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Kinetics of Mn-based Sorbents for Hot Coal Gas Desulfurization

Quarterly Report for the period of June 15, 1996 to September 15, 1996.
Task 2: Exploratory Experimental Studies: Single Pellet Tests; Rate Mechanism Analysis.

By
M.T. Hepworth, Principal Investigator, Department of Civil Engineering, University of Minnesota, Minneapolis, MN 55455.

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1. INTRODUCTION

Currently, the Morgantown Energy Technology Center, Department of Energy (DOE/METC) is actively investigating alternative hot fuel gas desulfurization sorbents for application to the Integrated Gasification Combined Cycle (IGCC)[1]. A sorbent must be highly active towards sulfur at high temperatures and pressures, and under varying degrees of reducing atmospheres. Also, it must regenerate nearly ideally to maintain activity over numerous cycles. Furthermore, regeneration must yield a sulfur product which is economically recoverable directly or indirectly.

Several metal oxides have been investigated[2-4] as regenerable sorbents for the removal of hydrogen sulfide (the primary sulfur bearing compound) from hot fuel gases. MnO was shown to have an intrinsic reaction rate approximately one order of magnitude greater than the rate or reaction with either CaO or ZnO and two orders of magnitude greater than the reaction rate with V_2O_3[3]. Manganese also shows desulfurization potential in the temperature range of 600-700°C where metal oxides currently known to be reactive with H_2S are unsatisfactory[2].

In response to stability difficulties of single and binary metal oxide sorbents, increasing effort is being directed towards incorporation of an inert component into sorbent formulation as witnessed by the various Zn-titanates[5-9]. Primarily, the inert component increases pore structure integrity while stabilizing the active metal oxide against reduction. This report will address the testing of Mn-based sorbents in an ambient pressure fixed-bed reactor. Steady-state H_2S concentrations and breakthrough times will be presented.

2. METHODS AND MATERIALS

Composition

Variables that were considered in formulating Mn-based sorbents included:

substrate composition,

Mn to substrate molar ratio,

non-volatile binder wt %,

The only source of manganese used was from a commercially available $MnCO_3$. Alundum and titanate were both tested as substrate based on previous considerations[10]. Molar ratios of Mn to substrate were varied from 1:1 to 4.33:1. Bentonite was used as a non-volatile binder at 0 and 2 % by weight. All chemical compositions, vender information, and particle sizes have been reported previously[11-14].

Preparation

Feed powders were hand mixed and pelletized in a balling wheel forming "green" pellets. Green pellets were air dried for one day and then dried to a constant weight at 105°C. Dry pellets were calcined for four hours at 350°C. Immediately after calcination, pellets were placed in a high-temperature furnace (pre-heated to 500°C), where the temperature was ramped up for 2 to 2.5 hours until final induration temperature was achieved. The pellets were indurated at this temperature for two hours. The indurated pellets were 1.2 to 2.6 mm in size.

Formulation Designations

Each pellet formulation can be fully described by the following designation, ex. C6-2-1100. The letter describes the manganese source (C for $MnCO_3$). The first number describes the substrate composition and molar ratio of Mn to substrate (4 for 4.33:1 Mn :alundum, 6 for 4.33:1 Mn:titania, 8 for 2:1 Mn:titania and 11 for 1:1 Mn:alundum. The second number is the weight percent bentonite binder. The last number is the temperature at which the pellets were indurated in degrees Centigrade. Table 1 summarizes the formulations tested in the fixed-bed reactor.

Formulation Designation	Molar Ratio Mn:Substrate	Substrate	Wt% Bentonite	Induration Temperature °C
C4-2-1175	4.33:1	Alundum	2	1175
C6-2-1100	4.33:1	Titania	2	1100
C8-0-1200	2:1	Titania	0	1200
C11-0-1160	1:1	Alundum	0	1160

Table 1. Formulations of Pellets Tested in the Fixed-bed Reactor and Their Designations

Characterization

Indurated pellets were characterized both physically and chemically using crush strength testing, fixed-bed testing, porosimetry, x-ray diffraction (XRD) and sulfur analysis. Crush strength testing and fixed-bed testing are describe in detail below. Porosimetry, XRD, and sulfur analysis will be presented in the next quarterly report.

Crush Strength

The first characterization done on the freshly indurated pellets was crush strength. Crush strength tests were conducted on all freshly indurated pellets with the requirement of 1 lb/pellet/mm^2 of diameter. Thus, a 1 mm pellet should have a crush strength of 1 lb/pellet and a 3 mm pellet should have a crush strength of 9 lb/pellet. This assumption was made previously[10] and assumes the crush straight increases proportionally with the pellet cross-sectional area. Pellets were indurated at the minimum temperature required to achieve this strength.

Fixed-Bed Testing

After crush testing proved satisfactory, indurated pellets were tested in an ambient pressure fixed-bed reactor to determine steady state H_2S concentrations, breakthrough times and effectiveness of the sorbent when subjected to recycle testing. Figure 1 is a schematic diagram of the fixed-bed experimental apparatus. The reactor consists of a 1" ID quartz tube positioned vertically in the two-zone furnace. Figure 2 is a schematic of the reactor. The reaction temperature was monitored using a Pt/Rd thermocouple positioned directly above the sorbent bed. Sulfidation and regeneration gases entered the reactor in an upward direction. Exit gases were cooled in a cold trap where vapors such as water and sulfur were condensed and collected. The gases were then scrubbed in a hypochlorous acid solution (sulfidation) or a hydrogen peroxide and sodium hydroxide solution (regeneration) prior to flaring and venting.

For each test, 3.5 to 3.75 inches (40 to 55 g) of sorbent was added to the reactor tube in the reaction zone. The reactor was heated in a nitrogen atmosphere to the desired operating temperature. Simulated coal gases spiked with H_2S were then introduced into the reactor at 3L/min. Exit gases were sampled after the cold trap and were analyzed using Gastec Detector Tubes (Gastec Corp.) for H_2S until breakthrough occurred. The test conditions for sulfidation are summarized in Table 2.

Sample mass	40-55 g
Sulfidation temperature	600°C
Average pellet diameter	1.2-2.6 mm
Gas composition	Shell (oxygen blown, see Figure 7)
Gas flow rate	3 L/min
H_2S concentration	2.2 mol %
Pressure	1 atm

Table 2. Conditions of Fixed-Bed Sulfidation Experiments for all Formulations

The sorbent was regenerated in air, oxygen depleted air, or steam after each sulfidation test. Regeneration of the sorbent was conducted at 750°C and 900°C. Regeneration in air was conducted at 900°C. Although it is theoretically possible to regenerate pellets in air at temperatures as low as 600°C, a fixed-bed reactor, where oxygen is supplied at higher chemical potential will cause sulfation. Figures 3-5 are stability diagrams showing the conditions under which sulfation will occur for 600, 800, and 1000°C respectively. Regeneration in oxygen depleted air, and steam was conducted at 750°C Five cycles of sulfidation and regeneration were conducted for each test to determine the sorbent's activity retention. The test conditions for regeneration are summarized in Table 3. The regeneration gas compositions and temperatures are listed in Table 4.

Sample mass	40-55 g
Regeneration temperature	750-900°C
Average pellet diameter	1.2-2.6 mm
Gas composition	Varied (see Table 4)
Gas flow rate	1 L/min
Pressure	1 atm

Table 3. Conditions of Fixed-Bed Regeneration Experiments for all Formulations

Test Number	Formulation	Regeneration Gas Composition	Regeneration Temperature (°C)
1	C6-2-1100	1000 cc/min air	900
2	C6-2-1100	100 cc/min O_2 900 cc/min N_2	750
3	C6-2-1100	50 cc/min O_2 950 cc/min N_2	750
4	C6-2-1100	400 cc/min steam 600 cc/min air	750
5	C8-0-1200	400 cc/min steam 600 cc/min air	750
6	C8-0-1200	800 cc/min steam 200 cc/min N_2	750
7	C4-2-1175	400 cc/min steam 600 cc/min air	750
8	C11-0-1160	800 cc/min steam 200 cc/min N_2	750

Table 4. Regeneration Gas Compositions and Temperatures

3. RESULTS

Results from the fixed-bed sulfidation testing will be presented in this section. Results from fixed-bed regeneration, sulfur analysis, porosimetry, crush strength testing and XRD will be presented in the next quarterly report.

Fixed-bed Testing

Figures 6 to 13 show the results of the fixed-bed sulfidation testing. Eight tests were conducted using four different formulations. Results from each formulation are describe separately below. A summary of the steady-state H_2S concentrations achieved in the fixed-bed and the breakthrough times for all tests conducted is given in Table 5. The breakthrough time based on the wt% Mn in the sorbent was calculated assuming a steady-state H_2S concentration of zero. Five cycles of sulfidation and regeneration were conducted for each test.

Formulation	Amount of Sorbent (g)	Steady-State H_2S(ppmv)	Breakthrough time based on wt% Mn (min)	Actual Breakthrough Time (min) Cycle				
				1	2	3	4	5
C6-2-1100 Figure 6	54.94	26.1	183.8	107	72	79	90	90
C6-2-1100 Figure 7	NA	46.3	NA	112	116	122	128	125
C6-2-1100 Figure 8	53.76	22.3	181.5	115	122	127	132	133
C6-2-1100 Figure 9	52.92	23.8	178.7	107	112	116	123	124
C8-0-1200 Figure 10	43.66	58.0	131.3	15	21	23	24	24
C8-0-1200 Figure 11	41.93	24.0	126	9	1	1	5	7
C4-2-1175 Figure 12	NA	24.7	NA	67	71	75	77	77
C11-0-1160 Figure 13	49.48	*	94.7	0	0	0	NA	NA

Table 5. Steady-State H_2S Concentrations and Breakthrough Times of Sorbent in Fixed-bed

Formulation C6-2-1100

Figures 6-9 are sulfidation breakthrough plots for formulation C6-2-1100. Four tests were conducted on this formulation. The conditions for each test are the same except that the sorbent was regenerated differently. The steady-state H_2S concentrations for each sulfidation cycle of each test ranged between 20 and 50 ppmv.

Figure 6 shows the breakthrough curves for sorbent regenerated in air at 900°C. As can be seen in this figure the sorbent did not regenerate completely. The second sulfidation cycle had a breakthrough time much earlier than the first sulfidation.

Figures 7 and 8 show the breakthrough curves for sorbent regenerated in oxygen depleted air and lower temperature. The breakthrough times are progressively better with progressing number of cycles. Cycle number 5 of Figure 8 shows a breakthrough time of 133 minutes which is 73% of the breakthrough time based on wt% Mn in sorbent.

Figure 9 shows the breakthrough curve for sorbent regenerated in steam and air. Again the breakthrough times are progressively better with progressing number of cycles.

Formulation C8-0-1200

Figures 10 and 11 are the sulfidation breakthrough plots for formulation C8-0-1200. Two tests were conducted on this formulation. For the first test, the sorbent was regenerated in air and steam, while the second was regenerated in steam and nitrogen. As can be seen in Figures 10 and 11, the sorbent did not regenerate as fully in steam and nitrogen as it did in air and steam.

Formulation C4-2-1175

Figure 12 is the sulfidation breakthrough plot of formulation C4-2-1175. This sorbent was regenerated in steam and air. As can be seen from the figure the breakthrough times become progressively better with progressing cycle numbers, however the steady-state H_2S concentration isn't as good for cycles 2-5 (60 ppmv) as compared to the first cycle (25 ppmv). Also, there is a large H_2S concentration early in cycles 2-5 that reduce to the steady-state after a short time. This may indicate the formation of sulfates during regeneration. When the sorbent is subsequently sulfided, the sulfates are reduced to SO_2 and is measured by the Detector Tubes incorrectly as H_2S.

Formulation C11-0-1160

Figure 13 is the sulfidation of a 1:1 molar ratio of Mn to substrate (alundum). As can be seen from the plot, this formulation was less effective in reducing the H_2S concentration than the sorbents that had >1:1 molar ratios of Mn:substrate. This is because the substrate combines with the Mn and is less effective as a reactant than MnO which is still present in sorbents with molar ratios >1:1.

4. CONCLUSIONS

Regeneration in a fixed-bed reactor, where oxygen is supplied at higher chemical potential, should be conducted at 900°C or greater to avoid sulfation which causes the pellets to fall apart.

Manganese based sorbents with molar ratios >1:1 Mn:substrate were effective in reducing the H_2S concentration in simulated coal gases to less than 100 ppmv over many cycles. Actual breakthrough time for formulation C6-2-1100 was as high as 73% of breakthrough time based on wt% Mn in sorbent.

Regeneration in steam and nitrogen did not effectively regenerate the pellets. Therefore steam should not be used as a reactant to regenerate the sorbent, rather it should be used as a diluent with air to keep the temperature from rising sharply during regeneration.

Titania and alundum should be used as a substrate, not as a reactant to combine with manganese, because if combined the manganese becomes much less effective in reaching the low levels of H_2S required by the desulfurization process for hot fuel gas.

Regeneration in oxygen depleted air at lower temperature gave the best sulfidation breakthrough curves for repeated cycles, however, the length and sulfur concentrations achieved in the regeneration exit gases are also an important consideration. This will be examined in the next quarterly report.

5. REFERENCES

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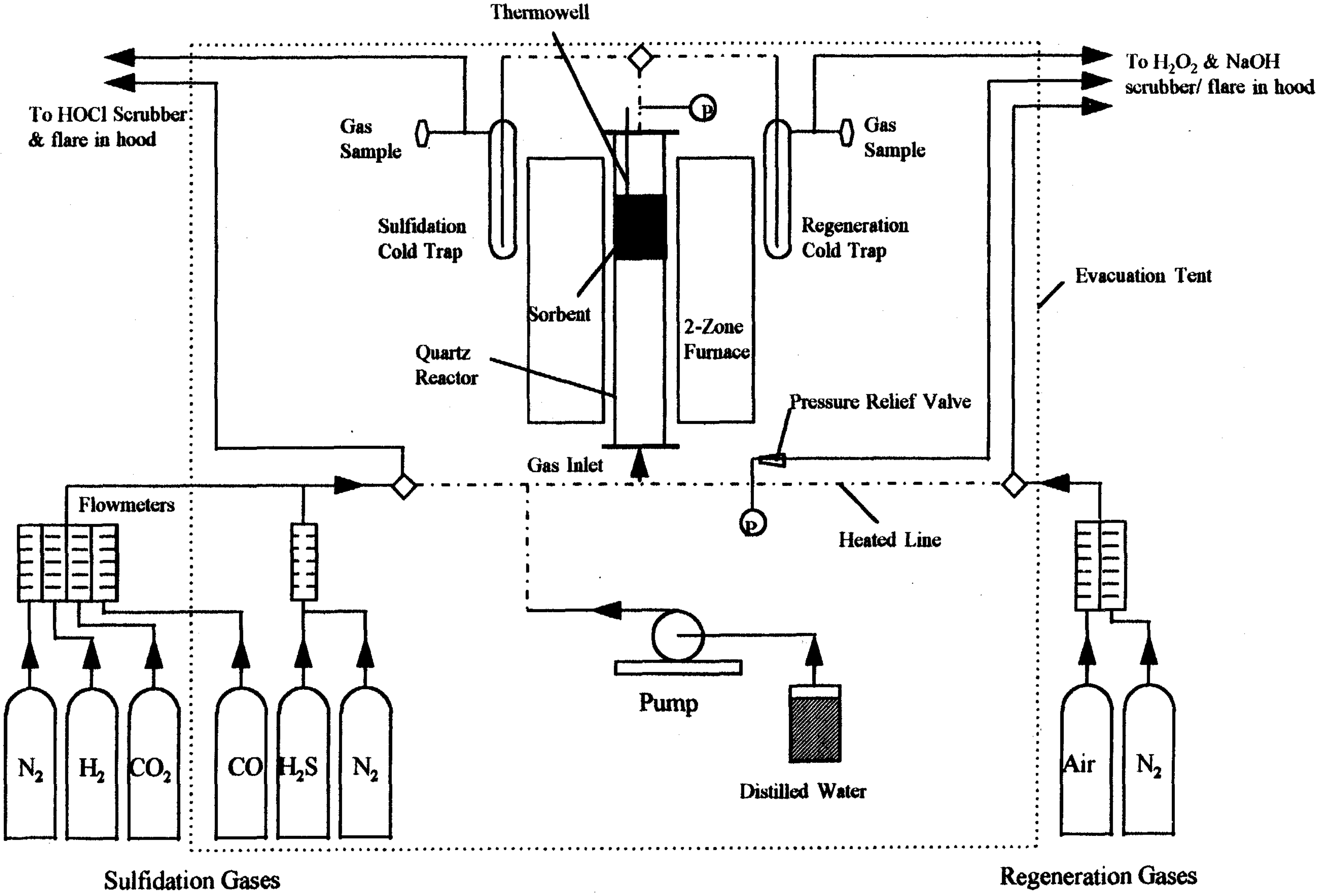

Figure 1. Schematic of Fixed-Bed Experimental Apparatus

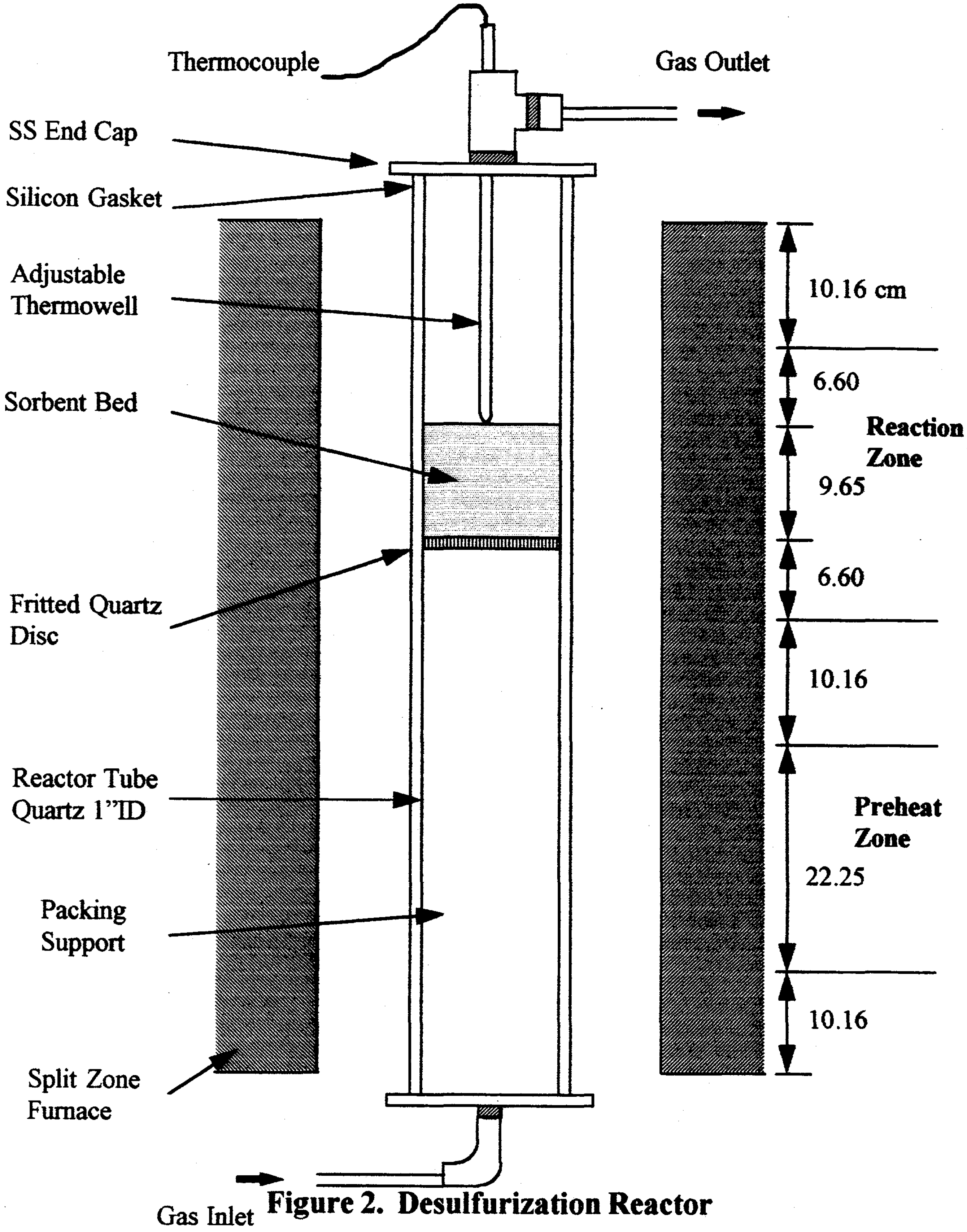

Figure 2. Desulfurization Reactor

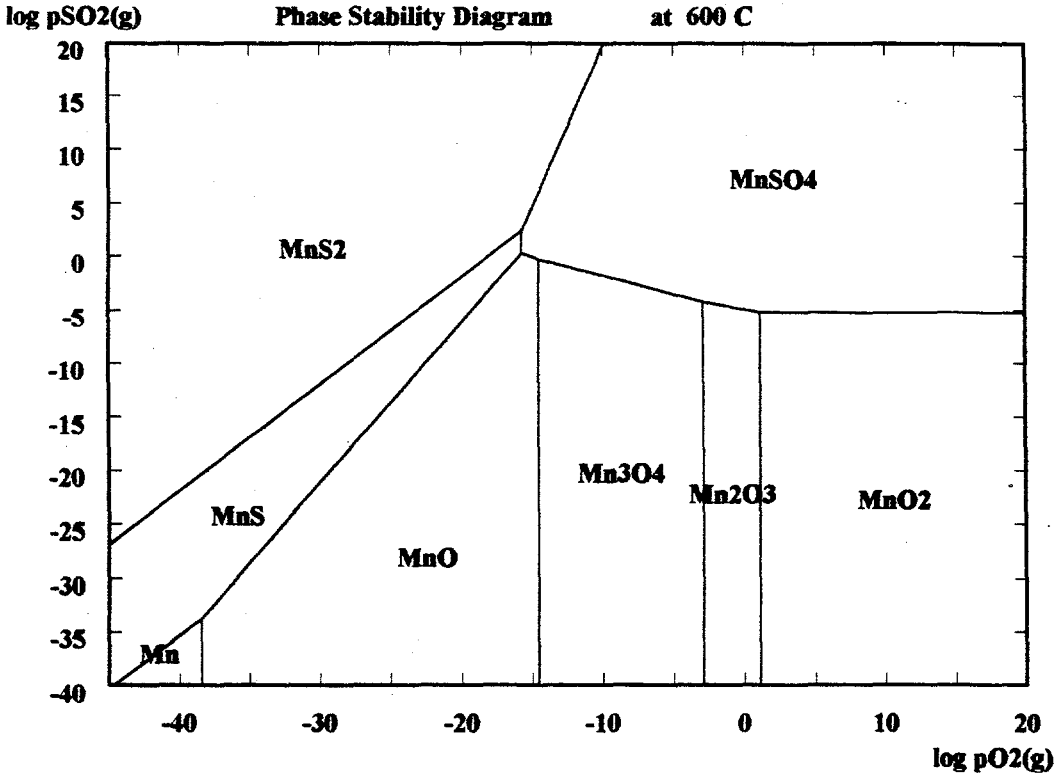

Figure 3. Phase Stability Diagram for the Mn-S-O System at 600°C

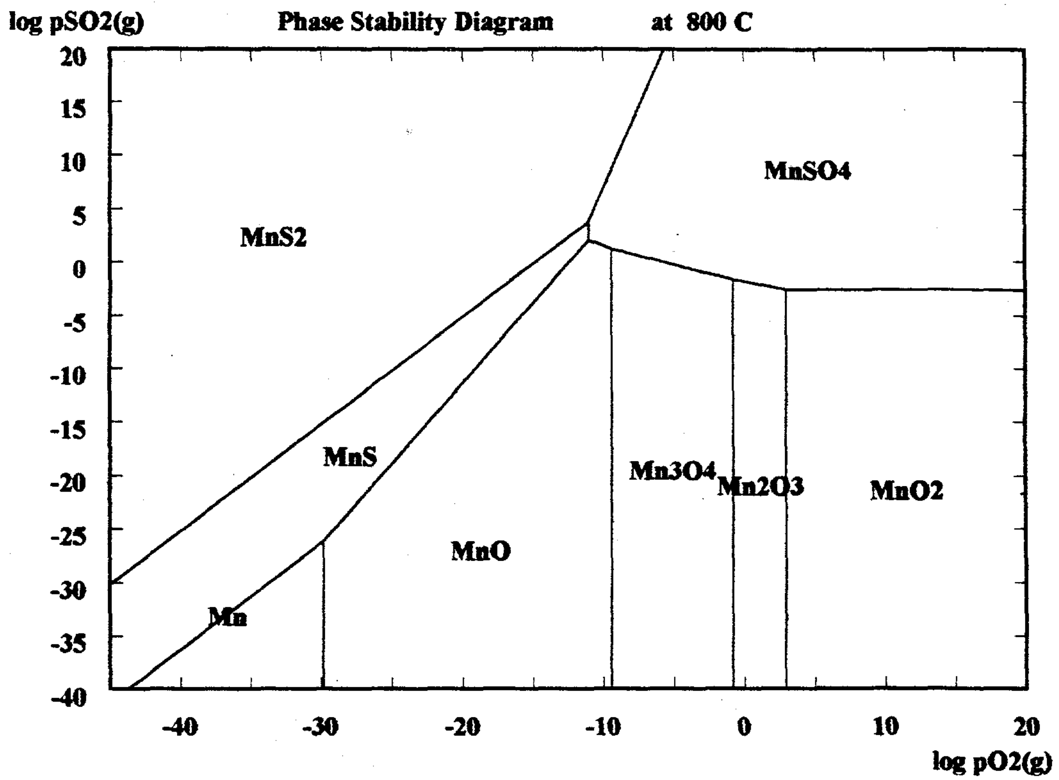

Figure 4. Phase Stability Diagram for the Mn-S-O System at 800°C

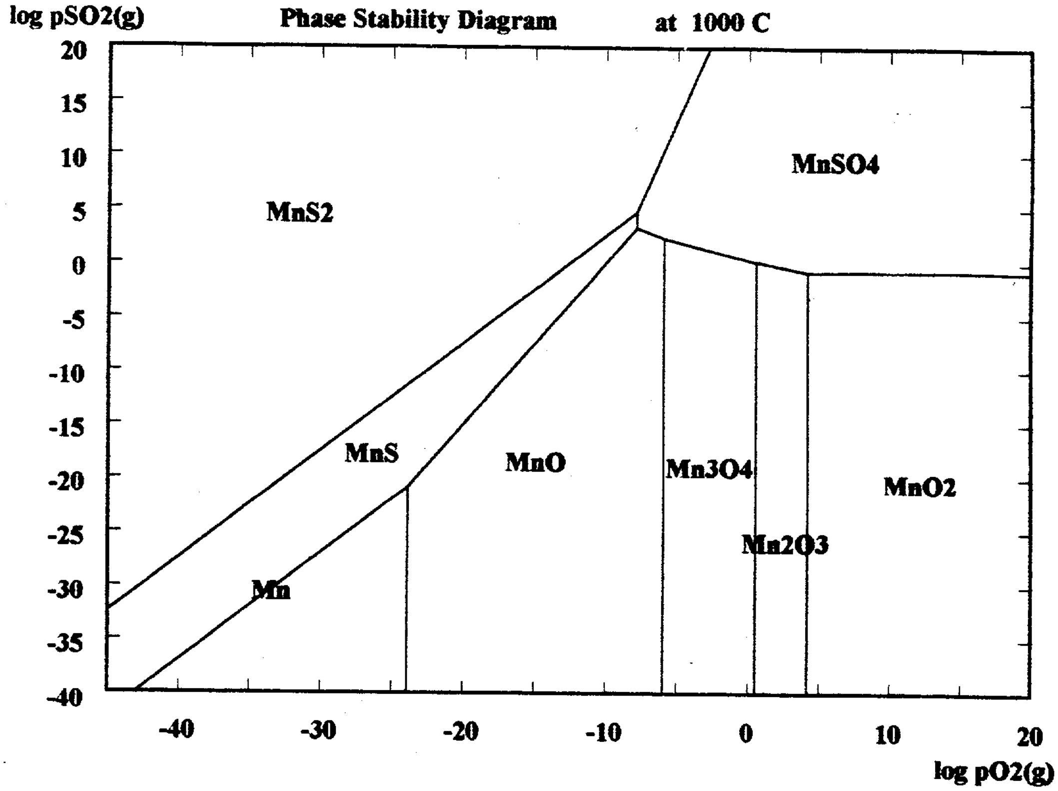

Figure 5. Phase Stability Diagram for the Mn-S-O System at 1000°C

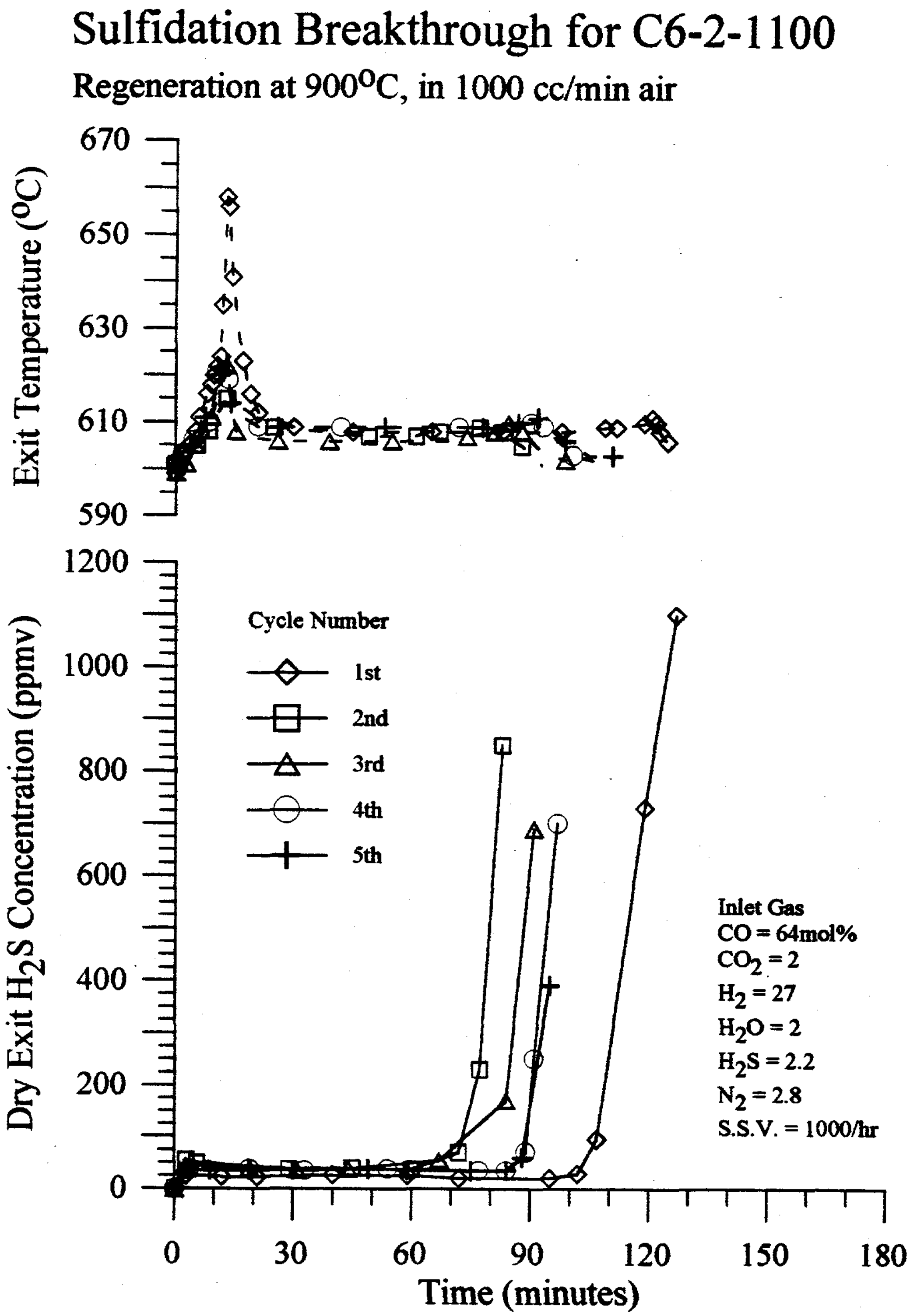

Figure 6. Sulfidation breakthrough curves for C6-2-1100 (5cycles).

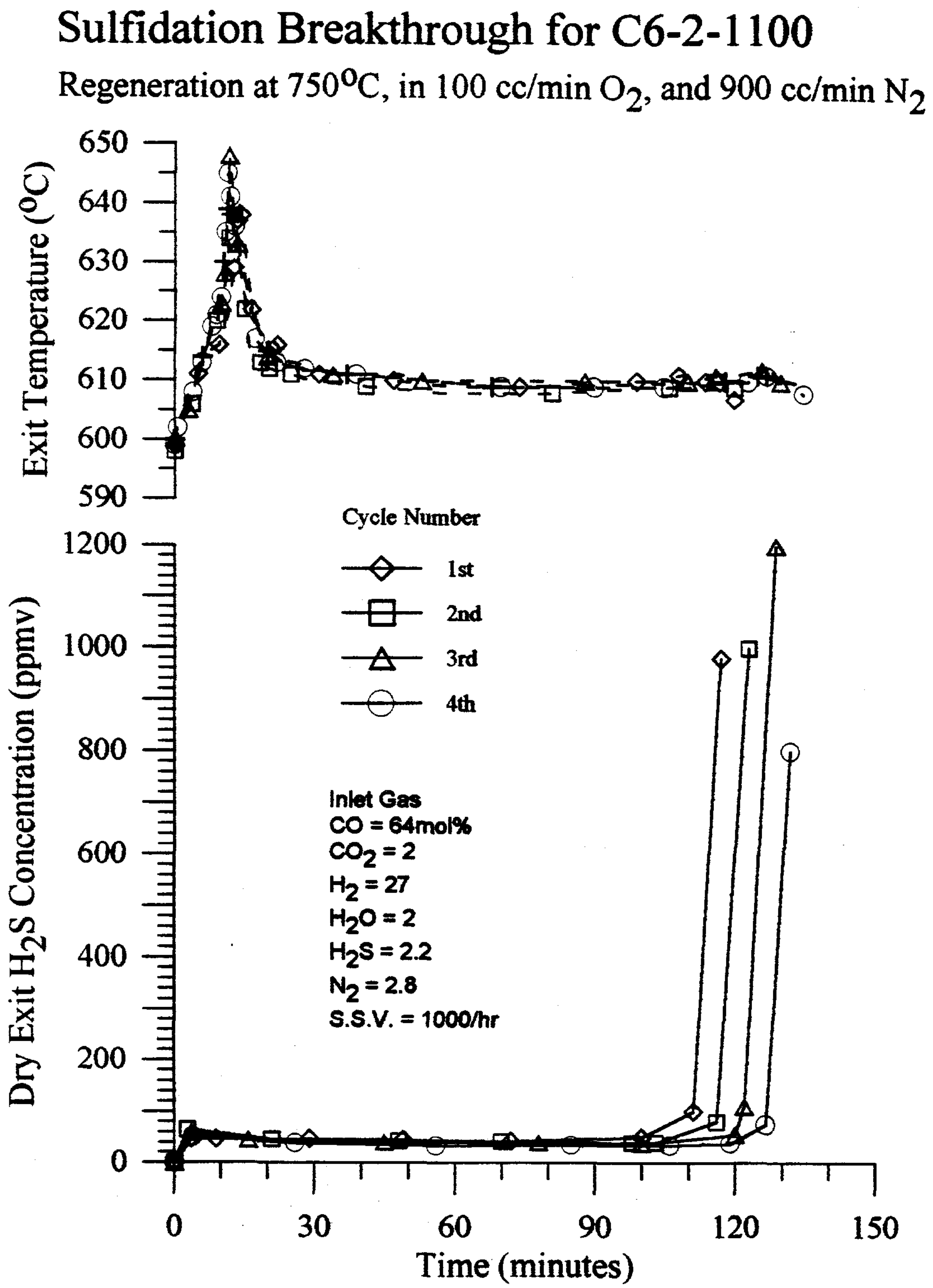

Figure 7. Sulfidation breakthrough curves for C6-2-1100 (4 cycles).

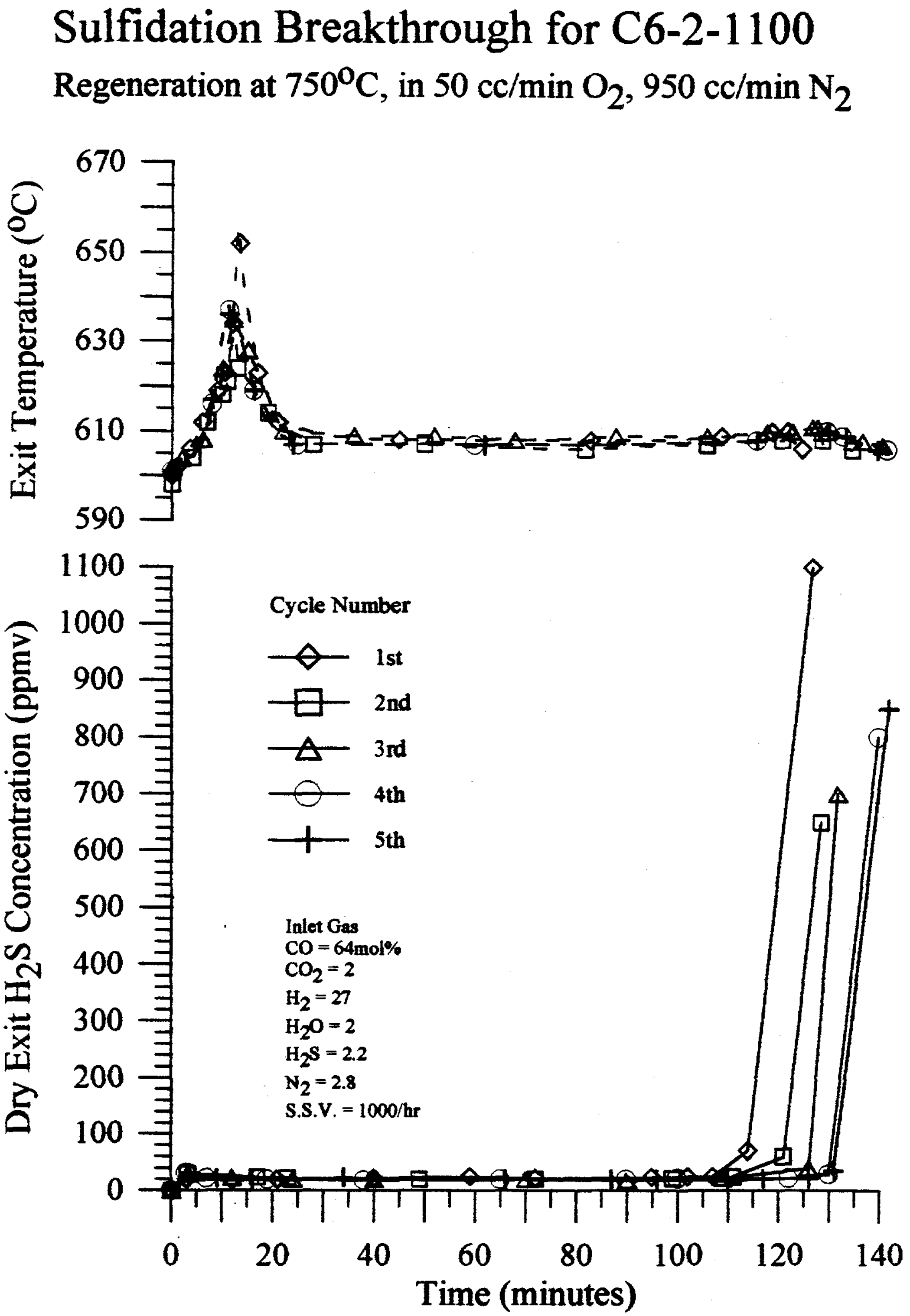

Figure 8. Sulfidation breakthrough curves for C6-2-1100 (5 cycles).

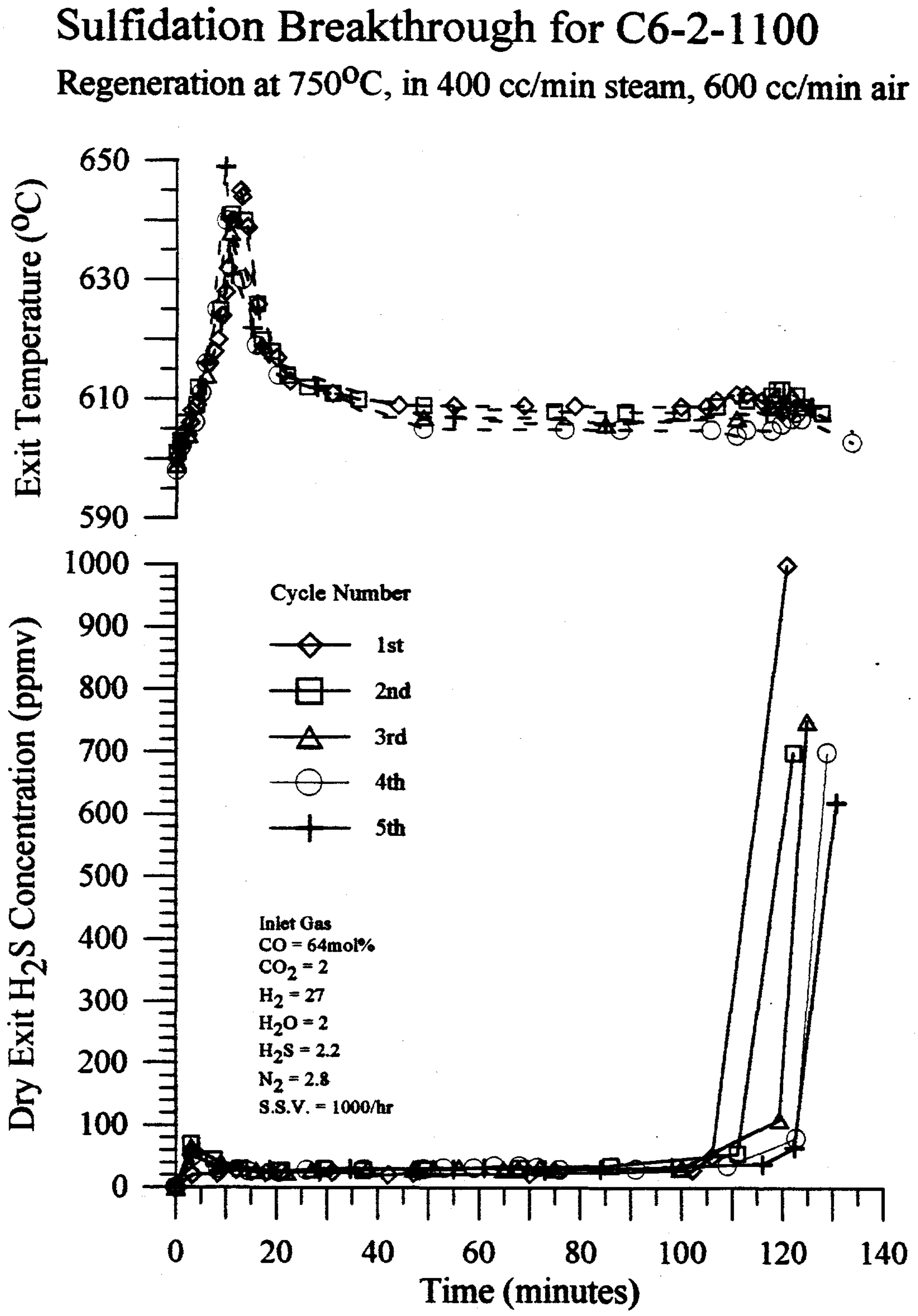

Figure 9. Sulfidation breakthrough curves for C6-2-1100 (5 cycles).

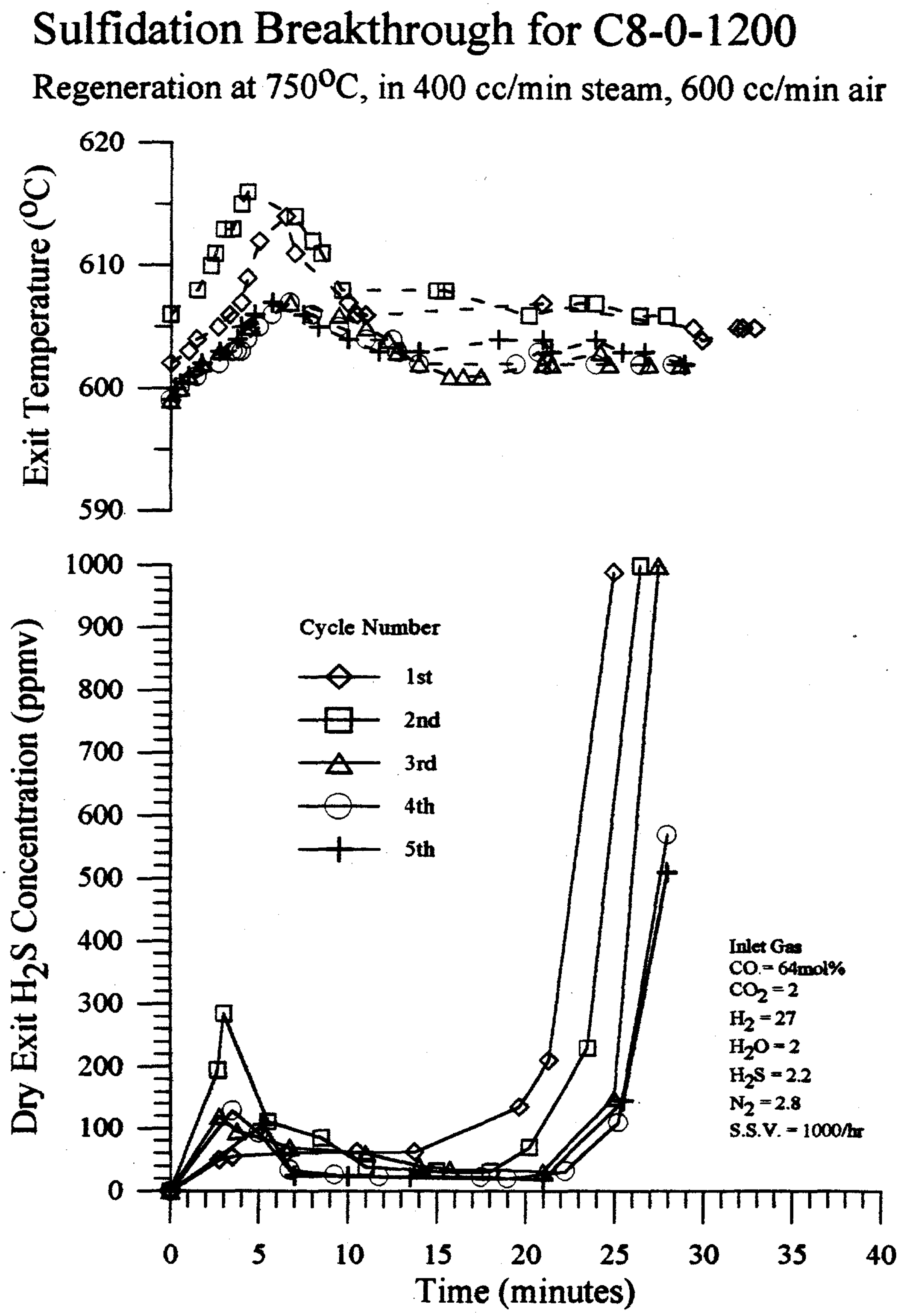

Figure 10. Sulfidation breakthrough curves for C8-0-1200 (5 cycles).

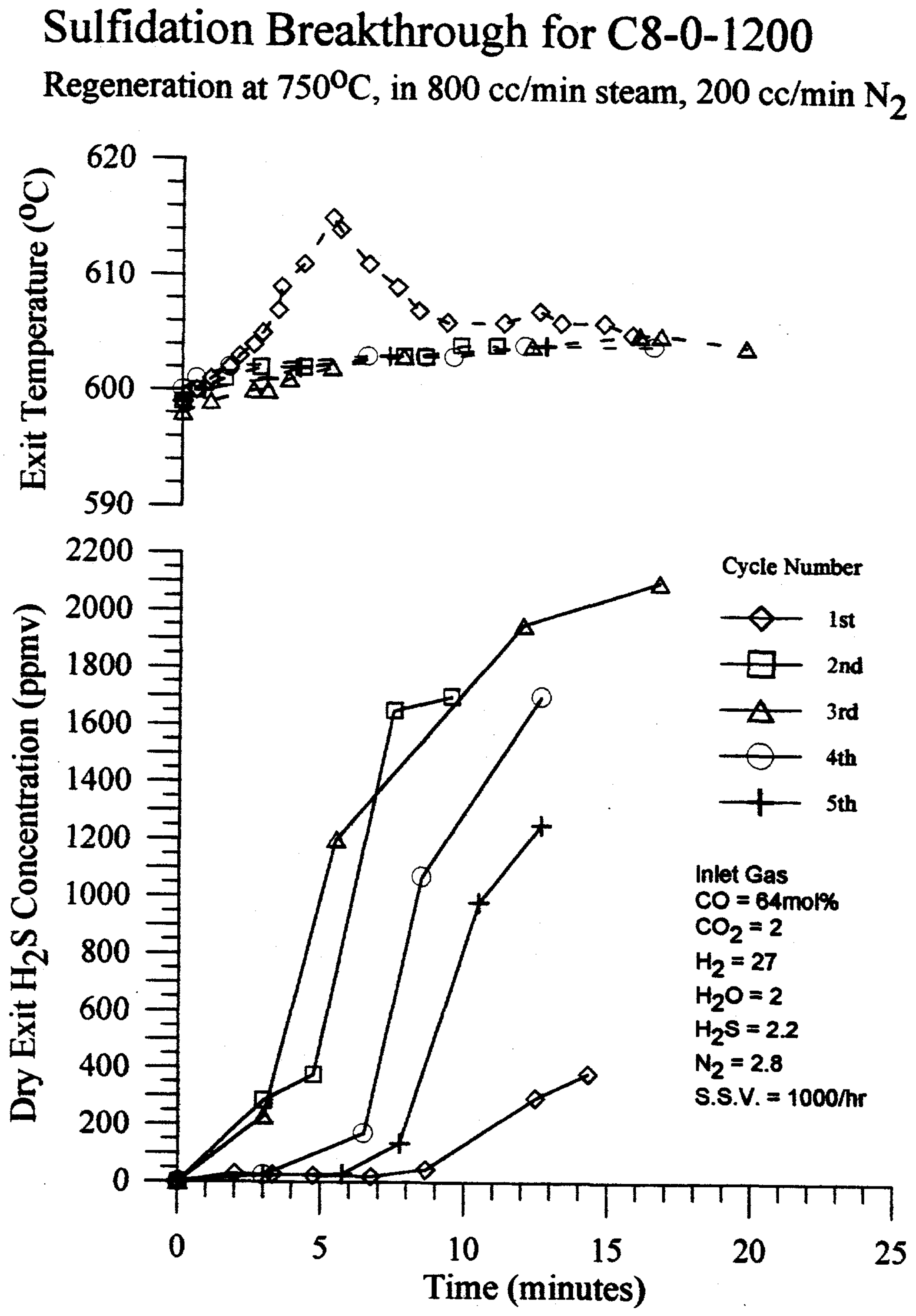

Figure 11. Sulfidation breakthrough curves for C8-0-1200 (5 cycles).

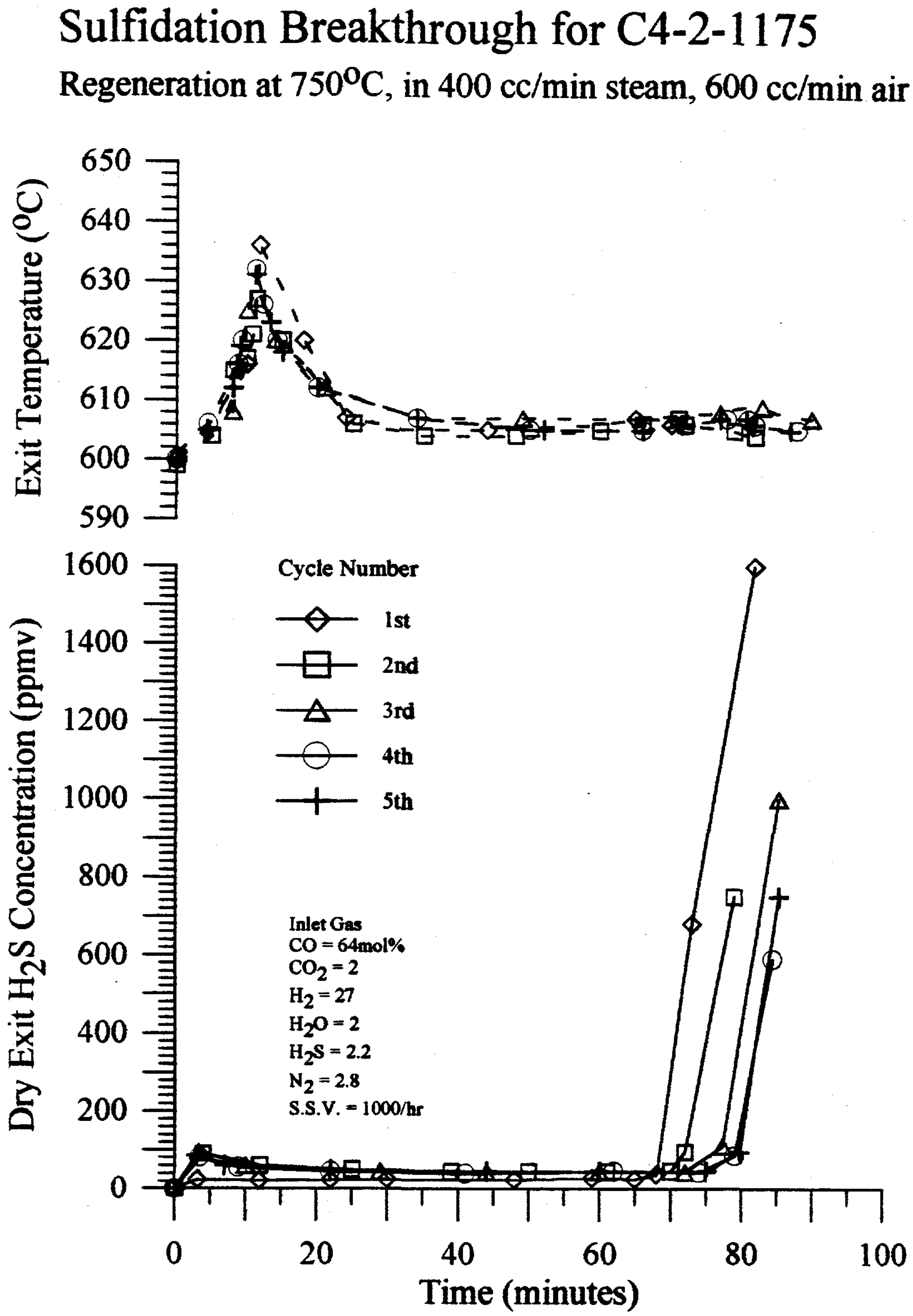

Figure 12. Sulfidation breakthrough curves for C4-2-1175 (5 cycles).

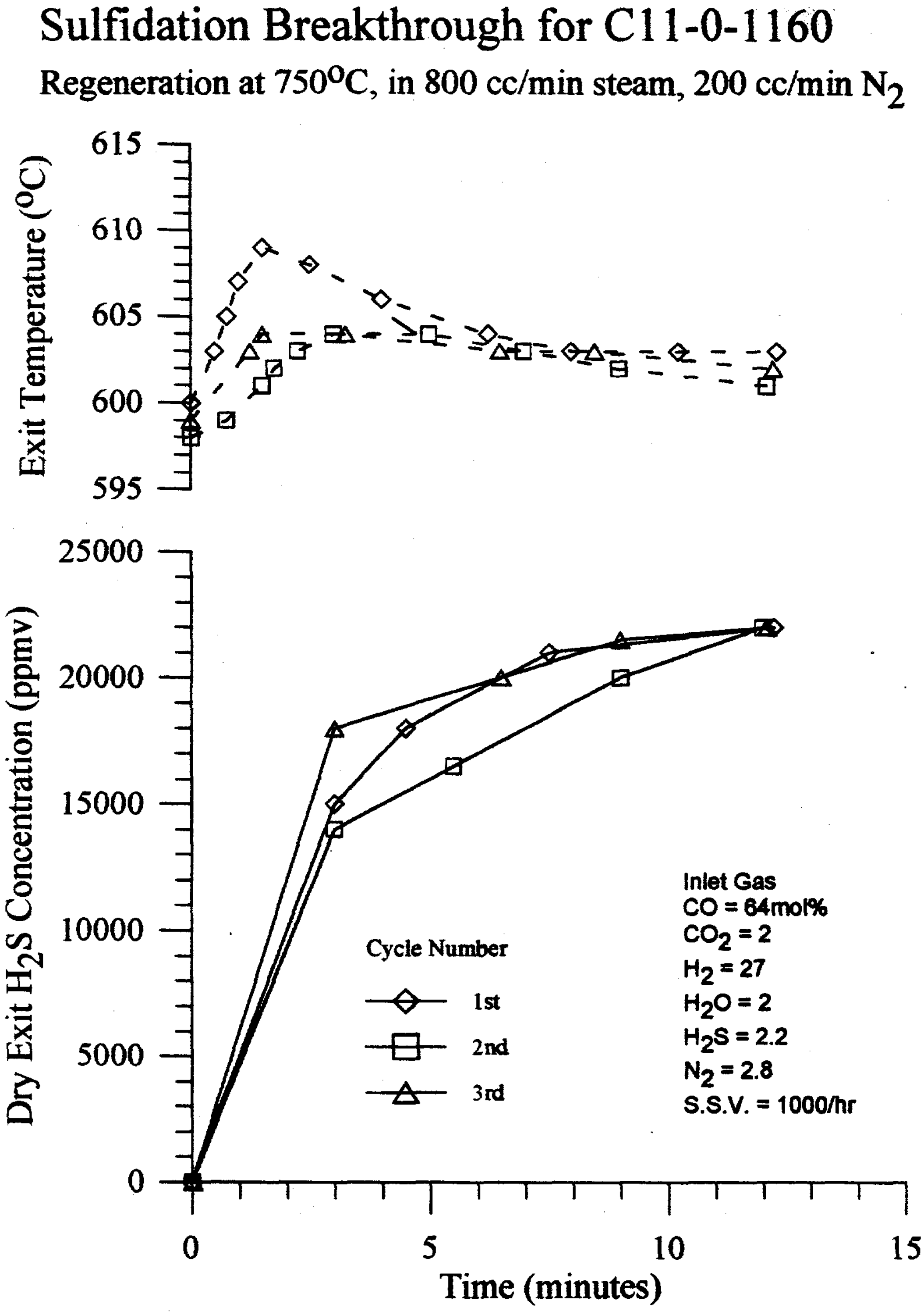

Figure 13. Sulfidation breakthrough curves for C11-0-1160 (3 cycles).