

DOE/ML/30092 --T1

**Advanced Sulfur Control Concepts in Hot-Gas
Desulfurization Technology**

**Quarterly Report
April 1 - June 30, 1997**

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**RECEIVED
JUN 18 1998
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Work Performed Under Contract No.: DE-AC21-94MC30012

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EXECUTIVE SUMMARY

Three areas of research were pursued during the past quarter. Experimental CeO_2 sulfidation and regeneration tests examined the effect of SO_2 concentration and gas flow rate on the production of elemental sulfur during regeneration. The maximum number of cycles using a single sorbent charge was increased to 13, and initial tests using a second source of CeO_2 (from Molycorp, Inc.) were carried out. Investigation of the thermodynamic possibility of reaching the IGCC target of about 20 ppmv H_2S using CeO_2 in a single-stage process was expanded. This concept is based on the reduction of CeO_2 to CeO_n ($n < 2$) at high temperature in highly reducing gas and the improved desulfurization potential of CeO_n compared to CeO_2 . A flame photometric detector for the gas chromatograph was ordered to enable H_2S concentration measurements down to 10 ppmv or less. In the process analysis effort, a third case study based on single-stage desulfurization using CeO_2 sorbent as described above was added. Capital and operating costs for this option were estimated under "base case" conditions. The sensitivity of the annual levelized cost of all three cases to variations in sorbent durability, sorbent unit cost, O_2 and N_2 unit cost, and capital cost was examined.

Experimental results continue to be favorable. The thirteen cycle run was conducted using "standard" sulfidation conditions in each cycle while both SO_2 concentration and gas feed rate were varied during the regeneration cycles. Little, if any, deterioration in performance was noted over the thirteen cycles. The SO_2 content of the feed was increased to 20% and elemental sulfur concentrations in the product (considered as S_2) approached 20%. As expected, the slope of the SO_2 breakthrough curve began to decrease as the feed rate increased due to reduced gas residence time in the sorbent bed. The maximum feed rate of 800 sccm corresponds to a space velocity of 18000 hr^{-1} (STP).

Initial tests using a second source of CeO_2 (from Molycorp, Inc.) showed good initial H_2S removal, but a somewhat slower global reaction rate. However, complete sulfidation was achieved, and material balance results corresponded to H_2S removals slightly greater than 100% of stoichiometric. The Molycorp CeO_2 sorbent was prepared in the standard manner involving dry pressing the powder into tablets which were subsequently crushed and sieved. Particles of 150 to 300 μ were used in the tests. The cause of the reaction differences between the two sorbents is not known, although we suspect differences in the characteristics of the original CeO_2 powders.

The equilibrium analysis was extended using approximate thermodynamic properties of CeO_n to predict ultimate H_2S removal potential in a Shell gas at high temperature. Free energies for CeO_n were estimated from known free energies of both CeO_2 and Ce_2O_3 ($\text{CeO}_{1.5}$). Although different equilibrium H_2S concentrations were predicted using the two approaches, achieving the 20 ppmv IGCC target level in a single stage appears possible.

At the end of the previous quarter, annual levelized cost estimates had been completed for two design cases, one involving two-stage desulfurization using CeO_2 for bulk H_2S removal followed by a zinc sorbent polishing step (case 5a), and the other involving single-stage desulfurization with ZnO and elemental sulfur recovery using DSRP (case 6). Cerium sorbent regeneration used SO_2 as the oxidant. Sorbent replacement costs were the dominant item in each case. During the present quarter, a third design case involving single-stage desulfurization with CeO_2 and SO_2 regeneration was completed (case 7). This case is based on the (as yet unproven) possibility of achieving H_2S

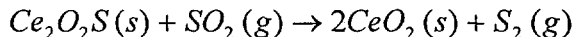
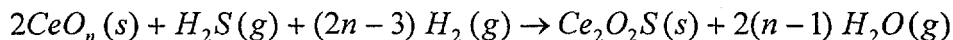
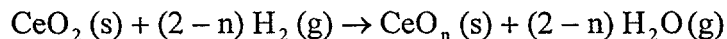
target levels in a single desulfurization stage using the reaction between CeO_n and H_2S . The total capital requirement for this case was considerably less, and the levelized cost was again dominated by the sorbent replacement cost.

The sensitivity of the annual levelized cost to sorbent replacement rate, sorbent unit cost, O_2 and N_2 unit cost, and capital cost was analyzed. Under base case conditions the single-stage process using ZnO and DSRP was found to be approximately 37% less expensive than either of the CeO_2 processes. The base cases, however, assumed a sorbent replacement rate equal to 1% of the sorbent circulation rate (100-cycle average sorbent lifetime). With this replacement rate it is probable that none of the processes would be economically attractive.

As the sorbent cost was reduced, based on smaller sorbent replacement rate and/or smaller sorbent unit cost, the annual levelized cost of all three processes decreased, and the cerium process became more attractive. For example, at a sorbent replacement rate of 0.1% of the sorbent circulation rate, both cerium processes should be less costly than the single-stage zinc sorbent process. As the sorbent replacement rate approaches zero (infinite sorbent lifetime), income from the sulfur by-product and export steam produced by the cerium processes exceeds the other process costs and a profit of \$2 to 2.5 million appears possible. In contrast, the annual levelized cost of the zinc-based process at zero sorbent replacement rate is about \$5 million.

CERIUM SULFIDATION AND REGENERATION

The reduction, sulfidation, and regeneration reactions are



The degree of reduction, i.e., the value of n , depends on the temperature and reducing power of the coal gas. In turn, the equilibrium concentration of H_2S depends on the value of n . These topics were discussed in the previous quarterly report and are elaborated upon in a separate section of this report.

Four sulfidation-regeneration tests consisting of twenty-one cycles were completed during the quarter. Reaction conditions are summarized in Table 1. Regeneration continued to be emphasized and the reactor system was only moderately cleaned between sulfidation and regeneration tests. For this reason, prebreakthrough H_2S plateaus during sulfidation were quite large. Regeneration tests examined the effect of gas composition (SO_2 content) and flow rate on regeneration performance. The maximum SO_2 content of the regeneration feed gas was 20%, and the elemental sulfur content of the product gas was approximately 20%. Good regeneration performance was achieved with gas

Table 1. Summary of Reaction Test Conditions: CeO₂ Sulfidation and Regeneration, April - June 1997

Run	Ce-20s01 through Ce-20s13	Ce-20r01	Ce-20r02	Ce-20r03	Ce-20r04	Ce-20r05	Ce-20r06	Ce-20r07	Ce-20r08	Ce-20r09	Ce-20r10
Date	4/14/97 to 5/23/97	4/14/97	4/16/97	4/18/97	4/21/97	4/23/97	4/25/97	4/29/97	4/30/97	5/02/97	5/09/97
Reactor Packing											
CeO ₂ , g	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
CeO ₂ Source	RP	RP	RP	RP	RP	RP	RP	RP	RP	RP	RP
Al ₂ O ₃ , g	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Reaction Conditions											
Temp., °C	800	600	600	600	600	600	600	600	600	600	600
Press., atm	5	1	1	1	1	1	1	1	1	1	1
Gas Composition											
% H ₂ S	1	0	0	0	0	0	0	0	0	0	0
% SO ₂	0	16	8	4	2	4	4	2	8	2	16
% H ₂	10	0	0	0	0	0	0	0	0	0	0
% N ₂	89	84	92	96	98	96	96	98	92	98	84
Total Gas Flow Rate, sccm	400	200	200	200	200	100	400	400	100	800	100

Table 1. (Continued)
 Summary of Reaction Test Conditions: CeO₂ Sulfidation and Regeneration, April - June 1997

Run	Ce-20r11	Ce-20r12	Ce-20r13	Ce-21s01 and Ce-21s02	Ce-21r01 And Ce-21r02	Ce-22s01	Ce-22r01	Ce-22s02	Ce-22r02	Ce-23s01 through Ce-23s04	Ce-23r01 through Ce-23r04
Date	5/12/97	5/19/97	5/23/97	6/03/97 through 6/04/97	06/03/97 through 6/04/97	6/09/97	6/09/97	6/11/97	6/11/97	6/19/97 through 6/30/97	6/19/97 through 6/30/97
Reactor											
CeO ₂ , g	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
CeO ₂ Source	RP	RP	RP	MC	MC	RP	RP	RP	RP	MC	MC
Al ₂ O ₃ , g	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Reaction Condition											
Temp., °C	600	600	600	800	600	900	600	1000	600	800	600
Press., atm	1	1	1	5	1	5.0	1	5	1	5	1
Gas Composition											
% H ₂ S	0	0	0	1	0	1	0	1	0	1	0
% SO ₂	20	16	20	0	12	0	12	0	12	0	12
% H ₂	0	0	0	10	0	10	0	10	0	10	0
% N ₂	80	84	80	89	88	89	88	89	88	89	88
Total Gas Flow Rate, sccm	100	100	100	400	200	400	200	400	200	400	200

feed rates up to 800 sccm corresponding to a space velocity of about 18000 hr^{-1} (STP). An alternate CeO_2 obtained from Molycorp, Inc. was used in tests Ce-21 and Ce-23. The sample was prepared in the standard manner in which the powder was dry-pressed into tablets, which were subsequently crushed and sieved. 6.0 g of particles having a size range between 150 and 300μ were charged to the reactor along with 3.0 g of Al_2O_3 . Although the Molycorp CeO_2 performed satisfactorily, H_2S breakthrough occurred earlier and the global sulfidation rate (as measured by the slope of the breakthrough curve) was somewhat smaller than previously seen with the Rhone-Poulenc CeO_2 .

Experimental problems associated with mass flow controller malfunctions and plugging of reactor exit lines with elemental sulfur were encountered periodically. As a consequence, results from some runs were not useful.

Run Ce-20

The same sulfidation conditions were used throughout this thirteen cycle run. The sulfur content of the regeneration feed gas was varied from 2% to 20% SO_2 while the flow rate ranged from 100 to 800 sccm. In some cycles, the SO_2 concentration and total flow rate were varied simultaneously in a manner such that the SO_2 feed rate remained constant. The reactor was only moderately cleaned between regeneration and sulfidation runs so that prebreakthrough H_2S concentrations during sulfidation were quite large. In addition to the sulfidation-regeneration tests, a number of nonreacting tracer tests were carried out at the end of run Ce-20 to supplement previous data regarding delay time and to assist in establishing the sulfur material balance. While regeneration received the primary emphasis in this test, useful information was also obtained from the sulfidation phase.

Figure 1 compares the sulfidation breakthrough curves from Ce-20s01 and Ce-20s10. Prebreakthrough H_2S concentrations were approximately 0.05% in each test due to the fact that the reactor was not cleaned rigorously following regeneration. A second plateau at about 0.2% H_2S appeared in Ce-20s10 in the 110 to 140 minute time span while the H_2S concentration in Ce-20s01 increased monotonically after about 100 minutes. However, the absence of significant sorbent deterioration through 10 cycles is particularly encouraging given that mass flow controller and sulfur plugging problems were encountered and since reaction conditions in each of the regeneration cycles were varied. Similar evidence of good sorbent durability is shown in Figure 2 where times corresponding to the H_2S product gas concentration reaching 0.1% are plotted versus cycle number. These times varied from 90 minutes in cycle 07 to 120 minutes in cycle 06 with a ten-cycle average of 100 minutes.

The regeneration conditions of Ce-20 were varied to permit us to examine the effect of SO_2 concentration at constant total flow rate, the effect of flow rate at constant SO_2 concentration, and the combined effects of total flow rate and SO_2 concentration at constant SO_2 flow rate.

The effect of SO_2 concentration is shown in Figure 3 where breakthrough curves from Ce-20r01 (16% SO_2), Ce-20r02 (8% SO_2), Ce-20r03 (4% SO_2) are combined with the breakthrough curves from the ten cycles of previous run Ce-16 (12% SO_2). The total flow rate in all cases was 200 sccm. Results from run Ce-20r04 using 2% SO_2 are not included since breakthrough occurred at 100

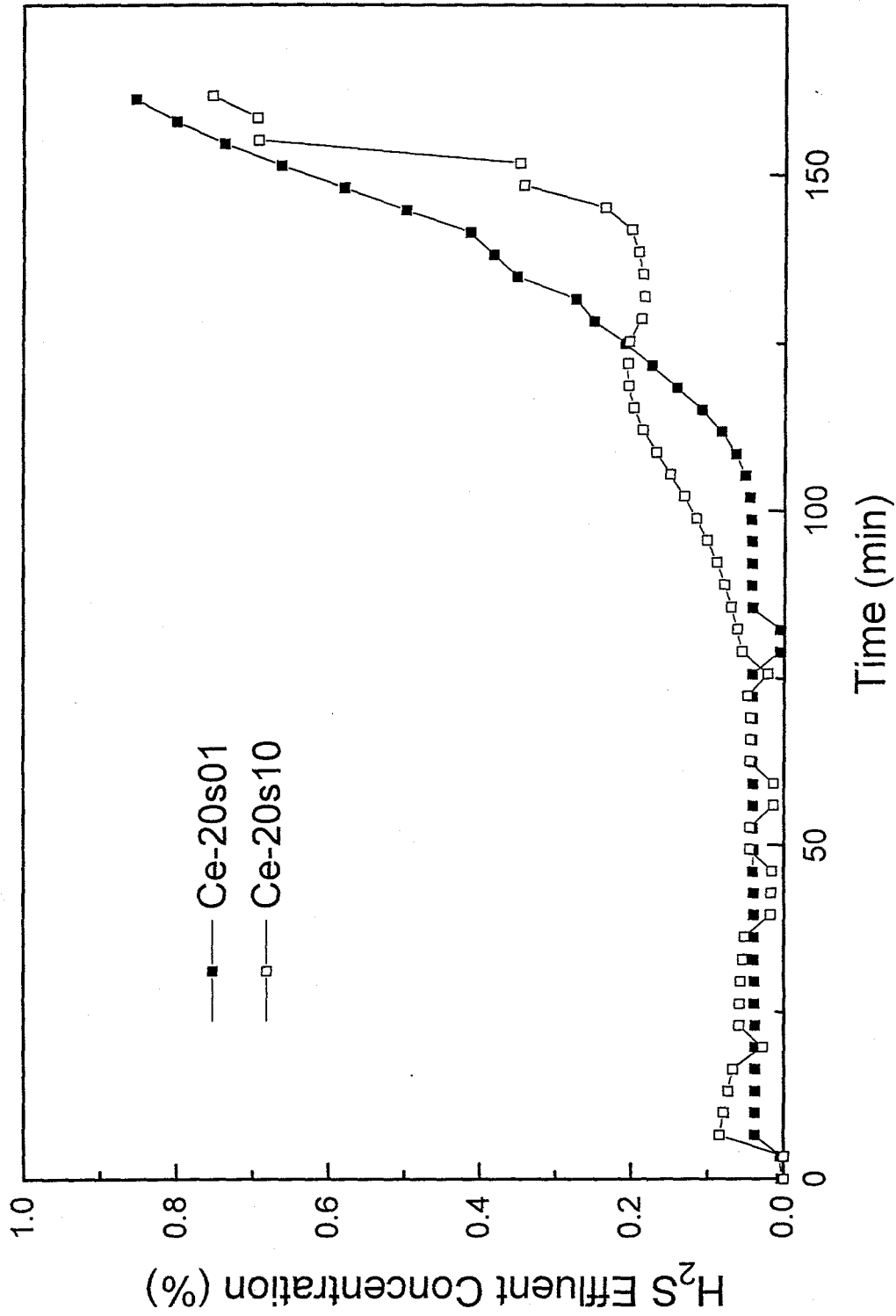


Figure 1. Comparison of Sulfidation Breakthrough Curves from the First and Tenth Cycles of Ce-20.

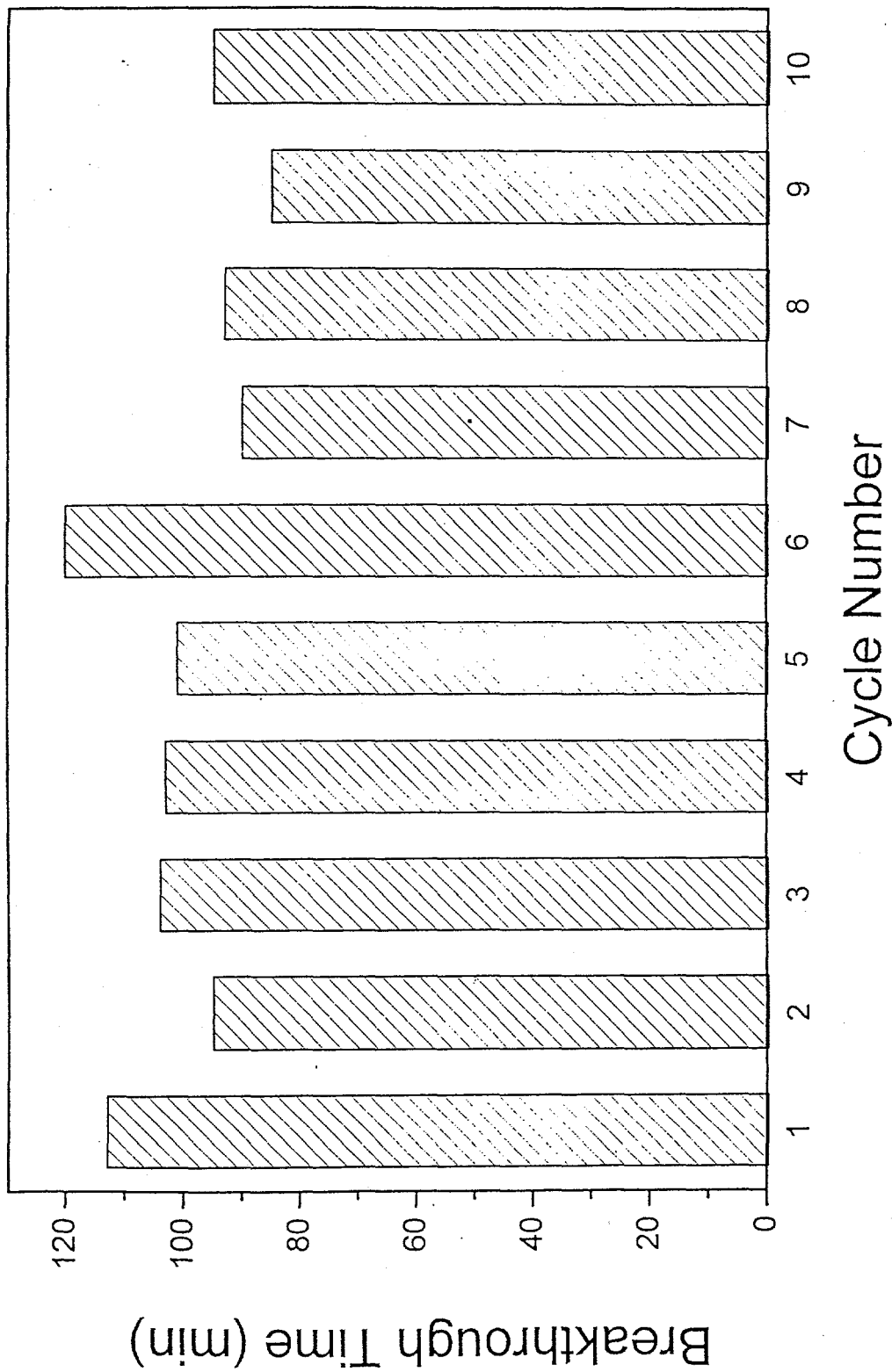


Figure 2. Breakthrough Times Corresponding to 0.1% H₂S in the First Ten Cycles of Ce-20.

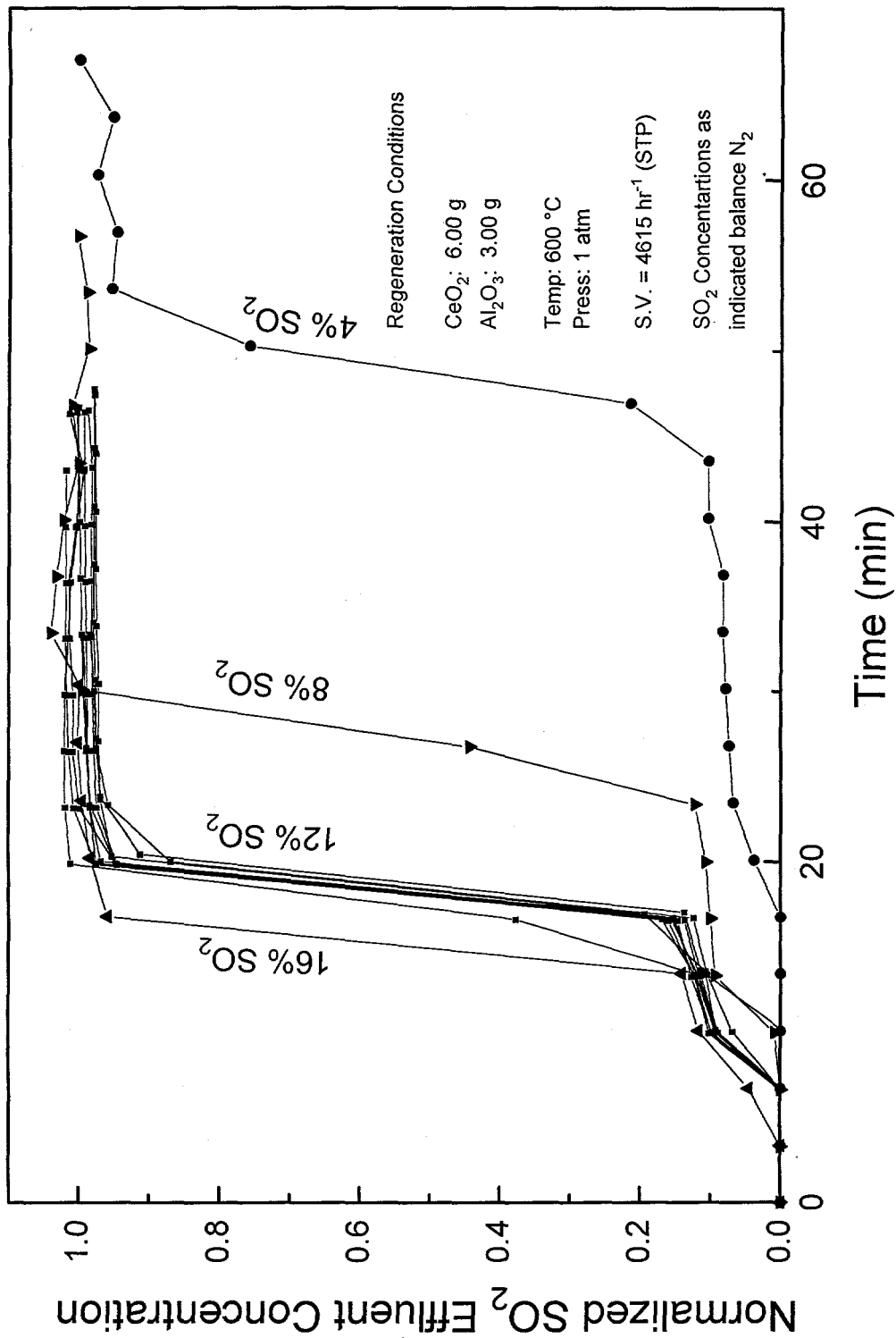


Figure 3. Regeneration Breakthrough Curves as a Function of SO₂ Concentration.

minutes and the time scale would have to be compressed to the point that the higher SO₂ concentration results would become overly crowded. The SO₂ concentration is presented on a normalized basis so that final concentration approaches 1.0 for all SO₂ feed concentrations. The important results from Figure 3 are that run Ce-20r02 was successfully completed using 16% SO₂, the fact that results from different tests using different sorbent charges (runs Ce-16 and Ce-20) were consistent, the near equal slope of the concentration curves during the active breakthrough period, and the fact that reaction time was roughly inversely proportional to SO₂ concentration.

The effect of total feed rate at a constant SO₂ concentration of 4% is shown in Figure 4. At the smallest feed rate of 100 sccm, the SO₂ product concentration reached half the feed concentration after 103 minutes. Doubling the feed rate to 200 sccm, which also doubled the SO₂ feed rate, reduced the time at which the product contained 2% SO₂ to 49 minutes without significantly altering the slope of the breakthrough curve. When the flow rate was again doubled to 400 sccm, the SO₂ concentration reached 2% after 29 minutes and the slope of the breakthrough curve was significantly smaller. The feed rates of 100, 200, and 400 sccm correspond to space velocities of 2300, 4600, and 9200 hr⁻¹ (STP), respectively, indicating that rapid regeneration can be achieved at reasonable gas throughputs.

Results of a series of tests in which the total feed rate and SO₂ concentration were varied in a manner to maintain a constant SO₂ feed rate of 16 sccm is shown in Figure 5. These results are from Ce-20r09 (2% SO₂ at 800 sccm), Ce-20r06 (4% SO₂ at 400 sccm), Ce-20r02 (8% SO₂ at 200 sccm), and Ce-20r12 (16% SO₂ at 100 sccm). The data for Ce-20r12 stop after 29 minutes when plugging due to elemental sulfur occurred. However, since most of the breakthrough curve was established by that time, the comparison with other tests is valid. There is essentially no difference in the slopes of the active portions of the breakthrough curves at flow rates of 100 and 200 sccm; only about 3 minutes were required for the product SO₂ concentration to increase from 20% to 80% of the feed concentration. At 400 sccm, the slope of the breakthrough curve was smaller and about 9 minutes were required to traverse the same concentration interval; the slope was still smaller at 800 sccm and about 14 minutes were required. The space velocity at this maximum flow rate was about 18400 hr⁻¹ (STP). The effect of flow rate (residence time) from Figures 4 and 5 is consistent.

Only one of the high SO₂ concentration regeneration runs ($\geq 16\%$) was completed due to elemental sulfur condensing and plugging the reactor exit tubing. However, the results at 16% SO₂ in Figure 5 prior to plugging were as expected, and there is no reason to believe that a larger-scale system, where downstream temperature can be more closely controlled, cannot operate continually without condensation and plugging. The process analysis phase of this project has shown that a commercial process might be expected to operate with elemental sulfur concentrations in the regeneration product gas of about 15%.

A series of nonreacting tracer tests at the regeneration conditions of run Ce-20 was carried out so that regeneration sulfur material balances could be completed. Figure 6 shows the nonreacting breakthrough curves as a function of feed rate at constant SO₂ concentration of 4% while Figure 7 shows the effect of SO₂ concentration at 200 sccm feed rate. From Figure 6, we see that approximately 10 minutes were required before the full 4% SO₂ concentration reached the sample valve at a feed rate of 100 sccm. At 200 sccm, the full concentration was reached before the second sample at about 6.5 minutes, and at 400 sccm the full concentration was reached before the first

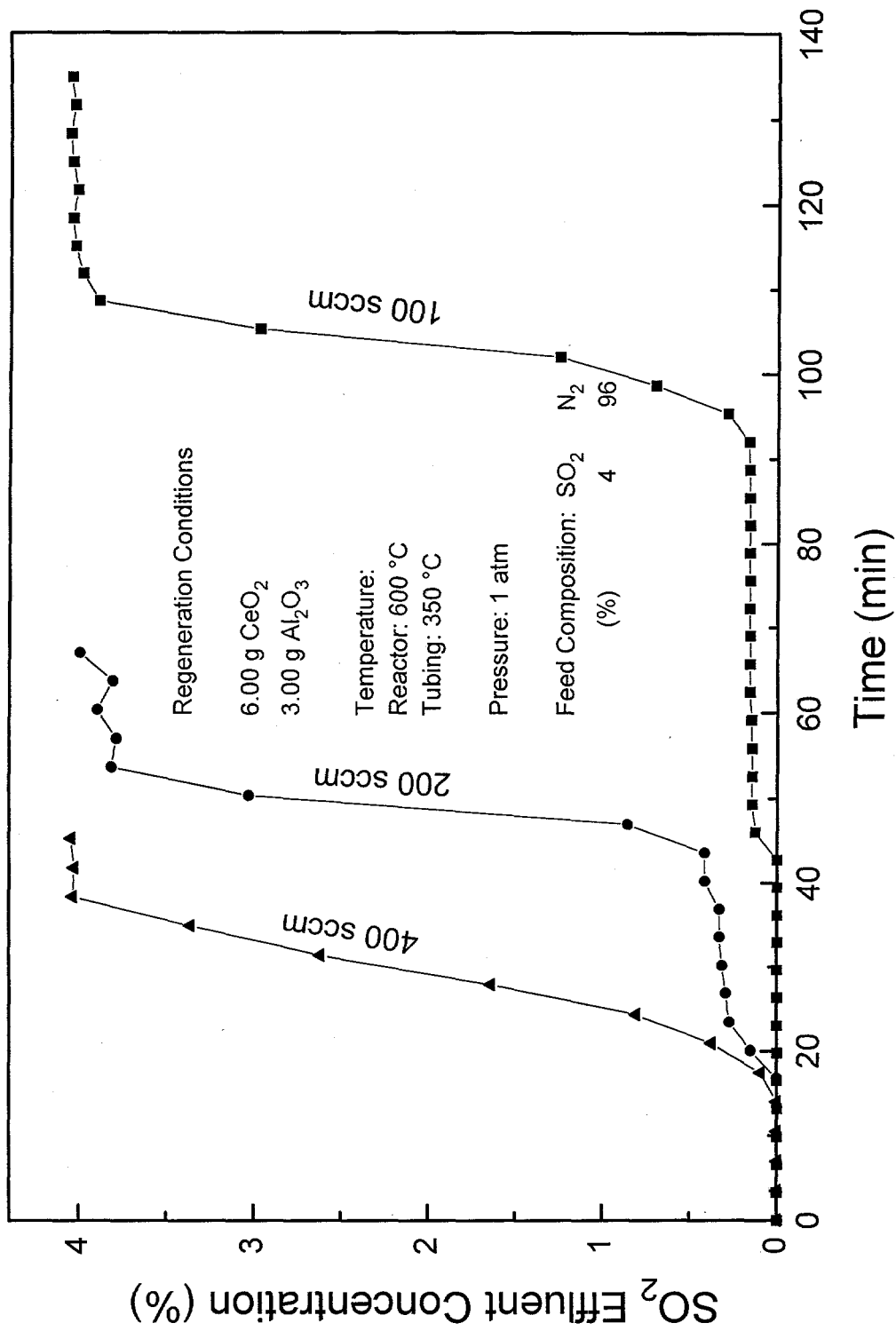


Figure 4. Regeneration Breakthrough Curves as a Function of Gas Flow Rate.

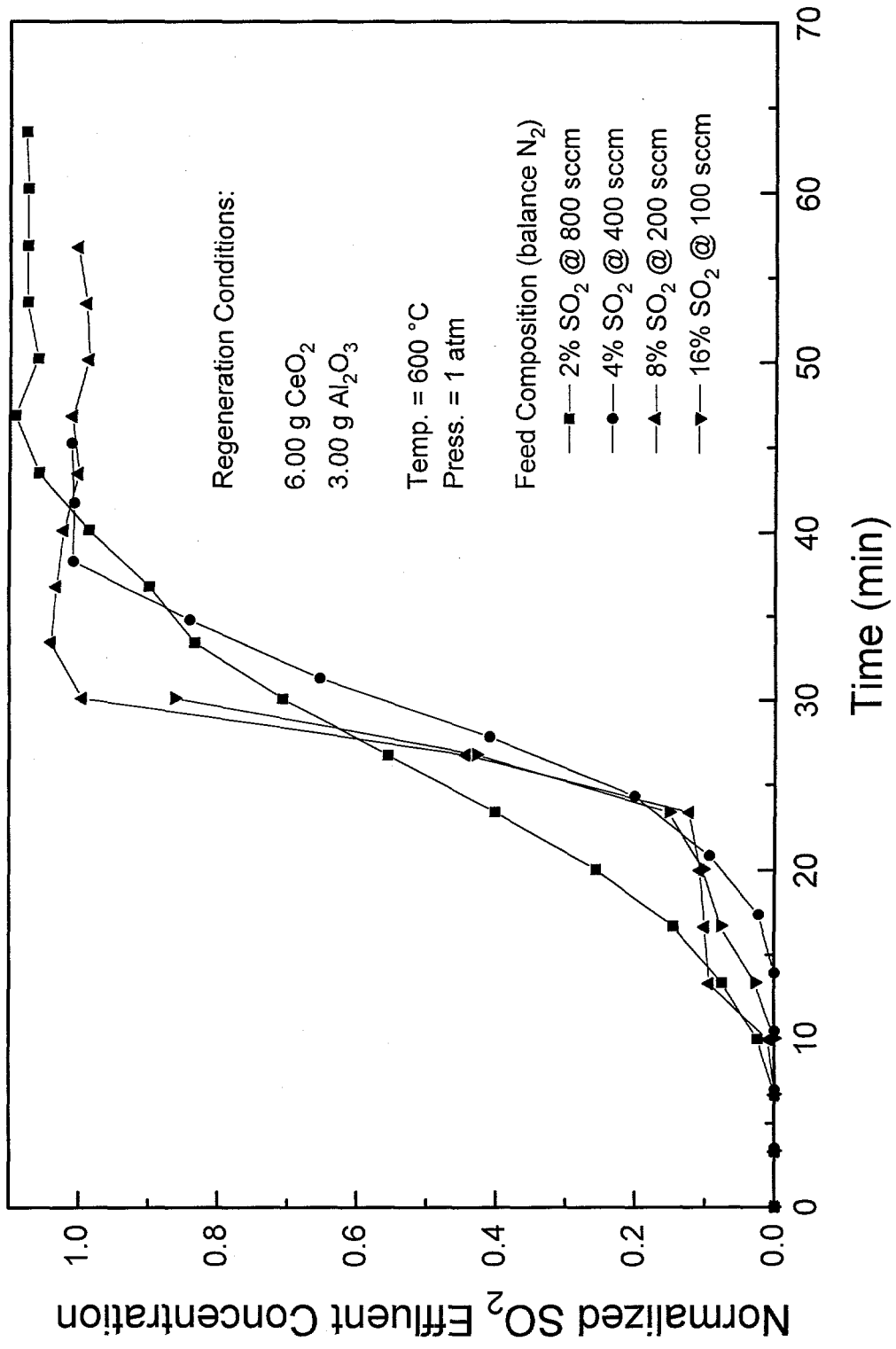


Figure 5. The Effect of Flow Rate and SO₂ Content at Constant SO₂ Feed Rate on Regeneration Breakthrough Curves.

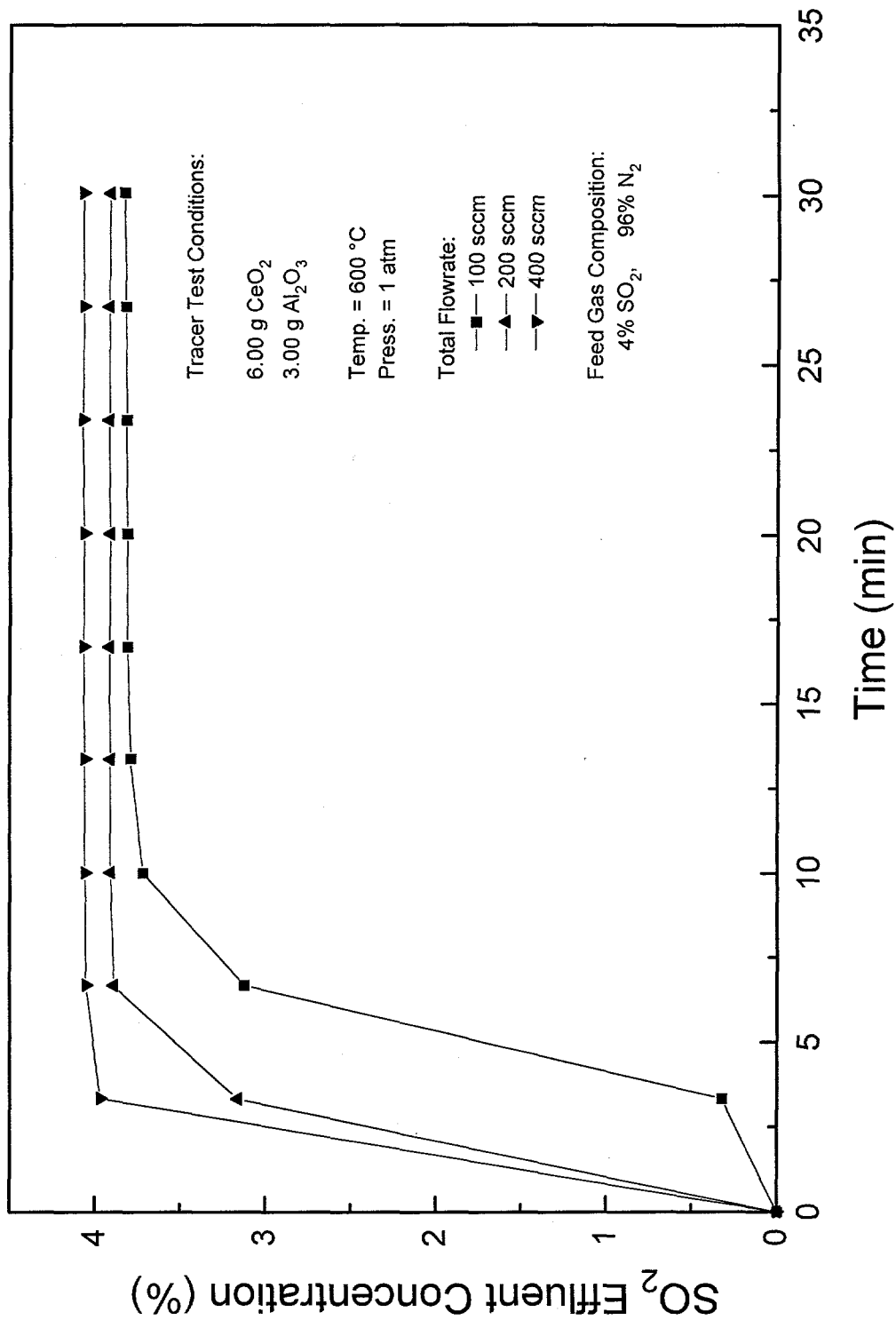


Figure 6. The Effect of Flow Rate on Delay Time: Non-Reacting Tracer Tests.

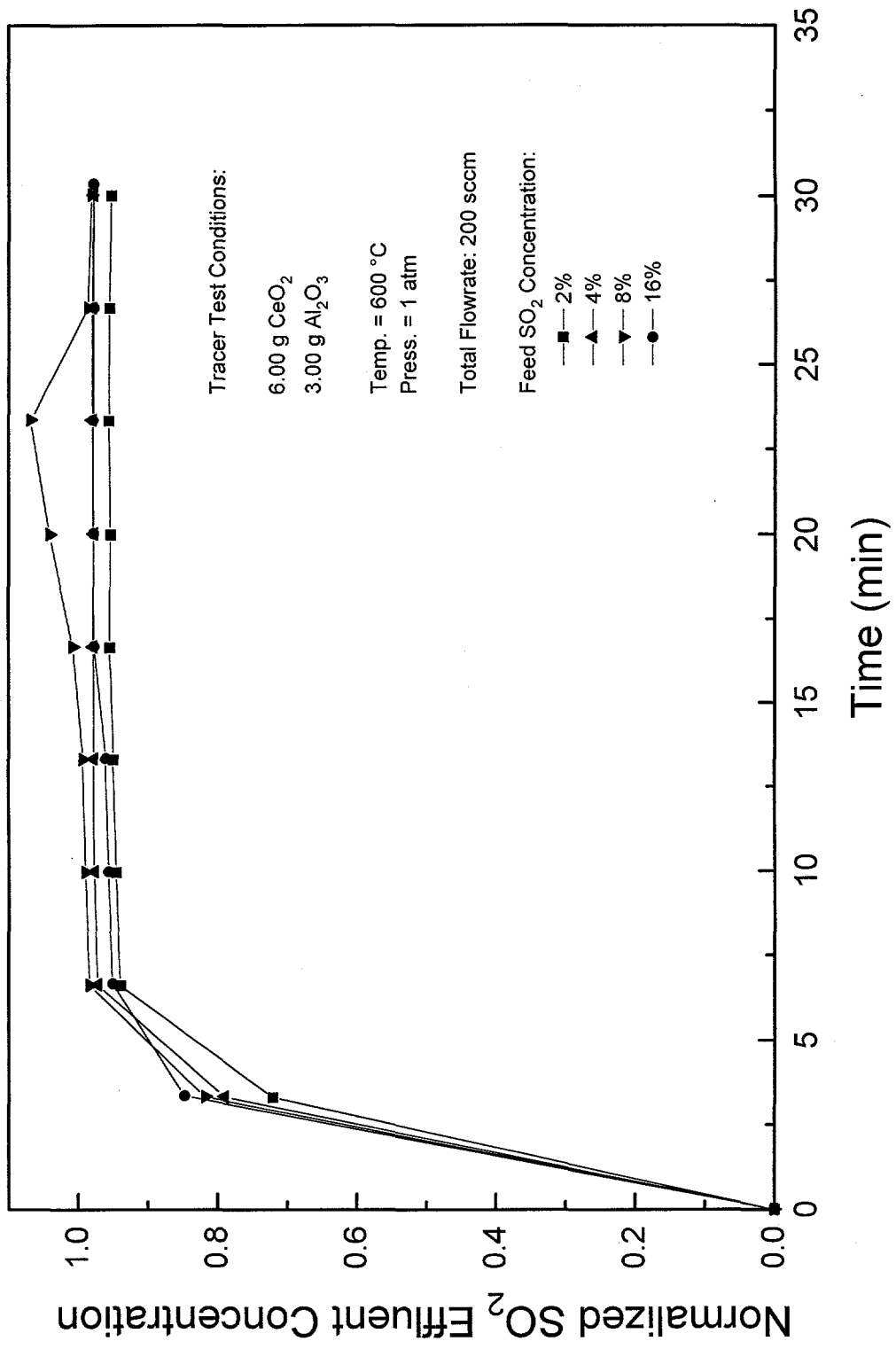


Figure 7. The Effect of H₂S Concentration on Delay Time: Non-Reacting Tracer Tests.

sample at just over 3 minutes. Figure 7 shows that the time required to reach full concentration was effectively independent of SO₂ concentration. Full concentration was achieved in each test by the second sample at about 6.5 minutes, which is in agreement with the Figure 6 results.

The tracer data were combined with the SO₂ breakthrough data from the regeneration cycles of run Ce-20 to evaluate sulfur material balance closure. Results for cycles Ce-20r01 through Ce-20r09 are shown in Figure 8. Results from Ce-20r10 through Ce-20r13 are not included because all of these runs were terminated prior to conclusion because of sulfur plugging. The material balance closure ranges from 91% of stoichiometric in Ce-20r03 to 110% in Ce-20r06 with a nine-cycle average of 98%. The fact that sulfur material balance closure was always within $\pm 10\%$ of theoretical is felt to be quite good, especially since these runs were at different flow rates and SO₂ feed gas concentration.

Run Ce-21

Run Ce-21 represented the first experimental test of the second source of CeO₂, from Molycorp, Inc. In addition, a quartz liner designed to further minimize contact between product gas and the hot surface of the pressure vessel was first tested in this run. The liner slips into the pressure vessel, rests on the bottom, and extends upward for most of the length of the vessel. A small hole in the bottom fits directly over the exit nipple leading to the downstream tubing.

Unfortunately, mass flow controller problems occurred, preventing any useful sulfidation or regeneration data from being obtained. However, the quartz liner performed as hoped.

Run Ce-22

Standard Rhone-Poulenc CeO₂ was again used in this run. Sulfidation temperature was increased to 900°C in Ce-22s01 and to 1000°C in Ce-22s02. We had hoped to accomplish three objectives with this run. The first objective was to test the sulfidation behavior at the higher temperatures. However, mass flow controller problems persisted and no useful reaction was obtained. The second objective was to test the performance of the quartz liner at the higher temperatures. No problems were observed. Finally, thermocouples were used to measure the temperature of the tubing near the exit of the reactor. We had hoped to use teflon-lined tubing with quick-connects in future sulfidation tests designed to determine the ultimate desulfurization capability of the cerium sorbent. However, quick-connect fittings cannot be used as the temperatures exceeded the limits of the quick-connect O-rings. As a result, we plan to use teflon-lined tubing but with standard connections.

Run Ce-23

Although not totally free of mass flow controller problems, reliable data were obtained from most of run Ce-23. Molycorp CeO₂ was used and four complete sulfidation-regeneration cycles were

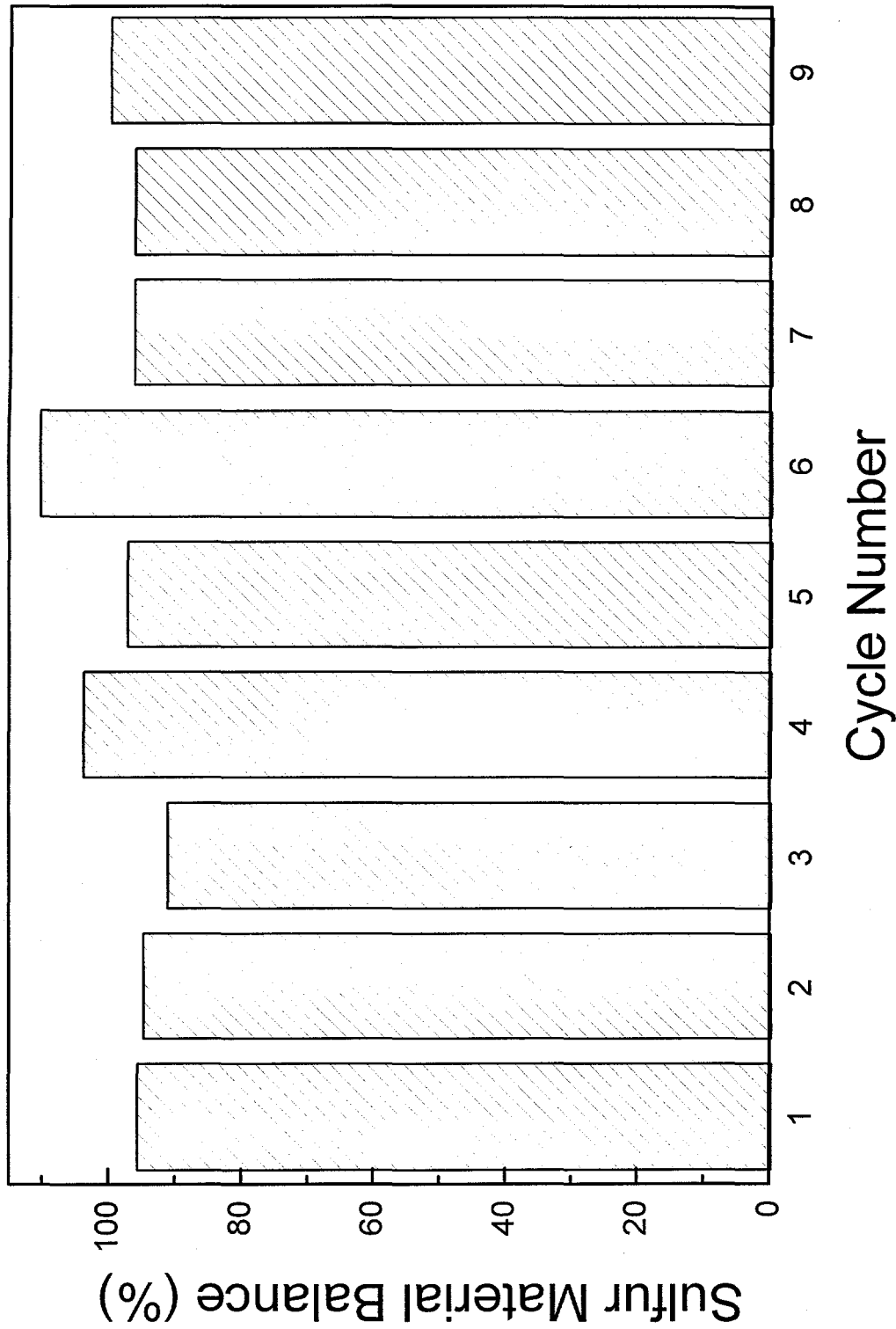


Figure 8. Sulfur Material Balance Closure in the First Nine Regeneration Cycles of Run Ce-20.

carried out at "standard" conditions. Figure 9 compares the early portions of the sulfidation breakthrough curve from Ce-23s01 with that obtained from earlier test Ce-17s01 at the same conditions except that Rhone-Poulenc CeO_2 was used in the earlier test. Similar extensive cleaning procedures were followed prior to each test in order to minimize the prebreakthrough H_2S plateau. H_2S concentrations were at or below 100 ppmv for the first 30 minutes of each test. Thereafter, the H_2S concentration increased rapidly in Ce-23s01 while it remained below 100 ppmv for 95 minutes in Ce-17s01. By the time breakthrough began in Ce-17s01, the H_2S concentration had increased to about 0.15% in Ce-23s01. Run Ce-17s01 was terminated after 120 minutes to minimize the possibility of downstream sulfur contamination; as a consequence, no sulfur material balance was possible in that run. Ce-23s01 was carried to completion and the total amount of sulfur removed corresponded to 113% of stoichiometric.

A similar comparison of regeneration breakthrough curves from Ce-23r01 and Ce-17r01 is presented in Figure 10. The regeneration results are quite similar. No SO_2 was detected in the first three samples. SO_2 concentration reached the 1% to 2% level during the next three samples, and then increased quickly. Regeneration was complete in Ce-17r01 by the eighth sample (about 23 minutes) while nine samples (about 27 minutes) were required for completion in Ce-23r01. In agreement with the sulfidation results from Ce-23s01, the total sulfur liberated in Ce-23r01 was 113% of stoichiometric.

The complete breakthrough curves for the four sulfidation cycles of Ce-23 are compared in Figure 11. All show the same general characteristics with H_2S concentrations less than 100 ppmv for about 30 minutes, followed by a plateau at the 0.1% to 0.2% level between 30 and 100 minutes. Active breakthrough then occurred and sulfidation was complete after about 150 minutes. The global rate of reaction using the Molycorp CeO_2 was smaller than with Rhone-Poulenc CeO_2 . The duration of the active breakthrough period is about 50 minutes with Molycorp CeO_2 compared to about 30 minutes with Rhone-Poulenc CeO_2 .

There is also some indication of decreased performance over the four cycles of Ce-23, as shown by the fact that active breakthrough occurred about 10 minutes earlier in cycle 04 than in cycle 01. In addition, the sulfur material balance, expressed as percent of stoichiometric, was relatively constant at 113% in cycle 01 and 114% in cycle 02, and then decreased to 108% in cycle 3 and to 106% in cycle 04.

Results from three of the four regeneration cycles of run Ce-23 are shown in Figure 12. No results are presented for Ce-23r03 because of mass flow controller problems. The regeneration results from the three cycles are effectively identical with no SO_2 detected in the first three samples, about 2% SO_2 in samples 4 through 6, and complete regeneration by sample 9 at about 27 minutes. Sulfur liberated during regeneration was 113% of stoichiometric in each cycle which is in good agreement with the sulfidation results.

Although firm conclusions should not be reached on the basis of these initial tests, the preliminary results show the Rhone-Poulenc CeO_2 to be superior to that from Molycorp. The most

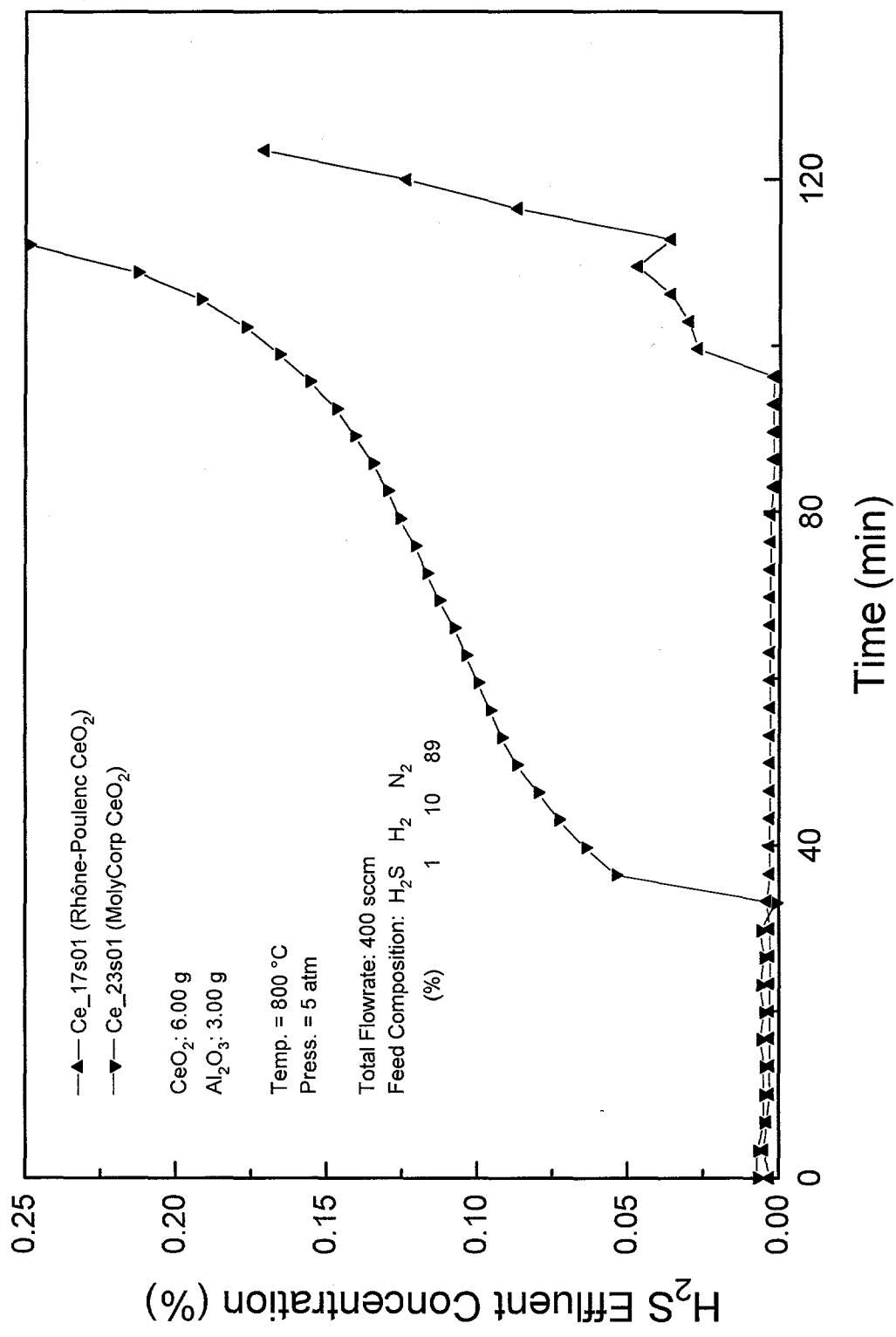


Figure 9. Comparison of the Early Portions of the Sulfidation Breakthrough Curves from Ce-17s01 (Rhône-Poulenc CeO₂) and Ce-23s01 (MolyCorp CeO₂).

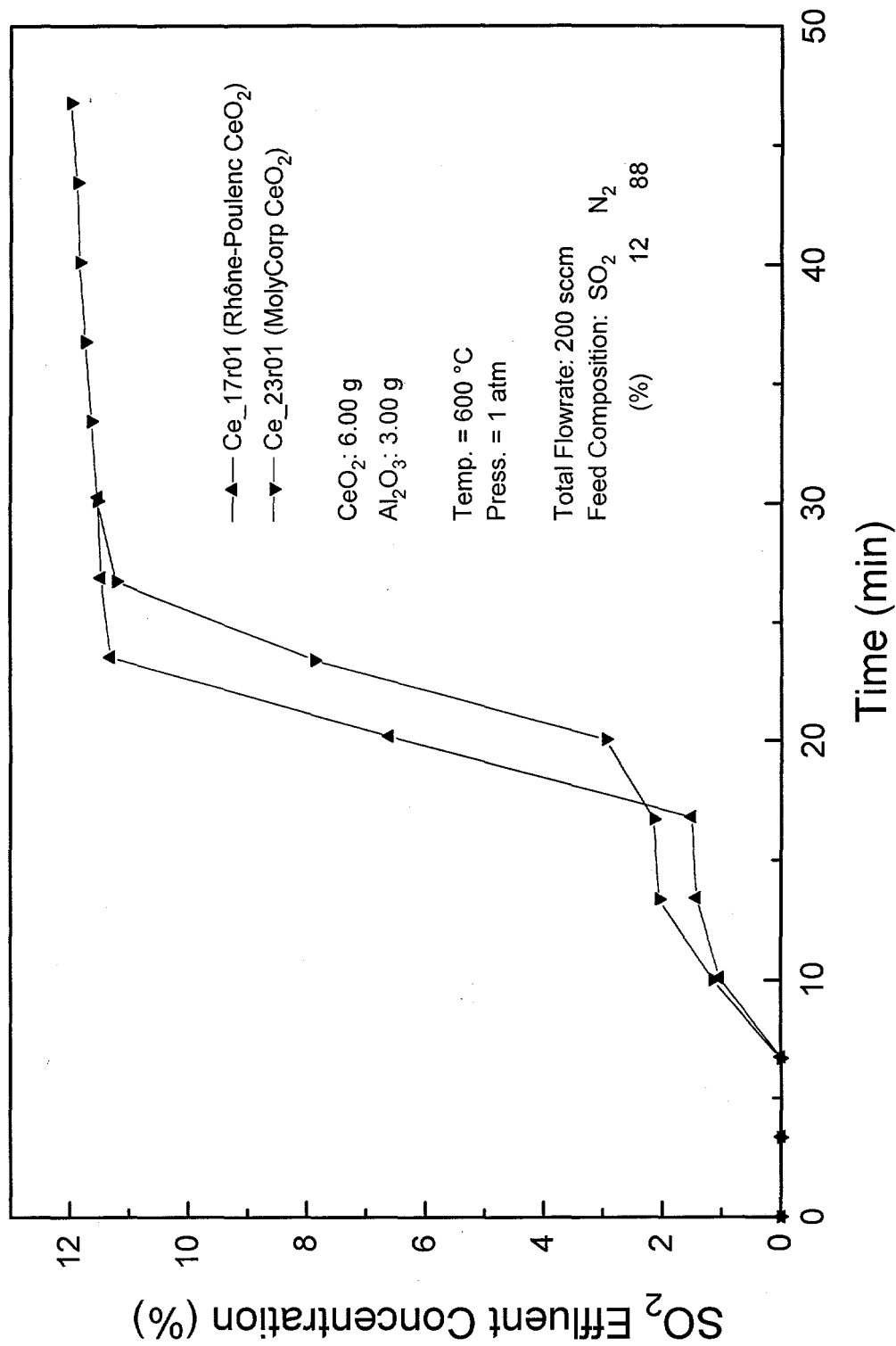


Figure 10. Comparison of the Regeneration Breakthrough Curves from Ce-17r01 (Rhône Poulenc CeO₂) and Ce-23r01 (Molycorp CeO₂).

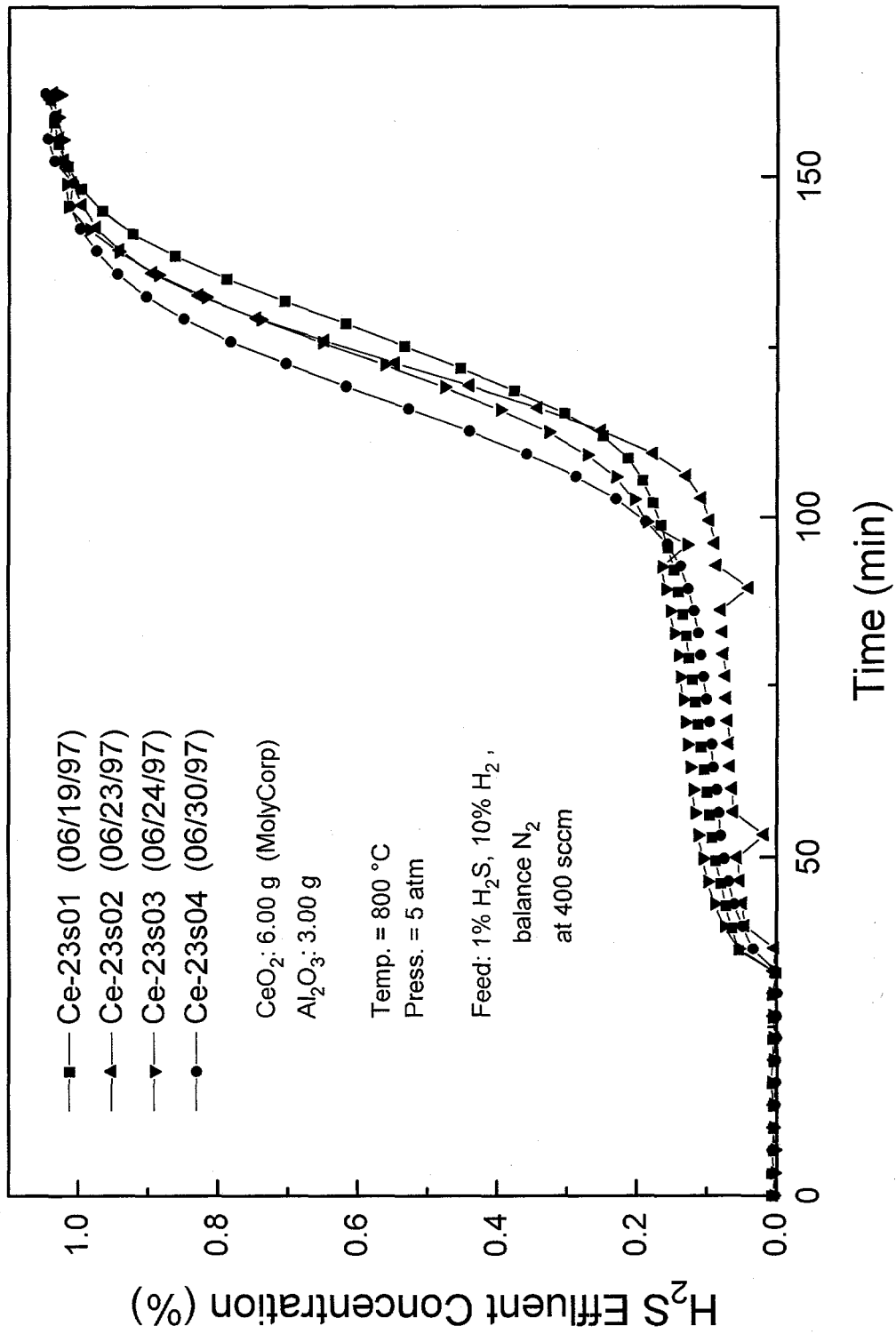


Figure 11. Sulfidation Breakthrough Curves from the Four Cycles of Run Ce-23.

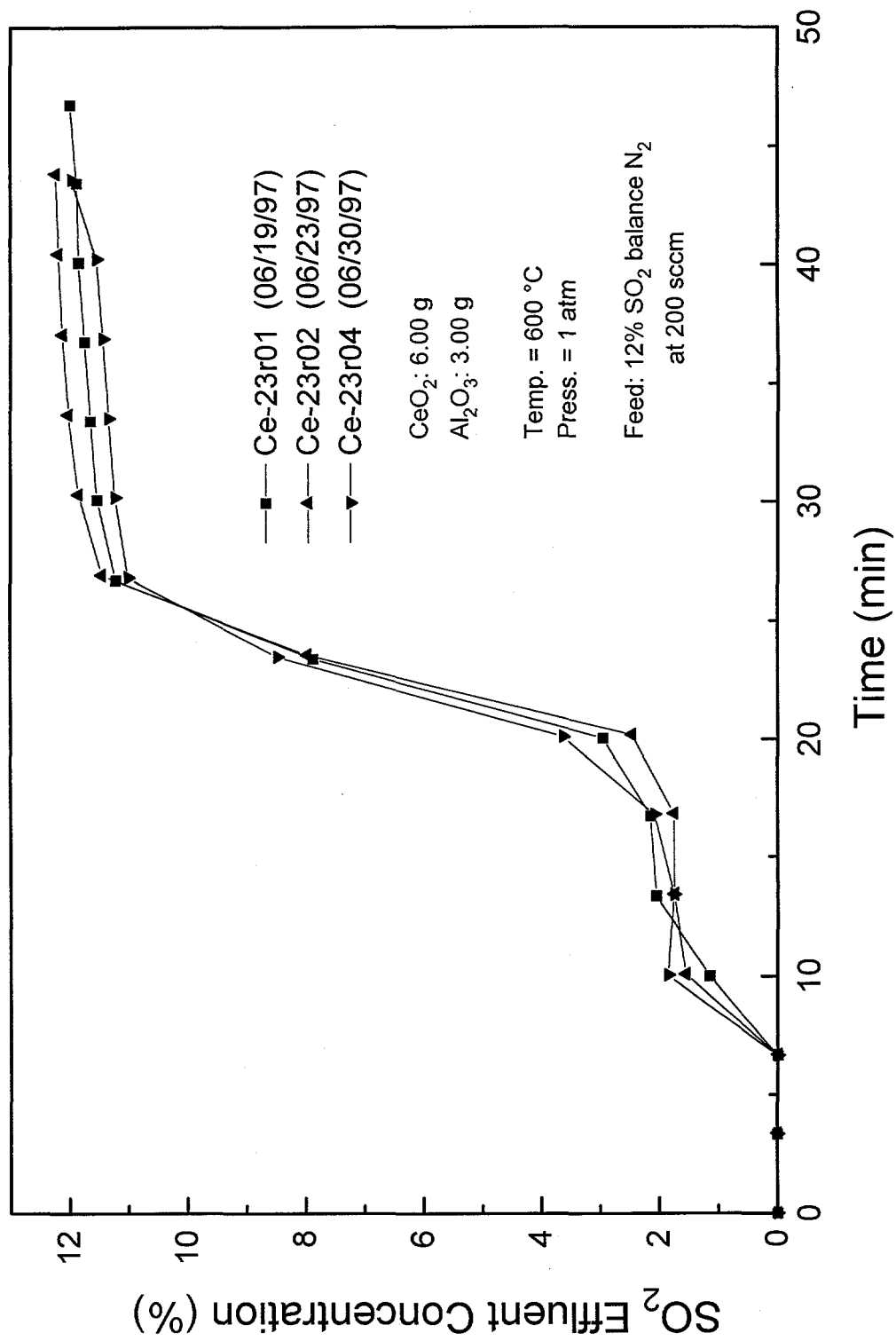


Figure 12. Regeneration Breakthrough Curves from Three of the Four Cycles of Run Ce-23.

probable explanation is differences in the size and structural characteristics of the two powders. Both were dry pressed into tablets which were subsequently crushed and sieved. The particles used were Figure 10. in the same size range, but the structural properties such as surface area, pore volume, and pore size distribution were, in all probability, different.

SULFIDATION THERMODYNAMICS

The potential for reducing H_2S concentration to the IGCC target level of 20 ppmv in a single stage using reduced cerium, CeO_n ($n < 2$), was discussed in the previous quarterly report. Additional effort on the desulfurization thermodynamics has been completed in this quarter and preparations are underway to modify the reactor and analytical systems to carry out experiments to determine the ultimate desulfurization potential of CeO_2 .

The current status of the thermodynamic analysis is summarized in Figure 13 where the equilibrium H_2S concentration (ppmv) from a Shell gas containing 1% H_2S is plotted versus temperature. A similar figure was shown in the previous quarterly report, but recent information has been added.

Thermodynamic data needed to predict equilibrium H_2S concentrations in contact with CeO_2 and Ce_2O_3 ($CeO_{1.5}$) is available. These results are represented by the top (CeO_2) and bottom (Ce_2O_3) solid lines in the figure. At the standard experimental sulfidation temperature of $800^\circ C$, CeO_2 is theoretically capable of reducing the H_2S concentration to about 300 ppmv, considerably above the IGCC target level. Ce_2O_3 , in contrast, can theoretically reduce the H_2S to about 0.1 ppmv at $800^\circ C$. These two curves, therefore, establish the bounds of the equilibrium H_2S concentration in contact with CeO_n . The actual limit is determined by the value of n , which is dependent on the temperature and reducing power of the coal gas.

The results of Bevan and Kordis (1964) showing the value of n as a function of temperature and equilibrium oxygen pressure have been combined with CHEMQ calculations to obtain the value of n in Shell gas as a function of temperature. These results, shown in Figure 14, indicate essentially no reduction at temperatures less than $650^\circ C$. The predicted value of n at the standard sulfidation temperature of $800^\circ C$ is 1.93, and the value of n decreases to 1.85 at $1000^\circ C$.

Thermodynamic data for CeO_n ($1.5 < n < 2.0$) are not available. However, the two dot-dash lines in Figure 13 present the results of approximate thermodynamic calculations for CeO_n based on reference data from both CeO_2 (upper dot-dash curve) and Ce_2O_3 (lower dot-dash curve). Using CeO_2 data as the starting point, it is clear that only moderate improvement in H_2S removal efficiency is predicted. At $800^\circ C$, the predicted equilibrium H_2S over $CeO_{1.93}$ is still near 300 ppmv. The results are more favorable when Ce_2O_3 data is used as the starting point. The lower dot-dash curve indicates an equilibrium H_2S concentration of about 6 ppmv in contact with $CeO_{1.93}$ at $800^\circ C$. Although the predicted H_2S equilibrium concentrations are considerably different, it is important to recognize that the estimated free energies of CeO_n from the two approaches are quite close. For example, at $800^\circ C$, the free energies differ by less than 2%. This illustrates the sensitivity of equilibrium calculations to the free energy data.

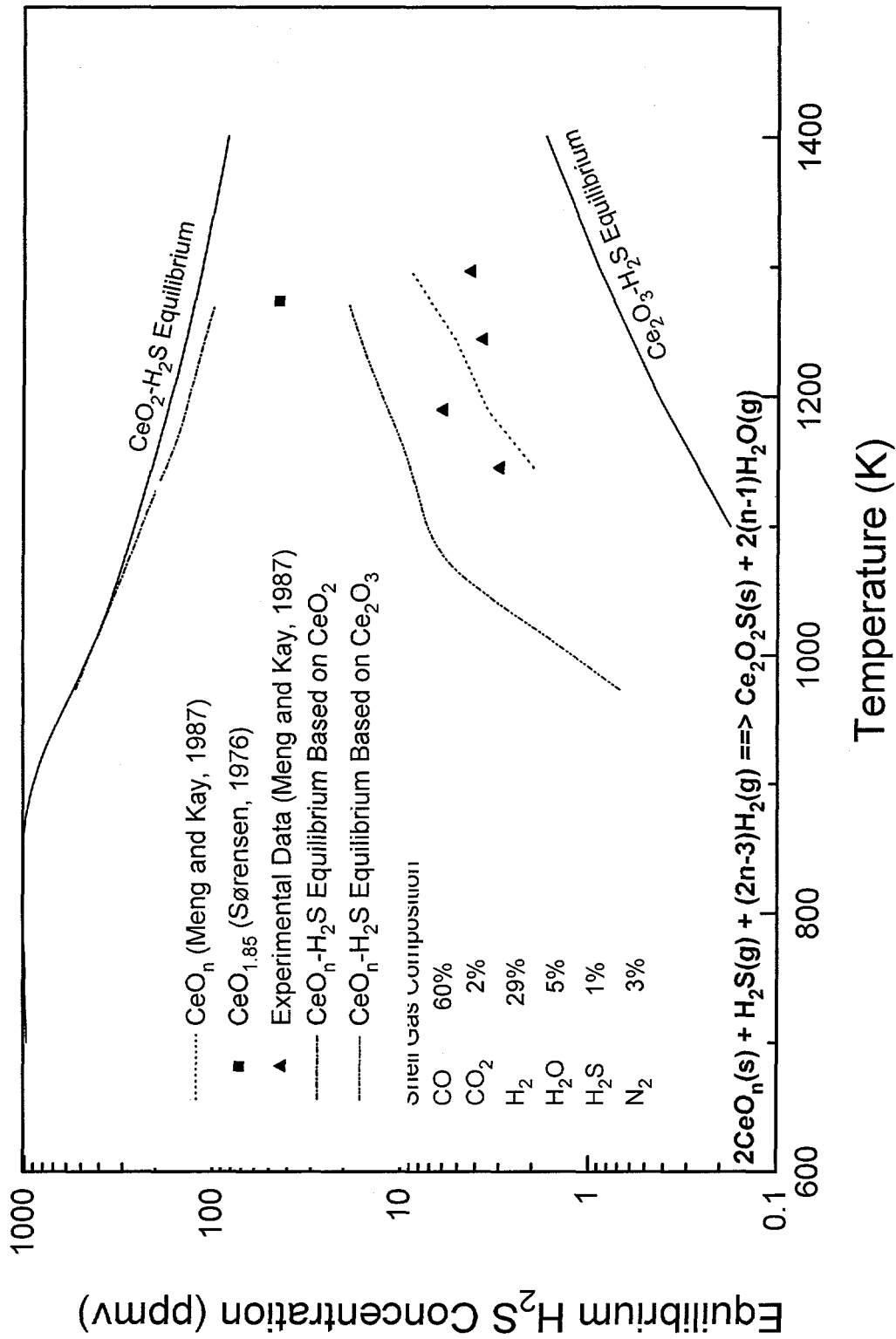


Figure 13. Equilibrium H_2S Concentration from Shell Gas in Contact with Cerium Oxide CeO_n with $1.5 < n < 2.0$.

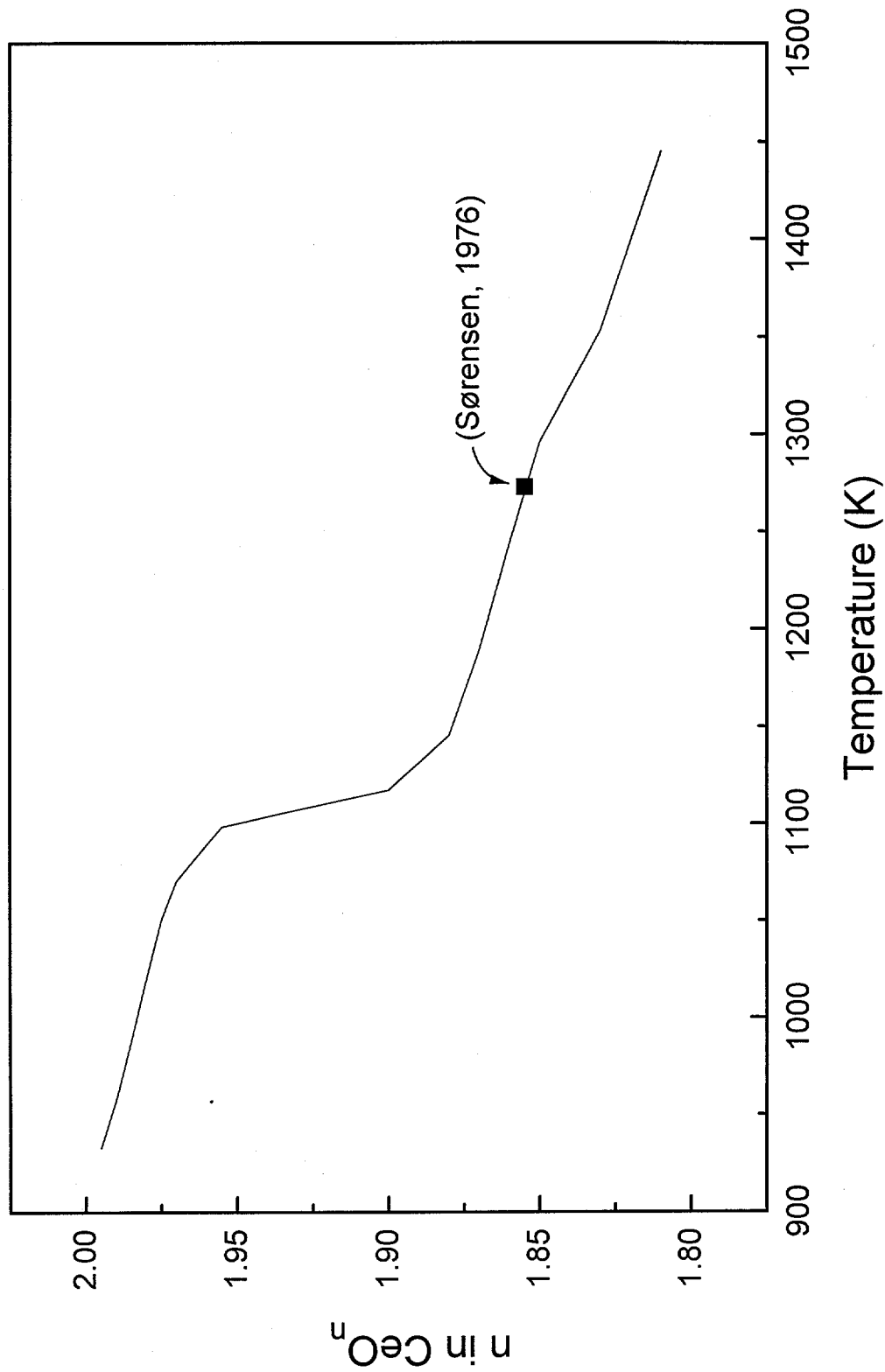


Figure 14. Equilibrium Value of n in CeO_n in Contact with Shell Gas Based on the Data of Bevan and Kordis.

Results from Meng and Kay (1987) indicate the possibility of even lower H₂S concentration than predicted by the lower dot-dash curve. Their experimental results are indicated by the triangular points while their equilibrium results are shown by the dashed line. They report experimental reductions of H₂S from 1.2% (12,000 ppmv) to 4 or 5 ppmv at temperatures up to 1300 K. The composition of the feed gas was similar, but not identical, to the Shell gas of current interest.

The sensitivity of the thermal conductivity detector (TCD) currently used for measuring H₂S concentrations is limited to about 100 ppmv. Hence, smaller concentrations such as shown in Figure 10 are at best approximate. A flame photometric detector (FPD) will be installed which will enable us to measure low ppmv values of H₂S and determine the ultimate desulfurization potential of CeO_n. These measurements will also require that changes be made in the reactor system to eliminate downstream contamination due to elemental sulfur deposition during regeneration tests. The elevated prebreakthrough H₂S concentrations are attributed to the formation of H₂S by the reaction between H₂ and elemental sulfur deposited in the regeneration runs.

Installation of the quartz liner within the pressure vessel was the first step in eliminating sources of sulfur contamination. Once the FPD is installed we plan to replace the standard stainless steel nipple, elbow, and tubing leading from the bottom of the reactor to the chromatograph sampling valve with a silica-treated nipple and elbow. Teflon-lined tubing will be used and the filters and sulfur condenser will be removed during sulfidation tests. Most sulfidation tests will be terminated before completion and the sorbent will not be regenerated. The regular tubing, filters, and condenser will be re-installed prior to regeneration tests.

PROCESS ANALYSIS

At the end of the previous quarter, base case economic estimates for two-stage desulfurization using CeO₂ with SO₂ regeneration (case 5a) and single-stage desulfurization using ZnO with DSRP (case 6) had been completed. Cost comparison, based on annual levelized cost, showed single-stage desulfurization with ZnO to be about 37% less expensive than the two-stage CeO₂ process. The dominant cost in each case was sorbent replacement which in the base case was arbitrarily set at 1% of the sorbent circulation rate (100 cycle average sorbent lifetime). However, even the less expensive zinc-sorbent process would not be economically competitive with low temperature desulfurization at these conditions. It is generally believed that sorbent lifetimes of several hundred cycles are required before hot gas desulfurization will be economically attractive.

In the current quarter the sensitivity of the annual levelized cost to variations in the cost of individual items, the most important of which was sorbent replacement rate, was investigated. In addition, the material and energy balances along with the base case cost estimate and cost sensitivity analysis for a third case based on single-stage desulfurization using CeO₂ with SO₂ regeneration (case 7) was developed. This case is based on the as yet unproven possibility that CeO_n will be able to reduce H₂S concentration to the 20 ppmv IGCC target level in a single stage. In the following discussion, the material and energy balances for this additional case are presented first. This is followed by the case 7 cost estimate under base conditions. Finally, the cost sensitivity analysis for all three cases is discussed.

Single-Stage CeO₂ Desulfurization Process

The flow diagram for this case (designated as case 7) is shown in Figure 15. The primary difference between this case and two-stage desulfurization using CeO₂ (case 5a) is that the secondary zinc-based sorber and regenerator are not needed. In addition, the quality of the clean coal gas is increased since it is available to the power generation section at 800°C instead of 600°C, and the gasification and desulfurization processes are uncoupled since recycle of the SO₂-containing secondary regeneration off-gas to the gasifier is no longer required.

Material and Energy Balance Comparison

The material and energy balances were based on the same assumptions used to develop previous cases. The overall material balance summary is presented in Table 2 along with comparable results from cases 5a and 6. The corresponding overall sulfur material balance summary for the three cases is presented in Table 3. The production rate of clean coal gas is equal in cases 5a and 7, but is somewhat less in case 6 because of the slip stream required for the DSRP reactor. Similarly, the quantity of sulfur fed and concentration of sulfur remaining in the clean coal gas is the same in each case. Case 6 involves the discharge of some sulfur as SO₂ to the atmosphere in the recycle purge stream while there is no sulfur discharge for either cases 5a or 7. The smaller recovery of elemental sulfur in case 5a is somewhat misleading since the SO₂ in the secondary regeneration off-gas is recycled to the gasifier and ultimately recovered as elemental sulfur. Thus, the production rates of elemental sulfur are effectively equal in each case.

Cerium sorbent make-up and discharge rates are the same in cases 5a and 7, and are considerably larger than the corresponding zinc sorbent rate in case 6. Sorbent make-up and discharge rates in each option are fixed at 1% of the sorbent circulation rate. The circulation rate, in turn, is fixed at twice the stoichiometric quantity required for complete removal of all sulfur. The primary reason for the different make-up/discharge rates is the lower theoretical sulfur capacity of 9.3g S per 100g CeO₂ compared to 26.4g S per 100g Zn₂TiO₄. The zinc sorbent make-up/discharge rate associated with the secondary sorber in case 5a is quite small since about 97% of the sulfur is removed in the primary sorber. Oxygen is required in the SO₂ regeneration of Ce₂O₂S with more O₂ needed in case 7 than case 5a because of the increased sulfur removal. Elimination of the secondary regenerator in case 7 also eliminates the need for steam and oxygen to that regenerator. Air and N₂ are required for the regeneration of sulfided zinc sorbent in case 6.

The significantly larger production rate of the elemental sulfur product stream in case 6 (Table 2) is due to the presence of water in this stream. As shown in Table 3, the actual sulfur content of this stream is approximately the same in each of the cases. The presence of the water, however, will reduce the value of the sulfur by-product. A recycle purge is required in case 6 to satisfy the CO₂ material balance, and, as shown in Table 3, this results in a small discharge of SO₂ to the atmosphere. No atmospheric discharge occurs in cases 5a and 7.

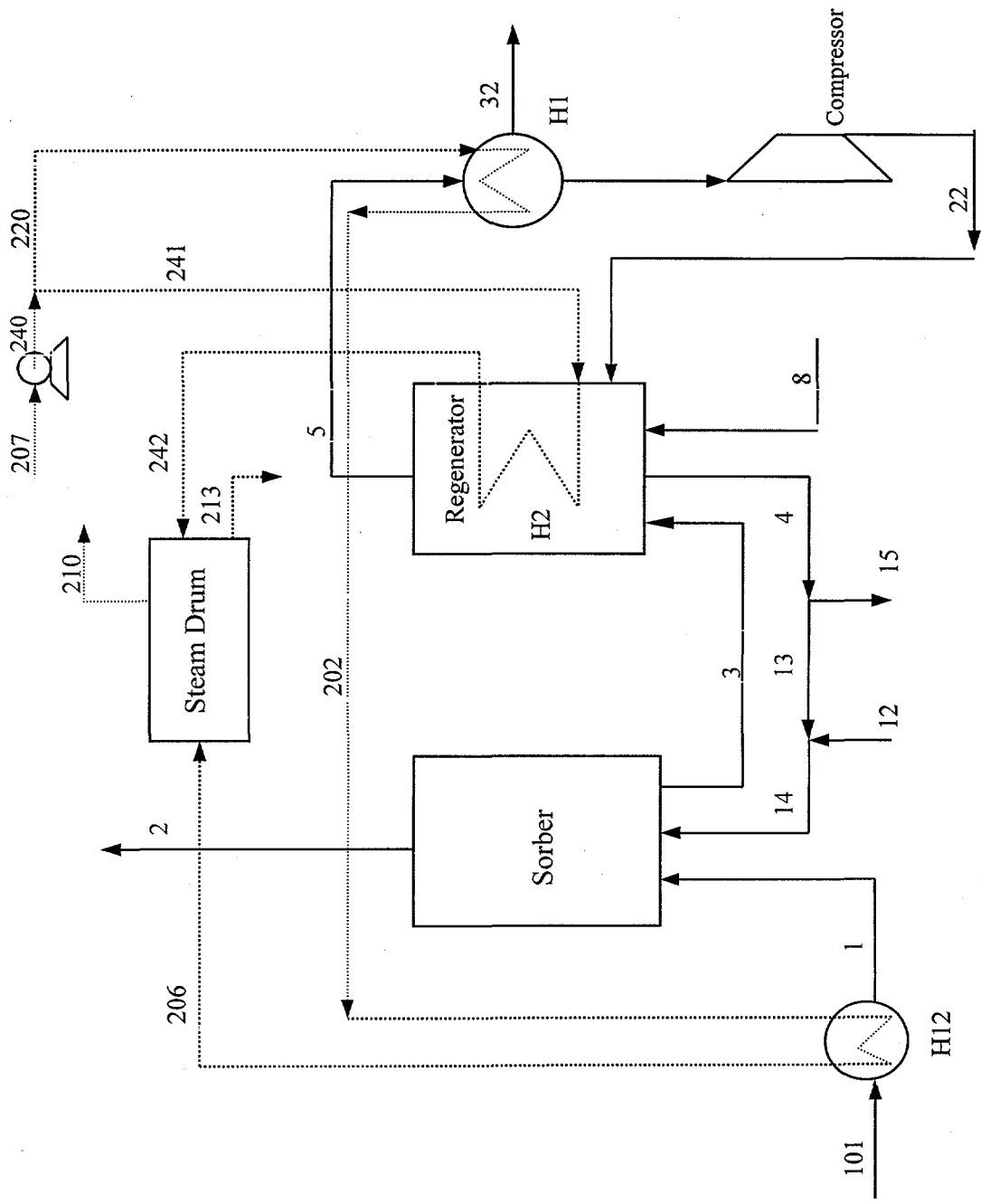


Figure 15. Process Flow Diagram for Single-Stage Desulfurization Using Cerium Sorbent with SO₂ Regeneration.

Table 2. Summary of Overall Process Material Balance Results for Three Design Cases.

Input Stream Description	Stream Flow Rate, lbmol/hr		
	Case 5a ¹	Case 6 ²	Case 7 ³
Coal Gas from Gasifier	17000	17000	17000
Cerium Sorbent Make-up	6.9	--	6.9
Zinc Sorbent Make-up	0.08	1.7	--
Oxygen to Primary Regenerator	164	--	172
Steam to Secondary Regenerator	424	--	--
Oxygen to Secondary Regenerator	13	--	--
Air to Regenerator	--	1320	--
Nitrogen to Regenerator	--	1100	--
Boiler Feed Water	6480	7560	4280
Output Stream Description			
Desulfurized Coal Gas	17000	16500	17000
Cerium Sorbent Discharge	6.9	--	6.9
Zinc Sorbent Discharge	0.08	1.7	--
Secondary Regenerator Off-gas	433	--	--
Recycle Purge Gas	--	2470	--
Elemental Sulfur Product	164	276	172
Product Steam	6060	7560	4280

¹Case 5a: Two-stage desulfurization using cerium and zinc sorbents and direct production of elemental sulfur using SO₂ regeneration.

²Case 6: Single-stage desulfurization using zinc sorbent with elemental sulfur recovery using DSRP.

³Case 7: Single-stage desulfurization using cerium sorbent and direct production of elemental sulfur using SO₂ regeneration.

Table 3. Summary of Sulfur Material Balance Results for Three Design Cases.

Input Stream (Sulfur Form)	Stream Flow Rate, lb/hr		
	Case 5a ¹	Case 6 ²	Case 7 ³
Coal Gas (H ₂ S)	5498	5498	5498
Output Stream (Sulfur Form)			
Desulfurization Coal Gas (H ₂ S)	5.9	5.4	6.0
Secondary Regenerator Off-Gas (SO ₂)	252	-	-
Recycle Purge Gas (SO ₂)	-	5.1	-
Elemental Sulfur Product (S _x)	5240	5487	5492

¹Case 5a: Two-stage desulfurization using cerium and zinc sorbents and direct production of elemental sulfur using SO₂ regeneration.

²Case 6: Single-stage desulfurization using zinc sorbent with elemental sulfur recovery using DSRP.

³Case 7: Single-stage desulfurization using zinc sorbent and direct production of elemental sulfur using SO₂ regeneration.

The quantities of boiler feed water and export steam are determined by the energy balance of the processes. The largest water and steam flows are associated with case 6 followed by case 5a and then case 7. The smaller rates in case 7 compared to case 5a are due to eliminating the exothermic energy released from the regeneration of zinc sorbent in the secondary regenerator.

Cost Comparison

The estimated purchased equipment cost and total capital requirement for the three cases are compared in Table 4. In each case the numbers represent the total cost of four identical parallel trains. All case 5a and 6 costs are as presented earlier. The cost of individual items in cases 5a and 7 are equal, except that the secondary sorber and regenerator and heat exchangers associated with those units are not needed in case 7. The total capital requirement of \$3.74 million for case 7 is 44% less than for case 5a and 72% less than for case 6.

The key factors in the operating costs are the consumption or generation rates of raw materials, by-products, and utilities coupled with the unit costs of these items. These flow rates are summarized in Table 5 for the three processes. The material in Table 5 was presented in the previous quarterly report for the initial design cases (cases 5a and 6), and has been enlarged in this report to include additional design case 7. Base unit costs are unchanged from the values reported in the previous quarterly report.

Annual operating costs (credits) for raw materials, by-products, and utilities for the three cases are summarized in Table 6. Again the values for cases 5a and 6 were reported in the previous quarterly report and the table has been updated to include the results from case 7. In all three cases sorbent replacement is the dominant cost item. Sorbent replacement cost actually exceeds the total operating costs for cases 5a and 7 where by-product income exceeds the total operating cost minus the sorbent replacement cost. It is also of interest to note that the \$18.70 million variable operating cost of case 7 is about 1.7% greater than the equivalent cost for case 5a even though the secondary sorber and regenerator are eliminated in the former case. The reason for this seeming contradiction is that the small savings gained from eliminating the zinc sorbent make-up is more than offset by the reduction in export steam produced by the exothermic secondary regeneration reaction. The higher variable costs are partially offset by the lower annual capital cost so that the \$18.79 million total operating cost for case 7a is only about 0.9% greater than the comparable value for case 5a.

The final comparison between process options is based on the annual levelized cost. Procedures for estimating annual levelized cost were described in the previous quarterly report and results for case 7 are summarized in Table 7. The total is dominated by the \$28.30 million cost of cerium sorbent replacement which is 111% of the estimated total levelized cost of \$25.56 million. This is about \$350,000 or 1.4% less than the \$25.91 million annual levelized cost of case 5a.

This estimated levelized cost saving of \$350,000 is almost negligible compared to the total cost associated with these base conditions, and is well within the uncertainty of the overall cost estimate. However, the magnitude of the savings is independent of the cerium sorbent cost which was estimated on the basis of the sorbent replacement rate being 1% of the sorbent circulation rate.

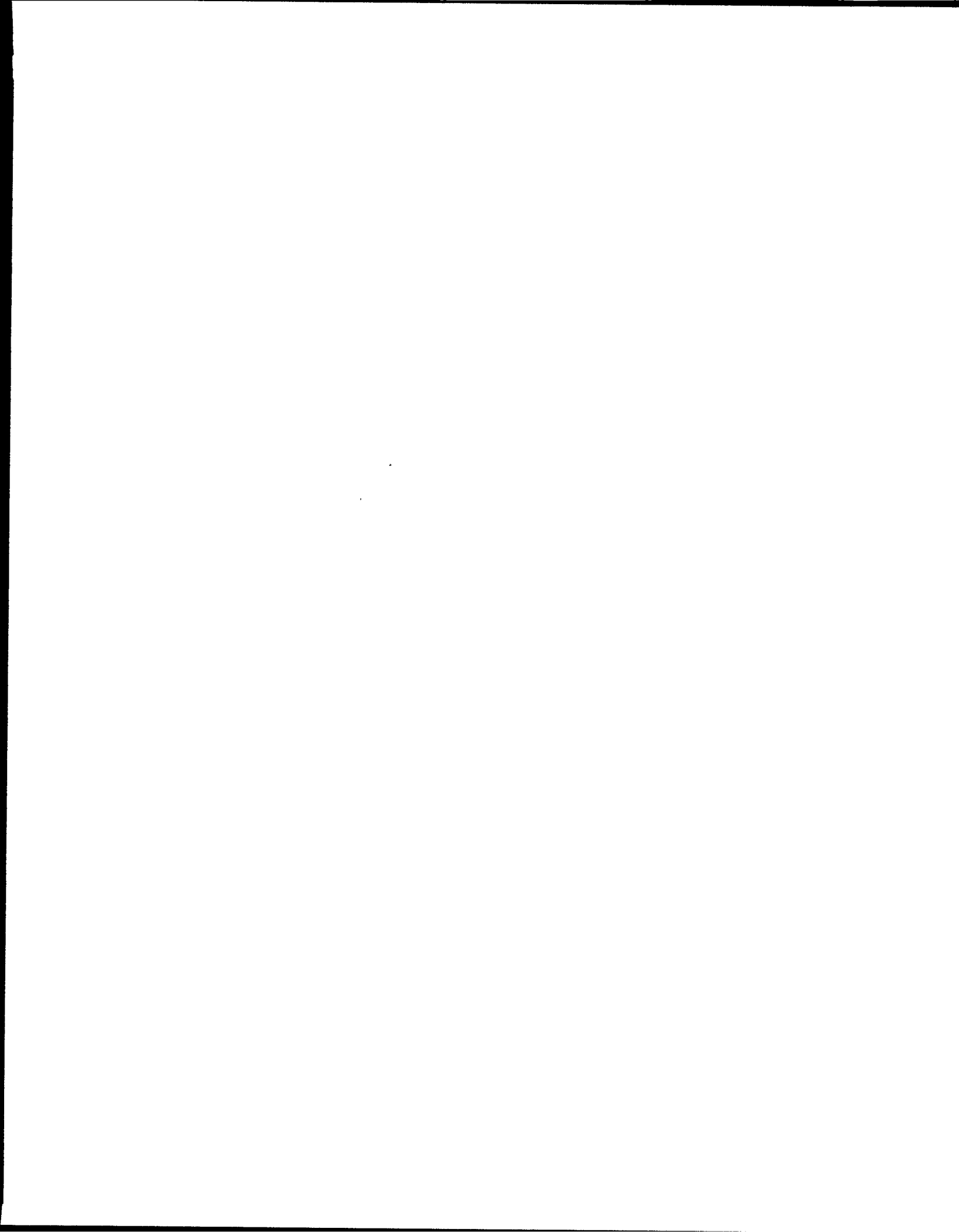


Table 5. Consumption and Production Rates of Raw Materials, By-Products and Utilities.

	Case 5a ¹	Case 6 ²	Case 7 ³
Raw Materials			
Zinc Sorbent	0.08 lbmol/hr	1.68 lbmol/hr	--
Cerium Sorbent	6.88 lbmol/hr	--	6.88 lbmol/hr
Coal Gas	--	435 lbmol/hr	--
Nitrogen	--	1100 lbmol/hr	--
Oxygen	177 lbmol/hr	--	172 lbmol/hr
By-Products			
Sulfur	164 lbmol/hr	171 lbmol/hr	172 lbmol/hr
Steam	6050 lbmol/hr	7560 lbmol/hr	4275 lbmol/hr
Utilities			
Boiler Feed Water	6480 lbmol/hr	7560 lbmol/hr	4280 lbmol/hr
Electricity	384 hp	3540 hp	293 hp

¹Case 5a: Two-stage desulfurization using cerium and zinc sorbents and direct production of elemental sulfur using SO₂ regeneration.

²Case 6: Single-stage desulfurization using zinc sorbent with elemental sulfur recovery using DSRP.

³Case 7: Single-stage desulfurization using cerium sorbent and direct production of elemental sulfur using SO₂ regeneration.

Table 6. Annual Variable and Fixed Operating Cost (Credit)
(10⁶ \$, 65% Capacity Factor).

	Case 5a ¹	Case 6 ²	Case 7 ³
Raw Materials			
Zinc Sorbent	0.41	8.62	--
Cerium Sorbent	21.42	--	21.42
Coal Gas	--	3.11	--
Nitrogen	--	2.20	--
Oxygen	0.65	--	0.63
By-Products			
Sulfur	(1.34)	(1.41)	(1.40)
Steam	(3.91)	(4.88)	(2.76)
Utilities			
Boiler Feed Water	1.05	1.23	0.69
Electricity	0.11	1.05	0.08
Total Variable Operating Costs	18.39	9.92	18.70
Fixed Operating Cost	0.24	0.48	0.13

¹Case 5a: Two-stage desulfurization using cerium and zinc sorbents and direct production of elemental sulfur using SO₂ regeneration.

²Case 6: Single-stage desulfurization using zinc sorbent with elemental sulfur recovery using DSRP.

³Case 7: Single-stage desulfurization using cerium sorbent and direct production of elemental sulfur using SO₂ regeneration.

Table 7. Levelized Cost for Single-Stage Desulfurization Using Cerium Sorbent with SO₂ Regeneration (Case 7), 10⁶ \$, 1996 Basis

Capital Cost	Levelized Cost	% of Capital Levelized Cost	% of Total Levelized Cost
Pressure Vessels	0.46	62.2	3.3
Heat Exchangers	0.17	23.0	1.3
Compressors	0.04	5.4	0.1
Pump	0.05	6.7	0.2
Steam Drum	0.02	2.7	0.1
Levelized Capital Cost	0.74	100	2.9
Levelized Fixed Operating Cost (65% of Total)	0.12		0.5
Variable Operating Cost		% of Vari. Operating Levelized Cost	
Boiler Feed Water	0.91	3.7	3.6
Power	0.11	0.4	0.4
Oxygen	0.83	3.4	3.2
Cerium Sorbent	28.30	114.6	110.7
Allocated Variable Operating Cost (35% of Total)	0.05	0.2	0.2
Credit			
Steam	(3.65)	-14.8	-14.3
Sulfur	(1.85)	-7.5	-7.2
Levelized Variable Operating Cost	24.70	100	96.6
Total Levelized Cost	25.56		100

As shown in the sensitivity analysis which follows, the total annual levelized cost decreases dramatically as sorbent durability increases (replacement rate decreases).

Cost Sensitivity

The annual levelized cost estimates for each process are dominated by sorbent replacement cost. The replacement cost is determined by two factors--sorbent lifetime and sorbent unit cost--both of which are highly uncertain at this time. The cost of other items, which are less important in the base case, are also uncertain and will become increasingly important if sorbent replacement cost is decreased. The cost sensitivity of the processes has been analyzed using sorbent lifetime, sorbent unit cost, oxygen and nitrogen unit costs, and capital cost as sensitivity parameters. Base case values and the range of values used in the sensitivity analysis are presented in Table 8.

The large sorbent replacement costs in the base case estimates are due primarily to the sorbent replacement rate being equal to 1% of the sorbent circulation rate, which corresponds to an average sorbent lifetime of 100 cycles. It is probable that none of the high temperature desulfurization cases would be competitive with low temperature desulfurization at these conditions. The high temperature desulfurization analysis completed by Buchanan et al. (1994) assumed three complete replacements of the zinc sorbent inventory per year while the Kellogg design of the hot gas desulfurization portion of the Pinon Pine IGCC demonstration unit is based on one complete replacement of the zinc sorbent inventory per year (Dorchak, 1997). We estimate that these replacement rates correspond roughly to 0.10% of the sorbent recirculation rate, which result in average sorbent lifetimes of about 1000 cycles. As shown in the following, the annual levelized cost of the cerium sorbent processes decreases more rapidly when the sorbent replacement rate is decreased than the annual levelized cost of the zinc sorbent process. At a replacement rate of 0.1% of the circulation rate, we estimate the cerium processes to be less expensive.

Results of the cost sensitivity analysis comparing the annual levelized cost of cases 5a and 6 as a function of sorbent replacement rate and sorbent unit cost is shown in Figure 16. Sorbent replacement rate is varied from the base value of 1% of the circulation rate down to 0.1% of circulation rate, while unit sorbent costs of \$3/lb, \$5/lb and \$8/lb are shown. All other cost items were maintained at the base values shown in Table 8.

The slopes of the lines representing cerium costs are greater than those of the zinc costs. Hence, the six lines of Figure 16 form nine intersections where the estimated annual levelized cost of the two processes are equal. For example, if the unit cost of both cerium and zinc sorbents is \$5/lb, the intersection occurs at a sorbent replacement rate of 0.25% of the circulation rate (400 cycles lifetime) and the estimated annual levelized cost of both processes is \$8.68 million. Larger sorbent replacement rates make the zinc sorbent option (case 6) more economical while with smaller replacement rates the cerium sorbent option (case 5a) is less costly. At these conditions, the \$350,000 savings for case 7 compared to case 5a is well within the uncertainty of the estimate.

Table 9 summarizes sorbent replacement rates and unit costs corresponding to the nine intersections of the lines of Figure 16. When the cost of zinc and cerium sorbents are equal, all intersections occur at the same total levelized cost of \$8.68 million, and the sorbent replacement rate

Table 8. Base Case and Range of Values Used in the Economic Sensitivity Analysis (1996 \$)

	<u>Base</u>	<u>Range</u>
Total Capital Requirement (10 ⁶ \$)		
Two-Stage Desulfurization	6.5	4.6 - 8.5
With SO ₂ Regeneration (case 5a)		
Single Stage Desulfurization	13.2	9.3 - 17.2
With DSRP (case 6)		
Sorbent Replacement Rate, % of Circulation Rate	1.0	0.1 - 1.0
Sorbent Unit Cost, \$/lb		
Cerium Sorbent	3.2	3.0 - 8.0
Zinc Sorbent	3.75	3.0 - 8.0
Nitrogen Unit Cost, \$/ton	25	10 - 40
Oxygen Unit Cost, \$/ton	40	30 - 50

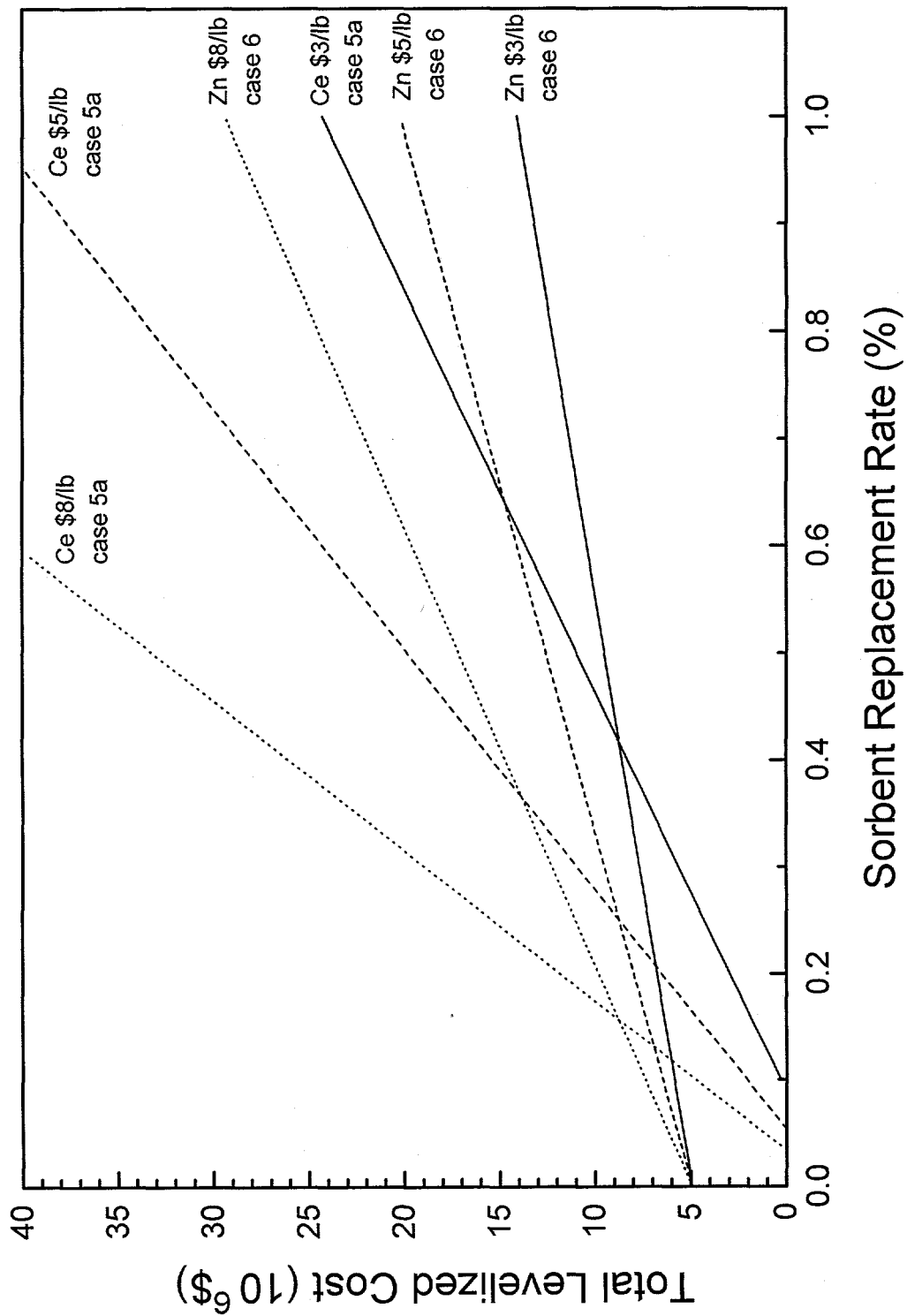


Figure 16. Total Annual Levelized Cost Comparison of Design Cases 5a and 6 as a Function of Sorbent Replacement Rate and Sorbent Unit Cost.

Table 9. Sorbent Replacement Rate and Total Levelized Cost at the Intersection Points of the Six Cost Lines in Figure 16.

Cerium Sorbent Unit Cost (\$/lb)	Zinc Sorbent Unit Cost (\$/lb)	Sorbent Replacement Rate (% of Circulation Rate)	Total Levelized Cost (10 ⁶ \$)
8	8	0.155	8.68
8	5	0.13	6.96
8	3	0.12	5.96
5	8	0.37	13.8
5	5	0.25	8.68
5	3	0.21	6.96
3	8	3.0*	76.42*
3	5	0.65	14.84
3	3	0.415	8.68

* Calculated values which are not shown in Figure 16.

shifts to lower values as the sorbent unit cost increases. Replacement rates of 0.155%, 0.25%, and 0.415% of the circulation rate produce equal annual levelized cost at sorbent unit costs of \$8/lb, \$5/lb, and \$3/lb respectively. Sorbent replacement rates less than 0.15% of circulation rate always result in two-stage desulfurization using cerium sorbent (case 5a) being more economical than single-stage desulfurization using zinc sorbent (case 6) over the range of sorbent unit costs considered.

Another example of the use of Figure 16 is illustrated by the following. Let us suppose that an annual levelized cost of, for example, \$7 million has been established as the maximum permissible cost for the desulfurization and sulfur recovery portions of the process. The maximum sorbent replacement rate for case 6 would be 0.13% of circulation rate if the unit cost of the zinc sorbent is \$5/lb. At a similar \$5/lb unit cost of cerium sorbent, the maximum allowable replacement rate for case 5a would be 0.21% of circulation rate.

It is also of interest to note that all cost lines for the zinc sorbent process converge to a value of \$5 million and the cerium process lines converge to \$-2.2 million at zero sorbent replacement rate (infinite sorbent lifetime). Thus, the cerium process could actually produce a profit through the sale of export steam and by-product sulfur if the sorbent is sufficiently durable, while the zinc sorbent process would always involve a cost of at least \$5 million.

The \$350,000 saving associated with single-stage cerium sorbent desulfurization (case 7) becomes increasingly important as the sorbent durability increases and total cost decreases. For example, at a cerium sorbent unit cost of \$5/lb and a replacement rate equal to 0.1% of the circulation rate, the \$350,000 savings is about 17% of the estimated annual levelized cost of \$2.1 for case 5a.

Although sorbent replacement is the dominant cost item for all three cases at the base sorbent replacement rate of 1% of the circulation rate, other items such as oxygen, nitrogen and capital cost become increasingly important as the sorbent replacement rate decreases. Oxygen is required in the secondary regenerator of the two-stage cerium-sorbent process (case 5a) while nitrogen is required in the regenerator of the single-stage zinc-sorbent process with DSRP (case 6). We assume that O₂ and/or N₂ would be "purchased" from the air separation unit required with the oxygen-blown gasifier. Unit cost of these materials depends on the size of the plant, the air separation method used, and, in some cases, on corporate accounting practices. For example, if the separation plant produces excess N₂, the unit price will be lower than if the demand for O₂ and N₂ are balanced. Cost ranges of \$30 to \$50 per ton for O₂ and \$10 to \$40 per ton for N₂ as shown in Table 8 were used in the sensitivity analysis.

The effect of O₂ and N₂ unit costs are shown in Figure 17 for sorbent replacement rates between 0.1% and 0.5% of circulation rate. The unit cost of both cerium and zinc sorbents was fixed at \$5/lb for this analysis. For single-stage desulfurization using zinc sorbent with DSRP (case 6), the annual levelized cost saving between N₂ at \$40/ton and \$10/ton is \$3.53 million. This is about 33% of the total levelized cost at a sorbent replacement rate of 0.5% and increases to 75% of the total at a sorbent replacement rate of 0.1%, with both percentages based on a unit N₂ cost of \$10/ton. For two-stage desulfurization using cerium sorbent with SO₂ regeneration (case 5a), the total levelized cost savings between O₂ at \$50/ton and \$30/ton is \$0.46 million, about 2% of the total levelized cost at a sorbent replacement rate of 0.5% but about 25% of the total levelized cost at a replacement rate

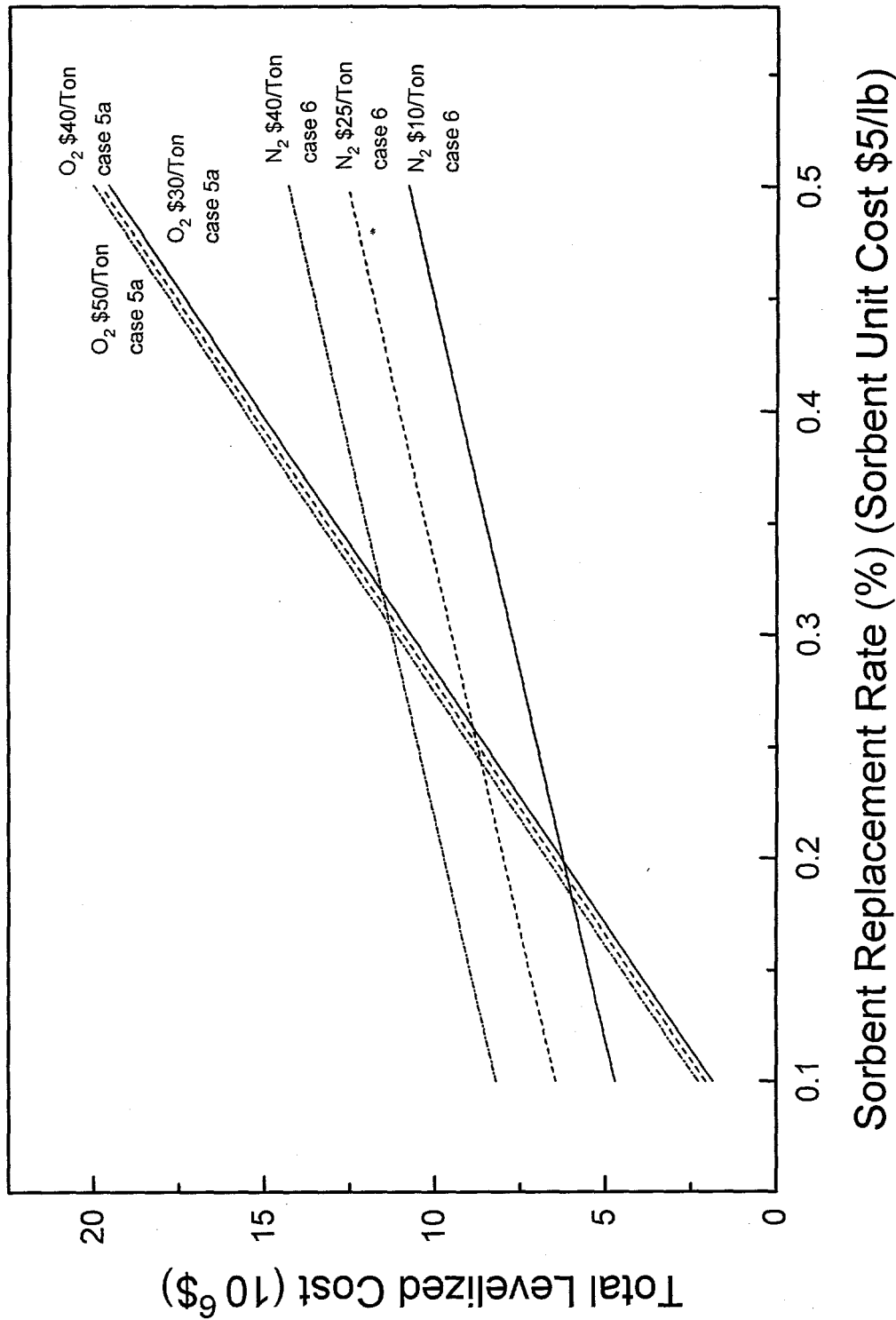


Figure 17. Total Annual Levelized Cost Comparison of Design Cases 5a and 6 as a Function of Sorbent Replacement Rate and Unit Costs of Oxygen and Nitrogen.

of 0.1%. Again, both percentages are based on the lower unit cost of \$30/ton. The \$0.35 million saving associated with the possible single-stage cerium sorbent process with SO₂ regeneration (case 7) would further reduce the cost. For example, at a sorbent replacement rate of 0.1%, the estimated annual levelized cost of case 5a using O₂ at \$50/ton is about 2.3 million. At the same sorbent replacement rate, the estimated annual levelized cost for case 7 with O₂ at \$30/ton is only about \$1.4 million.

Figure 17 also shows nine intersections of the six lines which represent equal cost for cases 5a and 6. Since the cost of case 5a is relatively insensitive to oxygen cost, the equal cost sorbent replacement rates are largely determined by N₂ cost. The equal cost sorbent replacement rate decreases from about 0.31% (320 cycles) for N₂ at \$40/ton to 0.25% (400 cycles) for \$25/ton N₂ and to 0.19% (530 cycles) when the unit cost of N₂ is \$10/ton.

Capital cost also becomes more important as the sorbent replacement rate decreases. The accuracy of the capital cost estimate is thought to be about $\pm 30\%$, and that range was selected to determine the sensitivity of the levelized cost to capital cost. Results are shown in Figure 18 for capital costs of 70%, 100%, and 130% of the base values. Numerical values corresponding to these percentages are shown in Table 8.

The capital cost variations correspond to a difference of \$0.78 million in total levelized cost for two-stage desulfurization with cerium sorbent and SO₂ regeneration (case 5a) and \$1.55 million for single-stage desulfurization using zinc sorbent and DSRP (case 6). On a percentage basis, the \$0.78 million is about 4% of the total levelized cost at a sorbent replacement rate of 0.5%, but is 46% of the total at a replacement rate of 0.1%. The \$1.55 million difference is about 13% of the levelized cost at a replacement rate of 0.5%, and is 27% of the total at a replacement rate of 0.1%.

Again, all percentages are based on the lower capital cost estimate. Once again, the six lines of Figure 18 form nine equal cost intersections, but the range of replacement rates varies only from 0.21% to 0.29% of the circulation rate, corresponding to a range in annual levelized cost from about \$10 million to \$7.5 million. The \$0.35 million potential levelized cost saving of case 7 compared to case 5a shifts the ranges of replacement rates corresponding to equal cost for cases 6 and 7 to about 0.22% to 0.3% of the circulation rate.

SUMMARY

The economic analysis has shown that sorbent durability is the key in determining the cost of high temperature desulfurization with elemental sulfur recovery. If the sorbent replacement rate exceeds 0.7% of circulation rate (143 cycles), single-stage desulfurization using zinc sorbent and elemental sulfur recovery using DSRP (case 6) will be less expensive than either of the options using cerium sorbent with direct recovery of elemental sulfur by SO₂ regeneration (cases 5a and 7). However, the annual levelized cost of single-stage desulfurization with DSRP at 0.7% sorbent replacement rate is estimated to be on the order of \$10 million, making it questionable if high temperature desulfurization would be economically competitive with standard low temperature desulfurization.

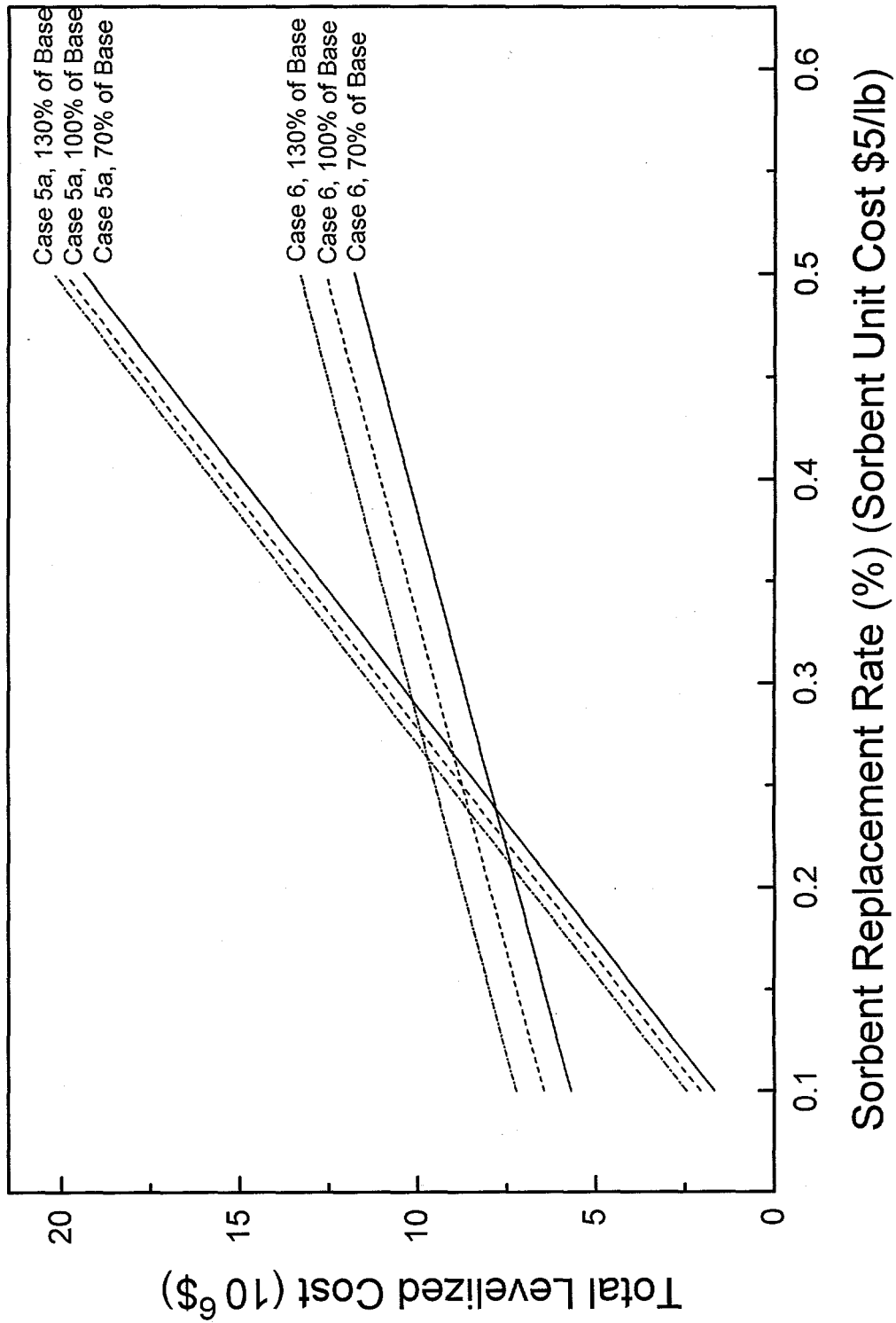


Figure 18. Total Annual Levelized Cost Comparison of Design Cases 5a and 6 as a Function of Sorbent Replacement Rate and Process Capitol Cost.

As the required sorbent replacement rate decreases, all high temperature desulfurization options become less expensive and the cerium-sorbent options become more attractive compared to the zinc-sorbent option. If the sorbent replacement rate can be reduced to about 0.1% of the circulation rate, the cerium sorbent processes should be less costly than the zinc process, and the annual levelized cost should be less than \$5 million. It is important to note that sorbent replacement rates in the range of 0.1% of circulation rate have been used as the basis for the design of the two clean coal demonstration processes which include hot gas desulfurization. It is also important to recognize that, as the sorbent replacement rate approaches zero, both cerium sorbent options could actually produce a profit through the sale of by-product sulfur and export steam. In contrast, the minimum levelized cost of the zinc sorbent option at zero sorbent replacement rate is about \$5 million. Between sorbent replacement rates of 0.1% and 0.7% of circulation rate, the least expensive high temperature desulfurization option will depend on the cost of other items such as the unit cost of sorbent, O₂, and N₂, as well as the total capital requirement.

According to Buchanan et al. (1994), the coal gas flow rate of 17,000 lbmol/hr used in this analysis should result in a nominal power generation capacity of 275 MW. With a 65% capacity factor, the conversion factor between levelized cost expressed in 10⁶ \$/yr and cost of electricity in mills/kWh is 0.65. Thus, \$10 million per year levelized cost is equivalent to an incremental cost of electricity of 6.5 mills/kWh while \$5 million per year levelized cost is equivalent to an increase of 3.25 mills/kWh in the cost of electricity. The latter value is thought to be a reasonable since McMichael and Gangwal (1991) estimated a ten-year levelized cost increment of 2.5 mills/kWh for sulfur recovery using DSRP, but not including the desulfurization and sorbent regeneration aspects.

The \$5 million cost target is achievable using the zinc sorbent process only as the sorbent replacement rate approaches zero. In contrast, the annual levelized cost of the two cerium sorbent options can achieve the target at sorbent replacement rates in the range of 0.1% to 0.3% of circulation rate, depending on other cost items

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Table 4. Estimated Purchased Cost of Major Equipment and Total Capital Requirement for Three Design Cases.

	Purchased Equipment Cost (10 ⁶ \$, 1996)		
	Case 5a ¹	Case 6 ²	Case 7 ³
Reactor Vessels			
Primary Sorber	0.380	0.325	0.380
Secondary Sorber	0.330	--	--
Primary Regenerator	0.082	0.252	0.082
Secondary Regenerator	0.054	--	--
DSRP Reactor	--	0.210	--
Refractory	0.040	0.048	0.020
Sub-Total	0.886	0.835	0.482
Heat Exchangers			
Waste Heat Boilers			
H1	--	0.177	--
H2	--	0.075	--
H4	--	0.117	--
H12	0.159	--	0.159
H15	0.050	--	--
H16	0.127	--	--
Shell and Tube			
H1	0.021	--	0.021
H3	--	0.043	--
H8	--	0.018	--
H9	--	0.214	--
Sub-Total	0.357	0.644	0.180
Compressors			
SO ₂ Recycle	0.043	--	0.043
Air	--	0.980	--
DSRP Recycle	--	0.150	--
Sub-Total	0.043	1.130	0.043
Pump	0.049	0.049	0.034
Total Purchased Equipment Cost	1.355	2.678	0.759
Total Capital Requirement (4.93 x Purchased Equipment Cost)	6.68	13.20	3.74

¹Case 5a: Two-stage desulfurization using cerium and zinc sorbents and direct production of elemental sulfur using SO₂ regeneration.

²Case 6: Single-stage desulfurization using zinc sorbent with elemental sulfur recovery using DSRP.

³Case 7: Single-stage desulfurization using zinc sorbent and direct production of elemental sulfur using SO₂ regeneration.