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Advanced Sulfur Control Concepts in Hot-Gas Desulfurization Technology

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EXECUTIVE SUMMARY

Professor Harrison, project principle investigator, visited Morgantown for a project review in February 1998. Following this review, the project was extended for five months and \$15,000 in incremental funding was approved. The new project completion date is August 18, 1998.

On the experimental front, the last six cycles of a 25-cycle sorbent durability test were completed, final installation of the flame photometric detector was accomplished, and fifteen tests whose aim was to determine the minimum prebreakthrough H_2S concentration over reduced CeO_2 were performed.

There was a little, if any, evidence of sorbent deterioration in the durability test. For example, the time required for the H_2S concentration in the product gas to reach one-half of the feed gas concentration, $t_{0.5}$, varied only between 97 minutes in cycle 2 and 110 minutes in cycle 17, with an overall average of 101.2 minutes. There was no apparent deterioration in $t_{0.5}$ as the number of cycles increased. The variation in $t_{0.5}$ for regeneration was also small, ranging from a minimum of 20.6 minutes in cycle 1 to a maximum of 23.0 minutes in cycle 6. The overall average was 21.9 minutes and again there was no apparent increase with increasing cycle number.

During the durability test we confirmed that, when using pre-reduced sorbent and a clean system, the prebreakthrough H_2S concentration was less than ~ 100 ppmv, the detection limit of the thermal conductivity detector (TCD). Consequently, a more sensitive flame photometric detector (FPD) which permitted measurements of H_2S concentrations of 1 ppmv or less was installed. The FPD and TCD were connected in parallel so that, when desired, the entire H_2S breakthrough curve could be measured.

Most of the quarter was devoted to conducting reduction-sulfidation tests to determine the minimum prebreakthrough H_2S concentrations which could be achieved using prereduced CeO_2 . Fifteen runs involving variations in reduction-sulfidation temperature, H_2S concentration in the feed gas, and feed gas volumetric flow rate were completed. In all tests the prebreakthrough H_2S concentration was less than 10 ppmv, and in many of the tests the H_2S concentration was equal to or less than 1 ppmv for an extended time period.

SORBENT DURABILITY TEST

The last six cycles of a twenty-five cycle sorbent durability test were completed in January. The initial sorbent charge consisted of 6g Rhone Poulenc CeO_2 mixed with 3g Al_2O_3 . Reaction conditions were as follows:

1. Reduction at 800°C and 5 atm. In cycles 1 through 15 the reduction gas contained 10% H_2 in N_2 at a flow rate of 400 sccm. In the remaining cycles reduction was carried out in 100% H_2 at a flow rate of 50 sccm. The reduction was generally carried out overnight.

2. Sulfidation at 800°C and 5 atm in 1% H₂S/10% H₂/N₂ at a rate of 400 sccm. Each sulfidation cycle was continued until H₂S breakthrough was complete, typically about 2 hours.

3. Regeneration at 600°C and 1 atm in 12% SO₂/N₂ at a rate of 200 sccm. Regeneration was continued until the SO₂ content of the product gas reached 12%, typically about 30 minutes.

4. Reactor cleaning at 800°C and 5 atm using air at 50 sccm. The purpose of this oxidation step was to remove, to the extent possible, all elemental sulfur deposited downstream of the sorbent bed during regeneration. As further precaution against contamination, different reactor exit lines were used during sulfidation and regeneration. During sulfidation the product gas flowed through teflon-lined tubing and a 7 μ stainless steel filter to the back pressure regulator and then through teflon tubing to the stainless steel chromatograph sampling valve. Stainless steel in contact with the sulfidation product gas consisted of three fittings, one filter, the back pressure regulator, the chromatograph sampling valve, and the TCD housing. During regeneration the product gas flowed through heat-traced stainless steel lines to the condenser and then through a series of filters and stainless steel tubing to the sampling valve. The back pressure regulator was not used during the atmospheric pressure regeneration tests and the only stainless steel parts exposed to both sulfidation and regeneration product gases were one fitting, the sampling valve, and the TCD housing.

Complete H₂S breakthrough curves for the 25 cycles are shown in Figure 1. Results of a nonreacting H₂S tracer tests at the same conditions are included for comparison. All concentration-time curves were similar except for the following exceptions.

In the 20 to 90 minute range the H₂S concentration from cycle 01 was clearly larger than from any of the remaining cycles. In the same time range the H₂S concentrations in cycles 02 through 15 are closely bunched at an intermediate level, while in cycles 16 through 25 H₂S concentration was below the TCD detection limit for about 80 minutes. These features are more clearly shown in Figure 2 where the concentration scale is expanded to emphasize results during the early reaction times. The improvement between cycles 15 and 16 is clearly due to the switch from 10% H₂ to 100% H₂ during the reduction step. The delayed breakthrough in cycle 16, which is particularly evident in Figure 1, is attributed to reduced H₂S feed rate caused by mass flow controller malfunction.

The time required for the product H₂S concentration to reach 0.5% (one-half of the feed concentration), $t_{0.5}$, provides a good comparison of sulfidation reproducibility during the active breakthrough stage. Figure 3 shows $t_{0.5}$ versus cycle number for the twenty-five cycles, excluding cycle 16 because of the mass flow controller problems. $t_{0.5}$ ranged from a minimum of 97 minutes in cycle 2 to a maximum of 110 minutes in cycle 17. The twenty-four-cycle average was 101.2 minutes and there was no indication of a decrease in $t_{0.5}$ with increasing cycle number.

Combining the H₂S breakthrough curves with the nonreacting tracer results shown in Figure 1 made it possible to estimate the overall percent conversion of CeO₂ to Ce₂O₂S at the conclusion of each cycle. These results are presented in Figure 4. The smallest value of 95% conversion occurred in cycle 01 while the largest value of 116% occurred in cycle 16. If this value

Figure 1. Complete Sulfidation Breakthrough Curves for the Sorbent Durability Test

Figure 2. Early Portions of the Sulfidation Breakthrough Curves in the Sorbent Durability Test

Figure 3. $t_{0.5}$ Versus Cycle Number for the Sulfidation Phase of the Sorbent Durability Test

Figure 4. Percent Conversion of CeO_2 to Ce_2O_3 s at the Conclusion of Each Cycle of the Sorbent Durability Test

is excluded because of the previously mentioned mass flow controller problems, the maximum of 108% conversion occurred in cycle 17. The twenty-five-cycle average (including cycle 16) was 102.5%. These conversion calculations are based on a loss of 9% of the CeO_2 charge due to formation of volatiles during the heating period. This 9% loss was measured in previous electrobalance tests.

Regeneration conditions were constant in all cycles and Figure 5 shows that the SO_2 breakthrough curves were also quite similar. Results from a nonreacting SO_2 tracer test are also included for comparison. Regeneration results from cycle 08 are omitted because of elemental sulfur plugging problems. Complete regeneration was achieved, however, as shown by the cycle 09 sulfidation results. Plugging also occurred near the end of cycles 06 and 10, but the regeneration breakthrough curves were effectively complete before the problem occurred.

$t_{0.5}$ corresponding to 6% SO_2 in the regeneration product gas (50% of the feed concentration) is shown for each regeneration cycle in Figure 6. Results from cycle 08 are omitted. During regeneration, $t_{0.5}$ varied from a minimum of 20.6 minutes in cycle 01 to a maximum of 23.0 minutes in cycle 06. The twenty-four cycle average was 21.9 minutes and, once again, there was no evidence of performance deterioration in the latter cycles.

Percent conversion of $\text{Ce}_2\text{O}_3\text{S}$ to CeO_2 for each cycle based on the SO_2 breakthrough curves and the nonreacting tracer test are shown in Figure 7. Results ranged from a low of 91% in cycle 05 to a high of 109% in cycle 06 with a twenty-four cycle average of 98.3%. The scatter in the regeneration results is somewhat larger than in sulfidation because only 9 or 10 data points collected during a regeneration cycle compared to about 40 data points during sulfidation. Nevertheless, the average of 98.3% for regeneration compared to 102.5% for sulfidation is felt to be quite good.

During the entire fifty-eight day duration of the durability test, the sorbent was continually exposed to a temperature of at least 600°C with the temperature being 800°C for approximately 90% of that time. During that time the sorbent was alternately exposed to H_2/N_2 during reduction, $\text{H}_2\text{S}/\text{H}_2/\text{N}_2$ during sulfidation, SO_2/N_2 during regeneration, air during cleaning, and N_2 purge between each phase. The durability of the sorbent is judged to be exceptionally good.

FLAME PHOTOMETRIC DETECTOR (FPD)

The ability to reduce H_2S concentrations during the prebreakthrough period to below the TCD detection limit led to installation of a FPD having a detection limit of about 1 ppmv. A great deal of trial-and-error experimentation was required before H_2S concentrations near the 1 ppmv level could be reliably measured. For example, the reactor and product lines downstream of the sorbent bed had to be free of residual sulfur. H_2S produced by the reaction between H_2 and contaminant sulfur could easily exceed the H_2S in the product gas. Stainless steel parts in contact with the product gas were minimized as described in the previous section. We also found the system would not operate reliably with the two detectors arranged in series with the TCD followed by the FPD. The

Figure 5. Complete Regeneration Breakthrough Curves for the Sorbent Durability Test

Figure 6. $t_{0.5}$ Versus Cycle Number for the Regeneration Phase of the Sorbent Durability Test.

Figure 7. Percent Conversion of $\text{Ce}_2\text{O}_2\text{S}$ to CeO_2 at the conclusion of Each Cycle of the Sorbent Durability Test

problem was determined to be caused by adsorption/desorption of H_2S on the stainless steel surface of the TCD.

A parallel arrangement of the detectors as shown in Figure 8 was finally implemented. Column 2 effluent flows into a remotely actuated three-way solenoid valve which, during the early prebreakthrough period, directs the product to the FPD. When the H_2S content increases to the FPD saturation level, the solenoid valve is switched and product is directed to the TCD. No additional stainless steel is introduced as all wetted parts of the solenoid valve are of teflon.

Alteration in the analytical system required that both detectors be recalibrated. In addition to installing the solenoid valve and parallel detectors, the volume of the sample loop and the carrier gas flow rate were changed to provide reasonable operating conditions for both detectors. As usual, the TCD calibration for both H_2S and SO_2 was linear through the origin. The equations relating concentration and area are:

$$\text{ppmv H}_2\text{S} = 1.287 \times 10^{-1} \text{ Area}$$

$$\% \text{ SO}_2 = 5.136 \times 10^{-5} \text{ Area}$$

The FPD response to H_2S was quadratic and separate equations were determined for low H_2S concentrations (0 to 3 ppmv), medium H_2S concentrations (3 to 15 ppmv) and high H_2S concentrations (15-108 ppmv). The quadratic equations are:

$$\text{ppmv H}_2\text{S} = 0.0612 [(1 + 5.444 \text{ Area})^{1/2} - 1]$$

$$\text{for } 1 \leq \text{ppmv H}_2\text{S} \leq 3$$

$$\text{ppmv H}_2\text{S} = 0.206 [(1 + 0.402 \text{ Area})^{1/2} + 1]$$

$$\text{for } 3 \leq \text{ppmv H}_2\text{S} \leq 15$$

$$\text{ppmv H}_2\text{S} = 6.942 [(1 + 0.000577 \text{ Area})^{1/2} - 1]$$

$$\text{for } 15 \leq \text{ppmv H}_2\text{S} \leq 108$$

Once again the minimum H_2S detection limit for the TCD was near 100 ppmv while the maximum and minimum detection limits of the FPD were near 100 ppmv and 1 ppmv, respectively.

Results of the first reduction-sulfidation test (Ce205s01) using the two detectors in parallel are shown in Figure 9. The standard $\text{CeO}_2\text{-Al}_2\text{O}_3$ mixture was prereduced at 800°C and 5atm in 10% H_2/N_2 overnight. Sulfidation was then carried out 800°C and 5 atm using 1% $\text{H}_2\text{S}/10\% \text{H}_2/\text{N}_2$. H_2S concentration is plotted on a logarithmic scale so that the entire concentration range from <10 ppmv to 10,000 ppmv (1%) is clearly visible. The product gas H_2S concentration was below 10 ppmv, corresponding to 99.9% H_2S removal, for the first 35 minutes and then increased gradually to 100

(a) GC Operation — Step One

(b) GC Operation — Step Two

Actuator: 115V Solenoid
 C_1 , C_2 , C_{ref} : Carrier gases (Helium)
 Column 1: Water trap column (PORAPAK Q)
 Column 2: Separation column (CHROMOSIL 310)

Figure 8. Parallel Arrangement of the FPD and TCD Detectors

Figure 9. Results of the First Sulfidation Test (Ce205s01) Using the Parallel Arrangement of the FPD and TCD

ppmv after about 50 minutes. At that time the three-way solenoid valve was switched to send product gas to the TCD. The TCD cannot operate while flow is directed to the FPD and the 30 minute gap in the data was necessary to allow the TCD to warm-up and stabilize after being turned on. The H_2S concentration from the first TCD sample at 83 minutes was about 250 ppmv, and by 106 minutes the H_2S concentration increased to near the feed value of 10,000 ppmv (1%).

The results from this test are in general agreement with results from succeeding runs discussed in the next section except that the FPD breakthrough (in the 30 to 60 minute time range) was more gradual than in the succeeding runs. As will be shown, the more normal response was for the H_2S concentration to increase from about 10 ppmv to greater than 100 ppmv in a single sample interval. The reason for this difference is not known.

REDUCTION-SULFIDATION TEST RESULTS

A total of 15 reduction-sulfidation tests (including Ce205s01) were completed using the FPD and, in some cases the FPD-TCD, for product analysis. Reaction conditions for the tests are summarized in Table 1. The standard reactor charge of 6.00g Rhone Poulenc C_2O_2 and 3.0g Al_2O_3 was used in all tests. The reduction gas composition was constant at 10% H_2 in N_2 and reduction and sulfidation pressures were constant at 5 atm. Reaction parameters investigated were reduction-sulfidation temperature (600 to 850°C), sulfidation feed gas composition (0.25% and 1.0% in 10% H_2/N_2), and sulfidation gas feed rate (200 to 800sccm). The sorbent was pre-reduced in all tests except Ce13s01. H_2S removal in that test was considerably smaller than in test Ce210s01 at equivalent reaction conditions and with pre-reduction. No regeneration tests were carried out in order to minimize sulfur contamination of the reactor system.

Duplicate Test Results

Test Ce205s01, Ce2s06s01, and Ce207s01 used identical reaction conditions except that Ce207s01 was terminated immediately after the product H_2S concentration exceeded the FPD saturation value (~100ppmv). In both Ce205s01 and Ce206s01 product gas flow was shifted to the TCD after FPD saturation so that the entire breakthrough curve was obtained.

H_2S concentrations from the first 30 minutes of the three tests are compared in Figure 10. The H_2S concentration is presented on a linear scale and is limited to 20 ppmv. All early concentrations were in the range of 3 to 8 ppmv (corresponding to 99.92 to 99.97% H_2S removal). However, there were significant differences after 20 minutes. In Ce206s01 the H_2S concentration increased between the fifth and sixth samples (~22 and 28 minutes) from 5 ppmv to greater than 100 ppmv. A similar increase from 3 ppmv to greater than 100 ppmv occurred in Ce207s01 between the sixth and seventh samples (~ 28 to 34 minutes). In contrast, the H_2S concentration in Ce20501 increased gradually and remained below 100 ppmv for 50 minutes (see Figure 9). However, as previously stated, the sharp increase observed in Ce206s01 and Ce207s01 is more common.

Table 1. Summary of Reduction - Sulfidation Reaction Conditions (January - March 1998)

Test	Ce205s0	Ce206s0	Ce207s0	Ce208s0	Ce209s0	Ce210s0	Ce211s0	Ce212s0	Ce213s0	Ce214s0	Ce215s0	Ce216s0	Ce217s0	Ce218s0	Ce219s01
Date	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3/30/98
		2/02/98	2/03/98	2/06/98	2/10/98	2/13/98	2/17/98	2/19/98	2/22/98	2/23/98	3/05/98	3/18/98	3/23/98	3/27/98	
Sorbent															
Al ₂ O ₃	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
CeO ₂	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Source	RP	RP	RP	RP	RP	RP	RP	RP	RP	RP	RP	RP	RP	RP	RP
Reduction															
Temp., °C	800	800	800	850	750	700	650	600	—	700	700	700	700	700	700
Press., atm	5	5	5	5	5	5	5	5	—	5	5	5	5	5	5
Gas Comp.															
% H ₂	10	10	10	10	10	10	10	10	—	10	10	10	10	10	10
% N ₂	90	90	90	90	90	90	90	90	—	90	90	90	90	90	90
Sulfidation															
Temp., °C	800	800	800	850	750	700	650	600	700	700	700	700	700	700	700
Press., atm	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Gas Comp.															
% H ₂ S	1	1	1	1	1	1	1	1	1	0.25	0.25	1.0	1.0	0.25	0.25
% H ₂	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
% N ₂	89	89	89	89	89	89	89	89	89	89.75	89.75	89	89	89.75	89.75
Flow Rate, sccm	400	400	400	400	400	400	400	400	400	400	400	200	800	200	800

Figure 10. Comparison of the FPD Prebreakthrough Concentrations From Duplicate Sulfidation Tests

Figure 11 shows the complete H₂S breakthrough curves from Ce205s01 and Ce206s01 including both FPD and TCD results. Except for the large difference in the time and slope of the FPD breakthrough the results are quite similar. The data gap in both tests is associated with switching product gas flow to the TCD and providing sufficient time for that detector to equilibrate. In both runs there appears to be a second H₂S concentration plateau in the 100 to 300 ppmv level which lasts for approximately 80 minutes. Major H₂S breakthrough then occurred in the 80 to 105 minute time span in both tests. This second concentration plateau and final breakthrough time correspond, at least qualitatively, to results of earlier runs in which only the TCD was used.

The Effect of Temperature

Tests Ce207s01 through Ce212s01 examined the effect of reduction-sulfidation temperature in intervals of 50°C between 600 and 850°C. Only the FPD was used so that only initial H₂S concentrations were obtained. Results from all tests except Ce212s01 at 600°C are shown in Figure 12. At this low temperature, the H₂S concentration in all samples exceeded the FPD saturation limit. In the remaining five tests, all initial concentrations were below 10 ppmv and decreased with decreasing temperature from about 6 ppmv at 850°C to less than 1 ppmv at both 650 and 700°C. This decrease in concentration with decreasing temperature is consistent with the sulfidation reaction being exothermic and equilibrium being closely approached. At 600°C, the kinetics of the reaction becomes too slow for equilibrium to be approached. As previously described, the GC-FPD operating conditions are such that the H₂S analysis becomes increasingly uncertain as the H₂S concentration approaches and goes below 1ppmv.

It is of interest to note that the prebreakthrough concentrations shown in Figure 12 compare quite well to previously published results from Meng and Kay (1987) at higher temperature. This is illustrated in Figure 13 where H₂S concentrations from the third sample of each of the Figure 12 tests have been added to previously reported data. While the feed gas composition used by Meng and Kay and in this study are different, and both are different from the Shell gas composition used to establish thermodynamic limits, the results are quite similar.

The importance of the prereduction step prior to sulfidation must be emphasized. The thermodynamics of the reaction between H₂S and substoichiometric CeO_n (n<2) are more favorable than the H₂S-CeO₂ reaction. This was proven in test Ce213s01 at 700°C where the prereduction step was omitted. Instead of the approximately 1ppmv H₂S levels formed in Ce210s01 (See Figure 12), all H₂S concentrations from Ce213s01 were above the FPD saturation limit.

The Effect of Feed Gas Composition

In tests in which the feed gas contained 1% H₂S such as shown in Figure 12, FPD breakthrough occurred in less than 30 minutes and the H₂S concentration increased from low levels (<10 ppmv) to above the FPD saturation limit in a single cycle. In order to extend the duration of

Figure 11. Comparison of the Complete FPD and TCD Breakthrough Curves from Duplicate Tests

Figure 12. The Effect of Temperature on FPD Prebreakthrough Concentrations

Figure 13. Comparison of FPD Prebreakthrough Concentrations
From This Work With Earlier Results From Meng and Kay

the FPD prebreakthrough period and, hopefully, to obtain more information on the shape of the breakthrough curve, the concentration of H_2S in the feed gas was reduced by a factor of 4 to 0.25% in tests Ce214s01 and Ce215s01. Reaction conditions in these tests were the same except that only the FPD was used in Ce214s01 and both the FPD and TCD were used in Ce215s01. Also reaction conditions in these tests were the same as in Ce210s01 except that the feed gas contained 1% H_2S in the latter case.

H_2S breakthrough curves from these runs are compared in Figure 14. An approximate correction for the increased H_2S feed concentration in Ce210s01 has been made by multiplying each sample time in that run by 4. Initial concentrations from all tests are at the 1 ppmv level or less. FPD breakthrough from ~1 ppmv to 100 ppmv occurred at approximately 120 minutes in both Ce214s01 and Ce215s01. FPD breakthrough appeared to occur at an earlier time in Ce210s01 but the factor of 4 used to adjust the reaction time in this test is at best approximate.

The FPD results from Ce214s01 and Ce215s01 show a secondary plateau in the 100 to 300 ppmv level. TCD results from Ce215s01 show that this plateau lasted until about 400 minutes when final breakthrough to 2500 ppmv H_2S occurred. FPD concentrations above 100 ppmv for both Ce214s01 and Ce215s01 must be treated cautiously as they are above the nominal saturation level and were estimated by extrapolation. Similarly, the TCD concentrations from Ce215s01 near 100 ppmv should be treated with caution as they are near the lower detection limit of the TCD. Thus the apparent concentration decrease in Ce215s01 following the switch from the FPD to the TCD may be attributed to analytic uncertainty.

The Effect Of Volumetric Feed Rate

The effect of volumetric feed rate at 200, 400, and 800 sccm was investigated at 700°C using feed concentrations of both 1% and 0.25% H_2S . However, prior to these reaction tests a series of nonreacting tracer tests was completed so that appropriate delay time corrections as a function of flow rate could be made. Delay time is defined as the time interval between opening the valve to feed reactive gases and those gases reaching the sorbent bed.

Results of the tracer tests are presented in Figure 15. The H_2S concentrations in the feed and product gases were effectively equal in the third sample (~10 min) at 200 sccm, in the second sample (~7 min) at 400 sccm, and in the first sample (~3 min) at 800 sccm. Delay time, t_D , was estimated by numerically integrating the area above the breakthrough curve and converting that area to a rectangle of the same area with height equal to the H_2S feed concentration and width equal to t_D . Resultant values of t_D at the three flow rates are:

200 sccm	$t_D = 5.5$ min
400 sccm	$t_D = 2.4$ min
800 sccm	$t_D = 1.2$ min

Figure 14. The Effect of H₂S Feed Composition on FPD Prebreakthrough Concentrations

Figure 15. Nonreacting Tracer Test Results as a Function of Volumetric Feed Rate

FPD prebreakthrough concentrations of 1 ppmv or less were achieved in all tests with breakthrough generally occurring earlier at the larger feed rates. FPD results from the three tests using 0.25% H₂S in the feed gas (Ce215s01, Ce218s01, and Ce219s01) are shown as a function of dimensionless time in Figure 16. Dimensionless time, t^* , is defined as

$$t^* = \frac{t - t_D}{t_E}$$

t_D is the delay time and t_E is the theoretical time at which all CeO₂ would be converted to Ce₂O₂S with complete removal of H₂S. When H₂S removal is essentially complete, as it is for all of the data in Figure 16, the value of t^* is effectively equal to the fractional conversion of CeO_n to Ce₂O₂S. From the figure we see that FPD breakthrough begins at $t^* \sim 0.17$ at 800 sccm, 0.31 at 400, and 0.32 at 200 sccm. However, at 200 sccm the H₂S concentration remained below 10 ppmv until $t^* \sim 0.41$.

FPD breakthrough occurred much sooner in the tests using 1% H₂S in the feed gas and severely limited the amount of data which could be obtained prior to FPD saturation. This was particularly true in test Ce217s01 at 800 sccm where only two samples were obtained prior to breakthrough. Results from Ce213s01, Ce216s01, and Ce217s01 all at 700°C at 5 atm are compared on a dimensionless time basis in Figure 17. Dimensionless times corresponding to the last sample in which the H₂S concentration was near 1 ppmv decreased from $t^* \sim 0.31$ at 200 sccm to $t^* \sim 0.18$ at both 400 and 800 sccm. There is, however, a reasonably large uncertainty in the last two values because, between samples, $\Delta t^* \sim 0.09$ at 800 sccm and $\Delta t^* \sim 0.045$ at 400 sccm.

CONCLUSIONS

With the more sensitive FPD, we have shown that initial H₂S concentrations in the range of 1 to 10 ppmv can be achieved over a temperature range of 650 to 850°C. The key to achieving the low prebreakthrough concentration is the prereduction step in which CeO₂ is reduced to CeO_n ($n < 2$). The prereduction requirement was proven by comparing initial H₂S concentrations at 700°C with and without prereduction. In the former case initial H₂S concentrations were about 1 ppmv and in the latter case all H₂S concentrations exceeded the saturation limit of the FPD (~ 100 ppmv). At 600°C even with a prereduction step the H₂S concentration always exceeded FPD saturation. This may be attributed to lack of reduction and/or slow sulfidation kinetics at the lower temperature.

The low initial H₂S concentrations were achieved using feed concentrations ranging from 0.25 to 1.0% H₂S and flow rates from 200 to 800 sccm. Of course the duration of the FPD prebreakthrough period decreased as both the inlet concentration and feed rate increased. In the most favorable case with a feed rate of 200 sccm and 0.25% H₂S, the H₂S concentration in the product remained below 20 ppmv until approximately 40% of the sorbent was converted to Ce₂O₂S.

Figure 16. FPD Breakthrough Curves Versus Dimensionless Time as a Function of Feed Rate: 0.25% H₂S

Figure 17. FPD Breakthrough Curves Versus Dimensionless Time as a Function of Feed Rate: 1% H₂S