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. 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 previous reports[16-18], the sulfidation and regeneration results from cyclic testing done at 550 and 600^oC 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 at 600^oC. Regeneration tests determined that loaded pellets can be essentially completely regenerated in air/steam mixture at 750^oC with minimal sulfate formation. In this report, the performance of the leading formulation (designated C6-2) was investigated for high temperature removal of H_2S from simulated coal-derived fuel gas under varying sorbent induration temperature, reaction temperature, and superficial gas velocity. Sulfidation experiments were performed in an ambient pressure fixed-bed reactor between 500^oC and 600^oC. Four tests were conducted with each test consisting of four cycles of sulfidation and regeneration. Results showed that the induration temperature of the sorbent and the reaction temperature greatly affected the H_2S removal capacity of the sorbent while the superficial gas velocity between 1090 and 1635 cm/min had minimal affect on the sorbent's breakthrough capacity. Sorbent also showed 30 to 53% loss of its strength over four cycles of sulfidation and regeneration. The former being sorbent indurated at 1115^oC and the prior being sorbent indurated at 1100^oC.

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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^oC 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.

Recent research conducted at the University of Minnesota has identified a sorbent consisting of 4.33 manganese to 1 titanium on a molar basis and 2 wt% bentonite as the leading manganese-based sorbent formulation (designated C6-2) for hot coal gas desulfurization. The objective of this research is to determine the effects of temperature, superficial gas velocity and induration temperature of the sorbent on the desulfurization performance of this leading formulation in an ambient pressure fixed-bed reactor. The crush strengths of the sorbent sulfided under varying conditions are compared after 4 cycles of sulfidation and regeneration; in addition x-ray, sulfur, and pore structure analysis results will be presented.

METHODS AND MATERIALS

Composition

Feed materials used to manufacture the sorbent consisted of manganese carbonate, titanium dioxide, and bentonite as an inorganic binder. 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^oC. Dry pellets were calcined for four hours at 350^oC. Immediately after calcination, pellets were placed in a high-temperature furnace (pre-heated to 500^oC), 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.

CHARACTERIZATION

Indurated pellets were characterized both physically and chemically using crush strength and fixed-bed testing, in addition to x-ray diffraction (XRD) and sulfur analysis.

Fixed-bed Testing

Indurated pellets were tested in an ambient pressure fixed-bed reactor to determine pre-breakthrough H_2S concentrations, breakthrough times (reaction kinetics), and effectiveness of the sorbent when subjected to multiple sulfidation and regeneration cycles. The reactor consisted of a 2.54 cm (1") ID quartz tube positioned vertically in a two-zone furnace. Schematics of the reactor and fixed-bed experimental apparatus is shown in a previous report[16]. The preheat zone was maintained at 200^oC. The reaction temperature was 500 to 600^oC 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. Mixing of the gases was achieved through quartz packing followed by an alumina gas distributor disk supporting the sorbent bed. 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 sodium hypochlorite solution (sulfidation) or a hydrogen peroxide and sodium hydroxide solution (regeneration) prior to flaring and venting.

For each test, 89 to 95 mm (3.5 to 3.75 ") 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. A simplified Shell gas spiked with 2.2 to 2.8 mol% H_2S was then introduced into the reactor at 2 to 3 L/min (STP). 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 Gastec™ detector tubes for H_2S until breakthrough occurred.

Four tests were conducted with varying sulfidation and regeneration temperatures or gas space velocity. Four cycles of sulfidation and regeneration were conducted for all four tests to determine the sorbents' strength and activity retention. The test conditions for sulfidation for all four tests are summarized in Table 1.

Table 1. Fixed-bed operating conditions for sulfidation

Test Designation	FB1A	FB2A	FB3A	FB4A
Sorbent Used	C6-2-1100	C6-2-1100	C6-2-1100	C6-2-1115
Amount of Sorbent (g)	47.87	47.88	40.16	49.08
Weight % Mn	55.8	55.8	55.8	54.1
Gas Composition	Shell[a]	Shell[a]	Shell[a]	Shell[a]
Gas Flow Rate (L/min, STP)	3	2	3	3
Temperature (°C)	550	550	500	600

[a] Refers to a simplified Shell gas with the following composition (mol%): 64 CO, 2 CO_2, 27 H_2, 2 H_2O, 1.8 - 2.8 H_2S, balance N_2.

The sorbent was regenerated in an air/steam mixture for all tests. The regeneration temperature was 650 to 750°C. The regeneration gas flow rate was 1 to 1.25 L/min (STP). The test condition for regeneration for all four tests are summarized in Table 2.

Table 2. Fixed-bed operating conditions for regeneration

Test Designation	FB1A	FB2A	FB3A	FB4A
Sorbent Used	C6-2-1100	C6-2-1100	C6-2-1100	C6-2-1115
Gas Composition	50% air 50% steam	50% air 50% steam	40% air 60% steam	50% air 50% steam
Gas Flow Rate (L/min, STP)	1	1	1.25	1
Temperature (°C)	750	750	650	750

Strength Testing

Crush (compressive) strength testing was conducted on all freshly indurated pellets with the requirement of 4.45 N/pellet/mm^2 (1 lb/pellet/mm^2) of diameter. To determine strength retention, pellets that had undergone cyclic fixed-bed testing were also tested for crush strength. Crush strength was measured with a radial compressive test using a John Chatillon and Sons, New York, NY, crusher, model TCM-TT. Testing was done in accordance with ASTM designation 4179-88a. The pellet diameter was measured using a vernier caliper. The lbs-forces it took to crush the pellet was then divided by the diameter. Due to strength variations in pellets prepared identically, crush strength was determined as an average of 15 crush strengths for pellets with similar diameters.

X-ray Diffraction (XRD)

Wide angle XRD using a Siemens D-500 apparatus was employed to determine what crystalline phases were present in the manganese-based sorbent. Four tests were conducted using fresh, reduced fresh, regenerated, and sulfided sorbent. Reduced fresh sorbent was prepared in a fixed-bed at 600^oC with H_2 flowing at 1 L/min for 45 minutes. Phases search for included: hausmannite (Mn_3O_4), bixbyite (Mn_2O_3), manganosite (MnO), rutile (TiO_2), pyrophanite ($MnO.TiO_2$), manganese titanium oxide (Mn_2TiO_4), alabandite (MnS), manganese sulfate ($MnSO_4$) and sulfided spinels such as $MnS.TiO_2$.

Manganese Analysis

The weight percent manganese in the fresh sorbent was measured through Inductively Coupled Plasma analysis. Staff in the Geology Department of the University of Minnesota performed this analysis.

Sulfur Analysis

The weight percent sulfur in sulfided and regenerated sorbent was measured by a coulometric titration method with iodine. Sample sizes of 20 to 125 mg were used. Staff in the Civil Engineering Department of the University of Minnesota performed this test.

RESULTS AND DISCUSSION

Results from the fixed-bed sulfidation and regeneration tests FB1A-FB2A were presented in previous reports[16-17]. Results from fixed-bed (FB3A and FB4A) testing and cyclic crush strength testing in addition to sulfur and x-ray analysis will be presented in this section.

Fixed-bed Testing

Four tests were conducted in an ambient pressure fixed-bed reactor with each test consisting of four cycles of sulfidation and regeneration. Sulfidation and regeneration results were presented in a previous report[17]. Sulfidation results for tests FB3A and FB4A will be presented first then the regeneration results will be presented. Finally, the effects of sulfidation temperature, superficial gas velocity and the sorbent induration temperature on the desulfurization performance of the sorbent will be presented.

Sulfidation

The operating conditions of all four tests for sulfidation are summarized in Table 1. H_2S concentration in the reactor effluent was measured as a function of time using Gastec™ detector tubes. Reactor effluent was sampled after the cold trap, thereby giving H_2S concentrations on a dry basis.

The fixed-bed sulfidation breakthrough curves for tests FB3A and FB4A are shown in figures 1 to 4. T_{th} is the theoretical time to breakthrough based on the moles of manganese in the packed-bed. The theoretical breakthrough time was calculated assuming one mole of manganese per mole of sulfur and exit H_2S concentrations prior to breakthrough of zero. The sulfidation breakthrough curves for each test are followed by sulfidation breakthrough curves plotted against dimensionless time (time/theoretical breakthrough time). When the H_2S concentration in the exit stream is low, the dimensionless time approximates the conversion of the total mass of MnO. Thus, the desulfurization performance of a sorbent tested under varying conditions can be compared.

The breakthrough time was defined to be the time at which the concentration of H_2S reached and stayed above 100 ppmv. This concentration was chosen because it is the maximum level of H_2S acceptable for IGCC. Each test was terminated shortly after this concentration had been reached to minimize corrosion of downstream equipment and H_2S release.

Prior to breakthrough, the H_2S concentration (dry basis) was below 100 ppmv for all sulfidations of both tests. The typical pre-breakthrough H_2S concentration was 10 to 50 ppmv. During the first sulfidation of test FB3A, very low H_2S concentrations (10 ppmv) were achieved, however, during subsequent sulfidations, higher concentrations (up to 50 ppmv) were realized. A possible reason for this is that sulfate could have been formed during previous regenerations and this sulfate was then reduced to SO_2 during subsequent sulfidations. The SO_2 could have been incorrectly detected by the detector tube as H_2S.

The observed breakthrough sorbent conversion was determined by dividing the actual time to achieve breakthrough by the theoretical time to breakthrough. Observed sorbent conversion ranged from 0.18 to 0.27, with the lowest conversion being attained by cycle 1 of test FB3A and the highest from cycle 2 of test FB4A. Sulfidation tests from FB3A showed improved sorbent conversions at breakthrough from cycle 1 to cycle 4. This may be due to a small amount of sulfate formation during regeneration. This sulfate formation may have caused small cracks and these cracks may help to decrease transport resistances. Test FB4A did not show improvement in sulfidation conversion, which may be due to the fact that the sorbent used in this test was indurated at a higher temperature than the sorbent in all other test, giving it a stronger crush strength and thus more resistance to cracks. Table 6.2 summarizes the results for the fixed-bed sulfidation tests.

Table 3. Lowest H_2S concentrations achieved and observed sorbent conversions in fixed-bed tests

Test Designation	Cycle	Lowest H_2S Concentration Achieved (ppmv)	Observed Sorbent Conversion at Breakthrough	Relative Percent Change*
FB3A	1	10	0.18	
FB3A	4	30	0.27	+50
FB4A	1	25	0.28	
FB4A	4	25	0.28	0

*Percent change is defined as (cycle 1 conversion - cycle 4 conversion)/cycle 1 conversion

Regeneration

After each sulfidation process, the sorbent was regenerated in an air/steam mixture flowing at approximately 1 L/min. The operating conditions of all four tests for regeneration are summarized in Table 2. The regeneration curves are shown in Figures 5 and 6.

A thermocouple placed at the exit of the packed-bed indicated that the temperature rose as much as 125°C. This increase in temperature occurred immediately prior to a sudden drop in SO_2 exit gas concentration as seen in Figure 5. This is due to the placement of the thermocouple. The thermocouple, which is positioned right at the sorbent bed exit, reads high temperatures in the vicinity of the reaction zone. Thus when the temperature gets very high, it indicates that the reaction is occurring near the exit of the bed, near the completion of regeneration. Although, the thermocouple only read a rise in temperature of 125°C, it is suspected that the temperature actually rose higher since regeneration temperatures as low as 650°C were used with minimal sulfate formation (the fact that the pellets remained intact and did not show noticeable cracks was an indication for minimal sulfate formation).

Another important aspect of regeneration besides sulfate formation is the off-gas composition. As seen in figures 5 and 6, the maximum SO_2 concentration achieved in tests FB3A and FB4A for all regeneration processes was at least 5 % (dry basis) with more typical concentrations of approximately 6 %. This SO_2 concentration held fairly steady until a sharp decrease in the concentration occurred, indicating regeneration breakthrough. The breakthrough occurred rapidly when the bed was almost completely regenerated. The remaining low concentrations of SO_2 following breakthrough were attributed to the small amount of sulfate formed during regeneration, decomposing back to SO_2.

Effects of Varying Sulfidation Conditions

To determine the best operating conditions, the effects of reaction temperature, superficial gas velocity and sorbent induration temperature on the desulfurization performance of the sorbent were investigated. To compare the sorbent's performance under varying conditions, the first sulfidation results of each test (including tests 7FB, FB1A and FB2A) were used.

Figure 7 shows the effect of reaction temperature on the desulfurization performance of the sorbent (C6-2-1100). As discussed in the previous section, the sulfidation temperature had a negligible affect on the pre-breakthrough concentration of H_2S. Pre-breakthrough concentrations ranged from 10 to 50 ppmv, all of which are acceptable for IGCC application.

The observed sorbent breakthrough conversion as approximated by the dimensionless time, however, is greatly affected by the sulfidation (reaction) temperature. The sorbent conversion at breakthrough increased as the sulfidation temperature increased. The observed sorbent breakthrough conversion increases from 0.18 at 500^{o}C to 0.60 at 600^{o}C. Thus a small change in the sulfidation temperature results in a large increase in the capacity without much compromise in the pre-breakthrough concentration.

Figure 8 shows the effect of the superficial gas velocity on the desulfurization performance of the sorbent. As seen in the figure, there is a slight increase in the observed sorbent breakthrough conversion as the velocity is decreased. This can be explained by the nature of the reaction. There is more than one reaction mechanism (reaction, gas film diffusion, product layer diffusion) occurring. One mechanism may be very fast and independent of time while another needs time to proceed (time dependent). As the gas velocity increases the contribution of the time dependent mechanisms becomes less, and consequently the breakthrough conversion is lower. However, between superficial gas velocities of 1090 cm/min and 1635 cm/min the difference in breakthrough conversion is minimal.

Figure 9 shows the effect of the sorbent induration time on the desulfurization performance of the sorbent. The sorbent induration temperature greatly affected the observed sorbent conversion at breakthrough. The observed sorbent breakthrough conversion was 0.60 for sulfidation of sorbent indurated at 1100^{o}C (C6-2-1100). The conversion dropped to 0.28 when sulfiding sorbent that was indurated at 1115^{o}C (C6-2-1115). This is a considerable drop for such a small change in induration temperature. The much lower conversion of C6-2-1115 must be attributed to a difference in physical properties as compared to C6-2-1100. The higher induration temperature of C6-2-1115 caused more sintering to occur which decreased the pore sizes, thereby increasing transport resistances.

Strength Testing

The crush strength of cycled sorbent (sorbent that had undergone 4 cycles of sulfidation and regeneration in a fixed-bed reactor) was also measured. Cycled samples used for strength testing were collected from the middle one-third, along the axial dimension, of the sorbent bed. Figure 10 shows the results of crush strength testing on sorbent after four cycles of sulfidation and regeneration. The crush strength of the fresh sorbent is also given for comparison reasons. Note that the sorbent from FB3A is actually the crush strength of the sorbent after 3.5 cycles (sulfided state) whereas FB1A, FB2A, and FB4A are crush strengths of the sorbent after four full cycles (regenerated state).

The crush strength of all sorbent after several cycles of sulfidation and regeneration decreased. The largest loss of sorbent strength (53 %) occurred during test FB2A. This test utilized sorbent C6-2-1100 (indurated at $1100^{o}C$). The smallest loss in sorbent strength (30 %) occurred during test FB4A. This test utilized sorbent C6-2-1115 (indurated at $1115^{o}C$) It is not known whether the sorbent would have continued to lose strength after additional cyclic testing or if the sorbent strength had stabilized. A minimum required pellet strength is typically establish for desulfurization processes. Therefore, if the pellet strength had stabilized, the minimum strength could be achieved and maintained. This could be accomplished by indurating the pellets at the minimum temperature that will achieve a sorbent crush strength that is approximately 50 % greater than the minimum strength requirement.

Sulfur Analysis

Sulfur analysis was performed to determine the regenerability of the sorbent. If the amount of sulfur left in the sorbent is low, then it can be assumed that the sorbent was satisfactorily regenerated. For this reason, the sorbent from test FB1A after the fourth regeneration was analyzed for sulfur. It was found that the sorbent contained 0.60 % sulfur. This was considered to be low, thus indicating that the sorbent regeneration was essentially complete.

X-Ray Diffraction (XRD)

Figures 11 through 14 represent the x-ray diffraction patterns for fresh, fresh reduced, sulfided and regenerated pellets. The top plot is the experimental x-ray diffraction patterns, while the bottom plot represents the "cards" or peaks that correspond to the pure substance. The fresh reduced pellets were prepared in a fixed-bed at $600^{o}C$ with H_2 flowing at 1 L/min for 45 minutes. Cycled sorbent was collected from the middle one-third, along the axial dimension, of the sorbent bed.

As seen in figures 11 through 14, the background is moderately high which is an indication that there is a non-crystalline phase present. Crystalline phases identified in fresh sorbent were bixbyite-C (Mn_2O_3) and pyrophanite, syn ($MnO.TiO_2$). Crystalline phases present in fresh reduced pellets were pyrophanite and manganosite (MnO). As discussed in Chapter 3, the reduction of Mn_2O_3 to MnO was expected. Also, as expected, no crystalline phase of metallic Mn was detected in the reduced sample.

The sulfided sample was obtained from test FB3A after 3.5 cycles. Crystalline phases identified in this sample were rutile, syn (TiO_2) and alabandite (MnS). No sulfided spinel was detected ($MnS.TiO_2$) therefore, it appears that the pyrophanite dissociates in the presence of H_2S. Also compounds that contain more than one mole of sulfur to Mn were not detected.

The regenerated sample was obtained from test FB1A after 4 cycles. Crystalline phases identified in this sample were Mn_2O_3 and TiO_2. A significant finding is that the sorbent was regenerated to Mn_2O_3, a higher oxide than both MnO and Mn_3O_4. This is somewhat undesirable in that the higher oxide will consume hydrogen from the fuel-gas during subsequent sulfidations. Another important finding is that no $MnSO_4$ was detected, in fact no compounds containing sulfur were detected. This is an indication of essentially complete regeneration.

CONCLUSIONS

Sorbent C6-2 showed excellent desulfurization performance in the temperature range of 500 to 600^oC and gas flow rates between 2 to 3 L/min (STP). The pre-breakthrough concentrations were below 100 ppmv for all tests. The pre-breakthrough concentrations remained below 100 ppmv over 4 consecutive sulfidations.

The sulfidation temperature and sorbent induration temperature greatly affected the sorbent's capacity at breakthrough. The breakthrough sorbent conversion increased only slightly as the superficial gas velocity decreased. The gas velocity also had no significant affect on the pre-breakthrough H_2S concentration.

It has been concluded that the optimum sulfidation temperature should be as high as possible before equilibrium and valve limitations occur. The optimum gas velocity should be as low as economically feasible; however, lowering the gas velocity will probably not improve sorbent performance that much. Finally the optimum sorbent induration temperature should only be as high as needed to achieve pellet strength requirements. Alternatively, a new method for preparing stronger pellets that provide the same level of desulfurization performance could be developed.

Regeneration in 50% air and 50% steam regenerated the sorbent essentially to completion while minimizing sulfate formation and large increases in temperature. Regeneration in 50% air and 50% steam produced SO_2 concentrations as high as 6.8% and may be used in sulfuric acid or elemental sulfur production.

Crush strength testing done after 4 cycles of sulfidation and regeneration showed decreases in strength from 30 to 53%. It is not known whether the sorbent's strength would have continued to decrease over additional cycles or if the sorbent's strength had stabilized.

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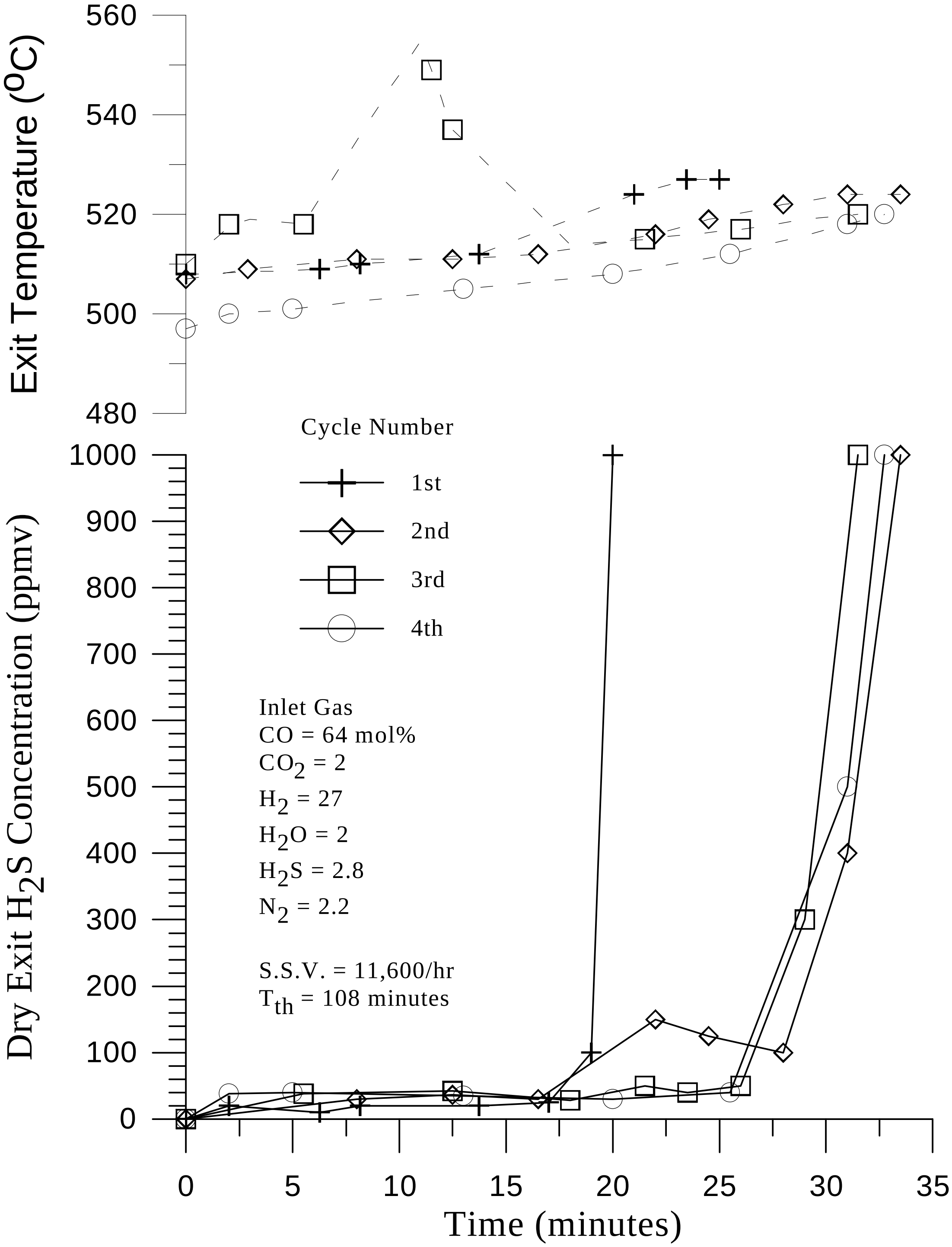

Figure 1. **Sulfidation breakthrough curves for test FB3A using C6-2-1100 sorbent. T_{th} is the theoretical time to breakthrough.**

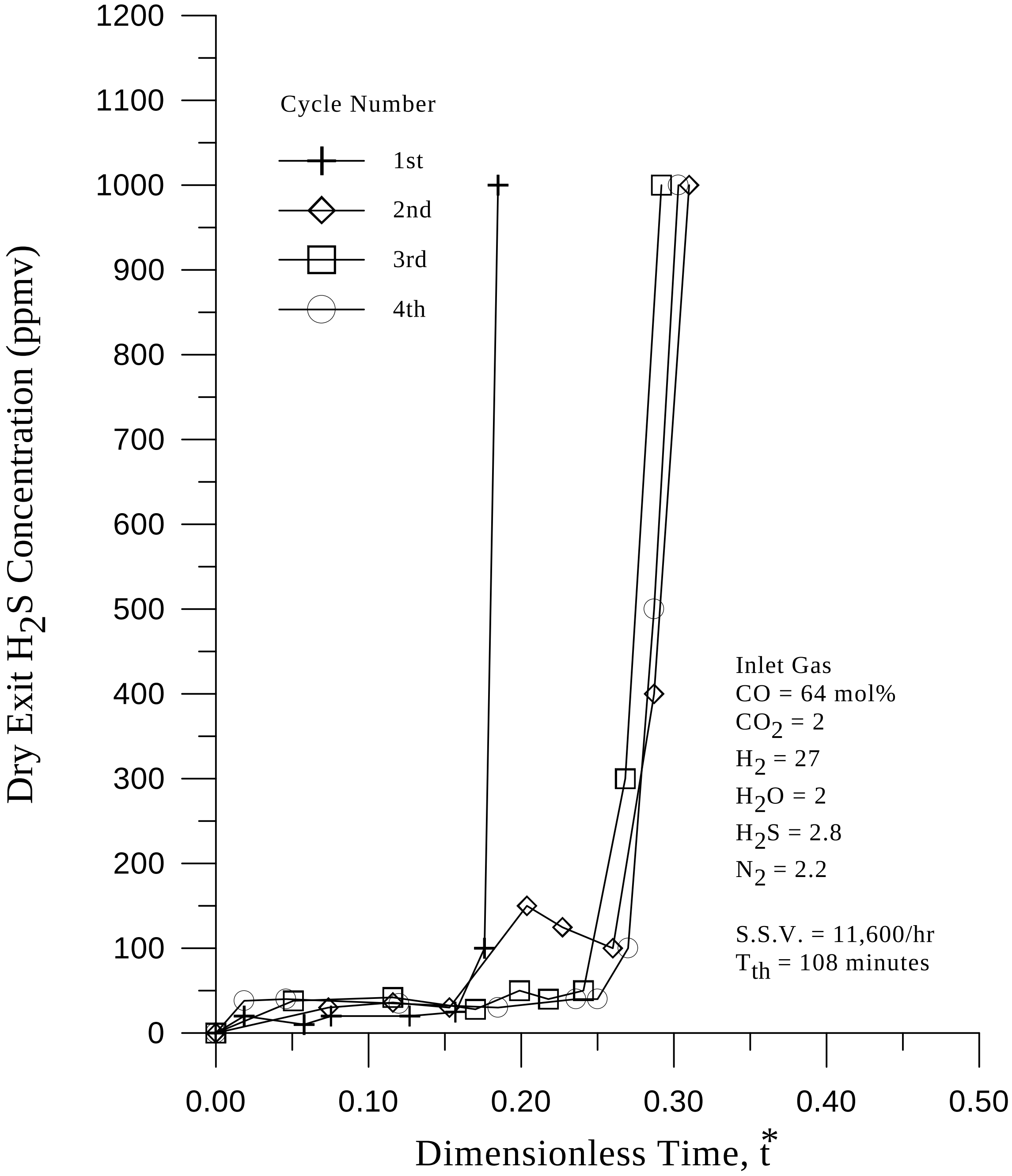

Figure 2. **Sulfidation breakthrough curves for test FB3A using sorbent C6-2-1100 at 500°C, plotted as H_2S concentration versus dimensionless time.**

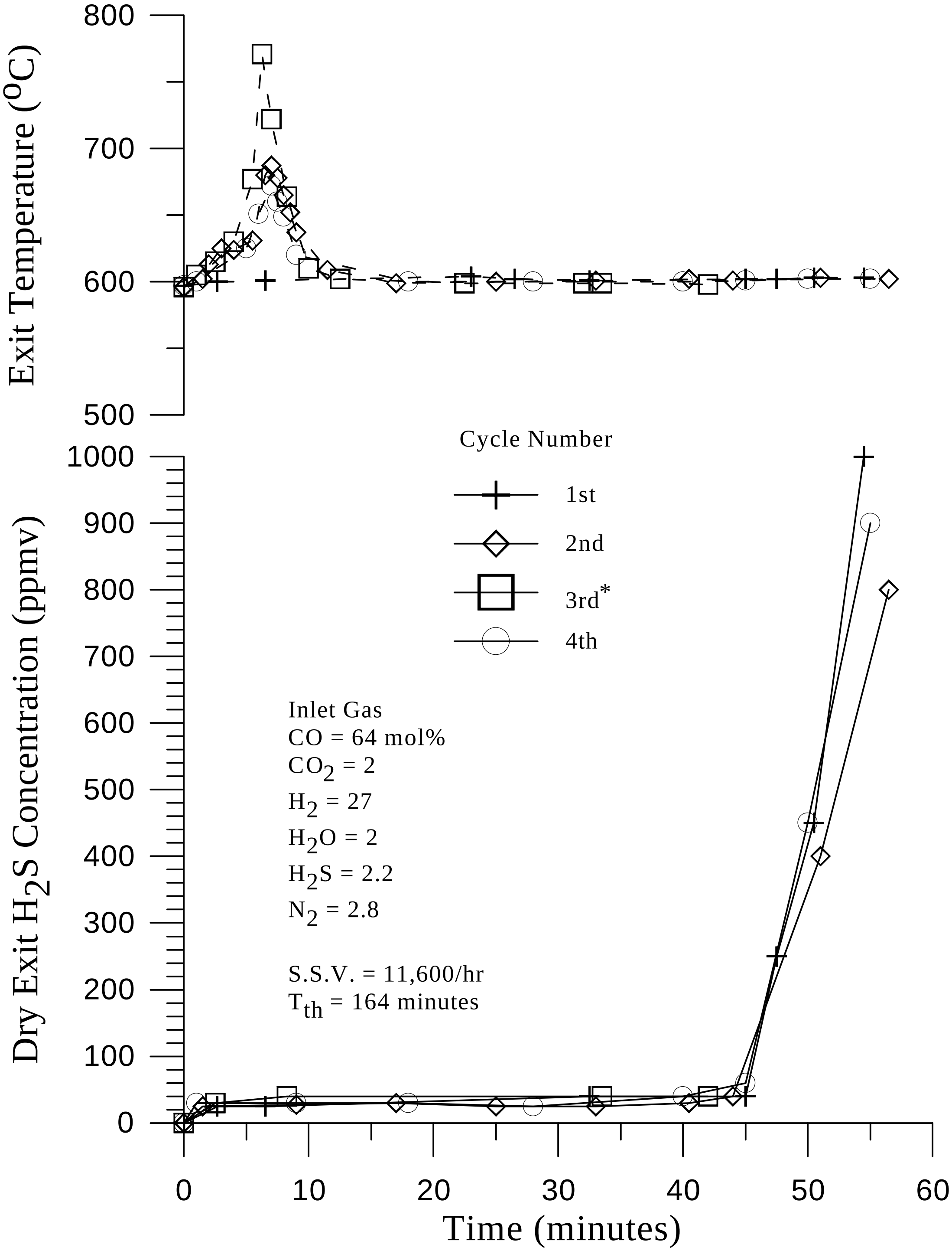

Figure 3. **Sulfidation breakthrough curves for test FB4A using C6-2-1115 sorbent. T_{th} is the theoretical time to breakthrough. *H_2S tank ran out at 44 minutes, cycle terminated.**

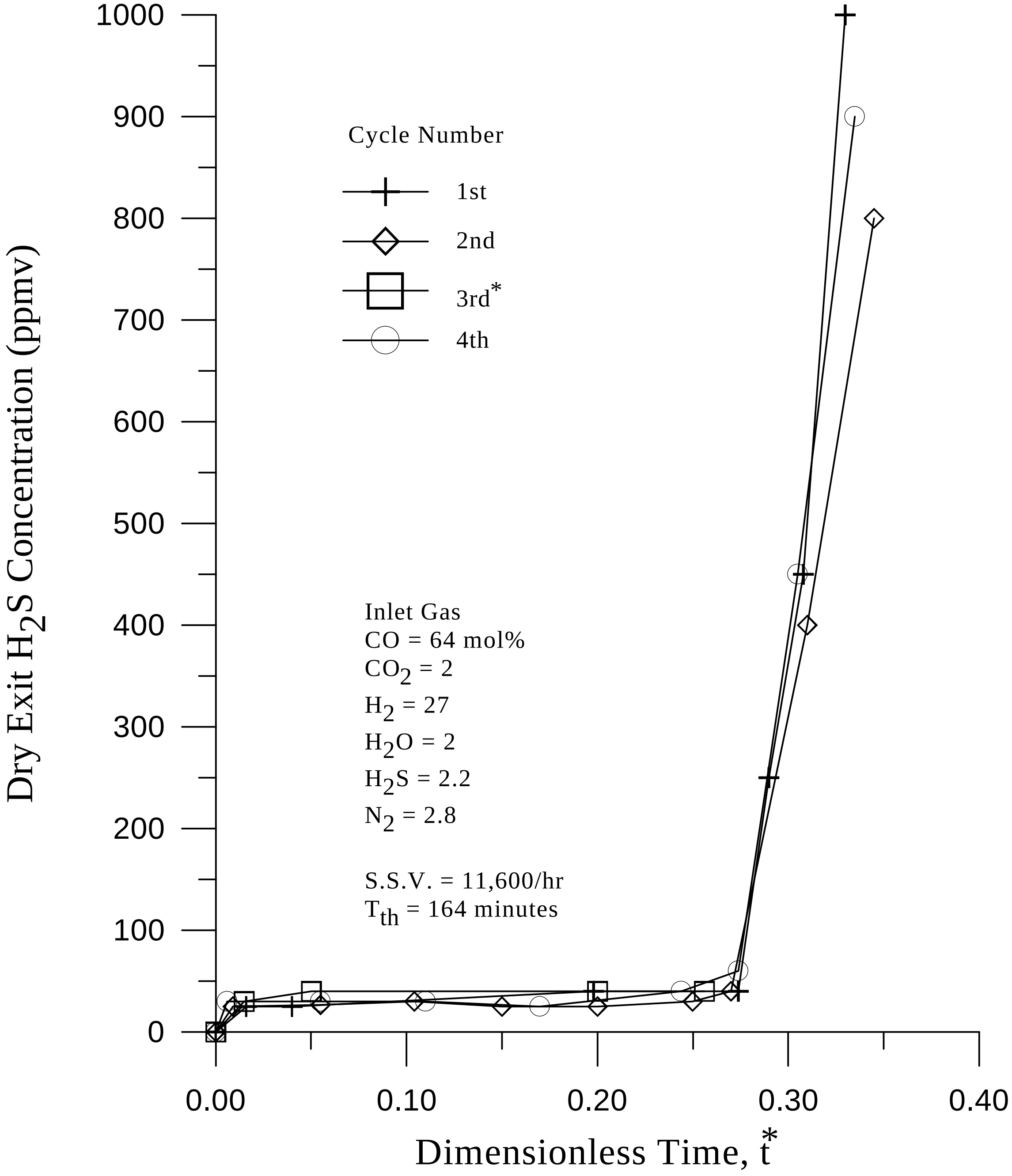

Figure 4. **Sulfidation breakthrough curves for test FB4A using sorbent C6-2-1115 at 600°C, plotted as H_2S concentration versus dimensionless time. *H_2S tank ran out at 44 minutes, cycle terminated.**

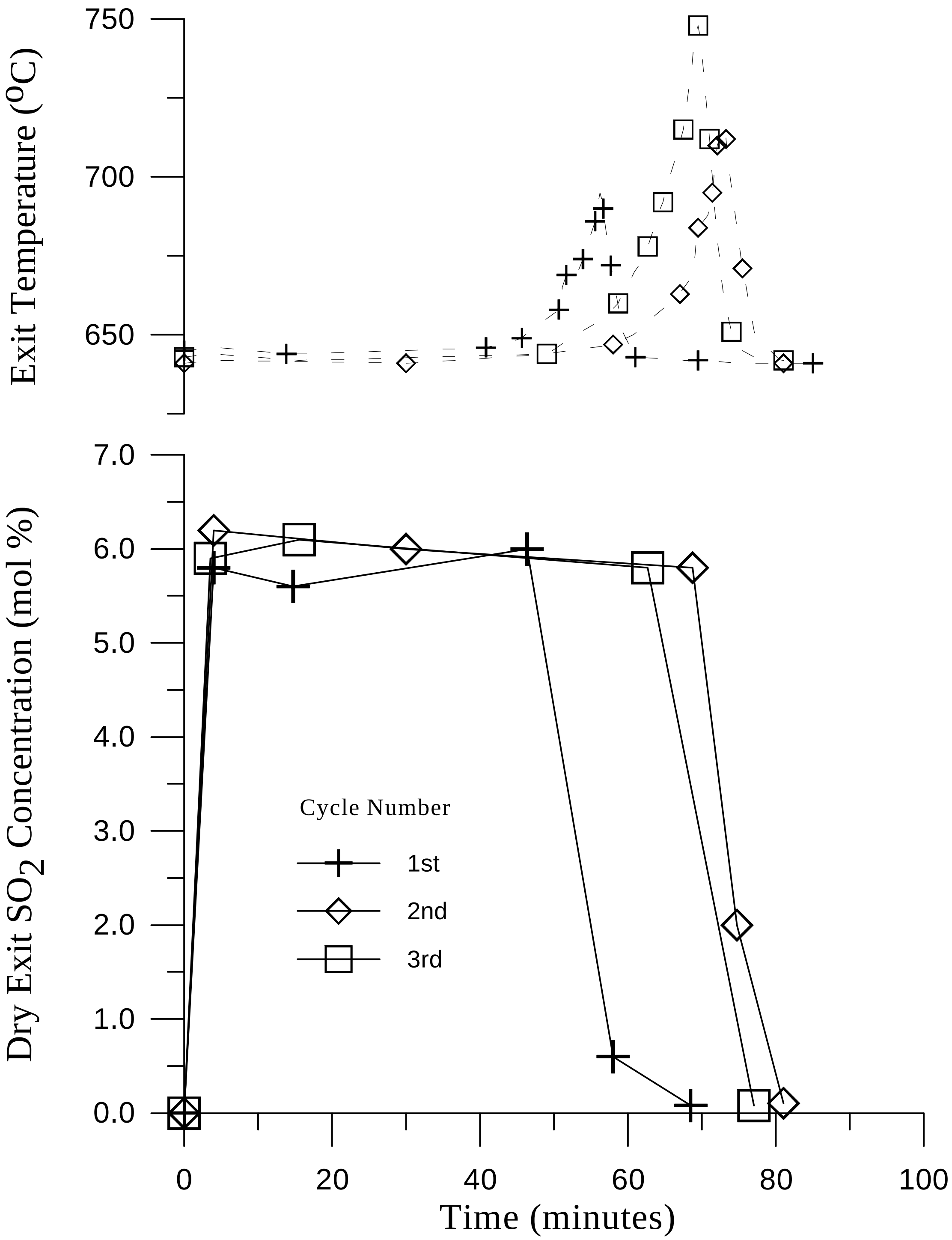

Figure 5. **Regeneration curves for test FB3A using C6-2-1100 sorbent. Regeneration in 40 mol% air and 60 mol% H_2O, with a standard space velocity of 4800/hr at 650 ^{0}C.**

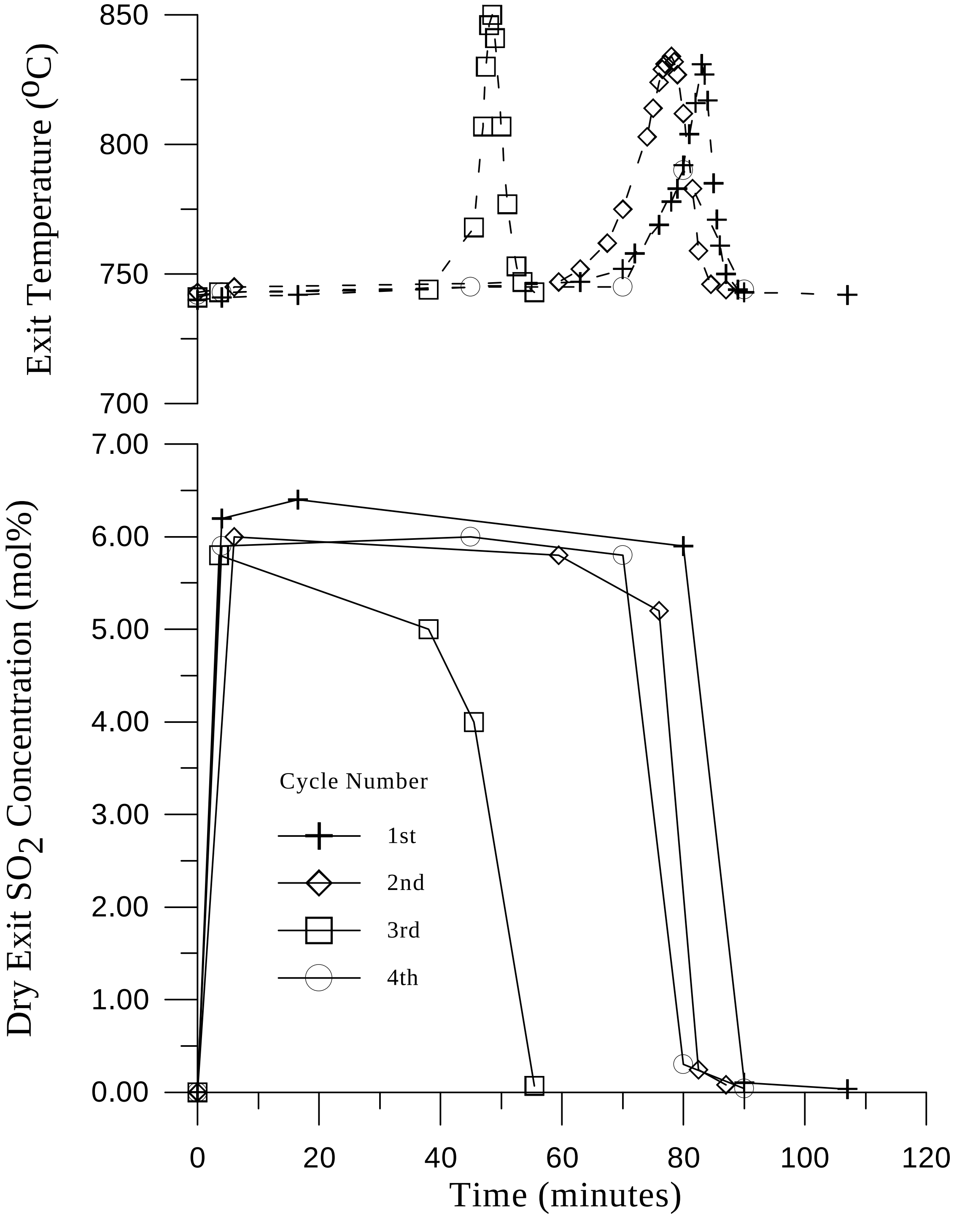

Figure 6. **Regeneration curves for test FB4A using C6-2-1115 sorbent. Regeneration in 50 mol% air and 50 mol% H_2O, with a standard space velocity of 3900/hr at 750°C.**

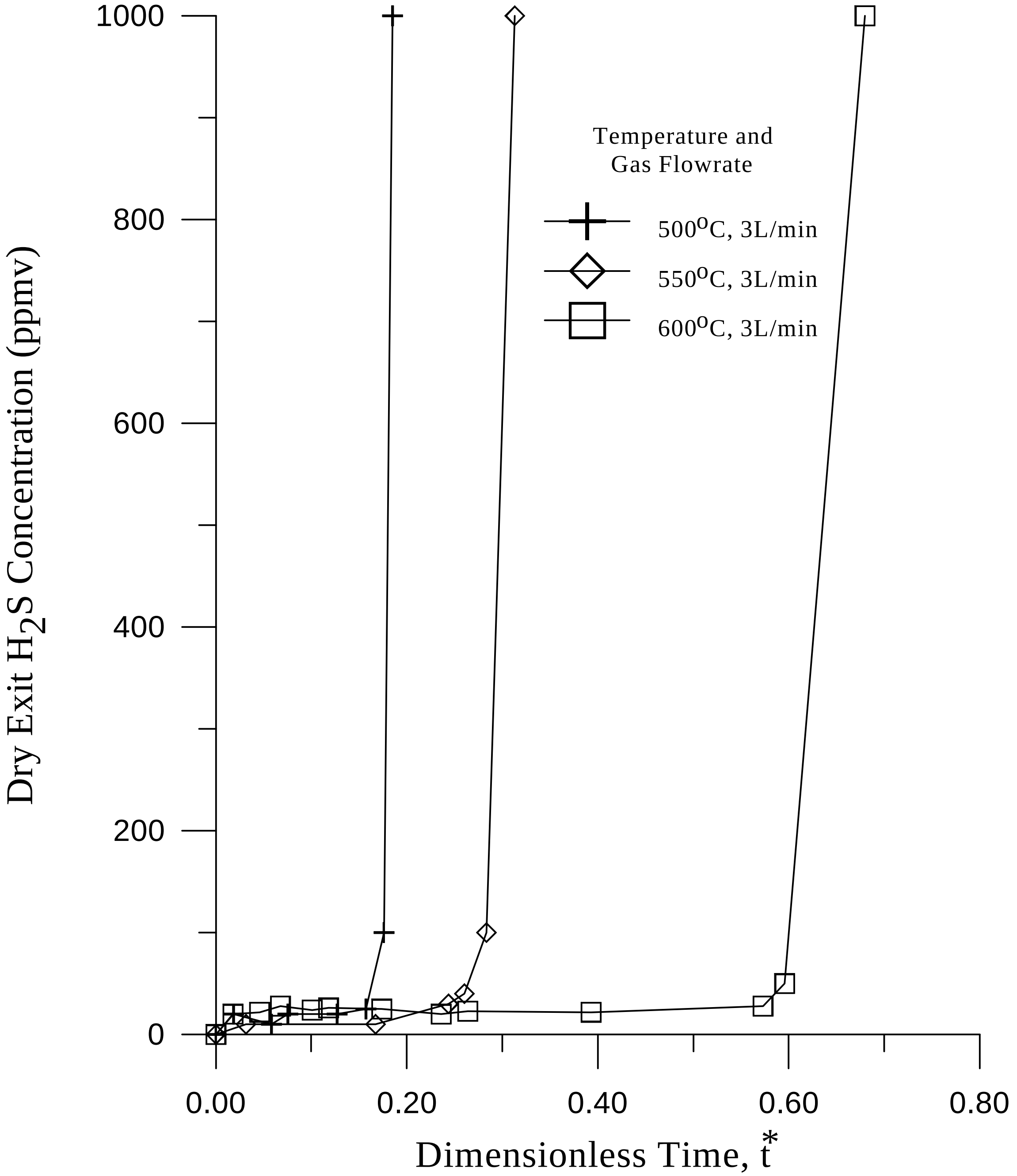

Figure 7. **Effect of sulfidation temperature on sorbent performance (C6-2-1100).**

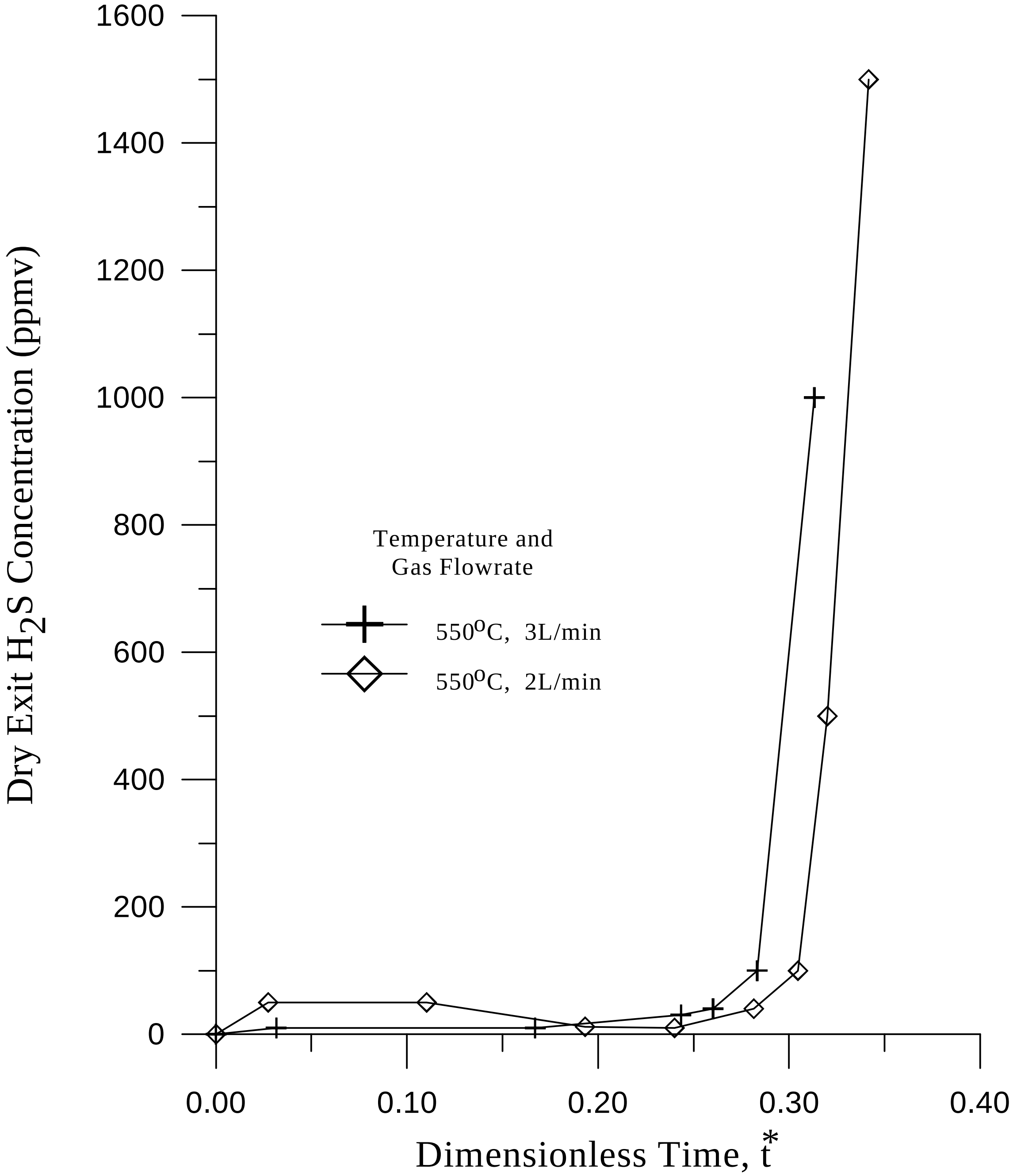

Figure 8 **Effect of sulfidation gas flow rate on sorbent performance (C6-2-1100).**

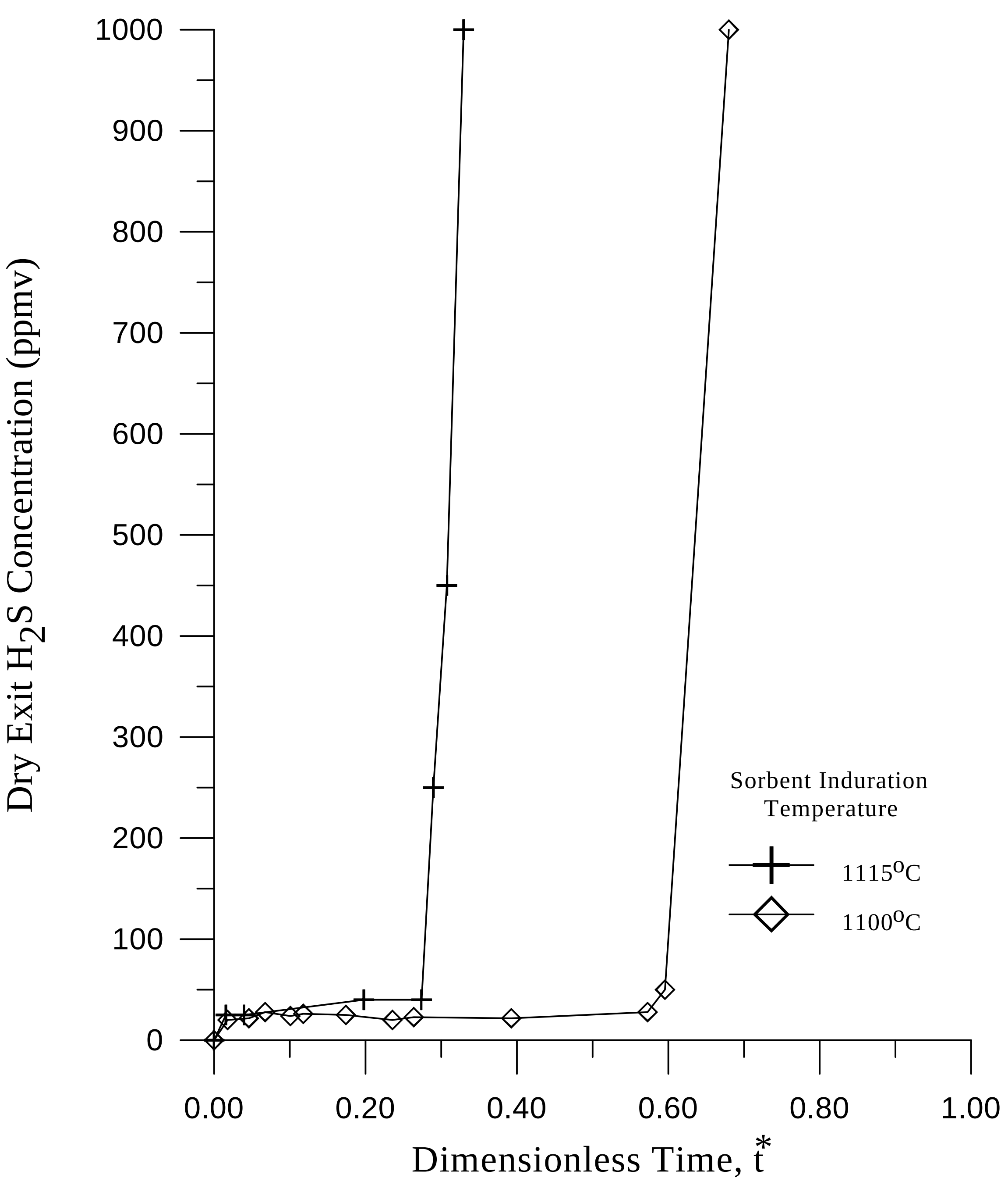

Figure 9. **Effect of sorbent induration temperature on sulfidation breakthrough.**

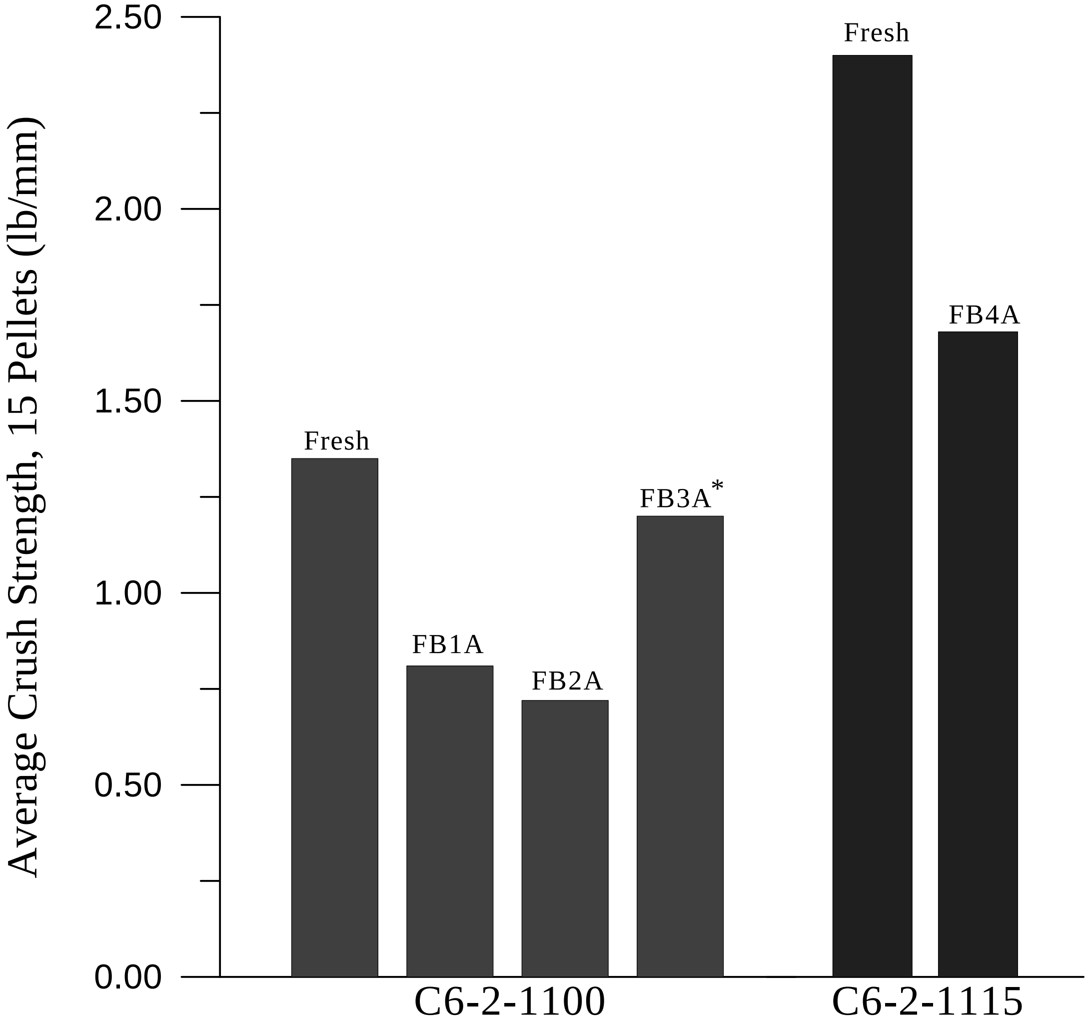

Figure 10. **Crush strength of sorbents after 4 cycles of sulfidation and regeneration in a fixed-bed reactor. *Crush strength of sorbent after 3.5 cycles (sulfided state).**

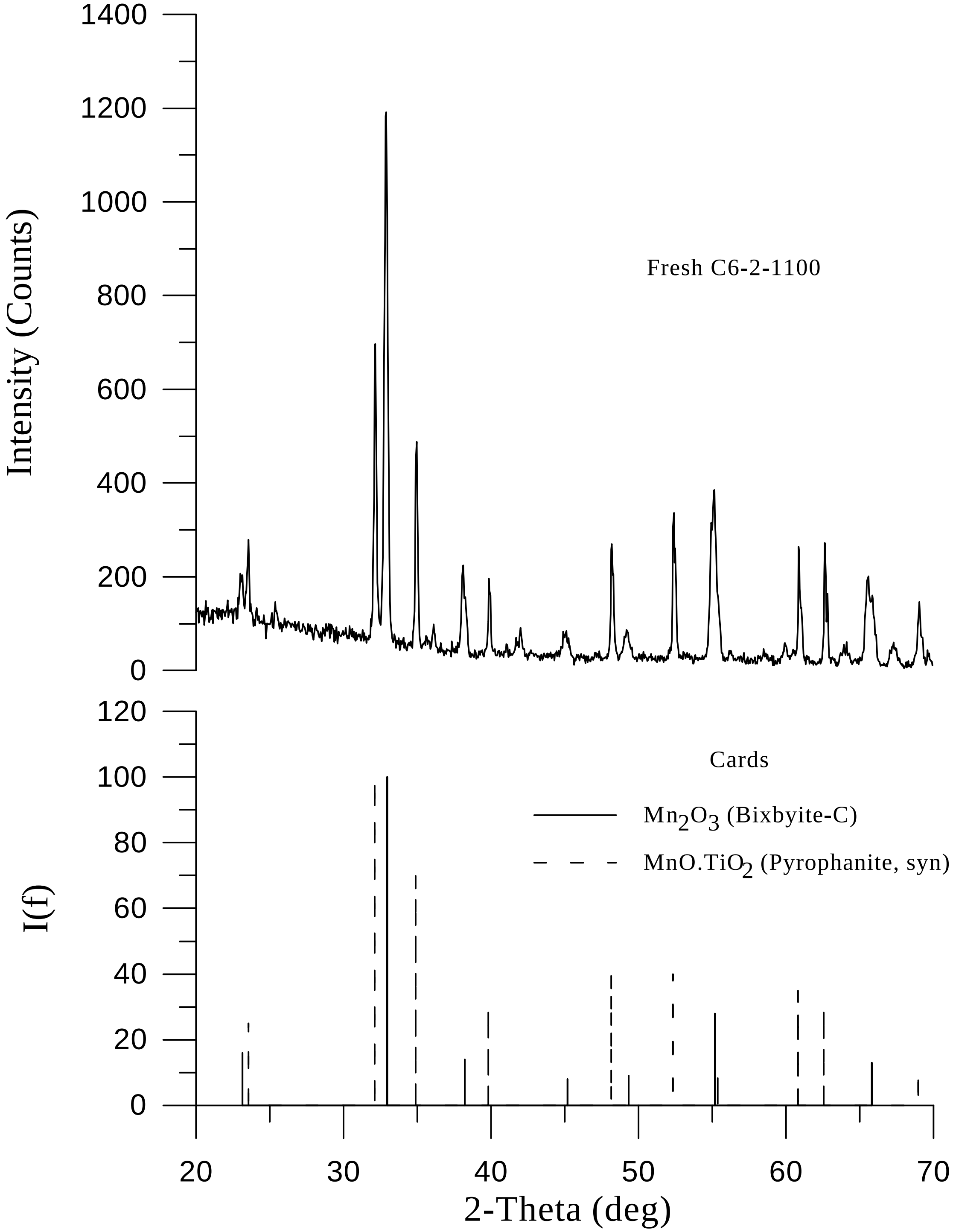

Figure 11. **X-ray diffraction patterns of fresh C6-2-1100**

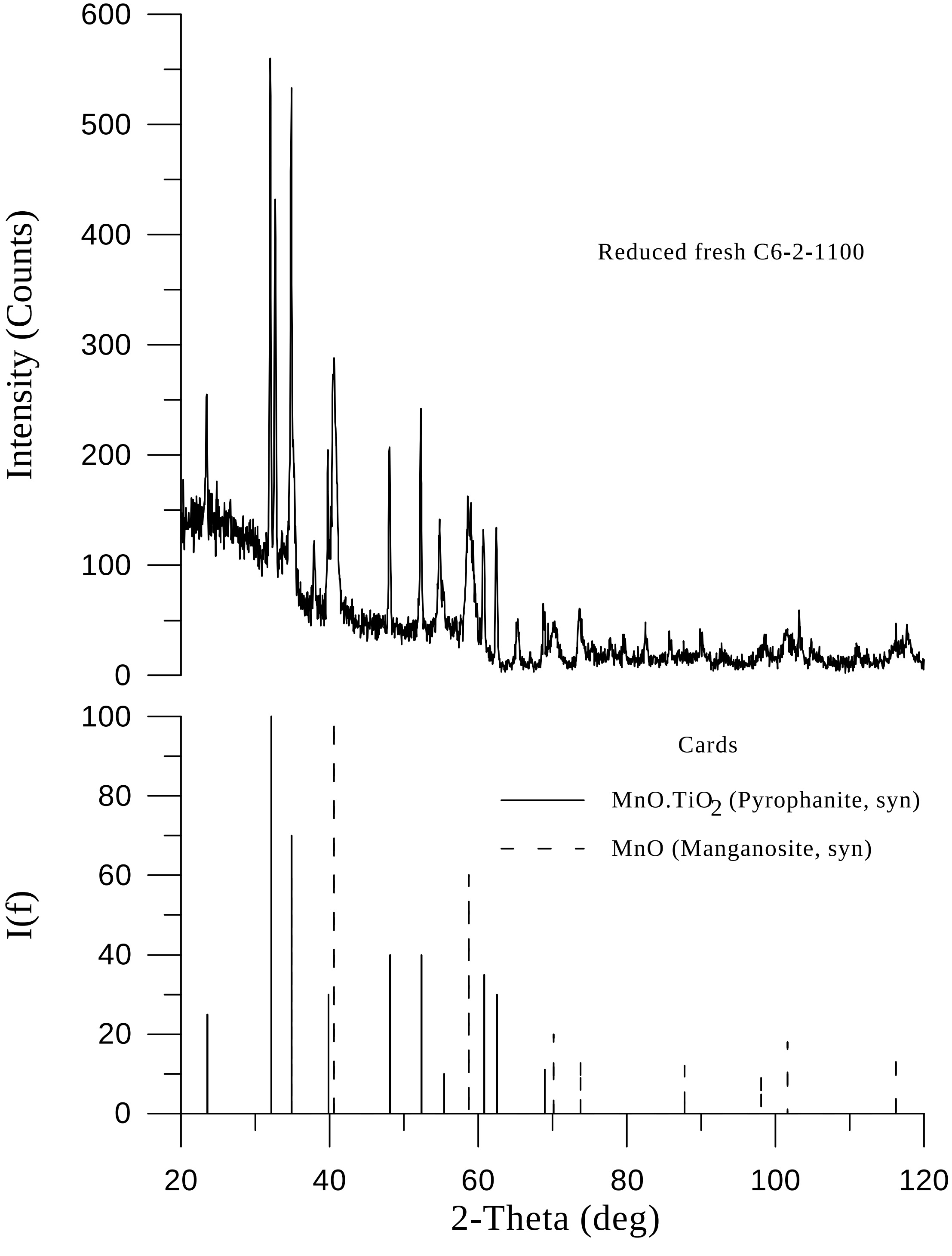

Figure 12. **X-ray diffraction patterns of reduced fresh C6-2-1100.**

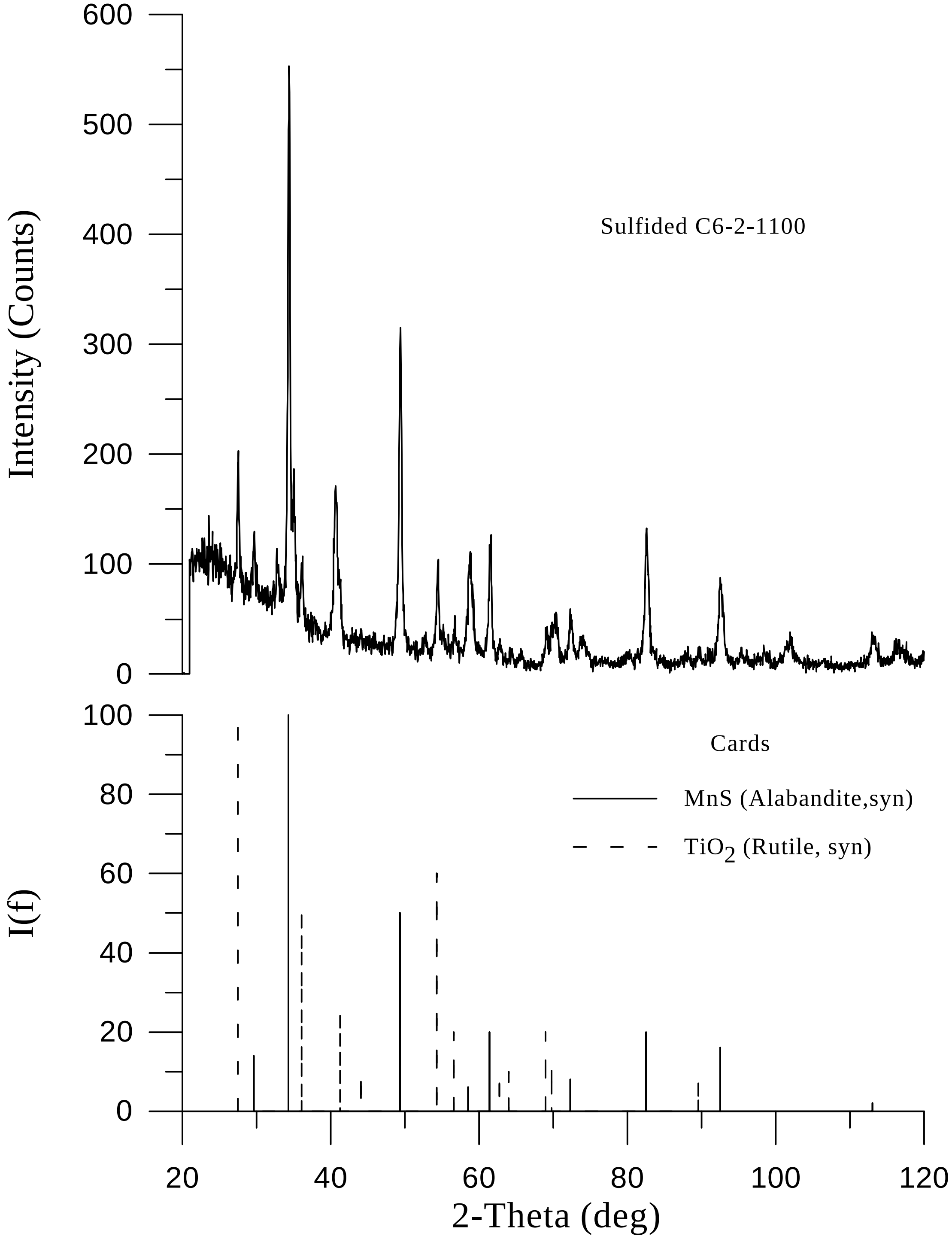

Figure 13. **X-ray diffraction patterns of sulfided C6-2-1100 from test FB3A, 3.5 cycles.**

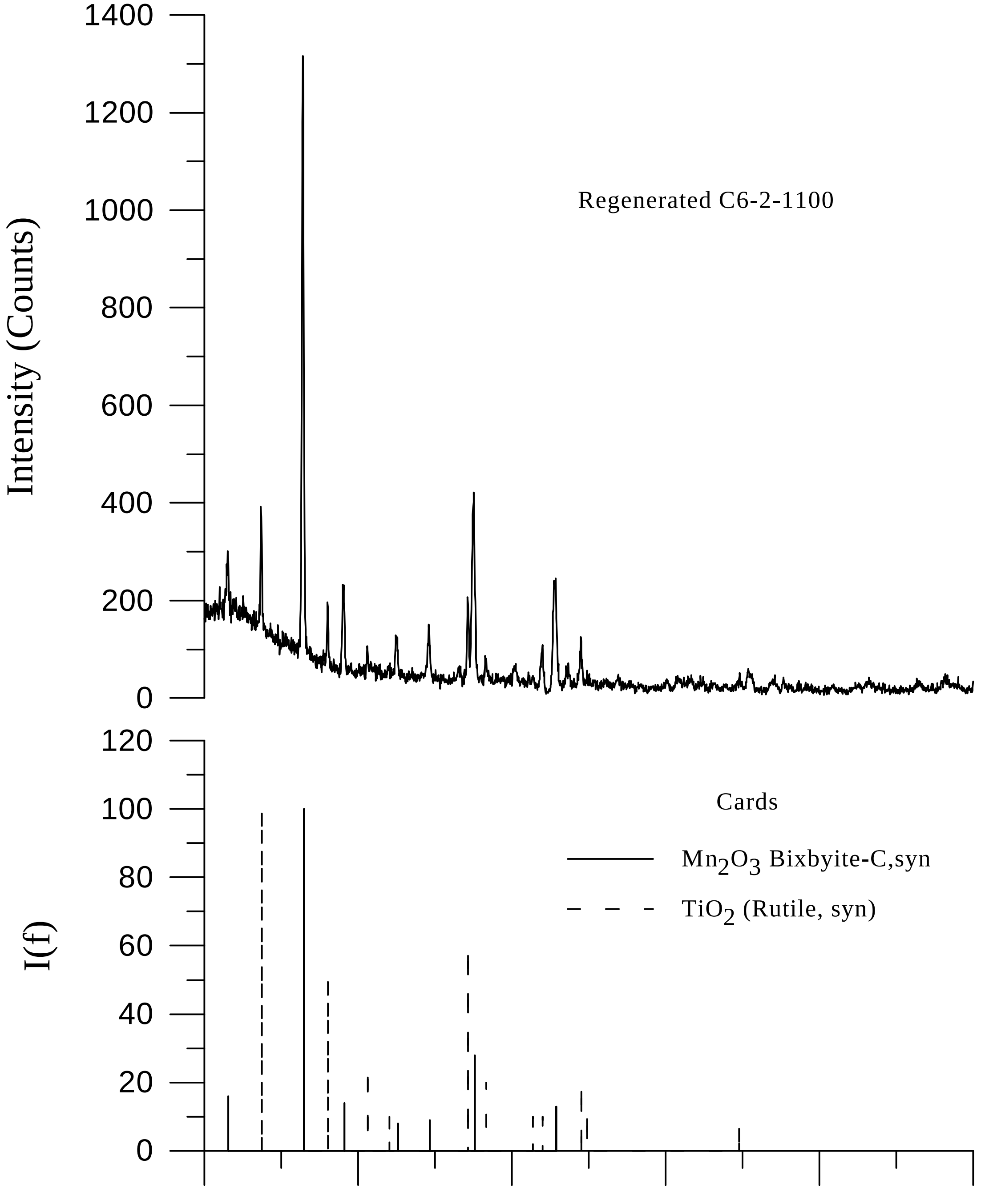

Figure 14. **X-ray diffraction patterns of regenerated C6-2-1100 from test FB1A after 4 cycles.**