N2O from Circulating Fluidized Bed Boilers - Present Status

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N2O from Circulating Fluidized Bed Boilers – Present Status

L-E. Åmand, B. Leckner, S. Andersson and L. Gustavsson
Chalmers University of Technology
Department of Energy Conversion
S–412 96 Göteborg, Sweden
(L–E. Åmand, tel +46–31721439, fax +46–31721192)

INTRODUCTION

Our first measurements of N_2O emissions in an 8 MW circulating fluidized bed CFB boiler were reported in [1], where it is concluded that the levels of N_2O emissions are high compared to the emissions of NO. Furthermore, the dependence of bed temperature is opposite to that of NO, that is, a higher bed temperature causes the emission of N_2O to decrease, while the emission of NO increases. In Fig.1 and Fig.2 some of the results are presented in the form of fuel-nitrogen conversion to either NO or N_2O. The calculation of the conversion is based on a molar balance over the combustion chamber and takes into account the fact that two moles of fuel nitrogen are found in every mole of N_2O, while half the amount is found in one mole of NO. Furthermore, it is assumed that the emission of NO and N_2O originates from the fuel nitrogen only and no formation from the nitrogen in the air takes place. With this representation, the difference between the NO and N_2O emissions becomes even more pronounced. In [1] it was not possible to draw any conclusions about the dependence of the excess air ratio on the emissions of N_2O. The reason for this is seen in Fig.3, where the temperature at the top of the combustion chamber decreases when the excess air ratio is increased, which means that the observed increase of the N_2O emission can be related to the decrease of temperature as well as to the increase in excess air. We have therefore carried out further measurements in the new 12 MW CFB boiler at CTH where it is shown that there is a dependence of excess air level. In these measurements special attention is paid to the heterogeneous reactions which characterize the fluidized bed.

THE 12 MW CFB BOILER AT CHALMERS

A schematic picture of the boiler is seen in Fig.4. Fuel is fed to the bottom of the combustion chamber through the fuel chute (1). The height of the combustion chamber is 13 m and the cross-section is 2.9 m^2. The entrained bed material is separated from the gases in the hot cyclone (2) and passed back to the combustion chamber through the return leg (3) and the particle seal (4). Primary air is introduced through air nozzles in the bottom plate (5) and secondary air is added through a secondary air register located about 2 metres above the bottom plate. An additional cold cyclone, which is not seen in Fig.4, makes it possible to recycle fly ash back to the combustion chamber. The boiler is well equipped for research purposes. For example, a continuous IR analyser is used for on-line analysis of N_2O (a Spectran 647 from Perkin Elmer) parallel with other conventional flue gas analyzers. Further details on the IR analyser are given in [7].

INFLUENCE OF EXCESS AIR

In Fig.5 the emission of N_2O has been recorded during 4 hours continuous operation when cold bed material was added on three occasions, leading to an almost instantaneous decrease of the temperature at the top of the combustion chamber. The change of the bottom bed temperature is much slower due to thermal inertia. The emission of N_2O follows closely both the small and the large changes in top temperature, which means that the temperature level in the top as well as in the bottom of the combustion chamber is important for the fuel-nitrogen conversion to N_2O.

Fig.6 shows an evaluation of minute mean values during 8 hours continuous operation when both the bottom bed temperature and the top temperature have been kept constant. It is evident that the emission of N_2O is dependent upon the excess air ratio. The dependence is similar to that of NO.

THE INFLUENCE OF CHAR LOADING ON N_2O EMISSION

In Fig.2 it can be seen that the fuel giving the highest char loading in the bed, the petroleum coke, leads to the highest conversion of fuel nitrogen to N_2O. The reason for this can be that N_2O is formed when NO is reduced by the well-known char reaction which is further enhanced by the unburned CO. The gradual increase of the N_2O in the vertical direction of the combustion chamber at the same time as the NO concentration decreases was shown in [1] and subsequently confirmed in a small-scale facility in Japan [3]. Both sets of measurements are compared in Fig.7 [3]. These measurements have been repeated also in the Chalmers CFB boiler, and the same qualitative behaviour is found. The decrease of NO is explained as being caused by the reduction on char surfaces. It is then likely that the corresponding increase of the N_2O concentration is caused by an incomplete reduction of NO to N_2O. A third support for this assumption is presented in Fig.8, which shows the results from a transient test in which the fly ash recirculation is stopped. This stop of recycling of fine char and ash particles causes the NO emission to increase, an effect which was observed already at the 8 MW CFB boiler at Cityvarvet [4]. During the present investigation the N_2O has been recorded as well and Fig.8 shows a simultaneous decrease of the N_2O emission when the NO emission increases. In other words, the NO and N_2O emissions are closely linked to each other in a combustion system characterized by a high char loading in the combustion chamber.

THE INFLUENCE OF LIME ADDITION ON N_2O EMISSION

The influence of lime on the N_2O emission was first observed in a 40 MW CFB boiler [8], Fig.9. It is also illustrated with a transient test carried out at the 12 MW CFB boiler, Fig.10. When the lime addition was started we saw a marked decrease in the SO_2 emission. At the same time the NO emission increased and the N_2O concentration decreased. This example illustrated the effect of further reactions involving particles and points out the special care that has to be taken when dealing with a complex fluidized bed combustion system where the heterogeneous reactions play a significant role.

DECREASE OF N_2O EMISSION

What can we do to reduce the N_2O emission without increasing either the NO, CO or SO_2 emissions? If the excess air is decreased, both the N_2O and the NO emissions decrease. For instance, an excess air ratio of 1.10 can be maintained with only a small increase of the CO emission compared to the conventional operating condition with excess air ratios of 1.20 to 1.30. However, the influence on combustion efficiency and on sulphur retention remains to be examined. A decrease of the excess air may lead to the formation of reducing zones in the combustion chamber which are known to be detrimental to sulphur capture [5].

An alternative way to reduce the N_2O emission is to raise the temperature after the combustion chamber in order to increase the rate of N_2O reduction. Fig.11 shows an example from a test programme carried out at the 12 MW CFB boiler in which propane or methane has been supplied to the hot cyclone. The temperature measured after the cyclone increases from 830^{0}C up to 880^{0}C. At the same time the N_2O concentration decreases from 120 ppm N_2O down to 60 ppm. The test shown in Fig.11 is an example taken out from a large test program [6]. The inlet oxygen concentration was 2%, which was decreased to 0.9% oxygen when the propane was supplied. This low oxygen concentration leads to unacceptable peaks in CO which are also shown in Fig.11. This can be improved, however, by air addition after the cyclone. A drawback is the large amounts of expensive gas that have to be supplied in order to produce a 50^{0}C increase of the gas temperature. The gas burner used has a power of about 700 kW, which corresponds to nearly 10% of the actual load of the boiler.

The two strategies for lower N_2O emissions, lower oxygen concentration and increase of the temperature after the combustion chamber, are summarized together with a reference case in Fig.12. In this figure, based on mean values during 15 minutes, the emissions of CO, NO and N_2O have been normalized to 6% oxygen measured on a dry basis at the outlet from the boiler.

CONCLUSIONS

Several conclusions can be made about the N_2O emissions from CFB boilers, for instance:

- Much more of the fuel nitrogen leaves with the flue gases in the form of N_2O than NO (Figs 1 and 2).

- The N_2O emission decreases with increasing bed temperature, unlike the NO emission (Figs 1 and 2).

- The N_2O emission decreases with decreasing excess air, similar to the NO emission (Fig.6).

- High volatile fuels result in lower N_2O emission than low volatile fuels (Fig.2).

- The N_2O concentration increases in the vertical direction of the combustion chamber (Fig.7).

- Heterogeneous reactions, for instance with lime and fly ash, are important for the N_2O emission (Figs 8, 9 and 10).

- The N_2O emission can be decreased by increasing the bed temperature and decreasing the excess air ratio, but then the sulphur capture with limestone becomes less efficient (Fig.12).

- The residence time at a high temperature is important to the resulting N_2O emission (Figs 3 and 5).

- A temperature increase in the cyclone decreases the N_2O emission but a considerable amount of fuel is needed to achieve the increase in gas temperatures (Fig.11).

The N_2O analyzer used (Spectran 647, Perkin Elmer) performs in an excellent way and is useful and convenient for flue gas analyses but not for analysis in the combustion chamber itself where methane is present.

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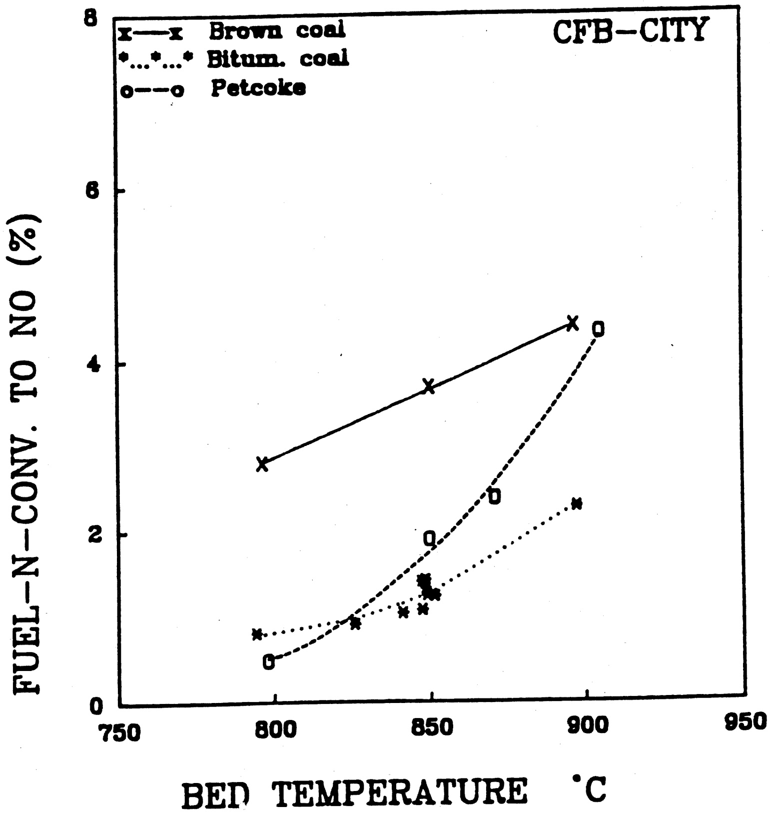

Figure 1 Fuel–nitrogen conversion to NO in the bed temperature series. Primary air stoichiometry = 0.7–0.8. Excess air ratio = 1.20–1.25. [2]

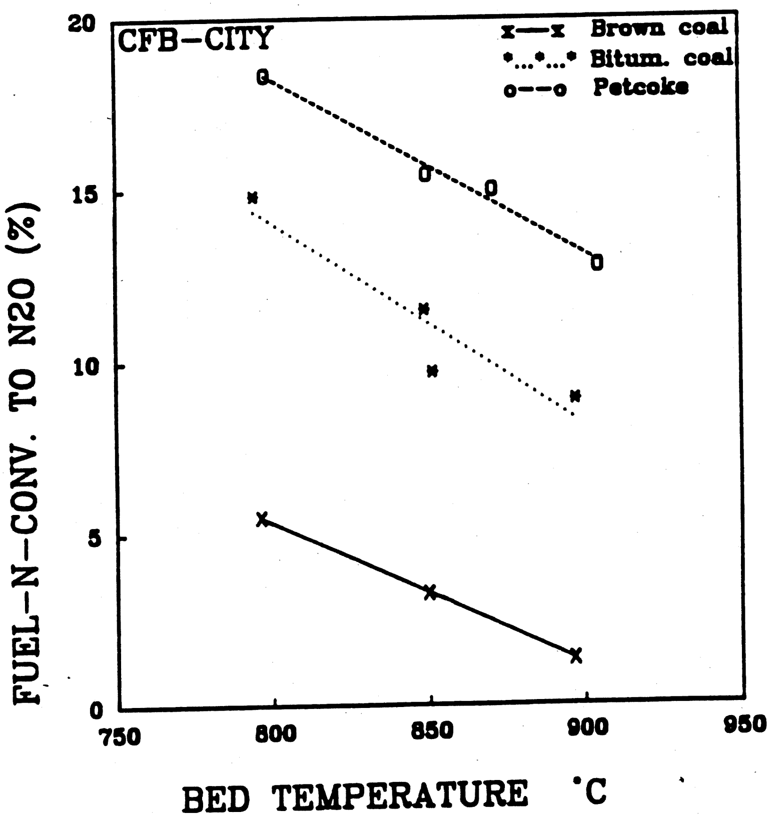

Figure 2 Fuel–nitrogen conversion to N_2O in the bed temperature series. Primary air stoichiometry = 0.7–0.8. Excess air ratio = 1.20–1.25. [2]

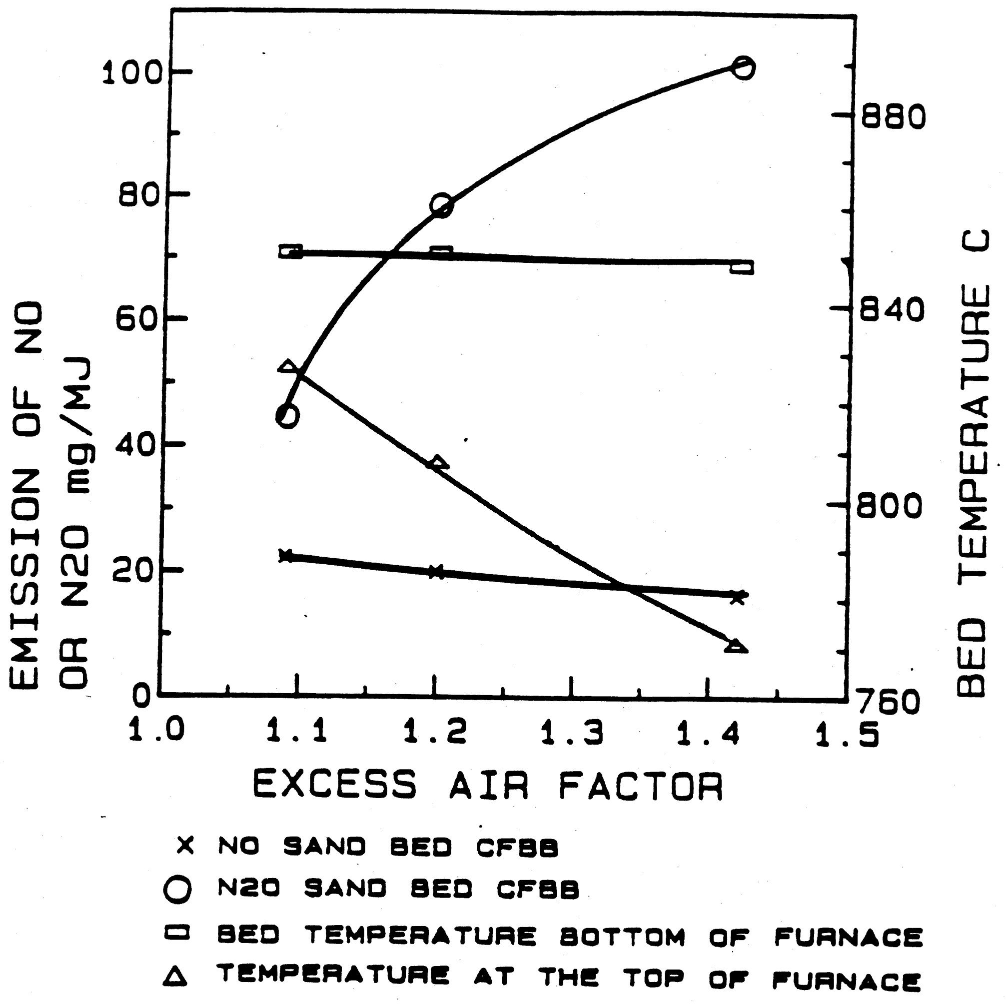

Fig. 3 Emissions of NO (mg NO_2/MJ) and N_2O (mg N_2O/MJ) versus excess air factor in the CFBB. Bottom and top temperatures are also shown.
Fuel: Petroleum coke.

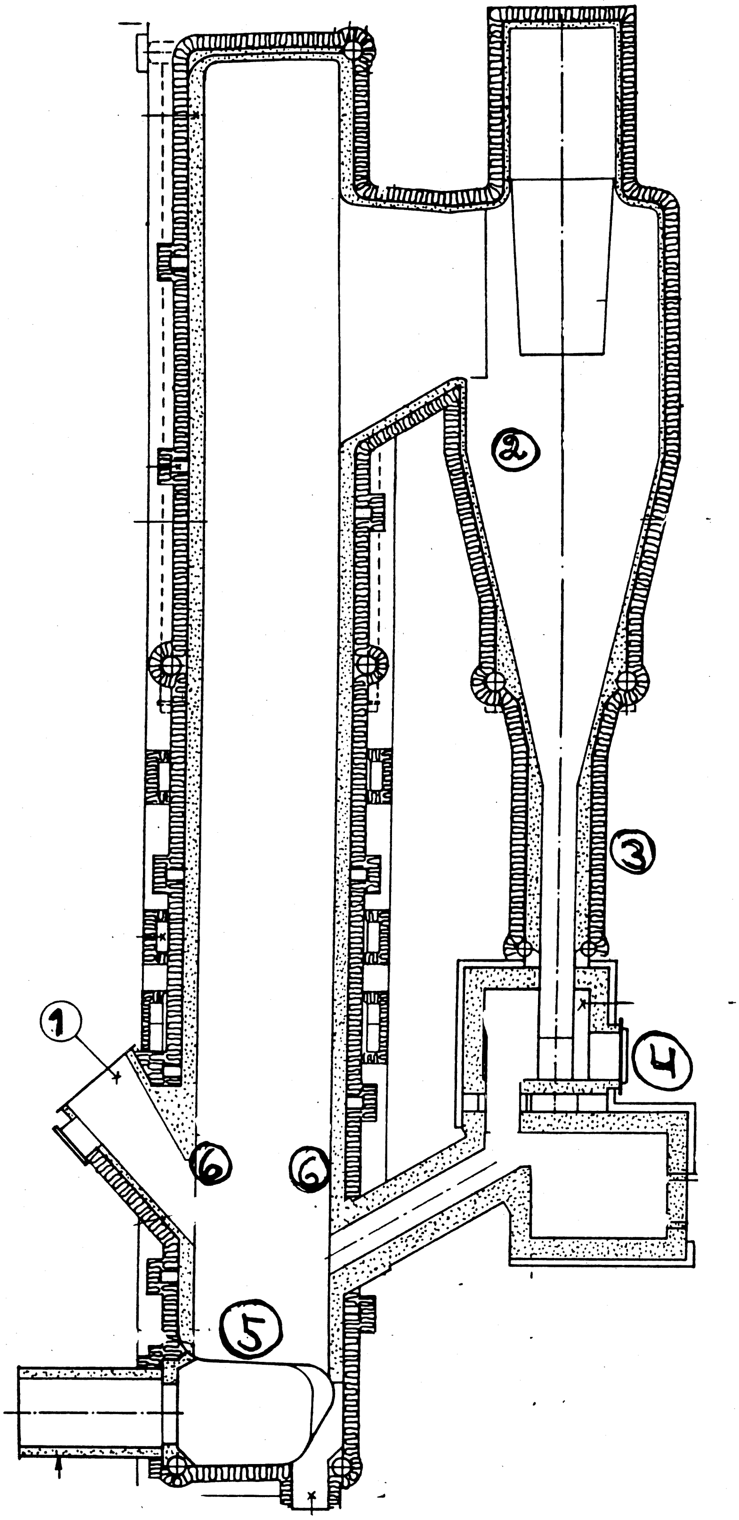

Fig. 4. The 12MW CFB-boiler at Chalmers University.

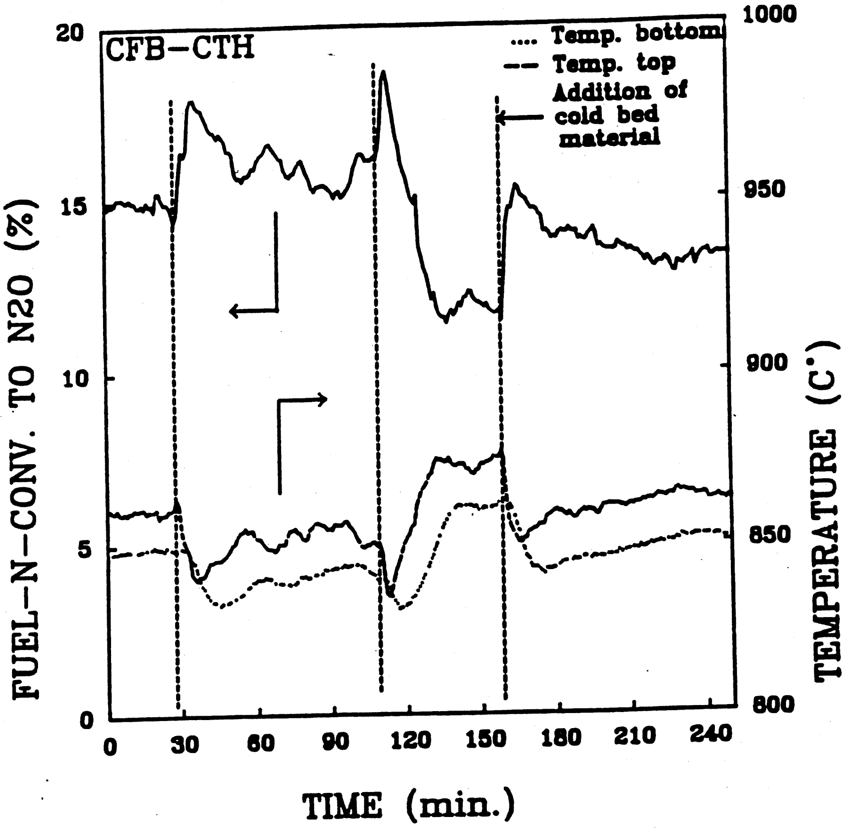

Figure 5 Characterisation of the dependence of the temperature on the fuel–nitrogen conversion to N_2O. Dotted vertical lines show times of addition of cold bed material. [2]

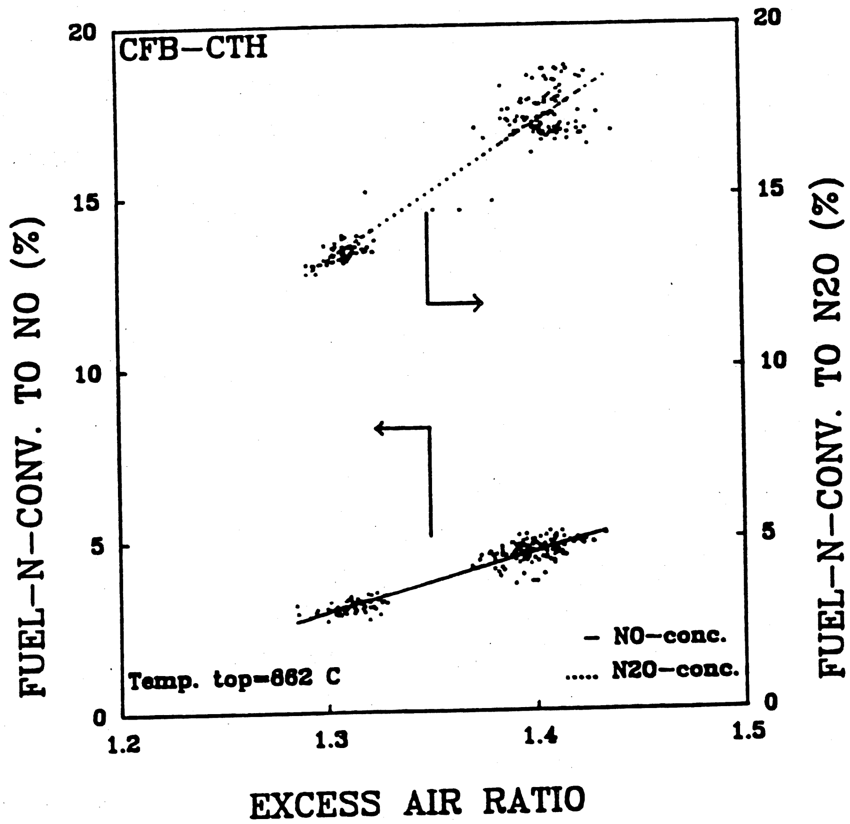

Figure 6 Fuel–nitrogen conversion to NO and N_2O as a function of the excess air ratio. Evaluation of minute mean values during 8 hours of continuous operation. [2]

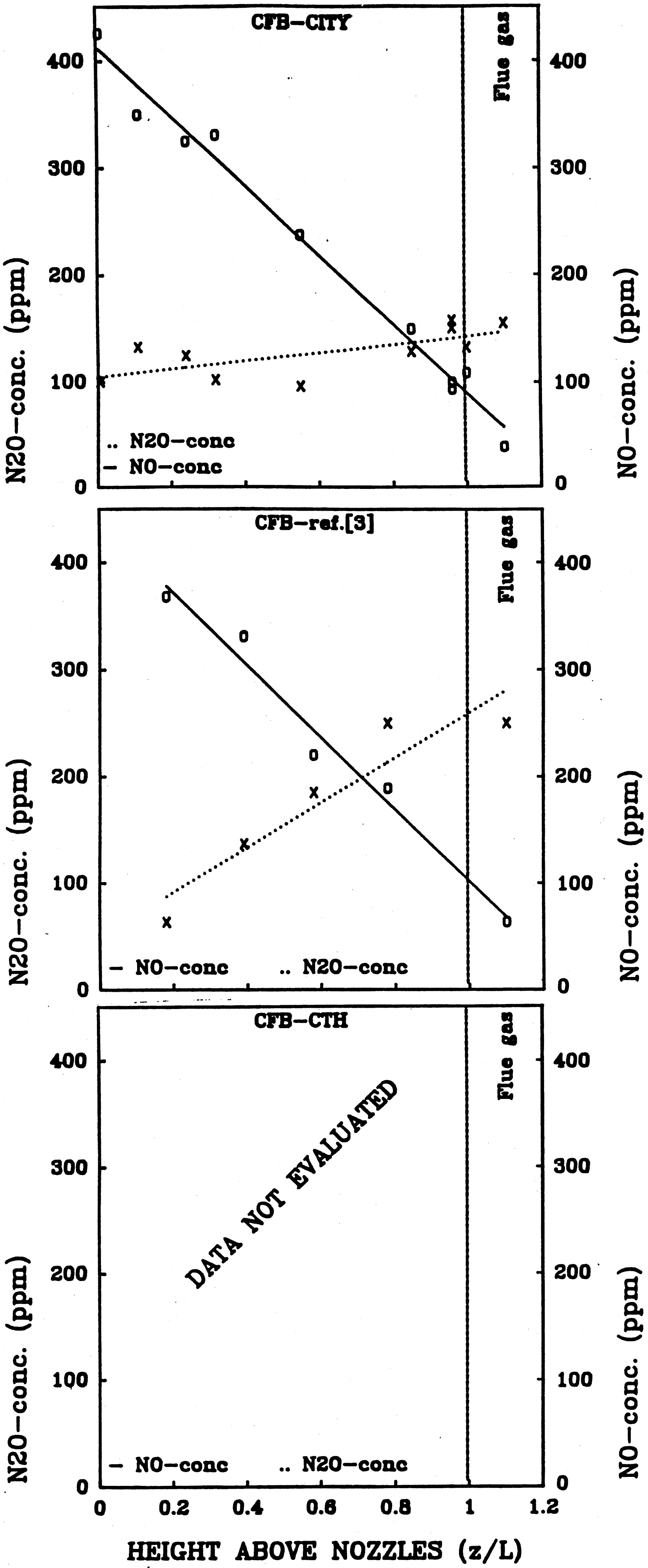

Fig. 7. Concentrations of NO and N2O in the combustion chambers of three different CFB-boilers

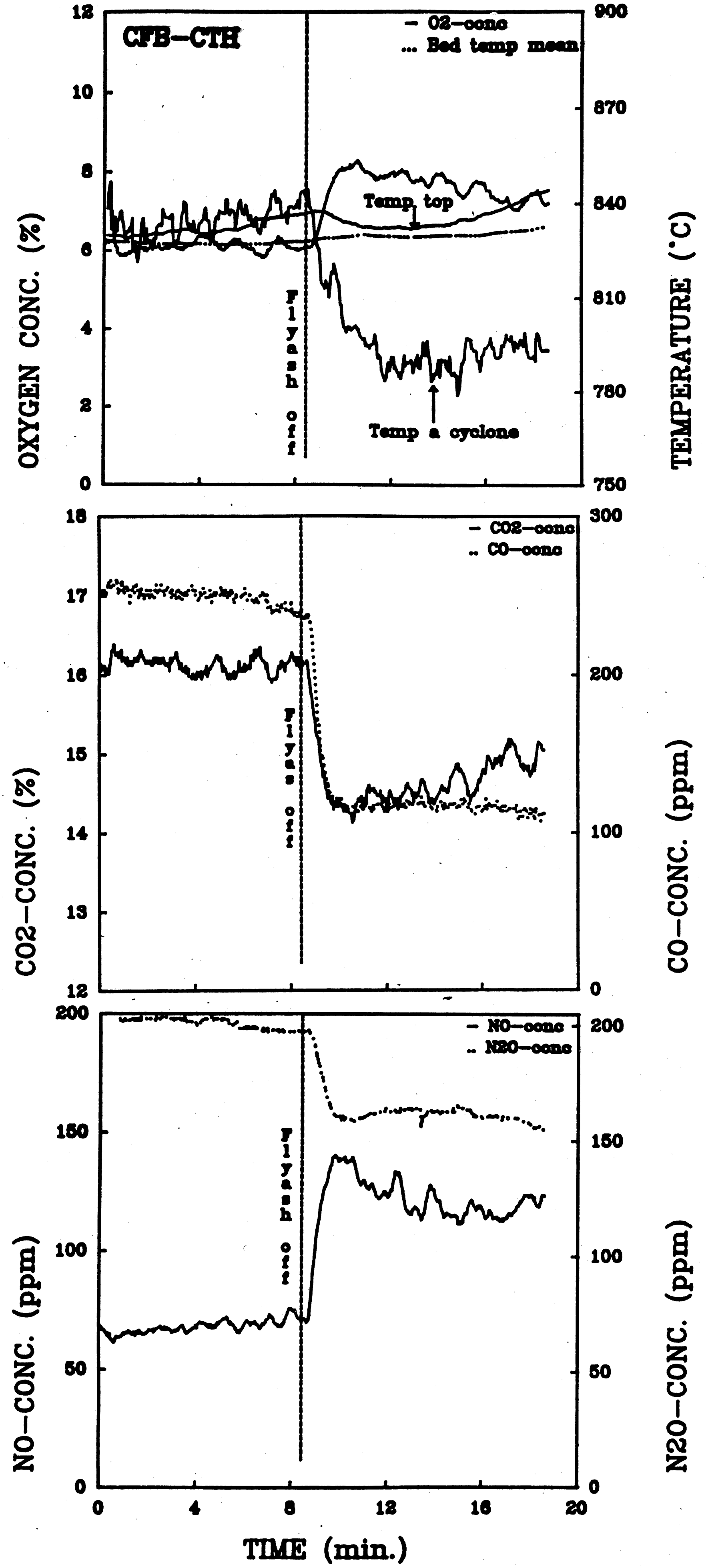

Fig. 8. Transient test of stop of the fly-ash recirculation flow. Flow flyash/fuel flow = 1 (before stop). Fuel: bituminous coal

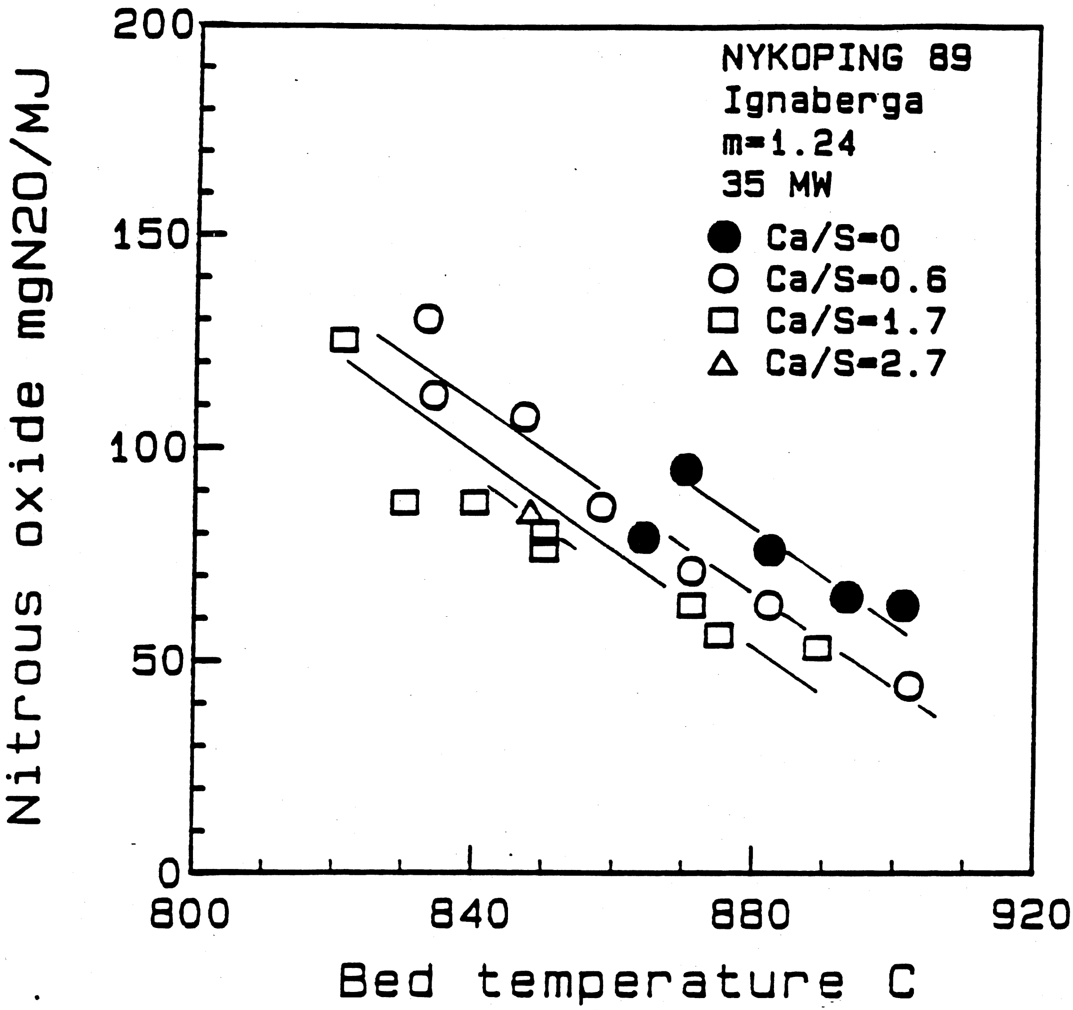

Figure ~~20a~~ 9. Temperature dependence of the N_2O emission at different feed rates of Ignaberga limestone. [8]

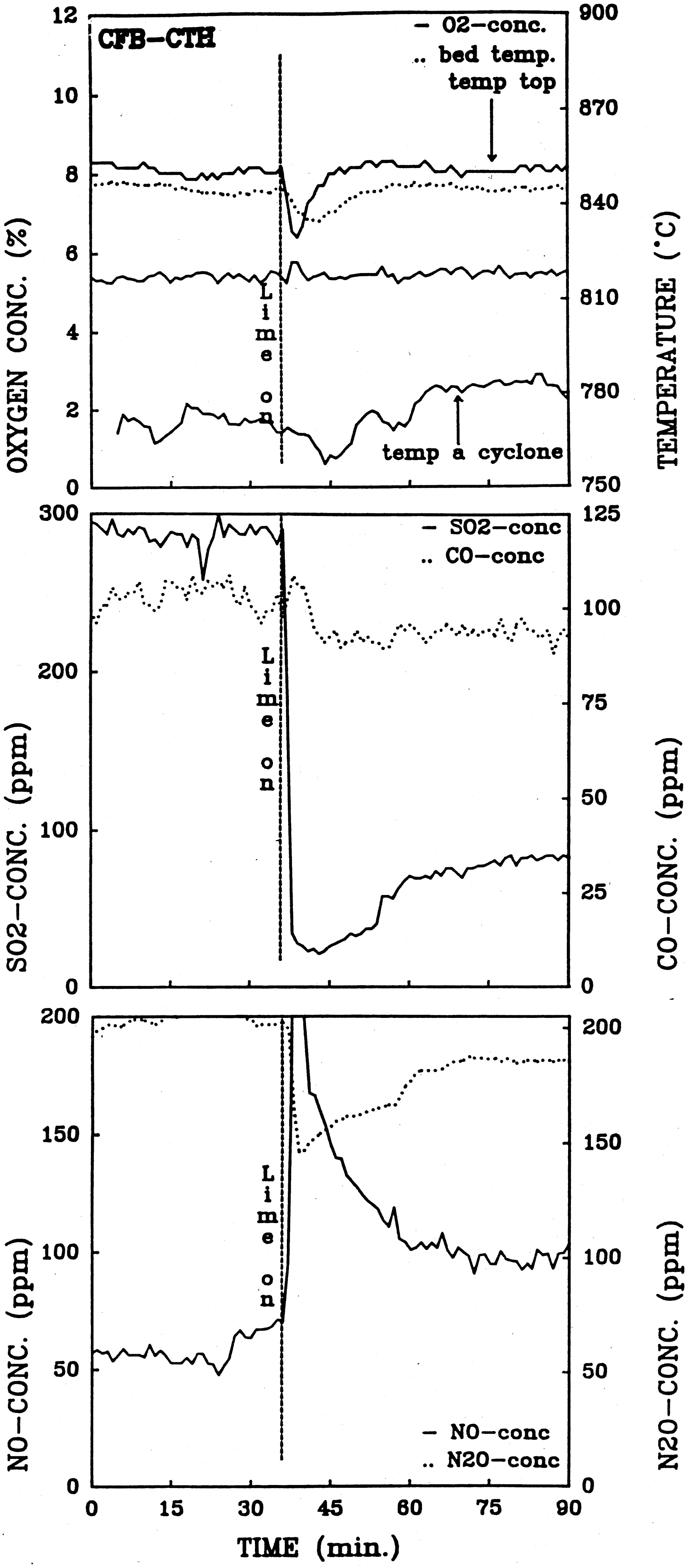

Fig. 10. Transient test of start of the lime addition.
Fuel: bituminous coal with low sulphur content.

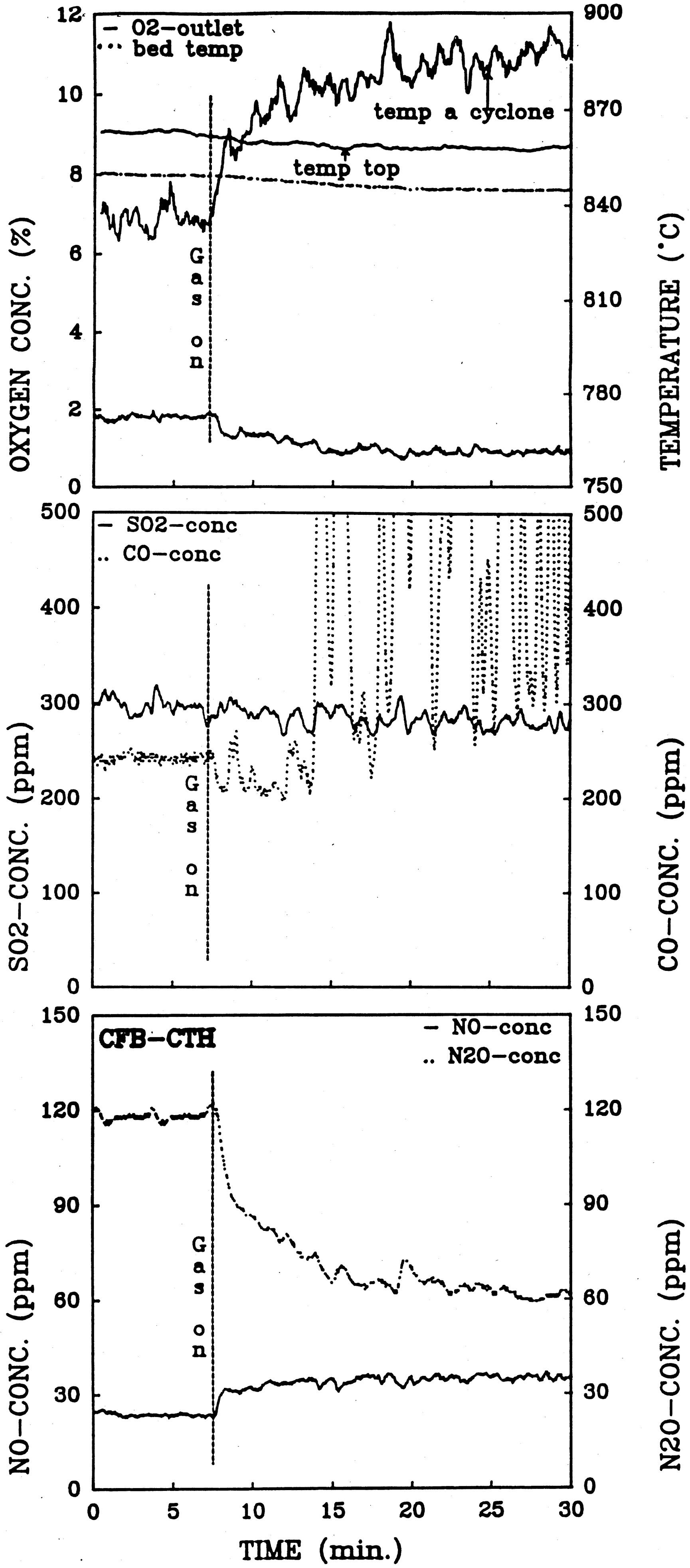

Fig. 11. Transient test of start of propane supply to the hot cyclone. Effect of gasburner: 700kW. Load of the boiler: 8MW. Fuel: bituminous coal.

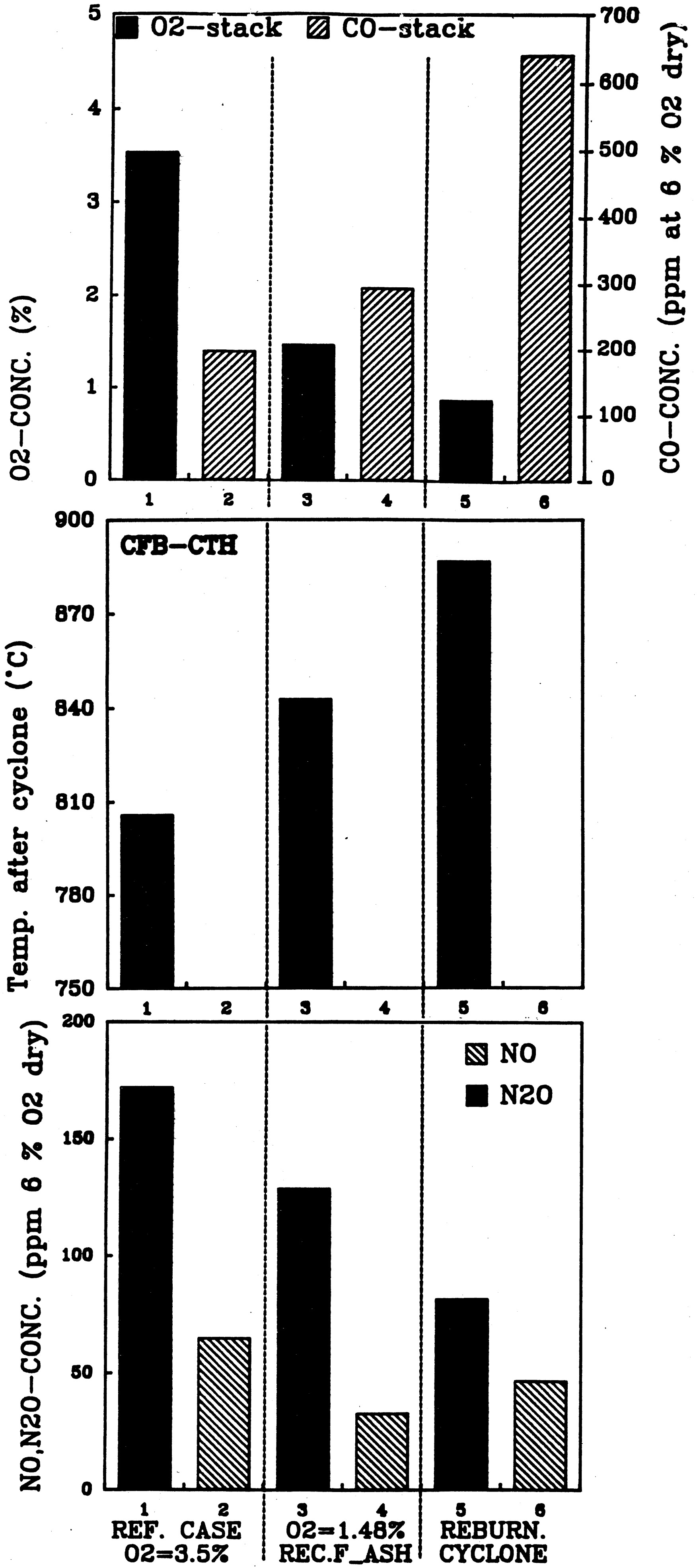

Fig. 12 Effect of low excess air ratio combined with additional supply of gas to the cyclone on the emission of N2O. Fuel: bituminous coal.