

Advanced Sulfur Control Concepts for Hot Gas Desulfurization Technology

**Quarterly Report
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EXECUTIVE SUMMARY

Experimental effort on Task 3.2 - Laboratory Development - was completed during the quarter. Professor Harrison, project Principal Investigator, reviewed the overall project status in a presentation in Morgantown in January 1997. The presentation emphasized the favorable results recently achieved in the sulfidation of CeO_2 by H_2S and the regeneration of $\text{Ce}_2\text{O}_2\text{S}$ by SO_2 . Successful removal of approximately 99% of the H_2S from the sulfidation gas to levels of about 100 ppmv (or lower), and the production of approximately 12% elemental sulfur (as S_2) in the regeneration product gas were highlights. Incremental funding of \$60,000 and a one-year time extension to continue the cerium-sorbent work was approved. The test plan for the additional work was submitted.

On the experimental front, the quarter represented a transition period which included final tests in the preliminary phase of the study, and initial work in the more detailed phase. Final effort in the preliminary phase included a ten-cycle test at "standard" sulfidation and regeneration conditions with little or no sorbent deterioration. In this multicycle test the cause of the high prebreakthrough H_2S concentration plateau was identified as being due to residual sulfur compounds downstream of the sorbent bed and in the transfer tubing between the reactor and analytical system. Chemical cleaning by flowing a H_2/N_2 mixture through the reactor and downstream tubing at high temperature was effective in reducing the prebreakthrough H_2S plateau to the 400-500 ppmv level. The use of high temperature air to remove sulfur compounds by converting them to SO_2 was even more effective. Prebreakthrough H_2S concentrations of 100 ppmv or less were achieved after oxidative cleaning.

In the initial test of the detailed experimental phase of the program, we investigated the effect of temperature on the regeneration reaction. Results of preliminary tests showed that the $\text{Ce}_2\text{O}_2\text{S}-\text{SO}_2$ reaction did not occur at 350°C , and all subsequent regeneration tests were at 600°C where the reaction was rapid. A series of regeneration tests between 450 and 700°C found essentially no reaction at 450°C , and rapid and complete regeneration at higher temperature but with little effect of temperature on the reaction rate.

The original justification for the CeO_2 sorbent study was the probability of the direct production of elemental sulfur during sorbent regeneration. Experimental results to date have confirmed this advantage. Primary disadvantages of CeO_2 include reduced sulfur capacity (the sulfur content of $\text{Ce}_2\text{O}_2\text{S}$ is only 9wt% compared to 33wt% in pure ZnS), and the less favorable thermodynamics of the $\text{CeO}_2-\text{H}_2\text{S}$ reaction compared to the $\text{ZnO}-\text{H}_2\text{S}$ reaction. The thermodynamics limitation led to the two-stage desulfurization concept with CeO_2 used for bulk H_2S removal followed by a ZnO polishing step. Obviously, the attractiveness of the CeO_2 process would be increased if the second desulfurization stage could be eliminated. Both experimental and thermodynamic evidence, based on the reduction of CeO_2 to CeO_n ($n < 2$) and subsequent reaction between CeO_n and H_2S , has been found which indicates that single-stage desulfurization may, indeed, be possible. We propose to examine this possibility during the remainder of the project.

Significant progress has been made on the process analysis effort during the quarter. Detailed process flow diagrams along with material and energy balance calculations for six design case studies were completed in the previous quarter. Two of the cases involved two-stage desulfurization with steam regeneration, three used two-stage desulfurization with SO₂ regeneration, and the sixth was based on single-stage desulfurization with elemental sulfur recovery using the DSRP concept.

In the present quarter, major process equipment was sized for each of the six cases. Capital cost estimates indicated that two-stage desulfurization with SO₂ regeneration could be accomplished with the least capital cost, followed by single-stage desulfurization with DSRP, and two-stage desulfurization with steam regeneration being the most capital intensive. The incremental capital cost required for single-stage desulfurization with DSRP was due primarily to the large air compressor required in the sorbent regeneration step. Capital costs were relatively insensitive to the operating temperature of the primary (first-stage) sorber and regenerator.

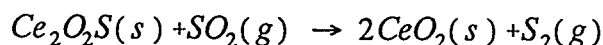
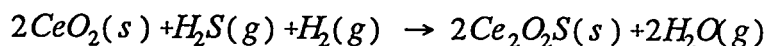
Preliminary annual operating and levelized total cost estimates were then completed for two design cases -- one involving two-stage desulfurization with SO₂ regeneration and the second based on single-stage desulfurization with DSRP. These calculations used "base case" estimates of the unit costs of raw material and by-product chemicals and utilities. The final levelized cost in both cases was quite high, but the estimated annual levelized cost of the single-stage desulfurization with DSRP was about 60% less than that of two-stage desulfurization with SO₂ regeneration.

Sorbent replacement cost, which was the dominant cost item in each case, was based upon an assumed sorbent replacement rate equal to 1% of the sorbent circulation rate, equivalent to an average sorbent life of 100 cycles. If either process is to be economically attractive, the sorbent replacement rate must be lowered considerably. This will reduce the cost of the cerium sorbent-based two-stage desulfurization process with SO₂ regeneration at a faster rate than the cost of the zinc sorbent-based single-stage desulfurization process with DSRP. At some replacement rate the cerium sorbent process will become more economical as its lower capital requirement becomes a more important cost factor.

In future economic analysis, a number of parameters, including sorbent unit cost and sorbent replacement rate, will be varied to illustrate the sensitivity of the process cost to key items.

CERIUM SULFIDATION AND REGENERATION

The primary reactions of interest are:



The research was originally justified on the basis of the potential for the direct production of elemental sulfur during the sorbent regeneration step. However, because $Ce_2O_2S(s)$ is not available commercially, both the sulfidation and regeneration reactions must be studied.

Most early CeO_2 sulfidation tests were performed at $800^\circ C$ and 5 atm using a sulfidation gas containing 1% H_2S , 10% H_2 , and balance N_2 . Sulfidation is rapid and complete and good sulfur material balance closure has been achieved. The only negative result was an unexpectedly large H_2S concentration plateau prior to breakthrough. Near the end of the previous quarter, the cause of this plateau was tentatively attributed to sulfur contamination in the reactor system downstream of the sorbent bed. Sulfidation studies during the present quarter have examined the cause and elimination of the contamination and have studied sorbent durability through ten complete cycles. Evidence has been found in the literature suggesting that the sulfidation effectiveness of cerium sorbent in highly reducing, high temperature gases might be increased to the point that a single-stage desulfurization process using cerium sorbent might be feasible. This work is discussed in a subsequent section of this report.

Regeneration results continue to be favorable. The regeneration reaction is rapid and complete at $600^\circ C$ and elemental sulfur concentrations (expressed as S_2) as high as 12% have been produced. The ten-cycle test completed during this quarter showed little, if any, sorbent deterioration. A series of tests in which the regeneration temperature was varied showed the reaction to be rapid and complete over the range of $500 - 700^\circ C$. The effect of temperature on regeneration kinetics was quite small.

A summary of reaction conditions used in all experimental tests during the quarter is presented in Table 1. The first three cycles of run Ce-16 were completed in the previous quarter. All sulfidation runs were conducted at $800^\circ C$ and 5 atm using 400 sccm of feed gas containing 1% H_2S /10% H_2 /balance N_2 . Regeneration runs were at 1 atm using 200 sccm of feed gas containing 12% SO_2 /balance N_2 . $600^\circ C$ regeneration temperature was used in Ce-16, Ce-17, and Ce-18, while the regeneration temperature in the multiple cycles of Ce-19 was varied between 450 and $700^\circ C$. The initial sorbent charge consisted of 6.0g CeO_2 and 3.0g of inert Al_2O_3 except in run Ce-18 where the Al_2O_3 was omitted.

Run Ce-16

The primary purpose of this run was to test the durability of the CeO_2 sorbent through ten complete sulfidation-regeneration cycles. In addition, initial effort testing different reactor cleaning procedures between regeneration and sulfidation cycles was instituted, and the sulfur material balance was carefully monitored.

H_2S concentrations in the sulfidation product gas as a function of time for cycles Ce-16s03 through Ce-16s10 are shown in Figures 1 and 2. Figure 1 is the traditional

Table 1. Summary of Reaction Test Conditions: CeO₂ Sulfidation and Regeneration
January - March 1977

Run	Ce-16s04 through Ce-16s10	Ce-16r04 through Ce-16r10	Ce-17s01 and Ce-17s02	Ce-17r01 and Ce-17r02	Ce-18s01	Ce-19s01 through Ce-19s05	Ce-19r01	Ce-19r02	Ce-19r03	Ce-19r04	Ce-19r05
Date	1/03/97 - 1/18/97	1/03/97 - 1/18/97	2/27/97 - 2/28/97	2/27/97 - 2/28/97	3/14/97	3/25/97 - 3/31/97	3/25/97	3/26/97	3/27/97	3/28/97	3/31/97
Reactor Packing											
CeO ₂ ,g	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
AL ₂ O ₃ ,g	3.0	3.0	3.0	3.0	0.0	3.0	3.0	3.0	3.0	3.0	3.0
Reaction Conditions											
Temp, °C	800	600	800	600	800	800	450	550	650	700	500
Press., atm	5	1	5	1	5	5	1	1	1	1	1
Gas Composition											
%H ₂ S	1	0	1	0	1	1	0	0	0	0	0
%SO ₂	0	12	0	12	0	0	12	12	12	12	12
%H ₂	10	0	10	0	10	10	0	0	0	0	0
%N ₂	89	88	89	88	89	89	88	88	88	88	88
Total Gas	400	200	400	200	400	400	200	200	200	200	200
Flow rate, SCCM	400	200	400	200	400	400	200	200	200	200	200

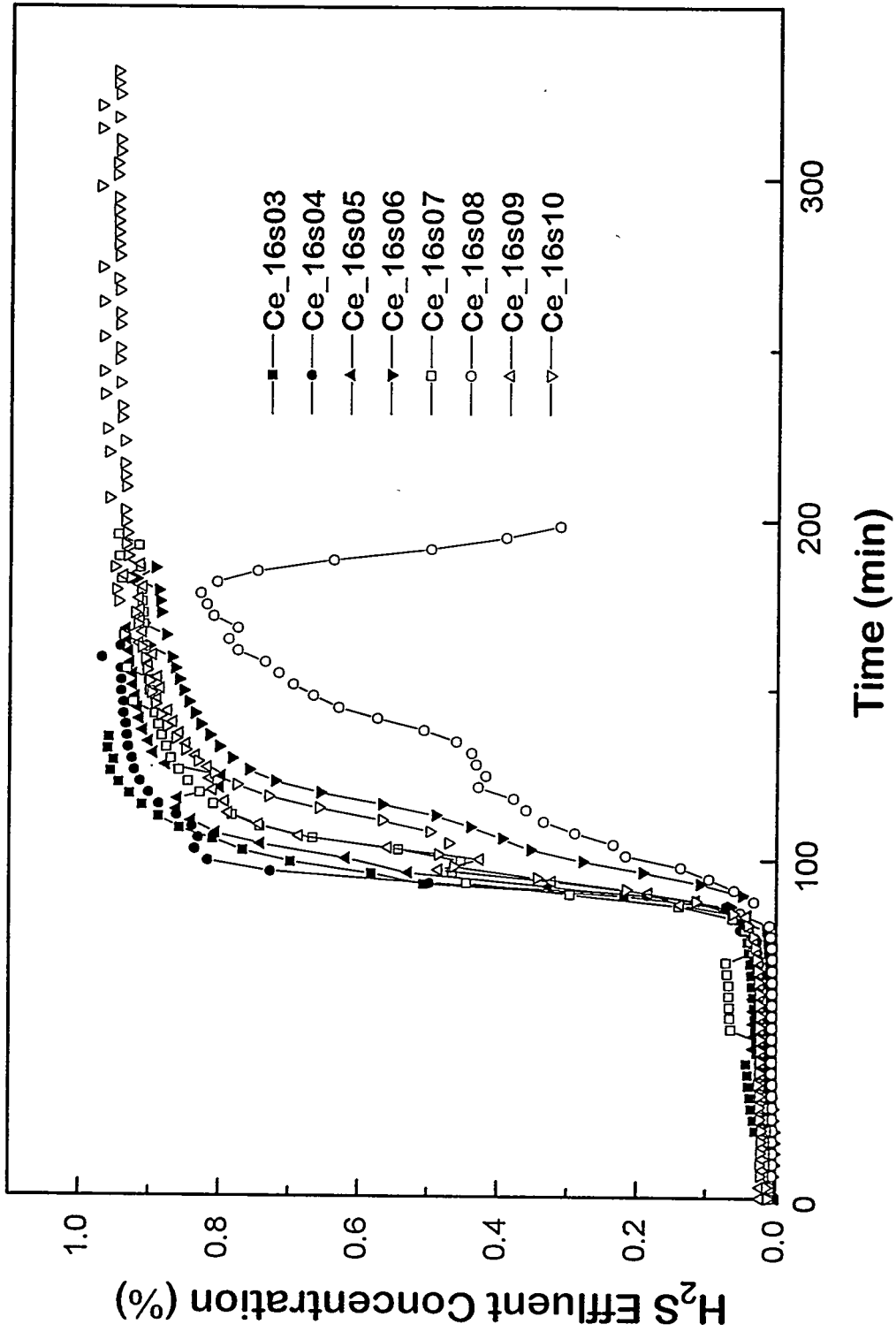


Figure 1. Sulfidation Breakthrough Curves for Tests Ce-16s03 through Ce-16s10.

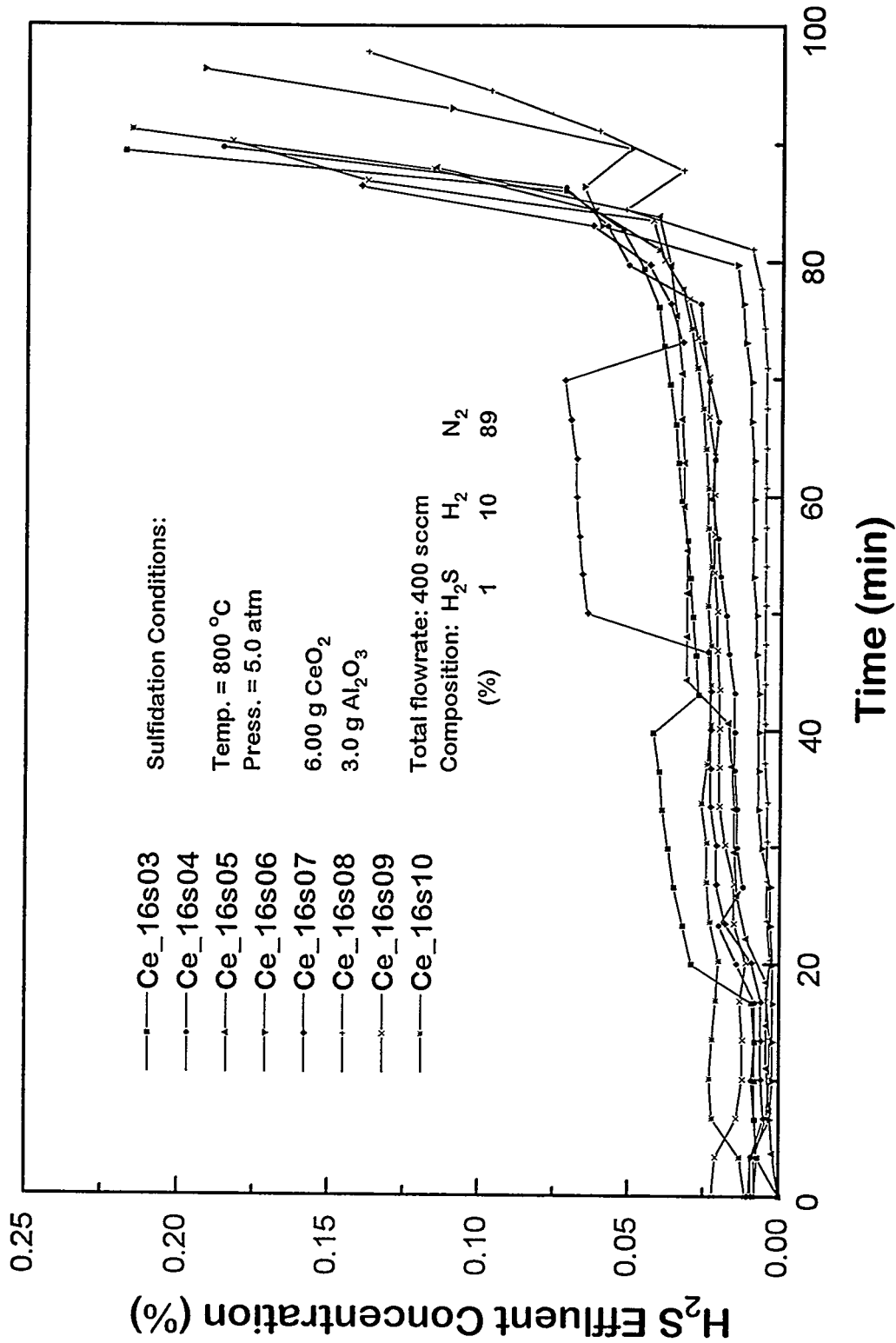


Figure 2. Sulfidation Prebreakthrough Curves for Ce-16s03 through Ce-16s10.

breakthrough curve showing the complete cycle results; in Figure 2 the concentration scale has been expanded to emphasize H₂S concentrations during the prebreakthrough period. All sulfidation tests, with the exception of Ce-16s08, went to completion in the same general time period. In Ce-16s08, the H₂S mass flow controller malfunctioned after about 175 minutes, which may also have been responsible for the earlier differences in the H₂S breakthrough curve for that cycle.

The important results from Figure 2 include the facts that initial H₂S concentrations were all equal to or less than 0.025% H₂S (250ppmv), and that, with the exception of the unexplained upset in Ce-16s07 in the 50 to 70 minute period, the H₂S concentration was less than 0.05% (500 ppmv) for the first 80 minutes of each cycle. Of particular interest, the H₂S concentrations in Ce-16s06 and Ce16s08 were below 150 ppm for 80 minutes. H₂S breakthrough time, taken as 0.05%(500 ppm), was approximately constant as shown in Figure 3. The times ranged from a low of 79.5 minutes in Ce-16s04 to a maximum of 84.3 minutes in Ce-16s05. The unexplained upset in Ce16s07 was ignored in determining the breakthrough time.

It was prior to Ce-16s03 that the importance of cleaning the reactor system between regeneration and sulfidation cycles was first recognized. A H₂/N₂ mixture was passed through the high temperature reactor to remove (at least partially) downstream sulfur compounds prior to each of the sulfidation cycles shown in Figures 1 and 2. The presence of residual sulfur was proven by the fact that significant H₂S concentrations were present when the H₂/N₂ cleaning gas was analyzed. In general, this cleaning step was effective in reducing the initial H₂S concentration to about 400 ppmv.

All ten regeneration cycles of run Ce-16 used the same reaction conditions; SO₂ breakthrough curves for all cycles are shown in Figure 4. With the exception of two samples -- one at 17 minutes in Ce-16r03 and the other at 10 minutes in Ce-16r10 -- the results were almost identical. The first measurable quantity of SO₂, about 1%, was detected after 10 minutes, and by 23 minutes regeneration was effectively complete. The final steady-state SO₂ content in the product gas ranged from 11.8 to 12.2%.

Sulfur material balance results, expressed as percent of stoichiometric sulfur removed during sulfidation and liberated during regeneration, are presented in Figure 5. Results from the previous quarter (cycles 1 and 2) are included except for Ce-16s01 where an error was made in the sulfidation gas flow rate. Results from Ce-16s08 are also omitted because of the mass flow controller malfunction.

Sulfur material balance closure in the eight sulfidation cycles of run Ce-16 included in Figure 5 ranged from a minimum of 75.0% in Ce-16s02 to a maximum of 96.8% in Ce-16s10. Regeneration results ranged from a minimum of 86.0% of stoichiometric in Ce-16r03 to 92.6% of stoichiometric in Ce-16r10. Ideally, the sulfidation and regeneration results from a single cycle should be equal. That is, the quantity of sulfur removed during sulfidation should be equal to the quantity liberated during regeneration. Differences are

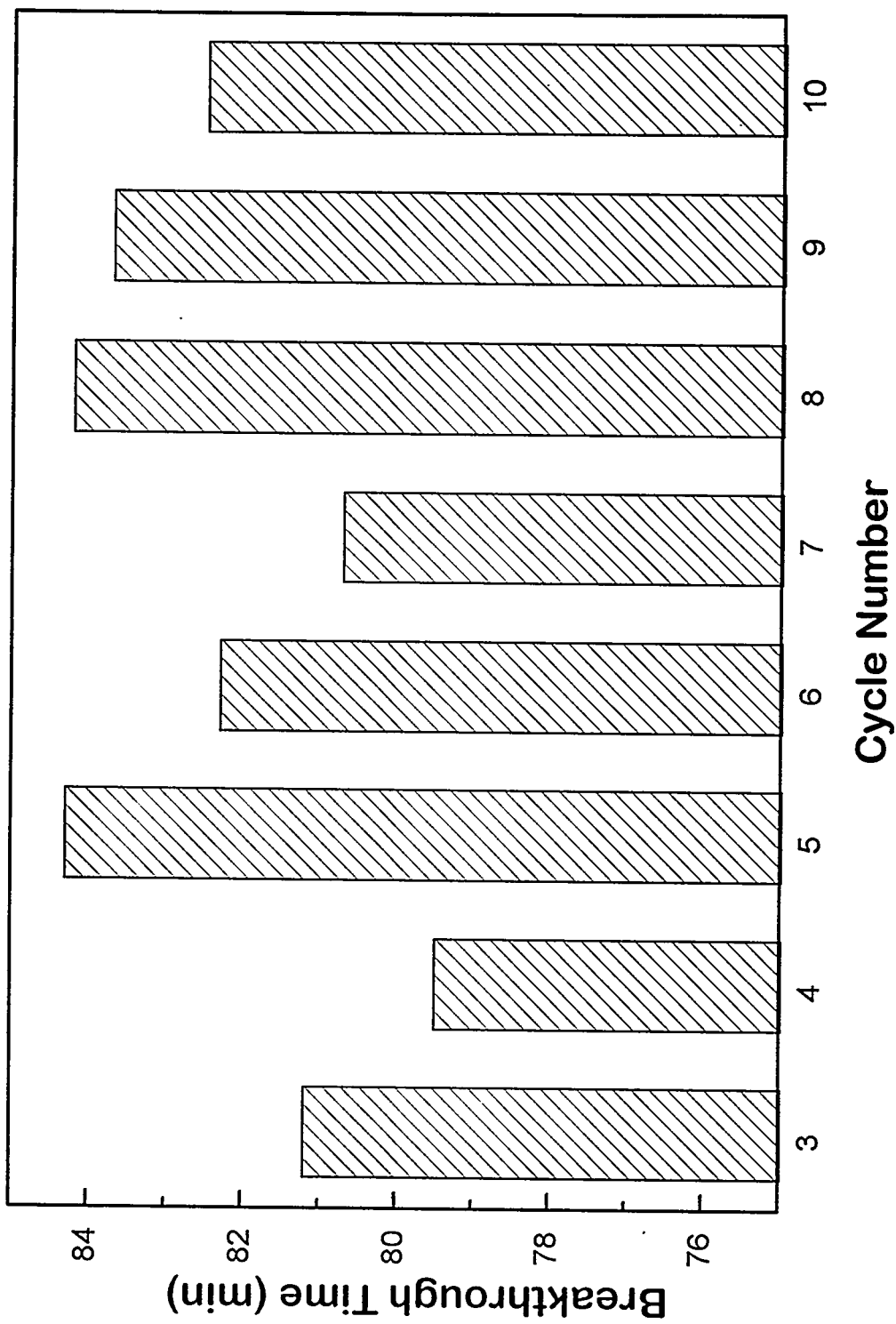


Figure 3. Sulfidation Breakthrough Times Corresponding to 0.05% H₂S: Runs Ce-16s03 through Ce-16s10.

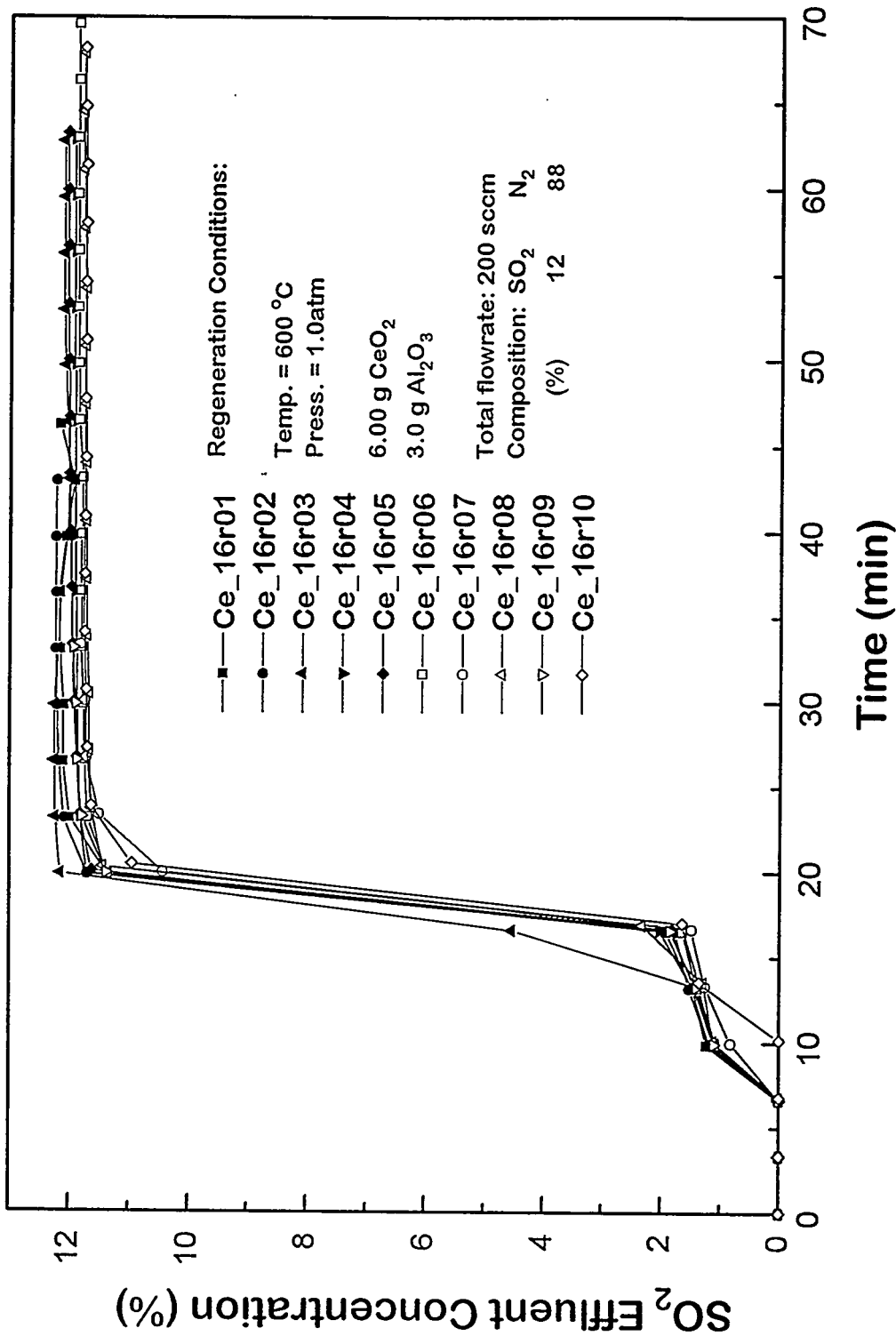


Figure 4. Regeneration Breakthrough Curves for Tests Ce-16r01 through Ce-16r10.

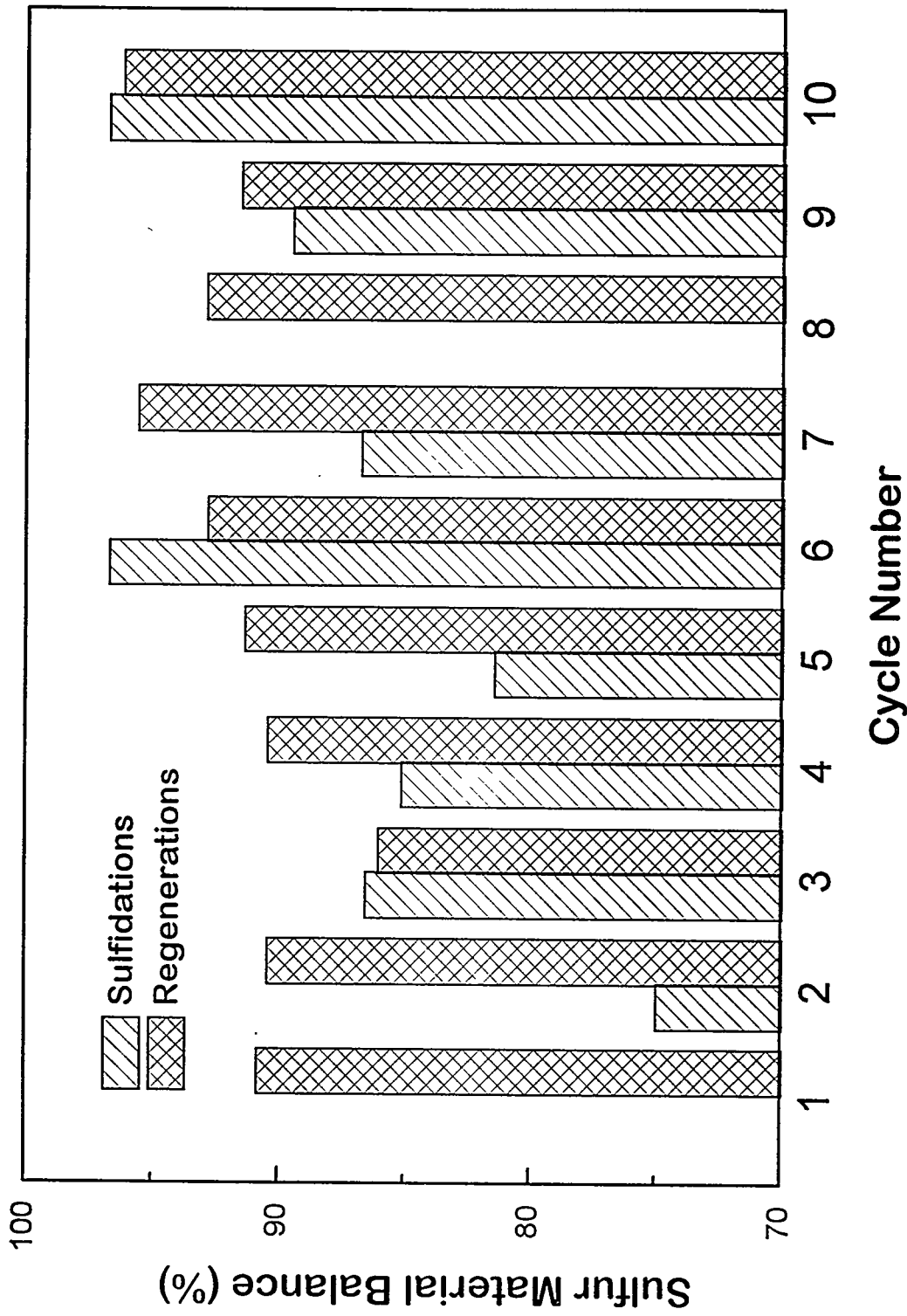


Figure 5. Sulfur Material Balance Closure During Cycles 1 through 10 on Ce-16.

caused by errors in flow rates (mass flow controllers), product gas analysis, and numerical integration of the breakthrough curve data. The maximum difference occurred in cycle 5 where sulfur removal and liberation were 81.5% and 91.4% of stoichiometric, respectively. However, the agreement was quite good when results from all cycles are averaged. Sulfur removal in the eight sulfidation cycles in Figure 5 averaged 87.2% of stoichiometric (88.9% if the low value associated with Ce-16s02 is omitted), while sulfur liberated in the ten regeneration cycles averaged 91.8% of stoichiometric.

The results of this extended ten-cycle run were quite favorable. The relative constancy of the slopes of the sulfidation and regeneration breakthrough curves, the small variation in breakthrough times, and the sulfur material balance closure all suggest little, if any, sorbent deterioration. In addition, the source of the elevated H₂S prebreakthrough concentration was identified and a method of reducing the concentration by about one order of magnitude was identified. It is important to recognize that the sulfur contamination problem would not exist in a commercial system where the reactor is not alternately exposed to sulfidation and regeneration conditions.

Run Ce-17

The primary purpose of two-cycle run Ce-17 was to continue to examine the effect of the severity of reactor cleaning on prebreakthrough H₂S concentration. While cleaning with H₂/N₂ was effective in reducing the prebreakthrough H₂S concentration to about 400 ppmv, this concentration was still larger than expected on the basis of thermodynamics. Prior to run Ce-17s01 and following Ce-17r01, air flowed through the reactor at 850°C with downstream tubing at 360°C. Approximately 150 hours at these conditions were required before SO₂ disappeared from the product gas prior to Ce-17s01. The air cleaning cycle lasted 10 hours before Ce-17s02.

H₂S concentration-time results for the two sulfidation cycles are shown in Figure 6. The runs were terminated when the H₂S content reached about 0.2% (2000 ppmv) in order to minimize sulfur contamination downstream of the sorbent bed. The significant result is that prebreakthrough concentrations ranged from 20 to 40 ppmv H₂S in Ce-17s01, and were approximately constant at 40 ppmv in Ce-17s02. It is important to realize that these low H₂S concentrations are, at best, approximate, since the sensitivity limit of the thermal conductivity detector for H₂S is about 100 ppmv. Although approximate, the results suggest that concentrations significantly below 100 ppmv can be achieved. The fact that Ce-17s02 concentrations were slightly larger may indicate that residual sulfur contamination remained after the abbreviated air cleaning cycle prior to Ce-17s02.

Regeneration breakthrough curves for Ce-17r01 and Ce-17r02 are presented in Figure 7. Standard regeneration conditions were used and results in the two cycles were effectively equal. In both cycles, the SO₂ concentration was zero in the first three samples (t < 7min), increased to about 2% during the next three samples, and closely approached the feed

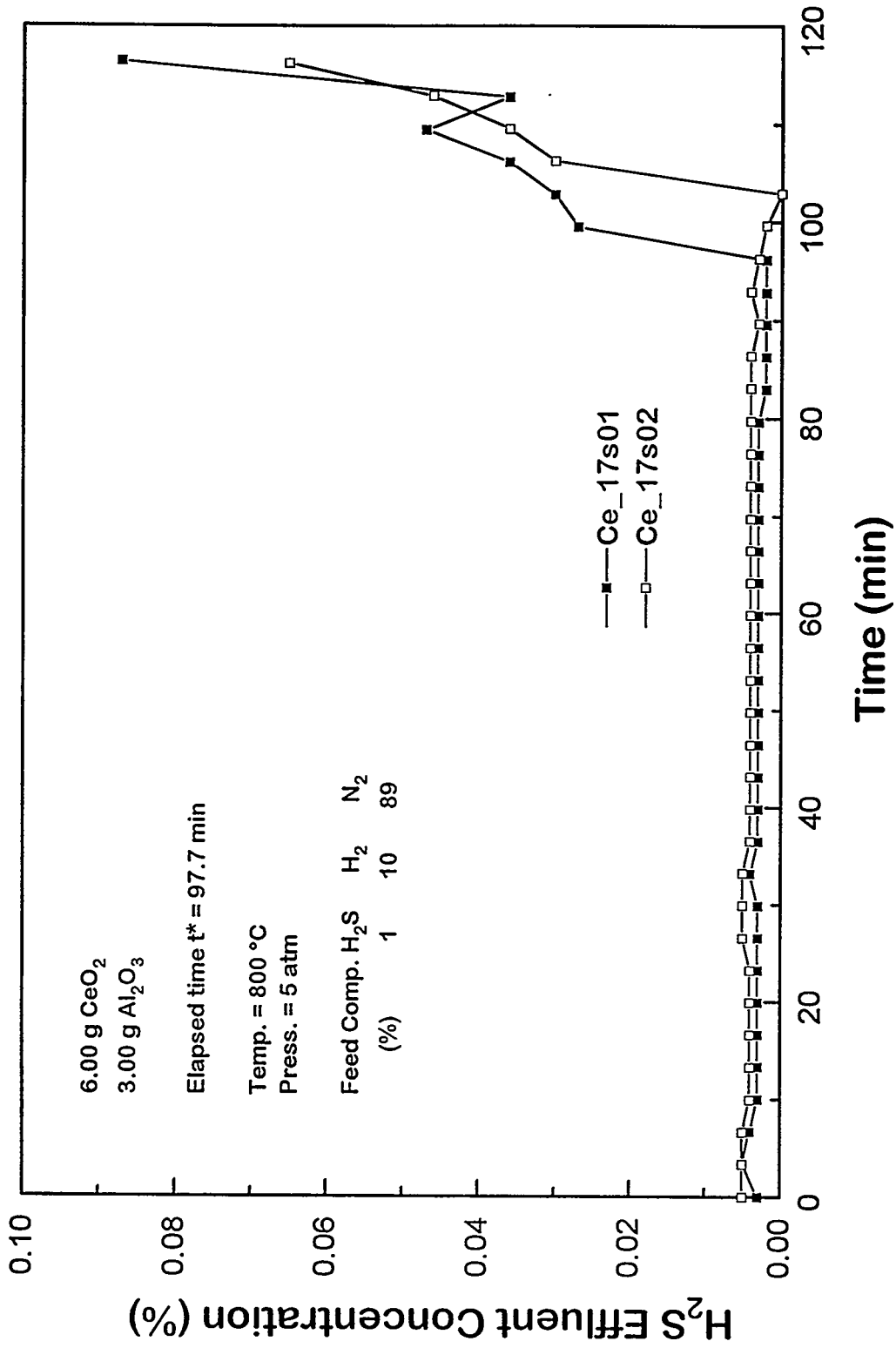


Figure 6. Sulfidation Response Curves: Run Ce-17s01 and Ce-17s02.

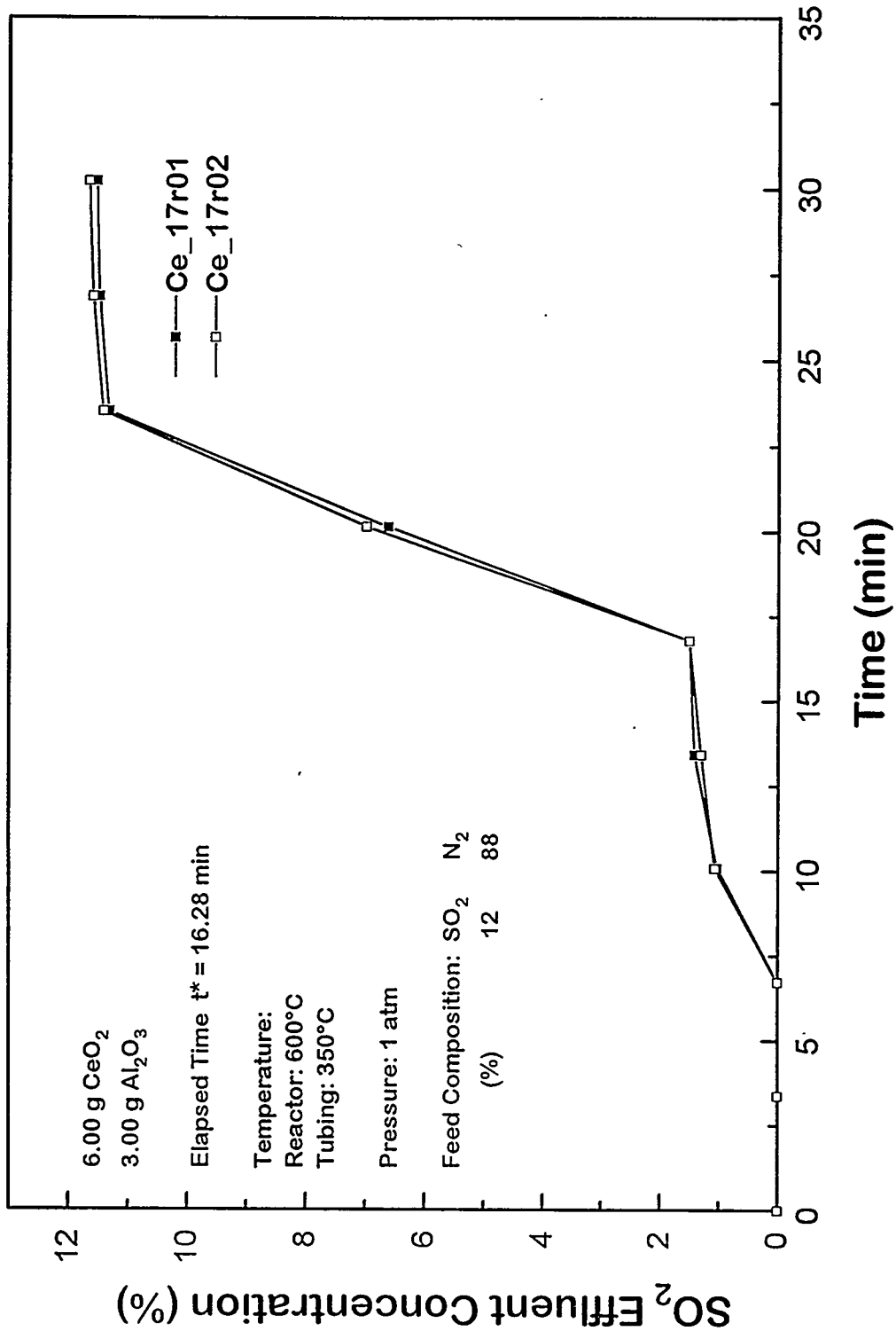


Figure 7: Regeneration Response Curves: Run Ce-17r01 and Ce-17r02.

composition of 12% by the eighth sample at about 23 minutes. Elemental sulfur concentration (considered as S₂) exceeded 10% for the first 17 minutes of each cycle.

Run Ce-18

In all recent cerium tests, the sorbent charge consisted of CeO₂ and inert Al₂O₃ in a 2-to-1 mass ratio. The Al₂O₃ was added to prevent sintering which occurred in earlier runs using pure CeO₂. Originally a 1-to-1 mass ratio was used and this was later changed to the 2-to-1 ratio without adverse effect. Completely eliminating the Al₂O₃ would permit the charge of CeO₂ to be increased, and would extend the duration of the regeneration cycle and/or allow still higher SO₂ concentrations to be used. However, severe sintering occurred in Ce-18s01, again confirming the need for at least some Al₂O₃. The volume of the cylinder of sintered sorbent removed from the reactor following Ce-18s01 was approximately 30% less than the volume of the original CeO₂ charge. Concentration-time results under these conditions were meaningless.

Run Ce-19

CeO₂ and Al₂O₃ were again mixed in the standard 2-to-1 ratio, and five sulfidation-regeneration cycles were completed. Regeneration temperature was varied over a range of 450°C to 700°C, while the chemical cleaning procedure between regeneration and sulfidation cycles was varied to obtain more information of the effect on prebreakthrough H₂S concentration. The cleaning procedures used are summarized below:

- Cycle 1. 10% H₂/N₂ was passed through the system for 3 hours with the reactor at 800°C and downstream tubing at 350°C.
- Cycle 2. The H₂ content was increased to 20% with the cleaning time and temperature as in cycle 1.
- Cycle 3. No cleaning. Run Ce-19s03 followed directly after Ce-19r02.
- Cycle 4. Air was passed through the system for about 17 hours with the reactor at 800°C and downstream tubing at 350°C.
- Cycle 5. The cleaning procedure was the same as in cycle 4 except that cleaning was extended over an entire weekend.

Sulfidation conditions in each cycle of Ce-19 were the same so that variations in prebreakthrough concentration should be attributed directly to the type and extent of cleaning. H₂S breakthrough results on an expanded concentration scale are shown in Figure 8. With the exception of Ce-19s05, the results were as expected based upon previous knowledge of the effect of cleaning. In Ce-19s01 and Ce-19s02, which followed H₂ cleaning, the H₂S concentration gradually increased from about 0.04% (400 ppmv). Concentrations of 0.1% and 0.25% were reached in Ce-19s01 after 93 and 100 minutes, respectively; in Ce-19s02 these same concentrations were reached after 100 and 105 minutes. The cleaning step was omitted following Ce-19r02, and a large peak in H₂S concentration

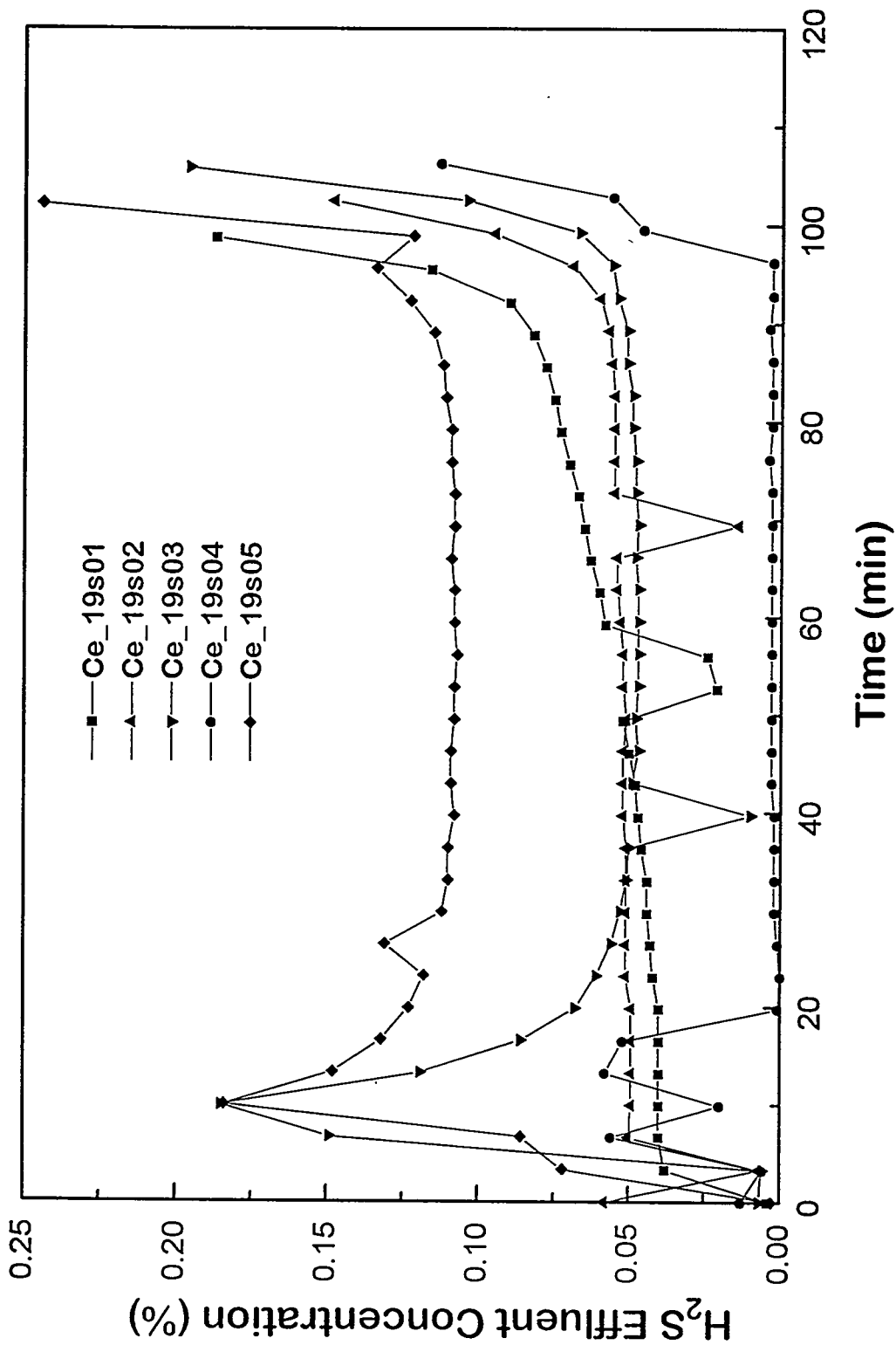


Figure 8. H₂S Breakthrough Curves During the Five Sulfidation Cycles of Run Ce-16.

was present in Ce-19s03 after 10 minutes. The concentration then decreased to about 0.05%, and concentrations of 0.1% and 0.25% occurred after 102 and 112 minutes, respectively. Thus, it appears that relatively brief (3 hours) cleaning in H₂ is effective in eliminating the initial H₂S peak, but does not remove the more refractory sulfur responsible for the 0.04% to 0.05% prebreakthrough concentrations.

Extended air cleaning preceded Ce-19s04 and, as shown in Figure 8, following an initial H₂S peak at about 0.06% at 10 minutes, the concentration dropped to the 0.001% to 0.004% range during the 20 to 95 minute time span. This prebreakthrough result was consistent with the results from Ce-17s01 and Ce-17s02 shown previously in Figure 6. The H₂S concentration in Ce-19s04 reached 0.1% after 105 minutes and 0.25% after 108 minutes, in quite good agreement with the results from Ce-19s01 through Ce-19s03.

Air at high temperature was also used to clean the system prior to Ce-19s05. The air cleaning cycle extended over an entire weekend, and we expected the Ce-19s05 sulfidation results to be as good or better than the Ce-19s04 results. However, as shown in Figure 8, this was not the case. After an initial peak near 0.2% after 10 minutes, the concentration decreased but remained above 0.1% throughout the test. There are two possible explanations for this poor performance. First, the performance is consistent with sintering which might have occurred during the prolonged high temperature cleaning. The second possibility is that the decreased reactivity was caused by the high temperature (700°C) of the previous regeneration cycle, Ce-19r04.

As stated previously, each regeneration cycle of run Ce-19 was carried out at a different temperature, covering the range of 450 to 700°C. The standard 600°C regeneration temperature, which had been used in all but one of the earlier tests, was omitted. This earlier test showed that regeneration was negligibly slow at 350°C. Similarly, the regeneration rate was quite slow at the 450°C regeneration temperature of Ce-19r01. Once the fact of the slow rate was established, the temperature was increased to 600°C to complete the regeneration and prepare the sorbent for the next sulfidation cycle.

Regeneration was rapid and complete over the temperature range 500 to 700°C, as shown by the SO₂ breakthrough curves of Figure 9. The effect of temperature was unexpectedly small, with the times corresponding 10% SO₂ in the product gas varying only between 20 minutes in Ce-19r05 at 500°C and 23 minutes in Ce-19r04 at 700°C. Perhaps the most significant difference is that in the two lower temperature tests (Ce-19r05 at 500°C and Ce-19r02 at 550°C) the SO₂ concentration in the product was significantly greater than zero by the third sample at about 6 minutes. In contrast, at the two higher temperatures (Ce-19r03 at 650°C and Ce-19r04 at 700°C) the SO₂ concentration was near zero until the fourth sample at about 10 minutes.

These results confirm that the 600°C standard regeneration temperature is a good choice. Significant positive or negative temperature excursions should not have a serious negative effect on the regeneration rate.

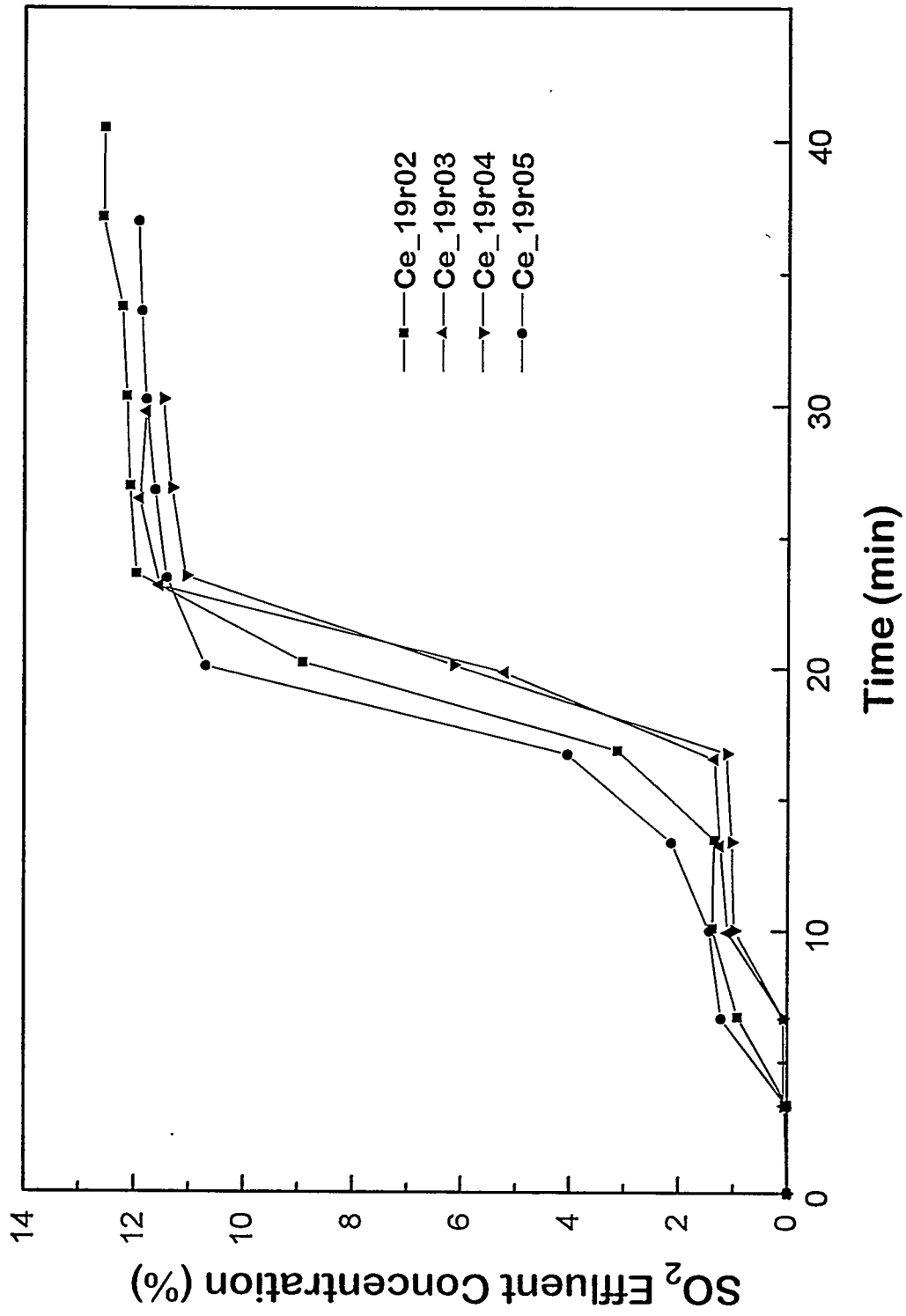


Figure 9. SO₂ Breakthrough Curves as a Function of Regeneration Temperature, Run Ce-19.

H₂S REMOVAL POTENTIAL

The possibility of the direct production of elemental sulfur during sorbent regeneration served as original justification of the cerium sorbent studies. Experimental results to date have confirmed this fact. The primary disadvantages of CeO₂ compared to ZnO include reduced sulfur capacity and less favorable sulfidation thermodynamics. The sulfur content of Ce₂O₂S is only 9 wt% compared to 33 wt% of ZnS. The poorer thermodynamics led to the two-stage desulfurization concept with bulk H₂S removal using CeO₂ followed by a polishing step using zinc-based sorbent. Obviously, the attractiveness of the cerium-based process would be improved if the second desulfurization stage could be eliminated. Evidence from the literature suggesting that this may, indeed, be possible has recently been found. We have begun to analyze the problem in more detail and results to date are summarized below.

Meng and Kay (1987) published results from two CeO₂ sulfidation tests in which H₂S concentration was reduced from 1.2% (12,000 ppmv) in the feed gas to less than 10 ppmv during a 20 minute prebreakthrough period. Sulfidation temperature was 1145K (872°C) and the feed gas contained 55% CO, 10.8% CO₂, 33.0% H₂, and 1.2% H₂S. Results of these tests are reproduced as Figure 10. The CeO₂ had been pre-reduced at 1145K in 5% H₂/N₂ for 24 hours. The explanation for the low prebreakthrough H₂S concentration was that the reaction was between H₂S and reduced cerium oxide, CeO_n (1.5 < n < 2), instead of CeO₂.

Bevan and Kordis (1964) published the results reproduced in Figure 11 showing the equilibrium value of n in CeO_n as a function of temperature and oxygen pressure. Using CHEMQ, we estimate the equilibrium O₂ pressure at 1145K in the gas composition used by Meng and Kay to be about 3x10⁻¹⁹ atm (1/2 log P_{O₂} = -9.3). According to the results of Bevan and Kordis, the equilibrium composition at these conditions should be CeO_{1.93}, which possessed more favorable thermodynamic properties than CeO₂.

Results of CHEMQ calculations showing the equilibrium O₂ pressure from a Shell gas as a function of temperature are summarized in Table 2 along with the estimated value of n in CeO_n obtained from Figure 11. A temperature slightly greater than 850°C would be required to achieve the same level of oxide reduction as achieved by Meng and Kay.

Thermodynamic data for reduced cerium oxide is not available, but it is reasonable to expect that the equilibrium H₂S pressure, and consequently the prebreakthrough H₂S concentration would be lower. This logic is illustrated in Figure 12 which presents the results of equilibrium calculations giving H₂S concentration as a function of temperature over CeO₂ and Ce₂O₃. The extended temperature range from 300 to 1600K is covered. The upper curve represents equilibrium between CeO₂ and H₂S in a Shell gas of the indicated composition. This is the type of calculation that has served as the basis for evaluating the desulfurization potential of cerium-based sorbents to this point. From 300 to 800K, the CeO₂-H₂S reaction is exothermic and equilibrium H₂S concentration increases with increasing temperature. Above 800K, however, the reaction becomes endothermic and potential H₂S

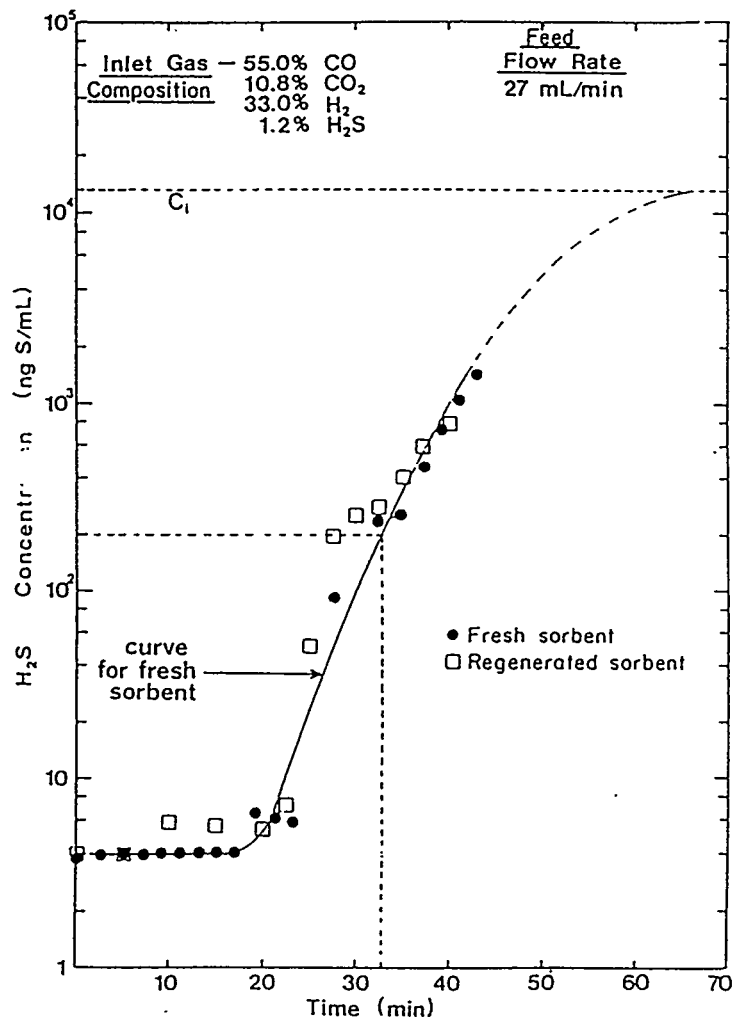
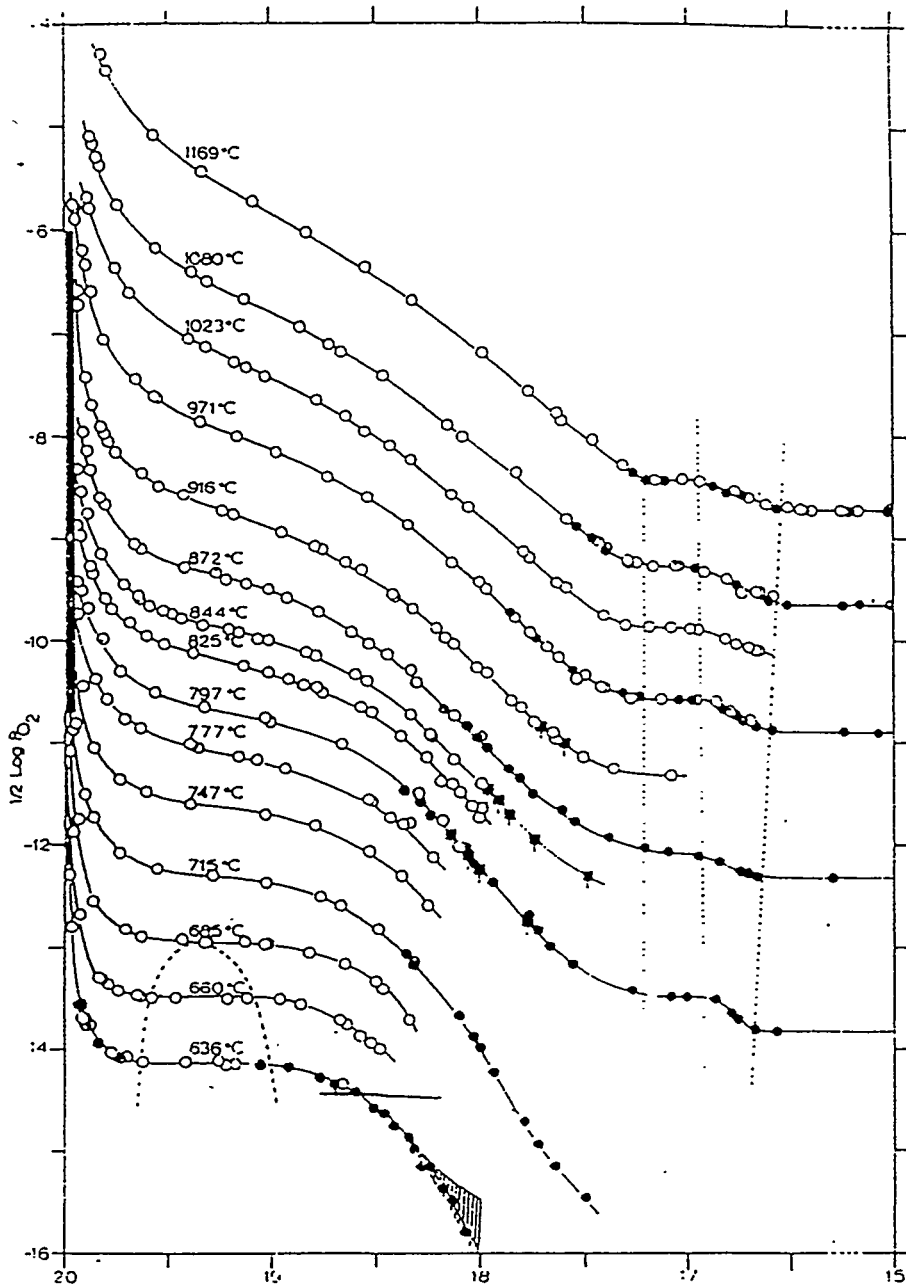


Figure 10. H₂S Breakthrough Curves During Two Sulfidation Cycles of CeO_n (n<2) (Meng and Kay, 1987)



Equilibrium Value of n in CeO_n

Figure 11. Reduction of CeO_2 to CeO_n as a Function of Oxygen Concentration and Temperature (Bevan and Kordis, 1964)

Table 2. Equilibrium Oxygen Pressure and CeO_n Composition in Shell Gas as a Function of Temperature.

Temperature, °C	Gas Composition, mol%						
	CO - 60	H ₂ - 29	CO ₂ - 2	H ₂ O - 5	H ₂ S - 1	N ₂ - 3	
700	750	800	850	900	950	1000	
P _{O₂} , atm.	8x10 ⁻²³	5.4x10 ⁻²²	2.8x10 ⁻²¹	3.8x10 ⁻²⁰	4.3x10 ⁻¹⁹	4.0x10 ⁻¹⁸	3.1x10 ⁻¹⁷
n in CeO _n	1.99	1.98	1.97	1.94	1.89	1.88	1.85

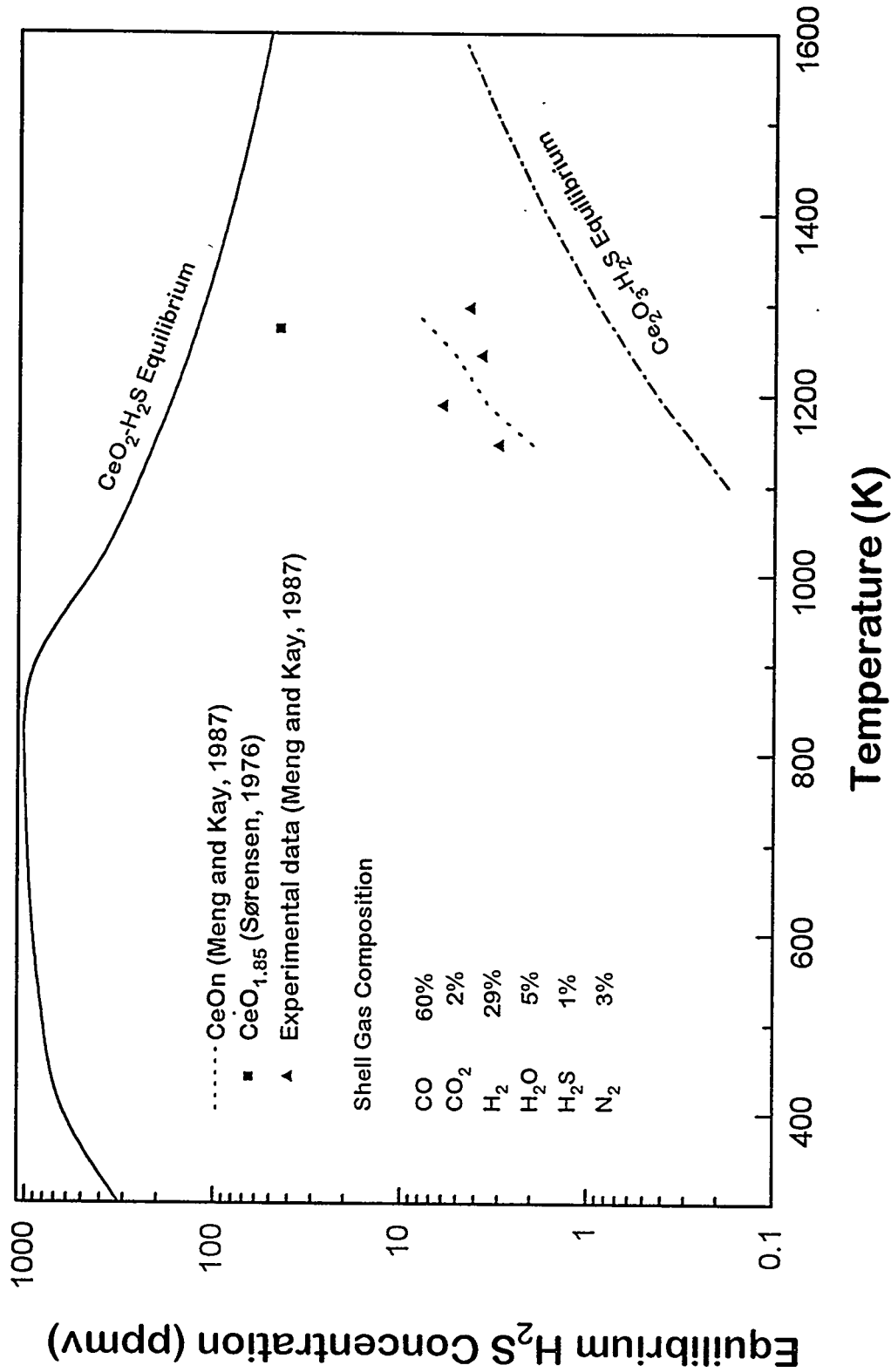


Figure 12. H_2S Equilibrium Concentration From Shell Gas in Contact with CeO_n .

removal efficiency improves with increasing temperature. At the standard experimental sulfidation temperature of 1073K, the equilibrium H_2S concentration is about 300 ppmv, which corresponds to the assumed H_2S concentration leaving the primary sorber in the systems analysis portion of the study. Still higher operating temperatures would improve the H_2S removal potential, but at 1600K the equilibrium level of H_2S would be about 50 ppmv.

Above a certain temperature, however, the reaction would be between CeO_n ($n < 2$) and H_2S , and the equilibrium H_2S concentration would presumably be lower. The limit of improvement is shown by the lower dashed line which represents equilibrium between Ce_2O_3 ($n=1.5$) and H_2S . This reaction is exothermic throughout the temperature range and H_2S removal potential decreases with increasing temperature. However, for all temperatures below 1300K, the equilibrium H_2S concentration is below 1 ppmv. Even at 1600K, Ce_2O_3 is thermodynamically capable of reducing H_2S to about 5 ppmv.

The thermodynamics of H_2S removal using CeO_n ($1.5 < n < 2.0$) should lie between these limits. To illustrate, the intermediate dotted line between 1145 and 1296K in Figure 12 represents the equilibrium H_2S concentration reported by Meng and Kay (1987), while individual points near this line represent their experimental results. Although the gas composition in Meng and Kay's study was different from the Shell gas composition, the equilibrium oxygen pressure was similar so that equilibrium H_2S concentration should also be similar. Finally, the single point at 1273K and 43 ppmv H_2S was calculated using the Shell gas composition and CeO_n free energy data from Sorensen (1976), who presented data only at this temperature.

Although there is considerable uncertainty in the thermodynamics, there appears to be a reasonable chance that cerium-based sorbent could be used to reduce H_2S concentration in a single sulfidation step to the level required for IGCC operation. Two significant experimental changes will be required to test this possibility. The thermal conductivity detector (TCD) currently used for H_2S analysis must be supplemented by a flame photometric detector (FPD). The TCD is reliable only to H_2S concentrations of above 100 ppmv while the FPD is capable of detecting H_2S to 1 ppmv or less. In addition, the reactor system downstream of the sorbent bed must be clean. As previously shown, sulfur contamination can result in apparent H_2S concentrations of 400 ppmv or more. We hope to acquire the FPD and examine the feasibility of single-step desulfurization using cerium-based sorbents in the remaining portion of the project.

PROCESS MODELING

At the conclusion of the previous quarter, detailed process flow sheets with material and energy balances had been completed for seven design case studies. Two involved the concept of two-stage desulfurization with steam regeneration and elemental sulfur recovery using a Claus process. Four cases involved two-stage desulfurization and direct production of elemental sulfur using SO_2 regeneration. In these six cases bulk H_2S removal was

accomplished in the primary sorber using a cerium-based sorbent, and zinc-based sorbent was used for polishing in the secondary sorber. The seventh case involved single-stage desulfurization with zinc sorbent and elemental sulfur recovery using the DSRP process. Details of the assumptions involved in these cases as well as material and energy balance results were presented in the previous quarterly report.

Effort in the present quarter involved the design of major process equipment, and estimation of capital, operating, and annual levelized costs. Six of the seven case studies were included in the vessel design effort. These cases are identified in Table 3 by the nominal operating temperatures of the sorbers and regenerators. Operating temperatures for case 5a involving two-stage desulfurization with SO₂ regeneration are effectively equal to the temperatures being used in the experimental study, while temperatures for case 6 involving single-stage desulfurization with DSRP are taken from values reported by Research Triangle Institute. Operating temperatures for other cases are arbitrarily selected to permit the effect of operating conditions on process cost to be estimated.

A list of major equipment, equipment sizes, and estimated purchased equipment cost is presented in Tables 4, 5 and 6 for the two cases of two-stage desulfurization with steam regeneration, three cases of two-stage desulfurization with SO₂ regeneration, and single case of single-stage desulfurization with DSRP, respectively. Sizes of each equipment type are expressed in the units required by the sources of the cost estimation data. All costs are expressed in 1996 dollars and the Chemical Engineering Plant Cost Index has been used to update earlier cost data to the 1996 level.

The following material describes the basis used for the design and costing of each major equipment type.

Reactors

Four primary reactor vessels are required for all two-stage desulfurization cases while only three are needed for single-stage desulfurization with DSRP. All four vessels required for two-stage desulfurization with steam regeneration are assumed to be adiabatic bubbling fluidized beds. While all four vessels required for two-stage desulfurization with SO₂ regeneration are bubbling fluidized beds, only the primary and secondary sorbers and secondary regenerator operate adiabatically. Nonadiabatic operation of the primary regenerator is required because of the highly exothermic nature of the reaction between Ce₂O₂S and SO₂. The SO₂ recycle rate was fixed to simultaneously satisfy the heat transfer and fluidization velocity requirements. The single sorber and regenerator used in the single-stage desulfurization with DSRP option were designed on the basis of adiabatic bubbling fluidized beds, while the DSRP reactor is a nonadiabatic fixed-bed. Energy liberated by the exothermic DSRP reaction is too large to permit adiabatic operation.

The fluidized beds were sized following the procedure described by Chen et al. (1992). Superficial gas velocity was set at 1ft/s which is approximately 5 to 7 times the

Table 3. Identification of the Six Case Studies by the Operating Temperature of the Reactors.

Two-Stage Desulfurization With Steam Regeneration		Nominal Temperature, K		
Case		1	2	
Reactor	Type			
Primary Sorber	Adiabatic Fluidized Bed	1000		900
Secondary Sorber	Adiabatic Fluidized Bed	873		873
Primary Regenerator	Adiabatic Fluidized Bed	1000		900
Secondary Regenerator	Adiabatic Fluidized Bed	1000		1000
Two-Stage Desulfurization With SO ₂ Regeneration				
Case		3a	4a	5a
Reactor	Type			
Primary Sorber	Adiabatic Fluidized Bed	1000	900	1073
Secondary Sorber	Adiabatic Fluidized Bed	873	873	873
Primary Regenerator	Nonadiabatic Fluidized Bed	1000	900	873
Secondary Regenerator	Adiabatic Fluidized Bed	1000	1000	1000
Single-Stage Desulfurization With DSRP				
Case		6		
Reactor	Type			
Sorber	Adiabatic Fluidized Bed		873	
Regenerator	Adiabatic Fluidized Bed		1000	
DSRP	Nonadiabatic Fixed Bed		873	

Table 4. Major Equipment List and Estimated Purchased Cost for Two-Stage Desulfurization with Steam Regeneration Cases.

	Case 1 1000K Primary Sorber		Case 2 900K Primary Sorber	
	Equipment Size (various units)	Purchased Cost (10 ⁶ \$, 1996)	Equipment Size (various units)	Purchased Cost (10 ⁶ \$, 1996)
Reactor Vessels (vessel weight, lb)				
Primary Sorber	3.81 x 10 ⁴	0.36	3.42 x 10 ⁴	0.34
Secondary Sorber	3.32 x 10 ⁴	0.33	3.32 x 10 ⁴	0.33
Primary Regenerator	3.73 x 10 ³	0.08	3.35 x 10 ³	0.07
Secondary Regenerator	2.40 x 10 ³	0.06	3.40 x 10 ³	0.07
Refractory	--	0.04	--	0.04
Subtotal	--	0.87		0.86
Heat Exchangers				
Waste Heat Boilers (lb steam/hr)				
H3	--	--	36,000	0.13
H13	3,200	0.03	--	--
H12	60,800	0.17	25,200	0.10
H15	30,600	0.12	13,000	0.07
H16	36,000	0.13	--	--
H17	--	--	68,000	0.19
Shell and Tube (ft ²)				
H1	450	0.01	400	0.01
Subtotal		0.46		0.50
Pump				
Flow Rate (gpm)	200	0.04	190	0.04
Head (ft)	2900		2900	
Steam Drum (gal)	1600	0.02	1500	0.02
Sour Water Stripper				
Diameter (ft)	2.4	--	2.4	--
Height (ft)	48	--	48	--
Pressure Swing Adsorption				
Flow Rate (lbmol/hr)	320	--	310	--
Claus Unit and Tail Gas Unit				
(S intake, (ton/day)	56	--	53	--
Total		1.38		1.41

Table 5. Major Equipment List and Estimated Purchased Cost for Two-Stage Desulfurization With SO₂ Regeneration Cases.

	Case 3a		Case 4a		Case 5a	
	1000K Primary Sorber	Purchased Cost (10 ⁶ \$, 1996)	900K Primary Sorber	Purchased Cost (10 ⁶ \$, 1996)	1073K Primary Sorber	Purchased Cost (10 ⁶ \$, 1996)
Reactor Vessels (vessel weight, lb)	Equipment Size (various units)		Equipment Size (various units)		Equipment Size (various units)	
Primary Sorber	3.81 x 10 ⁴	0.36	3.42 x 10 ⁴	0.34	4.09 x 10 ⁴	0.38
Secondary Sorber	3.32 x 10 ⁴	0.33	3.33 x 10 ⁴	0.33	3.32 x 10 ⁴	0.33
Primary Regenerator	3.98 x 10 ³	0.08	3.98 x 10 ³	0.08	3.98 x 10 ³	0.08
Secondary Regenerator	2.4 x 10 ³	0.06	3.44 x 10 ³	0.07	2.08 x 10 ³	0.05
Refractory	--	0.04	--	0.04	--	0.04
Subtotal	--	0.87	--	0.86	--	0.88
Heat Exchanger						
Waste Heat Boilers (lb steam/hr)						
H12	64,000	0.18	86,400	0.21	52,300	0.16
H15	9,900	0.06	17,500	0.08	7,630	0.05
H16	24,700	0.10	3,100	0.03	36,200	0.13
Shell and tube (ft ²)						
H1	1330	0.02	1,250	0.02	1,530	0.02
Subtotal		0.36		0.34		0.36
Compressor (hp)	103	0.04	106	0.04	118	0.04
Pump						
Flow Rate (gpm)	250	0.05	250	0.05	240	0.05
Head (ft)	2,930		2,900		2,930	
Steam Drum (gal)	3,000	0.02	2600	0.02	2,800	0.02
Total		1.33		1.30		1.34

Table 6. Major Equipment List and Estimated Purchased Cost
for Single-Stage Desulfurization With DSRP.

Case 6

	Equipment Size (various units)	Purchased Cost (10 ⁶ \$, 1996)
Reactor Vessels (vessel weight, lb)		
Sorber	3.23 x 10 ⁴	0.32
Regenerator	2.20 x 10 ⁴	0.25
DSRP Reactor	1.67 x 10 ⁴	0.21
Refractory	--	0.05
Subtotal		0.83
Heat Exchangers		
Waste Heat Boilers (lb steam/hr)		
H2	15,000	0.08
H4	31,500	0.12
H1	62,400	0.18
Shell and Tube (ft ²)		
H8	1,200	0.02
H3	3,600	0.04
H9	14,700	0.21
Subtotal		0.65
Compressors (hp)		
3-Stage Air	2,800	0.98
Recycle	390	0.15
Pump		
Flow Rate (gpm)	270	0.05
Head (ft)	2,930	
Steam Drum (gal)	3400	0.02
Total		2.67

minimum fluidization velocity. Contact time in the fluidized bed was fixed at 6 s which corresponds to a bed height of 6 ft. 50% freeboard height was added so that all fluidized-bed reactors are 9 ft in height. Six inches of refractory was included in each reactor because of the high operating temperature. An approximate heat transfer calculation was used to estimate the shell temperature, and shell thickness was determined in accordance with ASME codes as described by Peters and Timmerhaus (1991).

The volume of the fixed-bed reactor was determined from the space velocity of 4560hr^{-1} (STP) specified by Gangwal et al. (1993). This volume was then distributed appropriately between diameter and height. Six inches of refractory lining was added and the shell thickness was calculated in the manner described above.

Internal heat transfer for the DSRP reactor and the primary regenerator in the SO_2 regeneration cases was based on 1 1/4 inch OD heat transfer tubes. The overall heat transfer coefficient of $U=30\text{ Btu/hrft}^2\text{°F}$ was based on literature values reported by Seko et al. (1983), Piepers et al. (1983), and Donsi et al. (1983).

Reactor vessel dimensions are presented in Table 7. The height of all fluidized-bed reactors is 9 ft while the fixed-bed DSRP reactor is 11.5 ft in height. The open vessel diameter is the inside diameter to the beginning of the refractory lining. Six inches of refractory adds 1 foot to the metal wall inside diameter, and the outside diameter of the pressure vessel is equal to the inside metal wall diameter plus two times the wall thickness. Heat transfer tubes are included only in the nonadiabatic reactors.

All sorbers are approximately the same size. The difference in open vessel diameters, which ranges from 7.9 ft to 8.8 ft is due primarily to different operating temperatures. The smaller open vessel diameter of the sorber used in single-stage desulfurization with DSRP is also due partially to the diversion of a small amount of coal gas to the DSRP reactor. Regenerators are smaller, with diameters ranging from 1.6 ft to 6.5 ft. These differences are due to both gas flow rate and temperature, with the flow rate to the regenerator used in single-stage desulfurization with DSRP significantly larger because of the large nitrogen diluent flow. The DSRP reactor is of intermediate diameter, but is somewhat higher than the fluidized-bed reactors.

The purchased cost of individual reactors was estimated from an equation in Peters and Timmerhaus (1991) based on the vessel weight

$$K=80w^{0.66}$$

K is the vessel cost in 1990 dollars with a cost index of 356 and W is the vessel mass in lb_m . The cost entries in Tables 4, 5, and 6 represent the total cost of the four parallel reaction trains. Cost of refractory lining in each reactor is based on an informal estimate from a vendor (Milton, 1996). Note that the total purchased cost of the reactor vessels varies only

Table 7. Reactor Sizes for the Six Case Studies.

	Height (ft)	Open Vessel Diameter (ft)	Metal Wall Inside Diameter (ft)	Metal Wall Thickness	No. of Heat Transfer Tubes
Case 1 - Two-Stage Desulfurization with H₂O Regeneration					
Primary Sorber (adiabatic)	9	8.5	9.5	2.0	0
Secondary Sorber (adiabatic)	9	8	9	1.9	0
Primary Regenerator (adiabatic)	9	2.2	3.2	0.8	0
Secondary Regenerator (adiabatic)	9	1.6	2.6	0.6	0
Case 2 - Two-Stage Desulfurization with H₂O Regeneration					
Primary Sorber (adiabatic)	9	8.1	9.1	1.9	0
Secondary Sorber (adiabatic)	9	8	9	1.9	0
Primary Regenerator (adiabatic)	9	2.0	3.0	0.7	0
Secondary Regenerator (adiabatic)	9	2.1	3.1	0.7	0
Case 3a - Two-Stage Desulfurization with SO₂ Regeneration					
Primary Sorber (adiabatic)	9	8.5	9.5	2.0	0
Secondary Sorber (adiabatic)	9	8	9	1.9	0
Primary Regenerator (nonadiabatic)	9	2.3	3.3	0.8	100
Secondary Regenerator (adiabatic)	9	1.6	2.6	0.6	0
Case 4a - Two-Stage Desulfurization with SO₂ Regeneration					
Primary Sorber (adiabatic)	9	8.1	9.1	1.9	0
Secondary Sorber (adiabatic)	9	8	9	1.9	0
Primary Regenerator (nonadiabatic)	9	2.3	3.3	0.8	118
Secondary Regenerator (adiabatic)	9	2.1	3.1	0.7	0
Case 5a - Two-Stage Desulfurization with SO₂ Regeneration					
Primary Sorber (adiabatic)	9	8.8	9.8	2.0	0
Secondary Sorber (adiabatic)	9	8	9	1.9	0
Primary Regenerator (nonadiabatic)	9	2.3	3.3	0.8	102
Secondary Regenerator (adiabatic)	9	1.4	2.4	0.6	0
Case 6 - Single-Stage Desulfurization with DSRP					
Sorber (adiabatic)	9	7.9	8.9	1.8	0
Regenerator (adiabatic)	9	6.5	7.5	1.6	0
DSRP Reactor (nonadiabatic)	11.5	5.0	6.0	1.3	64

between \$0.83 million (case 6) and \$0.88 million (case 5a), and that the reactor costs are only weak functions of operating conditions. Only three primary reaction vessels are required for single-stage desulfurization with DSRP (case 6) compared to four vessels in all two-stage desulfurization options (cases 1 through 5a). However, all three vessels in case 6 are large while primary regenerators in cases 1 through 5a are much smaller. Thus, the final costs are relatively equal.

Heat Exchangers/Waste Heat Boilers

Four waste heat boilers and one shell-and-tube heat exchanger are required for each of the two-stage desulfurization with steam regeneration cases. Three waste heat boilers and one shell-and-tube exchanger are required for two-stage desulfurization with SO₂ regeneration, and three waste heat boilers and three shell-and-tube exchangers are needed for single-stage desulfurization with DSRP. The waste heat boilers include the units which are integral to the primary regenerators in the two-stage desulfurization with SO₂ regeneration cases and the DSRP reactor in the single-stage regeneration with DSRP option.

The size of the waste heat boilers was based on the pounds per hour of steam generated, numbers obtained directly from the PRO/II energy balance. An informal vendor quote (Willis, 1996) provided a purchased cost of \$75,000 for a unit having a capacity of 15,000 lb/hr of steam. The "0.6 factor rule" was used to estimate the cost for other capacities.

For all shell-and-tube heat exchangers, the values of UA (Btu/hr°F) came directly from the PRO/II energy balance. Exchanger area was then determined after estimating the heat transfer coefficient, U. Exchangers H1 in cases 1 through 5a and exchanger H9 in case 6 are the elemental sulfur condensers. The heat transfer coefficients, estimated from Kern (1950) depend on the quantity of noncondensables in the feed gas. The estimated coefficients ranged from 30 Btu/hrft²°F for case 6 where 95% of the feed gas is noncondensable to 180 Btu/hrft²°F in cases 1 and 2 where only 30% of the feed gas is noncondensable. Exchanger costs were estimated from a correlation in Peters and Timmerhaus (1991) and updated to 1996 levels using the Chemical Engineering Cost Index.

The combined cost of waste heat boilers and heat exchangers was only weakly dependent on operating conditions. For example, the purchased cost for the three two-stage desulfurization with SO₂ regeneration cases varied only between \$0.34 million and \$0.36 million (Table 5). This option resulted in the lowest cost while the highest cost was associated with the single-stage desulfurization with DSRP with an estimated cost of \$0.64 million (Table 6).

Compressors and Pumps

Compressor and pump horsepower requirements were obtained directly from the PRO/II simulation and were based on efficiencies of 0.85 and 0.65 for the compressors and

pumps, respectively. All cases require a large boiler feed water pump with the power depending upon the amount of steam generated. No compressors are required by the two-stage desulfurization with steam regeneration options, while a SO₂ recycle compressor is required for the two-stage desulfurization with SO₂ regeneration cases. The single-stage desulfurization with DSRP requires a recycle compressor and a large three-stage air compressor. The air compressor is primarily responsible for the higher cost for pumps and compressors associated with the single-stage desulfurization with DSRP option.

Compressor cost estimates were based directly on horsepower using information from Peters and Timmerhaus (1991). The pump cost data was obtained from Kirk-Othmer (1976) based on a combination of feed water flow rate and pump head.

Steam Drum

The steam drum is a minor cost item common to all cases. Although the design volume of the steam drum was somewhat variable, the estimated purchased cost rounded off to \$0.02 million in all cases.

Note that no purchased equipment costs are included in Table 4 (two-stage desulfurization with steam regeneration) for the sour water stripper, pressure swing absorber, and Claus and tail gas units. The estimate of their cost is introduced at the total process capital requirement level which is presented subsequently.

Comparison of the total purchased equipment cost estimates from Tables 4, 5, and 6, shows little dependence on operating conditions for any of the two-stage desulfurization with steam or SO₂ regeneration options. However, as previously noted, major equipment items have been omitted from the steam regeneration cases. The purchased equipment cost estimate for single-stage desulfurization with DSRP is approximately twice as large as the equivalent cost for either of the two-stage desulfurization with SO₂ regeneration options. The three-stage air compressor is responsible for most of this difference.

Total Capital Requirement

The total capital requirement includes such items as construction expenses, engineering fees, and working capital as listed in Table 8. The estimated cost of individual items is based on the indicated percent of the purchased equipment cost. The percentage of all items contributing to the process capital subtotal is taken from Peters and Timmerhaus (1991) while the percentage of all items below the process capital is taken from Buchanan et al. (1994). As shown in Table 8, the estimated total capital requirement for case studies 3a through 6 is 4.93 times the purchased equipment cost. The total capital investment for cases 1 and 2 involving two-stage desulfurization with steam regeneration is even larger because the estimated cost of the sour water stripper, pressure swing absorber, Claus unit, and tail gas unit were included at this stage. With the additional units, the total capital requirement,

Table 8. Total Capital Estimation Basis

Direct Cost	% of Purchased Equipment
Purchased Equipment	100
Purchased Equipment Installation	39
Instrumentation and Controls	13
Piping (Installed)	31
Electrical (Installed)	10
Buildings (Including services)	29
Yard Improvements	10
Service Facilities	55
Land	6
Subtotal	293
Indirect Cost	
Construction Expenses	34
Process Capital Total	327
Engineering Fees	33
Process Contingency	26
Project Contingency	49
Total Plant Cost	435
AFDC Cost	28
Total Plant Investment	463
Prepaid Royalties	2
Initial Catalysts	1
Startup Costs	13
Spare parts	2
Working Capital	10
Land	2
Total Capital Investment	493

as shown in Table 9, for two-stage desulfurization with steam regeneration is by far the largest, followed by single-stage desulfurization with DSRP, and leaving two-stage desulfurization with SO₂ regeneration with the smallest capital requirement.

Two previous economic studies, by McMichael and Gangwal (1991) and by Buchanan et al. (1994), have also considered the cost of the single-stage desulfurization with DSRP option. Direct comparison of the results is not possible because of the different time periods, plant sizes, and operating conditions. McMichael and Gangwal (1991) considered only the cost of sulfur recovery using DSRP (not including desulfurization and regeneration costs) for a plant having a coal gas feed rate about one-half the rate used in the current study and a pressure of 20 atm compared to 25 atm in the current study. Their estimate of the process capital requirement was \$2.15 million on a 1987 basis. Buchanan et al (1994) evaluated the cost of an entire IGCC plant having the same coal gas feed rate as the present study, but also at a lower operating pressure of 20 atm. Fortunately, Buchanan et al. reported capital costs of individual sections of the IGCC plant. On a 1993 basis, their estimate of the process capital required for the desulfurization, regeneration, and sulfur recovery portions was \$7.16 million. The process capital required for the combined desulfurization and regeneration sections was \$3.3 million compared to \$3.85 million for sulfur recovery.

We have used the above information and made approximate corrections to compare the capital requirements from the three studies on a common basis of 17,000 lbmol/hr of coal gas feed, an operating pressure of 20 atm, and using 1996 dollars. The only correction needed for the LSU study was to reduce the pressure from 25 atm to 20 atm. The resulting process capital estimate was reduced from \$8.8 million to \$8.5 million. The original process capital estimate of Buchanan et al. (1994) was increased from \$7.15 million to \$7.6 million in updating their costs to 1996 dollars. Several adjustments were required to bring the McMichael and Gangwal (1991) study to the common basis. First, their estimate of \$2.15 million in 1987 dollars for sulfur recovery only was increased to \$4.0 million to include the desulfurization and regeneration sections as well. This adjustment was made using the ratio of process capital for desulfurization and regeneration compared to sulfur recovery ($3.85/3.3=1.17$) reported by Buchanan et al. (1994). Next, the 0.6 factor was applied to increase the coal gas throughout to the common 17,000 lbmol/hr basis. Finally the costs were updated to 1996 using the appropriate cost indices. The final process capital estimate was \$7.4 million.

Although the methods are very approximate, the resultant process capital estimates from the three studies are reasonably close, ranging from \$7.4 million (McMichael and Gangwal) to \$7.6 million (Buchanan et al.) to \$8.5 million in this study. For practical purposes these estimates may be considered as being equal since the uncertainty in the estimate is larger than the minimum to maximum variation.

Operating Cost

At this stage the number of case studies was reduced to two -- one involving two-stage desulfurization with SO₂ regeneration (case 5a) and the other involving single-stage

Table 9. Summary of the Total Capital Investment
for the Six Case Studies

Case	Description	Total Capital Requirement (10 ⁶ \$, 1996)
1.	Two-Stage Desulfurization, Steam Regeneration, 1000K Primary Sorber	21.43
2.	Two-Stage Desulfurization, Steam Regeneration, 900K Primary Sorber	21.58
3a.	Two-Stage Desulfurization, SO ₂ Regeneration, 1000K Primary Sorber	6.55
4a.	Two-Stage Desulfurization, SO ₂ Regeneration, 900K Primary Sorber	6.45
5a.	Two Stage Desulfurization, SO ₂ Regeneration, 1073K Primary Sorber	6.65
6.	Single-Stage Desulfurization, DSRP	13.2

desulfurization with DSRP (case 6) -- for the purposes of operating cost estimation. Further consideration of two-stage desulfurization with steam regeneration was dropped when it became obvious that this concept would not be economically attractive. The capital requirement was significantly greater, the process was more complex, and the sorbent replacement rate, which (as will be shown) is the major operating cost, was comparable to the less capital intensive and simpler two-stage desulfurization with SO₂ regeneration option. In addition, operating cost estimates were carried out for only one (case 5a) of the three two-stage desulfurization with SO₂ regeneration options when it became obvious that capital and operating costs were relatively weak functions of the temperatures of the primary sorber and regenerator.

The key factors in estimating operating costs are consumption or generation rates of raw materials, by-products and utilities coupled with the unit costs of these items. Consumption and generation rates were obtained directly from the PRO/II simulation and are summarized in Table 10. Unit costs for these materials are presented in Table 11. Column 1 identifies the cost (or credit) item. Columns 2, 3, and 4 present the unit cost, the date of the unit cost, and the source of the unit cost data. Finally, the numbers in column 5 represent the unit costs updated to 1996. For example, the unit cost for zinc titanate sorbent of \$7000/ton in 1993 was taken from Buchanan et al. (1994), and the estimate of \$7500/ton in 1996 was obtained from the ratio of the cost indices. The unit costs of other items, with the exception of the DSRP catalyst, were estimated in the same manner. The annual cost of DSRP catalyst was taken directly from Buchanan et al. (1994) and updated to 1996 using cost factors.

Annual operating costs (credits) for raw materials, by-products, and utilities are summarized in Table 12. The values represent the product of the unit costs (Table 11) and the annual consumption (production) rate (Table 10). The annual cost of raw materials, by-products, and utilities for the two-stage desulfurization with SO₂ regeneration option (case 5a) is about twice that of the single-stage desulfurization with DSRP case (case 6), and almost all of the additional cost is directly attributable to the cost of the cerium sorbent compared to the zinc sorbent.

Also included in operating costs are such items as operating labor, maintenance labor, administration and support labor. These costs, designated as fixed operating costs, were estimated to be 5.45% of the process capital requirement following McMichael and Gangwal (1991), and are shown near the bottom of Table 12.

Levelized Cost

Final cost comparisons are based on the annual levelized cost (Electric Power Research Institute, 1982) which permits comparison of competing cases using single numbers in contrast with a display of full cash flow or present worth. Levelization of the operating costs is achieved by multiplying the first year's operating cost by a factor L_n which

Table 10. Consumption and Production Rates of Raw Materials, By-Products and Utilities.

	Two-Stage Desulfurization With SO ₂ Regeneration (Case 5a)	Single-Stage Desulfurization with DSRP (Case 6)
Raw Materials		
Zinc Sorbent	0.08 lbmol/hr	1.68 lbmol/hr
Cerium Sorbent	6.88 lbmol/hr	--
Coal Gas	--	435 lbmol/hr
Nitrogen	--	1100 lbmol/hr
Oxygen	177 lbmol/hr	--
By-Products		
Sulfur	164 lbmol/hr	171 lbmol/hr
Steam	6050 lbmol/hr	7560 lbmol/hr
Utilities		
Boiler Feed Water	6480 lbmol/hr	7560 lbmol/hr
Electricity	384 hp	3540 hp

Table 11. Base Unit Cost of Raw Materials, By-Products and Utilities.

Raw Materials	Unit Cost	Date	Reference	1996 Unit Cost
Zinc Sorbet	\$7,000/ton	1993	Buchanan et al. (1994)	\$7,500/ton
Cerium Sorbent	\$6,400/ton	1996	Stanford Materials (1997)	\$6,400/ton
DSRP Catalyst	\$4,000/yr	1996	Buchanan et al. (1994)	\$4,250/ton
Coal Gas	\$1.07/lbmol	1987	McMichael and Gangwal (1991)	\$1.25/lbmol
Nitrogen	\$25/ton	1996	Cammarnata (1997)	\$25/ton
Oxygen	\$40/ton	1996	Cammarnata (1997)	\$40/ton
By-Products				
Sulfur	\$76.40/ton	1987	McMichael and Gangwal (1987)	\$90/ton
Steam	\$4.9/1000lb	1981	EPRI (1982)	\$6.3/1000lb
Utilities				
Boiler Feed Water	\$11.2/1000 gal	1987	McMichael and Gangwal (1991)	\$13.2/1000 gal
Electricity	\$0.059/kwh	1987	McMichael and Gangwal (1991)	\$0.07/kwh

Table 12. Annual Variable and Fixed Operating Cost (Credit)
(10⁶ \$, 65% Capacity Factor).

	Two-Stage Desulfurization With SO ₂ Regeneration (Case 5a)	Single-Stage Desulfurization With DSRP (Case 6)
Raw Materials		
Zinc Sorbent	0.41	8.62
Cerium Sorbent	21.42	--
Coal Gas	--	3.11
Nitrogen	--	2.20
Oxygen	0.65	--
By-Products		
Sulfur	(1.34)	(1.41)
Steam	(3.91)	(4.88)
Utilities		
Boiler Feed Water	1.05	1.23
Electricity	0.11	1.05
Total Variable Operating Costs	18.39	9.92
Fixed Operating Cost	0.24	0.48

distributes the sum of the present worth of all future operating costs equally over the lifetime of the project. Levelization of capital costs over the lifetime of the project is achieved by multiplying the capital costs by the factor P_n . For an annual escalation factor of 6% and a ten-year analysis period, the values of L_{10} and P_{10} are 1.321 and 0.195 (O'Hara et al., 1987), respectively.

Final annual levelized costs for the two cases are compared in Table 13, along with the percent contribution to the total cost of each item. Two-stage desulfurization with SO_2 regeneration (case 5a) is shown to be almost 60% more expensive, with an annual total levelized cost of \$25.9 million compared to \$16.3 million for single-stage desulfurization with DSRP. Sorbent replacement is the dominant cost item in both cases. Cerium sorbent replacement cost alone is greater than the total cost of case 5a since credits for steam and sulfur exceed the cost of all other items.

Other items contributing significantly to the cost of two-stage desulfurization with SO_2 regeneration (case 5a) include boiler feed water (5.4%), fixed cost (5.1%), oxygen (3.3%), and zinc sorbent (2.1%). The credits for steam (20%) and sulfur (6.8%) more than offset the costs of other items. Other items contributing significantly to single-stage desulfurization with DSRP include coal gas (25.2%), nitrogen (17.8%) and fixed costs (15.8%). Credits associated with steam (39.6%) and sulfur (11.4%) partially offset these costs.

From the beginning, we recognized that the sorbent replacement rate equal to 1% of the sorbent circulation rate was unrealistically large. 1% replacement rate corresponds to an average sorbent life of 100 cycles, and sorbent lifetimes of several hundred cycles are thought to be necessary. In all probability, neither of the two cases presented in Table 13 would be economically viable.

The next step in the economic study will be a sensitivity analysis in which items which contribute significantly to the total cost and which involve significant uncertainty will be varied over a range of possible conditions to evaluate the effect on total annual levelized cost. Key sensitivity parameters to be considered include the unit cost and replacement rate of both the zinc and cerium sorbents. Reducing the sorbent replacement rate (increasing sorbent life) will reduce the annual levelized cost of both options, but will have a much greater effect on case 5a since the cerium sorbent cost is so large. At some replacement rate the cost of the two options will be equal, and for still smaller replacements rates, the two-stage desulfurization with SO_2 regeneration case will be less expensive. In the limit as the sorbent replacement rate approaches zero, the two-stage desulfurization with SO_2 regeneration option will actually become profitable since the credits for sulfur and steam exceed the total of all cost items less sorbent replacement. In contrast, there is no sorbent replacement rate at which the single-stage desulfurization with DSRP option will become profitable since by-products credits are less than the sum of the cost items less the zinc sorbent replacement cost.

Table 13. Total Levelized Cost Comparison for Two-Stage Desulfurization With SO₂ Regeneration (Case 5a) and Single-Stage Desulfurization With-DSRP (Case 6): 10⁶ \$, 65% Capacity Factor.

	Two-Stage Desulfurization With SO ₂ Regeneration (Case 5a)			Single-Stage Desulfurization With DSRP (Case 6)		
	Total Capital Requirement	Levelized Cost	% of Levelized Cost	Total Capital Requirement	Levelized Cost	% of Levelized Cost
Fixed Cost	6.70	1.31	5.1	13.21	2.58	15.8
Operating Cost (Credit)	Annual Cost			Annual Cost		
Fixed Operating Cost	0.24	0.31	1.2	0.48	0.63	3.9
Zinc Sorbent	0.41	0.54	2.1	8.62	11.38	69.8
Cerium Sorbent	21.42	28.29	109.2	--	--	--
DSRP Catalyst	--	--	--	0.004	0.005	0.0
Coal Gas	--	--	--	3.11	4.11	25.2
Nitrogen	--	--	--	2.20	2.91	17.8
Oxygen	0.65	0.86	3.3	--	--	--
Sulfur	(1.34)	(1.77)	(6.8)	(1.41)	(1.86)	(11.4)
Steam	(3.91)	(5.17)	(20.0)	(4.88)	(6.45)	(39.6)
Boiler Feed Water	1.05	1.39	5.4	1.23	1.62	9.9
Electricity	0.11	0.15	0.6	1.05	1.38	8.5
Total Levelized Cost	--	25.91	100	--	16.30	100

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