Report Title:

Kinetics of Mn-Based Sorbents for Hot Coal Gas Desulfurization

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ABSTRACT

Manganese-based sorbents have been investigated for the removal of hydrogen sulfide (the primary sulfur bearing compound) from hot coal gases prior to its use in combined cycle turbines. Four formulations of Mn-based sorbents 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 cyclic sulfidation and regeneration testing. In a previous report[16], the sulfidation results were presented. 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 five cycles. Actual breakthrough time for formulation C6-2-1100 was as high as 73% of breakthrough time based on wt% Mn in sorbent. In this report, the regeneration results will be presented. Regeneration tests determined that loaded pellets can be fully regenerated in air/steam mixture at 750°C with minimal sulfate formation.

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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 temperature 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 either 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]. The inert component increases pore structure integrity, stabilizes the active metal oxide against reduction and increases the pellet durability. 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 were presented in a previous report[16]. This report will present the results from regeneration and crush strength testing of four manganese-based sorbents.

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[15]. 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[10-14].

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 will be presented in this section.

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 4.45 N/pellet/mm^2 (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[15] and assumes the crush strength 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. The reactor consists of a 2.54 cm (1") ID quartz tube positioned vertically in the two-zone furnace. The preheat zone was maintained at 200°C. The reaction temperature was 600°C and was monitored using a type K 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. See the previous report[16] for schematics of the reactor tube and fixed-bed experimental apparatus.

For each test, 8.9 to 9.5 cm (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 2.2 mol% H_2S were then introduced into the reactor at 3L/min. Volumetric flow rates of the gases were calibrated with rotameters using a wet test meter. Elevated H_2S concentrations were employed to reduce the sulfidation breakthrough time. Exit gases were sampled after the cold trap and were analyzed using detector tubes 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)*
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. *Refers to a simplified Shell-type fuel gas with the following composition: 64 mol% CO, 27% H_2, 2.2% H_2S, 2% H_2O, 2% CO_2 and 2.8% N_2

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. Regeneration in oxygen depleted air and air/steam mixtures 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

RESULTS AND DISCUSSION

Results from the fixed-bed sulfidation testing were presented in the previous report[16]. Results from fixed-bed regeneration and crush strength testing will be presented in this section.

Crush Strength

Figure 1 shows the results from the crush strength testing of freshly indurated sorbent. As can be seen in the figure, a small increase in temperature can result in a large difference in crush strength. Induration time for all sorbent tested was restricted to two hours due to manpower limitations. Thus, the sensitivity of the crush strength to temperature may be minimized with longer induration times at lower temperatures. The induration length and temperature need to be further investigated. All sorbent tested in the fixed-bed reactor met the strength criteria represented by the horizontal dashed line in figure 1.

Fixed-bed Testing

Results from the sulfidation fixed-bed testing were presented in the previous quarterly report[16]. Figures 2 to 9 show the results from the fixed-bed regeneration testing. Eight tests were conducted using four different formulations. Five cycles of sulfidation and regeneration were conducted for each test. Results from each formulation are described separately. A summery of the SO_2 or H_2S concentrations achieved in the exit gases and the time for regeneration is given in Table 5. Regeneration time is based on the time to achieve an exit SO_2 or H_2S gas concentration of less than 10% of the highest concentration achieved. The regeneration times were then average over five cycles.

Formulation	Highest concentration of SO_2 (or H_2S*) achieved in exit gases (mol%)	Average regeneration time (min)
C6-2-1100 Figure 2	8.3	95
C6-2-1100 Figure 3	4.5	190
C6-2-1100 Figure 4	2.1	435
C6-2-1100 Figure 5	7.8	115
C8-0-1200 Figure 6	9.0	45
C8-0-1200 Figure 7	1.5	280
C4-2-1175 Figure 8	7.2	76
C11-0-1160 Figure 9	0.8	150

Table 5. Highest Concentration of SO_2 or H_2S Achieved in Exit Gases and Average Regeneration Times. *Figures 7 and 9 refer to H_2S concentrations.

Formulation C6-2-1100

Figures 2-5 are the regeneration breakthrough plots for formulation C6-2-1100. Figure 2 shows the regeneration curves for sorbent regenerated in air at 900°C.

Regeneration in air produced a dry SO_2 concentration of 8.3 mol% in the exit gases and an average regeneration time of 95 minutes, however due to the exothermic character of the desulfurization reaction, high temperatures were also produced. This is undesirable because of sintering effects. As described in the previous quarterly report the sorbent's capacity was reduced considerably from the first sulfidation cycle to the second cycle. A regeneration temperature similar to the sulfidation temperature is also desirable, however to prevent sulfate formation, which may cause the pellets to crack, a higher temperature is needed when regenerating in air.

A lower temperature is possible when regenerating in atmospheres with lower oxygen potentials. Figures 3 and 4 show the regeneration curves for sorbent regenerated in oxygen depleted air at 750°C. The pellets were shown to be completely regenerated, however, the exit SO_2 concentration is lower and the average regeneration time is longer than regeneration in air. The SO_2 at this concentration may not be economically recoverable.

Figure 5 shows the regeneration curves for sorbent regenerated in an air/steam mixture. Regeneration in 60% air and 40% steam regenerated the sorbent completely while minimizing sulfate formation and large increases in temperature. The highest SO_2 concentration achieved in the exit gases was 7.8 mol%.

Formulation C8-0-1200

Figure 6 is the regeneration curves for sorbent regenerated in air and steam. The sorbent was regenerated completely with exit SO_2 concentrations as high as 9 mol%, however, some sulfate formation was indicated during subsequent sulfidation testing.

Figure 7 is the regeneration curves for sorbent regenerated in steam and nitrogen. Steam regeneration produced low concentrations of H_2S in the gas exit stream and did not completely regenerate the pellets.

Formulation C4-2-1175

Figure 8 is the regeneration curves for sorbent regenerated in air and steam. The sorbent was regenerated completely with exit SO_2 concentrations as high as 7.2 mol%. Some sulfate formation was indicated, however, this was minimal.

Formulation C11-0-1600

Figure 9 is the regeneration curves for sorbent regenerated in steam and nitrogen. Again steam regeneration produced low concentrations of H_2S in the gas exit stream and did not fully regenerate the pellets.

CONCLUSIONS

The crush strength of a manganese-based pellet was highly sensitive to the temperature at which it was indurated. The relationship of the induration temperature and length to the pellet's crush strength needs to be further investigated. All pellets tested in the fixed-bed reactor had the required strength.

Regeneration in 95% N_2 and 5% O_2, appeared to regenerate the sorbent the best (see previous quarterly report), however, the % SO_2 achieved in the exit gases was low and the time required to achieve complete regeneration was high (approximately 2% and 450 minutes respectively). Regeneration of the sorbent should produce a sulfur product that is recoverable either directly or indirectly and the time to regenerate should also be considered.

Steam regeneration did not reach equilibrium with H_2S at 750°C in fixed-bed operation. This was true for both titania and alumina supported sorbents. Regeneration in air produced fast rising temperatures that may have caused sintering of the pellets.

Regeneration in 60% air and 40% steam regenerated the sorbent completely while minimizing sulfate formation and large increases in temperature. Regeneration in 60% air and 40% steam appeared to give the best combination of regenerabilty, sulfate control, length of regeneration and dry SO_2 exit concentrations.

Future work will focus on the durability of the manganese pellets over many sulfidation and regeneration cycles with regeneration in an air/steam mixture.

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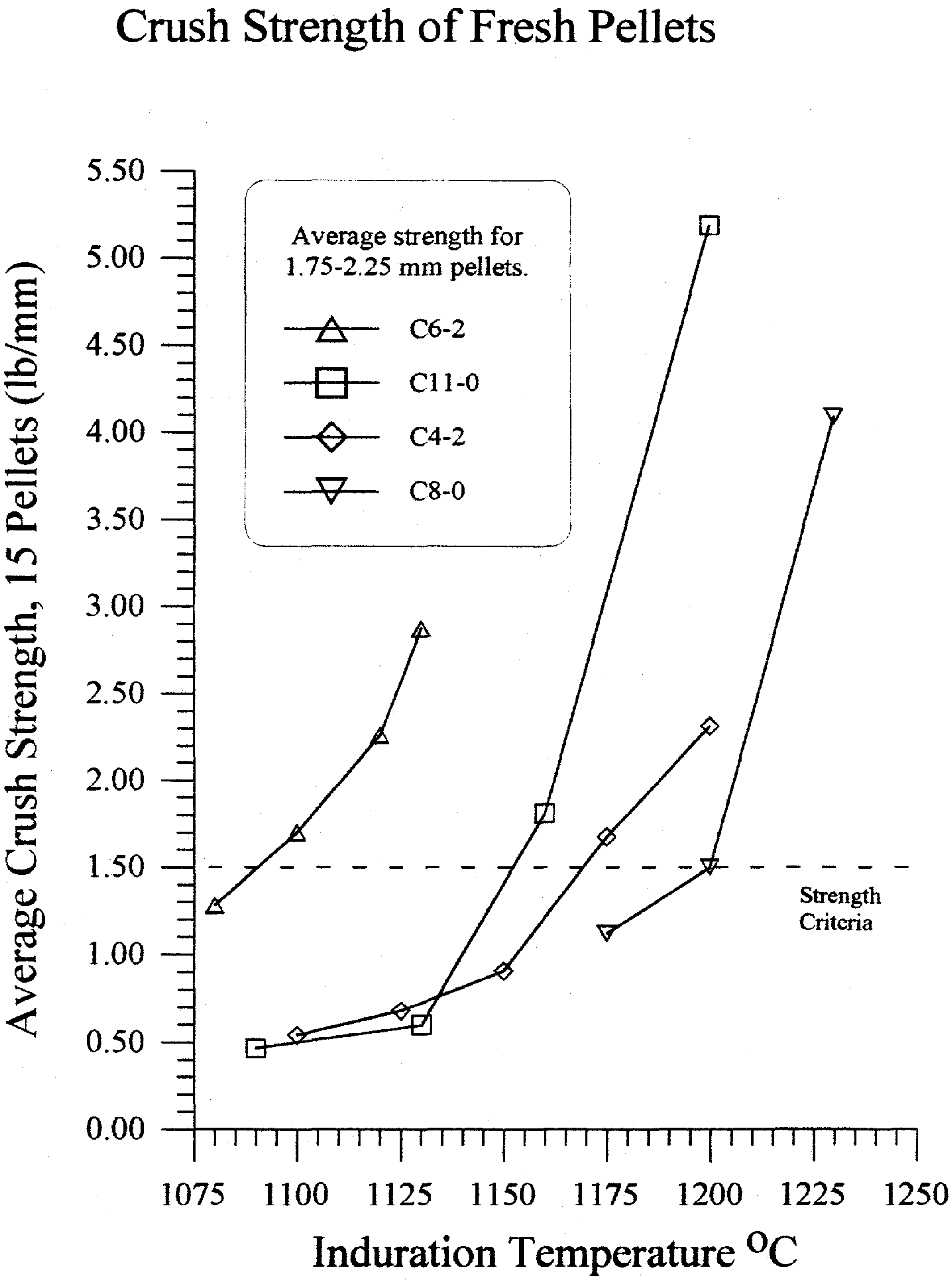

Figure 1. Average crush strength for fresh pellets, 1.75 to 2.25 mm in diameter

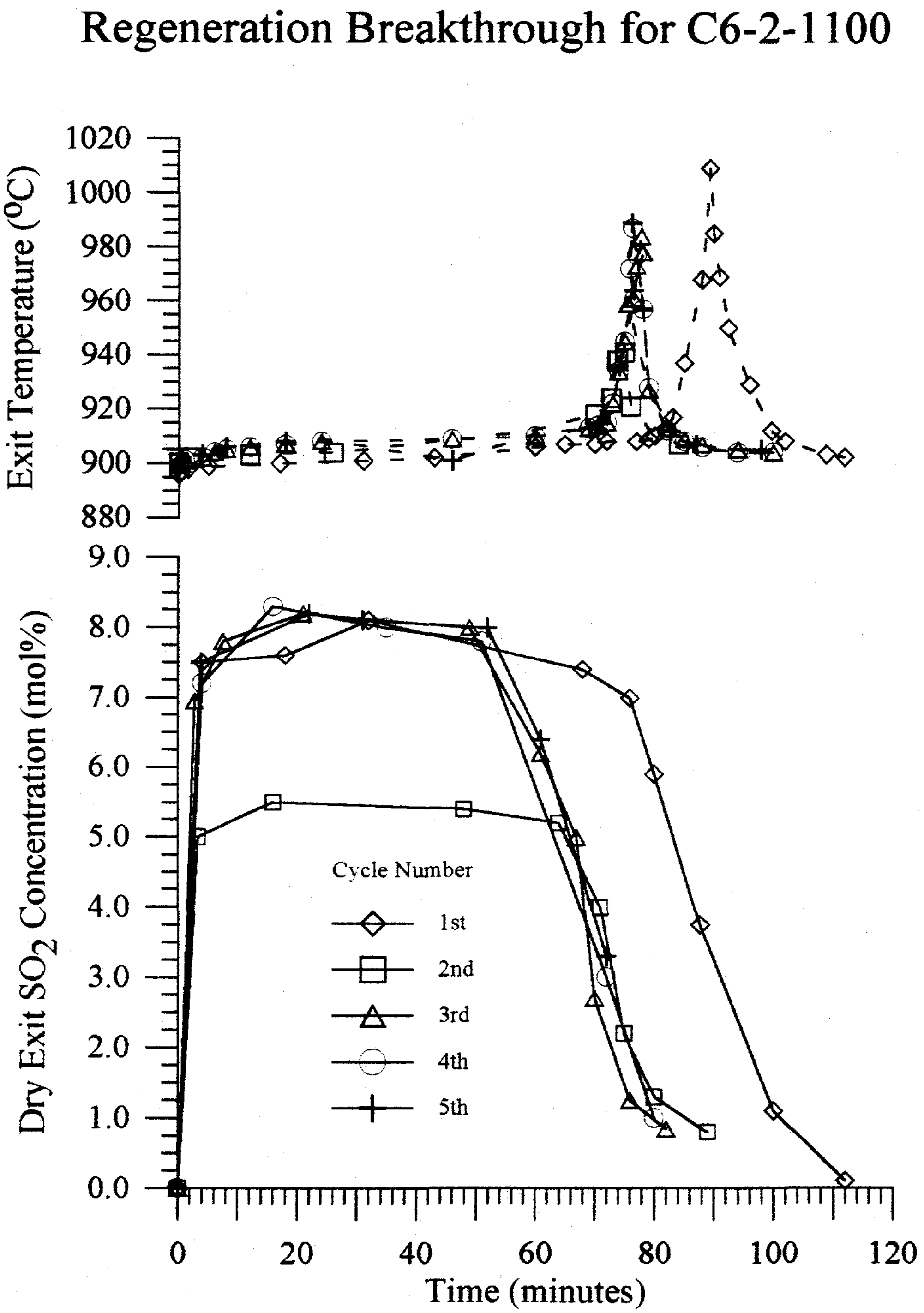

Figure 2. Regeneration curves for C6-2-1100. Regeneration in air with a standard space velocity of 333/hr.

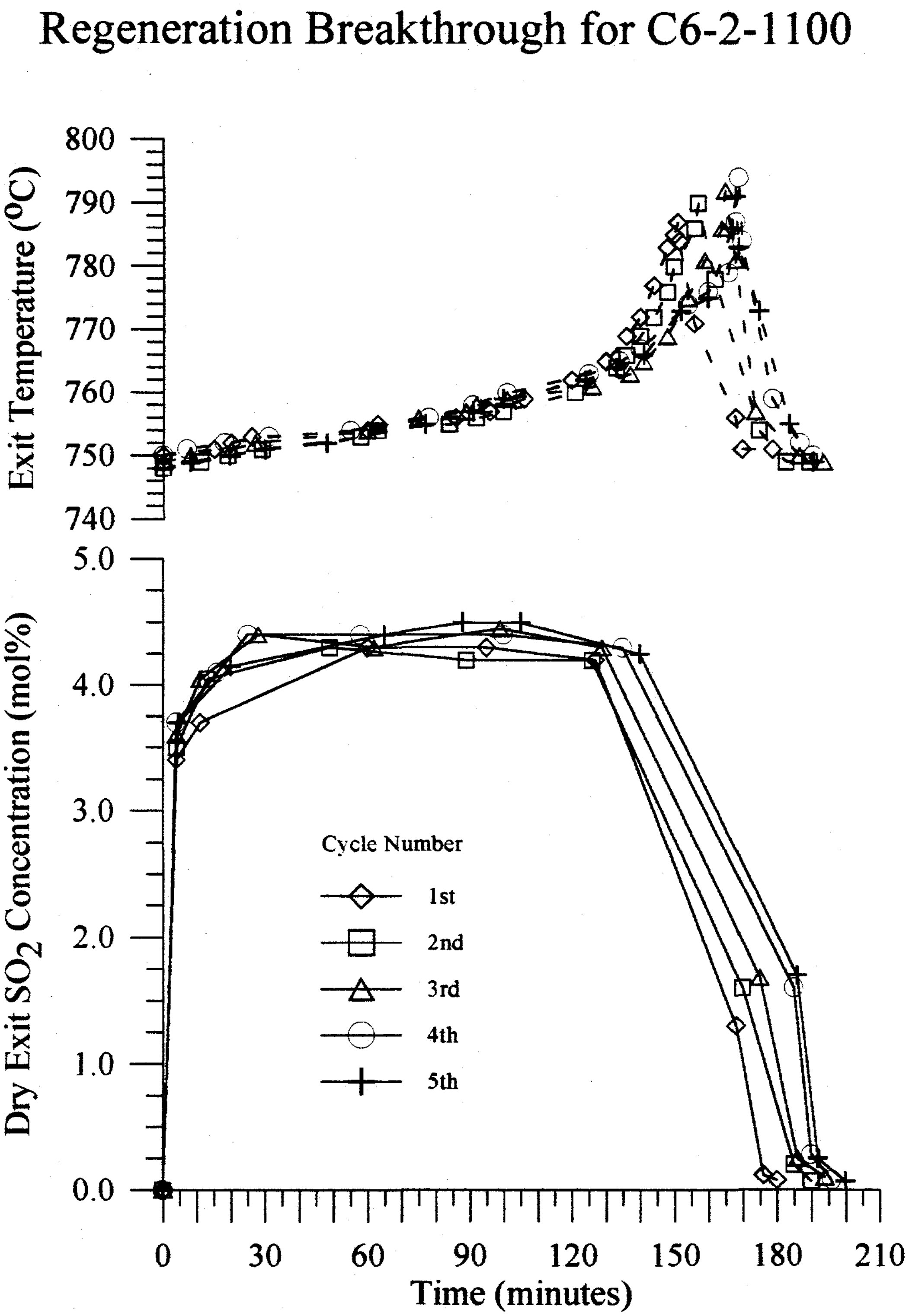

Figure 3. Regeneration curves for C6-2-1100. Regeneration in 90% N_2 and 10% O_2, with a standard space velocity of 333/hr.

Regeneration Breakthrough for C6-2-1100

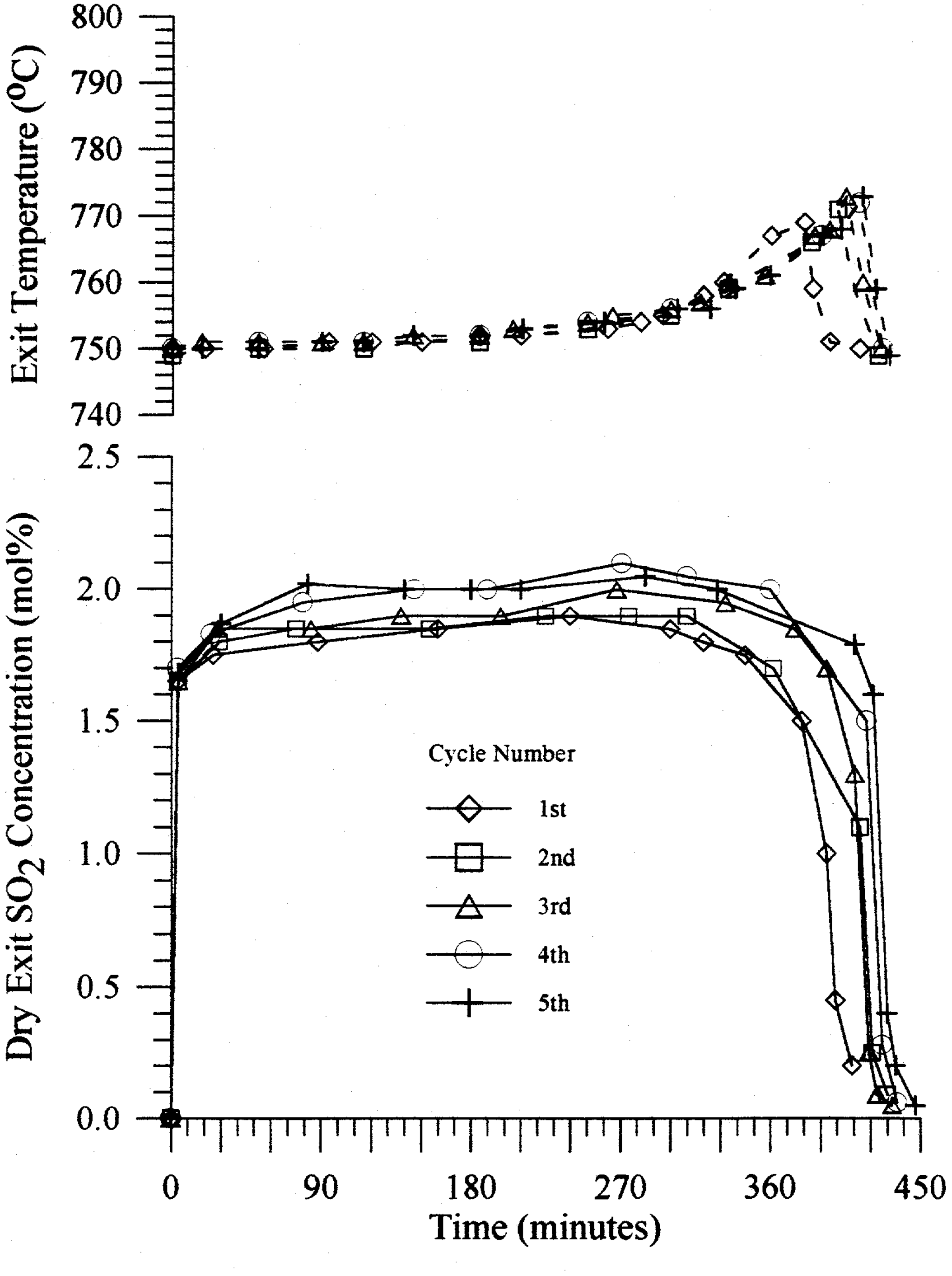

Figure 4. Regeneration curves for C6-2-1100. Regeneration in 95% N_2 and 5% O_2, with a standard space velocity of 333/hr.

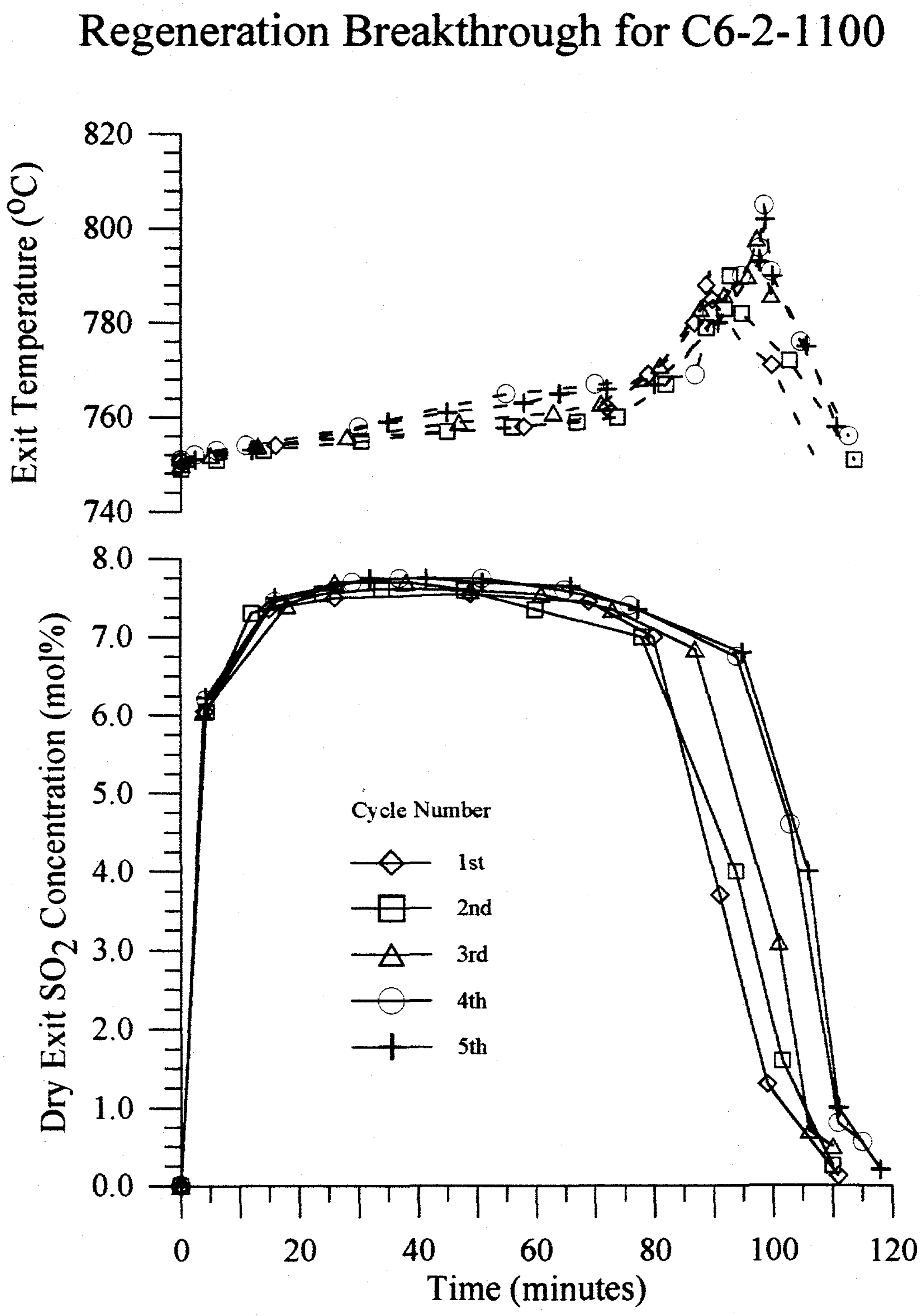

Figure 5. Regeneration curves for C6-2-1100. Regeneration in 47.4 mol% N_2, 12.6% O_2 and 40% H_20, with a standard space velocity of 333/hr.

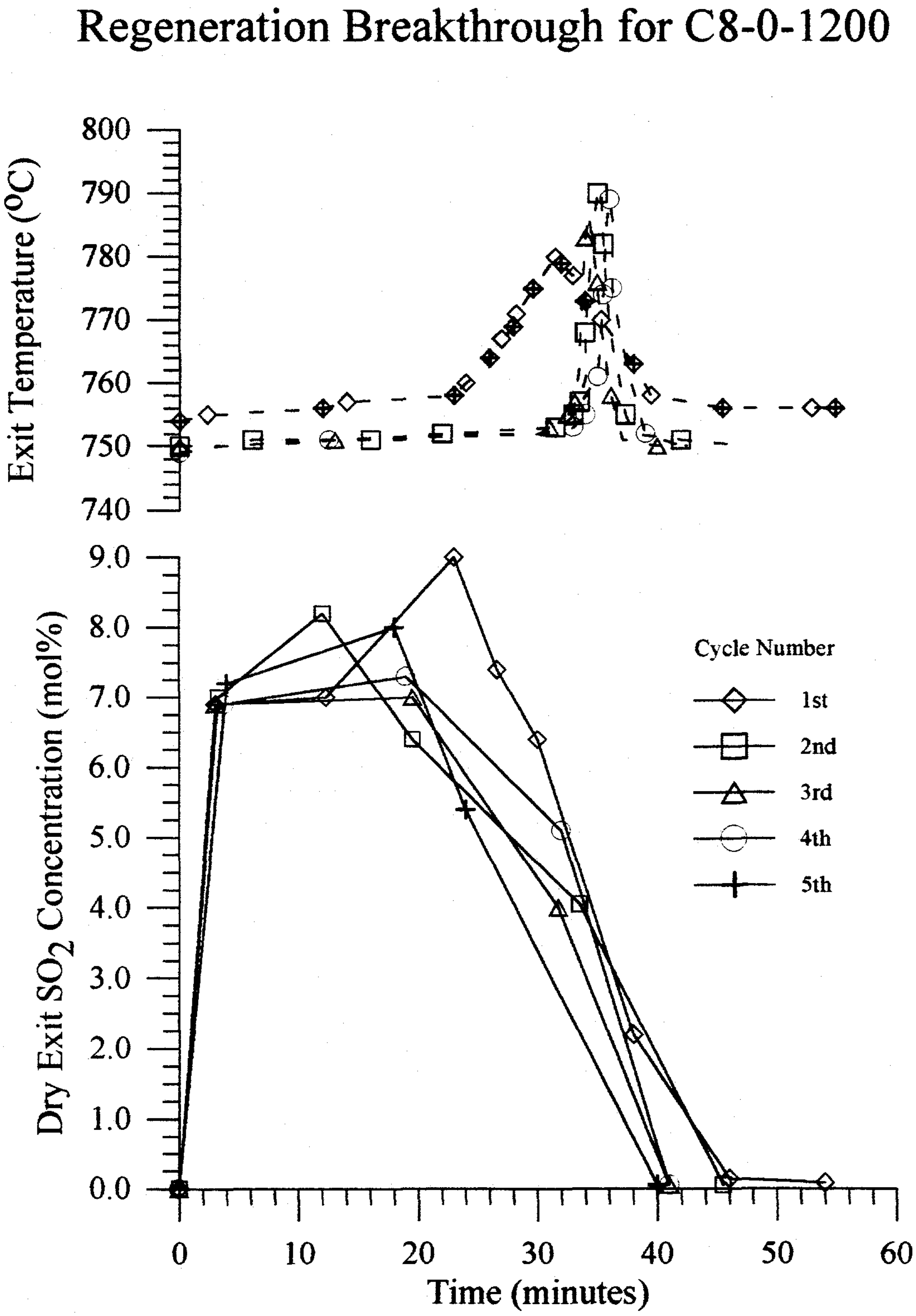

Figure 6. Regeneration curves for C8-0-1200. Regeneration in 47.4 mol% N_2, 12.6% O_2 and 40% H_2O, with a standard space velocity of 333/hr.

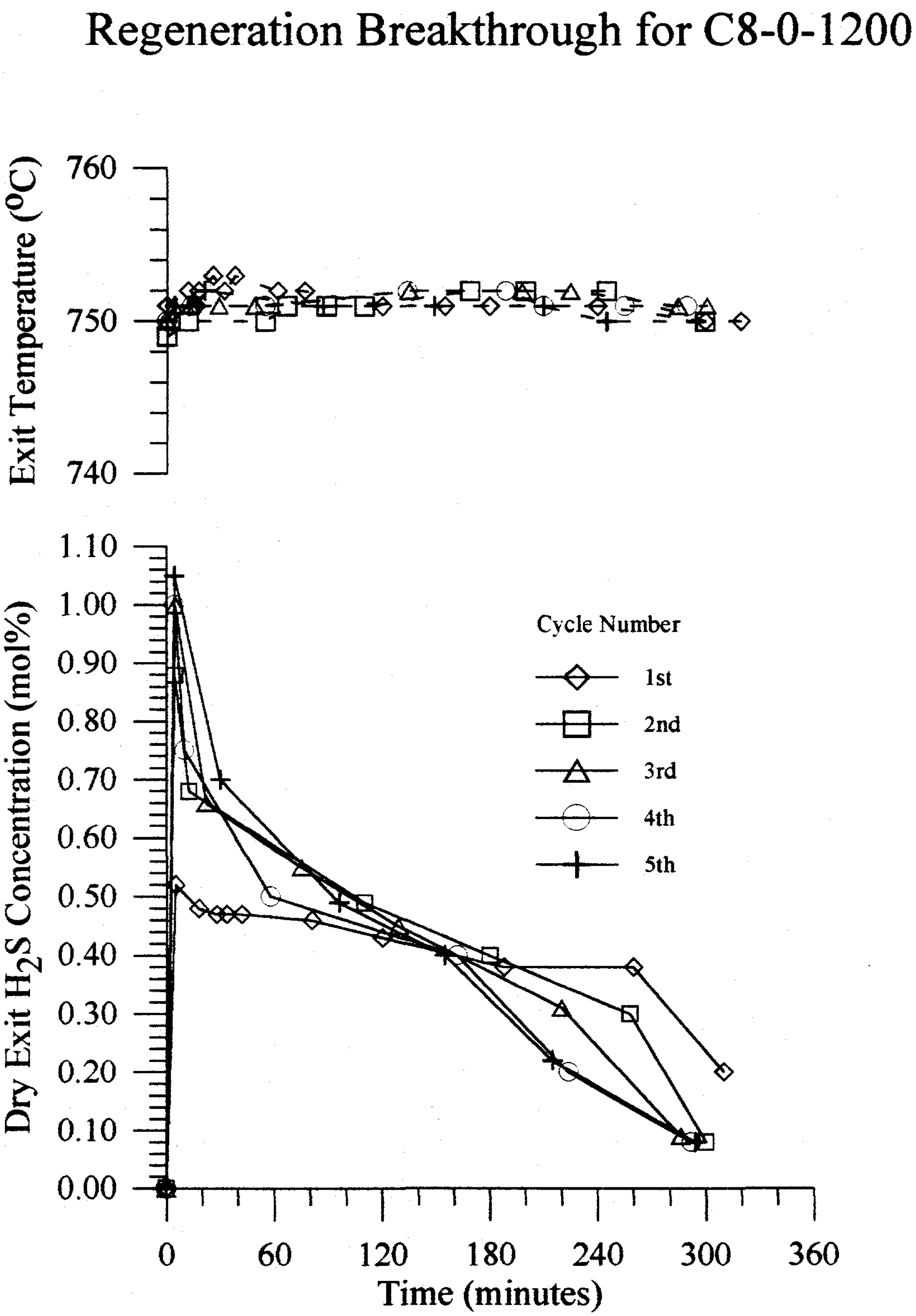

Figure 7. Regeneration curves for C8-0-1200. Regeneration in 80 mol% H_2O and 20% N_2, with a standard space velocity of 333/hr.

Regeneration Breakthrough for C4-2-1175

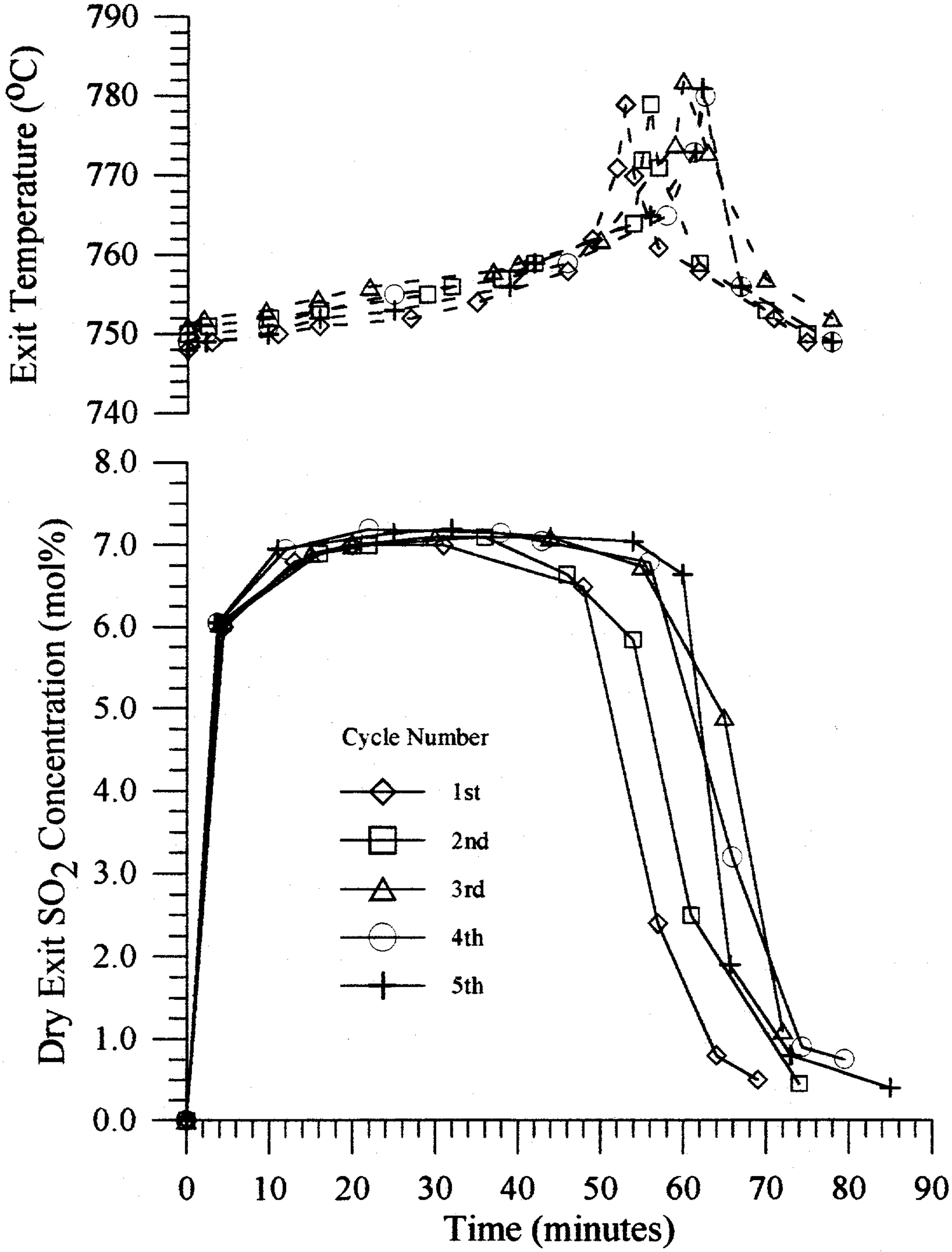

Figure 8. Regeneration curves for C4-2-1175. Regeneration in 47.4 mol% N_2, 12.6% O_2 and 40% H_2O, with a standard space velocity of 333/hr.

Regeneration Breakthrough for C11-0-1600

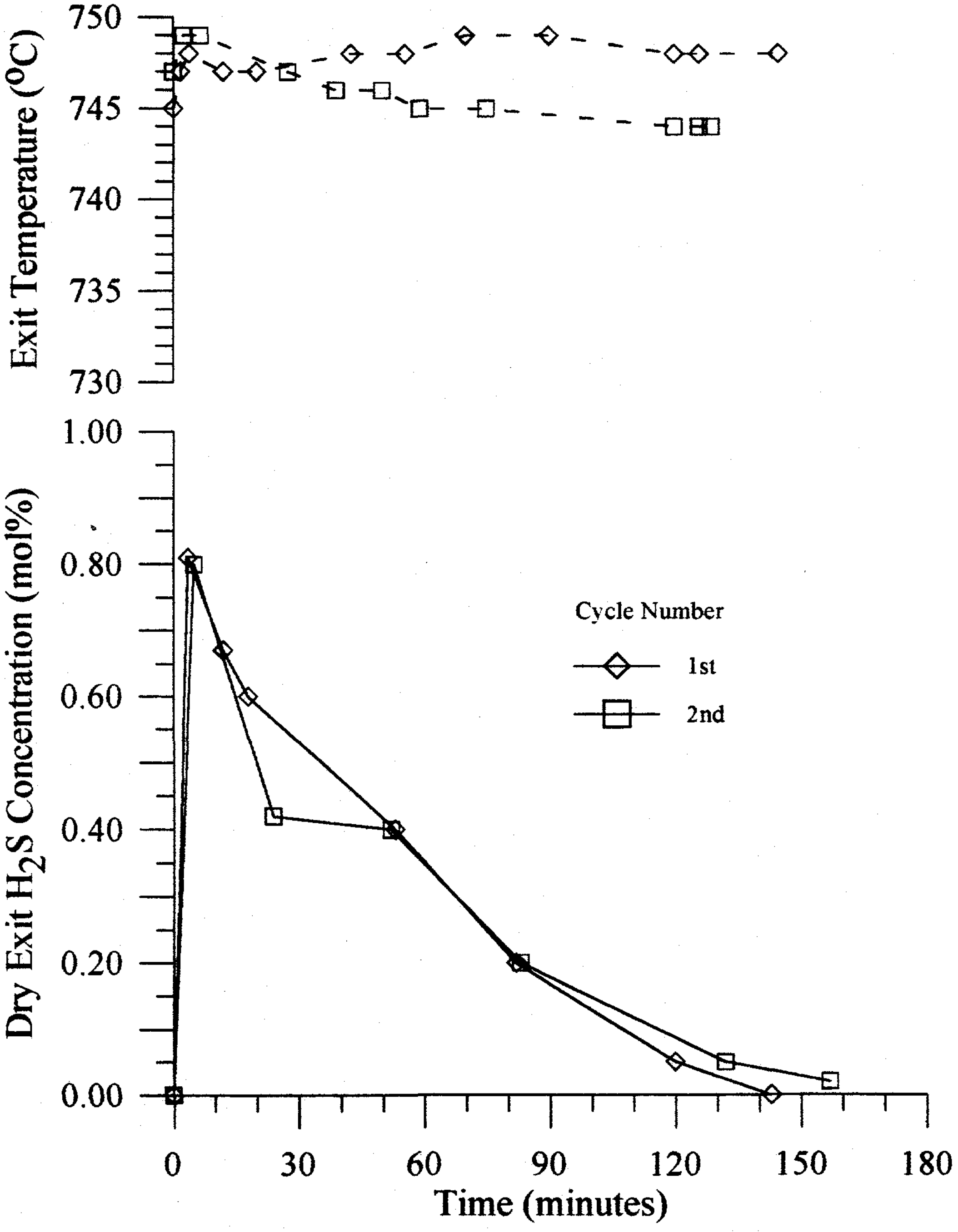

Figure 9. Regeneration curves for C8-0-1600. regeneration in 80 mol% H_2O and 20% N_2, with a standard space velocity of 333/hr.