

Advanced Sulfur Control Concepts in Hot-Gas Desulfurization Technology

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U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
Louisiana State University
Department of Chemical Engineering
Baton Rouge, Louisiana 70803

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EXECUTIVE SUMMARY

Experimental effort during the past quarter was restricted to the fixed-bed reactor. Effort during April was devoted to the sulfidation and regeneration of cerium oxide. Sulfidation tests were plagued by "over-sulfidation", i.e., the quantity of H_2S removed from the gas phase exceeded the stoichiometric amount associated with the conversion of CeO_2 to Ce_2O_2S . This was initially attributed to the formation of Ce_2S_3 which was found to be thermodynamically possible in the highly reducing feed gas. However, the addition of steam to the feed gas to prevent Ce_2S_3 formation did not eliminate the "over-sulfidation" problem. Later tests indicated that the apparent "over-sulfidation" was due to reaction between H_2S and the walls of the reaction vessel. Apparently the alonizing treatment to passivate the reactor walls was either ineffective at the reaction conditions or had deteriorated with use to the point that protection was no longer viable. Limited Ce_2O_2S regeneration results, although very qualitative, were quite favorable. In one regeneration test in an O_2-N_2 atmosphere, no SO_2 or H_2S were detected by the chromatograph in the regeneration product. Significant amounts of total sulfur were detected, and the test had to be terminated prematurely when elemental sulfur, which escaped the condenser and filter, caused the product line leading to the chromatograph to plug.

Experimental tests during May and June examined the regeneration of FeS as a function of temperature, gas feed composition, and gas flow rate. Complete regeneration was achieved with as much as 75% of the sulfur liberated in elemental form. Low regeneration temperature and large ratios of H_2O to O_2 in the feed gas promote the formation of elemental sulfur.

A number of changes in the reactor system were made during the quarter, including improvements to the sulfur condenser and filters on the reactor product line leading to the gas chromatograph. The condenser has been packed with glass wool to provide increased surface for elemental sulfur removal, and a second in-line filter having $2\mu m$ openings has been added. While we cannot claim that problems in capturing elemental sulfur have been eliminated, a number of runs in which significant amounts of elemental sulfur were formed were carried to completion without plugging the product line to the chromatograph. In addition, a quartz reactor insert has been designed to minimize the problem of H_2S reacting with the vessel walls during CeO_2 sulfidation runs. Finally, a SiO_2 -coated stainless steel capillary flow restrictor and pyrotube have been fabricated to avoid the breakage problems which have been experienced with quartz. Testing of both the quartz insert and the flow restrictor/pyrotube is awaiting completion of the FeS regeneration tests currently being carried out.

The Antek total sulfur analyzer continues to give erratic readings which we attribute to variable flow rates through the unit, and, in some cases, to excessive steam concentrations which exceed the capacity of the membrane dryer. The problems of variable flow are believed due to periodic partial plugging of the capillary flow restrictor due to particle carryover from the reactor and elemental sulfur deposition. The plugging problem is probably inherent to the system while the capacity of the membrane dryer limits the steam concentration which can be used in the regeneration feed gas. Both problems cause fluctuations in the output from the UV-fluorescence analyzer, and it has been necessary to smooth some of the total sulfur results. As

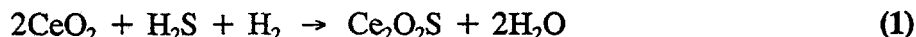
a result, the total sulfur material balance closure depends upon whether and how the data were smoothed.

The process simulation effort was initiated during the quarter and results of a base case material balance result involving two-stage desulfurization-regeneration of a Shell gas using CeO_2 are included in this report.

CERIUM OXIDE SULFIDATION AND REGENERATION

Fixed-bed reactor conditions for the series of cerium oxide sulfidation and regeneration runs are summarized in Table 1. The small "r" at the end of the run number designates a regeneration test. Note that all sulfidation tests were carried out at 750°C , 5 atm, and 300 scfm total gas flow, with approximately 1% H_2S in the feed gas. The last entry in Table 1 identifies the time, t_e , in hours at which the cumulative amount of gaseous reactant (H_2S for sulfidation and either O_2 or steam for regeneration) fed to the reactor is stoichiometrically sufficient to provide complete conversion of the solid reactant. The calculation, which does not take into account the delay between feeding reactive gas and the time that those gases reach the analyzer, is based upon the following idealized stoichiometries:

Sulfidation (Runs CeO_2 -05, CeO_2 -06, and CeO_2 -07)



Regeneration with O_2 (Runs CeO_2 -05r and CeO_2 -06r)



Regeneration with steam (Run CeO_2 -07r)



The equation used to calculate t_e is

$$t_e = \frac{\nu_G n_s}{\nu_s y n_G} \quad (4)$$

where ν_G and ν_s are the stoichiometric coefficients of gaseous and solids reactants from eqns. (1), (2) or (3), n_s is the initial mols of solid reactant in the reactor, y is the mol fraction of reactive gas in the reactor feed, and n_G is the total molar feed rate of reactive gas. For regeneration tests, the value of n_s was based on complete sulfidation of CeO_2 during the preceding sulfidation. The dimensionless time, $t^* = 1$, corresponds to the dimensional elapsed time shown in the table.

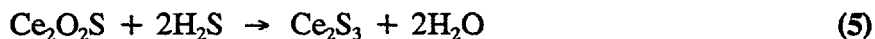
Table 1. Summary of Fixed-Bed Reactor Conditions:
CeO₂ Sulfidation and Regeneration

Run	CeO ₂ -05	CeO ₂ -05r	CeO ₂ -06	CeO ₂ -06r	CeO ₂ -07	CeO ₂ -07r
Date	04-01-96	04-02-96	04-11-96	04-12-96	04-25,26,29-96	04-25-96
Reactor Packing						
CeO ₂ , g	6.08	6.08	3.36	3.36	3.03	3.03
Al ₂ O ₃ , g	3.04	30.4	2.97	2.976	3.01	3.01
Reaction Conditions						
Temp., °C	750	600	750	750	750	750
Press., atm	5	5	5	5	5	5
Gas Comp., nominal						
% H ₂ S	1.0	--	1.0	--	0.98	--
% H ₂	25.0	--	25.0	--	14.7	--
% N ₂	74.0	99.0	73.0	99.0	81.2	97.0
% O ₂	--	1.0	--	1.0	--	--
% H ₂ O	--	--	--	--	3.1	3.0
% CO ₂	--	--	1.0	--	--	--
Gas Flow, sccm	300	300	300	300	306.5	300
Space Velocity, hr ⁻¹	3430	3430	5050	5050	5050	5050
Elapsed Time For t* = 1, hr.	2.20	2.20	1.21	1.21	1.09	0.73

r = regeneration test

Results from all three of the sulfidation tests indicated severe over-sulfidation, i.e., the apparent amount of H₂S removed by the sulfidation reaction based on the difference between the amount of H₂S fed and the amount in the reactor product gas far exceeded the stoichiometric amount indicated by eqn (1). This is illustrated in Figure 1 where the mol fraction of H₂S in the reactor product for run CeO₂-05 is plotted versus dimensionless time. The H₂S concentration increased slowly for t* < 0.5, then increased rapidly between 0.5 < t* < 1.0, and more slowly again for t* > 1.0. When the run was terminated at t*=2.6, the H₂S concentration in the product was only about 50% of the feed concentration. The cumulative H₂S removal, expressed as a fraction of the stoichiometric quantity given by eqn (1), is shown on the right ordinate of Figure 1. This value reached 1.0 at t*=1.2 and was still increasing at 1.75 when the run was terminated.

The "over-sulfidation" was initially attributed to the further sulfidation of cerium oxysulfide to cerium sulfide according to the reaction



Ce₂O₂S is thermodynamically favored when CeO₂, H₂S, H₂ and N₂ are allowed to react. However, the continuous removal of H₂O(g) in the reactor product would reduce the oxygen potential to the point that reaction (5) could occur. The feasibility of Ce₂S₃ formation is illustrated by the CHEMQ analysis shown in Table 2. The composition of the initial mixture is shown at the top of the table. Ce₂O₂S and H₂S are present in the stoichiometric proportions required by reaction (5) while the gas phase components -- H₂(g), N₂(g), and H₂S(g) -- are in the same proportions as the run CeO₂-05 reactor feed. Equilibrium composition is reported at the temperature and pressure of run CeO₂-05, and at 50°C higher and lower temperatures. The important result is that equilibrium corresponds to approximately 5% conversion of Ce₂O₂S to Ce₂S₃. The results of Figure 1 could, therefore, be explained on the basis of initial conversion of CeO₂ to Ce₂O₂S, followed by the slow conversion of Ce₂O₂S to Ce₂S₃.

While further sulfidation is possible under the laboratory experimental conditions, the presence of CO, CO₂, and H₂O would increase the oxygen potential to a level that would prevent further sulfidation in an actual coal gas atmosphere. CHEMQ calculations suggested that the addition of small amounts of oxygen-containing components -- CO, CO₂, H₂O -- to the reactor feed would be sufficient to prevent further sulfidation to Ce₂S₃. Consequently, 1% CO₂ was added to the reactor feed in run CeO₂-06, and 3.1% H₂O was added in run CeO₂-07. However, neither was effective in eliminating the apparent "over-sulfidation." For example, in run CeO₂-06 the cumulative amount of H₂S removed was 204% of stoichiometric when the reaction was terminated at t*=4.6.

By this time it appeared that formation of Ce₂S₃ was not the cause of "over-sulfidation," and we suspected that H₂S was reacting with the stainless steel surfaces of the reactor. In order to test this explanation, gas containing 1% H₂S, 15% H₂, and balance N₂ was fed at 600 sccm to an empty reactor at 750°C and 5 atm. The H₂S content of the product gas as a function of dimensional time is presented in Figure 2, which shows that the H₂S concentration in the product

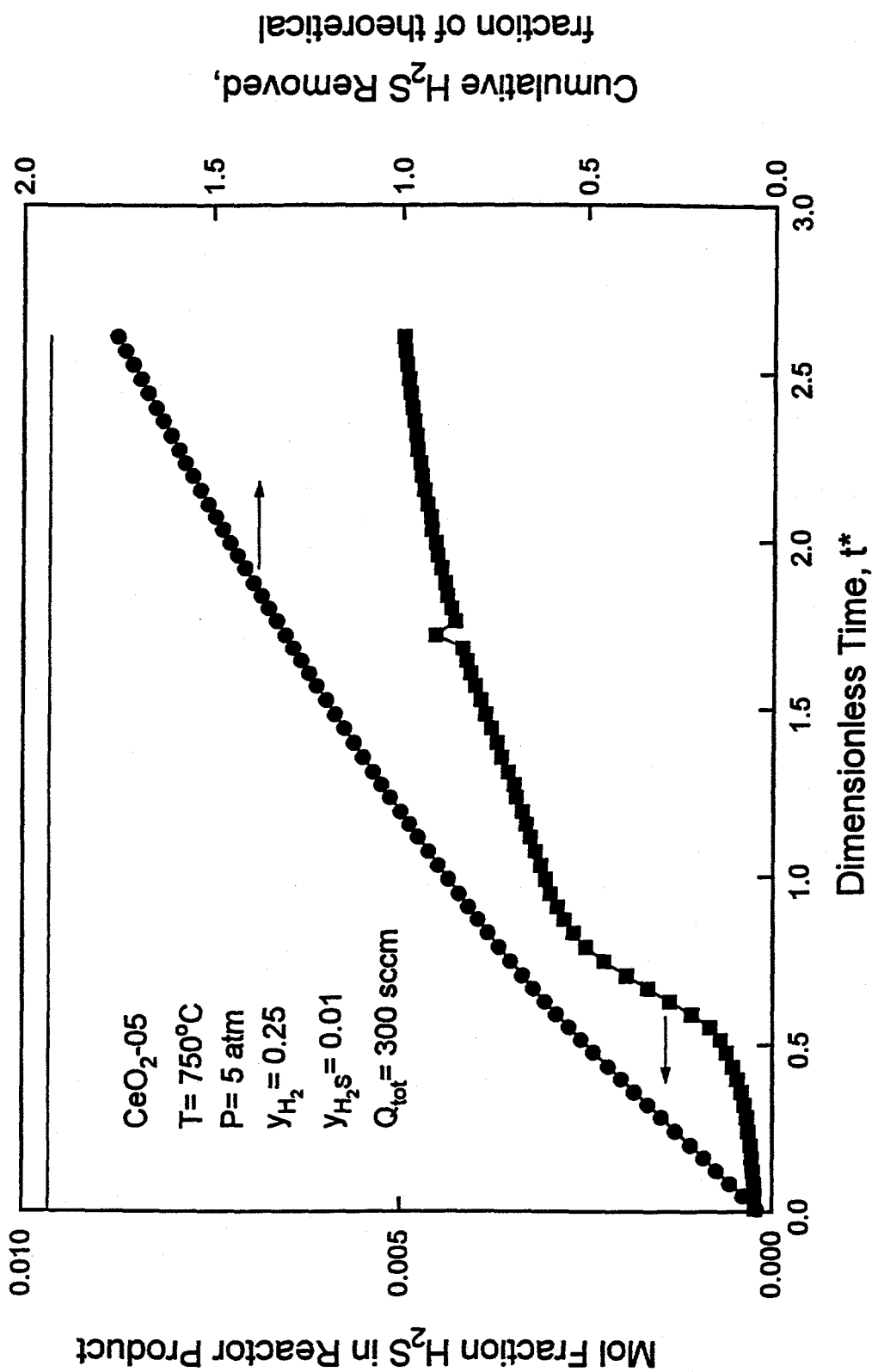


Figure 1. Fixed-Bed Reactor Response: Run CeO₂-05

Table 2. CHEMQ Analysis Showing
the Feasibility of Ce_2S_3 Formation

Initial Mixture

Component	Mols
$\text{Ce}_2\text{O}_2\text{S}$ (s)	0.10
H_2 (g)	5.00
N_2 (g)	14.80
H_2S (g)	0.20

Equilibrium Mixture at Indicated Temperature and Pressure

Temp., °C	700	750	800
Press., atm	5	5	5
Component	Mols		
H_2 (g)	4.9885	4.9920	4.9939
H_2O (g)	0.0085	0.0093	0.0102
H_2S (g)	0.1915	0.1907	0.1898
NH_3 (g)	0.0076	0.0055	0.0040
N_2 (g)	14.7963	14.7974	14.7981
$\text{Ce}_2\text{O}_2\text{S}$ (s)	0.0958	0.0953	0.0949
Ce_2S_3 (s)	0.0042	0.0047	0.0051

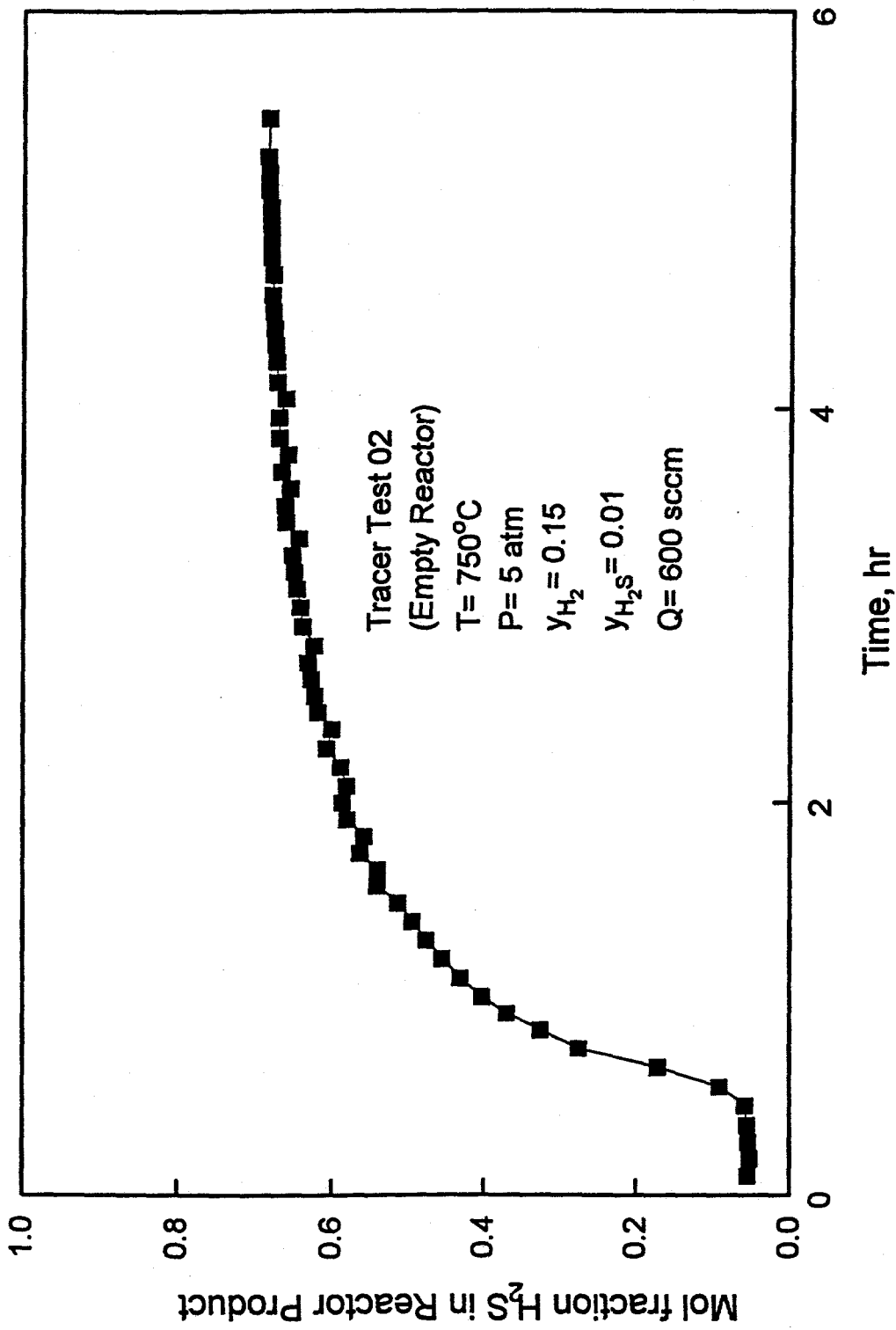


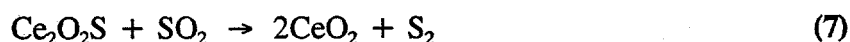
Figure 2. Fixed-Bed Reactor Response: H_2S Tracer Test 02

was only 68% of the feed concentration after 5.5 hours. In the absence of reaction, the inlet and outlet H₂S concentrations should have been approximately equal after a brief delay time.

This test confirmed that the Alon coating was not preventing the reaction between H₂S and the reactor walls. As a result, a quartz reactor insert which will minimize high temperature contact between H₂S and stainless steel is being fabricated. In the meantime, experimental effort turned to FeS regeneration studies.

Information gained from the Ce₂O₂S regeneration tests was obviously quite limited because of the sulfidation problems just described. However, qualitative results such as shown in Figure 3 were quite favorable. The initial sorbent, which contained an unknown amount of Ce₂O₂S, was regenerated at 750°C and 5 atm with the regeneration feed gas containing 1% O₂ in N₂. Both the gas chromatograph and total sulfur analyzers were used to determine the distribution of sulfur species in the product. No SO₂ or H₂S was detected by the chromatograph during the run. The total sulfur analyzer showed no sulfur in the product gas for the first 0.4 hours, followed by a rapid increase to 0.0011 mol fraction at 0.5 hours, a decrease to 0.0002 mol fraction at 0.56 hours, and a steady increase thereafter to a second maximum of 0.0022 mol fraction at 1.04 hours. The run had to be terminated after 1.05 hours because elemental sulfur plugged the product gas lines downstream of the condenser.

The fact that no H₂S or SO₂ was detected by the chromatograph suggests that all sulfur transferred to the gas phase during regeneration was in elemental form. This was consistent with the fact that the quantity of elemental sulfur produced was sufficient to plug the lines. In the presence of excess oxygen, we would expect SO₂ to be liberated. Therefore, the production of elemental sulfur may have resulted from the following pair of reactions



The first reaction should dominate near the entrance of the packed bed where the O₂ concentration is large. SO₂ produced near the entrance would then react downstream where the O₂ concentration is small.

Several changes were made in the product gas lines following this run in order to eliminate, or at least minimize, the sulfur plugging problem. First, the condenser was packed with glass wool to enhance the removal of aerosol-size particles of elemental sulfur. Thick-wall 1/8-inch diameter tubing downstream of the condenser was replaced with 1/4-inch tubing to provide an increase in the cross-sectional flow area by a factor of 8.7. Finally, a second filter was added just downstream of the condenser. Plugging has not occurred in the FeS regeneration runs conducted since these changes. No additional Ce₂O₂S tests have been attempted pending installation of the quartz reactor insert.

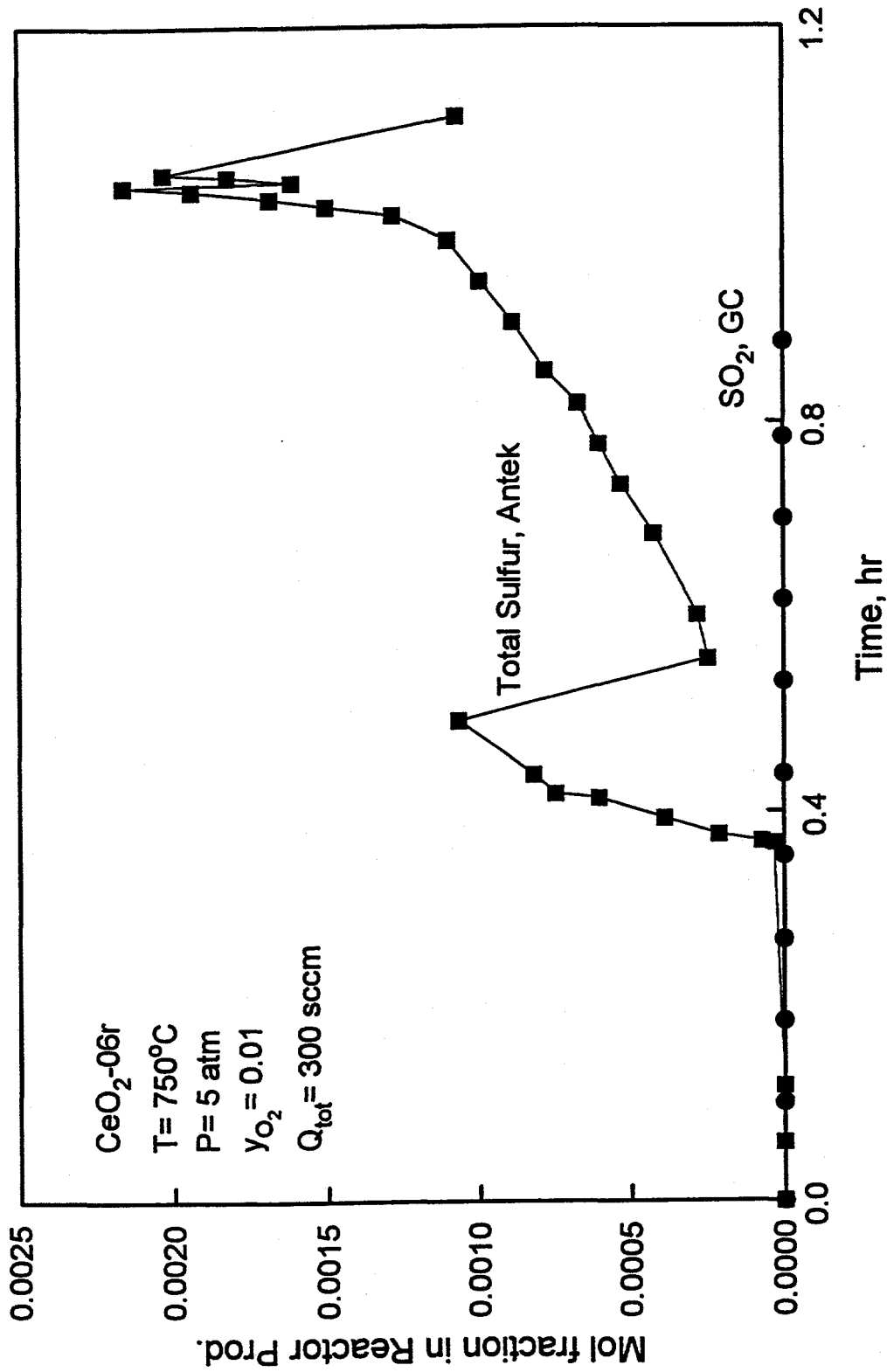


Figure 3. Fixed-Bed Reactor Response: Run CeO₂-06r

FeS REGENERATION

FeS regeneration tests have been conducted between 4.4 atm and 16.3 atm over a temperature range of 300 to 700°C. Total gas flow rates between 300 and 1800 sccm were used and the initial charge of FeS varied between 0.50 and 24.4 g. In most tests the FeS was mixed with between 3.0 and 3.8 g of inert Al₂O₃ to minimize sintering and to provide a reasonable size packed bed. Also, in most tests the feed gas contained O₂/H₂O/N₂ although some tests were conducted in atmospheres of O₂/N₂ or H₂O/N₂. Table 3 summarizes test conditions for all FeS regeneration tests completed to date, with the asterisk denoting those completed during the present quarter.

Regeneration in O₂/N₂

Figure 4 shows the fixed-bed reactor response from test FeS-13 at 700°C using a regeneration feed gas containing 1.5% O₂ in N₂. Product gas analysis was based upon the gas chromatograph only because effectively all of the sulfur transferred to the gas phase should be in the form of SO₂. After a brief delay, the SO₂ content increased quickly to about 0.0071 mol fraction at t* ~ 0.14, increased slowly thereafter to 0.008 mol fraction at t* ~ 1.05, and then decreased quickly to zero at t* ~ 1.3. The theoretical SO₂ mol fraction based on complete conversion of oxygen is 0.0087 and is shown by the horizontal line in Figure 4. Thus the maximum measured SO₂ content was approximately 90% of theoretical. The cumulative amount of SO₂ produced, expressed as a fraction of the theoretical SO₂ and shown on the right ordinate, was 0.97 at the conclusion of the test.

The Figure 4 results are typical of four oxygen regeneration tests in the temperature range of 600 to 700°C (runs FeS-07, FeS-11, FeS-12, and FeS-13). All exhibited an extended period of relatively constant SO₂ concentration within ± 10% of the theoretical maximum concentration based on complete oxygen conversion. Negative deviation from the theoretical maximum, such as shown in Figure 4, may be due to incomplete oxygen conversion, and/or errors in feed gas composition and product gas analysis. Positive deviation from the theoretical maximum may be due to errors in feed gas composition and/or product gas analysis, or to initial formation of Fe₂(SO₄)₃ followed by decomposition to form additional SO₂. The latter is particularly reasonable since both cases of positive deviation occurred in runs FeS-07 and FeS-11 at the minimum regeneration temperature of 600°C.

The cumulative production of SO₂ in the four runs ranged from a minimum of 92% of theoretical in FeS-11 to a maximum of 97% of theoretical in Fe-13, levels of sulfur material balance closure which are considered to be quite good.

Regeneration in H₂O/N₂

Early tests in which the regeneration feed gas contained steam showed extreme scatter in the product gas H₂S concentration with time. This was attributed to uneven steam concentrations in the feed gas caused by condensation on cool surfaces in the upper portion of

Table 3. Summary of Fixed-Bed Reactor
Test Conditions: FeS Regeneration

Run	FeS-01	FeS-02	FeS-03	FeS-04	FeS-05	FeS-06	FeS-07	FeS-08	FeS-09	FeS-10	FeS-11	FeS-12*	FeS-13*
Date	1-29-96	2-5-96	2-8-96	2-12-96	2-14-96	2-16-96	2-21-96	2-26-96	2-28-96	3-1-96	3-8-96	5-9-96	5-14-96
Reactor Packing													
FeS, g	24.2	24.4	8.84	5.97	5.97	6.00	3.26	3.27	3.20	3.20	3.27	3.27	3.34
Al ₂ O ₃ , g	--	--	--	--	--	--	3.29	3.26	3.22	3.22	3.29	3.28	3.13
Reactor Conditions													
Temp., °C	300→420	400→500	500	550	600	600	600	600	650	700	600	650	700
Press., atm	16.3	16.3	16.5	16.7	16.7	4.4	4.4	4.4	4.5	4.7	4.4	4.4	4.4
Gas Comp.													
% O ₂	1.0	1.0	1.0	1.5	1.5	1.5	1.5	--	--	--	1.5	1.5	1.5
% H ₂ O	--	--	--	--	--	--	--	5→10	10.0	10.0	--	--	--
% N ₂	99.0	99.0	99.0	98.5	98.5	98.5	98.5	95→90	90.0	90.0	98.5	98.5	98.5
Gas Flow, sccm	600	600	1050	600	600	600	600	600→1800	600	600	600	600	600

Run	FeS-14*	FeS-15*	FeS-16*	FeS-17*	FeS-18*	FeS-19*	FeS-20*	FeS-21*	FeS-22*	FeS-23*	FeS-24*	FeS-25*
Date	5-17-96	5-21-96	5-23-96	5-27-96	5-29-96	6-4-96	6-7-96	6-11-96	6-13-96	6-29-96	6-24-96	6-27-96
Reactor Packing												
FeS, g	3.22	3.25	3.21	1.73	1.24	0.8311	0.8322	1.022	0.8309	0.8327	0.5175	0.5037
Al ₂ O ₃ , g	3.21	3.26	3.27	3.04	3.29	3.3073	3.077	3.059	3.2801	3.2837	3.8301	3.8027
Reactor Conditions												
Temp., °C	700	700	700	700	700	700	700	600	600	600	550	600
Press., atm	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4
Gas Comp.												
% O ₂	--	--	1.5	0.5	0.25	0.25	--	0.25	0.25	0.50	0.25	0.26
% H ₂ O	10.0	30→20	10.0	23.3	20.5	20.0	20	20.0	20.0	40.0	20.0	52.0
% N ₂	90.0	70→80	88.5	76.2	79.3	79.75	80	79.75	79.75	59.5	79.5	47.75
Gas Flow, sccm	600	687→600	600	304	605	300	600	300	300	300	300	435

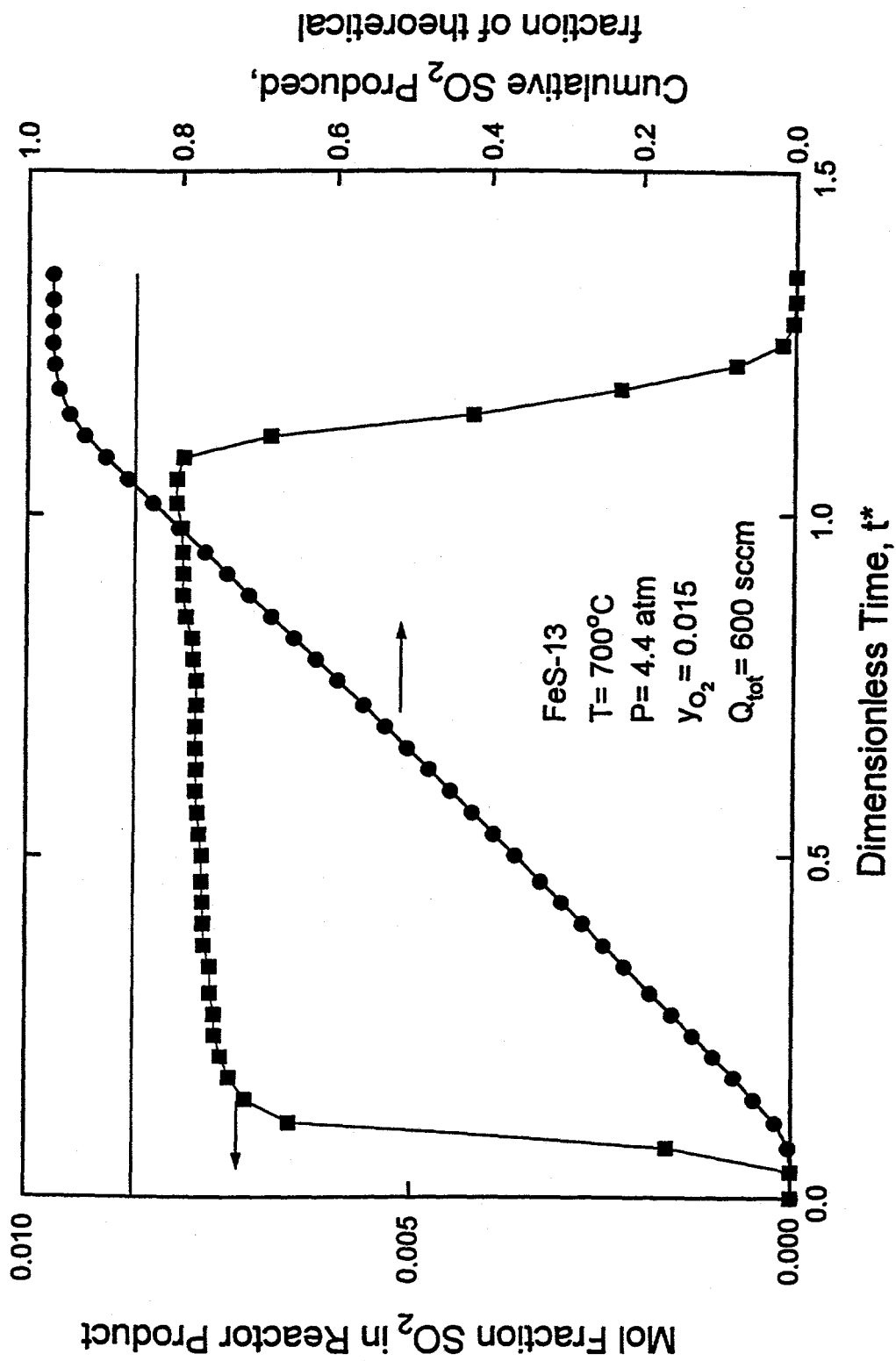


Figure 4. Fixed-Bed Reactor Response: Run FeS-13

the reactor vessel. Improvements in heat tracing and insulation were made prior to steam regeneration test FeS-14.

Results of run FeS-14 in which the regeneration feed gas contained 10% H₂O and balance N₂ are shown in Figure 5. Mol fraction H₂S in the reactor product, as determined by gas chromatography, and cumulative H₂S production, as a fraction of theoretical, are plotted versus dimensionless time. The scatter in successive data points, although still greater than observed with O₂ regeneration, was greatly reduced from previous tests. The H₂S mol fraction gradually increased to about 0.0015 at t* ~ 3.0 and was reasonably constant thereafter until the test was voluntarily terminated at t* = 8.3. The small rate of reaction between FeS and H₂O is emphasized by the fact that the 0.0015 mol fraction H₂S is only about 2% of the stoichiometric maximum of 0.075 mol fraction corresponding to complete conversion of 10% H₂O. In addition, the cumulative H₂S produced was only about 13% of theoretical at t* = 8. These values contrast to O₂ regeneration where the SO₂ mol fraction was quite close to the theoretical maximum and where the cumulative SO₂ produced exceeded 90% of theoretical in much smaller dimensionless reaction times.

Regeneration in O₂/H₂O/N₂

Run FeS-16 was the first in which true partial oxidation conditions involving both O₂ and H₂O in the feed gas were used. Regeneration product gas analysis was based upon both the gas chromatograph and total sulfur analyzer. The results of FeS-16 are shown in Figure 6 where the mol fractions of H₂S, SO₂, and total sulfur are plotted versus elapsed time. Dimensionless time has little meaning in cases where the feed gas contains both O₂ and H₂O.

Raw data from both the chromatograph and total sulfur analyzer are on a dry basis since H₂O is separated from both streams before entering the detectors. The raw data were corrected for the presence of steam and the mol fractions in Figure 6 are on a wet basis. After a delay time of about 10 minutes, H₂S and SO₂ were detected by the chromatograph and sulfur was detected by the total sulfur analyzer. H₂S mol fraction increased to about 0.0011 and remained near that level for about 1.5 hours before beginning a slow decrease to zero after about 2.25 hours. SO₂ mol fraction increased quickly to about 0.006 after 0.25 hours, slowly increased to 0.0077 over the next two hours, and then decreased steadily to zero after about 3.25 hours. The mol fraction of total sulfur was approximately constant at 0.008 between 0.5 and 2.25 hours, and then decreased to near zero after 3.25 hours.

Visual examination of Figure 6 shows that the total sulfur content is approximately equal to the sum of the H₂S and SO₂ contents at all reaction times. This means, of course, that little elemental sulfur was produced during the run. The absence of elemental sulfur and the agreement between the chromatograph and total sulfur analyzer are shown quantitatively in Figure 7 where the cumulative amounts of sulfur compounds, obtained by integrating the concentration-time data, is plotted versus time. The total amount of H₂S produced corresponded to about 9% of the theoretical sulfur while the total SO₂ produced was 77% of theoretical. The

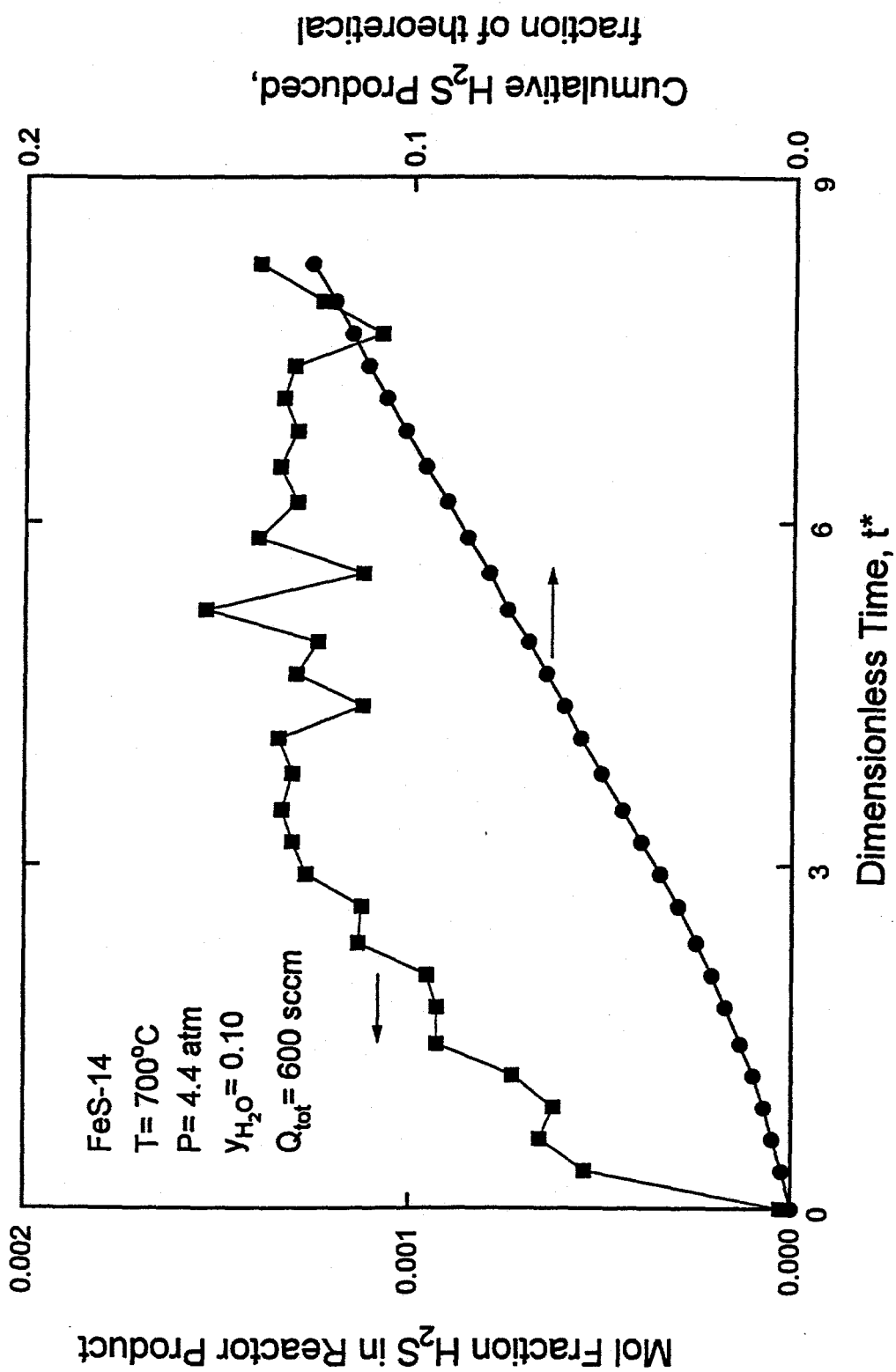


Figure 5. Fixed-Bed Reactor Response: Run FeS-14

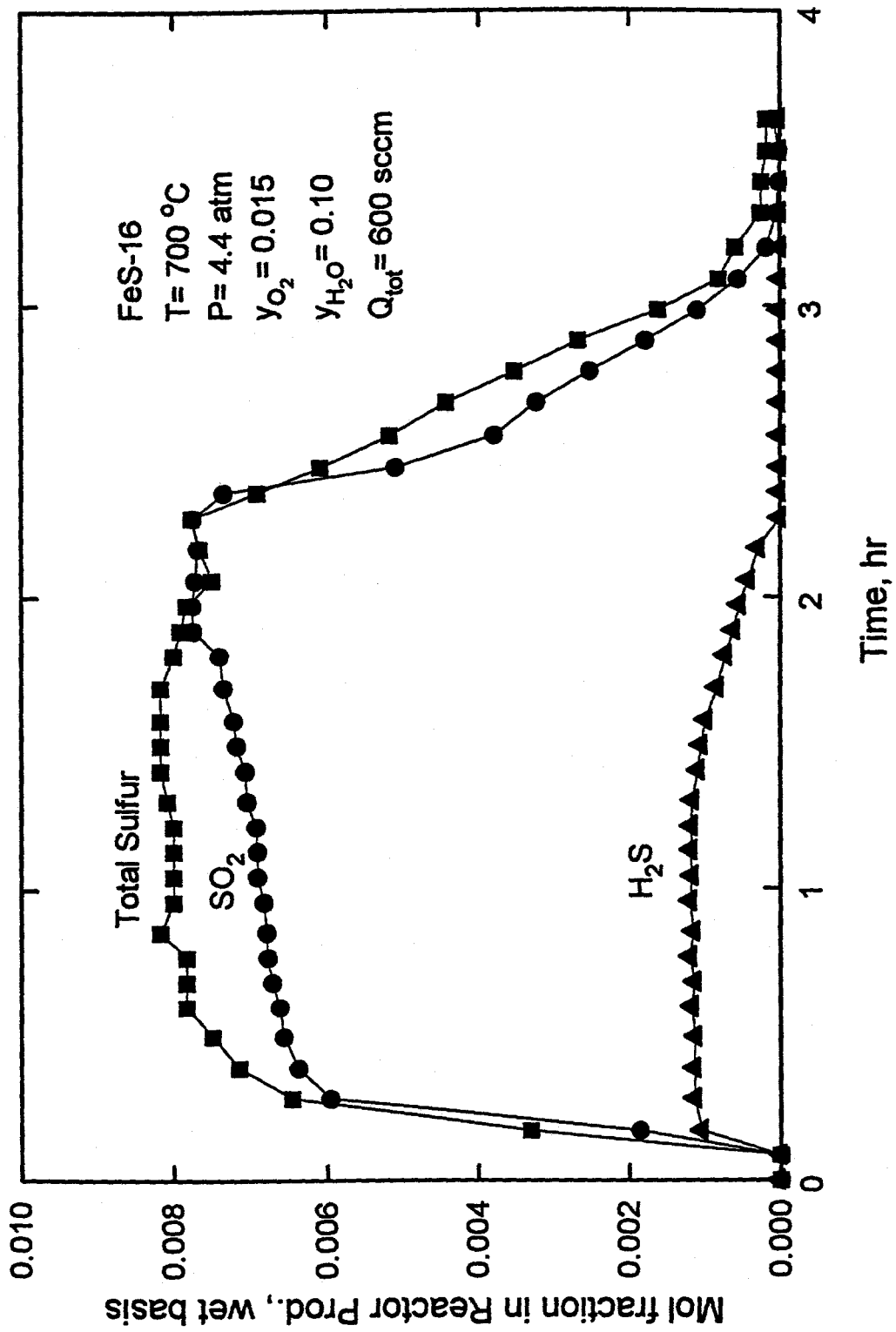


Figure 6. Fixed-Bed Reactor Response: Run FeS-16

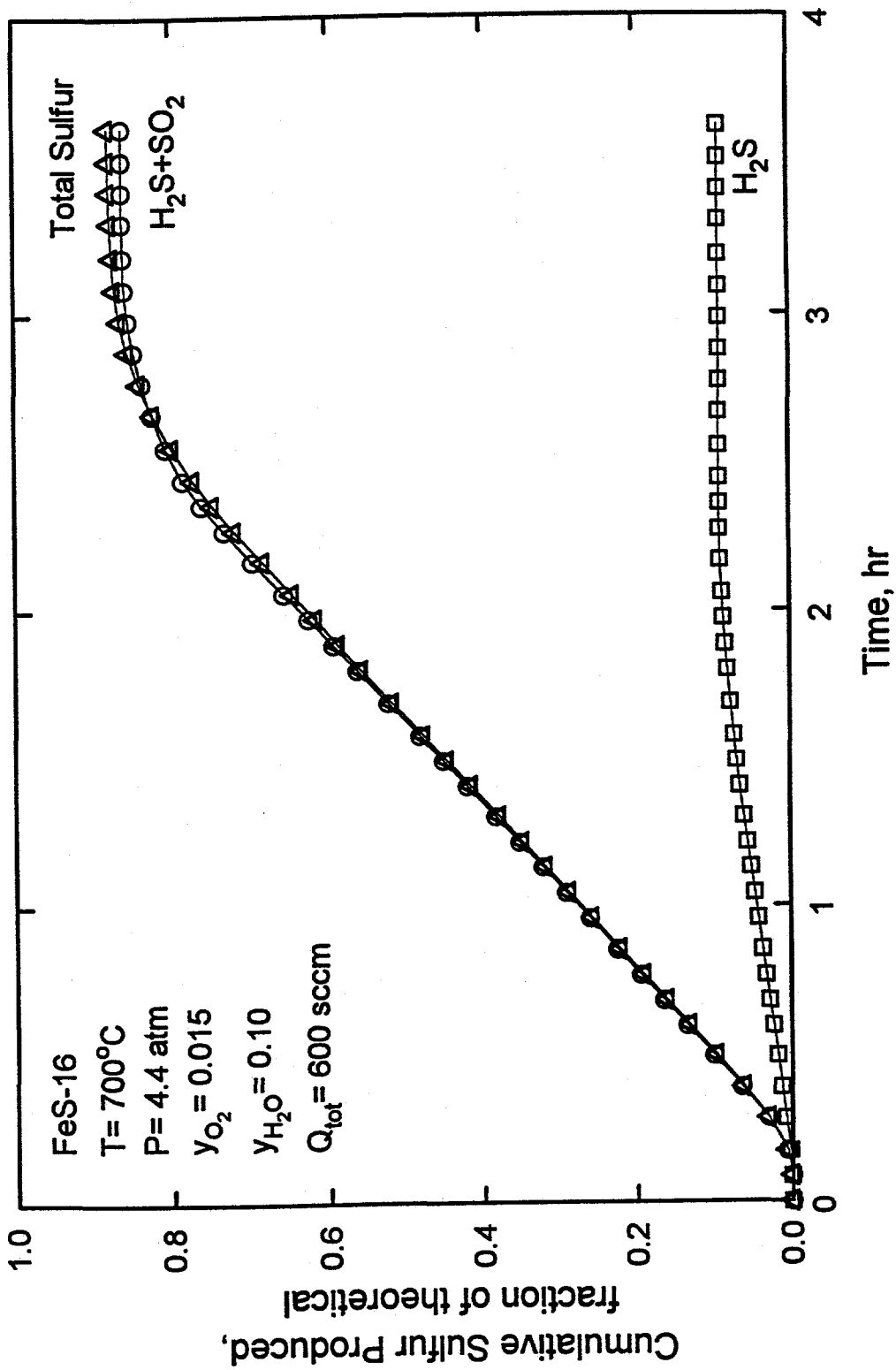


Figure 7. Cumulative Production of Sulfur Compounds: Run FeS-16

sum of these two agrees quite closely with the total sulfur analyzer which accounted for 88% of the total sulfur in the original charge of FeS.

The relatively poor sulfur material balance closure may have been caused by variations in reactor pressure which occurred during the run. The pressure was relatively constant at 4.4 atm for the first 2.25 hours. Pressure then increased to 5.6 atm after 3 hours and decreased to 4.7 atm at the conclusion of the run. The variation in pressure indicates a variation in flow resistance upstream of the back pressure regulator, probably caused by partial plugging of filters or product flow lines. The pressure variation produced a variation in the flow rate of product gas through the total sulfur analyzer. While the calculations of mol fraction total sulfur included an approximate pressure correction, this calculation was subject to error. The gas chromatograph sample is taken downstream of the back pressure regulator, and the analysis is effectively independent of pressure. If we assume that results from the total sulfur analyzer and gas chromatograph are both correct, then only 2% of the sulfur was liberated in elemental form while 12% of the sulfur remained unregenerated in the solid phase. The failure to produce significant quantities of elemental sulfur in this run was not surprising because of the small ratio of H₂O to O₂ in the feed gas. However, since the maximum source of error in the product gas analysis is associated with the total sulfur analyzer, complete or near complete regeneration may have occurred at these conditions. Therefore, if we assume that regeneration was complete and that the H₂S and SO₂ results from the gas chromatograph are correct, we conclude that as much as 14% of the total sulfur was liberated in elemental form.

In run FeS-18, the H₂O to O₂ ratio in the feed gas was increased to 82:1 in an effort to increase the production of elemental sulfur. This large ratio was achieved by reducing the O₂ content of the feed gas to 0.25% and increasing the H₂O content to 20.5%. The initial charge of FeS was also reduced so that complete regeneration could be obtained in a reasonable amount of time. Reaction temperature, pressure, and total gas flow rate were the same as in run FeS-16.

Component mol fraction versus time curves for run FeS-18 are shown in Figure 8 while the cumulative production of sulfur compounds is presented in Figure 9. Both H₂S and total sulfur were detected in the product gas soon after the reaction began while no SO₂ was detected for the first 0.5 hours. The H₂S mol fraction reached a maximum of 0.0014 at about the time that SO₂ first appeared. The H₂S concentration then gradually decreased and approached zero after about 3.5 hours. The SO₂ mol fraction gradually increased to a maximum of 0.0009 after about 3.5 hours and then decreased to zero after 5 hours. The maximum mol fraction of total sulfur of 0.0036 was reached early in the test after which the mol fraction decreased steadily to zero after 5 hours. Visual examination of Figure 8 indicates that the total sulfur content is larger than the sum of the SO₂ and H₂S contents, meaning that significant amounts of elemental sulfur were formed. This is confirmed by the cumulative production curves of Figure 9. The cumulative production of SO₂ during the run was 32% of theoretical while H₂S production was 38% of theoretical. Therefore, on a difference basis assuming complete regeneration, the amount of elemental sulfur formed was 30% of theoretical. However, the amount of total sulfur (from the total sulfur analyzer) was 112% of theoretical, suggesting the possibility of somewhat

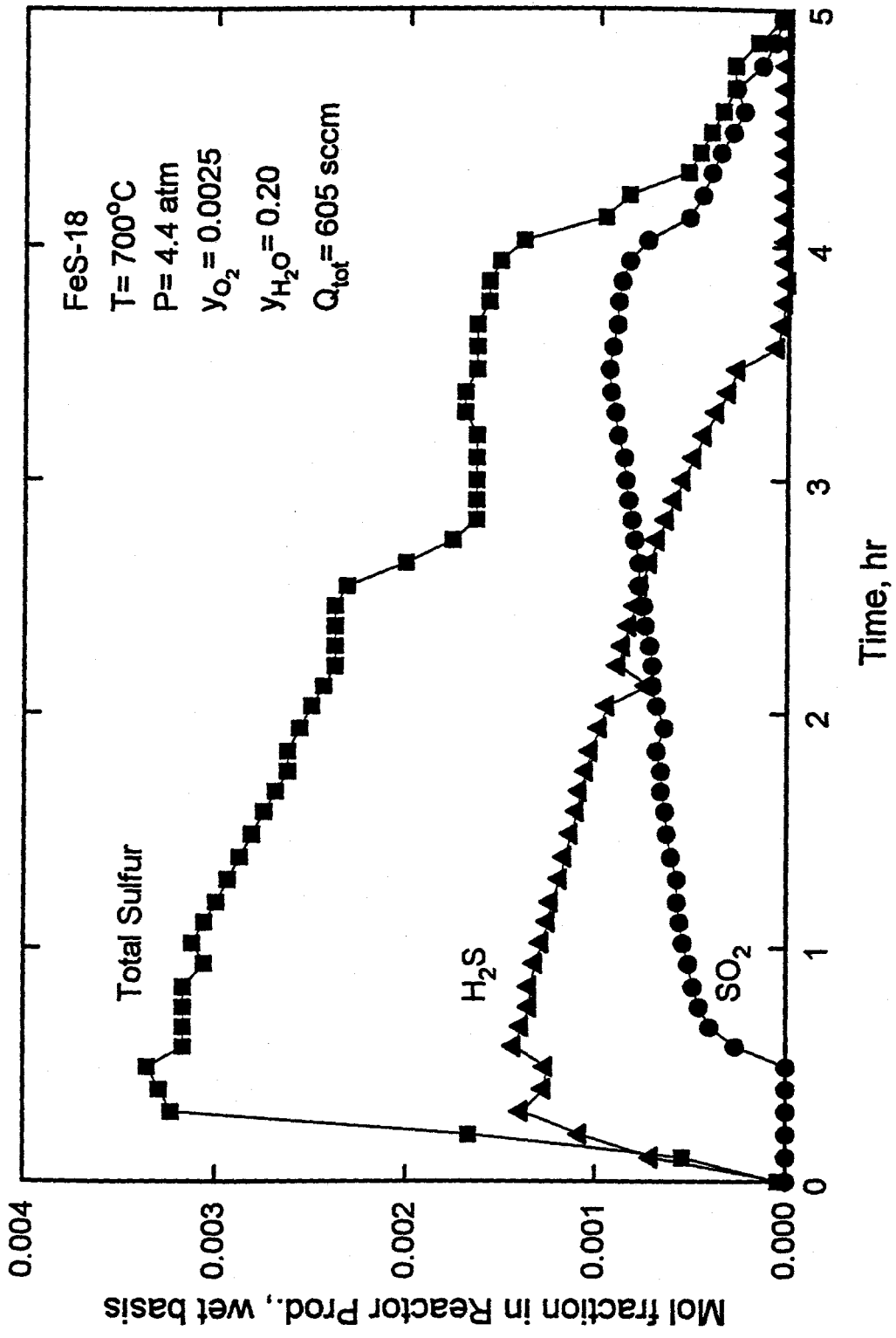


Figure 8. Fixed-Bed Reactor Response: Run FeS-18

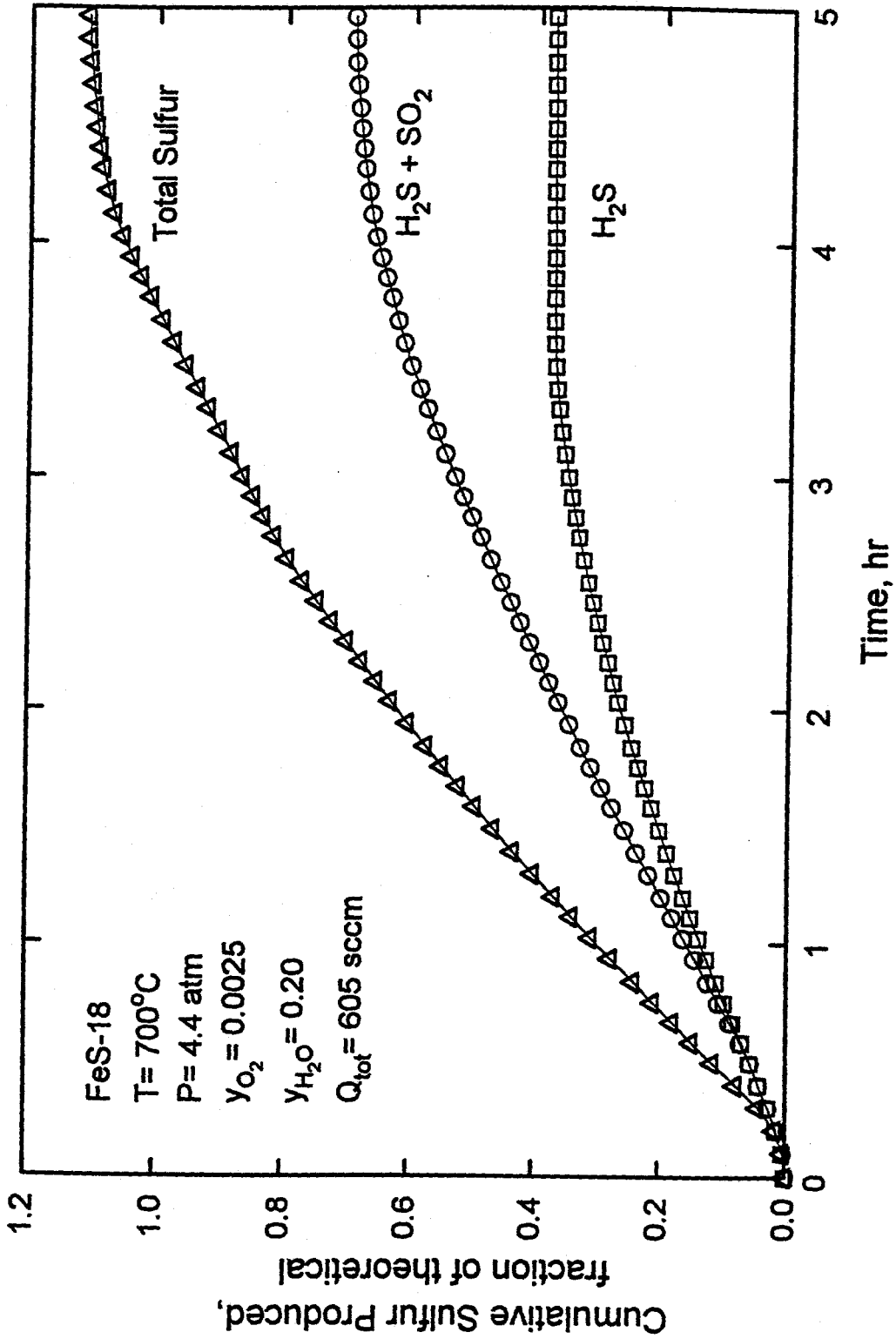


Figure 9. Cumulative Production of Sulfur Compounds: Run FeS-18

larger elemental sulfur yield. This was the first run in which a positive deviation in sulfur material balance closure was obtained.

The effect of residence time was then examined in run FeS-19 by reducing the volumetric flow rate from 600 to 300 sccm. The initial charge of FeS was also reduced so that the run could be completed in reasonable time. Other reaction conditions -- temperature, pressure, and feed gas composition -- were the same in runs FeS-18 and FeS-19. Results from FeS-19 in terms of component mol fraction versus time and cumulative component production versus time are shown in Figures 10 and 11, respectively.

The general characteristics of the component mol fraction curves in Figures 8 and 10 are similar. H_2S and total sulfur mol fractions reached a maximum early in the run and gradually declined thereafter. The SO_2 mol fraction remained at zero during the early stages, then increased gradually and reached a maximum at about the time that the H_2S mol fraction reached zero. The biggest difference is that the total sulfur mol fraction in run FeS-19 (Figure 10) was significantly larger than in run FeS-18 throughout the run.

The component production curves of Figures 9 and 11 are also qualitatively similar. At the conclusion of run FeS-19 (Figure 11), the H_2S and SO_2 productions were 34% and 28% of theoretical, respectively. Compared to run FeS-18 (Figure 9), these values represent a 4 percentage point decrease in both SO_2 and H_2S production. Therefore, by subtraction, the proportion of elemental sulfur increased from 30% in run FeS-18 to 38% in run FeS-19. The major difference between the two runs was volumetric gas feed rate which is inversely proportional to residence time. Since elemental sulfur is presumably formed from the gas phase Claus reaction between H_2S and SO_2 , we believe that the increased residence time is responsible for the increased amount of elemental sulfur in FeS-19. Once again, as shown in Figure 11, there was a positive error in the overall sulfur material balance, as the total amount of gas phase sulfur amounted to 116% of theoretical.

The effect of temperature was then examined in runs FeS-19 (700°C), FeS-22 (600°C), and FeS-24 (550°C). These runs were at constant pressure (4.4 atm), flow rate (300 sccm), and composition (0.25% O_2 and 20% H_2O). Results of FeS-22 are shown in Figures 12, 13, and 14. The component mol fraction versus time curves shown in Figure 12 are qualitatively similar to those in Figures 8 and 10, and the component production curves of Figure 13 are similar to those in Figures 9 and 11. The most important difference is that almost perfect sulfur material balance closure was obtained in this run as the quantity of sulfur measured by the total sulfur analyzer was 99% of the theoretical value. 21% of the total sulfur was liberated as H_2S and 25% as SO_2 , leaving about 54% of the total sulfur liberated in elemental form.

The excellent overall material balance achieved with run FeS-22 permitted the selectivity to elemental sulfur to be calculated as a function of time with results shown in Figure 14. There is considerable scatter in the data, particularly at the beginning and end of the run when reaction rates were quite small. However, there is a clear trend in the data throughout most of the run. The selectivity decreased from approximately 80% after 1 hour to 20% after 7 hours in an

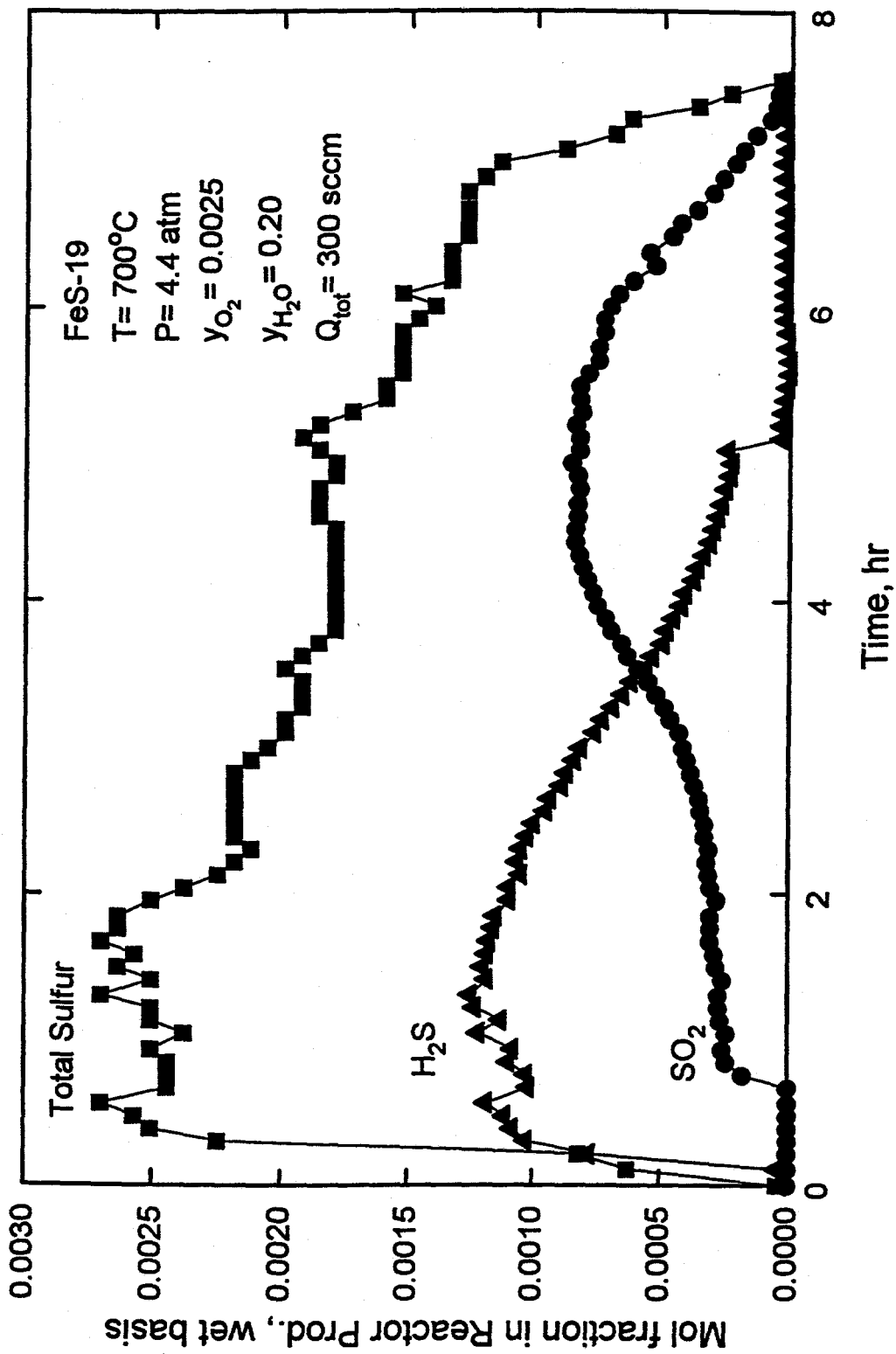


Figure 10. Fixed-Bed Reactor Response: Run FeS-19

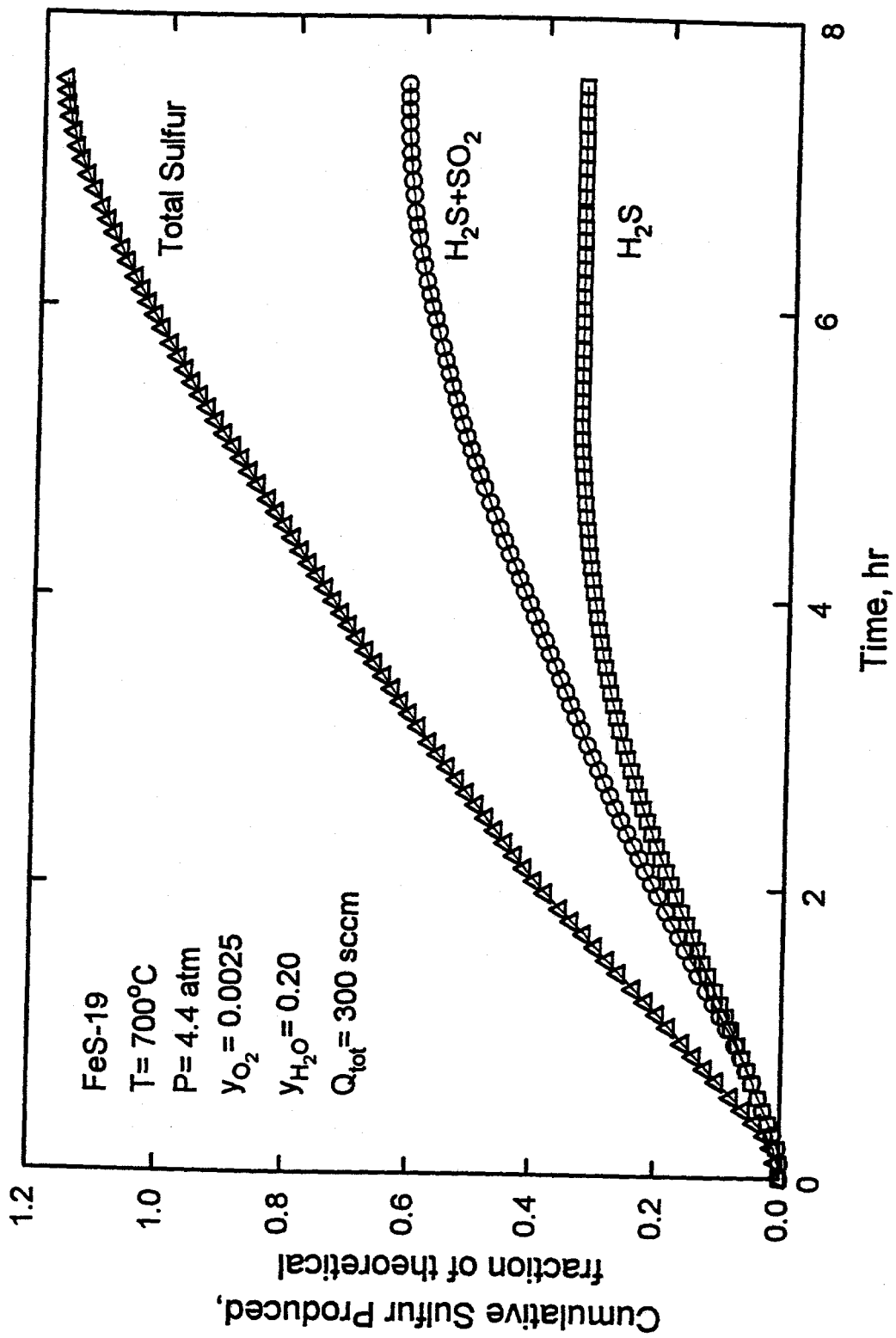


Figure 11. Cumulative Production of Sulfur Compounds: Run FeS-19

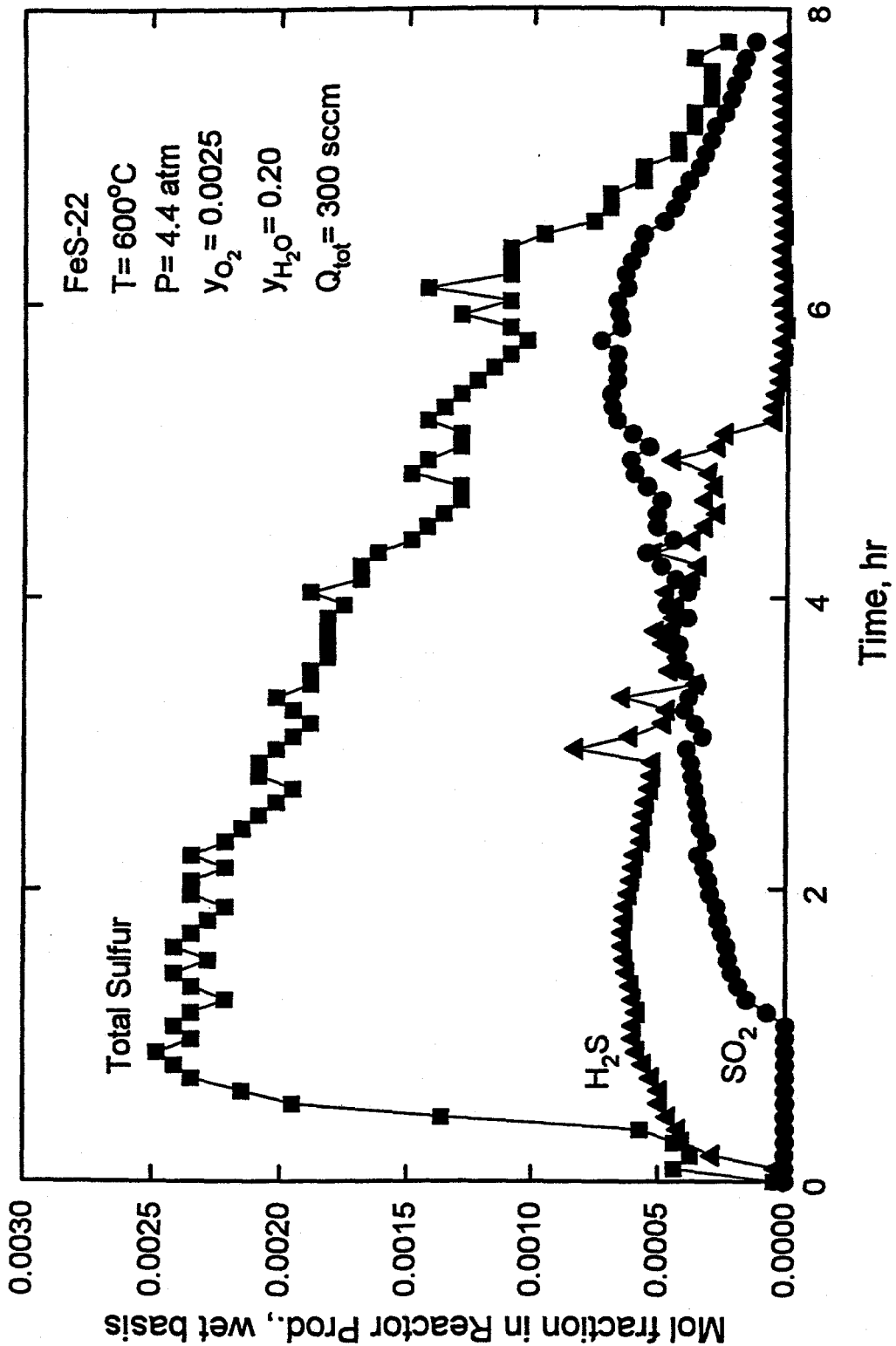


Figure 12. Fixed-Bed Reactor Response: Run FeS-22

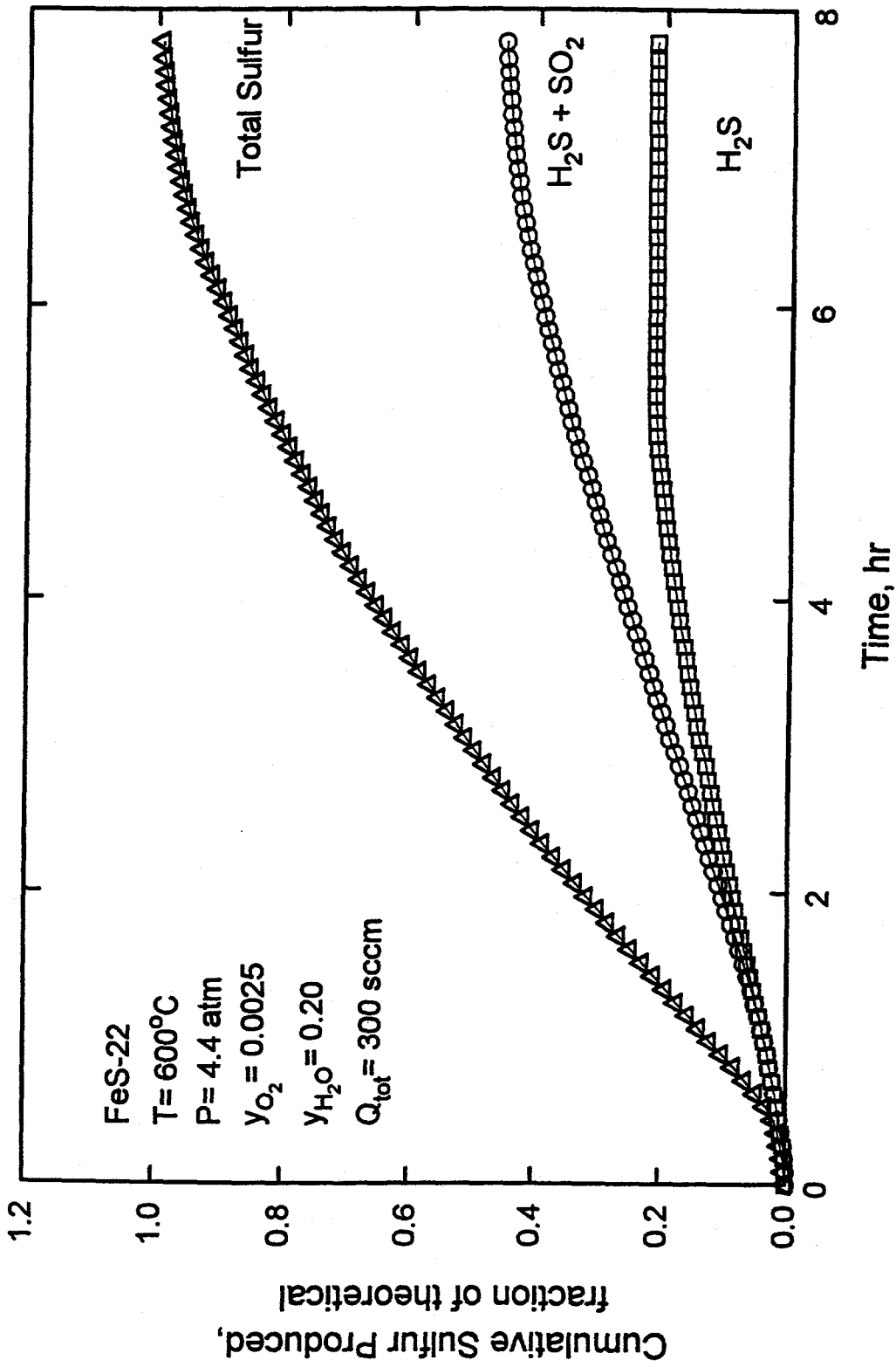


Figure 13. Cumulative Production of Sulfur Compounds: Run FeS-22

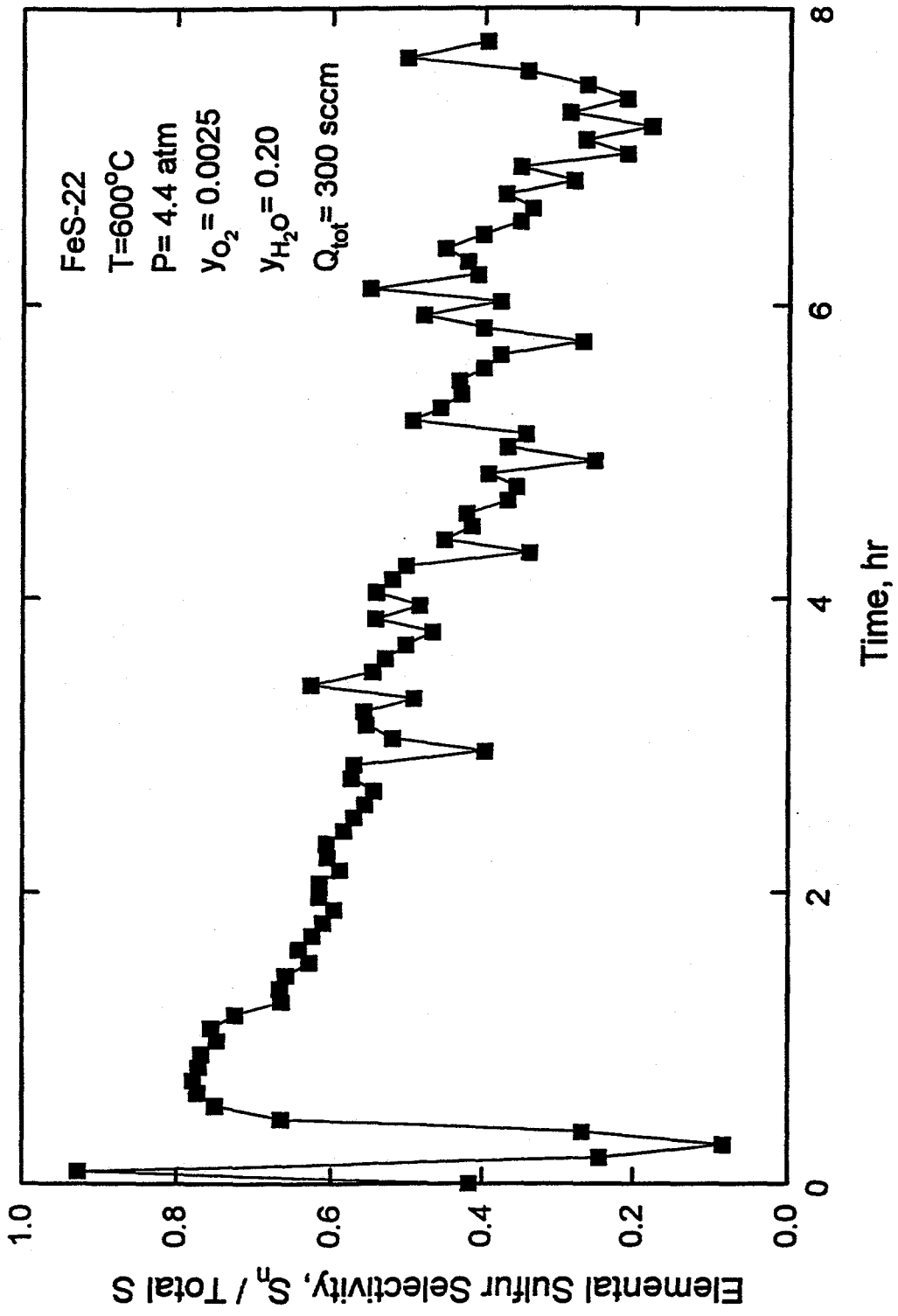


Figure 14. Instantaneous Selectivity to Elemental Sulfur: Run FeS-22

almost linear fashion. The overall (time average) selectivity was, as previously stated, about 54%.

The temperature was further reduced to 550°C in run FeS-24, and results are shown in Figures 15 and 16. Component mol fraction versus time curves (Figure 15) are similar to those from previous runs except that less H₂S was formed and there was considerable scatter in H₂S results in the vicinity of 1 hour. SO₂ mol fraction remained near zero for about 1½ hours, and the maximum was less than observed in tests at higher temperature. Similarly, the maximum in the total sulfur mol fraction was lower than in higher temperature tests. Figure 16 shows that the cumulative quantity of H₂S produced was only 4% of theoretical while the amount of SO₂ was 17% of theoretical, and the total amount of sulfur liberated was only 80% of theoretical. Failure to achieve complete regeneration in this test may be due to the fact that as the temperature is lowered, there is an increasing tendency for Fe₂(SO₃)₄ to be formed.

Runs FeS-21 and FeS-22 were at the same reaction conditions except for a 19% reduction in the mass of FeS in the reactor charge in FeS-22. The difference in FeS mass should change the time at which various events should occur but should have little effect on maximum component mol fractions and selectivity. These parameters were reasonably reproducible as indicated in Table 4.

In runs FeS-23 and FeS-25, the composition of the feed gas was altered to evaluate the effects of doubling both the O₂ and H₂O gas concentrations in FeS-23 and increasing the steam-to-oxygen ratio in FeS-25. Total sulfur mol fraction readings versus time were extremely erratic during both tests, perhaps due to uneven steam flow caused by periodic condensation and/or by the fact that the capacity of the membrane dryer on the total sulfur analyzer was exceeded at the high steam levels. However, smoothing of the total sulfur mol fraction versus time data produced believable results as illustrated for run FeS-25 in Figures 17 and 18. The key result from Figure 17 is the significantly higher mol fraction of total sulfur during the early stages of the test. The maximum mol fraction of total sulfur increased from 0.0025 in run FeS-22 (Fig. 12) to about 0.009 in run FeS-25 (Fig. 17). Otherwise, the results were similar except that the total run time was shorter due to the increased H₂O concentration and the decreased initial amount of FeS. Elemental sulfur production also increased to about 75% of theoretical in FeS-25 (Fig. 18) as the sum of the H₂S and SO₂ productions amounted to only 25% of theoretical.

PROCESS MODELING

The process modeling effort began during the quarter. A two-stage process for the desulfurization of coal gas using CeO₂ for primary desulfurization and a zinc-based sorbent for secondary desulfurization is shown in Figure 19. Regeneration of Ce₂O₂S is accomplished by reaction with steam to liberate H₂S followed by conversion of H₂S to elemental sulfur using a Claus process. Regeneration of the zinc-based sorbent is accomplished in the traditional manner using dilute oxygen and the resultant SO₂ is to be recycled back to the gasifier.

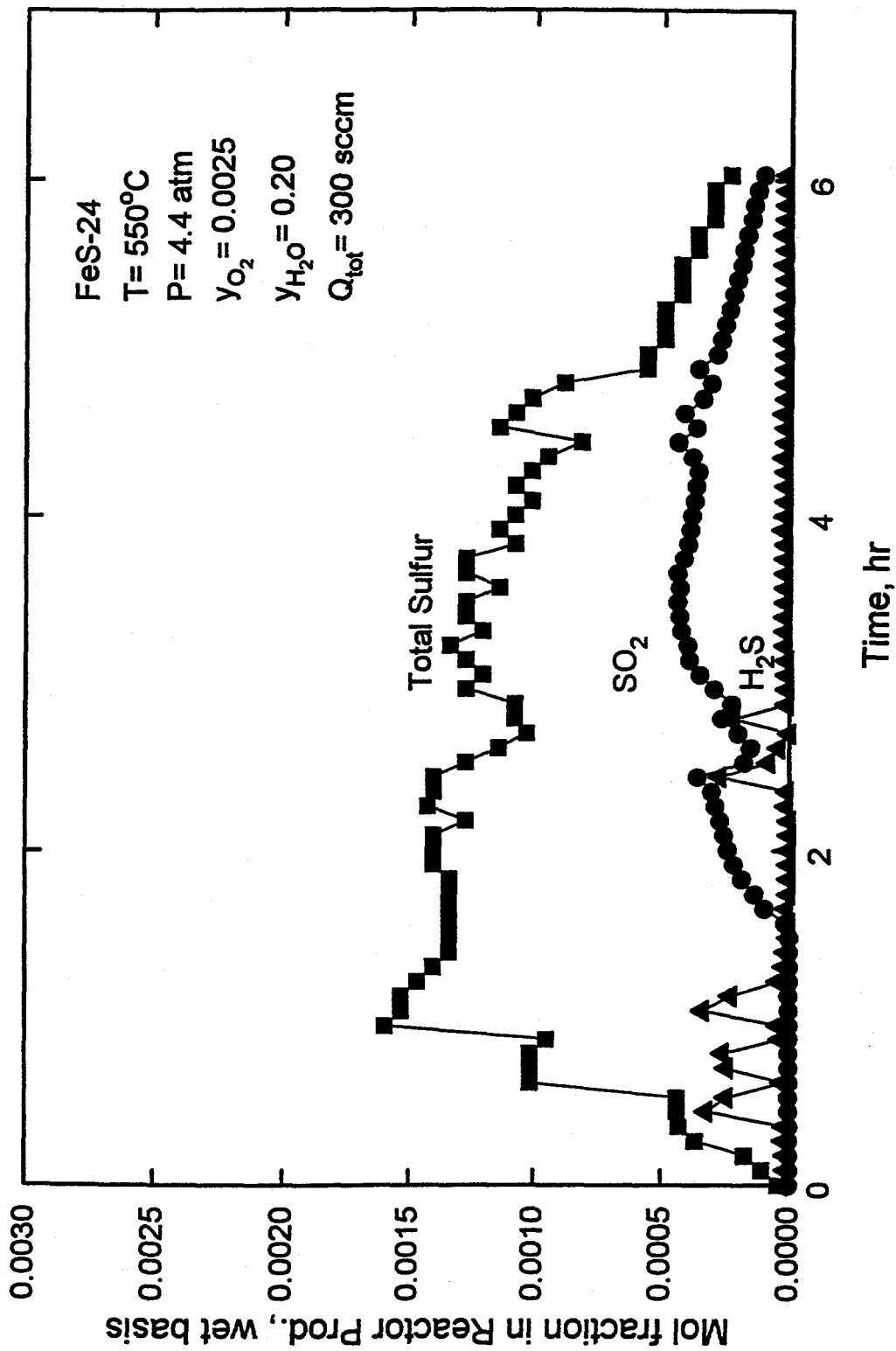


Figure 15. Fixed-Bed Reactor Response: Run FeS-24

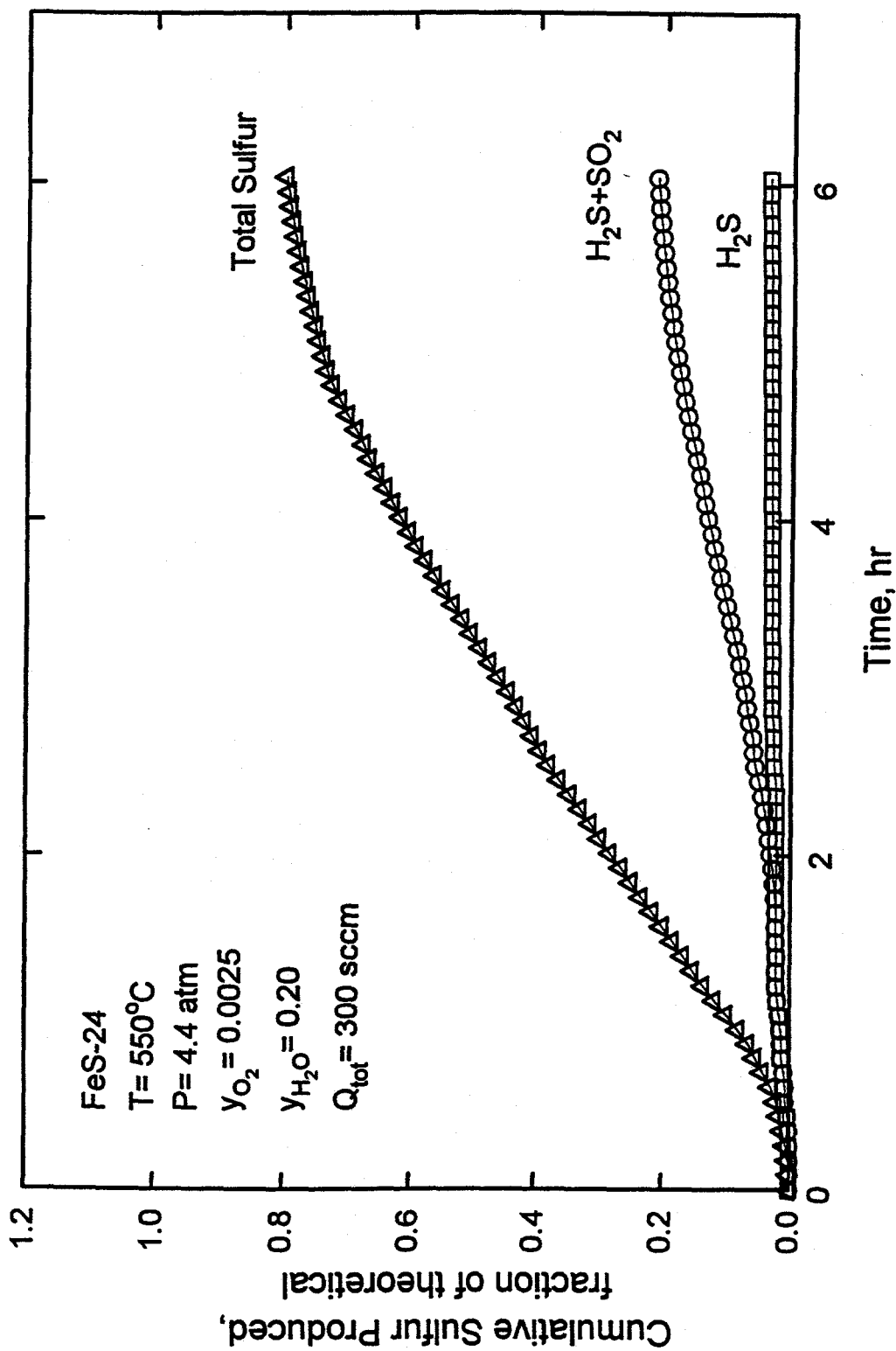


Figure 16. Cumulative Production of Sulfur Compounds: Run FeS-24

Table 4. Comparison of Duplicate FeS Regeneration Experiments
600°, 4.4 atm, 0.25% O₂, 20.0% H₂O, 79.75% N₂, 300 sccm

Run	FeS-21	FeS-22
Maximum H ₂ S mole fraction	0.00065	0.00063
Maximum SO ₂ mole fraction	0.00085	0.00087
Selectivity to elemental sulfur	0.50	0.54

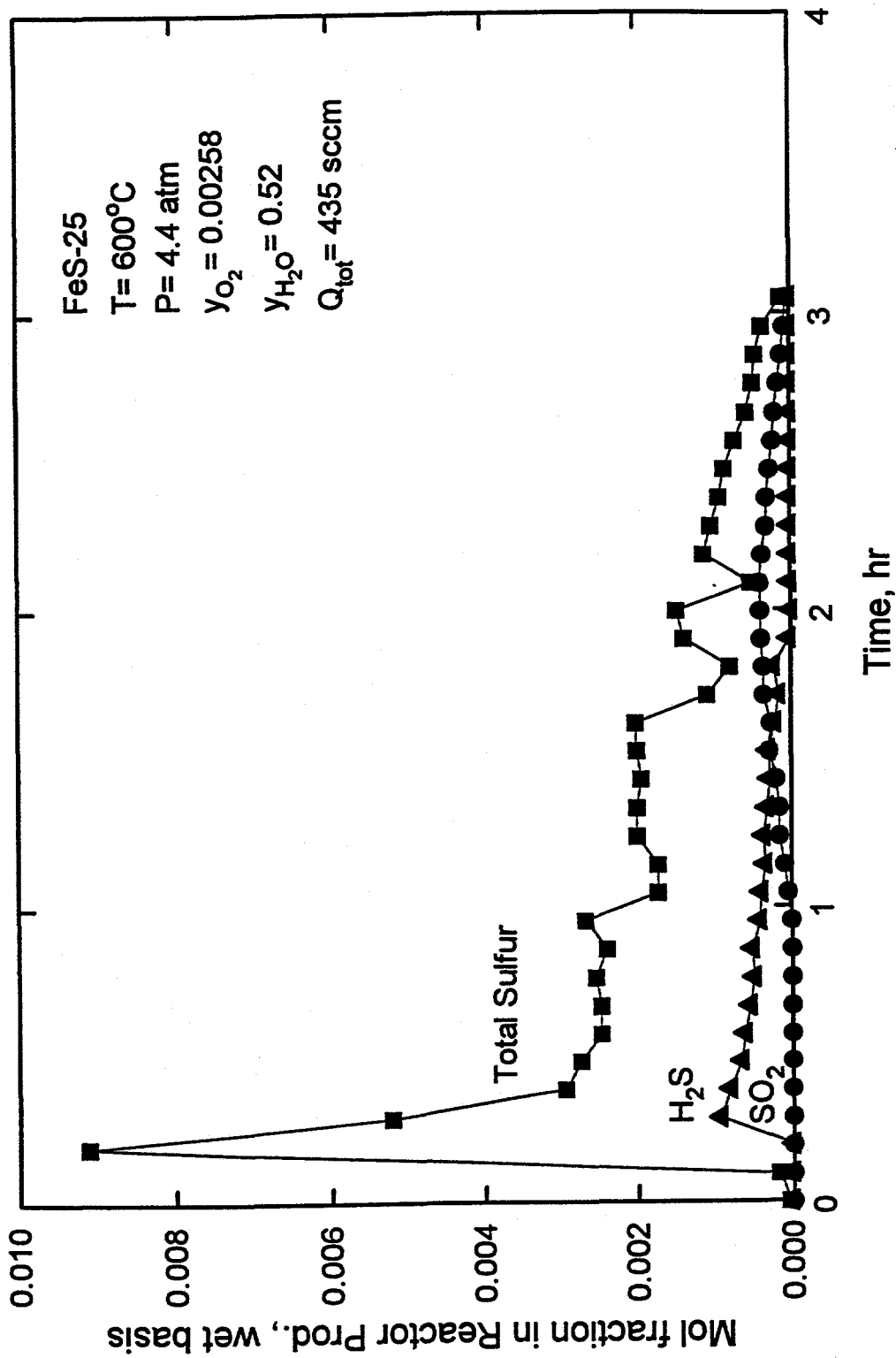


Figure 17. Fixed-Bed Reactor Response: Run FeS-25

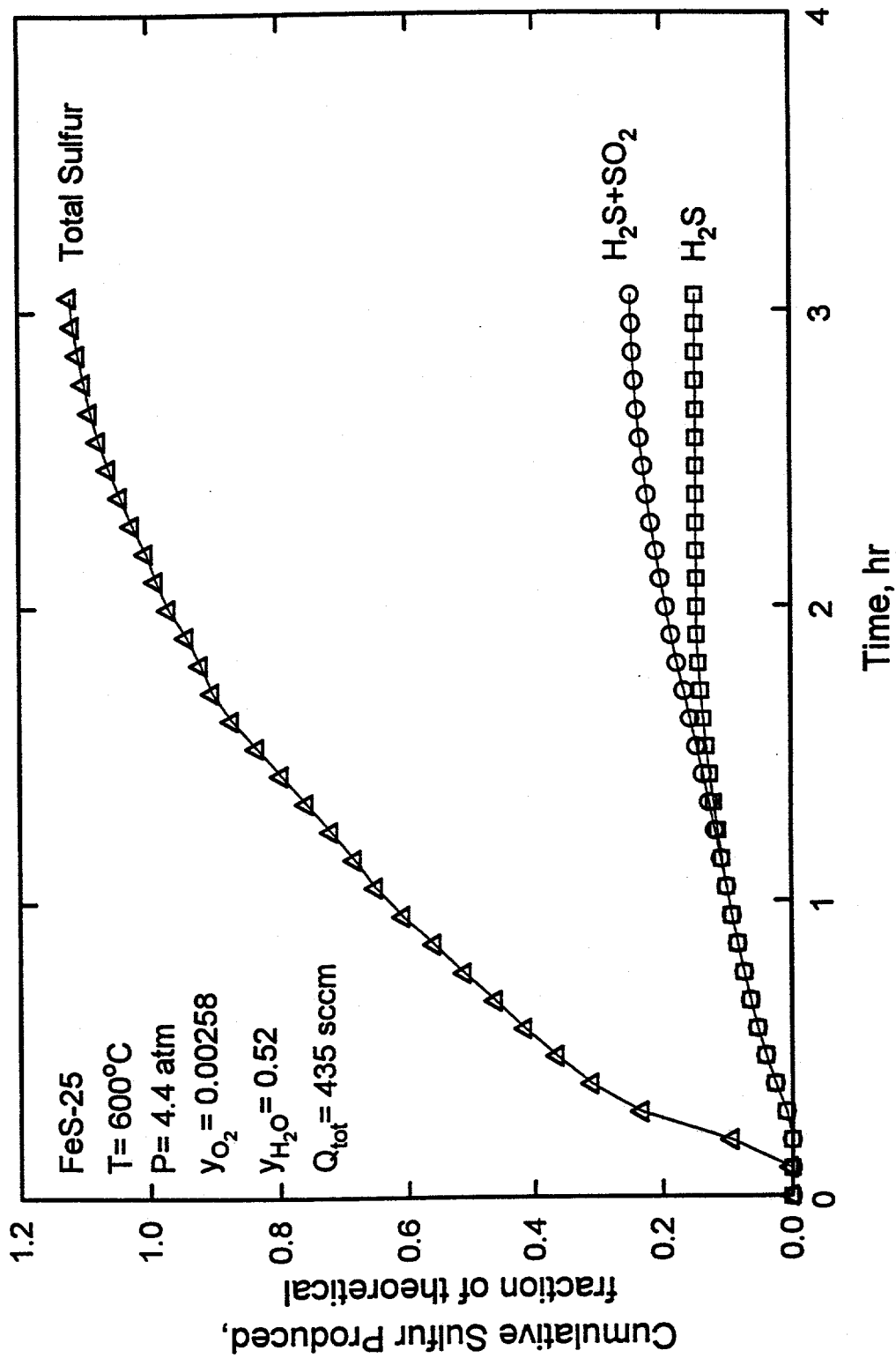


Figure 18. Cumulative Production of Sulfur Compounds: Run FeS-25

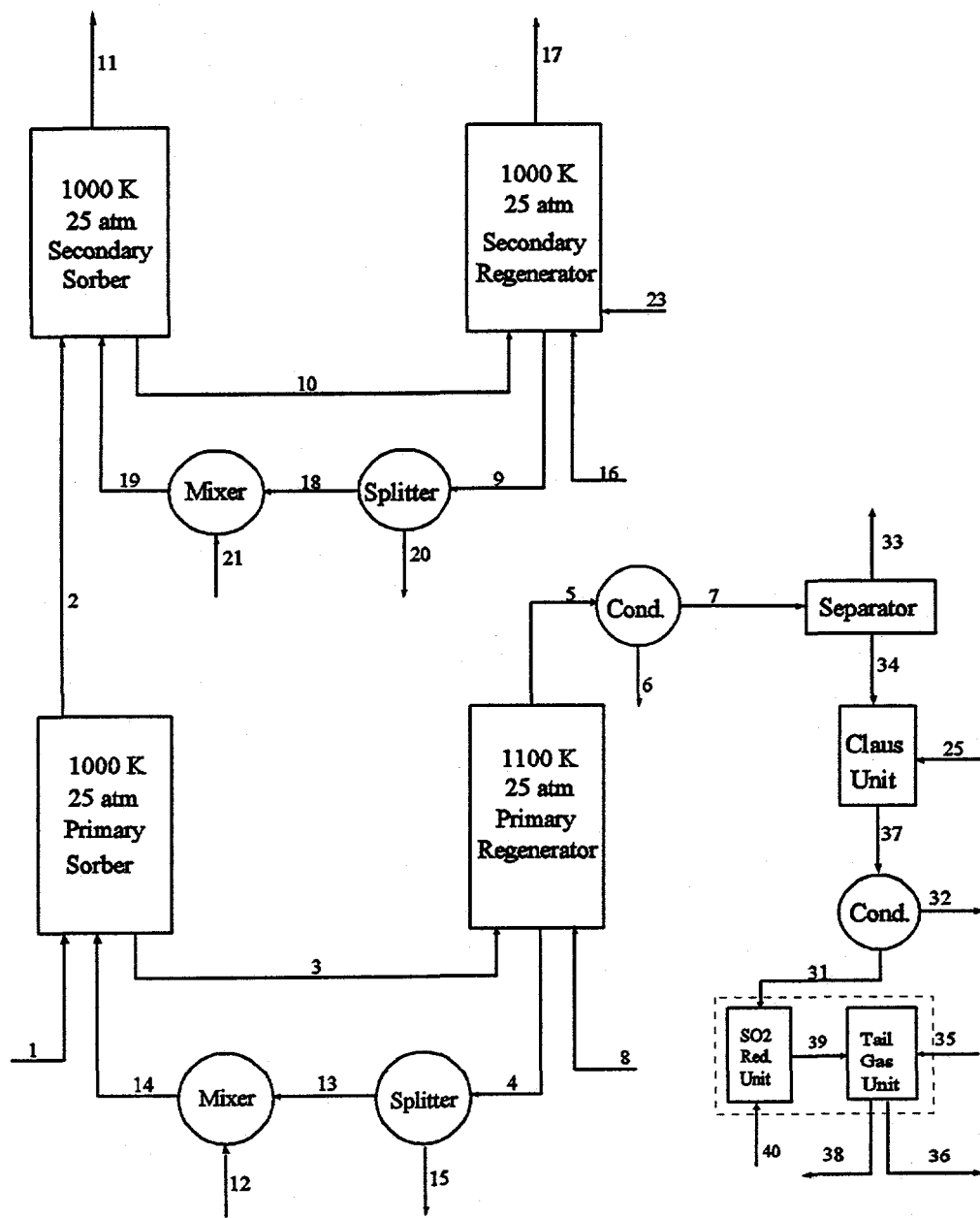


Figure 19. Flow Diagram of the Two-Stage Process for Coal Gas Desulfurization Using CeO_2

Table 6 identifies each stream in terms of the stream numbers from Figure 19. The software package PRO-II was used in conjunction with CHEMQ thermodynamic equilibrium calculations to complete the base-case material balance for the process which is presented in Table 7.

9395 lb mol/hr of raw coal gas (stream 1) at 1000K and 25 atm are fed to the primary desulfurization unit. The gas contains 100 lb mol/hr of H_2S (1.06% by volume and the composition is representative of a Shell gas). Primary desulfurization occurs at 1000K and 25 atm using CeO_2 sorbent. The composition of the partially desulfurized product gas (stream 2) is adjusted to thermodynamic equilibrium at 1000K and 25 atm. 94.7% desulfurization is achieved in the primary sorber using 400 lb mol/hr of CeO_2 sorbent (stream 14). 47% conversion of CeO_2 to Ce_2O_2S is achieved under these conditions.

The partially desulfurized coal gas (stream 2) enters the secondary sorber where final desulfurization is achieved using Zn_2TiO_4 sorbent at 1000K and 25 atm. The desulfurized coal gas (stream 11) contains approximately 23 ppmv H_2S . The flow rate of Zn_2TiO_4 to the secondary sorber (stream 19) is 5.3 lb mol/hr and 65% of the zinc in Zn_2TiO_4 is converted to ZnS in the secondary sorber (stream 10).

Regeneration of the primary sorbent (stream 3) is accomplished by reaction with steam (stream 8) at 1100K and 25 atm to produce gaseous product (stream 5) containing excess steam, H_2S and H_2 . H_2S and H_2 are produced in equal molar quantities in the steam regeneration of Ce_2O_2S . The flow rate of steam (stream 8) is equal to the thermodynamic quantity required to achieve complete conversion of Ce_2O_2S at the reaction conditions (6.3 mol steam per mol of Ce_2O_2S). Regenerated CeO_2 (stream 4) is recycled to the primary sorber with 1% (4 lb mol/hr) of the sorbent circulation rate discharged (stream 15) and replaced by an equal quantity of fresh sorbent (stream 12).

Zinc-based sorbent from the secondary sorber (stream 10) enters the secondary regenerator, and regeneration occurs using 3% O_2 in steam (streams 16 and 23) to liberate SO_2 and reform Zn_2TiO_4 . Discharge and make-up (streams 20 and 21) of the zinc titanate sorbent is also set at 1% of the circulation rate of 5.3 lb mol/hr. Off-gas from the secondary regenerator (stream 17), which contains 1.7% SO_2 , 0.4% O_2 , and 97.9% H_2O , will be recycled to the gasifier.

Off-gas from the primary regenerator (stream 5) contains 15.8% H_2S , 15.8% H_2 and balance excess steam. This stream flows through a condenser where the temperature is reduced to 80°C and the majority of the steam is condensed leaving a gas product (stream 7) containing 50% H_2 , 48.1% H_2S and 1.9% steam. Hydrogen separation is achieved using pressure swing adsorption to produce a pure H_2 product (stream 33) and a concentrated H_2S stream (stream 34) for feed to a Claus process. The Claus process coupled with the tail gas unit provides about 99.8% recovery of the sulfur in stream 34.

Table 6. Description of the Streams Associated With the Two-Stage Desulfurization Process of Figure 11

1. Coal Gas
2. Partially Desulfurized Coal Gas
3. Sulfided Sorbent from Primary Sorber
4. Sorbent from Primary Regenerator
5. Product Gas from Primary Regenerator
6. Condensed Water
7. Feed to Hydrogen Separator
8. Steam to Primary Regenerator
9. Sorbent from Secondary Regenerator
10. Sulfided Sorbent from Secondary Sorber
11. Desulfurized Coal Gas
12. Primary Sorbent Makeup
13. Recycled Regenerated Primary Sorbent
14. Sorbent Feed to Primary Sorber
15. Spent Primary Sorbent Discharge
16. Steam to Secondary Regenerator
17. Secondary Regeneration Outlet Gas (recycle to gasifier)
18. Recycled Regenerated Secondary Sorbent
19. Sorbent Feed to Secondary Sorber
20. Spent Secondary Sorbent Discharge
21. Secondary Sorbent Makeup
22. Air to Secondary Regenerator
25. Air to Claus Unit
31. Claus Tail Gas
32. Sulfur Condensate From Claus Unit
33. High Pressure Hydrogen
34. Claus Reactor Feed
35. Regenerated Solvent to Tail Gas Unit
36. Tail Gas Discharge
37. Off Gases from Claus Unit
38. Spent Solvent From Tail Gas Unit
39. Hydrogen Feed to SO₂ Reduction Unit
40. Reduced Tail Gas

Table 7. Material Balance for Cerium
Oxide Sorber with Steam Regeneration

SIMULATION SCIENCES INC.
PROJECT ce
PROBLEM general

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OUTPUT
STREAM MOLAR COMPONENT RATES

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=====
STREAM ID          1          2          3          4
NAME
PHASE              VAPOR        VAPOR        SOLID        SOLID

FLUID RATES, LB-MOL/HR
 1 O2              0.0000      0.0000      0.0000      0.0000
 2 S               0.0000      0.0000      0.0000      0.0000
 3 SO2            0.0000      0.0000      0.0000      0.0000
 4 H2O           499.9999     288.8800     0.0000      0.0000
 5 H2            2850.0000     634.9002     0.0000      0.0000
 6 H2S           100.0000       5.3000      0.0000      0.0000
 7 CO            5889.9995     2968.5596     0.0000      0.0000
10 CH4            0.0000      1260.4598     0.0000      0.0000
11 CO2            22.0000     1682.9800     0.0000      0.0000
12 NH3            0.0000       0.0000      0.0000      0.0000
13 N2             33.0000      33.0000      0.0000      0.0000
17 MEA            0.0000       0.0000      0.0000      0.0000
TOTAL FLUID, LB-MOL/HR  9395.0000   6874.0796     0.0000      0.0000

MW SOLID RATES, LB-MOL/HR
 8 ceo2           0.0000      0.0000      210.6000     400.0000
 9 ce2o2s        0.0000      0.0000      94.7000       0.0000
14 zn2tio4       0.0000      0.0000      0.0000       0.0000
15 zns           0.0000      0.0000      0.0000       0.0000
16 TIO2          0.0000      0.0000      0.0000       0.0000
TOTAL MW SOLID, LB-MOL/HR  0.0000      0.0000     305.3000     400.0000

TOTAL RATE, LB-MOL/HR  9395.0000   6874.0796     305.3000     400.0000

TEMPERATURE, C      726.8500     726.8500     726.8500     826.8500
PRESSURE, ATM       25.0000     25.0000     25.0000     25.0000
ENTHALPY, MM BTU/HR  84.0636     92.3108    -158.0342    -177.0747
MOLECULAR WEIGHT    19.6954     26.9172     225.3521     172.0000
MOLE FRAC VAPOR     1.0000      1.0000      0.0000      0.0000
MOLE FRAC LIQUID    0.0000      0.0000      0.0000      0.0000
MOLE FRAC MW SOLID  0.0000      0.0000      1.0000      1.0000
WEIGHT FRAC MW SOLID 0.0000      0.0000      1.0000      1.0000
    
```

Table 7. Material Balance for Cerium
Oxide Sorber with Steam Regeneration

SIMULATION SCIENCES INC.

PROJECT ce
PROBLEM general

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STREAM MOLAR COMPONENT RATES

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STREAM ID          5          6          7          8
NAME
PHASE             VAPOR      LIQUID      VAPOR      LIQUID
FLUID RATES, LB-MOL/HR
1  O2              0.0000      0.0000      0.0000      0.0000
2  S                0.0000      0.0000      0.0000      0.0000
3  SO2              0.0000      0.0000      0.0000      0.0000
4  H2O              410.6000    407.0828    3.5172      600.0000
5  H2                94.7000      0.0770     94.6230      0.0000
6  H2S              94.7000      3.7788     90.9212      0.0000
7  CO                0.0000      0.0000      0.0000      0.0000
10 CH4              0.0000      0.0000      0.0000      0.0000
11 CO2              0.0000      0.0000      0.0000      0.0000
12 NH3              0.0000      0.0000      0.0000      0.0000
13 N2                0.0000      0.0000      0.0000      0.0000
17 MEA              0.0000      0.0000      0.0000      0.0000
TOTAL FLUID, LB-MOL/HR      600.0001    410.9385    189.0615    600.0000

MW SOLID RATES, LB-MOL/HR
8  ceo2             0.0000      0.0000      0.0000      0.0000
9  ce2o2s           0.0000      0.0000      0.0000      0.0000
14 zn2tio4          0.0000      0.0000      0.0000      0.0000
15 zns               0.0000      0.0000      0.0000      0.0000
16 TIO2             0.0000      0.0000      0.0000      0.0000
TOTAL MW SOLID, LB-MOL/HR      0.0000      0.0000      0.0000      0.0000

TOTAL RATE, LB-MOL/HR      600.0001    410.9385    189.0615    600.0000

TEMPERATURE, C      826.8500     79.8500     79.8500     228.8500
PRESSURE, ATM       25.0000     24.7500     24.7500     27.3000
ENTHALPY, MM BTU/HR  16.1970     1.0636     0.7087     4.5772
MOLECULAR WEIGHT     18.0253     18.1597     17.7330     18.0150
MOLE FRAC VAPOR     1.0000      0.0000      1.0000      0.0000
MOLE FRAC LIQUID    0.0000      1.0000      0.0000      1.0000
MOLE FRAC MW SOLID  0.0000      0.0000      0.0000      0.0000
WEIGHT FRAC MW SOLID 0.0000      0.0000      0.0000      0.0000
    
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Table 7. Material Balance for Cerium
Oxide Sorber with Steam Regeneration

SIMULATION SCIENCES INC.

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STREAM MOLAR COMPONENT RATES

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STREAM ID          9          10          11          12
NAME
PHASE             SOLID         SOLID         VAPOR         SOLID

FLUID RATES, LB-MOL/HR
 1 O2              0.0000        0.0000        0.0000        0.0000
 2 S                0.0000        0.0000        0.0000        0.0000
 3 SO2             0.0000        0.0000        0.0000        0.0000
 4 H2O             0.0000        0.0000        294.0210       0.0000
 5 H2              0.0000        0.0000        634.9001       0.0000
 6 H2S             0.0000        0.0000         0.1590        0.0000
 7 CO              0.0000        0.0000       2968.5596      0.0000
10 CH4            0.0000        0.0000       1260.4598      0.0000
11 CO2            0.0000        0.0000       1682.9800      0.0000
12 NH3            0.0000        0.0000         0.0000        0.0000
13 N2             0.0000        0.0000        33.0000        0.0000
17 MEA            0.0000        0.0000         0.0000        0.0000
TOTAL FLUID, LB-MOL/HR
                    0.0000        0.0000       6874.0796      0.0000

MW SOLID RATES, LB-MOL/HR
 8 ceo2            0.0000        0.0000         0.0000         4.0000
 9 ce2o2s          0.0000        0.0000         0.0000         0.0000
14 zn2tio4         5.3000        2.7295         0.0000         0.0000
15 zns             0.0000        5.1410         0.0000         0.0000
16 TIO2            0.0000        2.5705         0.0000         0.0000
TOTAL MW SOLID, LB-MOL/HR
                    5.3000       10.4410         0.0000         4.0000

TOTAL RATE, LB-MOL/HR
                    5.3000       10.4410       6874.0796         4.0000

TEMPERATURE, C    726.8500     726.8500     726.8500     826.8500
PRESSURE, ATM     25.0000     25.0000     25.0000     25.0000
ENTHALPY, MM BTU/HR
-3.4822          -2.9267         92.3677        -1.7707
MOLECULAR WEIGHT  242.0000     130.6910     26.9052     172.0000
MOLE FRAC VAPOR  0.0000       0.0000       1.0000       0.0000
MOLE FRAC LIQUID 0.0000       0.0000       0.0000       0.0000
MOLE FRAC MW SOLID
1.0000          1.0000          0.0000         1.0000
WEIGHT FRAC MW SOLID
1.0000          1.0000          0.0000         1.0000
    
```


Table 7. Material Balance for Cerium
Oxide Sorber with Steam Regeneration

SIMULATION SCIENCES INC.

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R

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OUTPUT

STREAM MOLAR COMPONENT RATES

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STREAM ID	13	14	15	16
NAME				
PHASE	SOLID	SOLID	SOLID	LIQUID
FLUID RATES, LB-MOL/HR				
1 O2	0.0000	0.0000	0.0000	0.0000
2 S	0.0000	0.0000	0.0000	0.0000
3 SO2	0.0000	0.0000	0.0000	0.0000
4 H2O	0.0000	0.0000	0.0000	291.0000
5 H2	0.0000	0.0000	0.0000	0.0000
6 H2S	0.0000	0.0000	0.0000	0.0000
7 CO	0.0000	0.0000	0.0000	0.0000
10 CH4	0.0000	0.0000	0.0000	0.0000
11 CO2	0.0000	0.0000	0.0000	0.0000
12 NH3	0.0000	0.0000	0.0000	0.0000
13 N2	0.0000	0.0000	0.0000	0.0000
17 MEA	0.0000	0.0000	0.0000	0.0000
TOTAL FLUID, LB-MOL/HR	0.0000	0.0000	0.0000	291.0000
MW SOLID RATES, LB-MOL/HR				
8 ceo2	396.0000	400.0000	4.0000	0.0000
9 ce2o2s	0.0000	0.0000	0.0000	0.0000
14 zn2tio4	0.0000	0.0000	0.0000	0.0000
15 zns	0.0000	0.0000	0.0000	0.0000
16 TIO2	0.0000	0.0000	0.0000	0.0000
TOTAL MW SOLID, LB-MOL/HR	396.0000	400.0000	4.0000	0.0000
TOTAL RATE, LB-MOL/HR	396.0000	400.0000	4.0000	291.0000
TEMPERATURE, C	826.8500	826.8500	826.8500	228.8500
PRESSURE, ATM	25.0000	25.0000	25.0000	27.3000
ENTHALPY, MM BTU/HR	-175.3039	-177.0747	-1.7707	2.2199
MOLECULAR WEIGHT	172.0000	172.0000	172.0000	18.0150
MOLE FRAC VAPOR	0.0000	0.0000	0.0000	0.0000
MOLE FRAC LIQUID	0.0000	0.0000	0.0000	1.0000
MOLE FRAC MW SOLID	1.0000	1.0000	1.0000	0.0000
WEIGHT FRAC MW SOLID	1.0000	1.0000	1.0000	0.0000

Table 7. Material Balance for Cerium
Oxide Sorber with Steam Regeneration

SIMULATION SCIENCES INC.
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OUTPUT
STREAM MOLAR COMPONENT RATES

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STREAM ID		17	18	19	20
NAME					
PHASE		VAPOR	SOLID	SOLID	SOLID
FLUID RATES, LB-MOL/HR					
1	O2	1.2885	0.0000	0.0000	0.0000
2	S	0.0000	0.0000	0.0000	0.0000
3	SO2	5.1410	0.0000	0.0000	0.0000
4	H2O	291.0000	0.0000	0.0000	0.0000
5	H2	0.0000	0.0000	0.0000	0.0000
6	H2S	0.0000	0.0000	0.0000	0.0000
7	CO	0.0000	0.0000	0.0000	0.0000
10	CH4	0.0000	0.0000	0.0000	0.0000
11	CO2	0.0000	0.0000	0.0000	0.0000
12	NH3	0.0000	0.0000	0.0000	0.0000
13	N2	0.0000	0.0000	0.0000	0.0000
17	MEA	0.0000	0.0000	0.0000	0.0000
TOTAL FLUID, LB-MOL/HR		297.4295	0.0000	0.0000	0.0000
MW SOLID RATES, LB-MOL/HR					
8	ceo2	0.0000	0.0000	0.0000	0.0000
9	ce2o2s	0.0000	0.0000	0.0000	0.0000
14	zn2tio4	0.0000	5.2470	5.3000	0.0530
15	zns	0.0000	0.0000	0.0000	0.0000
16	TIO2	0.0000	0.0000	0.0000	0.0000
TOTAL MW SOLID, LB-MOL/HR		0.0000	5.2470	5.3000	0.0530
TOTAL RATE, LB-MOL/HR		297.4295	5.2470	5.3000	0.0530
TEMPERATURE, C		726.8500	726.8500	726.8500	726.8500
PRESSURE, ATM		25.0000	25.0000	25.0000	25.0000
ENTHALPY, MM BTU/HR		9.0736	-3.4474	-3.4822	-0.0348
MOLECULAR WEIGHT		18.8715	242.0000	242.0000	242.0000
MOLE FRAC VAPOR		1.0000	0.0000	0.0000	0.0000
MOLE FRAC LIQUID		0.0000	0.0000	0.0000	0.0000
MOLE FRAC MW SOLID		0.0000	1.0000	1.0000	1.0000
WEIGHT FRAC MW SOLID		0.0000	1.0000	1.0000	1.0000

Table 7. Material Balance for Cerium
Oxide Sorber with Steam Regeneration

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STREAM MOLAR COMPONENT RATES

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=====
STREAM ID          21          23          25          31
NAME
PHASE             SOLID          VAPOR          VAPOR          VAPOR

FLUID RATES, LB-MOL/HR
1  O2             0.0000         9.0000         52.1000         1.9128
2  S              0.0000         0.0000         0.0000         1.6083E-04
3  SO2            0.0000         0.0000         0.0000         2.4499
4  H2O            0.0000         0.0000         0.0000         46.5608
5  H2             0.0000         0.0000         0.0000         0.0000
6  H2S            0.0000         0.0000         0.0000         4.9077
7  CO             0.0000         0.0000         0.0000         0.0000
10 CH4            0.0000         0.0000         0.0000         0.0000
11 CO2            0.0000         0.0000         0.0000         0.0000
12 NH3            0.0000         0.0000         0.0000         0.0000
13 N2             0.0000         0.0000         204.0000        203.9997
17 MEA            0.0000         0.0000         0.0000         0.0000
TOTAL FLUID, LB-MOL/HR          0.0000         9.0000         256.1000        259.8311

MW SOLID RATES, LB-MOL/HR
8  ceo2           0.0000         0.0000         0.0000         0.0000
9  ce2o2s         0.0000         0.0000         0.0000         0.0000
14 zn2tio4        0.0530         0.0000         0.0000         0.0000
15 zns            0.0000         0.0000         0.0000         0.0000
16 TIO2           0.0000         0.0000         0.0000         0.0000
TOTAL MW SOLID, LB-MOL/HR        0.0530         0.0000         0.0000         0.0000

TOTAL RATE, LB-MOL/HR          0.0530         9.0000         256.1000        259.8311

TEMPERATURE, C          726.8500         26.8500         26.8500         79.8500
PRESSURE, ATM           25.0000         25.0000         1.0000         1.0000
ENTHALPY, MM BTU/HR    -0.0348         -0.0103         -0.5039         0.7084
MOLECULAR WEIGHT        242.0000         31.9990         28.8239         26.7052
MOLE FRAC VAPOR         0.0000         1.0000         1.0000         1.0000
MOLE FRAC LIQUID        0.0000         0.0000         0.0000         0.0000
MOLE FRAC MW SOLID      1.0000         0.0000         0.0000         0.0000
WEIGHT FRAC MW SOLID    1.0000         0.0000         0.0000         0.0000

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Table 7. Material Balance for Cerium
Oxide Sorber with Steam Regeneration
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STREAM MOLAR COMPONENT RATES

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=====
STREAM ID          32          33          34          35
NAME
PHASE             LIQUID         VAPOR         VAPOR         LIQUID
FLUID RATES, LB-MOL/HR
1  O2             1.1028E-06     0.0000        0.0000        0.0000
2  S              83.5612       0.0000        0.0000        0.0000
3  SO2            4.2973E-04     0.0000        0.0000        0.0000
4  H2O            52.4303       0.0000        3.5172        4999.9995
5  H2             0.0000        85.1607       9.4623        0.0000
6  H2S            2.0064E-03     0.0000        90.9212       0.0000
7  CO             0.0000        0.0000        0.0000        0.0000
10 CH4            0.0000        0.0000        0.0000        0.0000
11 CO2            0.0000        0.0000        0.0000        0.0000
12 NH3            0.0000        0.0000        0.0000        0.0000
13 N2             7.8274E-06     0.0000        0.0000        0.0000
17 MEA            0.0000        0.0000        0.0000        4999.9995
TOTAL FLUID, LB-MOL/HR      135.9939      85.1607      103.9008      9999.9990

MW SOLID RATES, LB-MOL/HR
8  ceo2           0.0000        0.0000        0.0000        0.0000
9  ce2o2s        0.0000        0.0000        0.0000        0.0000
14 zn2tio4       0.0000        0.0000        0.0000        0.0000
15 zns           0.0000        0.0000        0.0000        0.0000
16 TIO2          0.0000        0.0000        0.0000        0.0000
TOTAL MW SOLID, LB-MOL/HR      0.0000        0.0000        0.0000        0.0000

TOTAL RATE, LB-MOL/HR      135.9939      85.1607      103.9008      9999.9990

TEMPERATURE, C      79.8500      72.6430      72.6430      49.8500
PRESSURE, ATM       1.0000      24.7500      1.7500      1.0000
ENTHALPY, MM BTU/HR 0.2521      -0.1199      0.8286      23.5845
MOLECULAR WEIGHT    26.6453      2.0160      30.6152      39.5490
MOLE FRAC VAPOR     0.0000      1.0000      1.0000      0.0000
MOLE FRAC LIQUID    1.0000      0.0000      0.0000      1.0000
MOLE FRAC MW SOLID  0.0000      0.0000      0.0000      0.0000
WEIGHT FRAC MW SOLID 0.0000      0.0000      0.0000      0.0000

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Table 7. Material Balance for Cerium
Oxide Sorber with Steam Regeneration

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STREAM MOLAR COMPONENT RATES

STREAM ID		36	37	38	39
NAME					
PHASE		VAPOR	VAPOR	LIQUID	VAPOR
FLUID RATES, LB-MOL/HR					
1	O2	1.8957	1.9128	0.0171	1.9128
2	S	5.7234E-12	83.5612	1.6083E-04	1.6083E-04
3	SO2	0.0000	2.4503	0.0000	0.0000
4	H2O	13.3017	98.9910	5038.1582	51.4606
5	H2	0.2500	0.0000	3.1770E-04	0.2503
6	H2S	1.1937E-03	4.9098	7.3564	7.3576
7	CO	0.0000	0.0000	0.0000	0.0000
10	CH4	0.0000	0.0000	0.0000	0.0000
11	CO2	0.0000	0.0000	0.0000	0.0000
12	NH3	0.0000	0.0000	0.0000	0.0000
13	N2	203.5048	204.0000	0.4958	203.9997
17	MEA	0.3455	0.0000	4999.6538	0.0000
TOTAL FLUID, LB-MOL/HR		219.2989	395.8250	10045.6816	264.9812
MW SOLID RATES, LB-MOL/HR					
8	ceO2	0.0000	0.0000	0.0000	0.0000
9	ce2O2s	0.0000	0.0000	0.0000	0.0000
14	zn2tio4	0.0000	0.0000	0.0000	0.0000
15	zns	0.0000	0.0000	0.0000	0.0000
16	TIO2	0.0000	0.0000	0.0000	0.0000
TOTAL MW SOLID, LB-MOL/HR		0.0000	0.0000	0.0000	0.0000
TOTAL RATE, LB-MOL/HR		219.2989	395.8250	10045.6816	264.9812
TEMPERATURE, C		49.8500	736.8500	49.8500	426.8500
PRESSURE, ATM		1.0000	1.0000	1.0000	1.0000
ENTHALPY, MM BTU/HR		-0.1150	11.3754	23.5016	2.0358
MOLECULAR WEIGHT		27.4635	26.6846	39.4619	26.2440
MOLE FRAC VAPOR		1.0000	1.0000	0.0000	1.0000
MOLE FRAC LIQUID		0.0000	0.0000	1.0000	0.0000
MOLE FRAC MW SOLID		0.0000	0.0000	0.0000	0.0000
WEIGHT FRAC MW SOLID		0.0000	0.0000	0.0000	0.0000

Table 7. Material Balance for Cerium
Oxide Sorber with Steam Regeneration

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PROJECT ce
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STREAM MOLAR COMPONENT RATES

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=====
STREAM ID              40
NAME
PHASE                 VAPOR

FLUID RATES, LB-MOL/HR
 1 O2                 0.0000
 2 S                  0.0000
 3 SO2                0.0000
 4 H2O                0.0000
 5 H2                 7.6000
 6 H2S                0.0000
 7 CO                 0.0000
10 CH4                0.0000
11 CO2                0.0000
12 NH3                0.0000
13 N2                 0.0000
17 MEA                0.0000
TOTAL FLUID, LB-MOL/HR 7.6000

MW SOLID RATES, LB-MOL/HR
 8 ceo2               0.0000
 9 ce2o2s             0.0000
14 zn2tio4            0.0000
15 zns                0.0000
16 TIO2               0.0000
TOTAL MW SOLID, LB-MOL/HR 0.0000

TOTAL RATE, LB-MOL/HR 7.6000

TEMPERATURE, C       21.8500
PRESSURE, ATM        1.0000
ENTHALPY, MM BTU/HR -0.0156
MOLECULAR WEIGHT     2.0160
MOLE FRAC VAPOR     1.0000
MOLE FRAC LIQUID    0.0000
MOLE FRAC MW SOLID  0.0000
WEIGHT FRAC MW SOLID 0.0000
  
```

Sulfur discharges to the environment occur in streams 6 (condensate) and 36 (tail unit off-gas) and amount to 3.8% of the sulfur in the coal gas feed. Most of this sulfur is present in the condensate (stream 6) and, if necessary, the H_2S can be removed from this stream by steam stripping so that sulfur emissions are reduced to near zero.