Sulfidation:	420-460	CO_2:	10
SO_2 regeneration:	625	H_2O:	10-15
Dilute air regeneration:	600-650	H_2S:	0.3
SO_2 gas (vol%)		Oxidizing gas (vol%)	
SO_2:	50-65	O_2:	1-2
N_2:	Balance	N_2:	Balance

Because of the proprietary nature of the sorbents, the results presented here are of a general nature while patent protection is being sought. Generally each of the sorbents was able to reduce the H_2S to below 100 ppmv and was regenerable over multiple cycles. Also, measurable (several grams) quantities of elemental sulfur were produced during SO_2 regeneration of each of the sorbents. As much as 60 to 80 percent of the sulfur adsorbed by the sorbents has been recovered as elemental sulfur. However, the sorbents produced by the first procedure, namely R-5-AWB and R-5-C, underwent excessive loss in reactivity with cycles. In addition, they underwent significant attrition, as measured by a three-hole attrition tester, following cyclic testing. On the other hand, the sorbents prepared by the second procedure, namely R-5-52 and R-5-58, showed no loss in reactivity over the cyclic operation and also very low attrition, comparable to FCC catalysts, as measured both before and after cyclic testing by the three-hole attrition tester. In fact, the reactivity of both R-5-52 and R-5-58 improved with cycling.

Table 2. No. of Cycles Completed

Sorbent	Active metal	No. of cycles
R-5-AWB	Zn, Fe	5
R-5-C	Zn, Fe	17
R-5-52	Fe	10
R-5-58	Zn, Fe	8

Applications

As briefly discussed, the HGD process envisioned in Figure 1 or other similar processes that could result in direct production of elemental sulfur during regeneration have potential advantages over existing process options if they can be economically integrated with IGCC. The other 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 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, where the SO_2 can be obtained by burning a portion of the elemental sulfur product, is a process option that needs to be developed further.

Future Activities

Approximately 15 cycles will be completed with sorbents R-5-58 and R-5-57 each. Then one of these sorbents will be tested for up to 50 cycles to demonstrate sorbent and process durability. Based on the results of testing, an economic evaluation for a 300 MWe plant will be conducted.

Acknowledgments

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