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Advanced Sulfur Control Concepts in Hot-Gas Desulfurization Technology

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EXECUTIVE SUMMARY

Twenty-five reduction/sulfidation tests plus one sulfidation/regeneration test were completed during the quarter. The reduction/sulfidation tests examined the behavior of six cerium oxide sorbents from different sources with reaction variables of temperature, pressure, gas composition and flow rate. Most significantly, steam was added to the sulfidation feed gas for the first time. Tests using pre-reduced sorbents and tests in which reduction and sulfidation occurred simultaneously were performed. Prebreakthrough H_2S concentrations less than 10 ppmv were obtained over a range of reaction conditions with prebreakthrough concentrations as low as 1 ppmv achieved at the most favorable conditions. The general response to reaction variables was as expected except when feed rate was varied. In some of these cases the FPD breakthrough time did not correspond to expectation.

The single regeneration run was conducted at 600 °C and 2 atm using 12% SO_2 in N_2 at a feed rate of 400sccm. This was the first regeneration test at other than 1 atm pressure; favorable results were obtained. The only experimental objective remaining is additional high pressure regeneration testing. We hope to complete this work in July.

REDUCTION-SULFIDATION USING RHONE-POULENC CeO_2

The majority of the reduction-sulfidation tests used the "standard" Rhone-Poulenc CeO_2. Reaction conditions for these tests are summarized in Table 1.

The Effect of Pressure and Feed Rate

Tests Ce220s01 through Ce225s01 as well as Ce233s01 at 10 and 15 atm were the first in which the reduction-sulfidation pressure was greater than 5 atm. The reaction temperature was 700°C in each test and the feed gas contained 0.25% H_2S and 10% in N_2. Feed rate was varied between 200 and 800sccm.

When the feed rate and temperature are constant, the gas velocity through the sorbent bed is inversely proportional to pressure but the H_2S feed rate is unchanged. Residence time in the sorbent bed is directly proportional to pressure. One would expect that the higher H_2S concentration and increased residence time within the sorbent bed associated with higher pressure would increase the slope of the breakthrough curve but have little effect on the breakthrough time. FPD breakthrough curves for the tests using 400sccm are shown in Figure 1. With the limited concentration range associated with the FPD (only ~4% of the feed concentration), it is not realistic to compare the slopes of the breakthrough curves. However, the breakthrough time varied from 95 minutes in one 10 atm test to 215 minutes at 15 atm. The difference in breakthrough times in the two 10 atm tests, 95 minutes in Ce222s01 and 120 minutes in Ce233s01, was also larger than expected. Only the results from tests Ce215s01 at 5 atm and Ce233s01 at 10 atm agree with expectations previously described. It is significant, however, that all prebreakthrough H_2S concentrations shown in Figure 1 are below 5 ppm and most are approximately 1ppmv.

Table 1. Summary of Reduction-Sulfidation Reaction Conditions Using Rhone Poulenc CeO_2 (April- June 1998)

Test	Ce220s01	Ce221s01	Ce222s01	Ce223s01	Ce224s01	Ce225s01	Ce232s01	Ce233s01	Ce234s01	Ce237s01	Ce238s01	Ce239s01	Ce240s01	Ce241s01	Ce242s01
Date	4-12-98	4-14-98	4-16-98	4-17-98	4-28-98	4-30-98	5-26-98	5-28-98	5-30-98	6-9-98	6-13-98	6-15-98	6-17-98	6-19-98	6-24-98
Sorbent, g															
CeO_2	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Al_2O_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
Pre-Reduction	Yes	Yes	Yes	Yes	Yes	Yes	None	Yes	Yes	None	None	None	None	None	None
Temp., °C	700	700	700	700	700	700	–	700	700	–	–	–	–	–	–
Press., atm	10	10	10	10	15	15	–	10	10	–	–	–	–	–	–
Gas Comp.															
% H_2	10	10	10	10	10	10	–	10	10	–	–	–	–	–	–
% N_2	90	90	90	90	90	90	–	90	90	–	–	–	–	–	–
Sulfidation															
Temp., °C	700	700	700	700	700	700	700	700	700	700	700	700	700	800	800
Press., atm	10	10	10	10	15	15	5	10	10	5	5	5	5	5	5
Gas Comp.															
% H_2S	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
% H_2	10	10	10	10	10	10	10	10	10	50.25	50.25	28.25	28.25	28.25	28.25
% H_2O	0	0	0	0	0	0	0	0	0	2.5	3.5	6.5	6.5	6.5	6.5
% N_2	89.75	89.75	89.75	89.75	89.75	89.75	89.75	89.75	89.75	47	46	65	65	65	65
Flow Rate, sccm	200	200	400	800	400	600	400	400	800	400	400	400	400	400	400

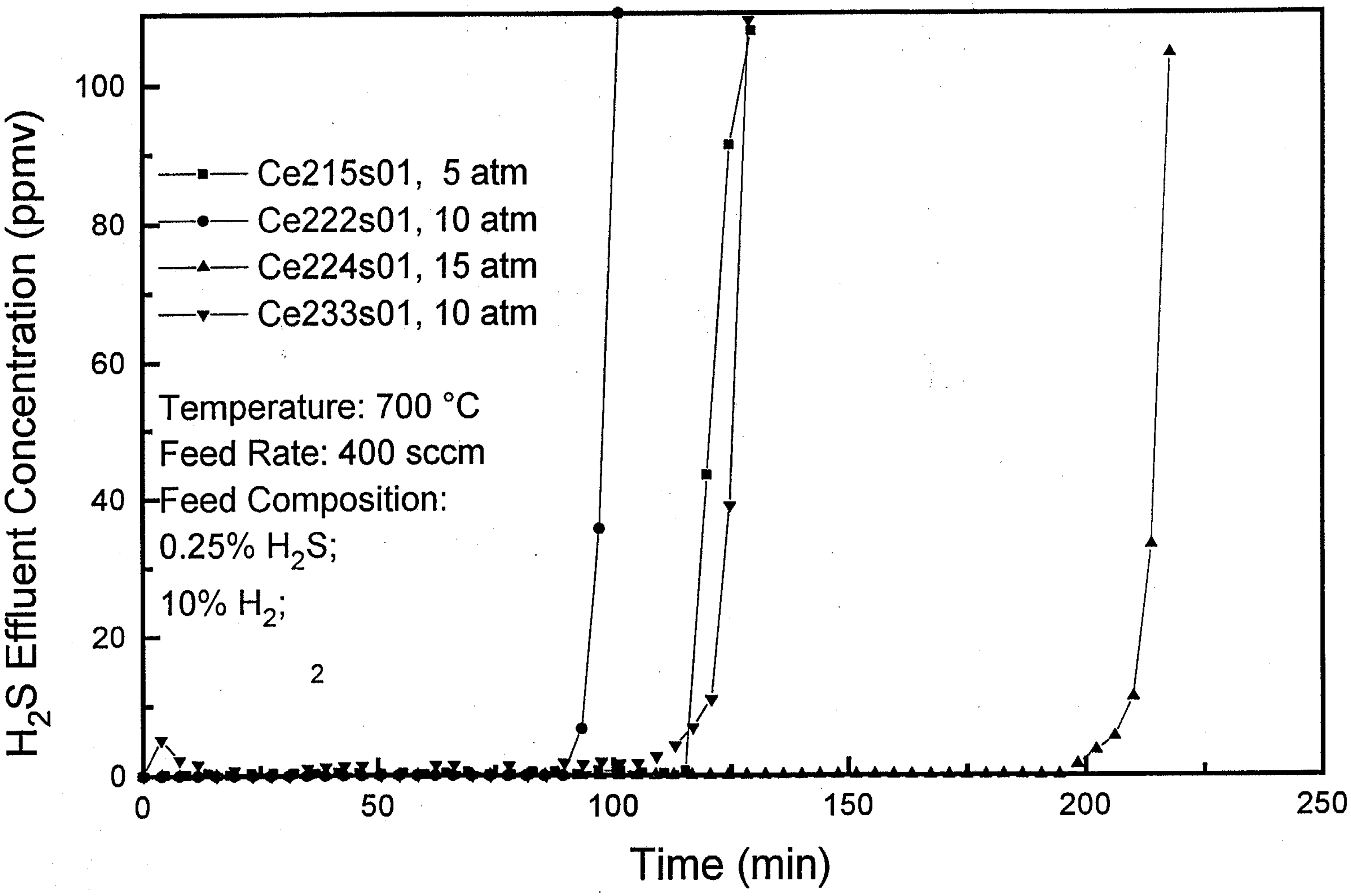

Figure 1. The Effect of Pressure at Constant Feed Rate.

Non-reacting tracer tests were run at each of the pressure-feed rate combinations so that delay time could be estimated. Results of the tracer tests at 10 atm and 200, 400, and 800 sccm feed rates are presented in Figure 2. Estimated delay times, based on the assumption of plug flow, are marked by the "x" on each tracer response. Each "x" is quite close to the H_2S concentration of 0.2% (80% of the feed concentration.) Table 2 presents the estimated delay times at the pressure-feed rate combinations studied. Dimensionless time, defined by the equation,

$$t^* = \frac{t - t_D}{t_E} \tag{1}$$

can be calculated once the delay time is known. t_E is the theoretical time corresponding to complete sorbent conversion with complete removal of H_2S; in an ideal system breakthrough would occur as a step function at $t^* = 1$. The value of t_E is calculated from the mass of sorbent charged and the H_2S feed rate.

The dimensionless breakthrough times for the tests shown in Figure 1 ranged from 0.23 (Ce222s01 at 10 atm) to 0.56 (Ce224s01 at 15 atm). When H_2S removal is complete, as it is effectively during the prebreakthrough period, the fractional conversion of sorbent is numerically equal to dimensionless breakthrough time. Thus the fractional conversion of CeO_2 to Ce_2O_2S also ranged from 0.23 to 0.56 prior to breakthrough.

In tests Ce220s01, Ce222s01, Ce233s01, Ce223s01, and Ce234s01 the sulfidation feed rate was varied between 200 sccm and 800 sccm at constant temperature and pressure. Duplicate runs were made at both 400 and 800 sccm. An increase in feed rate will reduce the bed residence time and increase the H_2S feed rate. The decreased residence time is expected to cause earlier initial breakthrough and a smaller slope of the breakthrough curve, while increasing the H_2S feed rate should simply shift the breakthrough curve to earlier time. The reactor response for these tests on a dimensional time basis is presented in Figure 3. Once again, all prebreakthrough H_2S concentrations were below 5 ppmv and most were approximately 1 ppmv. However, the effect of feed rate on breakthrough time agreed with expectation in only a qualitative way. If breakthrough is defined as the time corresponding to 10 ppmv H_2S, we see from Figure 3 that breakthrough time decreased from 260 minutes at 200 sccm to 90 and 125 minutes in the two 400 sccm tests and to 45 and 65 minutes in the two 800 sccm tests. On a dimensionless time basis, breakthrough time and fractional sorbent conversion at breakthrough ranged from 0.22 to 0.37. To a first approximation we would expect the dimensionless breakthrough times to be independent of feed rate.

Earlier test Ce218s01 coupled with Ce222s01, Ce233s01, and Ce225s01 provided simultaneous variation in pressure and flow rate in a manner to produce constant residence time. On a dimensional time basis the breakthrough time should be inversely proportional to feed rate because of the increased H_2S feed rate, while, as previously stated, pressure should have relatively little effect on breakthrough time. The experimental results are shown in Figure 4. In principle, conversion to dimensionless time should account for the H_2S feed rate variation and breakthrough curves at all conditions should be approximately equal. However, as shown in Figure 5, there is a wide variation in dimensionless breakthrough time, from 0.23 in Ce222s01 to 0.51 in Ce225s01.

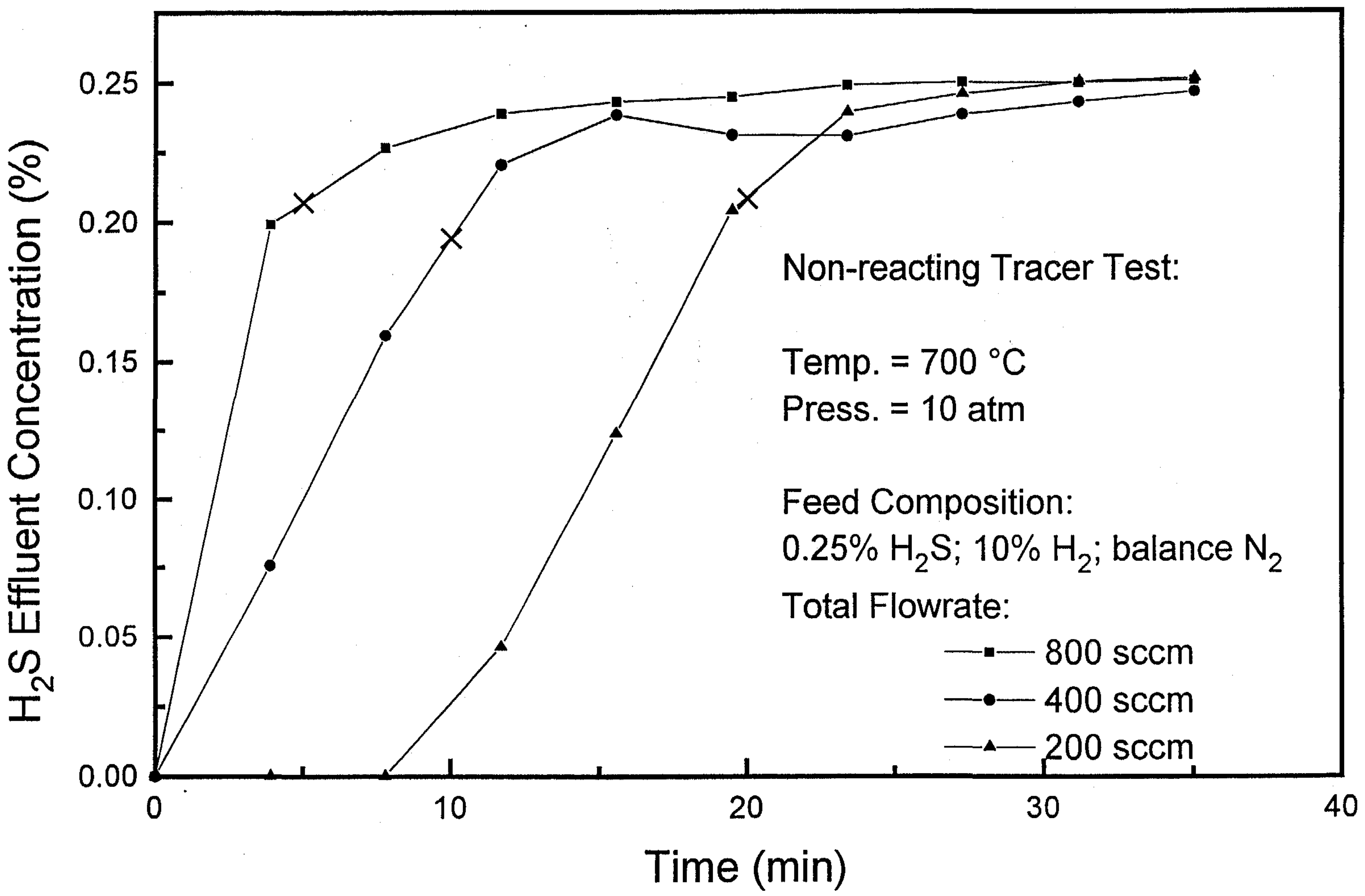

Figure 2. Non-Reacting Tracer Test Results at 10 atm.

Table 2. Estimated Delay Time as a Function of Reactor Pressure and Feed Rate (T = 700°C)

	Delay Time, min		
Pressure, atm	5	10	15
Feed Rate, sccm			
200	10	20	–
400	5	10	15
600	–		10
800	2.5	5	--

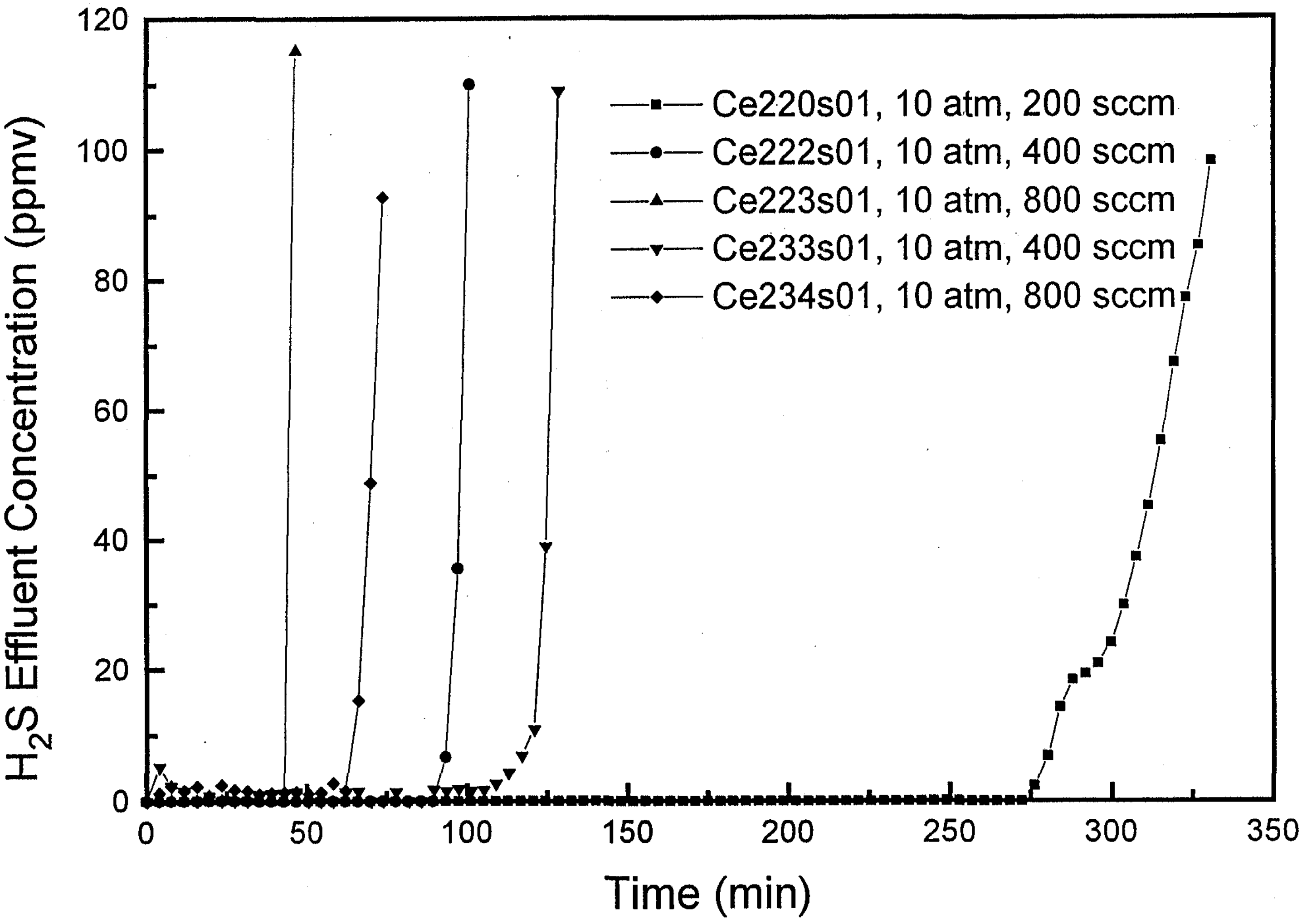

Figure 3. The Effect of Feed Rate at Constant Pressure.

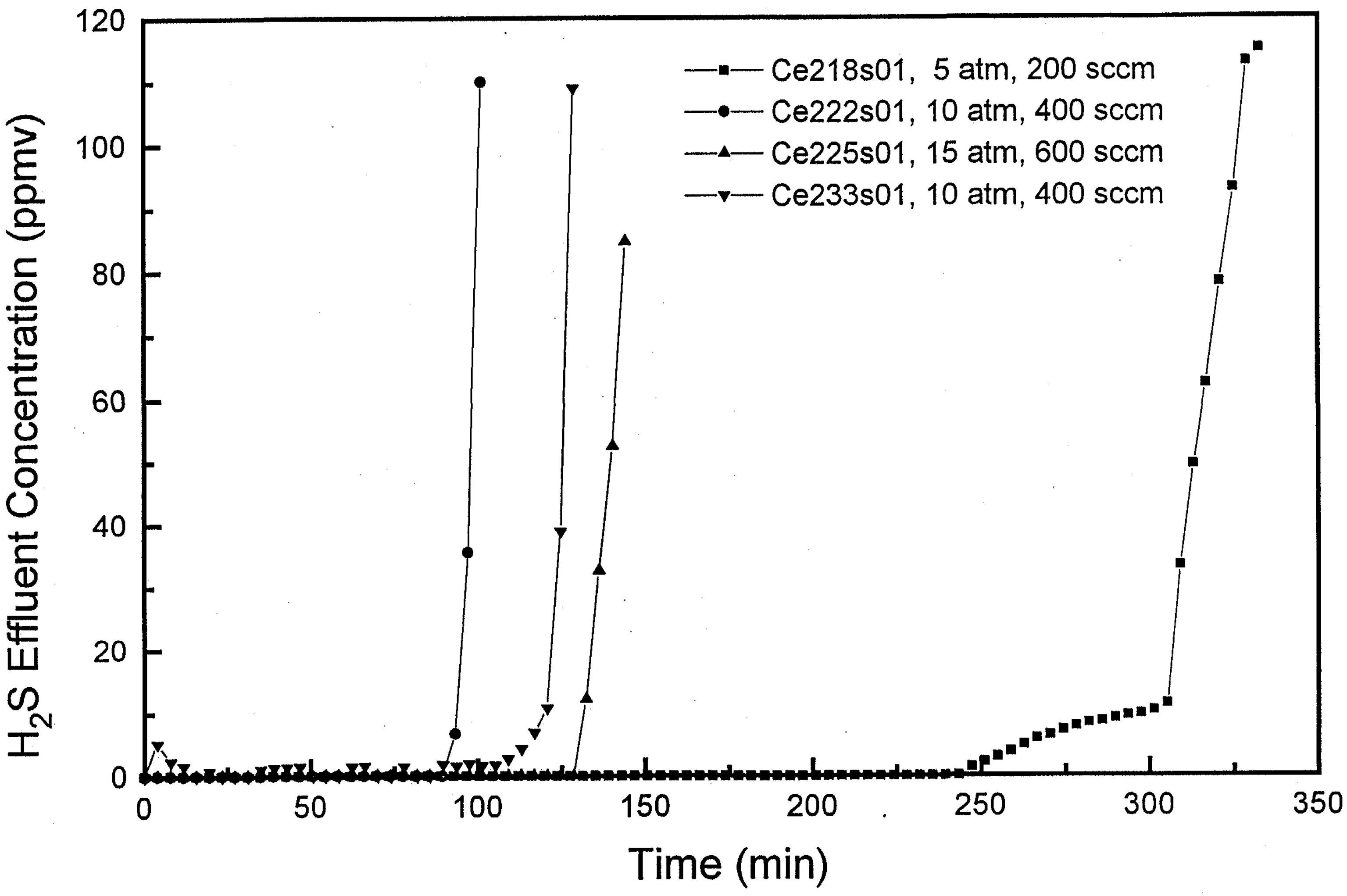

Figure 4. The Effect of Pressure and Feed Rate Variations to Produce Constant Gas Residence Time.

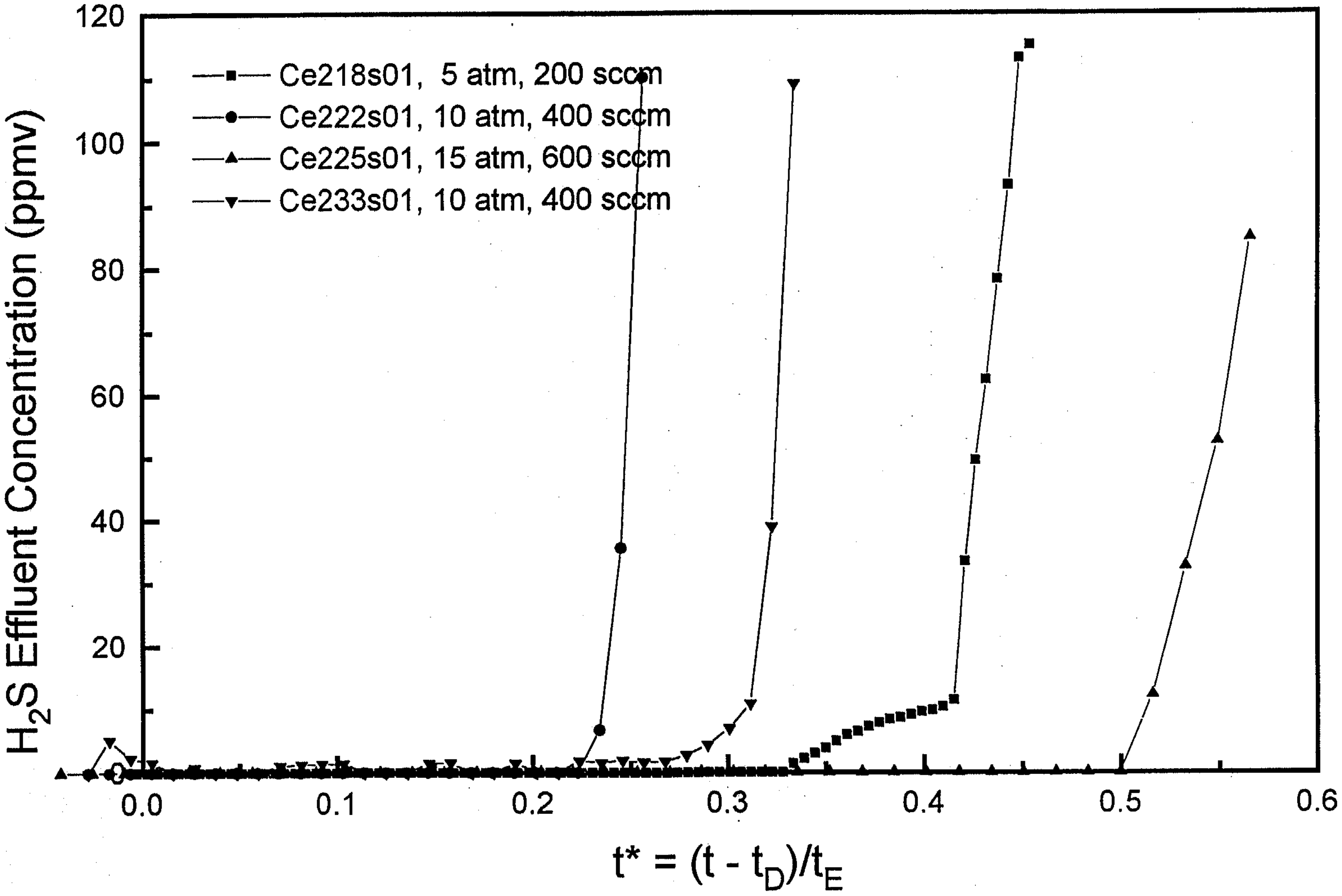

Figure 5. The Effect of Pressure and Feed Rate Variations to Produce Constant Residence Time: Dimensionless Time Basis.

The key feature from all of these tests in which the sorbent was pre-reduced in 10% H_2 - N_2 at the sulfidation temperature and pressure was that prebreakthrough H_2S concentrations were approximately 1ppmv for an extended period of time. As shown by the concentration versus dimensionless time plots, these low concentrations were maintained in some cases until approximately 50% of the cerium was sulfided. Unfortunately, the FPD breakthrough time (both dimensional and dimensionless) varied in an unpredictable manner. In all cases, however, approximately 25% of the cerium was sulfided prior to FPD breakthrough.

Comparison of Results With and Without Pre-reduction

To this point, pre-reduction was thought to be necessary if H_2S concentrations were to be reduced to low levels. However, as shown in Figure 6, this was found not to be the case. In tests Ce215s01 (with pre-reduction) and Ce232s01 (without prereduction) the same sulfidation conditions were used. With pre-reduction the H_2S concentration remained near the 1ppmv level for about 115 minutes. Without pre-reduction, there was an early peak in the H_2S concentration at 33 ppmv followed by a decrease to less than 5 ppmv between 23 and 115 minutes. FPD breakthrough then occurred at 125 minutes.

The following explanation is proposed to describe the performance difference. With pre-reduction the entire bed consists of CeO_n ($n < 2$) before being exposed to H_2S, with the value of n dependent on the temperature and H_2 concentration during reduction. Without pre-reduction, the entire bed is CeO_2 at the beginning of the test and reduction and sulfidation occur simultaneously. The early H_2S peak is associated with incomplete reduction. However, because of the large H_2 to H_2S ratio, reduction occurs downstream of the sulfidation reaction front and the subsequent reaction is between H_2S and CeO_m ($m < 2$). We expect m to be larger than n since with pre-reduction all CeO_2 is exposed to 10% H_2 reducing gas with no H_2O present. Without pre-reduction the upstream reaction of H_2S consumes a small quantity of H_2 and produces H_2O. The reducing power of this product gas is lower so that $m > n$ and H_2S removal is reduced. Nevertheless, during most of the prebreakthrough period of test Ce232s01, the H_2S concentration was below the 20 ppmv IGCC target level.

The Effect of Steam in the Feed Gas

Steam was introduced with the reactor feed gas in the remainder of the tests using Rhone-Poulenc CeO_2. As shown in Table 1, three different gas compositions were used at sulfidation temperatures of 700°C and 800°C. No pre-reduction step was included in any of the tests. The 2.5% H_2O, 50.25% H_2 composition used in test Ce237s01 and the 3.5% H_2O, 50.25% H_2 used in test Ce238s01 were chosen to closely match the equilibrium O_2 partial pressure of Shell gas. The 6.5% H_2O - 28.25% H_2 used in tests Ce239s01 through Ce243s01 approximated the actual H_2O and H_2 contents of the Shell gas. However, in the absence of CO and CO_2 the equilibrium O_2 pressure of the experimental gas was considerably larger than the Shell gas, i.e., the experimental gas was less reducing. Addition of CO and CO_2 at the levels present in Shell gas was impractical because of carbon deposition as the feed is preheated.

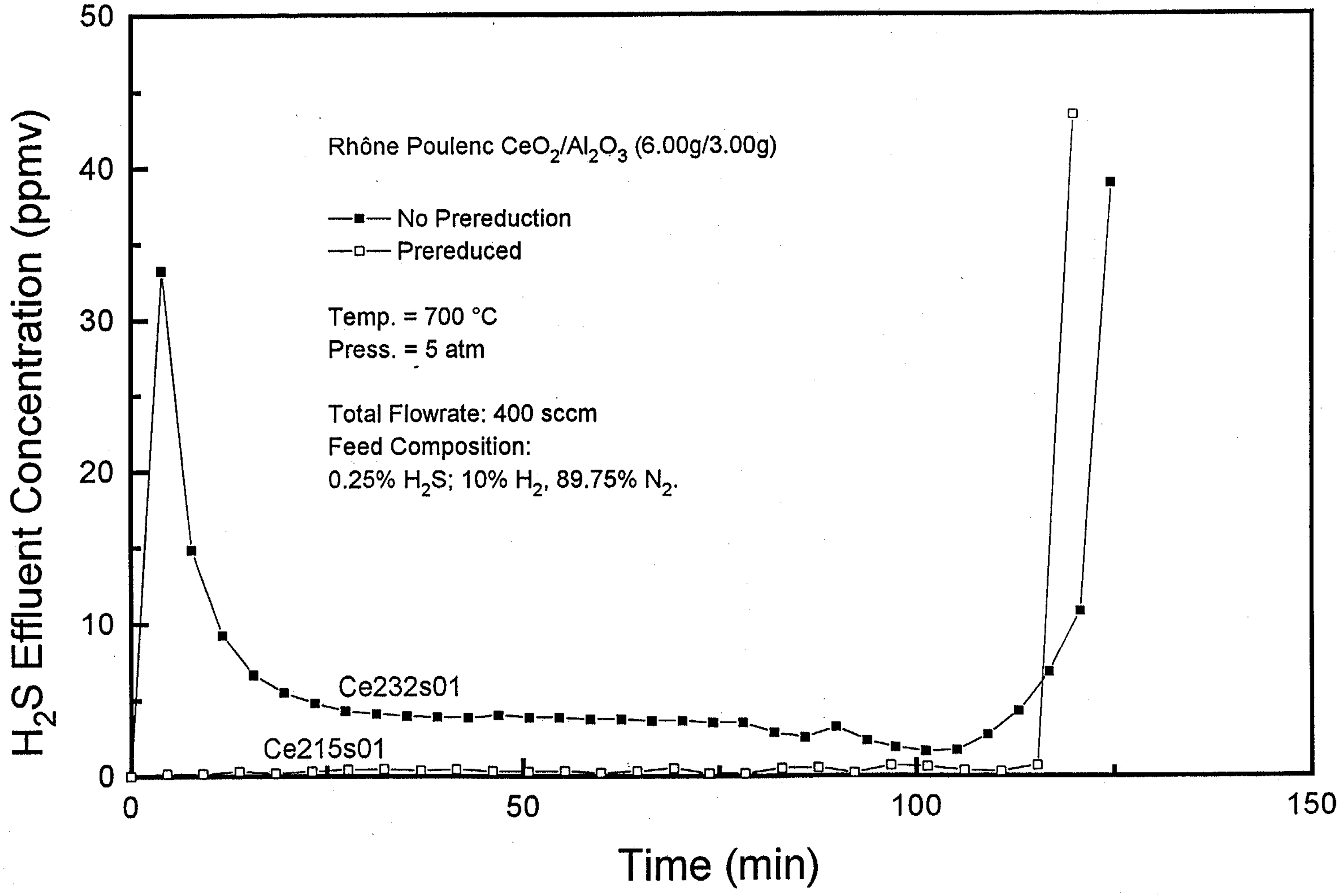

Figure 6. Comparison of Prebreakthrough Response With and Without Pre-Reduction.

Results from Ce237s01 and Ce238s01 with H_2O in the feed along results from earlier test Ce232s01 without H_2O, but otherwise the same reaction conditions, are shown in Figure 7. With the large H_2 and small H_2O contents, the presence of H_2O had no negative impact. The early H_2S peak was absent, prebreakthrough concentrations were slightly smaller (about 2 ppmv in both Ce237s01 and Ce238s01 compared to about 4 ppmv in Ce232s01), and the FPD breakthrough times were extended to 195 minutes from 120 minutes.

Our current explanation of these results is based on the equilibrium O_2 pressure exerted by the product gas from each of these feed gas compositions. Table 3 compares the composition of the experimental feed and product gases, with the product composition based on the complete removal of H_2S via the reaction

$$2CeO_2(s) + H_2S(g) + H_2(g) \longleftrightarrow Ce_2O_2S(s) + 2H_2O(g)$$

The sorbent downstream of the sulfidation reaction front is exposed to the product gas composition which determines the extent to which CeO_2 is reduced to CeO_n ($n < 2$) and, consequently, the desulfurization efficiency. Even though the feed gas in Ce232s01 was H_2O-free, the H_2O produced by reaction is sufficient to increase the equilibrium O_2 pressure (see last row of Table 3) to a value approximately one order of magnitude larger than the equilibrium O_2 pressure of the product gas from Ce237s01 and Ce238s01. The absence of the initial peak, the lower prebreakthrough concentration, and the extended duration of the prebreakthrough period are all attributed to the lower O_2 pressure.

While the H_2O and H_2 contents of the feed gas in test Ce239s01 were approximately equal to the Shell gas, the absence of CO and CO_2 made the equilibrium O_2 pressure even larger (see Table 3). As a result, the sulfidation behavior of test Ce239s01 shown in Figure 8 was poor. The FPD prebreakthrough period lasted only 20 minutes and the prebreakthrough H_2S concentration was about 70 ppmv.

Test Ce240s01 was identical to Ce239s01 except that both the FPD and TCD were used in the latter run. Ce241s01 also used both the FPD and TCD and the sulfidation temperature was increased to 800°C. In these tests product gas flow was diverted to the TCD after the FPD became saturated, and sulfidation was continued to completion. Results are shown in Figure 9. The data gap is associated with the time required for the TCD to equilibrate after flow was established. During the FPD portion of the tests the higher temperature produced lower initial H_2S concentrations (10 ppmv vs. 70 ppmv) but for a shorter time (20 min vs. 40 min). During the TCD portion of the tests the prebreakthrough concentrations at 800°C were slightly smaller, with both tests in the 300-400 ppmv range. TCD breakthrough time was effectively identical at 450 minutes in each test, and the fractional cerium conversions at the completion of the tests were 0.99 in Ce240s01 and 1.01 in Ce241s01.

In those tests with H_2O in the feed gas, the area near the o-rings holding the quartz insert in place was heated to prevent H_2O condensation. The o-rings also prevented the feed from bypassing the sorbent. At the conclusion of both Ce240s01 and Ce241s01 we found that the quartz

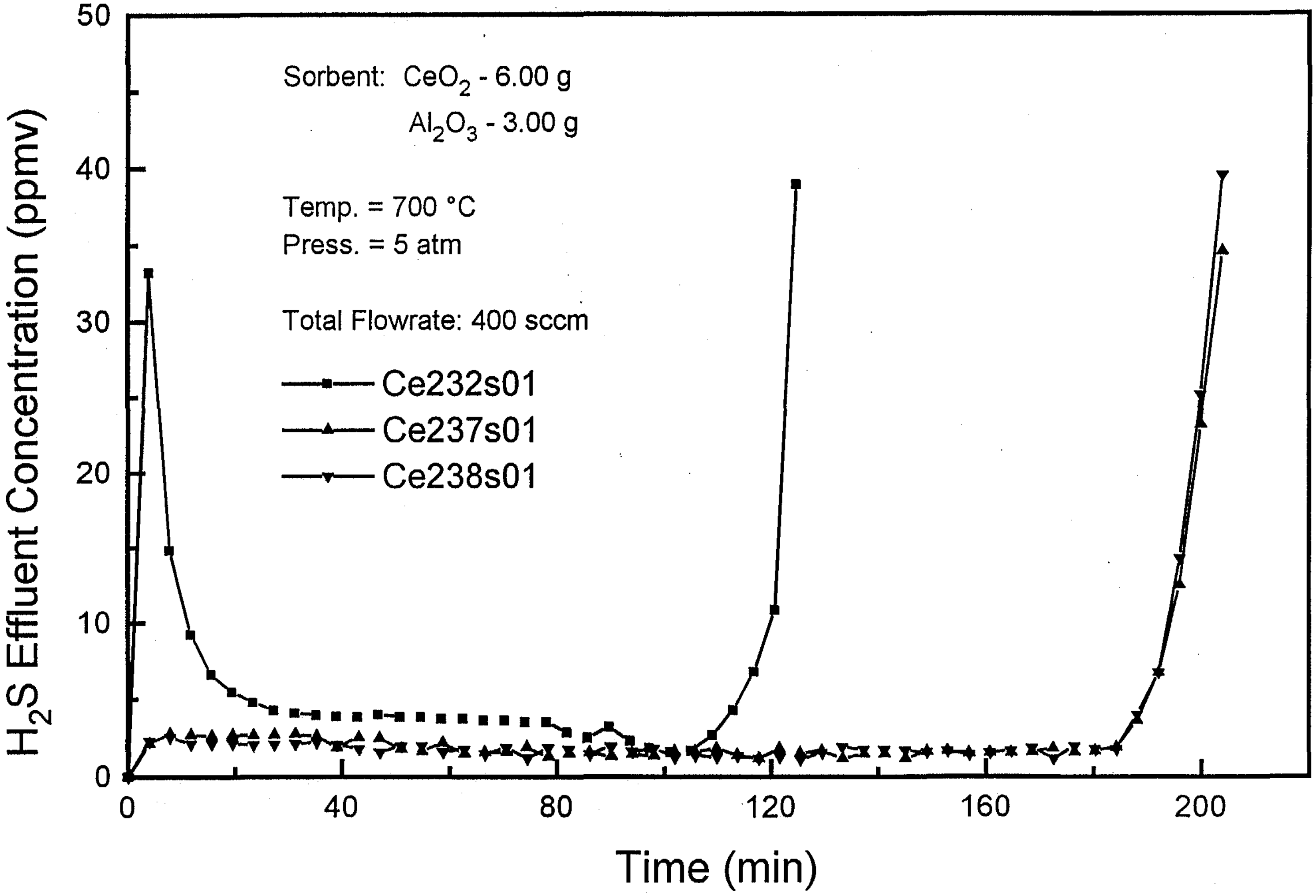

Figure 7. The Effect of Steam Addition With the Feed Gas Containing a Large H_2-to-H_2O Ratio.

Table 3. Comparison of Compositions and Equilibrium Oxygen Pressures of Experimental Gases

	Experimental Gases			
	Ce232s01	Ce237s01	Ce238s01	Ce239s01
Feed Comp., mol %				
H_2S	0.25	0.25	0.25	0.25
H_2O	0	2.5	3.5	6.5
H_2	10	50.25	50.25	28.25
CO	0	0	0	0
CO_2	0	0	0	0
N_2	89.75	47	46	65
Product Comp., mol %				
H_2S	0	0	0	0
H_2O	0.5	3.0	4.0	7.0
H_2	9.75	50	50	28
CO	0	0	0	0
CO_2	0	0	0	0
N_2	89.75	47	46	65
Product, H_2/H_2O Ratio	19.5	16.7	12.5	4
Equil. O_2 Press, atm at 700°C and 5atm	8.5×10^{-21}	0.62×10^{-21}	1.1×10^{-21}	12×10^{-21}

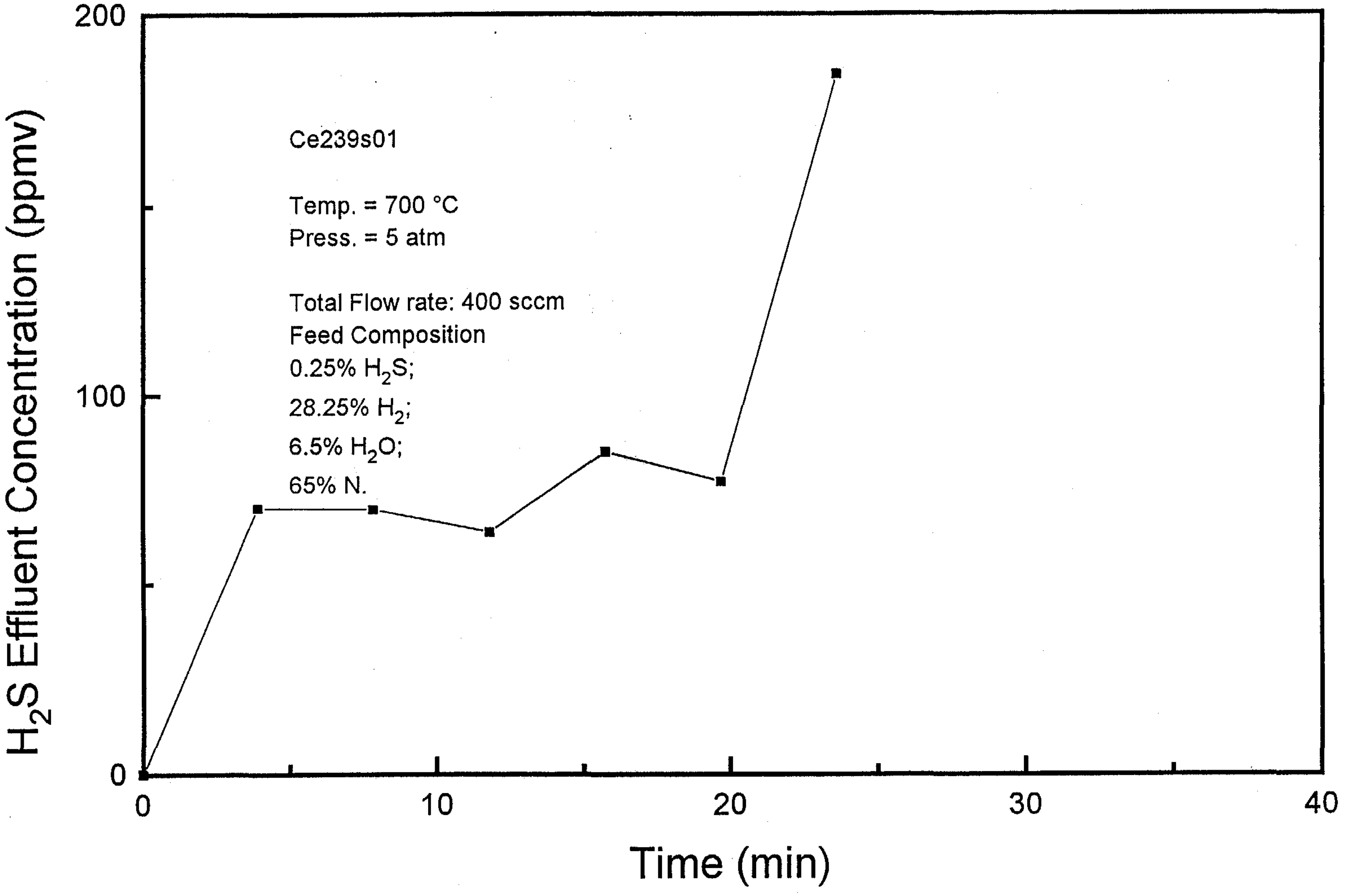

Figure 8. The Steam Addition With the Feed Gas Containing H_2 and H_2O Equivalent to Shell Gas.

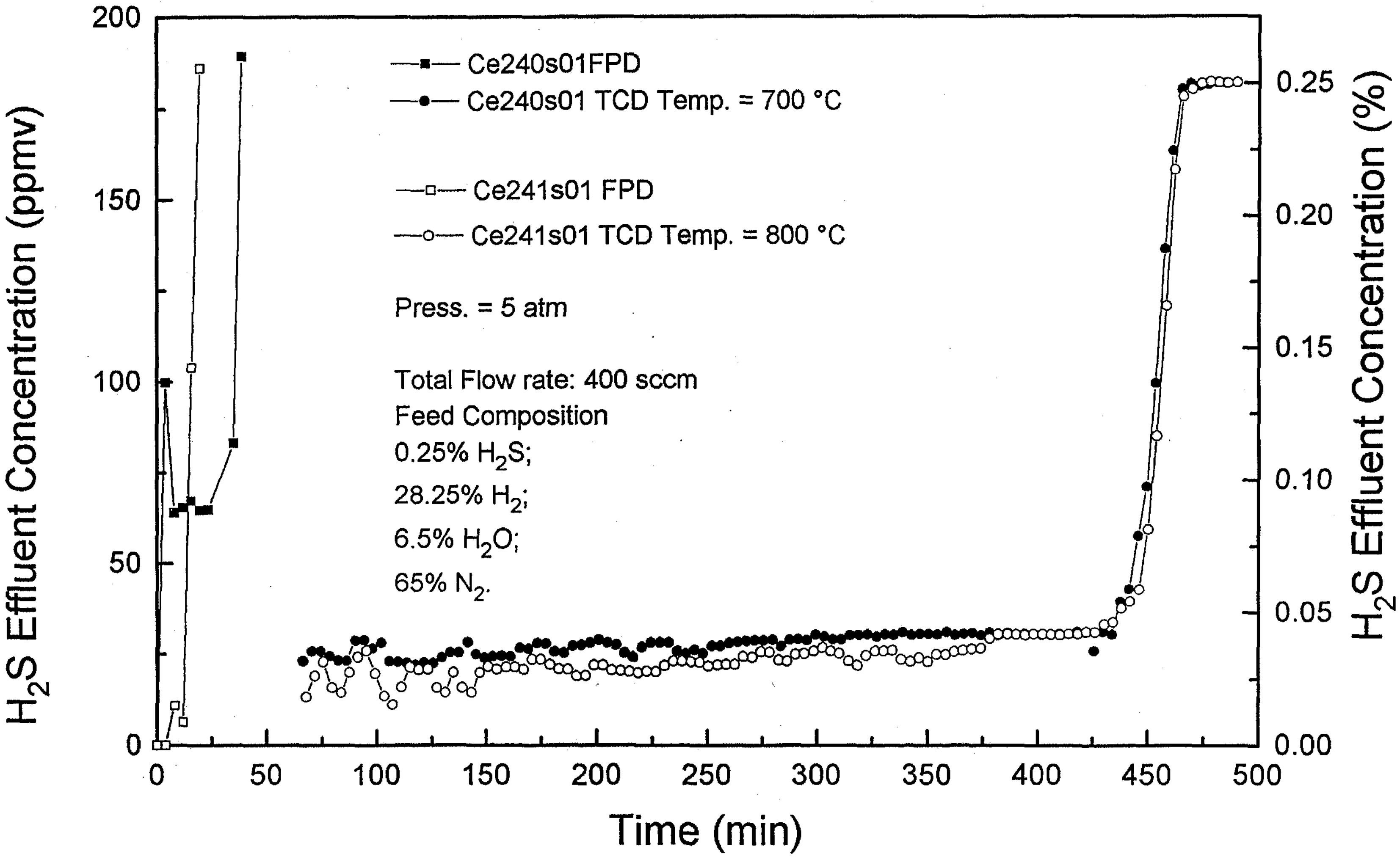

Figure 9. The Effect of Temperature on the Complete H_2S Breakthrough Curve With the Feed Gas Containing H_2 and H_2O Equivalent to Shell Gas.

insert had cracked at the shoulder where it was supported by o-rings. We attribute the cracking to the higher temperatures in the area of the o-rings necessitated by the higher H_2O concentration since no cracking had occurred in any of the previous runs. Consequently, test Ce242s01 was carried out at the same reaction conditions as used in Ce241s01, except that the o-ring area was heated to a lower temperature. H_2S breakthrough curves in Ce241s01 and Ce242s01 were similar, with the H_2S concentrations marginally higher in Ce242s01. TCD breakthrough time (1000 ppmv H_2S) was 458 minutes in Ce242s01 compared to 451 minutes in Ce241s01. The results showed that feed bypassing was not a problem.

REDUCTION-SULFIDATION USING OTHER CeO_2 SOURCES

Five additional sources of CeO_2 were tested during the quarter to compare results with the standard Rhone-Poulenc CeO_2. Brief descriptions of the alternate sorbents are found in Table 4 while Table 5 summarizes the reaction conditions used in the reduction-sulfidation tests. Three of the alternate sorbents (WGW1, WGW2, WGW3) were obtained from Gas Desulfurization Corp. and were prepared by Engelhard Corp. by depositing CeO_2, or CeO_2 and La_2O_3, on Al_2O_3 spheres approximately 1/8 inch diameter. These pellets were crushed and sieved to 150 to 300 μm, the same particle size as used in the Rhone-Poulenc CeO_2 tests. No surface area information is available on these sorbents. However, high surface areas are expected because of the Al_2O_3 support. Molycorp was the source of the other two sorbents. Sorbent MC was 96% CeO_2 which was tableted, crushed, sieved, and then mixed with Al_2O_3 using the same procedure as used with the Rhone-Poulenc CeO_2. However, as noted in Table 4 the specific surface area of MC sorbent was less than 10% that of the Rhone-Poulenc sorbent. $Ce_2(CO_3)_3$ was the CeO_2 precursor in tests Ce235s01 and Ce236s01. In test Ce235s01 the carbonate was calcined inside the reactor after being mixed with Al_2O_3. In test Ce236s01 the carbonate was calcined externally in a tube furnace and then mixed with Al_2O_3 and charged to the reactor. No data is available on the surface area of either the carbonate precursor or the oxide product.

As shown in Table 5 the quantity of CeO_2 was variable in these tests and, particularly with WGW1 and WGW2 sorbents, was significantly less than used in the Rhone-Poulenc tests. A pre-reduction step was included in only two of the nine tests involving the alternate sorbents. Except for the last test (Ce243s01) sulfidation temperature, pressure, and feed gas composition were equal in all tests. Ce243s01 used the higher sulfidation temperature of 800°C and the H_2 and H_2O contents of the feed gas matched the Shell gas composition. The sulfidation feed gas rate was 400 sccm in all except the first two tests where a feed rate of 200sccm was used.

H_2S breakthrough curves from tests Ce226s01 and Ce228s01, both using WGW1 sorbent, the first at a flow rate of 200 sccm without pre-reduction and the second at a flow rate of 400 sccm with pre-reduction are shown in Figure 10. Without pre-reduction the early peak in H_2S concentration at 15 ppmv was followed by a decrease to about 5 ppmv prior to FPD breakthrough at 150 minutes. With pre-reduction there was no early H_2S peak, the H_2S concentration was near zero for 23 minutes and below 5 ppmv for 55 minutes. Most of the difference between the breakthrough times of 150 minutes in Ce226s01 and 60 minutes in Ce228s01 is a result of the differences in feed rate.

Table 4. Alternate Sorbents Used in Reduction-Sulfidation Tests

Designation	Description
MC	96% CeO_2 from Molycorp. This sorbent was pressed into tablets which were subsequently crushed and sieved in a manner similar to that used for Rhone Poulenc sorbent. However, the surface area after tabletting, crushing, and sieving was only 11 m^2/g compared to 156 m^2/g for the Rhone-Poulenc CeO_2.
MC1	Cerium carbonate, $Ce_2(CO_3)_3$, from Molycorp served as the CeO_2 precursor in two tests. In one test (Ce235s01) 10g of the as-received $Ce_2(CO_3)_3$ was mixed with 3.0 g of Al_2O_3 and the mixture was calcined inside the reactor at 700°C in N_2. The 6.6g of CeO_2 shown in Table 5 for this run is based on measured weight loss at 200°C (presumably H_2O) followed by the presumption of complete calcination of pure $Ce_2(CO_3)_3$ to 2 CeO_2. In test Ce236s01, $Ce_2(CO_3)_3$ was calcined at 750°C in air in a tube furnace outside the reactor. 6.0g of the calcined product was then mixed with 3.0g of Al_2O_3 and added to the reactor.
WGW1	This sorbent was supplied by Gas Desulfurization Corp. and consisted of 22% (wt) CeO_2 deposited on Al_2O_3 substrate. The as-received sorbent was in the form of 1/8 inch diameter spheres cylinders which were crushed and sieved for use in tests Ce226s01 and Ce228s01.
WGW2	This sorbent was also obtained from Gas Desulfurization Corp. and was similar to WGW1 except that La_2O_3 as well as CeO_2 was deposited on the Al_2O_3 substrate. The composition (wt.%) was reported to be 18.2% CeO_2, 3.8% La_2O_3, and 78% Al_2O_3. This sorbent was also in the form of 1/8 inch diameter spheres, and was treated in the same manner as WGW1.
WGW3	This sorbent was similar to WGW1 except for a high loading of 50% CeO_2. This sorbent was received as 1/8 inch diameter spheres and was handled in the same manner as the other sorbents from Gas Desulfurization Corp. It was used in test Ce231s01.

Table 5. Summary of Reduction-Sulfidation Reaction Conditions Using Alternate CeO_2 Sorbents (April - June 1998)

Test	Ce226s01	Ce227s01	Ce228s01	Ce229s01	Ce230s01	Ce231s01	Ce235s01	Ce236s01	Ce243s01
Date	5-03-98	5-06-98	5-20-98	5-21-98	5-22-98	5-25-98	6-01-98	6-03-98	6-26-98
Sorbent, g	WGW1	WGW2	WGW1	WGW2	WGW3	MC	MC1	MC1	WGW2
CeO_2	2.2	1.8	2.2	1.8	5.0	6.0	6.6	6.0	1.8
La_2O_3	–	0.4	–	0.4	–	–	–	–	0.4
Al_2O_3	7.8	7.8	7.8	7.8	5.0	3.0	3.0	3.0	7.8
Pre-Reduction	None	None	Yes	Yes	None	None	None	None	None
Temp., °C	–	–	700	700	–	–	–	–	–
Press., atm	–	–	5	5	–	–	–	–	–
Gas Comp.	–	–			–	–	–	–	–
% H_2	–	–	10	10	–	–	–	–	–
% N_2	–	–	90	90	–	–	–	–	--
Sulfidation									
Temp., °C	700	700	700	700	700	700	700	700	800
Press., atm	5	5	5	5	5	5	5	5	5
Gas Comp.									
% H_2S	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
% H_2	10	10	10	10	10	10	10	10	28.25
% H_2O	0	0	0	0	0	0	0	0	6.5
% N_2	89.75	89.75	89.75	89.75	89.75	89.75	89.75	89.75	65
Flow Rate, sccm	200	200	400	400	400	400	400	400	400

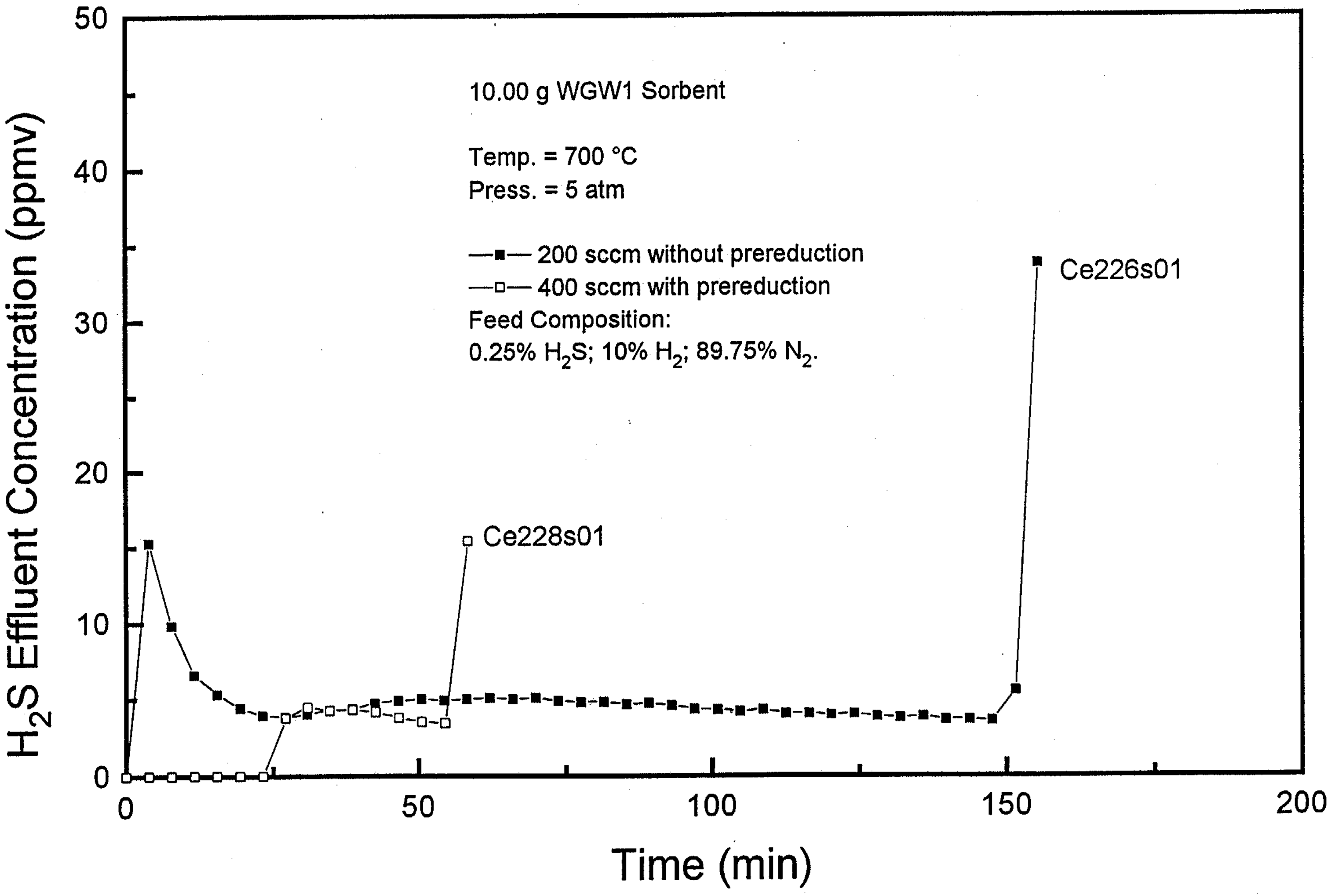

Figure 10. FPD Breakthrough Using WGW1 Sorbent.

Runs Ce222s01 using Rhone-Poulenc CeO_2 and Ce228s01 using WGW1 sorbent were at the same reaction conditions. H_2S concentrations were below 5 ppmv prior to breakthrough in each test, while the FPD breakthrough time was 90 minutes in Ce222s01 and 60 minutes in Ce228s01. The ratio of FPD breakthrough times (90/60 = 1.5) is considerably smaller than the ratio of the quantities (6.0/2.2 = 2.7) which suggests more efficient unitization of CeO_2 in the WGW1 sorbent.

The addition of La_2O_3 in WGW2 had no obvious effect either with or without pre-reduction. This is shown in Figure 11 where results from tests Ce226s01 and Ce228s01, both using WGW1 sorbent without and with pre-reduction, respectively, are compared to Ce227s01 and Ce229s01 using WGW2 sorbent, also without and with pre-reduction. The early H_2S peak at about 15 ppmv was present in both cases without pre-reduction, and the H_2S concentration then decreased to about 5 ppmv until FPD breakthrough at about 150 minutes. The two tests with pre-reduction were fed at 400 sccm which accounts for the earlier breakthrough. There was no early H_2S peak and the H_2S concentration was equal to or less than 5 ppmv for the entire time prior to breakthrough.

Figure 12 compares the H_2S breakthrough curves for four different sorbents – WGW1 (Ce226s01), WGW3 (Ce230s01), MC (Ce231s01) and RP (Ce232s01) – at the same sulfidation conditions. No pre-reduction was used in any of these tests. However, both the feed rate and quantity of CeO_2 in the initial charge were different which accounts for the different breakthrough times. The expected initial H_2S peak, associated with no pre-reduction, was present in each test and ranged from 15 to 35 ppmv. After the initial H_2S peak the H_2S concentration decreased to about 1 ppmv with MC sorbent, to about 5 ppmv with both WGW1 and RP sorbents, and to about 20 ppmv with WGW3. The 150 minute breakthrough time for RP sorbent corresponded to a dimensionless time of $t^* \sim 0.34$ while the 80 minute breakthrough time for MC sorbent corresponded to $t^* \sim 0.2$. The more rapid FPD breakthrough with MC may be associated with its smaller surface area. The dimensionless breakthrough times for WGW1 and WGW3 were about 0.50 and 0.45, respectively, again showing more efficient cerium utilization. While there are no surface area measurements available for either WGW1 or WGW3, we expect reasonably large values since both were prepared by depositing CeO_2 or high surface area Al_2O_3 carrier.

HIGH PRESSURE REGENERATION TEST

Test Ce243s01 competed the planned CeO_2 sulfidation series leaving only a limited number of high pressure regeneration tests on the schedule. All previous regeneration tests were run at 1 atm with this limit established by the low vapor pressure of SO_2. In order to carry out high pressure regeneration, a gas mixture containing 12% SO_2 in N_2 was purchased. The mixture pressure was supposed to be 180 psi which would permit regeneration at pressures to near 12 atm. However, the first cylinder contained only 60 psi of gas mixture and a single test at 2 atm regeneration pressure was completed at the end of the quarter.

Sulfidation and regeneration conditions for this test are presented in Table 6. The standard Rhone-Poulenc CeO_2 - Al_2O_3 mixture was used without pre-reduction. Sulfidation conditions were 800 °C and 5 atm using 1% H_2S and no H_2O in the feed gas. Regeneration at 600 °C and 2 atm using

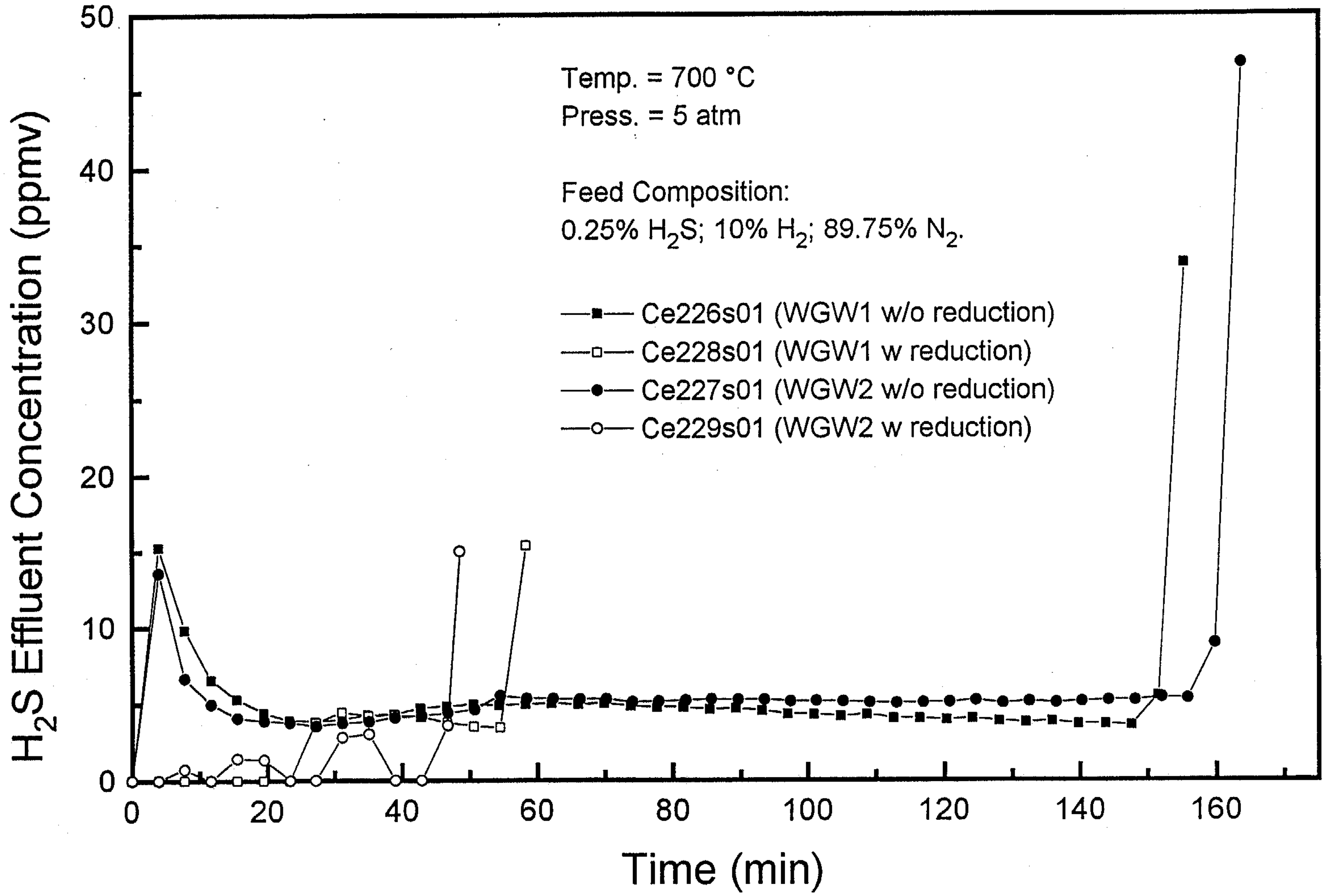

Figure 11. Comparison of FPD Breakthrough Curves Using WGW1 and WGW2 Sorbents.

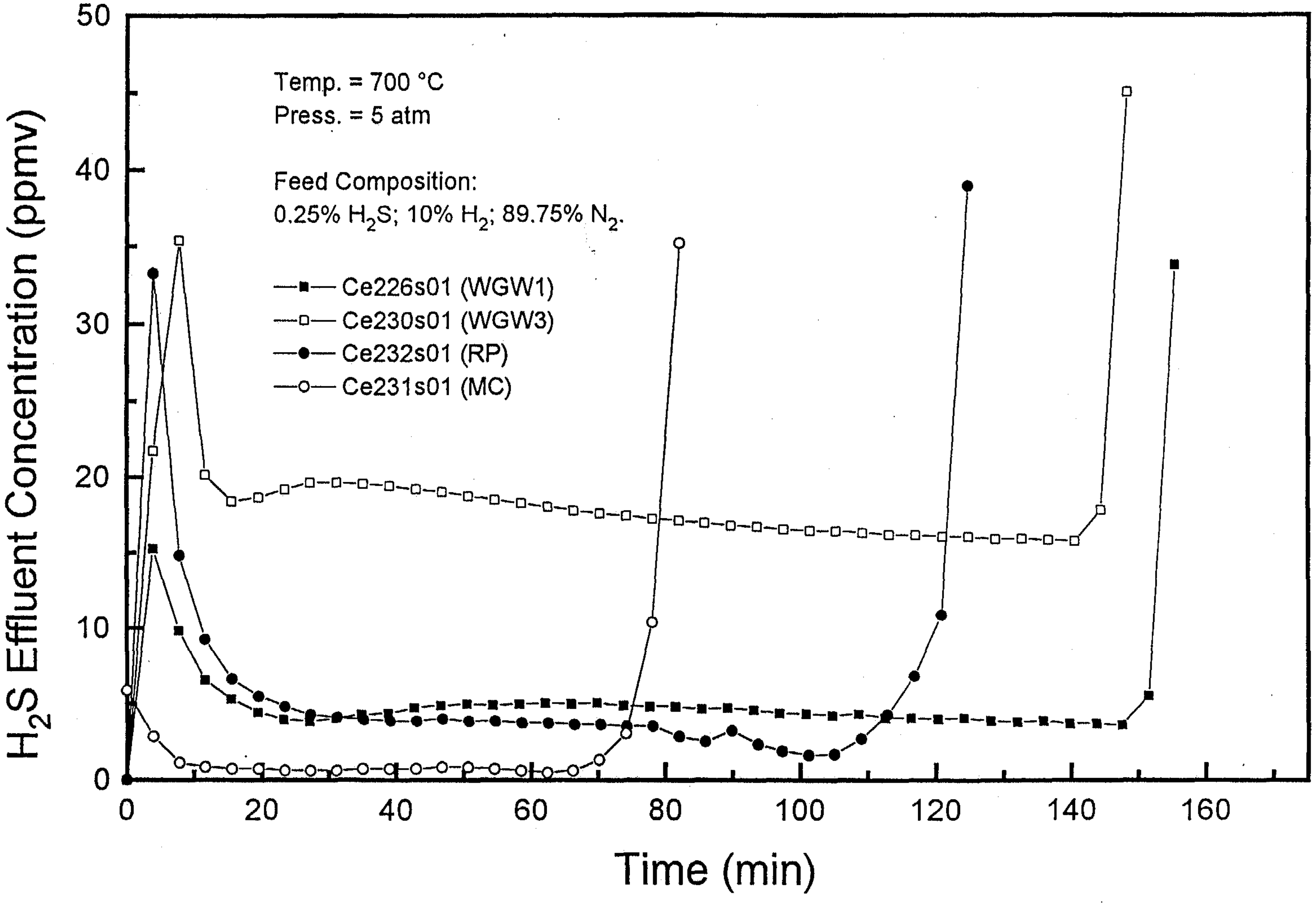

Figure 12. Comparison of FPD Breakthrough Curves From Four Cerium-Based Sorbents.

Table 6. Sulfidation and Regeneration Conditions Used in Initial High Pressure Regeneration Test

	Sulfidation	Regeneration
Test	Ce244s01	Ce244r01
Date	6/30/98	6/30/98
Sorbent, g	RP	RP
CeO_2	6.0	6.0
Al_2O_3	3.0	3.0
Reduction	None	None
Reactions		
Temp., °C	800	600
Press., atm	5	2
Gas Comp.		
% H_2S	1.0	–
% H_2	10	–
% N_2	89	88
% SO_2	–	12
Flow Rate, sccm	400	400

12% SO_2 in N_2 followed immediately. A feed rate of 400 sccm was used for sulfidation and regeneration, and all gas analysis was based on the TCD. The SO_2 breakthrough curve from Ce244r01 is shown in Figure 13 along with results from Ce204r01 using the same regeneration temperature and gas composition, but at 1 atm and 200 sccm feed rate. Doubling the pressure effectively halved the regeneration gas velocity, while doubling the feed rate countered the effect of pressure on velocity but also doubled the H_2S feed rate. The net result should be an approximate halving of the breakthrough time which, as shown in Figure 13, is consistent with the experimental data.

The only anticipated problems in carrying out high pressure regeneration are associated with preventing condensation of elemental sulfur and plugging reactor exit lines. For example, the 2 atm regeneration test using 12% SO_2 is, in terms of elemental sulfur concentration, the equivalent 24% SO_2 at 1 atm. The highest SO_2 concentration previously tested at 1 atm was 20%. For this reason, most high pressure regeneration runs will use dilute SO_2.

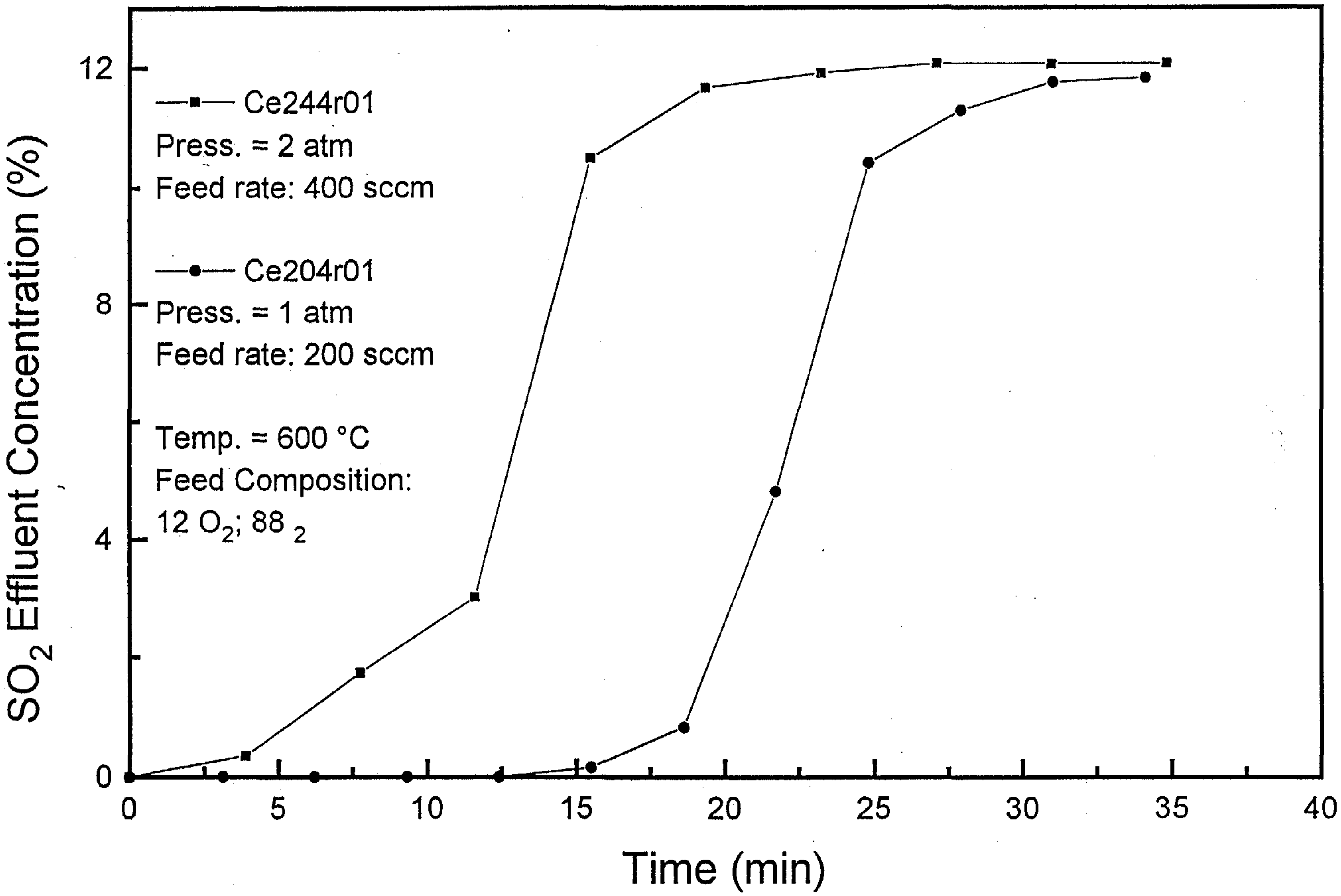

Figure 13. Results From First Regeneration Test at a Pressure Greater Than 1 atm.