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**Advanced Sulfur Control Concepts**

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**ABSTRACT**

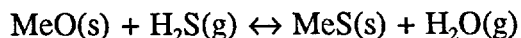
The primary objective of this study is the direct production of elemental sulfur during the regeneration of high temperature desulfurization sorbents. Three possible regeneration concepts were identified as a result of a literature search. The potential for elemental sulfur production from a number of candidate metal oxide sorbents using each regeneration concept was evaluated on the basis of a thermodynamic analysis. Two candidate sorbents, Fe<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>, were chosen for experimental testing.

The experimental test program using both electrobalance and fixed-bed reactors is now getting underway. The objective is to determine reaction conditions - temperature, pressure, space velocity, and regeneration feed gas composition-- which will maximize the yield of elemental sulfur in the regeneration product gas.

Experimental results are to be used to define a conceptual desulfurization-regeneration process and to provide a preliminary economic evaluation.

**BACKGROUND INFORMATION**

High temperature desulfurization of coal-derived gas is an important component in the integrated gasification combined cycle (IGCC) process for electric power generation. A number of metal oxide sorbents which are capable of reacting with H<sub>2</sub>S and reducing the outlet H<sub>2</sub>S concentration to acceptable levels have been studied. The generic desulfurization reaction may be represented by the following:



For the process to be economical, the sorbent must be regenerable and must maintain activity through many sulfidation-regeneration cycles. Most regeneration studies to date have used total oxidation in which the metal sulfide is reacted with oxygen to regenerate the metal oxide and liberate the sulfur as SO<sub>2</sub>. In addition to the problem of controlling SO<sub>2</sub> in the regenerator off-gas, the highly exothermic total oxidation reaction creates reactor temperature control problems which may accelerate the deterioration of the high surface area, porous sorbent. Decreasing the oxygen concentration of the regeneration gas to assist in temperature control reduces the SO<sub>2</sub> concentration in the regeneration product and complicates the SO<sub>2</sub> control.

Direct production of elemental sulfur during sorbent regeneration would alleviate both problems. Elemental sulfur is a marketable by-product which can be separated by condensation and safely stored and transported.

## PROJECT DESCRIPTION

Three concepts for the possible formation of elemental sulfur were identified from the literature. Thermodynamic analysis showed that sorbents having the strongest affinity for H<sub>2</sub>S removal, e.g., ZnO, would be less conducive to elemental sulfur production than oxides which are less effective for H<sub>2</sub>S removal. Other factors considered during the thermodynamic analysis were carbon deposition from the coal gas, the stability of the metal oxide in the reducing coal gas, the tendency for metal sulfate to be formed during regeneration, and the possible production of volatile reactants or products during both the reduction/desulfurization and regeneration cycles.

Experimental studies using the oxides of iron and cerium for high temperature desulfurization are getting underway. The objective of these studies is to determine reaction conditions--temperature, pressure, regeneration gas composition and space velocity, and sorbent

composition and properties--which maximize the production of elemental sulfur during regeneration. One unique feature involves the development of an analytical system to permit real-time analysis of the sulfur species in the regeneration gas product.

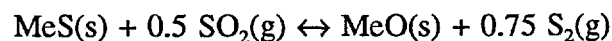
The experimental results will be used to define a conceptual desulfurization-regeneration process suitable for IGCC application. Material and energy balance calculations will be carried out and a preliminary economic evaluation will be performed. This paper summarizes the results of the literature search and thermodynamic analysis, and briefly describes the experimental plans.

## RESULTS--REGENERATION CONCEPTS

Three possible elemental sulfur production concepts were identified from the literature. The general chemistry of each as well as a brief summary of the literature is presented below.

### Reaction With SO<sub>2</sub>

The generic reaction between metal sulfide and SO<sub>2</sub> to yield elemental sulfur is:

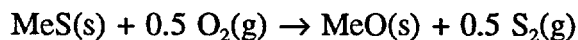


Copeland et al. (1994) have studied the regeneration of SnS(s) while Anderson and Berry (1987) have reported on the regeneration of a sulfided cobalt titanate sorbent. Several studies (Schrodt and Best, 1978; Tseng et al., 1981; Patrick et al., 1993) have examined the regeneration of sulfided iron oxide. Primary questions concern the rate of reaction between metal sulfide and SO<sub>2</sub> and thermodynamic limitations on the maximum partial pressure of S<sub>2</sub>(g) in the regeneration product.

### Partial Oxidation

The formation of elemental sulfur when metal sulfide is reacted with oxygen and steam

under "O<sub>2</sub>-starved" conditions is referred to as partial oxidation. The general stoichiometric reaction is:

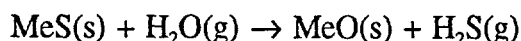


In reality, this stoichiometry represents the net result of a number of simultaneous reactions. In the presence of excess oxygen, total oxidation would occur with MeO(s) and SO<sub>2</sub>(g) as the primary products.

Several references suggest that partial oxidation to produce elemental sulfur may be possible. Joshi et al. (1979), Grindley and Steinfeld (1981), and Van der Waal (1987) have studied the partial oxidation of sulfided iron-based sorbents. As much as 75% of the sulfur released during regeneration was in elemental form, with most of the remainder as H<sub>2</sub>S. Kay and Wilson (1989) and Kay et al. (1993) have reported that elemental sulfur is formed during the regeneration of cerium oxysulfide, Ce<sub>2</sub>O<sub>2</sub>S, at conditions similar to those used for FeS regeneration.

### Reaction With H<sub>2</sub>O/Claus

By reversing the primary desulfurization reaction, regeneration to H<sub>2</sub>S is possible according to the generic reaction:



Although elemental sulfur is not a direct product, H<sub>2</sub>S may be converted to elemental sulfur by the Claus reaction if the H<sub>2</sub>S concentration is sufficiently high. Since regeneration with steam is the reverse of the desulfurization reaction, it is obvious that sorbents having the greatest affinity for H<sub>2</sub>S will be the most difficult to regenerate.

Nielsen et al. (1991) report H<sub>2</sub>S mol fractions in the regeneration product as high as 0.25 when SnS(s) was reacted with H<sub>2</sub>O. H<sub>2</sub> is also produced by this reaction and a separation step is required to recover H<sub>2</sub>S from the excess steam and H<sub>2</sub> by-product. Tamhankar et al.

(1985) and Wakker et al. (1993) have studied the regeneration of sulfided iron-based sorbents with steam while Sohn and Kim (1987) have studied the steam regeneration of ZnS.

### RESULTS--THERMODYNAMIC ANALYSIS

Thermodynamic analysis was used to evaluate the potential of selected metal oxide sorbents to remove H<sub>2</sub>S from Texaco and KRW coal gases, and the feasibility of producing elemental sulfur during regeneration using the concepts previously described.

The free-energy minimization program CHEMQ was used (Kirkpatrick and Pike, 1994). Implementation of CHEMQ requires that the composition of the initial mixture (which may include gaseous, liquid, and solid species) and the temperature and pressure be specified. The CHEMQ data base is searched and all species whose elements are present in the initial mixture are considered as possible components of the equilibrium mixture. The number of mols of each component which minimizes the free energy of the system subject to the elemental material balance constraint established by the initial mixture is then calculated.

Although the initial CHEMQ data base contained 1322 species, several species of interest were not included. Therefore, free energy data from Barin et al. (1993) for 52 compounds including a number of the gaseous sulfur allotropes, and metal compounds of cerium, cobalt, manganese, and molybdenum were added to the data base. Data for a single compound of interest, Ce<sub>2</sub>O<sub>2</sub>S(s), were taken from Kay et al. (1993) since that compound was missing from the compilation of Barin et al.

### Reduction/Desulfurization Cycle Analysis

Coal gas compositions representing a Texaco oxygen-blown gasifier and a KRW air-blown gasifier were considered (see Table 1). The

**Table 1.**  
**Composition of the Texaco Oxygen-Blown**  
**and KRW Air-Blown Gasifier Products**

|                                | Composition, mol% |       |
|--------------------------------|-------------------|-------|
|                                | Texaco            | KRW   |
| H <sub>2</sub>                 | 31.06             | 10.0  |
| CO                             | 39.87             | 15.0  |
| H <sub>2</sub> O               | 16.81             | 15.0  |
| CO <sub>2</sub>                | 10.62             | 5.0   |
| H <sub>2</sub> S               | 1.04              | 1.0   |
| N <sub>2</sub>                 | -----             | 54.0  |
| NH <sub>3</sub>                | 0.21              | ----- |
| CH <sub>4</sub>                | 0.31              | ----- |
| $\frac{H_2 + CO}{H_2O + CO_2}$ | 2.59              | 1.25  |
| $\frac{C}{O + H}$              | 0.29              | 0.22  |

ratios of  $[(H_2 + CO)/(H_2O + CO_2)]$  and  $[C/(O + H)]$  found at the bottom of Table 1 show that the Texaco gas is more highly reducing and exhibits a greater tendency for carbon deposition, which implies that the operating window for a particular sorbent will be different in different coal gases.

The reduction/desulfurization analysis was carried out by determining the composition resulting from "equilibrating" one mol of metal oxide sorbent in its highest oxidation state with 10 mol of coal gas at selected temperatures and pressures. This initial mixture provided a large excess of metal oxide to H<sub>2</sub>S and of reducing gas to metal oxide. This approach permitted the simultaneous determination of the oxidation state of the excess sorbent, the nature of the sulfided species, and the possible formation of molten or volatile metal species, as well as the potential of the sorbent for removing H<sub>2</sub>S. Eight metal oxide sorbents were examined over a temperature range

of 600 to 1150 K (620 to 1610°F) and pressure range of 1 to 25 atmospheres.

Results of the reduction/desulfurization analysis are summarized in Table 2. The first column identifies the eight sorbents by defining the highest oxidation state metal oxide. Column 2 identifies the chemical nature of the sulfided product; metal sulfide formation is favored from all sorbents except cerium where the favored product is the oxysulfide, Ce<sub>2</sub>O<sub>2</sub>S. In three of the systems -- iron, manganese, and molybdenum -- reduction of excess metal oxide to a lower oxidation state, or, in the case of copper and cobalt, to the elemental form is favored (column 3). At some conditions, ZnO may be reduced to gaseous metallic zinc (column 4) and SnO<sub>2</sub> may be reduced to the low melting metal. SnS(s) has an appreciable vapor pressure, and SnS(g) may be formed at appropriate conditions. Only CeO<sub>2</sub> is not subject to reduction over the range of conditions studied.

The maximum fractional H<sub>2</sub>S removal at conditions outside the region of equilibrium carbon deposition and/or the formation of molten or volatile species is shown in the last column of Table 2. The values range from a low of 0.88 for CeO<sub>2</sub> to 1.00 for both Co(s) and ZnO(s). Equilibrium fractional H<sub>2</sub>S removal is only a weak function of pressure, particularly at temperatures above the carbon deposition region. Three types of temperature effect on H<sub>2</sub>S removal were found. With most sorbents, equilibrium fractional sulfur removal decreased monotonically with increasing temperature. However, with SnO<sub>2</sub> the maximum H<sub>2</sub>S removal occurred at an intermediate temperature, and the equilibrium H<sub>2</sub>S removal with CeO<sub>2</sub> increased with increasing temperature. These effects are illustrated in Figure 1 for MnO, SnO<sub>2</sub>, and CeO<sub>2</sub> sorbents using a Texaco gas at 5 atmospheres.

Cobalt and copper were eliminated from the regeneration analysis because of the tendency for reduction to the metal. The remaining sorbents were analyzed for their potential to form elemental sulfur using the regeneration concepts.

**Table 2.**  
**Reduction/Desulfurization Analysis Summary**  
**600K < T < 1150K**  
**1 atm < P < 25 atm**

| Sorbent<br>in Highest<br>Oxidation State | Sulfided<br>Product              | Excess<br>Metal                     | Molten/<br>Volatile<br>Species | Maximum<br>Fractional<br>H <sub>2</sub> S Removal* |
|--|----------------------------------|-------------------------------------|--------------------------------|--|
| CeO <sub>2</sub>                         | Ce <sub>2</sub> O <sub>2</sub> S | CeO <sub>2</sub>                    | None                           | 0.88   |
| Co <sub>3</sub> O <sub>4</sub>           | Co <sub>3</sub> S <sub>4</sub>   | Co(s)                               | None                           | 1.00   |
| CuO                                      | Cu <sub>2</sub> S                | Cu(s)                               | None                           | 0.99   |
| Fe <sub>2</sub> O <sub>3</sub>           | FeS                              | FeO, Fe <sub>3</sub> O <sub>4</sub> | None                           | 0.96   |
| MnO <sub>2</sub>                         | MnS                              | MnO                                 | None                           | 0.99   |
| MoO <sub>3</sub>                         | MoS <sub>2</sub>                 | MoO <sub>2</sub>                    | None                           | 1.00   |
| SnO <sub>2</sub>                         | SnS                              | SnO <sub>2</sub>                    | SnS(g), Sn(l)                  | 0.98   |
| ZnO                                      | ZnS                              | ZnO                                 | Zn(g)                          | 1.00   |

\*at conditions where carbon is not deposited and molten/volatile species are not formed

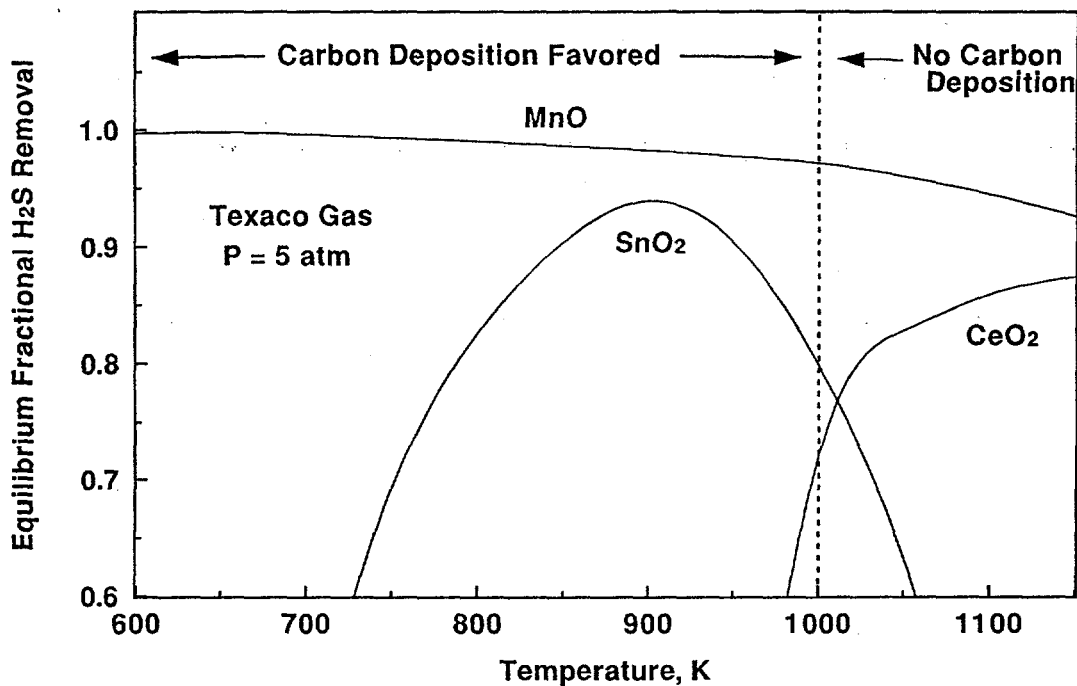


Figure 1. The Effect of Temperature on Equilibrium H<sub>2</sub>S Removal

## Regeneration Analysis

The thermodynamic analysis addressed a number of questions. Can the metal sulfide be regenerated under the specified conditions, and, if so, does the regeneration gas contain substantial quantities of elemental sulfur? Is metal sulfate likely to be formed? What is the oxidation state of the regenerated oxide, and are molten or volatile regeneration products likely to be formed?

**Concept 1: Reaction With SO<sub>2</sub>:** The thermodynamic analysis was carried out by "mixing" one mol of sulfided sorbent with three mols of SO<sub>2</sub> and determining the equilibrium product composition as a function of temperature and pressure. With excess SO<sub>2</sub>, complete regeneration would be possible if

thermodynamically favored. Ideal performance would correspond to complete regeneration, i.e., complete transfer of solid phase sulfur to the gas phase, with the gas phase sulfur consisting of equal quantities in the oxidized (SO<sub>2</sub>) and elemental (S<sub>x</sub>) forms. While the conditions of this analysis do not match actual regeneration conditions, the results provide a valid comparison of the potential of the different sorbents.

MnS, MoS<sub>2</sub>, and ZnS were effectively nonreactive with SO<sub>2</sub> over the temperature and pressure ranges considered, 600 to 1150 K and 1 to 25 atm. FeS exhibited moderate reactivity while both SnS and Ce<sub>2</sub>O<sub>2</sub>S were quite reactive. Results of the equilibrium calculation at 25 atmospheres and 900 and 1050 K for SnS, Ce<sub>2</sub>O<sub>2</sub>S, and MnS are summarized in Table 3. With SnS at 900 K and 25 atmospheres, sulfur is

**Table 3.**  
**Results of Equilibrium Analysis for the**  
**Regeneration of SnS, Ce<sub>2</sub>O<sub>2</sub>S, and MnS**  
**With SO<sub>2</sub> (1 mol metal sulfide : 3 mols SO<sub>2</sub>)**  
**P = 25 atm**

| System  | SnS  |       | Ce <sub>2</sub> O <sub>2</sub> S |      | MnS   |       |
|---|------|-------|----------------------------------|------|-------|-------|
| Temperature, K  | 900  | 1050  | 900                              | 1050 | 900   | 1050  |
| Condensed Phase Composition, mol fraction             |      |       |                                  |      |       |       |
| Oxide   | 0.00 | 1.00  | 1.00                             | 1.00 | trace | trace |
| Sulfide   | 0.00 | trace | 0.00                             | 0.00 | 1.00  | 1.00  |
| Sulfate   | 0.77 | 0.00  | 0.00                             | 0.00 | 0.00  | 0.00  |
| Sulfur (liq)  | 0.23 | 0.00  | 0.00                             | 0.00 | 0.00  | 0.00  |
| Sulfur Distribution (as S), fraction                  |      |       |                                  |      |       |       |
| Condensed   | 0.33 | trace | 0.00                             | 0.00 | 0.25  | 0.25  |
| Gas   | 0.67 | 1.00  | 1.00                             | 1.00 | 0.75  | 0.75  |
| Sulfur Distribution (as S) Within Gas Phase, fraction |      |       |                                  |      |       |       |
| Elemental (S <sub>x</sub> )                           | 0.62 | 0.47  | 0.49                             | 0.47 | trace | trace |
| Oxide (SO <sub>x</sub> )                              | 0.38 | 0.53  | 0.51                             | 0.53 | 1.00  | 1.00  |
| Sulfide (H <sub>2</sub> S)                            | 0.00 | 0.00  | 0.00                             | 0.00 | 0.00  | 0.00  |



added to the condensed phase, either as  $\text{SnSO}_4(\text{s})$  or  $\text{S}(\text{l})$ , meaning that fractional regeneration is actually negative. At higher temperature  $\text{SnSO}_4(\text{s})$  is unstable and  $\text{S}(\text{l})$  vaporizes so that complete regeneration is possible at 1050 K and 25 atmospheres. The equilibrium distribution of sulfur in the gas phase of 47% elemental and 53% oxide is reasonably close to the ideal 50 - 50 split between the two forms.

Complete regeneration of  $\text{Ce}_2\text{O}_2\text{S}$  is possible at both 900 and 1050 K with the solid product returning to the original  $\text{CeO}_2$  form. The gas phase sulfur distribution is reasonably close to the ideal split between elemental and oxide forms, with the distribution slightly improved at the low temperature. In contrast to  $\text{SnS}$  and  $\text{Ce}_2\text{O}_2\text{S}$ ,  $\text{MnS}$  is almost totally unreactive even at the higher temperature.

#### **Concept 2: Partial Oxidation:**

Duplication of the actual conditions in a regeneration reactor operated in an  $\text{O}_2$ -starved condition with large quantities of steam in the feed gas is impossible because of the inherent batch nature of the thermodynamic calculations. However, a legitimate comparison of sorbent performance was obtained by "mixing" one mol of sulfided sorbent with one mol of  $\text{O}_2(\text{g})$  and one mol of  $\text{H}_2\text{O}(\text{g})$ , and determining the equilibrium composition. The temperature and pressure ranges were 650 to 1100 K and 1 to 25 atmospheres.

Each of the six sulfided sorbents will react, at least to some extent, in the  $\text{O}_2 - \text{H}_2\text{O}$  atmosphere. However, effectively no elemental sulfur can be formed from either  $\text{ZnS}$  or  $\text{MoS}_2$ . A small amount of elemental sulfur may be produced from  $\text{MnS}$ , and a somewhat larger amount from  $\text{FeS}$ . Once again,  $\text{SnS}$  and  $\text{Ce}_2\text{O}_2\text{S}$  are quite reactive and the quantities of elemental sulfur which may be formed are significant.

Selected results of the partial oxidation regeneration analysis for  $\text{FeS}$ ,  $\text{ZnS}$ , and  $\text{Ce}_2\text{O}_2\text{S}$  are presented in Table 4 at 25 atmospheres and 900 and 1050 K. Regeneration of  $\text{FeS}$  is

incomplete at both temperatures with the fraction of sulfur transferred to the gas phase increasing from 0.52 at 900 K to 0.65 at 1050 K. At 950K, the condensed phase sulfur is present as the disulfide,  $\text{FeS}_2$ ; at 1050 K all condensed phase sulfur is  $\text{FeS}$ . The stable oxide is  $\text{Fe}_3\text{O}_4$  at both temperatures. A large majority of the gas phase sulfur is in form of  $\text{SO}_2$  at both temperatures, but both the elemental ( $\text{S}_x$ ) and reduced ( $\text{H}_2\text{S}$ ) sulfur contents increase at higher temperature. The fact that the maximum concentration of elemental sulfur at equilibrium is far below concentration levels which have been reported experimentally is to be expected for two reasons. First, as previously stated, it is not possible to duplicate the experimental conditions corresponding to  $\text{O}_2$ -starved flow in the thermodynamic analysis. In addition, partial oxidation experimental conditions are not expected to closely approach equilibrium.

The reaction of  $\text{ZnS}$  in the  $\text{O}_2 - \text{H}_2\text{O}$  atmosphere is essentially that of oxidation by  $\text{O}_2$  with the formation of  $\text{ZnO}$  and  $\text{SO}_2$ . The amount of  $\text{O}_2$  in the thermodynamic mixture is two-thirds of the stoichiometric requirement, and two-thirds of the  $\text{ZnS}$  is converted to  $\text{ZnO}$ .

$\text{Ce}_2\text{O}_2\text{S}$  is quite reactive. Complete regeneration to  $\text{CeO}_2$  is favored at both temperatures, and significant fractions of the gas phase sulfur should be in elemental form. The gas phase distribution of sulfur species is a relatively strong function of temperature with elemental sulfur formation increasing at lower temperature.

#### **Concept 3: Reaction With Steam/Claus:**

This regeneration concept is a direct reversal of the desulfurization reaction and the expected sulfur product is  $\text{H}_2\text{S}$  instead of elemental sulfur. The concept is of interest, however, if sufficiently high concentrations of  $\text{H}_2\text{S}$  to permit direct feed to a Claus reactor can be produced. It is obvious that sorbents having the greatest affinity for  $\text{H}_2\text{S}$  will be the least amenable to regeneration with steam. For this reason, only the  $\text{SnS}$  and  $\text{Ce}_2\text{O}_2\text{S}$  systems were considered.

Both systems should react with steam, and

**Table 4.**  
**Results of Equilibrium Analysis for the Regeneration**  
**of FeS, ZnS, and Ce<sub>2</sub>O<sub>2</sub>S With O<sub>2</sub> and H<sub>2</sub>O**  
**(1 mol sulfided sorbent : 1 mol O<sub>2</sub> : 1 mol H<sub>2</sub>O)**  
**P = 25 atm**

| System  | FeS  |      | ZnS   |       | Ce <sub>2</sub> O <sub>2</sub> S |      |
|---|------|------|-------|-------|----------------------------------|------|
| Temperature, K  | 900  | 1050 | 900   | 1050  | 900                              | 1050 |
| Condensed Phase Composition, mol fraction             |      |      |       |       |                                  |      |
| Oxide   | 0.52 | 0.38 | 0.67  | 0.67  | 1.00                             | 1.00 |
| Sulfide   | 0.00 | 0.72 | 0.33  | 0.33  | 0.00                             | 0.00 |
| Disulfide   | 0.48 | 0.00 | 0.00  | 0.00  | 0.00                             | 0.00 |
| Sulfate   | 0.00 | 0.00 | 0.00  | 0.00  | 0.00                             | 0.00 |
| Sulfur (liq)  | 0.00 | 0.00 | 0.00  | 0.00  | 0.00                             | 0.00 |
| Sulfur Distribution (as S), fraction                  |      |      |       |       |                                  |      |
| Condensed   | 0.48 | 0.35 | 0.33  | 0.33  | 0.00                             | 0.00 |
| Gas   | 0.52 | 0.65 | 0.67  | 0.67  | 1.00                             | 1.00 |
| Sulfur Distribution Within Gas Phase (as S), fraction |      |      |       |       |                                  |      |
| Elemental   | 0.01 | 0.03 | trace | 0.00  | 0.58                             | 0.49 |
| Oxide   | 0.96 | 0.91 | 1.00  | 1.00  | 0.14                             | 0.18 |
| Sulfide   | 0.03 | 0.06 | trace | trace | 0.28                             | 0.32 |

both reactions should proceed essentially according to stoichiometry. Only negligible quantities of SO<sub>2</sub> or S<sub>x</sub> should be formed. However, both regeneration reactions produce H<sub>2</sub> and H<sub>2</sub>S in equimolar quantities, so that a H<sub>2</sub> separation step will be required. In order to achieve complete regeneration, it will only be necessary to supply sufficient excess steam to satisfy the thermodynamics.

Figure 2 shows the minimum steam to sorbent ratio required for complete regeneration as a function of temperature at 15 atm. For SnS, the ratio is in the 20 to 25 range and is almost independent of temperature. It is interesting to note that the experimental work on SnS regeneration with steam described by Nielsen et al. (1991) used a ratio of H<sub>2</sub>O to SnS of 30 to 1,

only slightly above the thermodynamic minimum. Ce<sub>2</sub>O<sub>2</sub>S is even more amenable to regeneration with steam. As shown in Figure 2, the minimum steam to Ce<sub>2</sub>O<sub>2</sub>S ratio is in the range of 5 to 10, and increases slightly with increasing temperature. These results are independent of pressure since the reactions do not result in a change in the number of gas phase mols.

### Discussion

The thermodynamic analysis has shown that sorbents having the greatest affinity for H<sub>2</sub>S in the reduction/desulfurization cycle will be the most difficult to regenerate with elemental sulfur (or H<sub>2</sub>S) as a direct product. For practical purposes, this eliminates zinc, manganese,

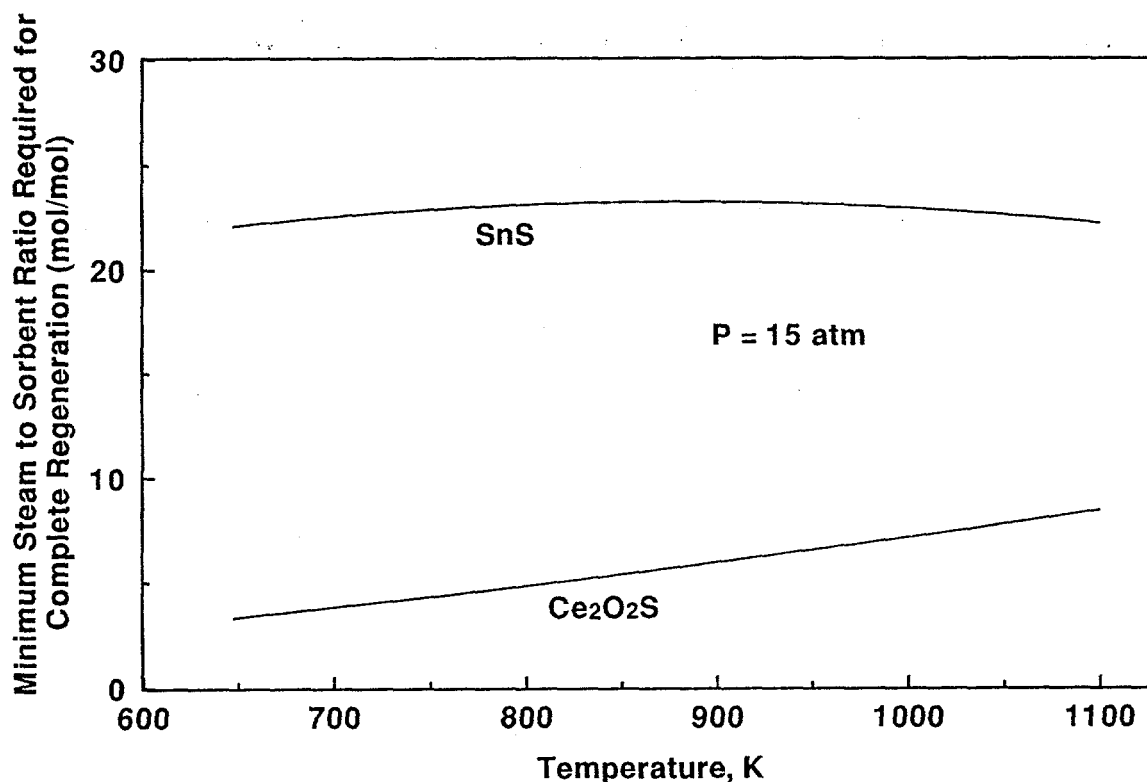


Figure 2. Minimum Steam to Sorbent Ratio for the Complete Steam Regeneration of SnS(s) and Ce<sub>2</sub>O<sub>2</sub>S(s) Sorbents

and molybdenum sorbents, each of which is thermodynamically capable of desulfurization efficiencies which approach 100%. Iron oxide sorbents are less effective for H<sub>2</sub>S removal, and are somewhat more amenable to elemental sulfur production. The most promising regeneration concept for FeS appears to be partial oxidation in which the regeneration atmosphere is deficient in O<sub>2</sub> and contains excess steam. Numerous simultaneous reactions such as listed in Table 5 are expected to occur. Hence, the objective of the experimental study will be to determine conditions which maximize the rate of those reactions producing elemental sulfur to the rate of reactions which produce SO<sub>2</sub>. Regeneration of FeS with SO<sub>2</sub> or H<sub>2</sub>O, while feasible, would require such large quantities of reactant that the concept would not be practical.

The thermodynamic properties of SnS and Ce<sub>2</sub>O<sub>2</sub>S make these systems uniquely suitable to elemental sulfur production. All three of the regeneration concepts show promise with both SnS and Ce<sub>2</sub>O<sub>2</sub>S. Although the thermodynamic characteristics of SnS and Ce<sub>2</sub>O<sub>2</sub>S are similar with respect to elemental sulfur production, there are significant differences in other respects. Under appropriate conditions, either SnS<sub>2</sub> or Sn<sub>2</sub>S<sub>3</sub> may be produced during regeneration. SnSO<sub>4</sub> is moderately stable and high temperatures are required to prevent its formation, particularly at high pressure. The reduction of SnO<sub>2</sub> to liquid metallic Sn may occur in a highly reducing coal gas. Finally, SnS(s) may vaporize at appropriate conditions, a potential problem in both desulfurization and regeneration cycles. The condensed phase of the cerium system is less

**Table 5.**  
**Simultaneous Reactions Involved**  
**in the Partial Oxidation of FeS to Produce**  
**Elemental Sulfur**

Gas - Solid Reactions

1.  $2\text{FeS(s)} + 1.5 \text{O}_2\text{(g)} \rightarrow \text{Fe}_2\text{O}_3\text{(s)} + \text{S}_2\text{(g)}$
2.  $2\text{FeS(s)} + 3.5 \text{O}_2\text{(g)} \rightarrow \text{Fe}_2\text{O}_3\text{(s)} + 2\text{SO}_2\text{(g)}$
3.  $3\text{FeS(s)} + 4\text{H}_2\text{O(g)} \rightarrow \text{Fe}_3\text{O}_4\text{(s)} + 3\text{H}_2\text{S(g)} + \text{H}_2\text{(g)}$
4.  $3\text{FeS(s)} + 2\text{SO}_2\text{(g)} \rightarrow \text{Fe}_3\text{O}_4\text{(s)} + 2.5 \text{S}_2\text{(g)}$
5.  $2\text{Fe}_3\text{O}_4\text{(s)} + 0.5 \text{O}_2\text{(g)} \rightarrow 3\text{Fe}_2\text{O}_3\text{(s)}$

Gas-Phase Reactions

6.  $\text{SO}_2\text{(g)} + 2\text{H}_2\text{S(g)} \rightarrow 2\text{H}_2\text{O(g)} + 1.5 \text{S}_2\text{(g)}$
7.  $\text{H}_2\text{S(g)} \rightarrow \text{H}_2\text{(g)} + 0.5 \text{S}_2\text{(g)}$
8.  $\text{SO}_2\text{(g)} + 2\text{H}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(g)} + 0.5 \text{S}_2\text{(g)}$
9.  $\text{S}_2\text{(g)} + 2\text{O}_2\text{(g)} \rightarrow 2\text{SO}_2\text{(g)}$

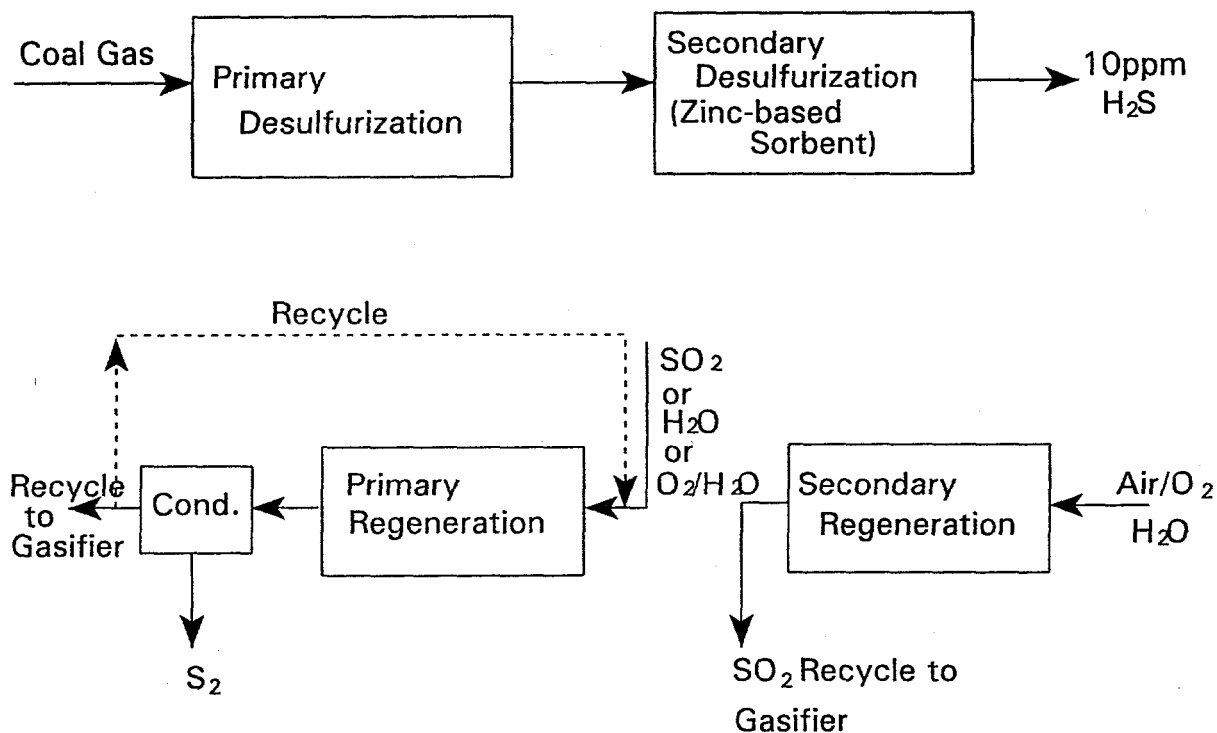
complex.  $\text{CeO}_2$  is nonvolatile and there is no danger of it being reduced.  $\text{Ce}_2\text{O}_2\text{S}$ , also nonvolatile, is the only sulfided product. As an added advantage, the desulfurization potential of  $\text{CeO}_2$  increases with increasing temperature and in more highly reducing coal gas.

Because of the reduced desulfurization capability of the sorbents of interest, a two-step desulfurization process such as shown in Figure 3 may be required. A primary desulfurization reactor containing an oxide such as iron, tin, or cerium would be followed by a secondary desulfurization reactor containing a high efficiency sorbent such as  $\text{ZnO}$ . Regeneration of  $\text{ZnS}$  would be accomplished in the traditional manner and product gas containing  $\text{SO}_2$  would be recycled to the gasifier. By removing the majority of  $\text{H}_2\text{S}$  in the primary desulfurization step, the secondary

reactor would be smaller and/or require less frequent regeneration. Regeneration of the sorbent in the primary desulfurization reactor would be accomplished using one of the three concepts previously described. Elemental sulfur would be condensed, and the remaining product gas would be recycled to the regeneration reactor or to the gasifier.

#### FUTURE WORK

In the experimental phase of the project, we are studying the regeneration of  $\text{FeS}$  using the partial oxidation concept, and the sulfidation and regeneration of  $\text{CeO}_2$  using all three regeneration concepts. Both atmospheric and high pressure electrobalance reactors are now being used and a



**Figure 3. Two-Step Desulfurization-Regeneration Process**

high-pressure laboratory-scale fixed-bed reactor is being constructed.

The flow rates and the distribution of sulfur species in the reactor product gas will vary with time because of the inherent unsteady state behavior of the fixed-bed reactor. An analytical system is being developed to permit real-time analysis of the distribution of sulfur species in the regeneration product gas. A slip stream of the product gas will be expanded from reaction to atmospheric pressure through a specially designed quartz capillary tube into an oxidizer where all sulfur species will be converted to SO<sub>2</sub> for total sulfur analysis. The remainder of the product gas will pass through condensers where elemental sulfur and H<sub>2</sub>O will be removed. SO<sub>2</sub> and H<sub>2</sub>S concentrations will then be determined using gas chromatography. This will permit elemental sulfur to be determined by difference. Although analysis

by difference is not generally desirable, no alternative has been identified. In addition, the results should be acceptable if we are able to achieve the goal of producing high concentrations of elemental sulfur.

The experimental studies, which will receive primary emphasis during the next year, will be followed by simulation studies, including material and energy balances and a preliminary economic evaluation.

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