

# Hot Gas Desulfurization With Sulfur Recovery<sup>1</sup>

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## Abstract

Cerium-based high temperature sorbent as an alternative to zinc-based sorbent is being investigated. Initial interest in cerium was justified on the potential for producing elemental sulfur directly during regeneration. The regeneration reaction is highly favored thermodynamically. No side reactions occur and the reaction is rapid between 500 °C and 700 °C. Preliminary multicycle tests showed good sorbent durability. Process analysis suggested the optimum elemental concentration in the regeneration product should be about 15%, and experimental concentrations as high as 20% have been achieved. These results were reported last year.

The thermodynamics of desulfurization have been considered to be the limiting factor in cerium sorbents. High temperatures ( $\approx 800$  °C) and highly reducing gas compositions were required before CeO<sub>2</sub> sulfidation would proceed to any significant extent. Even under these conditions the equilibrium H<sub>2</sub>S concentration was well above the 20-ppmv target for IGCC application.

During the past year we have found that reduction of CeO<sub>2</sub> to CeO<sub>n</sub> ( $n < 2$ ) greatly increases the ability of the sorbent to remove H<sub>2</sub>S. Using reduced CeO<sub>n</sub>, prebreakthrough H<sub>2</sub>S concentrations of 10-ppmv or less have been achieved over a range of temperatures, pressures, and feed gas compositions and flow rates. More extensive multicycle tests have confirmed the sorbent durability. No significant change in reactivity was observed after twenty-five reduction-sulfidation-regeneration cycles. Other advantages of cerium sorbents are the absence of cerium volatility and the lack of sulfate formation during regeneration.

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## Introduction

High temperature desulfurization is a key element in the optimal development of the integrated gasification combined cycle (IGCC) process. Research on the development of regenerable sorbents capable of reducing the H<sub>2</sub>S concentration to approximately 20-ppmv and with sufficient durability to survive many sulfidation-regeneration cycles has been ongoing for a number of years. Extensive studies on zinc-based sorbents have led to their use in clean coal demonstration projects. While zinc sorbents are capable of reaching the 20-ppmv target level, their use is restricted to relatively low temperatures and moderately reducing gases because of the tendency for ZnO to be reduced to volatile Zn. In addition, problems and questions remain in the regeneration and durability areas. Because of the strong affinity between zinc and sulfur, regeneration of ZnS can only be accomplished using a strong oxidant such as O<sub>2</sub> to reform ZnO and liberate SO<sub>2</sub>. Dilute O<sub>2</sub> must be used to control the temperature of this highly exothermic reaction, which means that the regeneration product gas contains dilute SO<sub>2</sub>. Additional processing is required for ultimate sulfur control. Also, the partial pressure of O<sub>2</sub> and SO<sub>2</sub> in the regeneration gas favor the formation of ZnSO<sub>4</sub>, which is believed to be a major contributor to sorbent deterioration.

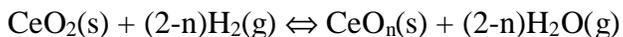
## Objective

The primary objective of this study is to identify a second-generation sorbent capable of producing elemental sulfur directly during regeneration and avoiding, or at least minimizing, other problems associated with the first-generation zinc sorbents.

## Approach

An initial literature search identified three concepts for the direct production of elemental sulfur during sorbent regeneration. This was followed by a thermodynamic analysis in which each concept was evaluated using several candidate metal oxide sorbents. Sorbents having the greatest affinity for H<sub>2</sub>S during sulfidation such as ZnO were found to be least conducive to elemental sulfur production during regeneration. Less efficient sulfidation sorbents, Fe<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>, were selected for experimental study based on favorable thermodynamics for elemental sulfur production during regeneration. As much as 80% of the sulfur in FeS was liberated in elemental form using an O<sub>2</sub>-H<sub>2</sub>O regeneration gas containing large H<sub>2</sub>O concentrations (White et al. 1998). This approach, while technically feasible, was judged to be commercially impractical because of the large steam consumption and the small concentration of elemental sulfur in the regeneration product gas.

The majority of the experimental effort has been devoted to the CeO<sub>2</sub> sorbent system in which three reactions are important. At high temperatures in a reducing atmosphere CeO<sub>2</sub> is reduced to CeO<sub>n</sub> (n < 2) according to

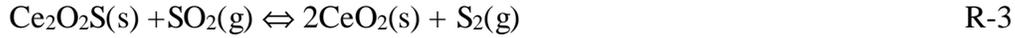


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The sulfidation reaction is



$\text{Ce}_2\text{O}_2\text{S}$  may be regenerated using weakly oxidizing  $\text{SO}_2$  by the following reaction



The sulfur product is represented as  $\text{S}_2$  for simplicity. In reality, a mixture of sulfur allotropes  $\text{S}_x$  with  $1 \leq x \leq 8$  may be formed.

In addition to forming elemental sulfur directly, the  $\text{CeO}_2$  system has additional advantages of not producing volatile cerium species, of eliminating sulfate formation, and reducing temperature control problems since the  $\text{Ce}_2\text{O}_2\text{S}$ - $\text{SO}_2$  reaction is less exothermic than the  $\text{ZnS}$ - $\text{O}_2$  reaction. The disadvantages of cerium compared to zinc sorbent are poorer sulfidation thermodynamics, lower theoretical capacity (0.093 kg S per kg  $\text{CeO}_2$  compared to 0.39 kg S per kg of pure  $\text{ZnO}$ ), and higher oxide cost.

Early phases of the cerium sorbent experimental work concentrated on the regeneration reaction as elemental sulfur production was the primary goal of the study. Details of the reaction system along with favorable regeneration results were presented at last year's meeting (Zeng et al. 1997). Effort during the past year has concentrated on the reduction and sulfidation phases and on multicycle sorbent durability.

## Results

**Thermodynamics:** The limitations of  $\text{CeO}_2$  during the sulfidation phase of the cycle are clearly seen by the three solid lines of Figure 1. These lines represent, respectively, the equilibrium  $\text{H}_2\text{S}$  concentrations from KRW, Texaco, and Shell gas compositions in contact with  $\text{CeO}_2$  as a function of temperature. Nominal compositions of these gases are shown in the first three columns of Table 1; in each case the  $\text{H}_2\text{S}$  content was arbitrarily set to 1 mol% (10,000-ppmv).

Table 1. Compositions of Coal Gases and Experimental Gases Used in This Study

Component	Gasifier Product Composition			Experimental Gas Composition		
	KRW Air-Blown	Texaco O <sub>2</sub> -Blown	Shell O <sub>2</sub> -Blown	Gas A	Gas B	Gas C
CO	15	40	60	--	--	--
H <sub>2</sub>	10	31	29	10	50.25	28.25
CO <sub>2</sub>	5	11	2	--	--	--
H <sub>2</sub> O	15	17	5	--	3.5	6.5
N <sub>2</sub>	54	--	3	balance	balance	balance
H <sub>2</sub> S	1	1	1	1/0.25	0.25	0.25

Essentially no H<sub>2</sub>S removal from the KRW gas is possible until the temperature exceeds 700°C and at 900°C the equilibrium H<sub>2</sub>S concentration of about 4000-ppmv corresponds to only 60% H<sub>2</sub>S removal. Increased H<sub>2</sub>S removal from the Texaco gas is possible but temperatures in excess of 900°C are required to achieve 90% removal. With the Shell gas, greater than 90% H<sub>2</sub>S removal is thermodynamically possible at all temperatures shown. However, the 320-ppmv equilibrium concentration (96.8% H<sub>2</sub>S removal) at 800 °C is well above the IGCC target level. As a result, a two-stage desulfurization process using cerium sorbent for bulk H<sub>2</sub>S removal followed by a zinc-based sorbent polishing step was proposed (Zeng et al. 1997).

The potential for increased H<sub>2</sub>S removal by reducing CeO<sub>2</sub> is illustrated by the three dashed lines of Figure 1 that represent equilibrium H<sub>2</sub>S concentration from the three coal gases

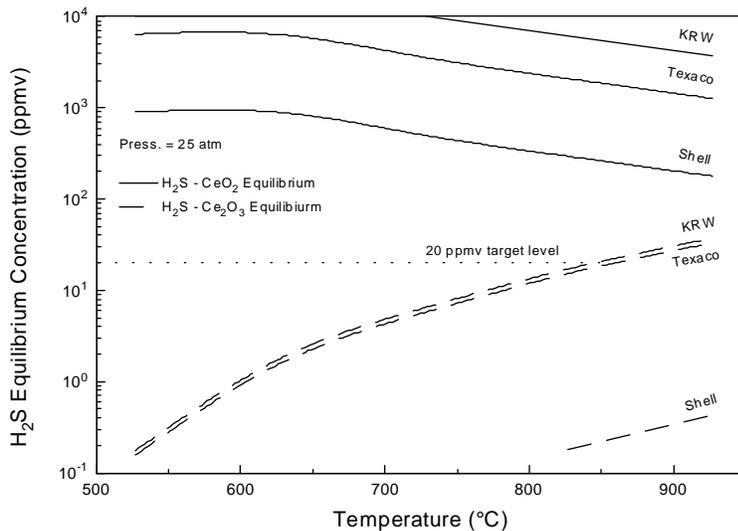


Figure 1. Equilibrium H<sub>2</sub>S Concentrations from Three Coal Gases With CeO<sub>2</sub> and Ce<sub>2</sub>O<sub>3</sub>

in contact with Ce<sub>2</sub>O<sub>3</sub> (CeO<sub>1.5</sub>). Equilibrium H<sub>2</sub>S concentrations below 20-ppmv are possible with the KRW and Texaco gases at temperatures below 850 °C while Ce<sub>2</sub>O<sub>3</sub> is capable of reducing the H<sub>2</sub>S concentration in Shell gas to less than 1-ppmv at all temperatures shown. The problem, of course, is that CeO<sub>2</sub> cannot be reduced to Ce<sub>2</sub>O<sub>3</sub> at conditions of interest. Reliable thermodynamic data for CeO<sub>n</sub> (1.5 < n < 2) are not available, but it is reasonable to presume that the H<sub>2</sub>S equilibrium would fall between the CeO<sub>2</sub> and Ce<sub>2</sub>O<sub>3</sub> limits.

In contrast to the limited ability of CeO<sub>2</sub> sorbent to remove H<sub>2</sub>S, the thermodynamics of the Ce<sub>2</sub>O<sub>2</sub>S-SO<sub>2</sub> reaction are quite favorable. At 600 °C, the most common experimental regeneration temperature, the equilibrium constant for the reaction is about 250 and no side reactions occur. Regeneration is not limited by thermodynamics, but by reactor heat transfer considerations and the need to prevent condensation of elemental sulfur within the reactor. For example, at 600 °C and 25 atm, the elemental sulfur content of the regeneration product gas can approach 60 mol% before condensation. Heat transfer considerations show that the elemental sulfur content should be limited to about 15 mol%, well below either the condensation or thermodynamic limits. Elemental sulfur contents as large as 20 mol% have been produced experimentally (Zeng et al. 1997).

**CeO<sub>2</sub> Reduction:** The ability to reduce CeO<sub>2</sub> to CeO<sub>n</sub> (n < 2) is well established in the literature. Bevan and Kordis (1964) published data showing the equilibrium value of n as a function of temperature and O<sub>2</sub> partial pressure. Atmospheric pressure electrobalance tests were performed to confirm that CeO<sub>2</sub> could be reduced at temperatures of interest and to compare experimental results with those reported by Bevan and Kordis. Experimental and theoretical results as a function of temperature are compared in Figure 2. The experimental gas composition

of 40% H<sub>2</sub> and 3.5% CO<sub>2</sub> in He was chosen to closely match the equilibrium O<sub>2</sub> pressure of the Shell gas. At 800 °C the equilibrium O<sub>2</sub> pressures are 2.8x10<sup>-21</sup> atm and 3.4x10<sup>-21</sup> atm for the experimental and Shell gases, respectively. Helium was used instead of N<sub>2</sub> to reduce aerodynamic drag and increase electrobalance sensitivity.

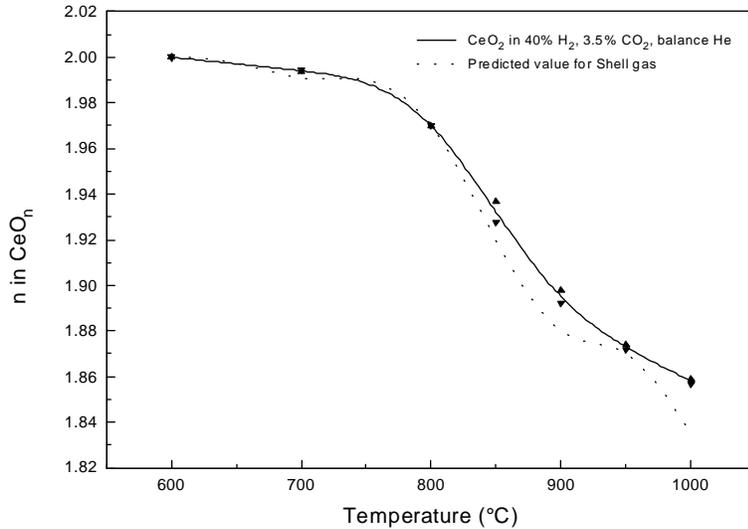


Figure 2. Reduction of CeO<sub>2</sub>

Results from duplicate experimental runs are indicated by the discrete points in Figure 2, while the solid line is drawn through the average of the two runs. The dashed line is based on equilibrium O<sub>2</sub> pressure for the Shell gas coupled with data from Bevan and Kordis. The agreement is quite good. Reduction becomes significant at about 750 °C, and both experimental and predicted weights correspond to CeO<sub>1.97</sub> at 800 °C. At the maximum temperature of 1000 °C the experimental data correspond to CeO<sub>1.86</sub> compared to the predicted value of CeO<sub>1.83</sub>.

**Reactor Modifications:** Three significant changes were made in the reactor and analytical system (Zeng et al. 1997) and the test procedure to enable lower H<sub>2</sub>S concentrations associated with reduced CeO<sub>n</sub> to be measured accurately.

First, a flame photometric detector (FPD) was installed in parallel with the thermal conductivity detector (TCD) in the gas chromatograph. Flow could be directed to either detector using a three-way teflon valve. The FPD permitted accurate H<sub>2</sub>S measurement in the range of 1-ppmv to 100-ppmv with an ultimate detection limit of about 0.3-ppmv (compared to 100-ppmv for the TCD).

In addition, contact between sulfidation product gas and stainless steel parts was reduced by adding a quartz liner inside the stainless steel pressure vessel, using teflon-lined stainless steel tubing between the reactor and back-pressure regulator, and replacing other stainless steel lines downstream of the back-pressure regulator with teflon. Sulfur contamination was minimized by using separate transfer lines for sulfidation and regeneration tests, and by feeding sulfur-free reducing gas through the reactor system following regeneration tests until no H<sub>2</sub>S was detected in the product gas. With these changes the only stainless surfaces left in contact with the sulfidation product gas were the chromatograph sampling valve, backpressure regulator, a filter, and a short pipe nipple between the pressure vessel and teflon-lined transfer tubing.

**Feed Gas Compositions:** Three experimental feed gas compositions shown in the last three columns of Table 1 were used in the test program. Gas A contained only H<sub>2</sub> and H<sub>2</sub>S in N<sub>2</sub>. Steam was added in gas B at a level such that the equilibrium O<sub>2</sub> pressure was approximately

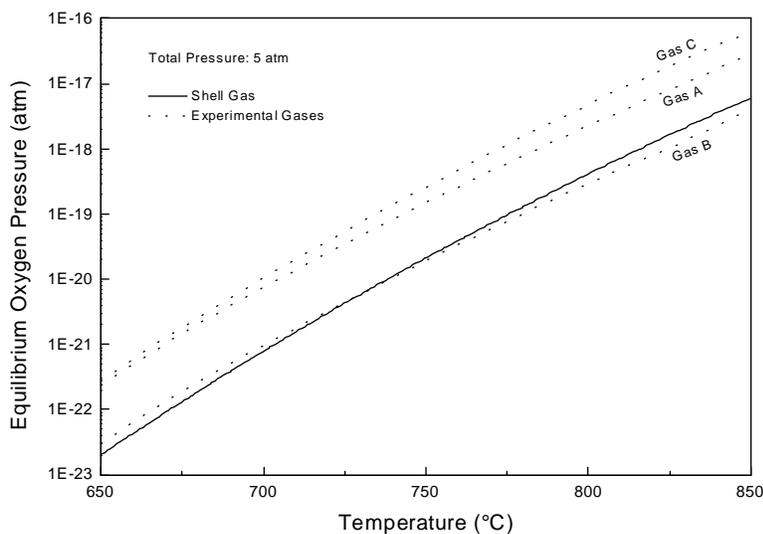


Figure 3. Equilibrium Oxygen Pressure of Shell Gas and Three Experimental Gases.

equal to that of Shell gas. Finally, the H<sub>2</sub> and H<sub>2</sub>O contents of gas C were almost equal to the Shell gas. However, in the absence of CO and CO<sub>2</sub>, the O<sub>2</sub> pressure was significantly larger. Equilibrium O<sub>2</sub> pressures for the three experimental gases evaluated at the product gas composition and the Shell gas as a function of temperature are presented in Figure 3. At a fixed temperature there is just over one order of magnitude difference in the O<sub>2</sub> pressure of the gas compositions, and the equilibrium O<sub>2</sub> pressure of each composition increases by about five orders of magnitude between 650 °C and 850 °C.

**Sulfidation of Reduced Cerium Oxide:** The effect of reduction-sulfidation temperature was examined between 600 °C and 850 °C using gas A containing 1 mol% H<sub>2</sub>S. In each case the sorbent was pre-reduced in sulfur-free gas A at the same temperature used for sulfidation. Results at the five highest temperatures are shown in Figure 4. 600 °C results are not shown since the H<sub>2</sub>S concentration in all samples exceeded the FPD saturation limit of about 100-ppmv. At the higher temperatures, all H<sub>2</sub>S concentrations were below 10-ppmv for at least 17 minutes. The initial concentrations decreased with decreasing temperature from about 6-ppmv at 850 °C to near the ultimate detection limit of the FPD (< 1-ppmv) at both 650 °C and 700 °C. In each test, the H<sub>2</sub>S concentration in the sample after the last data point shown in Figure 4 exceeded the FPD saturation limit.

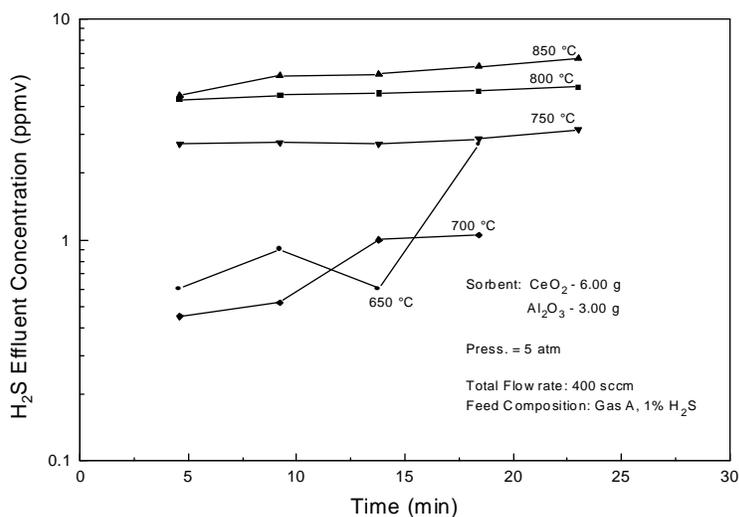


Figure 4. Prebreakthrough H<sub>2</sub>S Concentrations Over CeO<sub>n</sub>

The FPD prebreakthrough concentrations shown in Figure 4 compare quite well to previous results at higher temperatures reported by Meng and Kay (1987). This is illustrated in Figure 5 where concentrations from the third sample of the Figure 3 tests are compared to the Meng and Kay data. The calculated equilibrium concentrations for the CeO<sub>2</sub>-H<sub>2</sub>S and Ce<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>S reactions in contact with Shell gas are also shown for comparison. While the feed gas compositions used by Meng and Kay and in this study were

somewhat different, the results are quite similar. These results prove, without question, that reduced  $\text{CeO}_n$  is capable of achieving IGCC  $\text{H}_2\text{S}$  specifications at temperatures and gas compositions well beyond the limits of zinc-based sorbents.

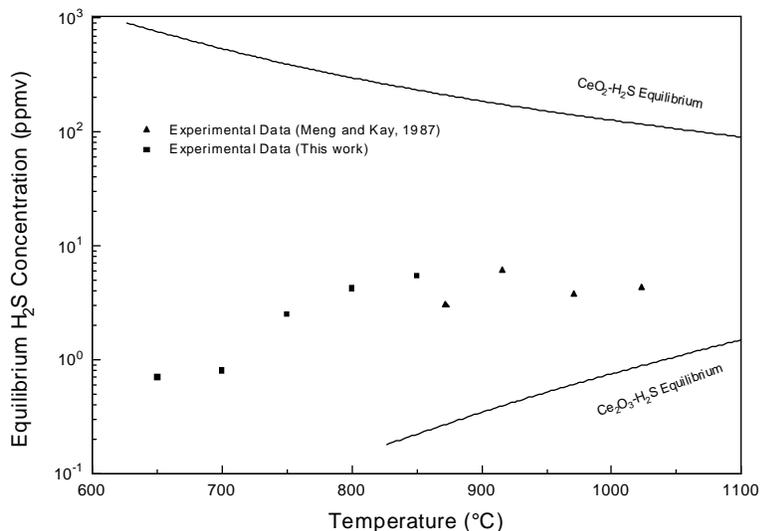


Figure 5. Comparison of Experimental Prebreakthrough  $\text{H}_2\text{S}$  Concentrations With Literature Results

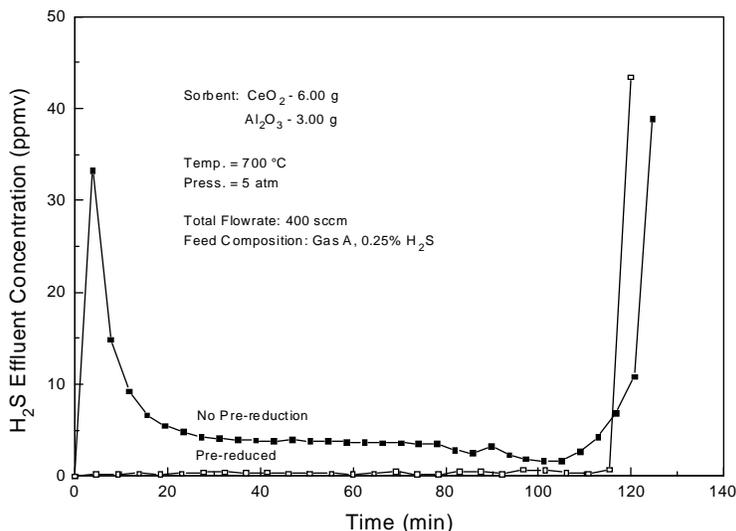


Figure 6. Prebreakthrough  $\text{H}_2\text{S}$  Concentrations With and Without Pre-Reduction

We expect  $m$  to be somewhat larger than  $n$  because with pre-reduction all  $\text{CeO}_2$  is exposed to the 10 mol%  $\text{H}_2$  reducing gas with no  $\text{H}_2\text{O}$  present. Without pre-reduction the upstream reaction of  $\text{H}_2\text{S}$  consumes  $\text{H}_2$  and produces  $\text{H}_2\text{O}$ , thus decreasing the reducing power of the downstream gas.

The effect of feed gas composition using gases A, B, and C, all containing 0.25%  $\text{H}_2\text{S}$  is shown in Figure 7. The sorbent was not pre-reduced in these tests. The best performance was achieved using Gas B where the  $\text{H}_2\text{S}$  concentration was below 3-ppmv for the first 185 minutes. From Figure 3 we see that Gas B also had the lowest equilibrium  $\text{O}_2$  pressure, about  $10^{-21}$  atm at

The FPD breakthrough curves with and without pre-reduction, but otherwise equivalent reaction conditions, are compared in Figure 6. The  $\text{H}_2\text{S}$  concentration of gas A was reduced to 0.25 mol% to prolong the prebreakthrough period. Without pre-reduction there was an initial peak in the  $\text{H}_2\text{S}$  concentration followed by a decrease to less than 5 ppmv between 23 and 115 minutes. With pre-reduction the early  $\text{H}_2\text{S}$  peak was absent and the concentration was near 1 ppmv for the first 110 minutes. FPD breakthrough occurred at 125 minutes without pre-reduction and 115 minutes with pre-reduction.

The following explanation for the different response is proposed. With pre-reduction, the entire bed consists of  $\text{CeO}_n$  ( $n < 2$ ) before being exposed to  $\text{H}_2\text{S}$ . Without pre-reduction the entire bed is  $\text{CeO}_2$  at the beginning of the test so that reduction and sulfidation occur simultaneously. Reduction occurs downstream of the sulfidation reaction front, and, after the early  $\text{H}_2\text{S}$  peak associated with partial  $\text{CeO}_2$  reduction, the subsequent sulfidation reaction is between  $\text{H}_2\text{S}$  and  $\text{CeO}_m$  ( $m < 2$ ).

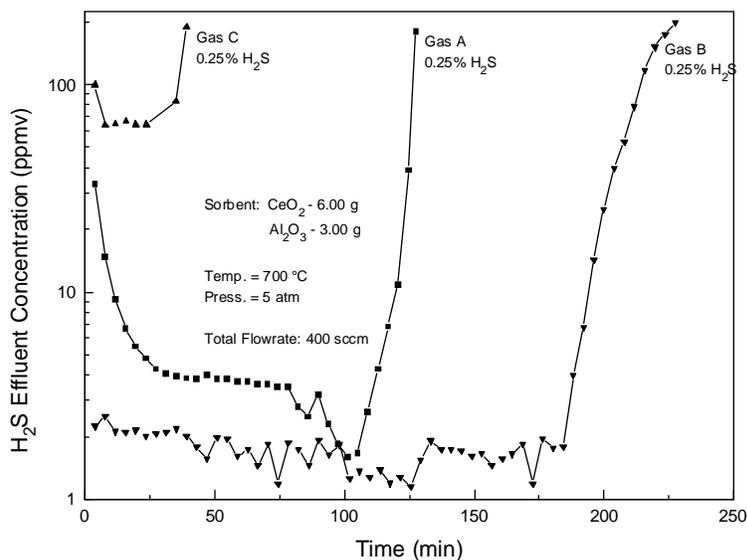


Figure 7. Prebreakthrough H<sub>2</sub>S Concentrations as a Function of Feed Gas Composition

the 700 °C reaction temperature. Gas A exhibited intermediate performance with the H<sub>2</sub>S concentration below 5-ppmv between 15 and 115 minutes; the equilibrium O<sub>2</sub> pressure of Gas A at 700 °C was just less than 10<sup>-20</sup> atm. While the equilibrium O<sub>2</sub> pressure of Gases A and C were about equal, sorbent performance with Gas C was clearly inferior. The minimum H<sub>2</sub>S concentration was between 60-ppmv and 70-ppmv, and FPD breakthrough occurred after about 50 minutes. Although Gases A and C should have produced about the same level of CeO<sub>2</sub> reduction, the poorer sulfidation performance of Gas C is attributed to its relatively large H<sub>2</sub>O-H<sub>2</sub> ratio.

**Sorbent Durability:** Results of process analysis and preliminary economic evaluation reported previously (Zeng et al. 1997) showed that sorbent durability was key to the commercial viability of either a zinc-based or cerium-based high temperature desulfurization process. Favorable ten-cycle results using cerium sorbent were presented in the previous paper. A twenty-five-cycle test with similarly favorable results was completed this year. The TCD was used for gas analysis since the overall behavior of the breakthrough curve was of greater interest than the minimum initial H<sub>2</sub>S concentration.

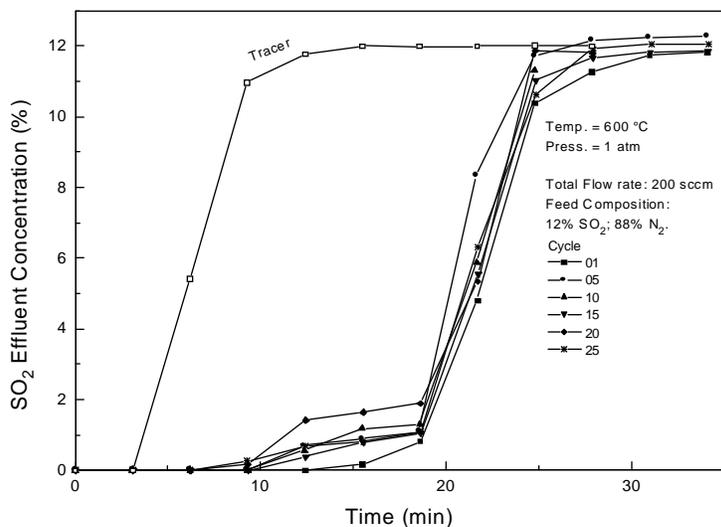


Figure 8. SO<sub>2</sub> Breakthrough Curves from Selected Regeneration Cycles of Twenty-Five-Cycle Test

SO<sub>2</sub> breakthrough curves from selected cycles of the twenty-five-cycle run are shown in Figure 8 with results from a non-reacting SO<sub>2</sub> tracer test at the same conditions included for comparison. In all cycles the elemental sulfur content of the regeneration product (considered as S<sub>2</sub>) exceeded 10 mol% between 8 and 17 minutes, and breakthrough occurred in the 17 to 25 minute period by which time regeneration approached completion. The scatter in the breakthrough curves appeared random. The time, t<sub>0.5</sub>, corresponding to 6 mol% SO<sub>2</sub> in

the regeneration product gas (50% of the feed concentration), varied from a minimum of 20.6 minutes in cycle 04 to a maximum of 23.0 minutes in cycle 06 with the average being 21.9 minutes. There was no evidence of sorbent deterioration as the number of cycles increased.

Percent conversion of  $CeO_n$  to  $Ce_2O_2S$  at the conclusion of each sulfidation cycle and of  $Ce_2O_2S$  to  $CeO_2$  at the end of each regeneration cycle is shown as a function of cycle number in Figure 9. These values were obtained by numerically integrating the area between the non-reacting tracer results and the breakthrough curves from individual sulfidation and regeneration cycles. Results from sulfidation cycle 16 and regeneration cycle 08 are omitted because of mass flow controller and sulfur plugging problems, respectively. Sulfidation conversion varied between 95% in cycle 01 to 108% in cycle 17 with an average of 101.9%. Regeneration ranged from 91% in cycle 05 to 109% in cycle 06 with an average of 98.3%. Thus, good sulfur material balance closure was achieved, and once again, there was no evidence of performance deterioration in the latter cycles.

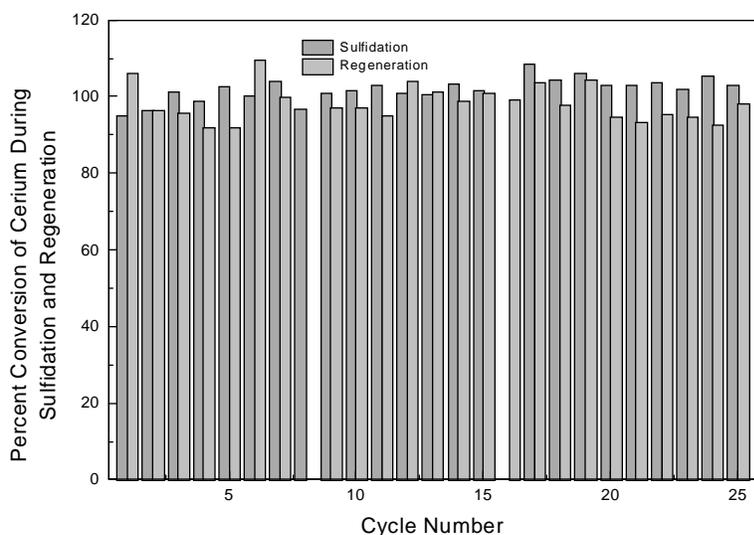


Figure 9. Sulfur Material Balance Closure in Twenty-Five-Cycle Sorbent Durability Test

During the fifty-eight day duration of this multicycle test, the sorbent was continually at a temperature of at least 600°C with the temperature being 800 °C for approximately 90% of that time period. The sorbent was alternately exposed to  $H_2/N_2$  during reduction,  $H_2/H_2S/N_2$  during sulfidation,  $SO_2/N_2$  during regeneration, and  $N_2$  purge between each phase. While twenty-five cycles are insufficient to establish commercial viability, these preliminary durability results are judged to be exceptionally promising.

### Application

The advantages of cerium-based high temperature desulfurization sorbent counter the disadvantages of first-generation zinc-based sorbent. The primary advantages of cerium sorbent are the ability to produce elemental sulfur directly during regeneration, lack of volatility and sulfate formation, improved intrinsic durability, and applicability to strongly reducing gases at higher temperatures. Because of the limited desulfurization ability of cerium sorbent, two-stage desulfurization with bulk  $H_2S$  removal using cerium sorbent followed by a zinc sorbent polishing step will be required when treating moderately reducing gases. The economics of the two-stage process may be competitive with single-stage zinc sorbent desulfurization if the cerium sorbent is sufficiently durable. Results of twenty-five-cycle durability tests are quite favorable. In special applications involving high temperature desulfurization of highly reducing gases, single-stage cerium sorbent desulfurization appears to be possible. At such conditions zinc-based sorbents are totally impractical.

## **Future Activities**

The experimental phases of the project have been completed and the final report is being prepared.

## **Acknowledgement**

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## **References**

- Bevan, D.J.M. and Kordis, J., 1964, *J. Inorg. Nucl. Chem.*, 26, 1509.
- Meng, V.V. and Kay, D.A.R., 1987, *Gas Desulfurization Using Rare Earth Oxides*, in *High Tech Ceramics*, P. Vincenzini ed., Elsevier Science Publishers, p. 2247.
- White, J.D., Groves, F.R., and Harrison, D.P., 1998, *Catalysis Today*, 40, 47.
- Zeng, Y., Zhang, S., Groves, F.R., and Harrison, D.P., 1997, *Hot-Gas Desulfurization With Sulfur Recovery*, Proceedings of the Advanced Coal-Based Power and Environmental Systems '97 Conference, DOE/FETC-97/1046 (on CD-ROM).