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Advanced Sulfur Control Processing

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Abstract

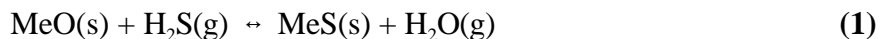
The primary objective of this project is to determine the feasibility of an alternate concept for the regeneration of high temperature desulfurization sorbents in which elemental sulfur, instead of SO₂, is produced. If successful, this concept will eliminate or alleviate problems caused by the highly exothermic nature of the regeneration reaction, the tendency for metal sulfate formation, and the need to treat the regeneration off-gas to prevent atmospheric SO₂ emissions.

Iron and cerium-based sorbents were chosen on the basis of thermodynamic analysis to determine the feasibility of elemental sulfur production. The ability of both to remove H₂S during the sulfidation phase is less than that of zinc-based sorbents, and a two-stage desulfurization process will likely be required.

Preliminary experimental work used electrobalance reactors to compare the relative rates of reaction of O₂ and H₂O with FeS. More detailed studies of the regeneration of FeS as well as the sulfidation of CeO₂ and regeneration of Ce₂O₂S are being carried out in a laboratory-scale fixed-bed reactor equipped with a unique analytical system which permits semi-continuous analysis of the distribution of elemental sulfur, H₂S, and SO₂ in the reaction product gas.

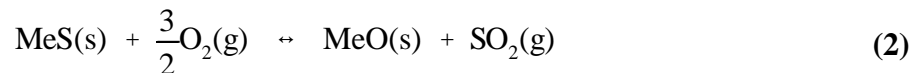
Introduction

High temperature desulfurization of coal-derived gas is an important component in the development of the integrated gasification combined cycle (IGCC) process for electric power generation. A number of metal oxide sorbents are capable of reacting with H₂S. The generic desulfurization reaction may be represented as follows:



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The sorbent must be regenerable and must maintain activity and structural integrity through many sulfidation-regeneration cycles. The standard reaction used for regeneration is as follows:



In addition to the obvious problem of SO₂ control in the product gas, the highly exothermic nature of the reaction creates temperature control problems which may accelerate the deterioration of the high surface area, porous sorbent. Decreasing the O₂ content of the regeneration feed gas to assist in temperature control will also reduce the SO₂ content of the product gas and complicate the SO₂ control problem. Finally, the combination of SO₂ and O₂ favors the formation of stable metal sulfates which, particularly in zinc-based sorbent systems, are believed to be a major contributor to sorbent pellet fragmentation and spalling.

The direct production of elemental sulfur during sorbent regeneration would eliminate or alleviate all of these problems. In addition, elemental sulfur is a marketable by-product which can be safely and economically stored and transported.

Project Description

The project began with a literature search to identify possible concepts for the direct production of elemental sulfur during sorbent regeneration. The literature search was followed by a detailed thermodynamic analysis to determine the feasibility of sulfur formation using a number of metal oxides known to have high temperature desulfurization capability. Results of the literature search and thermodynamic analysis have been reported (Harrison et al., 1995), and only a brief summary is presented here.

Three possible concepts for elemental sulfur formation were identified: (1) partial oxidation in a steam-oxygen atmosphere under oxygen-starved conditions, (2) reaction with SO₂, and (3) reaction with steam to produce H₂S concentrations suitable for conversion to elemental sulfur in a Claus unit. The thermodynamic analysis showed that metal oxides having the strongest affinity for H₂S in the sulfidation phase (e.g., ZnO) were least conducive to elemental sulfur production during regeneration. The thermodynamic properties of CeO₂, SnO₂ and, to a lesser degree, Fe₂O₃ provide a unique combination of H₂S removal capability and the potential for elemental sulfur production.

The regeneration of FeS using the partial oxidation concept, and the sulfidation of CeO₂ followed by regeneration of Ce₂O₂S using all three of the regeneration concepts are being studied in the experimental phase of the program. The experimental studies are designed to determine reaction conditions -- temperature, pressure, regeneration gas composition and flow rate -- which maximize the production of elemental sulfur.

Preliminary FeS regeneration experiments used an electrobalance reactor to compare the relative rates of reaction of O₂ and H₂O with FeS. More detailed studies of FeS regeneration

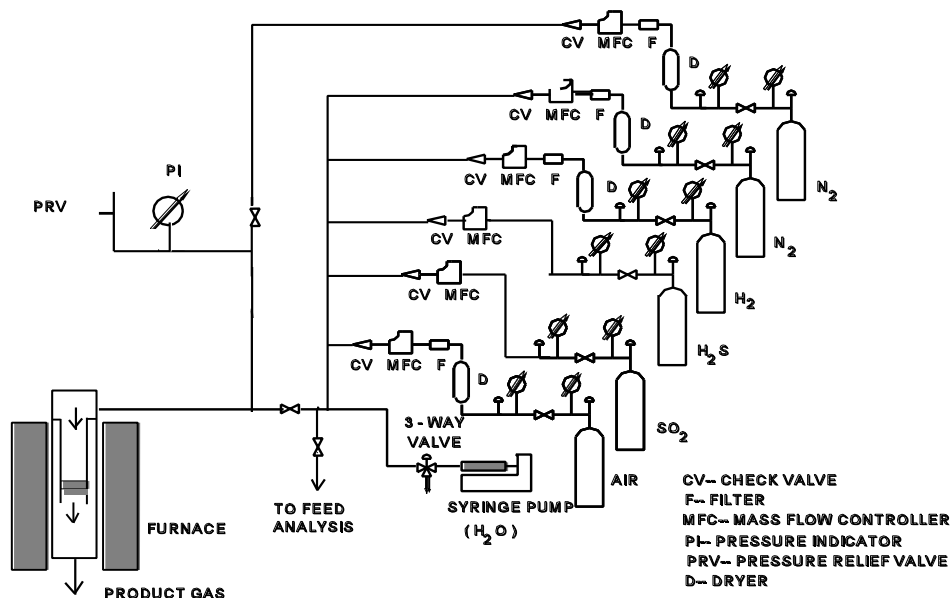


Figure 1. Schematic Diagram of the Fixed-Bed Reactor System

as well as CeO_2 sulfidation and Ce_2O_3 regeneration are being carried out in a laboratory-scale fixed-bed reactor. Conversion of 2CeO_2 to Ce_2O_3 does not involve a change in solid mass so that all cerium studies are limited to the fixed-bed reactor.

A schematic diagram of the fixed-bed reactor system is shown in Figure 1. Inert and reactive gases are obtained from high purity cylinders and their flow rates are controlled by high pressure mass flow controllers. Water is fed as a liquid using a high-pressure syringe pump, and gas feed lines are preheated to insure that the water is completely vaporized and mixed with other gases before entering the reactor. Combined gases enter near the top of the pressure vessel and flow downward over the sorbent which is contained in the reactor insert tube. The reactor is capable of operating at temperatures and pressures to about 800°C and 15 atm.

The unique gas analytical train, which provides semi-continuous analysis of the sulfur species in the product gas, is shown in Figure 2. The reactor product, which must be maintained above the condensation temperature of elemental sulfur, is split into two streams, with one portion flowing through a capillary flow restrictor into an oxidation chamber where all sulfur compounds are converted to SO_2 . From the oxidation chamber, the gases flow through a UV-fluorescence detector where the total sulfur content of the reactor product is measured. The sample flow rate through this leg of the analytical train is determined by the resistance of the capillary restrictor and the reactor pressure. Frequent recalibration of the flow through the capillary restrictor and the UV-fluorescence detector response are required.

The remainder of the reactor product flows through a condenser and series of filters for removal of water and elemental sulfur, through a back pressure regulator which establishes the reactor pressure, and to a gas chromatograph where the SO_2 and H_2S concentrations of the

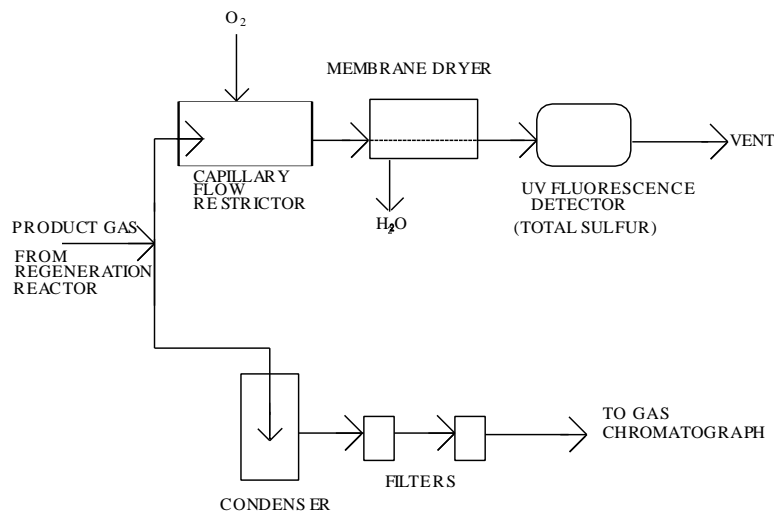


Figure 2. Product Gas Analysis Train

product gas are determined. Although this analytical method involves the determination of elemental sulfur by difference (total sulfur - H_2S - SO_2), it provides acceptable accuracy when sufficiently large quantities of elemental sulfur are present.

The gas and water feed systems for the electrobalance reactor are analogous to those of the fixed-bed reactor. The operating temperature and pressure limits are also the same. The difference is that the progress of the reaction in the electrobalance is followed by monitoring the change in mass of the solid reactant. Product gas composition is not monitored, and for this reason, the use of the electrobalance is largely limited to systems in which a single gas-solid reaction having known stoichiometry occurs.

Experimental Results

Electrobalance Studies

The electrobalance reactor was used in preliminary studies to compare the rates of reaction between O_2 -FeS and H_2O -FeS as a function of temperature (600-800°C), pressure (1-15 atm), and reactive gas composition (0.5 to 3.0% O_2 in N_2 and 10 to 50% H_2O in N_2). Complete regeneration of FeS to Fe_2O_3 in O_2 runs and to Fe_3O_4 in H_2O runs was achieved except in certain low temperature-high pressure runs where some $\text{Fe}_2(\text{SO}_4)_3$ was formed. Much of the data analysis was based upon the initial global reaction rate which was found to be first order in either O_2 or H_2O , only weakly dependent on temperature, and to decrease at high pressure. The rate of the reaction of FeS with O_2 was much faster than with H_2O as shown by the dimensionless mass versus time results in Figure 3. In spite of the fact that the H_2O concentration was 3.3 times greater than the O_2 concentration, the reaction required about 10 times as long to approach completion in H_2O .

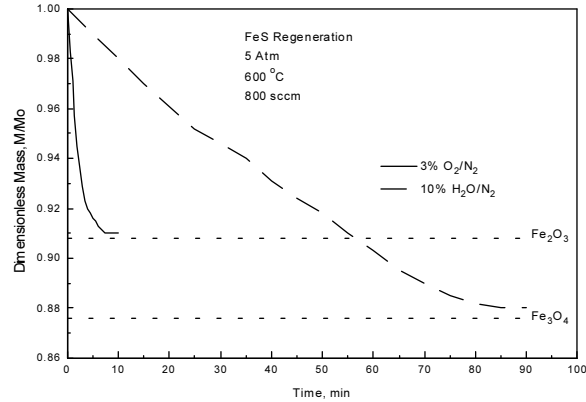


Figure 3. Comparison of the Reaction Rates of O₂ and H₂O with FeS

Initial reaction rates were correlated as a function of temperature and mol fraction of reactive gas to produce a rate equation of the form

$$r_i = k_{oi} \exp(-E_i/RT) y_i \quad (3)$$

r_i is the initial time rate of change of dimensionless mass, k_o is the frequency factor, E the activation energy, R the gas constant, T the absolute temperature, and y the mol fraction of reactive gas. The subscript i represents the reactive gas, either O₂ or H₂O. Table 1 presents the frequency factors and activation energies for both reactions at 15 atm, and compares the initial rates of the two reactions at equal reactive gas mol fractions as a function of temperature. In spite of the higher activation energy for the FeS-H₂O reaction, the initial rate was still more than two orders of magnitude larger in O₂ at the maximum temperature of 800 °C.

When O₂ and H₂O were both present in the feed gas, the initial regeneration rate was equal to the sum of the individual rates. This is illustrated in Figure 4 for a series of tests at 700 °C in which y_{H_2O} was held constant at 0.30, while y_{O_2} and pressure were varied between 0.0005 and 0.005 and 1 and 15 atm, respectively. The discrete points represent the measured initial reaction rates while the straight lines were calculated by summing the pure component initial rates using eqn.(3) and the appropriate values of k_{oi} , E_i , and y_i . This figure also shows the unexpected effect of pressure with an increase in initial rate from 1 to 5 atm, and then a decrease between 5 and 15 atm.

Fixed-Bed Reactor Studies

FeS Regeneration.

The regeneration of FeS is being studied using the partial oxidation concept, with key reaction parameters of temperature, pressure, and gas flow rate and composition.

Table 1. Parameters in the Initial Rate Equation for the Regeneration of FeS in O₂ and H₂O (P=15 atm)

$$r_i = k_{oi} \exp(-E_i/RT) y_i$$

Reacting Gas	k_{oi} (min ⁻¹)	E_i (cal/mol)
O ₂	4.65	1440
H ₂ O	1.52	9700

Ratios of Initial Rates at Equal y_i	r_{O_2}/r_{H_2O}
600	366
700	219
800	147

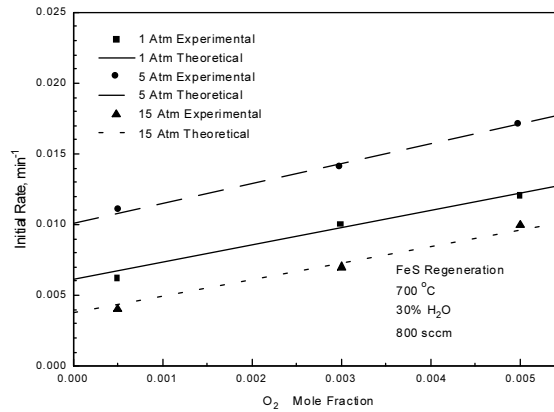


Figure 4. Initial Rate of Regeneration of FeS in O₂-H₂O-N₂

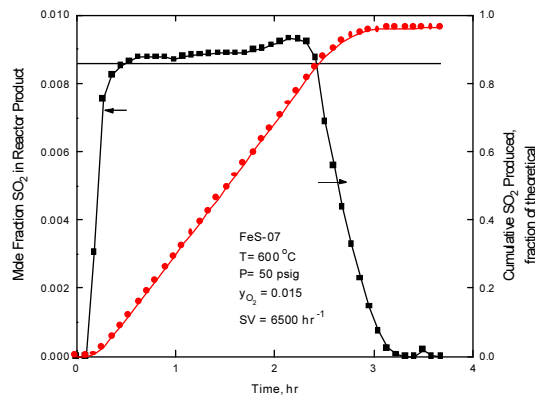
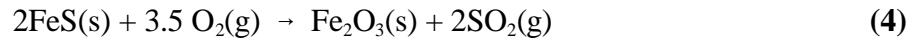


Figure 5. Fixed-Bed Reactor Response for the Regeneration of FeS With O₂

The results of an FeS regeneration run at 600°C and 4.4 atm with the feed gas containing 1.5% O₂/balance N₂ are shown in Figure 5. The mol fraction SO₂ in the reactor product and the cumulative amount of sulfur produced, expressed as a fraction of stoichiometric sulfur, are plotted versus time. SO₂ is the only sulfur compound which should be formed at these regeneration conditions, and product gas analysis was determined by gas chromatography. The horizontal line at y_{SO₂}= 0.0086 represents the stoichiometric maximum SO₂ mol fraction associated with complete conversion of the 1.5% O₂ according to the equation



After a brief time delay, the SO₂ content of the product gas increased to a value slightly above theoretical, remained relatively constant for about 2 hours, and then decreased to zero after about 3 hours. The cumulative production of SO₂ increased linearly during the time that the SO₂ content of the product gas was constant, and reached 96% of theoretical by the end of the run.

In contrast, the rate of the reaction between steam and FeS is much smaller, and the H₂S content of the product gas during a steam regeneration experiment is much less than the stoichiometric value. This is shown in Figure 6 where the mol fraction of H₂S in the regeneration product gas as well as the cumulative amount of sulfur produced, again expressed as a fraction of the stoichiometric sulfur, is plotted versus time. Again, gas chromatography was used for product gas analysis as H₂S was the only sulfur compound expected. In this test the H₂S content gradually increased for the first hour, and reached a steady-state value of about 0.0015 mol fraction after that time. The steady-state mol fraction is only about 2% of the stoichiometric value associated with 0.10 mol fraction steam in the feed gas. Only about 16% of the sulfur originally present as FeS was accounted for in the H₂S product when the run was terminated after 2.5 hours.

The production of elemental sulfur from FeS using the partial oxidation regeneration concept requires that the feed gas contain both O₂ and steam. Results from a partial oxidation regeneration test in which the feed gas contained 10% H₂O, 1.5% O₂ in N₂ are shown in Figure 7. H₂S and SO₂ were detected by the chromatograph at about the same time that total sulfur was detected by the UV analyzer. H₂S mol fraction increased quickly to about 0.0011, remained near that level for about 1.5 hours, and then slowly decreased to zero after about 2.25 hours. SO₂ mol fraction increased quickly to about 0.006, slowly increased to about 0.0077 over the next two hours, then decreased steadily to zero after about 3.25 hours. The gradual increase in SO₂ mol fraction corresponded quite well with the gradual decrease in H₂S. The mol fraction of total sulfur was approximately constant near 0.008 between 0.5 and 2.25 hours, after which the decrease in total sulfur closely matched the decrease in SO₂. The cumulative production of total sulfur was approximately equal to the sum of the SO₂ and H₂S production, indicating good closure of the sulfur material balance, and also that little elemental sulfur was formed at these conditions. The absence of elemental sulfur was not unexpected because a much higher ratio of steam-to-oxygen should be required for significant elemental sulfur formation.

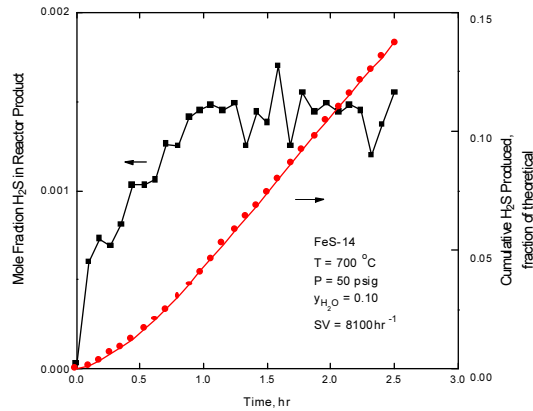


Figure 6. Fixed-Bed Reactor Response for the Regeneration of FeS With H₂O

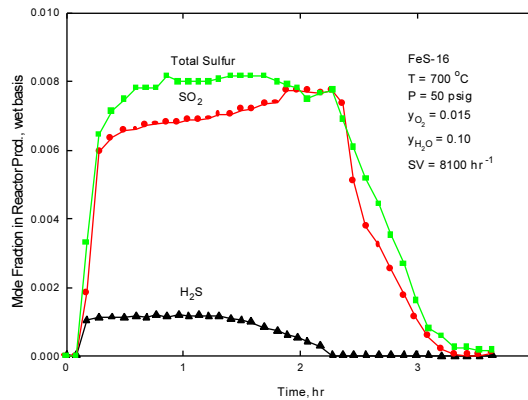


Figure 7. Fixed-Bed Reactor Response for the Partial Oxidation Regeneration of FeS (H₂O:O₂ = 3.3:1)

Increasing the H₂O to O₂ ratio in the regeneration feed gas results in the production of significant quantities of elemental sulfur as shown in Figure 8. FeS was reacted at 600 °C and 4.4 atm with a feed gas containing 20% H₂O, 0.25% O₂, and balance N₂ (a H₂O to O₂ ratio of 80 to 1). The H₂S concentration peaked at about .0006 mol fraction after about 1.5 hours and gradually decreased to near zero after 5.2 hours. The SO₂ mol fraction remained near zero for 1 hour, gradually increased to a maximum of 0.0007 at 5.5 hours, and was about 0.0001 when the run was terminated. It is significant that the maximum SO₂ mol fraction was only about 50% of the stoichiometric maximum associated with 0.0025 mol fraction O₂ in the feed gas. In other runs such as shown in Figure 5 in which the reactor feed gas contained only O₂, the SO₂ concentration in the product gas was always near the stoichiometric maximum. Similarly, the maximum H₂O mol fraction was only about 0.4% of the stoichiometric maximum, compared to typical values of about 2% of the stoichiometric maximum when H₂O was the only reactive gas in the reactor feed.

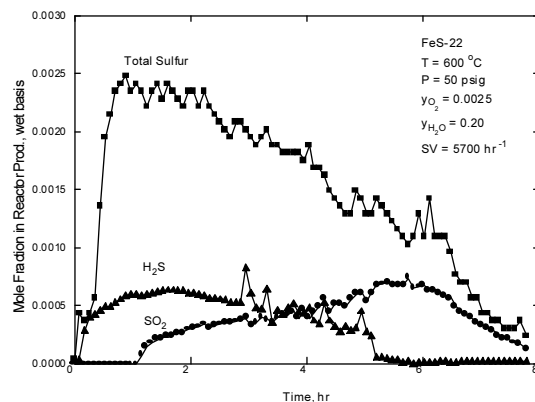


Figure 8. Fixed-Bed Reactor Response for the Partial Oxidation Regeneration of FeS
($\text{H}_2\text{O}:\text{O}_2 = 80:1$)

The areas under the respective curves are proportional to the quantities of H_2S , SO_2 and total sulfur produced. Of the sulfur originally present as FeS, approximately 22% was produced as H_2S and 24% as SO_2 . The area under the total sulfur curve represented 99% of the original sulfur charge so that about 50% of the sulfur produced was in elemental form.

We expect to be able to increase the proportion of elemental sulfur by further increasing the H_2O to O_2 ratio, decreasing the space velocity, and decreasing the reaction temperature.

CeO_2 Sulfidation and $\text{Ce}_2\text{O}_2\text{S}$ Regeneration.

Both the sulfidation and regeneration cycles must be carried out experimentally because $\text{Ce}_2\text{O}_2\text{S}$ is not commercially available. Sulfidation tests have been plagued by "over-sulfidation" in that the total quantity of H_2S removed from the feed gas exceeded the stoichiometric maximum associated with conversion of CeO_2 to $\text{Ce}_2\text{O}_2\text{S}$. The problem was attributed initially to further sulfidation of $\text{Ce}_2\text{O}_2\text{S}$ to Ce_2S_3 which was thermodynamically feasible in the feed gas containing only N_2 , H_2 , and H_2S . However, the addition of steam, which according to thermodynamics should prevent Ce_2S_3 formation, did not solve the problem. It soon became clear that the "over-sulfidation" was caused by reaction between H_2S and the walls of the reactor vessel. Apparently, the aluminized coating on the stainless steel was either ineffective at the reaction conditions or had deteriorated to the point that it no longer offered protection. A new quartz reactor insert has been designed, and, at the time of this writing, is being fabricated.

Although no quantitative information on elemental sulfur production during regeneration is available, limited qualitative results are encouraging. In run CeO_2 -06r, a mixture of CeO_2 and $\text{Ce}_2\text{O}_2\text{S}$ (unknown proportions) was regenerated at 750°C and 5 atm with the feed gas containing 1% O_2 in N_2 . The regeneration lasted for about 1 hour and had to be terminated due elemental sulfur plugging the product line. Effectively all of the sulfur produced prior to plugging was in elemental form as

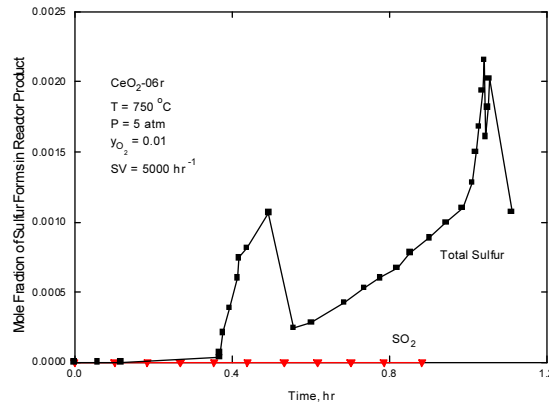
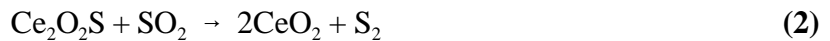


Figure 9. Fixed-Bed Reactor Response for the Regeneration of $\text{Ce}_2\text{O}_2\text{S}$

shown in Figure 9. No SO_2 or H_2S was detected using the GC while the mol fraction of total sulfur (= elemental sulfur) reached 0.002 just prior to the end of the run.

The formation of elemental sulfur at these conditions can be explained on the basis of the following pair of reactions



The first reaction should dominate near the entrance to the reactor where oxygen is plentiful. In downstream sections of the reactor, the oxygen will be depleted leaving SO_2 to react with $\text{Ce}_2\text{O}_2\text{S}$ and produce elemental sulfur.

Improvements have been made in the condenser and filters since this time so that plugging problems have been greatly reduced. Additional cerium tests are now awaiting the quartz reactor insert.

Applications

One of the major problems facing hot gas desulfurization processes is the proper control and disposal of sulfur compounds in the regenerator off-gas. The G.E. moving-bed process is designed to produce an off-gas containing SO_2 at concentrations suitable for conversion to sulfuric acid (Bevan et al., 1995). However, in many instances the location of the power plant will not correspond to the location of existing H_2SO_4 plants or markets. Long distance transportation of H_2SO_4 is both hazardous and expensive. When a fluidized-bed gasifier is used, in-bed bulk sulfur removal may be accomplished by limestone or dolomite injection. The off-gases from the regeneration phase of the polishing desulfurization step may be recycled to the gasifier for ultimate conversion to CaSO_4 (Ghazanfari et al., 1995). However, this option is not applicable to all gasification processes, and creates immense land disposal problems. Successful development of the

direct sulfur recovery process (DSRP) (Gangwal and Portzer, 1995) for reducing the SO₂ in dilute gases to elemental sulfur will solve the disposal problem, but with the penalty of adding an additional chemical processing step to the power plant and reducing the flow of clean coal gas by the amount required to reduce the SO₂. Clearly the direct production of elemental sulfur during sorbent regenerator is the preferred option.

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