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Advanced Sulfur Control Concepts

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DISCLAIMER

CONTRACT INFORMATION

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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

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

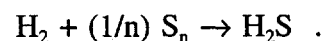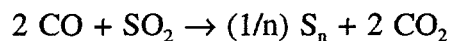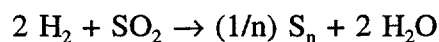### Leading Hot-Gas Desulfurization Technologies

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:

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

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

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

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 H₂S, and SO₂ 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 1/2-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 backpressure 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 SO₂ Regeneration

Like steam regeneration, SO_2 regeneration has thermodynamic constraints as the thermodynamic calculations presented later show. However,
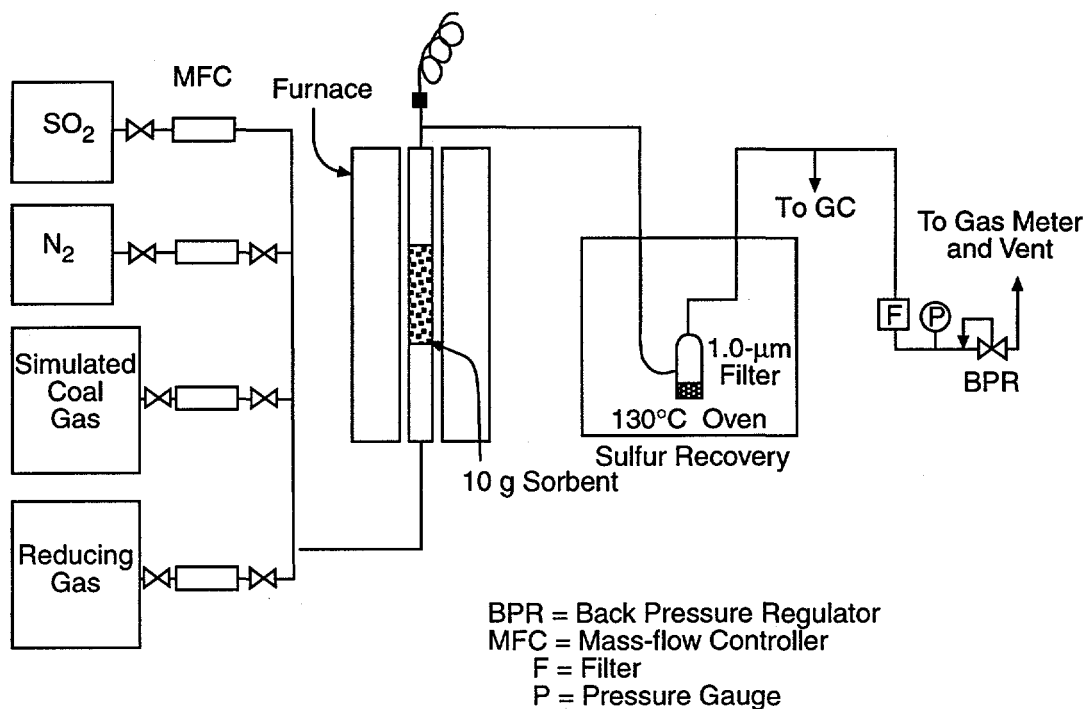
Figure 1. Laboratory-Scale SO$_2$ Regeneration Test System

high-pressure conditions are anticipated to enhance 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, non-ideal 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 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 regeneration with 3.3 percent SO_2 in N_2 at up to 800 °C and 10 atm. However, iron- and

Table 1. Thermodynamic Calculations for Sulfidation and SO_2 Regeneration

Sorbent	Sulfidation Equilibrium H_2S Concentration with 20% Steam at 800 K (ppm)	Equilibrium Constants for SO_2 Regeneration			
		800 K		1,000 K	
		S_2 ($\times 10^{-4}$)	S_8 ($\times 10^{-4}$)	S_2 ($\times 10^{-4}$)	S_8 ($\times 10^{-4}$)
ZnO	3	0.17	0.51	3.3	1.1
ZnO·TiO₂	3	0.19	0.56	3.7	1.2
FeO	107	6.2	19.0	55.0	18.0
ZnO·Al₂O₃	1,055	61.0	183.0	316.0	100.0
FeO·Al₂O₃	3,484	202.0	605.0	717.0	227.0

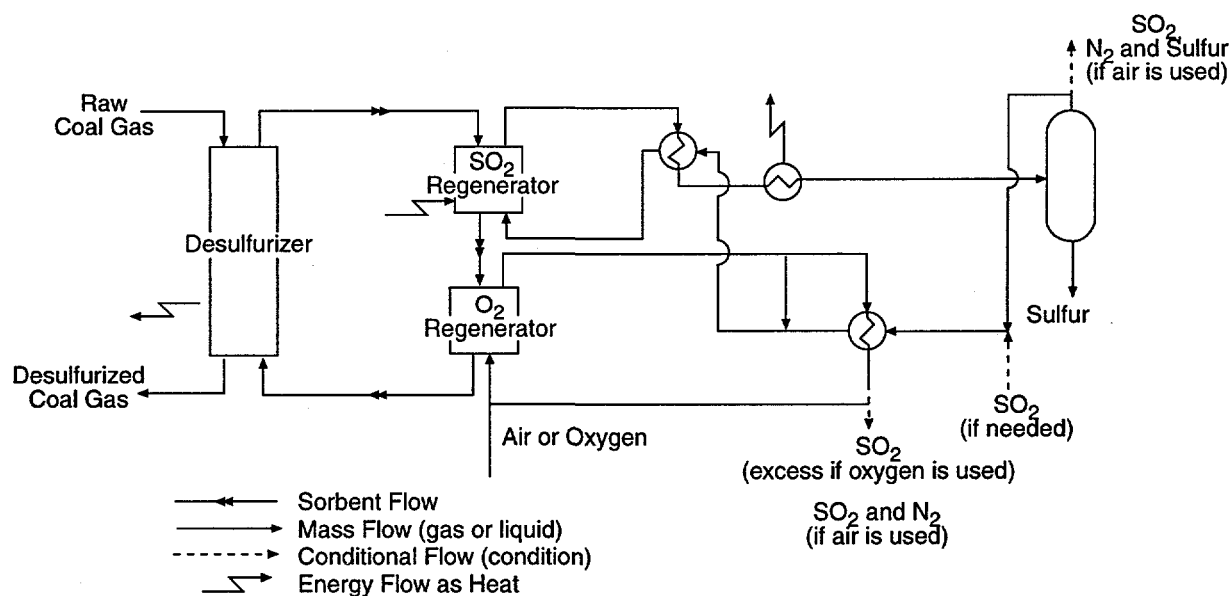

Figure 2. Three Reactor Systems for SO_2 Regeneration Followed by O_2 Regeneration

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_2S 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

**Table 2. Comparison of Sulfidation and SO_2 Regeneration for Several Sorbents
(3.3 percent SO_2, 10 atm)**

Sorbent Designation	Sorbent Type (P = proprietary additive)	Sulfidation Temperature (°C)	Regeneration Temperature (°C)	Sulfidation Rate ($\times 10^{-4}$) (g sulfur/g sorbent/min)	Regeneration Rate ($\times 10^{-4}$) (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	Fe+P	500	700	3.8	5.8
R-4	Fe+P	500	700	2.0	4.4
R-5	Zn+Fe+P	460	700	13.4	4.4

possible by increasing the SO_2 concentration and pressure and by modifying sorbent properties.

The L-7, R-2, and R-5 sorbents did not show complete regeneration in SO_2 because the zinc portion of the sorbent did not regenerate. The iron-only-based sorbents completely regenerated in SO_2. To test the potential of SO_2 regeneration (with higher SO_2 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 SO_2 regeneration with 3.3 to 15 percent SO_2 at 650 to 700 °C, and finally an air regeneration with 2 percent O_2 at 700 °C.

The sorbent showed consistent behavior over the three cycles of operation. The rates of sulfidation, SO_2 regeneration, and air regeneration are compared in Table 3. Results show that as SO_2 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, SO_2-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% H_2S)	460	13.4
SO_2		
3.3%	700	4.4
3.3%	650	0.22
15%	650	3.7
2% O_2 in N_2	700	5[a]

[a] Result probably limited by mass transfer.

Laboratory-scale tests of SO_2 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. SO_2 regeneration was then started at 7.8 atm and 700 °C with 15 percent SO_2 in N_2. 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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