Advanced Sulfur Control Concepts for Hot Gas Desulurization Technology

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EXECUTIVE SUMMARY

Experimental effort on the regeneration of FeS using the partial oxidation concept was completed during the quarter, and attention returned to the sulfidation of CeO_2 and regeneration of Ce_2O_2S. Progress was made in the process simulation effort involving two-step desulfurization using CeO_2 to remove the bulk of the H_2S followed by a zinc-titanate polishing step. The simulation effort includes regeneration of Ce_2O_2S using two concepts -- reaction with SO_2 and reaction with H_2O. Elemental sulfur is formed directly in the reaction with SO_2 while H_2S is the product of the regeneration reaction with steam. Steam regeneration is followed by a Claus process to convert the H_2S to elemental sulfur.

The last test involving partial oxidation regeneration of FeS was completed in early July. Experimental problems were encountered throughout this phase of the program, primarily associated with erratic readings from the total sulfur analyzer. The problems are attributed to variable flow rates through the capillary restrictor, and, in some cases, to steam concentrations which exceeded the capacity of the membrane dryer. Nevertheless, sufficient data was collected to confirm that large fractions of the sulfur in FeS could be liberated in elemental form. Low regeneration temperature ($\sim 600°C$), large steam-to-oxygen ratios, and low space velocities were found to favor elemental sulfur production.

Previous experimental effort on the sulfidation of CeO_2 was plagued with "over-sulfidation," i.e., the amount of H_2S removed from the gas exceeded the stoichiometric quantity associated with the formation of Ce_2O_2S. The problem was first attributed to further sulfidation of Ce_2O_2S to Ce_2S_3 in the highly reducing gas composition. Later troubleshooting suggested that reaction of H_2S with the walls of the reactor insert tube was the probably cause of "over-sulfidation."

A quartz insert tube was fabricated to replace the stainless steel tube. The quartz tube was initially used in a series of non-reacting tracer tests at successively higher temperatures to evaluate the stability of the tube and its o-rings, and to confirm that reaction between H_2S and reactor surfaces was sufficiently small that meaningful reaction results could be obtained. Upon successful completion of the non-reacting tracer tests, we returned to sulfidation tests using CeO_2. Some problems in the CeO_2 sulfidation studies which we attribute to gas by-passing caused by incomplete mixing of CeO_2 and Al_2O_3 diluent have been experienced. By-passing problems attributed to sintering of Ce_2O_2S were experienced when no Al_2O_3 was added to the bed. In spite of these problems, significant progress has been made in the CeO_2 sulfidation study. Greater than 95% H_2S removal has been achieved during the prebreakthrough period at reaction conditions of 800°C and 5 atm. Overall sulfur material balance closure for the duration of the tests is within $\pm 10\%$. Initial tests on the regeneration of Ce_2O_2S by reaction with SO_2 will be carried out during the next quarter.

Significant progress was also made in the process analysis phase of the study. Process flow diagrams and material and energy balance calculations for a number of case studies involving two-stage desulfurization using CeO_2 for bulk sulfur removal followed by zinc-titanate

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polishing have been completed. Regeneration of the sulfided zinc titanate is accomplished in the traditional manner with sulfur liberated as SO_2. The SO_2-containing off-gases are then recycled to the gasifier where they are reconverted to H_2S and re-enter the desulfurization process. The case studies consider regeneration of Ce_2O_2S both by reaction with SO_2 to form elemental sulfur directly and by reaction with steam to form H_2S followed by a Claus process to produce elemental sulfur.

Initial work on a single-stage desulfurization process using zinc titanate and the direct sulfur recovery process (DSRP) for recovery of elemental sulfur from the regeneration off-gases was carried out. Process analysis effort during the next quarter will concentrate upon further refining of the two-stage processes using CeO_2 sorbent, and further developing the single-stage process using DSRP to provide legitimate comparisons of the two approaches.

REGENERATION OF FeS BY PARTIAL OXIDATION

The last two tests involving FeS regeneration by partial oxidation were carried out in July. Reaction conditions for these tests are presented in Table 1. The regeneration feed gas in Fe-26 contained both O_2 and H_2O while H_2O was the only reactive component in the FeS-29 feed.

Results of FeS-26 in terms of sulfur component concentrations in the product gas as a function of time are presented in Figure 1. The results are qualitatively consistent with earlier partial oxidation runs in that H_2S and total sulfur concentrations increased soon after the reaction started, quickly reached a maximum, and decreased thereafter. SO_2 concentration remained near zero for 0.5 hours, gradually increased to a maximum of 0.008 mol fraction after 2.7 hours, and decreased thereafter. The total sulfur measurement stopped after 1.0 hour when the capillary flow restrictor plugged. Flow through the chromatograph was not affected, and SO_2 and H_2S measurements continued.

The cumulative production of sulfur compounds, expressed as a fraction of the stoichiometric sulfur, is shown in Figure 2 as a function of time. When the capillary restrictor plugged after 1 hour, the cumulative production was 10% H_2S, 3% SO_2, and 36% total sulfur, which implies that 23% of the sulfur had been transferred to the gas phase as elemental sulfur. At the conclusion of the test, 22% of the theoretical sulfur had been liberated as H_2S and 30% as SO_2, leaving (by difference) approximately 50% as elemental sulfur.

Figure 3 shows the instantaneous selectivity to elemental sulfur for the first hour of the test when both analyzers were operating. Although there is significant scatter in the data, it appears that the selectivity was about 80% at the beginning of the test and decreased to about 40% after 1 hour. These results are qualitatively consistent with results from earlier partial oxidation runs which have consistently shown maximum selectivity to elemental sulfur near the beginning of the run.

Table 1. Summary of Fixed-Bed Reactor Test Conditions:
FeS Regeneration, July 1996

Run	FeS-26	FeS-29
Date	7-2-96	7-17-96
Reactor Packing		
FeS, g	0.83	0.84
Al_2O_3, g	3.29	3.28
Reaction Conditions		
Temp., °C	600	600
Press., atm	4.4	4.4
Gas Comp.		
% O_2	0.25	0
% H_2O	20.0	20.0
% N_2	79.75	80.0
Gas Flow, sccm	600	300
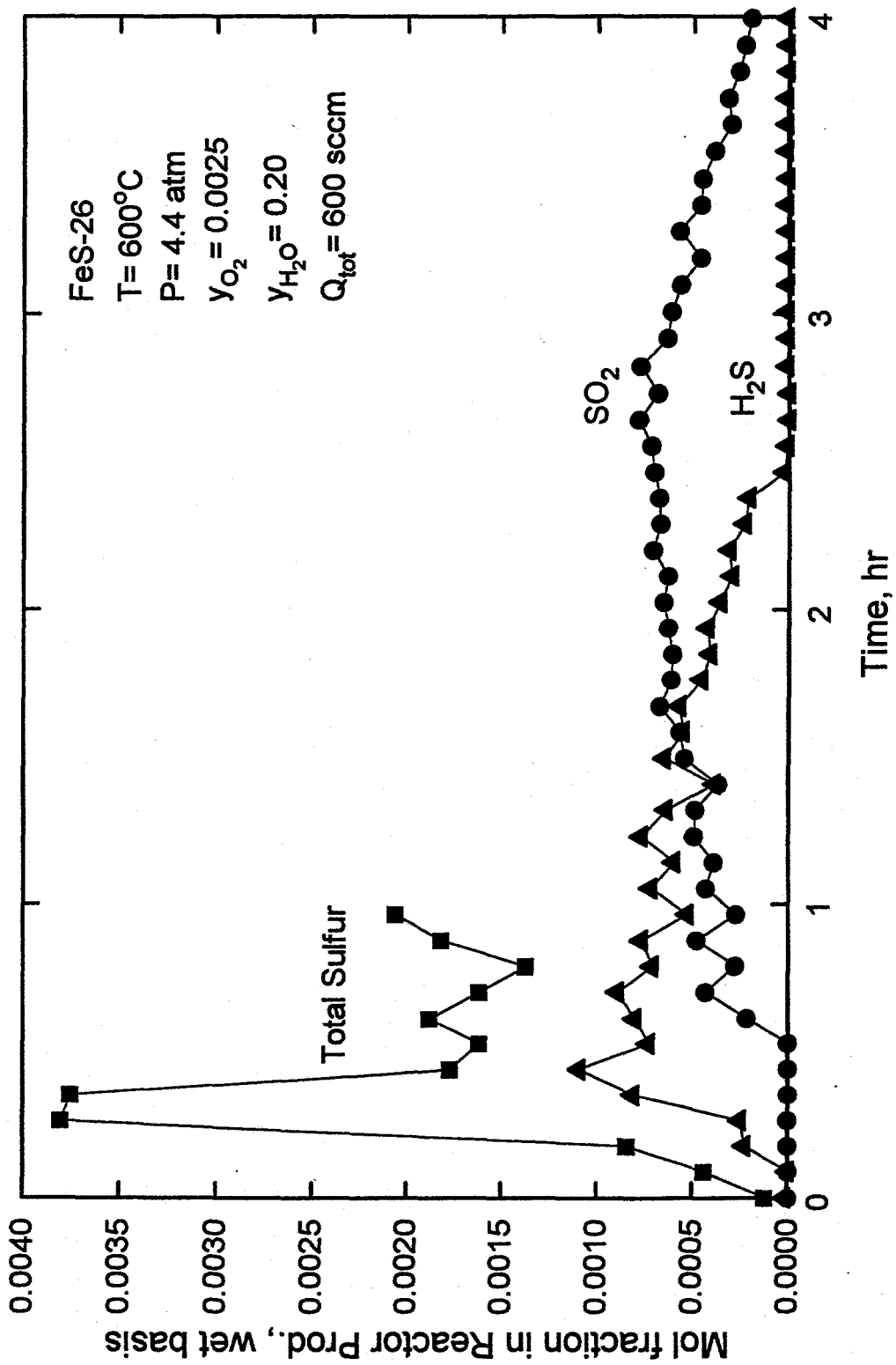
Figure 1. Fixed-Bed Reactor Response: Run FeS-26
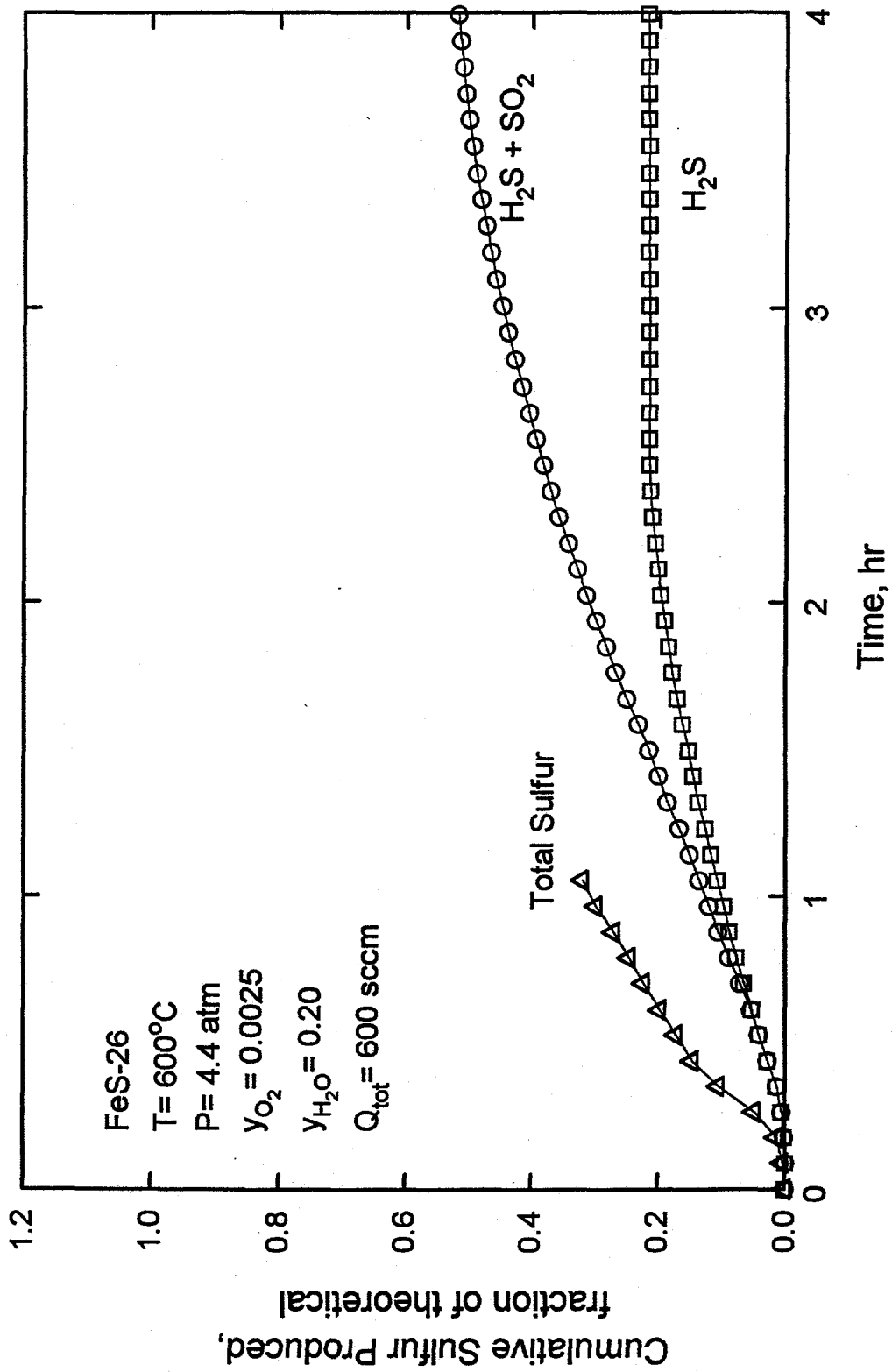
Figure 2. Cumulative Production of Sulfur Species: Run FeS-26

The figure is a plot with axes:

- X-axis: Time, hr (from 0 to 4)
- Y-axis: Cumulative Sulfur Produced, fraction of theoretical (from 0.0 to 1.2)

Conditions listed:

FeS-26
T = 600°C
P = 4.4 atm
$y_{O_2} = 0.0025$
$y_{H_2O} = 0.20$
$Q_{tot} = 600$ sccm

Curves labeled: Total Sulfur, $H_2S + SO_2$, H_2S
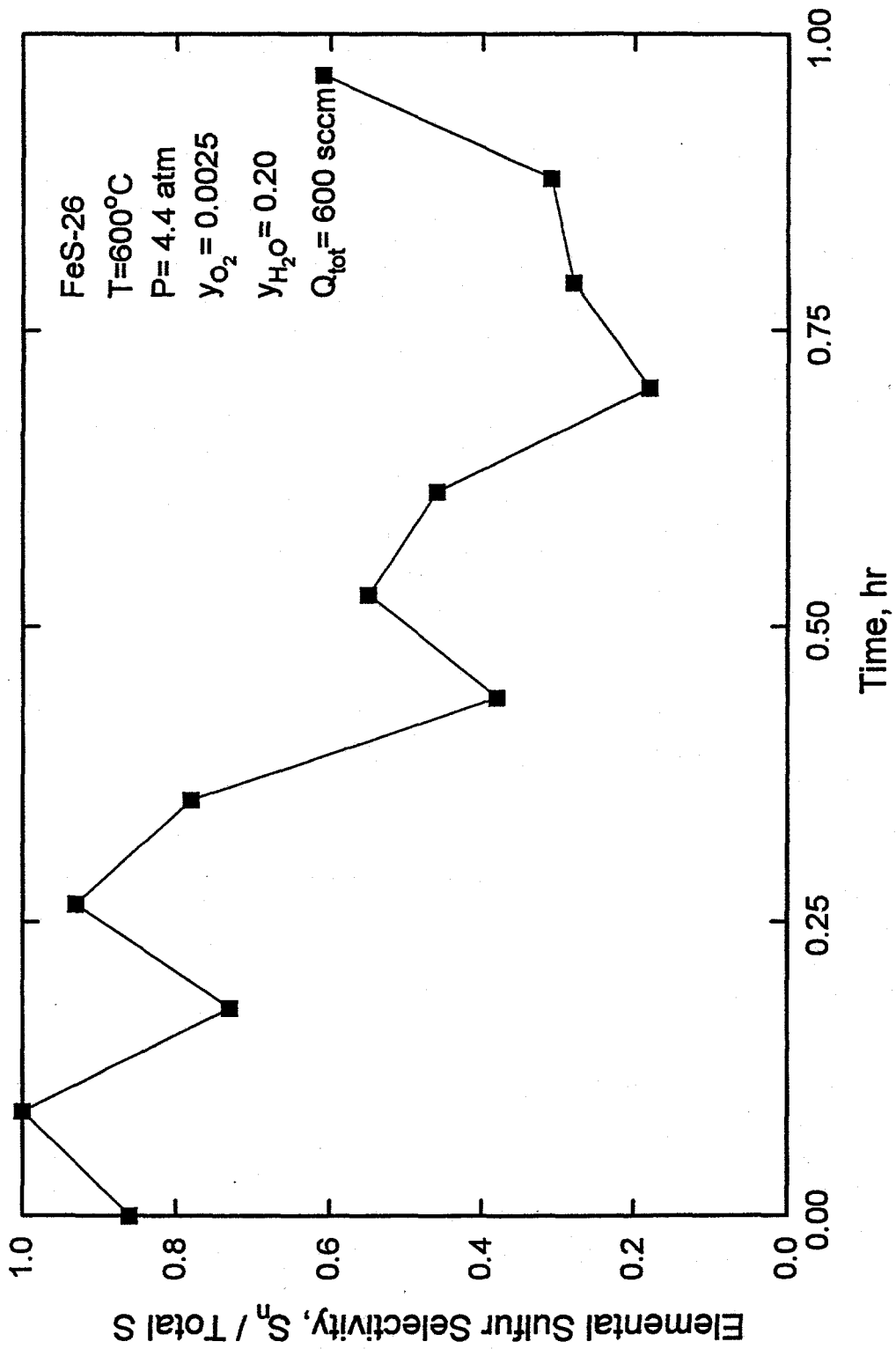
Figure 3. Instantaneous Selectivity to Elemental Sulfur During the First Hour of Run FeS-26

The plot shows Elemental Sulfur Selectivity, S_n / Total S (y-axis, 0.0 to 1.0) versus Time, hr (x-axis, 0.00 to 1.00).

Conditions:
FeS-26
$T = 600^\circ C$
$P = 4.4$ atm
$y_{O_2} = 0.0025$
$y_{H_2O} = 0.20$
$Q_{tot} = 600$ sccm

The feed gas in run FeS-29 (not shown) contained only H_2O and N_2 and all of the sulfur was liberated as H_2S. After a short delay time, the H_2S concentration increased quickly, reached a maximum after 2 hours, and decreased slowly until the run was terminated after 5.5 hours. The cumulative amount of H_2S produced during the run was about 36% of theoretical. This run emphasized once again that the reaction rate between FeS and H_2O was much slower than the FeS-O_2 rate. Run FeS-26 was effectively complete after 4 hours while FeS-29 was only 36% complete after 5.5 hours.

OVERALL ANALYSIS OF FeS PARTIAL OXIDATION RESULTS

The complete series of FeS partial oxidation tests examined the effects of (1) the mass of FeS charge, (2) regeneration temperature, (3) regeneration feed gas composition, and (4) regeneration feed gas volumetric flow rate on the regeneration kinetics and product distribution. The range of reaction parameters is summarized in Table 2. Total pressure was constant at 4.4 atm in all tests.

FeS Charge

The mass of FeS charged to the reactor was reduced from 3.21g in the first test to approximately 0.5g and 0.8g in later tests. These reductions were made in response to experimental system constraints and the need to keep the run time required for complete regeneration to a reasonable value. Examples of experimental constraints are the capacity of the high pressure syringe pump and the flow ranges of the mass flow controllers. Relatively small variations in FeS charge were expected to change the timing of key reaction events, but not to alter the distribution of sulfur compounds in the regenerator product. Table 3 compares results of two tests in which FeS charge was the only significant variable. The total reaction time and the times corresponding to maximum sulfur compound concentrations did not respond as expected. In spite of the smaller FeS charge in FeS-22 the total reaction time and the times corresponding to maximum H_2S and total sulfur concentrations increased. Only the time corresponding to the maximum SO_2 concentration decreased as expected. However, the total sulfur concentration exhibited a very sharp peak such as shown in Figure 1. The sharpness of the peak coupled with the general erratic response of the total sulfur analyzer creates the possibility of significant error in both the maximum concentration and the time corresponding to the maximum concentration. Run FeS-21 was also terminated before actual completion which explains the unexpected difference in total run time.

The maximum concentrations and cumulative selectivity of the sulfur compounds were quite similar. The differences in the H_2S and SO_2 selectivity are within the experimental error. Two values of elemental sulfur selectivity for run FeS-24 are shown for run FeS-21. The first is based on the difference in the cumulative production of total sulfur and H_2S and SO_2 (95-20-25=50). The second value represents the elemental sulfur selectivity assuming complete regeneration (100-20-25=55). The elemental sulfur selectivity of 54% for FeS-22 falls within the range of values for FeS-21.

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Table 2. Ranges of Reaction Parameters Covered in
the Partial Oxidation Regeneration of FeS

FeS, g	0.50	-	3.21
Al_2O_3, g	3.04	-	3.83
Temp	550	-	700°C
P		4.4 atm	
Gas Comp			
% O_2	0.25	-	1.5
% H_2O	10	-	52.0
H_2O/O_2 Ratio	6.7	-	200
Gas Flow	300	-	600 sccm

Table 3. The Effect of Initial FeS Change on Reaction
Times, Maximum Mol Fractions, and Product
Yields: Runs FeS-21 and FeS-22

Reaction Conditions		Feed Gas Composition
$T=600°C$		$0.25\%\ O_2$
$P=4.4$ atm		$20.0\%\ H_2O$
$Q=300$ sccm		$79.75\%\ N_2$

Run	FeS-21	FeS-22
FeS, g	1.02	0.83
Max. Mol Fraction		
H_2S	0.0006	0.0006
SO_2	0.0008	0.0009
Total S	0.0023	0.0025
Reaction Times (hr) for		
Max H_2S	1.4	1.7
SO_2	7.2	5.8
Total S	0.5	0.9
Total Reaction Time, hr	7.4	7.8
Cumulative Selectivity,		
$\%H_2S$	20	22
SO_2	25	24
S_x	50-55	54

Regeneration Temperature

Lower regeneration temperature definitely favors the production of elemental sulfur, as shown by the comparison of results from runs FeS-19, FeS-22, and FeS-24 presented in Table 4. Reaction temperature was the only difference between FeS-19 (700°C) and FeS-22 (600°C) while a smaller FeS charge as well as lower temperature (550°C) were used in FeS-24. Decreasing the temperature from 700 to 600°C increased the time required for complete regeneration by about 10%, decreased the maximum H_2S and total sulfur mol fractions, and produced no change in the maximum SO_2 mol fraction. However, the cumulative selectivity to elemental sulfur increased by about 50%, from 37% to 54%. A further 50°C decrease in regeneration temperature to 550°C (run FeS-24) produced a reduction in the maximum mol fraction of all sulfur species and in the selectivity to both H_2S and SO_2. The wide range in elemental sulfur selectivity for run FeS-24 found in Table 4, from 59 to 78%, is based on the fact that regeneration was incomplete at 550°C, perhaps due to the formation of $Fe_2(SO_4)_3$. The run was terminated after 6 hours even though small amounts of SO_2 and total sulfur were still present in the product gas; no H_2S was detected after 3 hours. Integration of the total sulfur versus time curve accounted for only 81% of the stoichiometric sulfur. The lower limit of 59% selectivity is based on this value (81% total sulfur - 4% H_2S - 18% SO_2) while the upper limit is based on complete regeneration (100-4-18=78). The actual value should be between these limits and is probably closer to the 59% lower limit. However, even this lower limit represents an additional 10% increase in the elemental sulfur selectivity.

Volumetric Flow Rate

Small volumetric flow rate (small space velocity) of regeneration gas also favors elemental sulfur production, as seen in Table 5 where the results from runs FeS-22 and FeS-26 are compared. The large feed rate in run FeS-26 produced an increase in the maximum concentrations of H_2S and total sulfur, decreased the times at which the maximum concentrations occurred as well as the total reaction time, increased to selectivity to SO_2, and decreased the selectivity to elemental sulfur. Most of the elemental sulfur is believed to be produced via the gas phase Claus reaction. Since gas residence time is inversely proportional to the gas volumetric flow rate, the small volumetric flow rate provides increased residence time needed for the gas phase reaction to occur.

Regeneration Gas Composition

The composition of the regeneration feed gas was varied in two ways. In one case the concentrations of both O_2 and H_2O were both doubled so that the H_2O to O_2 ratio remained constant. In the other case the H_2O to O_2 ratio was increased by increasing the H_2O concentration at constant O_2 concentration.

The effect of doubling both the O_2 and H_2O contents of the regenerator feed is summarized in Table 6 which compares the results of runs FeS-22 and FeS-23. It should be emphasized that the 40% H_2O content of the run FeS-23 feed gas caused increased scatter in the

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Table 4. The Effect of Regeneration Temperature on Elemental Sulfur Production: Runs FeS-19, FeS-22, and FeS-24

Reaction Conditions	Feed Gas Composition
P=4.4 atm	0.25% O_2
Q=300 sccm	20.0% H_2O
	79.75% N_2

Run	FeS-19	FeS-22	FeS-24*
FeS, g	0.83	0.83	0.52
T, °C	700	600	550
Max. Mol Fraction			
H_2S	0.0013	0.0006	0.0003
SO_2	0.0009	0.0009	0.0004
Total S	0.0027	0.0025	0.0016
Reaction Times (hr) for			
Max H_2S	1.4	1.7	1.1
SO_2	5.9	5.8	4.5
Total S	0.6	0.9	0.9
Total Reaction Time, hr	7.0	7.8	6.0
Cumulative Selectivity, %			
H_2S	35	22	4
SO_2	28	24	18
S_x	37	54	59-78

*incomplete regeneration perhaps due to $Fe_2(SO_4)_3$ production

Table 5. The Effect of Regeneration Gas Flow Rate (Space Velocity) on Elemental Sulfur Production
Runs FeS-22 and FeS-26

Reaction Conditions		Feed Gas Composition
T=600°C		0.25% O_2
P=4.4 atm		20.0% H_2O
0.83 g FeS		79.75% N_2

Run	FeS-22	FeS-26
Q, sccm	300	600
Max. Mol Fraction		
H_2S	0.0006	0.0011
SO_2	0.0009	0.0008
Total S	0.0025	0.0038
Reaction Times (hr) for		
Max H_2S	1.7	0.4
SO_2	5.8	2.7
Total S	0.9	0.3
Total Reaction Time, hr	7.8	4.0
Cumulative Selectivity, %		
H_2S	22	22
SO_2	24	30
S_x	54	48

Table 6. The Effect of O_2 and H_2O Concentrations (Constant $H_2O:O_2$ Ratio) on Elemental Sulfur Production: Run FeS-22 and FeS-23

Reaction Conditions		Feed Gas Composition
T=600°C		0.83 g FeS
P=4.4 atm		Q=300 sccm

Run	FeS-22	FeS-23
Feed Gas, % O_2	0.25	0.50
% H_2O	20.0	40.0
% N_2	79.75	59.5
Max. Mol Fraction		
H_2S	0.0006	0.0008
SO_2	0.0009	0.0018
Total S	0.0025	0.0188
Reaction Times (hr) for		
Max H_2S	1.7	0.5
SO_2	5.8	2.4
Total S	0.9	0.4
Total Reaction Time, hr	7.8	5.3
Cumulative Selectivity, %		
H_2S	22	4
SO_2	24	38
S_x	54	52-58

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product gas composition, particularly the total sulfur concentration. The problem may be due to uneven steam flow associated with periodic condensation and vaporization and/or by exceeding the capacity of the membrane dryer in the total sulfur analyzer. This erratic behavior makes the maximum total sulfur mol fraction in Table 6 for run FeS-23 particularly suspect. However, other results from Table 6 appear to be reasonable.

Doubling the concentration of O_2 and H_2O had the expected effect of increasing the maximum concentrations of the sulfur species, reducing the time at which the maxima occurred, and reducing the time required for complete regeneration. The cumulative H_2S selectivity was dramatically reduced, from 22% in run FeS-22 to only 4% in FeS-23. The SO_2 selectivity increased from 24% in FeS-22 to 38% in FeS-23. As a result, the cumulative selectivity to elemental sulfur was approximately constant near 55%.

No pair of runs provided a direct comparison of the effect of the H_2O to O_2 ratio while holding all other reaction parameters constant. The closest approach to satisfying this criterion is shown in Table 7 where selected results from runs FeS-22, FeS-25, and FeS-26 are compared. In FeS-22 and FeS-26 the H_2O to O_2 ratio was 80 to 1 while in FeS-25 the ratio was increased to 200 to 1. However, the mass of FeS was also reduced in FeS-25 and the volumetric feed rates were different in each run. Previous analysis has shown that the mass of FeS should not have significant impact on the selectivity while increases in the volumetric flow rate have a small negative effect on selectivity. Also important is the fact that the large steam concentration in the run FeS-25 feed gas caused erratic behavior in the total sulfur concentration similar to that previously described for run FeS-23.

The elemental sulfur selectivity in FeS-25 (H_2O to O_2=200) is significantly greater than in either FeS-22 or FeS-26 (both with H_2O to O_2=80), which confirms the expectation that larger H_2O to O_2 ratios favor elemental sulfur production. The smaller elemental sulfur selectivity for run FeS-25 listed in Table 7 is based on the stoichiometric sulfur minus the sulfur produced as H_2S and SO_2 (100-15-10=75) while the larger value is based on the fact that integration of the total sulfur-time curve accounted for 106% of the stoichiometric amount (106-15-10=81).

Summary

The results of the FeS regeneration tests using the partial oxidation concept suggest that the maximum selectivity to elemental sulfur occurs at low temperature, small O_2 concentration, large H_2O concentration, and small volumetric flow rate of regeneration gas. The minimum regeneration temperature of about 600°C is established by the tendency to form $Fe_2(SO_4)_3$ at lower temperatures. Of all the partial oxidation tests carried out, run FeS-25 came closest to satisfying the conditions needed to maximize the elemental sulfur selectivity while reaction conditions of run FeS-16 were the opposite. The cumulative elemental sulfur selectivity increased from about 10% in FeS-16 to approximately 80% in FeS-29.

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Table 7. The Effect of $H_2O:O_2$ Ratio (Constant O_2 Concentration on Elemental Sulfur Production: Runs FeS-22, FeS-25, and FeS-26

Reaction Conditions
   T=600°C
   P=4.4 atm

Run	FeS-22	FeS-25	FeS-26
FeS, g	0.83	0.52	0.83
Q, sccm	300	435	600
Feed Gas, % O_2	0.25	0.26	0.25
% H_2O	20.0	52.0	20.0
% N_2	79.75	47.74	79.75
$H_2O:O_2$ Ratio	80	200	80
Max. Mol Fraction			
H_2S	0.0006	0.0010	0.0011
SO_2	0.0009	0.0002	0.0008
Total S	0.0025	0.0091	0.0038
Reaction Times (hr) for			
Max H_2S	1.7	0.3	0.4
SO_2	5.8	1.5	2.7
Total S	0.9	0.2	0.3
Total Reaction Time, hr	7.8	3.1	4.0
Cumulative Selectivity, %			
H_2S	22	15	22
SO_2	24	10	30
S_x	54	75-81	48

CERIUM OXIDE SULFIDATION

Earlier attempts to study the sulfidation of CeO_2 were plagued by "over-sulfidation", i.e., the quantity of H_2S removed from the gas phase exceeded the stoichiometric quantity. This was initially attributed to the further sulfidation of Ce_2O_2S to Ce_2S_3 in the highly reducing gas. Thermodynamic analysis using CHEMQ showed that further sulfidation was possible, and also indicated that further sulfidation could be prevented by the addition of small amounts of oxygen-containing components such as CO_2 or H_2O to the sulfidation feed gas. However, the addition of 1% CO_2 in run CeO_2-06 and 3% H_2O in run CeO_2-07 did not prevent over-sulfidation. After a series of troubleshooting tests, the cause of over-sulfidation was traced to reaction between H_2S and the stainless steel walls of the reactor insert. The alonized coating on the stainless steel was either ineffective at the severe reaction conditions or it had deteriorated with time to the point that protection was no longer being offered.

In order to eliminate this problem, a quartz reactor insert was designed to replace the original stainless steel insert. A diagram of the new insert is shown in Figure 4. The quartz tube is 84 cm long and has an inside diameter of 11 mm. Dimples located 71 cm from the top support a porous quartz disk, a layer of quartz wool, and the CeO_2 sorbent diluted with Al_2O_3. The insert is attached to the top of the pressure vessel by a stainless steel ring and o-rings which fit over the shoulders at the top of the insert. The o-rings do not provide a pressure seal, but supply a flexible cushion to accommodate differences in the thermal expansion coefficients between the quartz and stainless steel.

Initial testing of the quartz insert was carried out under nonreacting conditions without the addition of CeO_2. These tests were intended to confirm the mechanical stability of the insert and o-rings at temperatures and pressures comparable to those to be used in the reaction tests, and to confirm that the reaction between H_2S and the walls of the reactor was eliminated, or at least reduced to the point that it did not interfere with the kinetics of the primary reaction.

Non-reacting H_2S tracer tests were conducted at room temperature and at 400 and 700°C. In some tests the reactor insert was packed with inert materials while in other cases no packing was used. A mixture of H_2S, H_2, and N_2 of known composition was established by the mass flow controllers and fed to the reactor. The composition of the reactor product as a function of time was determined by gas chromatography. The H_2 content was constant at 10% in all tests while the H_2S content was periodically varied in a step function between 0.5%, 1.0%, and 1.5%. The specified accuracy of the mass flow controllers is $\pm 1\%$ of full scale which leads to the following expected ranges of H_2S content:

$$0.50 \pm 0.03\%$$
$$1.00 \pm 0.04\%$$
$$1.50 \pm 0.05\%.$$

The gas chromatograph response to a nonreacting tracer test at 700°C is shown in Figure 5. The reactor insert contained the porous quartz disk, quartz wool, and alumina. The total gas
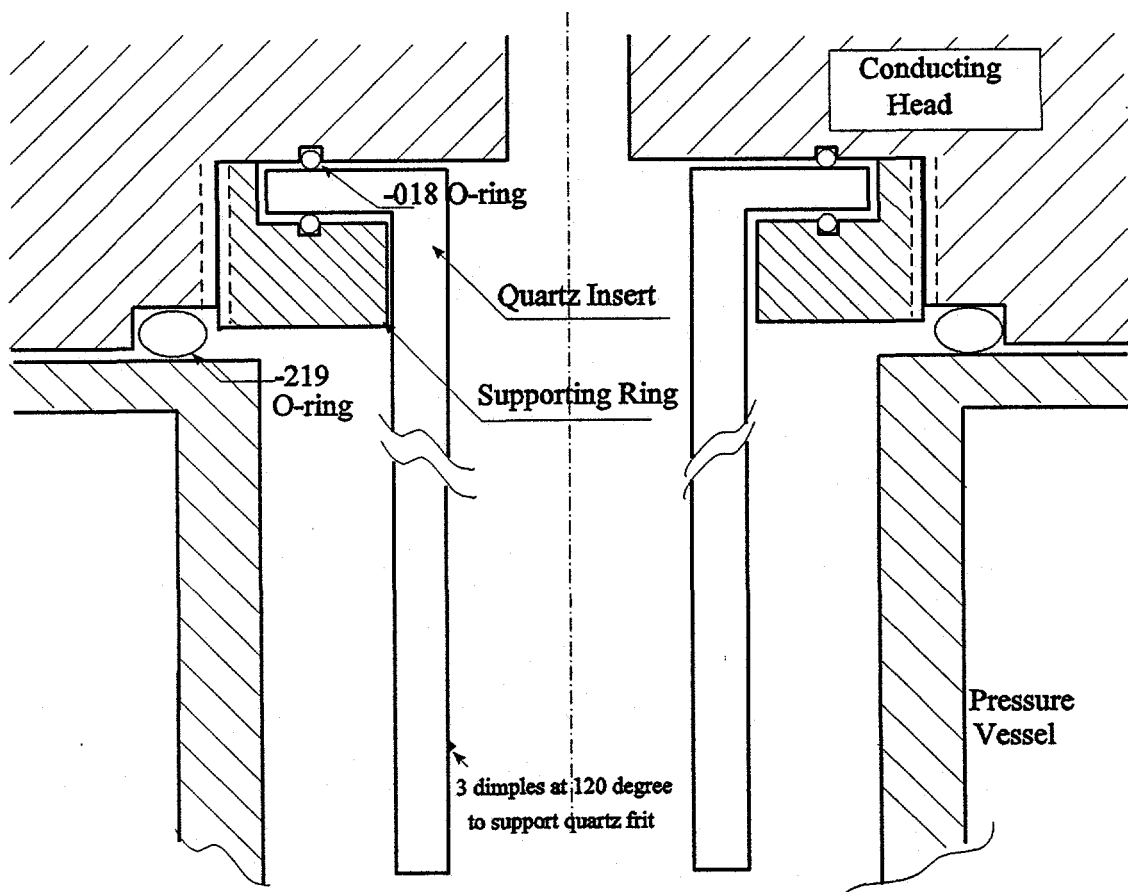
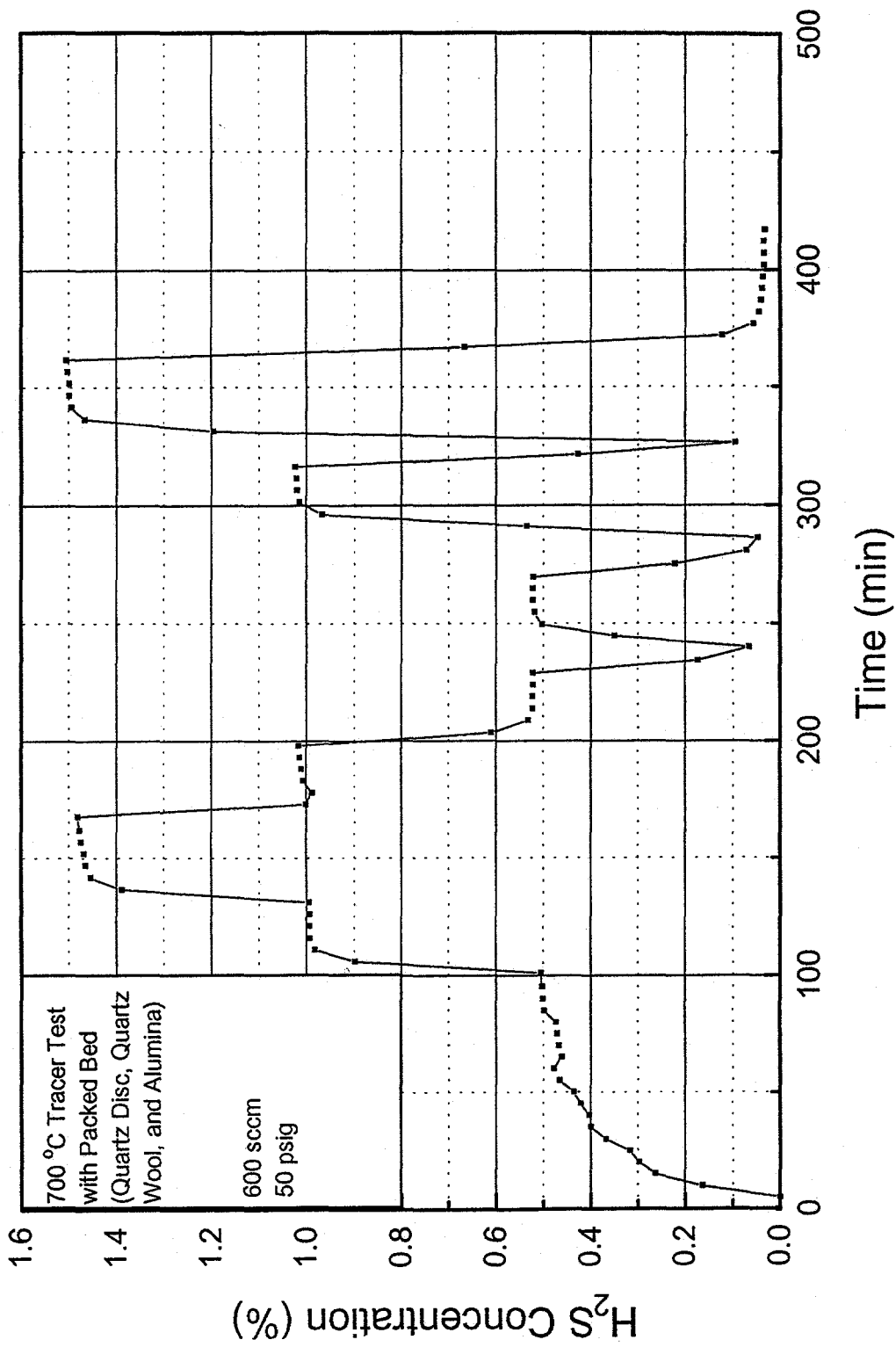Figure 4. The Quartz Reactor Insert

Conducting Head

-018 O-ring

Quartz Insert

-219 O-ring

Supporting Ring

3 dimples at 120 degree to support quartz frit

Pressure Vessel

Figure 5.   Results of a Non-Reacting Tracer Test Using the Quartz Insert

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feed rate was 600 sccm and the reactor pressure was 50 psig. Reactor temperature and pressure were first established in a H₂S-free mixture of N₂ and H₂. At $t=0$ H₂S flow was initiated at a rate sufficient to provide 0.5% H₂S in the feed gas. The reactor product was sampled at 5 min intervals. After a brief lag, the H₂S content increased and reached 0.4% after 35 minutes. A total of 85 minutes was required before the product gas concentration reached 0.5%. At 100 minutes, the feed rate of H₂S was increased to provide a feed composition of 1.0% H₂S. The response of the reactor product composition was much faster than initially. The H₂S content of the product increased to 0.9% within 5 minutes of the feed composition change and to 0.98% after 10 minutes. As shown in Figure 5, the response to subsequent step changes in the feed was quite rapid. Only the initial response was sluggish. We interpret the initial behavior as being caused by adsorption of H₂S on the walls of the feed and product lines. Once an adsorbed layer is formed, the response is quite rapid. The response illustrated in Figure 5 was typical of all the nonreacting tracer - response tests.

Table 8 compares the measured steady-state H₂S percentages to the feed H₂S percentages as a function of temperature. The feed percentages is column 1 were established by the mass flow controller settings. Test temperature is reported in column 2 while the number of measurements at each temperature - composition combination is found in column 3. Column 4 indicates that 0.5% and 1.0% H₂S values were approached from both larger and smaller H₂S values. 1.5% H₂S was approached only from below while 0.0% H₂S was approached only from above. Columns 5, 6, and 7 contain the minimum, maximum, and average steady-state compositions, while the standard deviation from the average presented in column 8. Finally, the percentage deviation of the average steady-state composition measured by the GC from the mass flow controller settings is found in the last column. There was little, if any, effect of temperature which indicated that reaction of H₂S was no longer a significant problem. In fact, the high temperature values were actually closer to the mass flow controller settings than the ambient temperature measurements.

Having established that the quartz insert and o-rings operated properly at high temperature and that the extent of reaction between H₂S and the reactor system walls was negligible, CeO₂ sulfidation tests were initiated. Three sulfidation tests were completed during the quarter and reaction conditions are summarized in Table 9. In each test the feed gas contained 1% H₂S, 10% H₂, balance N₂; approximately 6 grams of CeO₂ sorbent were used. The CeO₂ was mixed with an equivalent amount of Al₂O₃ in the first and third runs but no Al₂O₃ was added in the second. Sulfidation temperature was 700°C in the first run and 800°C in the second and third, while the volumetric flow rate of the feed gas was 600 sccm in the first run and 400 sccm in the second and third. The average reaction pressures of 2.9 atm and 4.7 atm in the first and third runs were established solely by the bed pressure drop. In the first run the inlet and outlet pressures were 4.8 and 1.0 atm to give the average pressure of 2.9 atm. Similarly, the inlet and outlet pressure of 8.4 and 1 atm in the third run produced the average pressure of 4.7 atm. Removing the Al₂O₃ in the second run reduced the bed pressure drop so that the inlet and outlet pressures were approximately equal and the reactor pressure of 2.7 atm was established using the back pressure regulator. The implications of the variations in the bed pressure drop are discussed more fully in the following.

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Table 8. Comparison of Steady-State H$_2$S Compositions from Mass Flow Controller Settings and Measured by the Gas Chromatograph

% H$_2$S Mass Flow Controllers	Temp., °C	Number of Measurements N	Direction of Approach Above or Below	GC Composition, % H$_2$S				% Dev. from Mass Flow Controllers
				Minimum	Maximum	Average	Std. Dev.	
0.0	25	8	Above	0.02	0.03	0.03	0.00	--
	400	3	Above	0.04	0.05	0.04	0.01	--
	700	2	Above	0.04	0.05	0.04	0.01	--
0.5	25	12	Both	0.39	0.51	0.46	0.03	-8.0
	400	3	Both	0.44	0.52	0.48	0.05	-4.0
	700	6	Both	0.50	0.52	0.51	0.01	+2.0
1.0	25	11	Both	0.87	0.99	0.94	0.04	-6.0
	400	3	Both	0.93	1.03	0.99	0.06	-1.0
	700	6	Both	1.00	1.03	1.01	0.01	+1.0
1.5	25	7	Below	1.38	1.47	1.42	0.04	-5.3
	400	2	Below	1.45	1.52	1.48	0.05	-1.3
	700	4	Below	1.48	1.52	1.50	0.02	0.0

Table 9. Summary of Fixed Bed Reactor Test
Conditions: CeO_2 Sulfidation, September 1996

Run	Ce01s	Ce02s	Ce03s
Date	9/20	9/27	9/30
Reactor Packing			
CeO_2, g	6.00	5.99	6.07
Al_2O_3, g	6.00	--	6.00
Reaction Conditions			
Temp., °C	700	800	800
Press., atm*	2.9	2.7	4.7
Gas Comp.			
% H_2S	1.0	1.0	1.0
% H_2	10.0	10.0	10.0
% N_2	89.0	89.0	89.0
Gas Flow, sccm	600	400	400

*Pressure is the average between the reactor inlet and outlet.

Run CeO1s

The mol fraction of H_2S in the product gas as a function of time for sulfidation run CeO1s and a nonreacting tracer test at the same conditions are shown in Figure 6. In the reaction test (solid line) no H_2S was detected in the first ten minutes; thereafter the H_2S concentration increased and reached a steady-state value of 0.97% after 3.3 hours. The H_2S concentration was zero for only the first five minutes in the nonreacting test and the H_2S concentration increased more quickly to a steady-state value of 0.98% after 1.5 hours. The area between the two curves is proportional to the amount of H_2S removed by the reaction

$$2 \; CeO_2 + H_2S + H_2 \rightarrow Ce_2O_2S + 2 \; H_2O.$$
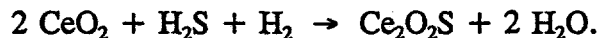
Numerical integration of this area showed that the total amount of H_2S reacted was 104% of the stoichiometric quantity. Thus, the sulfur material balance closure was quite good. However, the global rate of reaction, which is qualitatively measured by the slope of the breakthrough curve, was smaller than desired.

The quartz reactor insert provides an added advantage in that the reactor packing was visible after the insert was removed from the pressure vessel. Color gradients between the light brown Ce_2O_2S and white Al_2O_3 were clearly visible. Nonuniform mixing of the initial CeO_2 and Al_2O_3 may have contributed to the small slope of the breakthrough curve by allowing gas to bypass the sorbent.

Run CeO2s

Three significant changes were made in the operating conditions of run CeO2s, all aimed at increasing the global reaction rate, minimizing the opportunity for gas bypassing, and reducing the bed pressure drop. Omission of Al_2O_3 was intended to eliminate the solids mixing problem and reducing the bed pressure drop. The decreased volumetric feed rate was also expected to contribute to lower pressure drop. Finally, the reaction temperature was increased to 800°C in an effort to increase the global reaction rate.

Breakthrough curves under both reacting and nonreacting conditions are shown in Figure 7. Bed pressure drop was decreased and reactor pressure was controlled by the back pressure regulator as previously discussed. However, there was little improvement in the shape of the breakthrough curve. The duration of the prebreakthrough period increased to 20 min. but the slope of the breakthrough curve was smaller than in run CeO1s. The H_2S content of the reaction product gas approached a steady-state value of 0.92% after 4.9 hours. The sulfur material balance, as measured by the cross-hatched area between the reaction and tracer curves, was again quite good, corresponding to 105% of the stoichiometric sulfur.

The decrease in the slope of the breakthrough curve is again believed to be associated with gas bypassing, this time due to solid sintering. The pressure drop was significantly smaller than could be accounted for by the absence of Al_2O_3 and the reduced volumetric flow rate. At
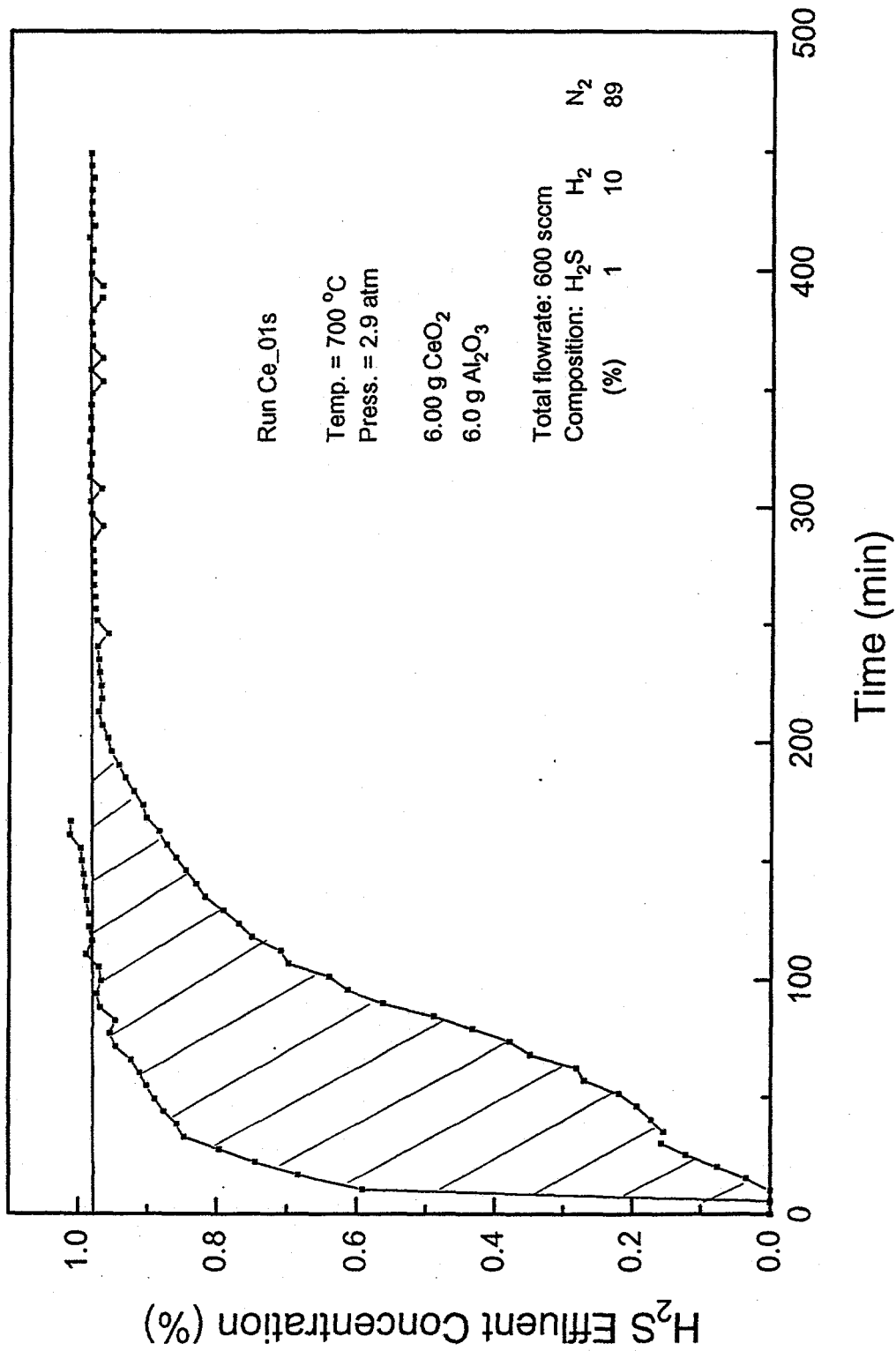
Figure 6. Fixed-Bed Reactor Response: Run Ce-01s

H₂S Effluent Concentration (%)

Run Ce_02s

Temp. = 800 °C
Press. = 2.7 atm

5.99 g CeO₂
6.0 g Al₂O₃

Total flowrate: 400 sccm
Composition: H₂S   H₂   N₂
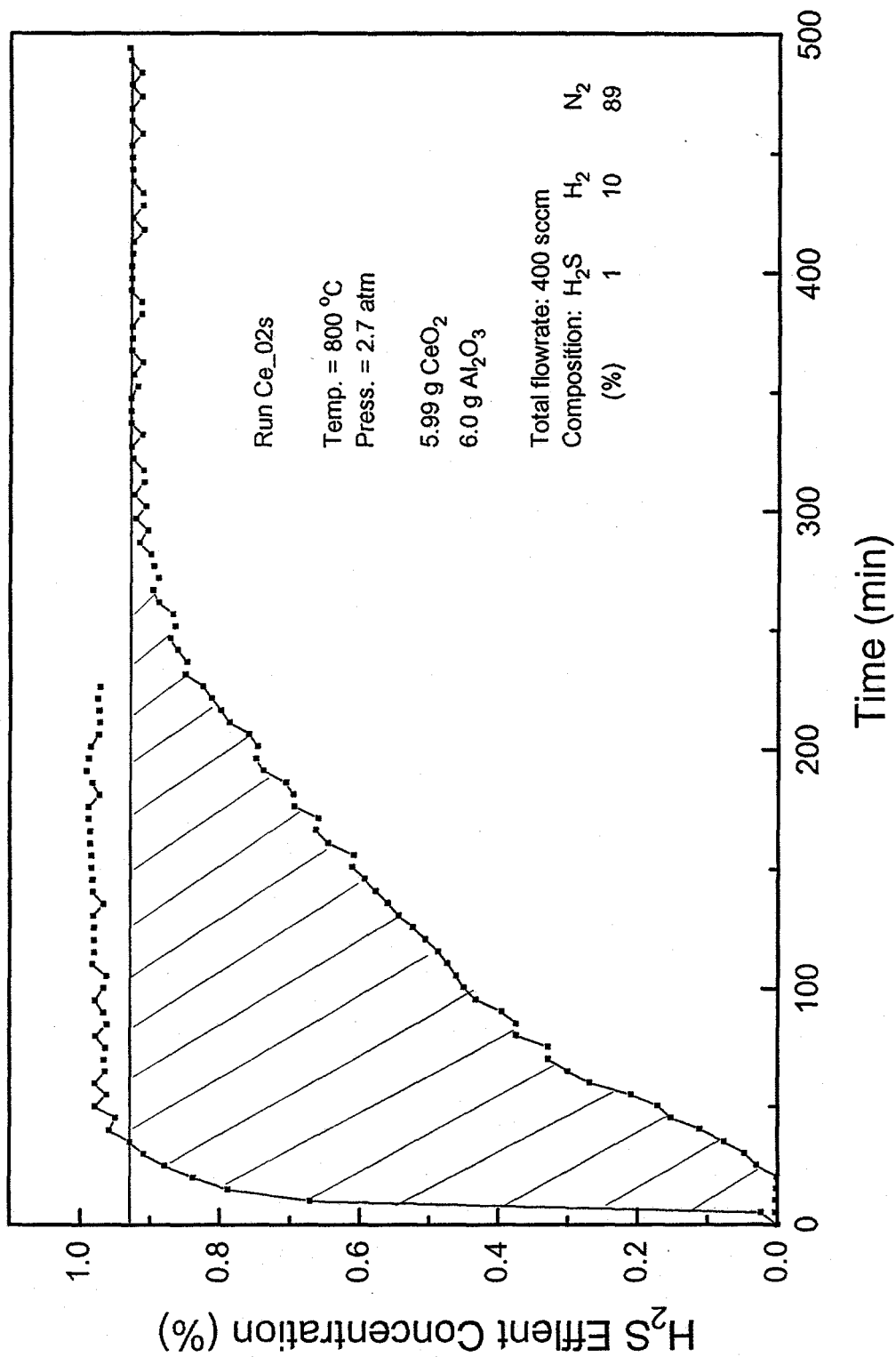   (%)   1   10   89

Time (min)

Figure 7. Fixed-Bed Reactor Response: Run Ce-02s

the conclusion of the run the solid slid out of the insert tube as a single cylinder which suggests sintering and the possibility of gas bypassing around the circumference of the bed. In other tests, the solid fit tightly into reactor insert and had to be carefully removed. Increased sintering due to the removal of Al_2O_3 was not expected since the 2600°C melting temperature of CeO_2 is about 500°C higher than the melting temperature of Al_2O_3. This, coupled with the observable decrease in the slope of the breakthrough curve at 1.3 hours, suggests that sintering was associated with the formation of Ce_2O_2S.

Run Ce03s

Equal masses of CeO_2 and Al_2O_3 were again used in order to minimize sintering, and extra care was taken to achieve intimate mixing of the CeO_2 and Al_2O_3. Otherwise, reaction conditions in runs Ce02s and Ce03s were the same. The bed pressure drop again increased to the point that the back pressure regulator was not used.

The changes had the desired effect on the breakthrough curve as shown in Figure 8. H_2S in the product gas remained near zero for about 45 minutes. This was followed by an unexpected plateau in the H_2S content at about 0.09% which lasted for another hour. Then the slope of the breakthrough curve became quite large and the steady-state H_2S level of 0.92% was reached after a total elapsed time of two hours. The quarter ended before the non-reacting tracer test at these conditions was completed. Consequently, sulfur material balance data for the run is not yet available.

PROCESS MODELING

The process modeling phase of the project was initiated during the quarter. Three desulfurization processes with elemental sulfur recovery are being considered. Two processes utilize CeO_2 for bulk H_2S removal followed by a zinc titanate polishing step. CeO_2 is not thermodynamically capable of reducing H_2S to the desired 100 ppmv level, and the secondary desulfurization using zinc titanate is required. In one process, Ce_2O_2S regeneration is accomplished by reaction with steam to produce H_2S, followed by elemental sulfur production using the Claus process. In the other, Ce_2O_2S is regenerated by reaction with SO_2 for the direct production of elemental sulfur. In the third process, H_2S is removed in a single desulfurization stage using zinc titanate. Regeneration of ZnS is accomplished in the traditional manner to produce SO_2, which is then reduced to elemental sulfur using the direct sulfur recovery process (DSRP). This third process will serve as the reference point against which the two CeO_2 processes will be compared.

16,987 lb mol/hr of coal gas whose composition (see Table 10) is similar to the product from a Shell gasifier has been chosen for each process. The flow rate is equal to that used in a recent DOE-sponsored process study by Buchanan et al. (1994). The highly reducing gas composition is necessary since the desulfurization thermodynamics of CeO_2 are not satisfactory in a low-Btu, high steam content gas.
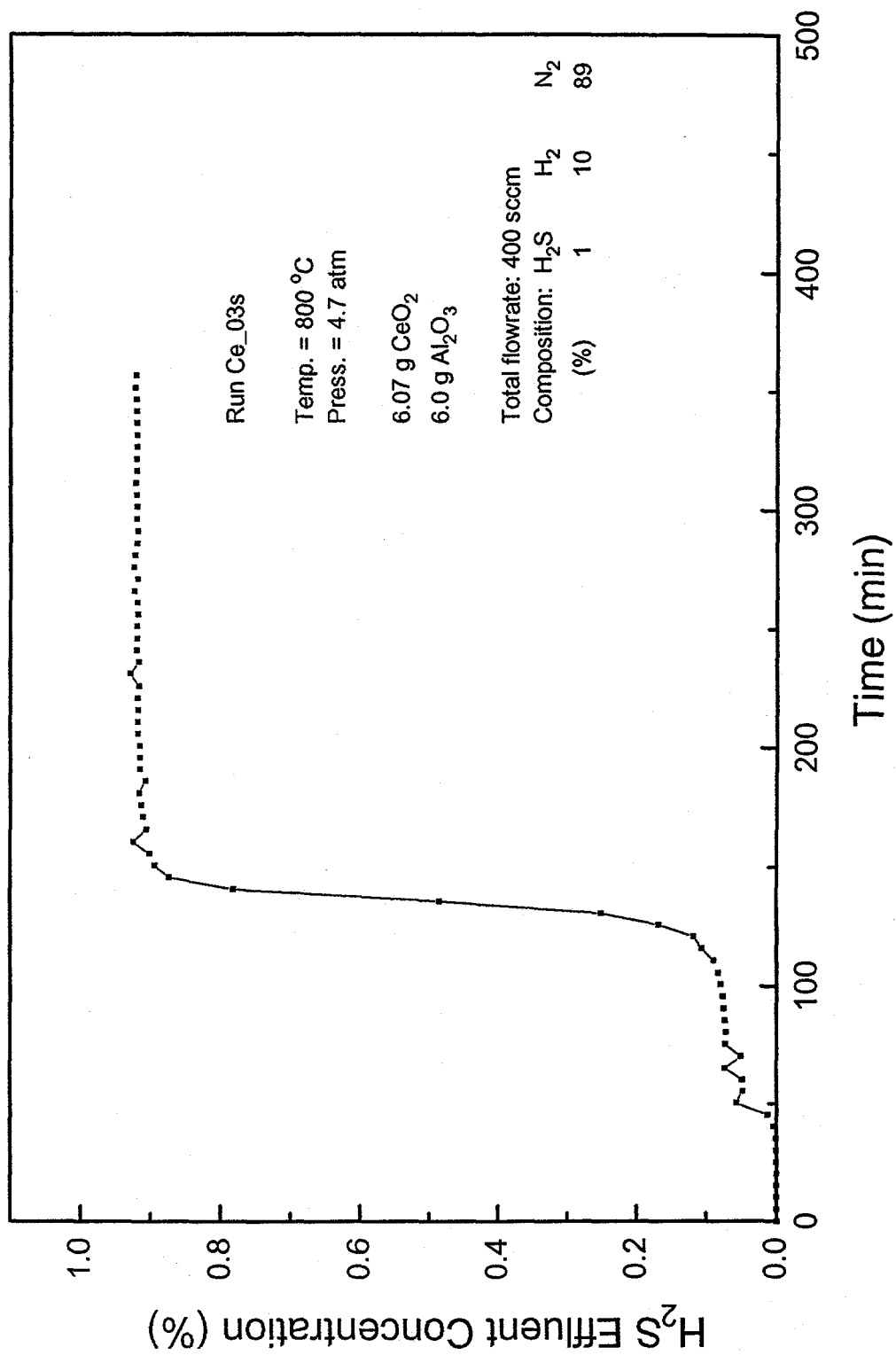
25

Figure 8. Fixed-Bed Reactor Response: Run Ce-03s

Table 10. Composition of the Coal
Gas Used in the Process
Analysis Studies

Component	Mol Fraction
CO	0.60
H_2	0.29
CH_4	0.00
CO_2	<0.02
H_2O	0.05
H_2S	0.01
N_2	0.03
Other	<0.01

Two Stage Desulfurization Using CeO_2 With Steam Regeneration

A flow diagram of this process is shown in Figure 9. The major process streams are identified in Table 11 and the stream numbers are coordinated with those in Figure 10. Coal gas (stream 1) enters the primary sorber where the majority of the H_2S is removed by reaction with CeO_2 to form Ce_2O_2S. Partially desulfurized coal gas (stream 2) then enters the secondary sorber where the sulfur content is reduced to less than 100 ppmv by reaction with zinc-titanate. The desulfurized coal gas product (stream 11) is then sent to the power generation section of the IGCC process.

Spent sorbent from the primary sorber (stream 3) is transferred to the primary regenerator where it reacts with steam (stream 8). Regenerated sorbent (stream 4) is recycled to the primary sorber as stream 14 after an appropriate discharge (stream 15) and make-up of sorbent (stream 12) required to maintain activity. Spent sorbent from the secondary sorber (stream 10) is transferred to the secondary regenerator where it is mixed with oxygen (stream 23) and steam (stream 16). Regenerated sorbent (stream 9) is recycled (stream 19) after appropriate discharge (stream 20) and fresh sorbent make-up (stream 21). The oxygen is presumed to be available from the air separation plant associated with the gasifier while steam will be generated by heat recovery within the desulfurization process. A more complete energy balance including heat recovery and steam generation is planned for the future. Secondary regenerator off-gas (stream 17) is recycled to the gasifier. There the SO_2 will be reduced to H_2S and then recycled with the coal gas feed (stream 1).

The gas product from the primary regenerator (stream 5), which contains the majority of the sulfur in the coal gas feed (stream 1), passes through a condenser where excess steam is condensed along with some dissolved H_2S (stream 6). The remaining gases (stream 7) flow to a hydrogen separator where essentially pure H_2 (stream 33) is separated from the H_2S-rich gas (stream 34). H_2S containing gases from the hydrogen separator (stream 34), the sour water stripper (steam 48), and recycle from the tail gas unit (stream 41) are mixed with air (stream 25) in the Claus reactor where the majority of the H_2S is converted to elemental sulfur. Claus reactor product (stream 37) flows into a condenser for removal of the elemental sulfur product (stream 32). The Claus reaction is equilibrium limited and appreciable amounts of H_2S and SO_2 remain in the gaseous product (stream 31) from the condenser. This stream is fed to an SO_2 reduction reactor along with a portion of the H_2 product (stream 40) from the hydrogen separator. SO_2 is reduced to H_2S and the product (stream 39) is fed to a sulfur tail-gas unit where the H_2S is separated and recycled to the Claus reactor (stream 41). H_2S is removed in the tail gas unit by amine scrubbing and the solvent make-up is represented by stream 50. Gaseous discharge from the tail gas unit (stream 47) consists primarily of N_2 which was fed with air to the Claus reactor (stream 25). Water is formed as a reaction product in the SO_2 reduction unit and this water is removed as a liquid discharge (stream 36) from the tail gas unit.
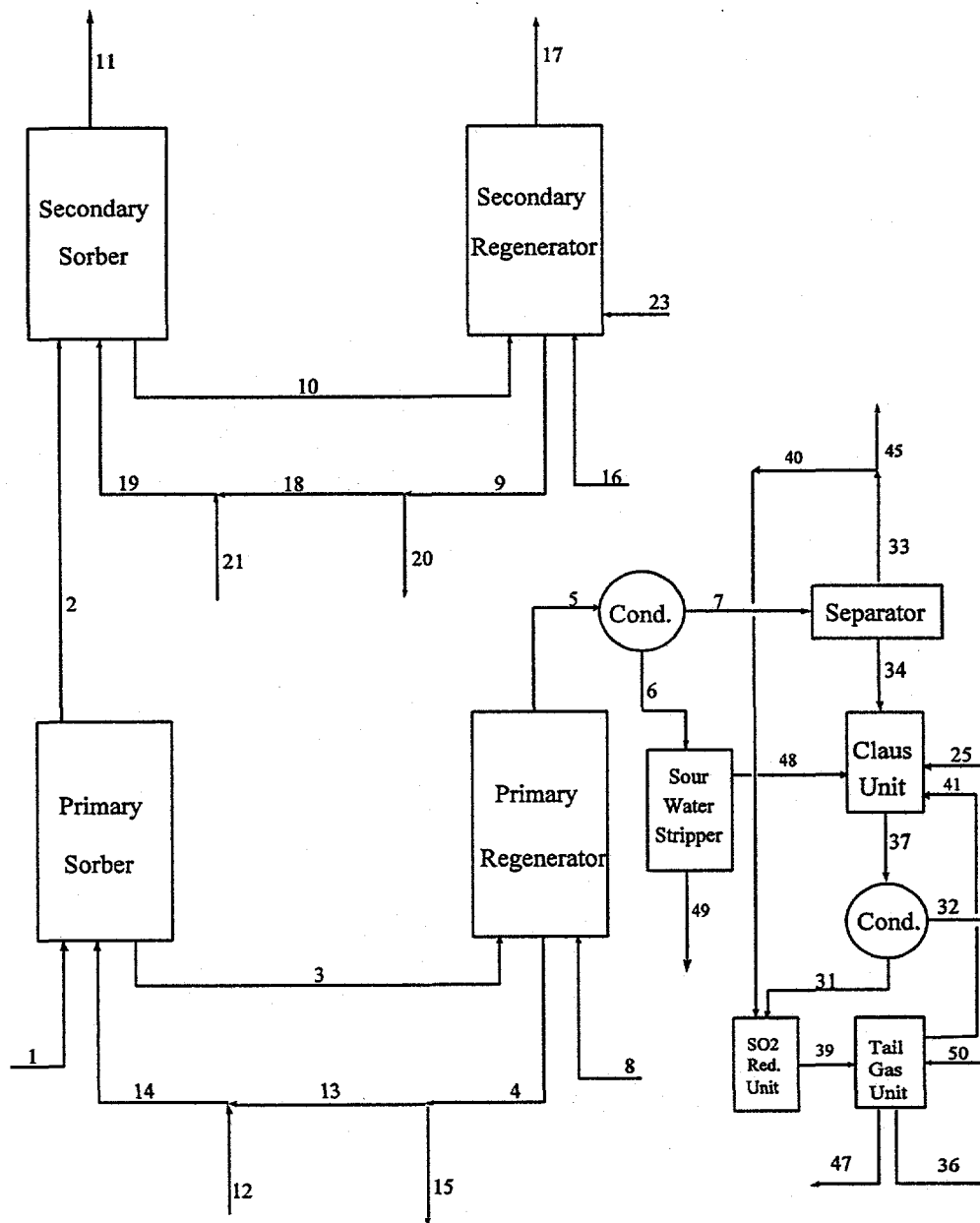
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Figure 10. The Two-Stage Desulfurization Process
Using Steam Regeneration

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. Sour Water Condensate
7. Feed Gas 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 Make-up
13. Recycled Primary Sorbent
14. Total Sorbent Feed to Primary Sorber
15. Spent Primary Sorbent Discharge
16. Steam to Secondary Regenerator
17. Secondary Regenerator Outlet Gas (recycled to gasifier)
18. Recycled Secondary Sorbent
19. Total Sorbent Feed to Secondary Sorber
20. Spent Secondary Sorbent Discharge
21. Secondary Sorbent Make-up
23. Oxygen to Secondary Regenerator
25. Air to Claus Reactor
31. Claus Unit Tail Gas
32. Elemental Sulfur Product
33. Hydrogen from Gas Separator
34. Claus Reactor Feed Gas
36. Discharge Gas from Sulfur Tail Gas Unit
37. Product Gas from Claus Reactor
39. Gas Feed to Sulfur Tail Gas Unit
40. Hydrogen Feed to Sulfur Reduction Unit
41. Product Gas from Tail Gas Stripper
45. Hydrogen Product Gas
47. Water Discharge from Tail Gas Unit
48. H_2S Product from Sour Water Stripper
49. Water Discharge from Sour Water Stripper
50. Solvent Make-up to Tail Gas Unit

Two-Stage Desulfurization Using CeO₂ With SO₂ Regeneration

The schematic flow diagram for this option is shown in Figure 11 and the streams are identified in Table 12. The portion of the flow diagram involving the primary sorber and primary and secondary regenerators are effectively the same as in the steam regeneration process. Major changes are associated with the primary regenerator and downstream units.

As before, spent sorbent from the primary sorber (stream 3) is transferred to the primary regenerator where recycled SO_2 (stream 22) and sub-stoichiometric oxygen (stream 8) are added. Regenerated sorbent is recycled to the primary sorber, again with appropriate discharge and make-up to retain constant reactivity. Product gas from the primary regenerator (stream 5) contains elemental sulfur and excess SO_2. The elemental sulfur product (stream 32) is removed by condensation and the excess SO_2 flows through a recycle compressor and back to the primary regenerator.

Single-Stage Desulfurization With Sulfur Recovery Using DSRP

Modeling of the single-stage desulfurization process using zinc titanate sorbent with elemental sulfur recovery using DSRP was initiated just before the end of the quarter. A flow diagram of the process is shown in Figure 12 while each stream is identified in Table 13. This process flow sheet is based upon work reported by researchers at the Research Triangle Institute.

The coal gas feed (stream 1) is split with the majority flowing to the zinc titanate desulfurization reactor (stream 2) and the remainder (stream 3) fed to the DSRP reactor. The zinc titanate is responsible for reducing the H_2S content of the coal gas to less than 100 ppmv in the desulfurized coal gas (stream 11) which is fed to the power generation section of the IGCC process. Spent sorbent (stream 9) is transferred to the regenerator where it is mixed with air (stream 10) and nitrogen diluent (stream 15). ZnS is converted back to ZnO which, with proper discharge (stream 6) and make-up (stream 5) to maintain reactivity, is recycled to the sorber (stream 4). Diluent N_2 is assumed to be available from the air separation plant associated with the gasifier.

Off-gases from the regenerator (stream 12), which contain SO_2, are mixed with the coal gas slip stream (stream 3) in the DSRP reactor where SO_2 is reduced to elemental sulfur. Elemental sulfur product (stream 32) is separated by condensation and the off-gases are recycled to the sorber (stream 14). [Author's note: The location of the recycle stream 14 is in error in Figure 12. Actually, this nitrogen-rich stream will be recycled to the regenerator instead of the sorber. This error was identified after the quarter ended, and will be corrected in the next monthly report.]

Material and Energy Balance Case Studies

Material and energy balance calculations for 12 case studies -- all utilizing CeO₂ for primary desulfurization with 6 using H_2O/Claus regeneration and 6 using SO_2 regeneration --
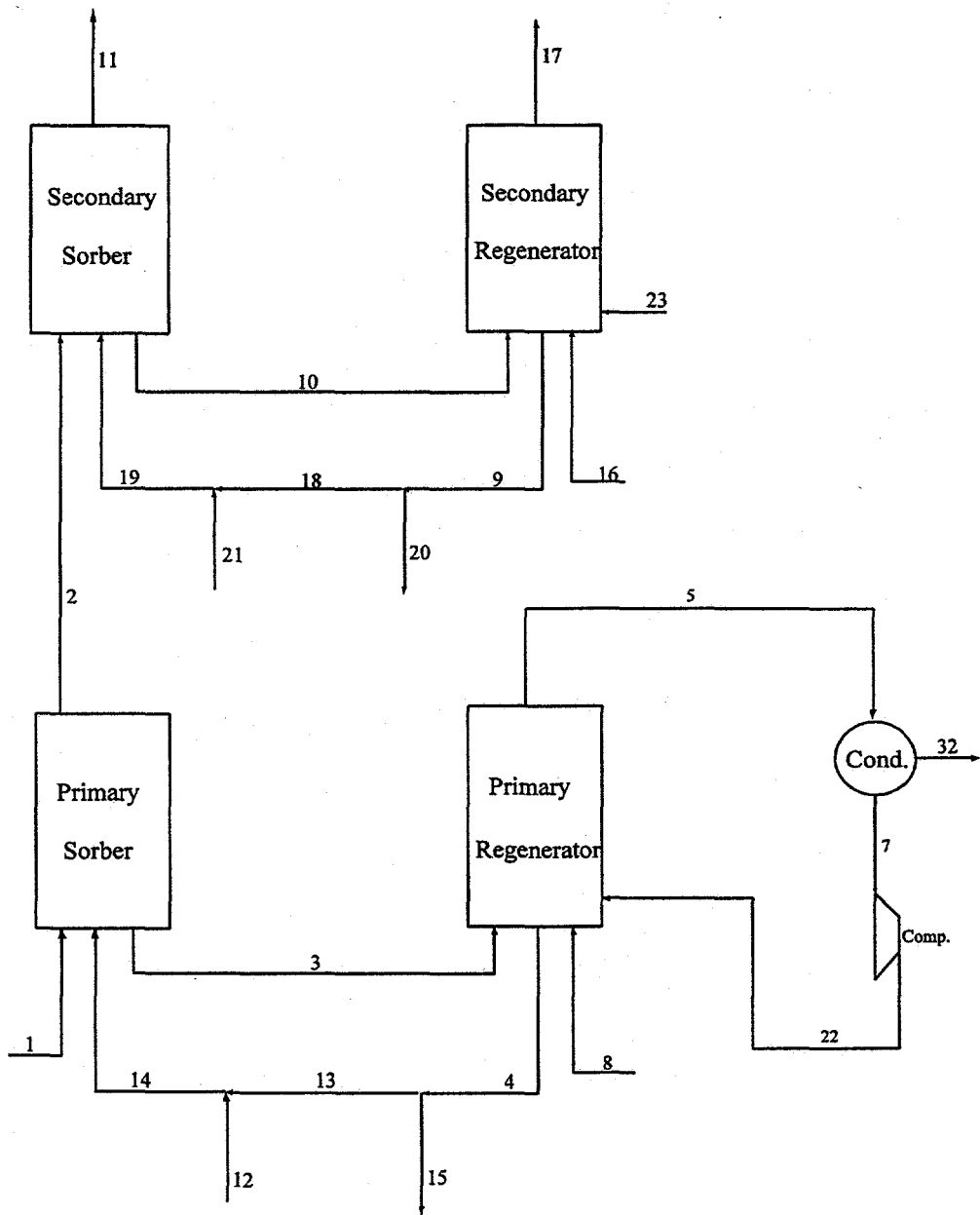
Figure 11. The Two–Stage Desulfurization
Process Using SO$_2$ Regeneration

Table 12. Description of the Streams Associated
With the SO_2 Regeneration 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
7. SO_2 from Elemental Sulfur Condenser
8.   Oxygen to Primary Regenerator
9.   Sorbent from Secondary Regenerator
10. Sulfided Sorbent from Secondary Sorber
11. Desulfurized Coal Gas
12. Primary Sorbent Make-up
13. Recycled Primary Sorbent
14. Total Sorbent Feed to Primary Sorber
15. Spent Primary Sorbent Discharge
16. Steam to Secondary Regenerator
17. Secondary Regenerator Outlet Gas (recycled to gasifier)
18. Recycled Secondary Sorbent
19. Total Sorbent Feed to Secondary Sorber
20. Spent Secondary Sorbent Discharge
21. Secondary Sorbent Make-up
22. Recycled SO_2 to Primary Regenerator
23. Oxygen to Secondary Regenerator
32. Elemental Sulfur Product
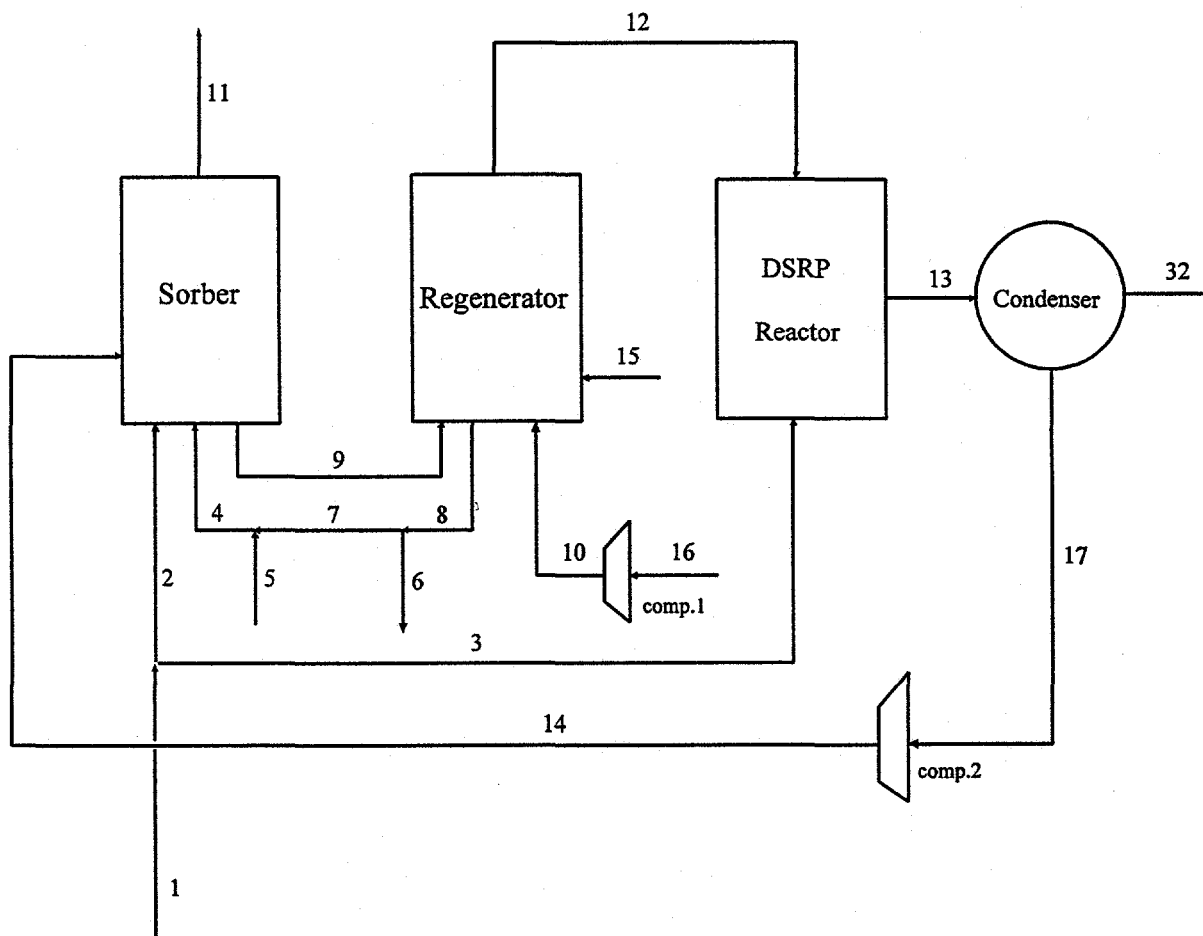
Figure 12.   The Single–Stage Desulfurization
Process With DSRP

Table 13. Description of the Streams Associated
With the Direct Sulfur Recovery Process

1.   Coal Gas from Gasifier
2.   Coal Gas to Sorber
3.   Slipstream of Coal Gas to the DSRP Reactor
4.   Sorbent Feed to Sorber
5.   Sorbent Make-up
6.   Spent Sorbent Discharge
7.   Recycled Regenerated Sorbent
8.   Regenerated Sorbent
9.   Sulfided Sorbent to Regenerator
10.   High Pressure Air to Regenerator
11.   Desulfurized Coal Gas
12.   Regenerator Product Gas
13.   DSRP Reactor Product Gas
14.   Recycle Gas From Sulfur Condenser
15.   Nitrogen Diluent to Regenerator
16.   Ambient Air
32.   Elemental Sulfur Product

have been completed. These are not considered to be final results; additional refinements are planned for the future. Work on the single-stage zinc titanate desulfurization with DSRP was initiated near the end of the quarter and no material and energy balance studies on this option have been completed.

The material and energy balances were based on the following assumptions. The assumptions in items 1 through 7 apply equally to both regeneration concepts.

1. The temperature of the coal gas to the desulfurization block was fixed at 800K. This implies that the coal gas would have been cooled for particulate removal prior to entering the desulfurization block. Case studies were run based on desulfurization pressures of both 15 and 25 atm, and the coal gas was assumed to be available at the operating pressure.

2. H_2S removal in both the primary and secondary sorbers was calculated based on the achievement of thermodynamic equilibrium at the specified temperature and pressure. No reactions other than desulfurization were allowed to occur.

3. All reactors were assumed to operate isothermally at the specified temperature. Thus, the energy balance reports the quantity of heat which must be added or removed in each reactor in order to maintain the specified isothermal temperature.

4. Spent sorbent discharge, streams 15 and 20 in Figures 11 and 12, and make-up, streams 12 and 21 in the figures, from both the primary and secondary desulfurization steps are fixed at 1% of the sorbent circulation rates. These rates are very important in cost estimation but do not affect the material balance of other process streams.

5. Sorbent feed rates to the primary and secondary sorbers, streams 14 and 19 in both figures, provide 100% excess of the stoichiometric amount required complete removal of all H_2S in the feed. Sorbent utilization (fractional conversion), therefore, is approximately 50% for each case. Complete regeneration of both the primary and secondary sorbents is also assumed.

6. The mol fraction of O_2 in the secondary regeneration feed gas was fixed at 0.03 with the balance being steam diluent. No N_2 diluent is permitted since the regeneration off-gas is to be recycled to the oxygen-blown gasifier.

7. The oxygen feed rate to the secondary regenerator, stream 23 in Figures 10 and 11, is set at 10% excess of the stoichiometric amount required for complete ZnS regeneration. This oxidation reaction is, for practical purposes, irreversible.

The following assumptions apply only to the design cases involving steam regeneration.

8. The steam feed rate to the primary regenerator, stream 8 in Figure 10, is 10% greater than the thermodynamic minimum required for complete Ce_2O_2S regeneration. Since the

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thermodynamic minimum greatly exceeds the stoichiometric minimum, this provides for a large stoichiometric excess of steam to the primary regenerator.

9. The temperatures of the products from the condenser located downstream of the primary regenerator, streams 6 and 7 in Figure 10, are set at 350K.

10. The hydrogen separator is assumed to operate with 90% recovery of pure H_2, stream 33 in Figure 10.

11. The flow rate of H_2 to the SO_2 reduction reactor, stream 40 in Figure 10, is set at 10% excess of the stoichiometric amount required to reduce all SO_2 and O_2 in stream 31 to H_2S.

12. The flow rate of air to the Claus reactor, stream 25 in Figure 10, is 10% greater than the stoichiometric amount needed to convert all H_2S fed in streams 34, 41, and 48 to elemental sulfur as well as to burn all H_2 in stream 34 to H_2O.

The twelve design cases differ in the specified operating temperatures and pressures in the primary and secondary sorbers and regenerators. The temperature and pressure combinations ranged from 800 to 100K and from 15 to 25 atm as indicated in Table 14. In most cases, the design was based on equal temperatures and pressures in the primary and secondary units. Temperature differences between the primary sorber and regenerator in cases 8, 9, and 12 involving SO_2 regeneration were necessary to avoid condensation of elemental sulfur inside the regenerator. A lower primary regenerator temperature was used in case 4 to get some idea of the effect of unequal temperatures.

Material balance results for the six case studies using steam regeneration are summarized in Table 15. The flow rates, in units of lb-mol/hr, of all overall process input and output streams are included. The flow rates of coal gas (stream 1) and desulfurized coal gas (stream 11) are equal and are constant for each of the design cases. Similarly, the primary sorbent make-up (stream 12) and discharge (stream 15) are equal and constant. Secondary sorbent make-up (stream 21) and discharge (stream 20) rates are equal and are independent of pressure, but increase as the temperature of the primary sorber decreases. The reaction between CeO_2 and H_2S is endothermic, and the amount of sulfur removed in the primary sorber decreases with decreasing temperature. The reaction between ZnO and H_2S is exothermic. Consequently, both the amount of H_2S to the secondary sorber and the H_2S removal efficiency in the secondary sorber increase with decreasing temperature. The required steam flow to the primary regenerator (stream 8) and the condensate flow from the primary regenerator condenser (stream 6) decrease with decreasing temperature since less sulfur is removed in the primary sorber. In response, the flow rates of oxygen and steam to the secondary regenerator (streams 16 and 23) and the flow rate of the secondary regenerator off-gas (stream 17) increase because of the increased sulfur load to the secondary sorber.

The flow rate of air to the Claus reactor (stream 25) and the production rates of hydrogen (stream 33) and elemental sulfur (stream 32) all decrease with decreasing temperature because

Table 14. Temperature and Pressure Combinations Chosen for
the LSU Material and Energy Balance Case Studies

Case	Primary Regeneration Concept	Primary Sorber		Primary Regenerator		Secondary Sorber		Secondary Regenerator	
		T,K	P,atm	T,K	P,atm	T,K	P,atm	T,K	P,atm
1	Rxn with H_2O	1000	25	1000	25	1000	25	1000	25
2		900	25	900	25	900	25	900	25
3		800	25	800	25	800	25	800	25
4		1000	15	800	15	1000	15	1000	15
5		900	15	900	15	900	15	900	15
6		800	15	800	15	800	15	800	15
7	Rxn with SO_2	1000	25	1000	25	1000	25	1000	25
8		900	25	930	25	900	25	900	25
9		800	25	930	25	800	25	800	25
10		1000	15	1000	15	1000	15	1000	15
11		900	15	900	15	900	15	900	15
12		800	15	900	15	800	15	800	15

Table 15. Summary of the Material Balance Results for the
Case Studies Using Steam Regeneration

Stream Flow Rates, lb-mol/hr

Case Study Number	1	2	3	4	5	6
Input Streams						
1. Coal Gas From Gasifier	16987	16987	16987	16987	16987	16987
12. Primary Sorbent Make-up	6.9	6.9	6.9	6.9	6.9	6.9
21. Secondary Sorbent Make-up	0.1	0.2	0.4	0.1	0.2	0.4
8. Steam to Primary Regenerator	1264	996	714	840	996	714
16. Steam to Secondary Regenerator	549	968	1865	549	968	1865
23. Oxygen to Secondary Regenerator	17	30	58	17	30	58
25. Air to Claus Reactor	526	501	447	526	501	447
50. Make-up Solvent to Tail Gas Unit	0.01	0.01	0.01	0.01	0.01	0.01
Output Streams						
11. Desulfurized Coal Gas	16987	16987	16987	16987	16987	16987
15. Primary Sorbent Discharge	6.9	6.9	6.9	6.9	6.9	6.9
20. Secondary Sorbent Discharge	0.1	0.2	0.4	0.1	0.2	0.4
17. Secondary Regenerator Off-Gas	561	989	1906	561	989	1906
49. Water From Sour Water Stripper	936	683	435	508	679	431
45. Hydrogen Product	108	103	92	108	103	92
32. Elemental Sulfur Product	256	244	218	259	247	220
36. Gas Discharge from Sulfur Tail Gas Unit	426	406	362	426	406	362
47. Liquid Discharge from Tail Gas Unit	120	114	102	121	116	103

Table 16. Summary of Sulfur Material Balance Results for the LSU Case Studies Using Steam Regeneration

Case Study Number	Sulfur Flow Rate, lb_m/hr					
	1	2	3	4	5	6
Sulfur Input Stream (Sulfur Form)						
1. Coal Gas From Gasifier (H_2S)	5498	5498	5498	5498	5498	5498
Sulfur Output Streams (Sulfur Form)						
11. Desulfurized Coal Gas (H_2S)	17	7	3	17	7	3
17. Secondary Regenerator Off-Gas (SO_2)	329	581	1119	329	581	1119
32. Elemental Sulfur Product (S)	5149	4907	4374	5149	4907	4374
36. Sulfur Tail Gas Unit Off-Gas (H_2S)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
47. Water Discharge from Tail Gas Unit (H_2S)	2	2	2	2	2	2
49. Water Discharge from Sour Water Stripper (H_2S)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

of the smaller amount of H_2S removed in the primary sorber. These flow rates all increase marginally at lower pressure. Both the gas and liquid discharge rates from the tail gas (streams 36 and 47) unit decrease with decreasing temperature because of the reduced sulfur removal in the primary sorber. Both streams are effectively independent of pressure. The make-up solvent to the tail gas unit (stream 50) is quite small and is necessary only to replace the amount of solvent lost in the tail gas unit discharge streams.

The overall sulfur balance associated with steam regeneration is summarized in Table 16. The rates are expressed in units of lb/hr as elemental sulfur. 5498 lb/hr of sulfur as H_2S enter the process with the coal gas. Elemental sulfur is recovered in stream 32 at a rate which decreases with decreasing temperature and is independent of pressure. The percentage recovery of elemental sulfur ranges from a high of 93.6 for design cases 1 and 4 to a low of 79.6% in cases 3 and 6. The majority of sulfur not captured as elemental sulfur emerges from the process in the secondary regenerator off-gas (stream 17). In an actual process this is not discharged but is recycled to the gasifier so that it would reappear as additional H_2S in the coal gas feed (stream 1), and most would eventually be removed as elemental sulfur. However, including this H_2S recycle would require that the gasifier be incorporated into the overall process, which is beyond the scope of the study. As a rough approximation, we could assume that all of this sulfur would eventually be captured as elemental sulfur, in which case the overall elemental sulfur recovery would be well in excess of 99% in all of the design cases.

Actual discharge of sulfur compounds from the process is limited to that in the desulfurized coal gas (stream 11) and in liquid discharge streams from the sour water stripper (stream 49) and the tail gas unit (stream 47) and the gas discharge stream from the tail gas unit (stream 36). The combined sulfur in these streams ranges from about 5 lb/hr in cases 3 and 6 to 17 lb/hr in cases 1 and 4. These quantities represent from about 0.09% to 0.3% of the total sulfur fed. The H_2S concentrations in the desulfurized coal gas (stream 11) range from 5 to 31 ppmv, depending on the operating temperature of the secondary sorber. Actual concentrations will, of course, be somewhat larger since the reported concentrations are based on thermodynamic equilibrium. However, a reasonable approach to equilibrium should result in the target concentration of 100 ppmv being met.

Material balance results for the six case studies using SO_2 regeneration are summarized in Table 17. As before, the flow rates, in units of lb mol/hr, of all overall process input and output streams are reported. Many of the entries in Tables 17 and 15 are identical. The coal gas feed rate, as well as the primary sorber and the secondary sorber and secondary regenerator are the same using both the steam and SO_2 regeneration concepts. Only streams associated with and downstream of the primary regenerator are different. This includes only the oxygen to the primary regenerator (stream 8) and elemental sulfur product (stream 32) in Table 17. The flow rates of these streams decrease with decreasing temperature because less sulfur is removed in the primary sorber at lower temperature.

Table 17. Summary of Material Balance Results for the LSU Case Studies Using SO_2 Regeneration

	Stream Flow Rate, lb mol/hr					
Case Study Number	7	8	9	10	11	12
Input Streams						
1. Coal Gas From Gasifier	16,987	16,987	16,987	16,987	16,987	16,987
12. Primary Sorbent Makeup	6.9	6.9	6.9	6.9	6.9	6.9
21. Secondary Sorbent Makeup	0.1	0.2	0.4	0.1	0.2	0.4
8. Oxygen to Primary Regenerator	161	153	137	161	153	137
16. Steam to Secondary Regenerator	549	968	1865	549	968	1865
23. Oxygen to Secondary Regenerator	17	30	58	17	30	58
Output Streams						
11. Desulfurized Coal Gas	16,987	16,987	16,987	16,987	16,987	16,987
15. Primary Sorbent Discharge	6.9	6.9	6.9	6.9	6.9	6.9
20. Secondary Sorbent Discharge	0.1	0.2	0.4	0.1	0.2	0.4
17. Secondary Regenerator Off-Gas	561	989	1905	561	989	1905
32. Elemental Sulfur Product	162	154	137	161	154	137

The overall SO_2 regeneration process is simpler than the steam regeneration process and the resulting sulfur balance presented in Table 18 is also simpler. 5498 lb/hr of sulfur as H_2S enter with the coal gas (stream 1). Sulfur compounds exit in the clean coal gas (stream 11), the secondary regenerator off-gas (stream 17), and as elemental sulfur product (stream 32). The amount of sulfur in the clean coal gas decreases with decreasing temperature because of the more favorable thermodynamics of the exothermic reaction between ZnO and H_2S. In contrast, the amount of sulfur (as SO_2) in the secondary regeneration product gas increases with decreasing temperature because of less favorable thermodynamics of the endothermic reaction between CeO_2 and H_2S. However, as with the steam regeneration option, the secondary regeneration product gas would be recycled to the gasifier so that effectively all of the sulfur in this stream would eventually be removed in the elemental sulfur product. The production rate of elemental sulfur (stream 32) decreases with decreasing temperature because less sulfur is removed in the primary sorber at low temperature. The flow rates of all input and output streams which contain sulfur compounds are effectively independent of pressure.

Tables 19 and 20 summarize the heat duties associated with the major processing units in the steam and SO_2 regeneration concepts, respectively. In these case studies, all reactors were assumed to operate isothermally at the temperature listed in Table 14. Thus the energy demand, positive when heat must be added and negative when heat must be removed, is based on the flow rate and specific enthalpy of the feed and product streams coupled with appropriate heats of reaction. The rate of heat removal from the condensers is based on the same factor except there is no heat of reaction.

In 11 of the 12 cases, heat must be added to the primary sorber in order to maintain the specified reaction temperature. The quantity is highly dependent on reaction temperature with the sorber being approximately thermally neutral at 800K (cases 3, 6, 9, and 12) and with relatively large heat demand at 1000K (cases 1, 4, 7, and 10). Heat demands associated with the secondary sorber and secondary regenerator are quite small for all of the design cases. Even though the secondary sorber reaction between H_2S and ZnO is exothermic, the required heat removal is small because of the low H_2S concentration in the secondary sorber feed. The oxidation reactions which occur in the secondary regenerator are highly exothermic. In spite of this, heat must be added to the secondary regenerator because of the low temperature of the oxygen and steam feeds (streams 16 and 23).

In the steam regeneration option, both condensers require that relatively large quantities of heat be removed. The magnitude depends on the amount of sulfur removed in the primary sorber, which is a function of primary sorber temperature. The only condenser required in the SO_2 regeneration option is the elemental sulfur product condenser. The heat duty for this condenser is only about 2/3 the heat duty for the elemental sulfur condenser in the steam regeneration options even though the production rate of elemental sulfur is almost the same. The larger duty in the steam regeneration option is due to the added flow rate from the sour water stripper and the recycle stream from the tail gas unit.

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Table 18. Summary of Sulfur Material Balance Results for the LSU
Case Studies Using SO$_2$ Regeneration

Case Study Number		Sulfur Flow Rate, lb/hr					
		7	8	9	10	11	12
Sulfur Input Stream (Sulfur Form)							
1. Coal Gas From Gasifier (H$_2$S)		5498	5498	5498	5498	5498	5498
Sulfur Output Stream (Sulfur Form)							
11. Desulfurized Coal Gas (H$_2$S)		17	7	3	17	7	3
17. Secondary Regenerator Off-Gas (SO$_2$)		329	581	1119	329	581	1119
32. Elemental Sulfur Product (S)		5152	4922	4394	5152	4922	4394

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Table 19. Heat Duties in Major Processing
Units Involved in Steam Regeneration

Heat Duty, 10^6 Btu/hr

Case Study	1	2	3	4	5	6
Primary Sorber	50.6	26.4	2.5	55.2	26.4	2.5
Primary Regenerator	8.1	4.1	1.2	-2.7	4.4	1.4
Secondary Sorber	-0.3	-0.5	-1.0	-0.3	-0.5	-1.0
Secondary Regenerator	2.9	3.3	3.1	3.0	3.6	3.6
Water Condenser	-29.6	-20.6	-12.6	-14.8	-20.5	-12.5
Sulfur Condenser	-20.3	-19.3	-17.2	-20.4	-19.4	-17.3

Table 20. Heat Duties in Major Processing
Units Involved in SO_2 Regeneration

	Heat Duty, 10^6 Btu/hr					
Case Study	7	8	9	10	11	
Primary Sorber	50.6	25.7	-0.5	50.6	26.4	0.2
Primary Regenerator	-181.6	-185.7	-193.4	-181.6	-186.5	-194.3
Secondary Sorber	-0.3	-0.5	-1.0	-0.3	-0.5	-1.0
Secondary Regenerator	2.9	3.3	3.1	3.0	3.6	3.6
Sulfur Condenser	-14.7	-13.7	-12.2	-14.7	-13.5	-12.0

Easily the largest difference in heat duties between the two options is that associated with the primary regenerator. Relatively small heat addition is required in five of the six case studies using steam regeneration. However, the SO_2 regeneration reaction is highly exothermic and large quantities of heat must be removed.