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Citation for the published paper:

Leckner, B. ; Åmand, L. (1987) "Primary Measures to Reduce the Emissions of Nitrogen Oxide in Circulating Fluidized Bed Boilers". In proceedings of the Swedish Flame Days held 8-9 September 1987 in Studsvik, Sweden

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Swedish Flame Days  
Studsvik  
8-9 September 1987

**PRIMARY MEASURES TO REDUCE THE EMISSIONS  
OF NITROGEN OXIDE IN CIRCULATING  
FLUIDIZED BED BOILERS**

by

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**ABSTRACT**

During the combustion of coal in a circulating fluidized bed boiler the conversion of the fuel-bond nitrogen to either nitrogen oxides or nitrogen can be influenced by design and operational measures.

The paper gives a summary of results obtained in a series of tests on a 40 MW circulating fluidized bed boiler in Nyköping, designed by Göta-verken Energy. In this commercial boiler it was not possible to study the influence of primary to secondary air addition independent of the bed temperature. For this reason, a smaller boiler designed by the same manufacturer was adapted to permit independent variations of the primary air ratio and the bed temperature. The results from the 40 MW and the 8 MW boilers are compared and the influence of the distribution of the air supply and of the bed temperature on the reduction of nitrogen oxide emissions are discussed.

**INTRODUCTION**

Nitrogen oxides in the flue gases can be reduced by adding a catalytic de-nox plant to the boiler or by suitably modifying the boiler combustion. Measures to decrease the  $\text{NO}_x$  emissions by optimizing the combustion process are called primary measures. Fluidized bed boilers are particularly promising for measures of this kind. They give low emissions even in designs which do not consider nitrogen oxides. With an active intention to reduce the emissions, very low values can be obtained. However, several requirements have to be fulfilled simultaneously and the necessary optimization requires more knowledge about the

possibilities of influencing the processes in the combustion chamber of the boiler. In the present paper results from investigations on commercial-type boilers will be used to show how the emissions of nitrogen oxide can be influenced.

## FLUIDIZED BED BOILERS

### General

The design of fluidized bed boilers is now well-known and only a few general comments need to be made. There are two types of fluidized bed boiler, the stationary fluidized bed boiler (SFBB), and the circulating fluidized bed boiler (CFBB).

The combustion chamber of the SFBB contains a dense bed fluidizing on the air distributor. Above the dense bed there is a splash zone with a particle density that decreases in the upward direction. The height of the splash zone is about the same as the height of the dense bed. Above the splash zone there is a freeboard which contains gases and a few particles elutriated from the bed. These particles may be recirculated to the bed from a particle separator which is situated after the convection section heat exchangers.

The bed particles of the CFBB are smaller than those of the SFBB and the fluidizing velocity is higher, in the order of 3 to 6 m/s. In the CFBB there is also a relatively dense part of the bed at the bottom of the combustion chamber, a transition zone corresponding to the splash zone, and a "transport zone" corresponding to the freeboard. In this case the freeboard is filled with particles streaming upwards with a density before the exit of 1 to 10 kg/m<sup>3</sup>. The particles are separated from the gases in a hot separator (which has the same temperature as the bed) and recirculated to the bottom of the combustion chamber.

In the SFBB, the combustion chamber contains the dense bed and the splash zone, which together form the bed, and a freeboard. In the CFBB, on the other hand, the bed fills the entire combustion chamber, the particle separator and the return leg.

The combustion takes place mainly in the bed. High volatile and fine particle fuels tend to

burn partly in the freeboard of the SFBB. Similarly in the CFBB they burn partly high up in the combustion chamber and even in the particle separator. Due to the high particle loading, temperature variations are to a great extent eliminated in the bed so that low combustion temperatures (800 to 900°C) and low total excess-air ratios can be maintained without seriously affecting the efficiency of combustion. An indication of this is given by the CO emission values registered at the Nyköping CFBB during the tests to be reported below, Figure 1.

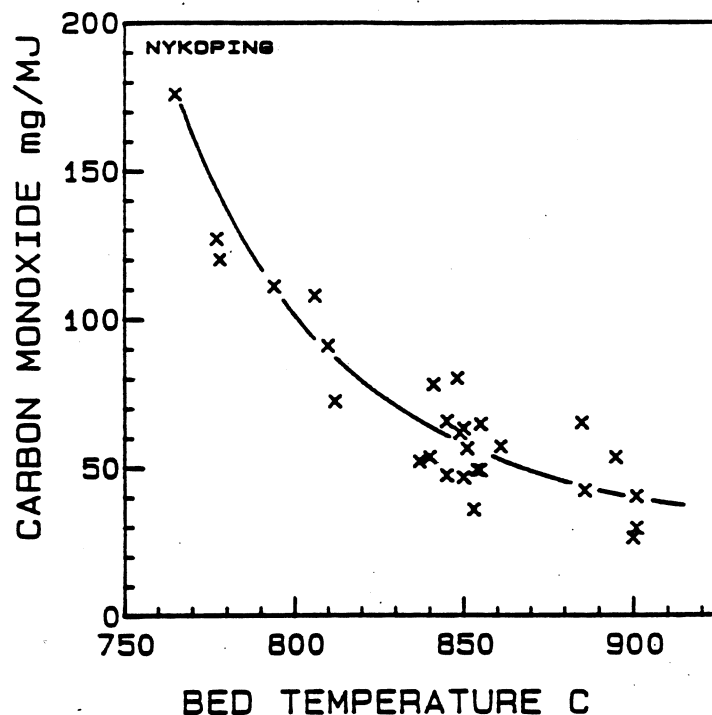


Figure 1. CO emissions registered in the CFBB of Nyköping. The total excess air ratios varied from 1.05 and to 1.4.

#### The boilers of the present tests

Two CFBB's have been used, both of the design of Götaverken Energy. Some data are given in Table 1 and the appearance is indicated in principle in Figure 2.

The Nyköping boiler is a commercial boiler for production of heat to the district heating system of the city of Nyköping. The design of the boiler is flexible enough to permit the large parameter

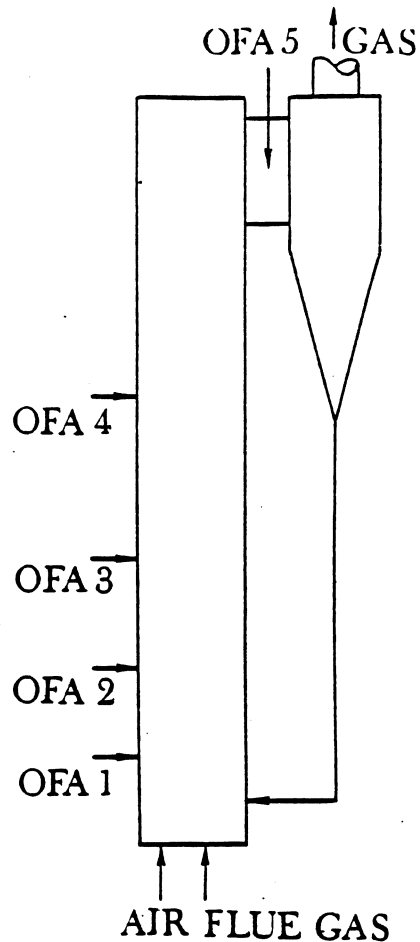


Figure 2. The combustion chamber of the circulating fluidized bed boilers. OFA means "Over-fire air"; secondary air or flue gas registers. The Nyköping boiler is not equipped with flue gas recirculation and OFA 2 to 5.

variations needed for testing the NO emissions. From a scientific view there was one disadvantage with the boiler. In order to change the bed temperature with a constant total excess air ratio, it was necessary to change the ratio of primary to secondary air. Thus, the variation of this ratio might have influenced the NO emission at the same time as the influence of the bed temperature was studied. For this reason the smaller 8 MW boiler was provided with a flue gas recirculation duct. In this boiler independent variations of bed temperature and primary air could then be carried out. In addition, several secondary air registers, see Figure 2, were also installed. These air registers could be run with flue gas as well as air.

The total excess air ratio is derived from the oxygen concentration of the flue gases measured after the convection section. The flow of pri-

mary air is expressed as primary air stoichiometry, the ratio of the primary air flow and the stoichiometric air demand of the fuel burned in the entire bed.

The fuels used during the tests are described in Table 2. The bed materials were limestone of the brand of Ignaberga, double-screened between 0.2 and 1.5 mm, and Silversand 35, a silica sand with a mass mean size of 0.35 mm. In Nyköping the sand was Silversand 17 with a mass mean size of 0.17 mm.

Table 1. Boiler data

	Nyköping	City- varvet
Thermal power, MW	40	8
Start of operation, year	1985	1981
Cross-section surface m <sup>2</sup>	10	1.8
Height of combustion chamber, m	17	8.5
Flue gas recirculation	no	yes
Secondary air registers	OFA 1	OFA 1-4
Separator	2 cyclones	1 cyclone

Table 2. Coals

	Nyköping	City- varvet
Type	North American	Pennsyl- vanian
Size, mass mean, mm	6.9	2.0
% smaller than 1 mm	20	40
Volatiles, % on m a f	36	39
Proximate analysis		
Combustibles	75	86
Ash	12	7
Moisture	13	7
Ultimate analysis %		
c	85	83
h	5	5
o	6	8
s	2	2.2
n	2	1.7

## REACTIONS

The formation and destruction of nitrogen oxides in fluidized bed boilers differ in two important respects from flame combustion in general. Firstly, the temperature level is low, which makes formation of thermal nitrogen oxides unimportant. Secondly, the gases in fluidized beds are in intimate contact with the surface of particles, which causes heterogeneous reactions and catalytic effects to dominate.

Reactions involved in the conversion of the fuel nitrogen to either nitrogen oxide or to nitrogen have been summarized by Furusawa (1985) in Table 3.

Table 3. Reactions concerned in the fate of fuel bond nitrogen in fluidized bed combustion.

Reaction	Gas-solid	Solids catalyzed	Gas phase
1. Char + NO	0	-	-
2. Reduction of NO by CO and H <sub>2</sub>	-	0	-
3. Decomposition of NH <sub>3</sub>	-	0	-
4. Reduction of NO by NH <sub>3</sub>			
Absence of oxygen	-	0	-
Presence of oxygen	-	0	-
5. Oxidation of NH <sub>3</sub>	-	0	0
0 Possible reaction at 700 to 900°C			
- No significant reaction at 700 to 900°C			

The volatile nitrogenous compounds evolving from thermal decomposition of the fuel are approximated by ammonia.

The solids known to be most active as catalysts are char and lime (calcium oxide). Silica sand is not deemed to be active, but it contributes to the decomposition of NH<sub>3</sub> as shown by Hiram (1983). The possible contribution of various components of fuel ashes as catalysts has not yet been studied.

The above reactions have mostly been investigated in small laboratory reactors, where well controlled experiments could be carried out. The combustion chambers of fluidized bed boilers are of course much more involved and the detailed processes occurring there are not fully known. The efforts to interpret the observations to be presented below must be understood against this background.

## PRIMARY MEASURES

### Bed temperature and air supply

In a bed that consists predominantly of silica sand, the principal agent for nitrogen oxide reduction is the surface of the char particles participating in the combustion process, reactions 1 and 2, Table 3. The rate of combustion decreases when the bed temperature and the total excess air ratio decrease. Both measures will increase the amount of carbon monoxide and char in the bed and thus decrease the nitrogen oxide emission. The resulting nitrogen oxide emissions from the two CFBB are seen in Figures 3 and 4. The levelling out of the curves at low temperatures and excess air does not readily fit the above explanation, which indicates that there are further influencing factors that remain to be considered. This is especially the case of the NO-temperature relationship.

At an excess air ratio of 1.2 and bed temperatures below 850°C the emissions of nitrogen oxide from the two boilers are very low indeed, about the same level as an SFBB with staged air supply, see for instance Leckner and Amand (1987). Without staged air supply, however, the SFBB emits about twice as much.

The importance of the air staging is studied by changing the primary air flow to the bottom of the bed and the secondary air to one of the overfire air registers (usually OFA 1) at a constant total excess air ratio. In the 8 MW boiler the bed temperature could also be kept constant, thanks to the flue gas recirculation.

Figure 5 shows the variation of nitrogen oxide emission to changes in the primary air stoichiometry in the 8 MW boiler. The insignificant dependence on the primary stoichiometry shown is astonishing considering the large effect of air staging in the SFBB. Due to this result it was decided to investigate if the secondary air was added to the combustion chamber in the right position (OFA 1). Fortunately, as seen from Figure 2, there are four air registers to manipulate. The result of adding air in one register after another is given in Figure 6. In all cases the momentum of the air jets was tested to be sufficient for the mixing of the secondary air with the bed. }

There was only a very small improvement when the secondary air supply was moved to higher positions in the combustion chamber. This is also in disagreement with previous experience with SFBB. Tatebayashi (1980) showed that in



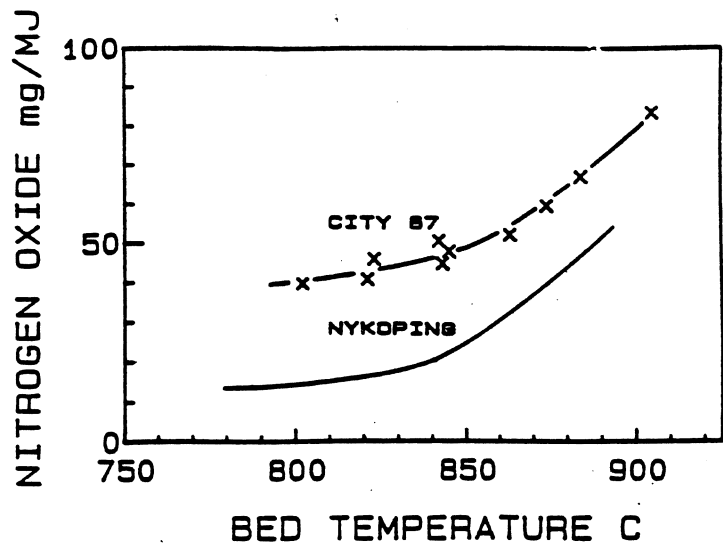


Figure 3. The NO emissions from the 40 MW boiler in Nyköping and the 8 MW boiler at Cityvarvet as a function of bed temperature. Sand beds.

	40 MW	8 MW
Excess-air ratio	1.20	1.22±0.03
Primary stoichiometry	varying	0.74±0.04
Register	OFA 1	OFA 1

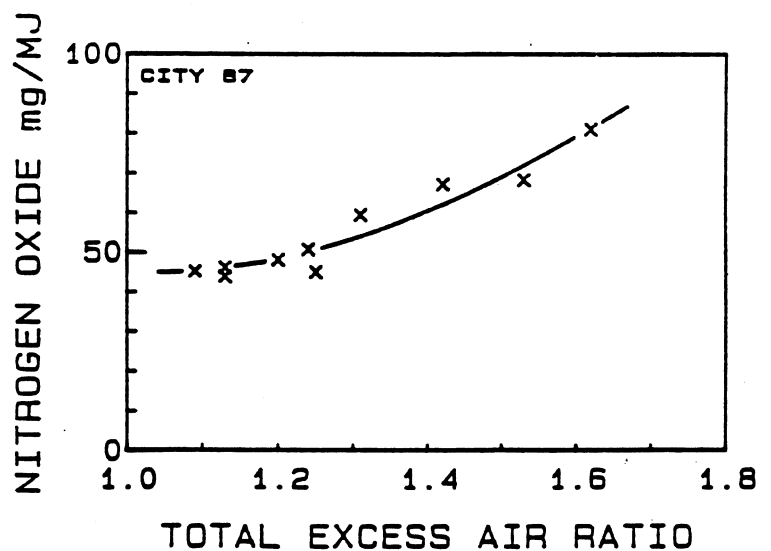


Figure 4. The NO emission from the 8 MW boiler as a function of the total excess air ratio. Sand bed.

Bed temperature	842±5°C
Primary stoichiometry	0.75±0.05
Register	OFA 1

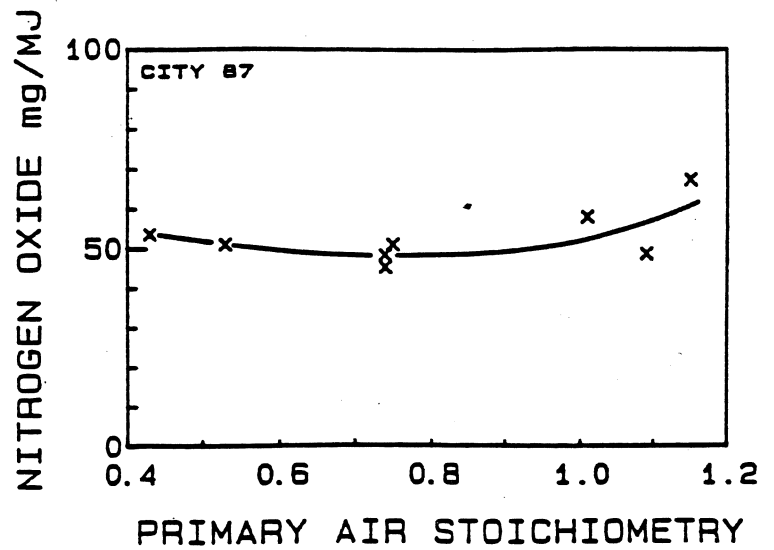


Figure 5. The NO emissions at different primary air stoichiometries at the 8 MW boiler. Sand bed.

Excess air ratio	1.22±0.03
Bed temperature	846±5°C
Register	OFA 1

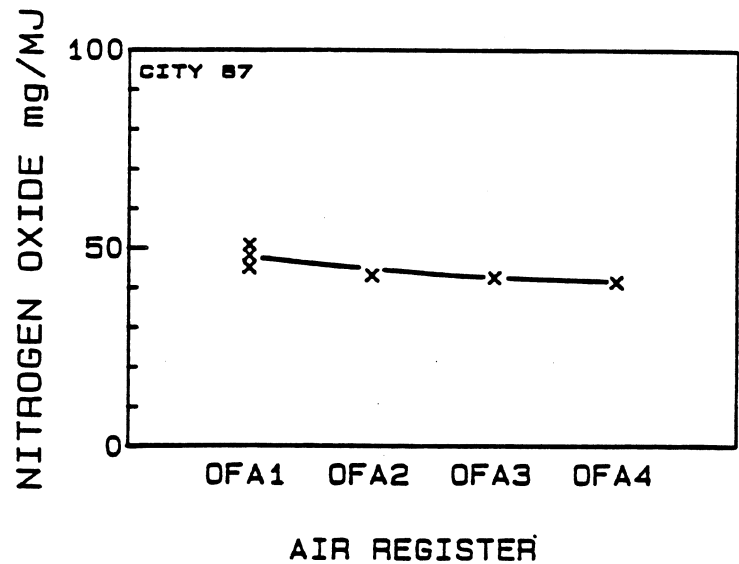


Figure 6. The NO emission when the secondary air is introduced through one of the four air registers in the 8 MW boiler. Sand bed.

Bed temperature	843±2°C
Primary stoichiometry	0.76±0.03
Excess air ratio	1.22±0.02

the SFBB the nitrogen oxide emission decreases considerably when the distance between the dense bed and the secondary air supply increases.

There are two reasons why staged air supply would be successful in reducing the nitrogen oxide emission. The first is that the rate of combustion slows down when the air supply to the primary combustion zone is decreased, thereby increasing the amount of char and carbon monoxide. The second reason has to do with the volatiles and will be treated in the next section.

The probable explanation of the lack of success of staged combustion in the present case, is that the active agent, the char, is distributed all over the combustion chamber in contrast to the case of an SFBB, where almost all the fuel is contained in the dense bed. Thus, changes in the air supply to the lower parts of the combustion chamber of a CFBB does not influence the distribution and the concentration of char very much. The use of coarser coal and lower fluidization velocities in the bottom zone of the combustion chamber might change the situation by locating more of the char surface to the bottom zone.

### Volatiles

In an SFBB volatiles escape from the dense bed and interact with the nitrogen oxides in the freeboard according to reaction 4 of Table 3. There are two cases (in an SFBB):

1. At staged combustion, not only does the above-mentioned increase in char and carbon monoxide concentrations lead to the reduction of nitrogen oxide in the dense bed, but an increased escape of  $\text{NH}_3$  may contribute to a reduction in the freeboard. This can be compared with the reduction of the NO emission at injection of ammonia in the freeboard.
2. The escape of  $\text{NH}_3$  from the bed should also be the explanation for the enhanced efficiency of reduction of NO in the freeboard at the combustion of more volatile fuels presented by Hampartsoumian and Gibbs (1984).

In such cases the height of the secondary air supply above the surface of the dense bed becomes important. The tests of Tatebayashi (1980) were mentioned above.

The volatiles may also influence the processes in the dense bed. However, the contribution of the volatiles in the dense bed is not well known.

In order to investigate the role of volatiles in the CFBB run with a sand bed, ammonia was injected through the OFA registers. Sufficient momentum for the penetration of the ammonia into the bed was ensured by the use of recirculated flue gas as a carrier gas. There was no effect of the ammonia injection in the OFA registers 1 to 4. Only at injection in OFA 5 there was a slight decrease in the NO emission. The conclusion is that ammonia is decomposed in the sand bed, reaction 3, Table 3. This result is supported by Hirama (1987) who carried out measurements in a circulating fluidized bed research reactor fired with coal. He detected very small amounts of ammonia at the same time as the NO concentration decreased with height in the reactor.

The lack of active participation of the volatiles in a CFBB with a bed of sand is another contribution to the explanation of the small influence of the OFA registers in contrast to the experience from an SFBB.

### Catalytic beds

In contrast to the beds of silica sand treated above, beds of other materials may have a significant effect on the reactions of Table 3. Such a bed material is lime, which is used for sulphur absorption. Several laboratory investigations, Hirama (1983), Furusawa (1985), Lee (1985, 1987), have shown the influence of lime on the nitrogen oxides emissions. The influence of limestone addition in a CFBB has been demonstrated by Leckner and Herstad (1986), Leckner and Amand (1987), and by Hirama and co-workers (1987).

In the Nyköping boiler an increase in the nitrogen oxide emission was observed even at small feed rates of limestone to the bed, Figure 7. When the feed of limestone, expressed by the molar ratio of calcium to sulphur,  $\text{Ca/S}$ , was further increased, a plateau in the emission is attained. When the limestone feed rate approaches  $\text{Ca/S}=2$ , where the sulphur capture is almost complete, the emission increases again, and at an excess feed the nitrogen oxide concentration rises drastically. At  $\text{Ca/S}=3$  a nitrogen oxide concentration of around 230 mg/MJ was reached. This jump in emission level can be explained by the excess of calcium oxide surface present in the bed when all sulphur is already consumed. The lower emission level seen at  $\text{Ca/S}$

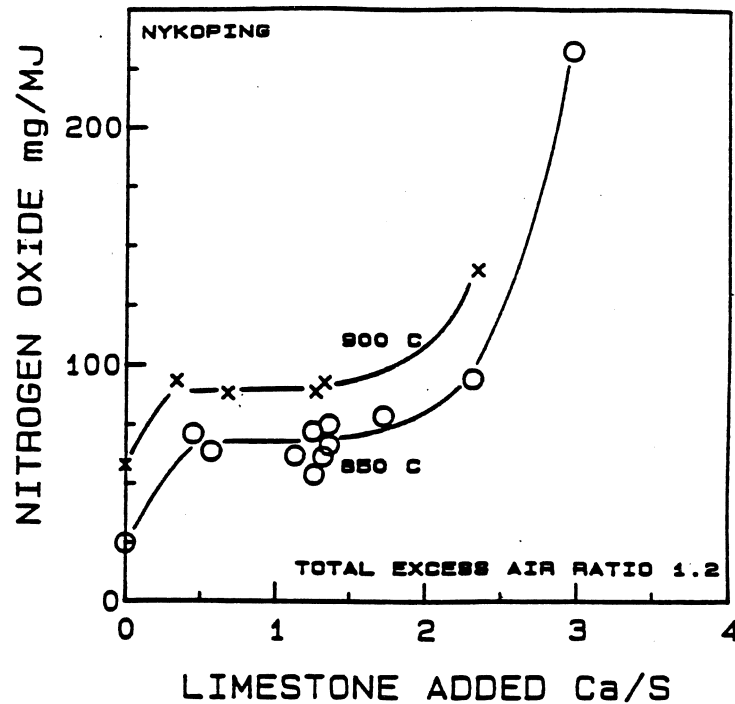


Figure 7. The influence of limestone addition on the NO emission from the 40 MW boiler.

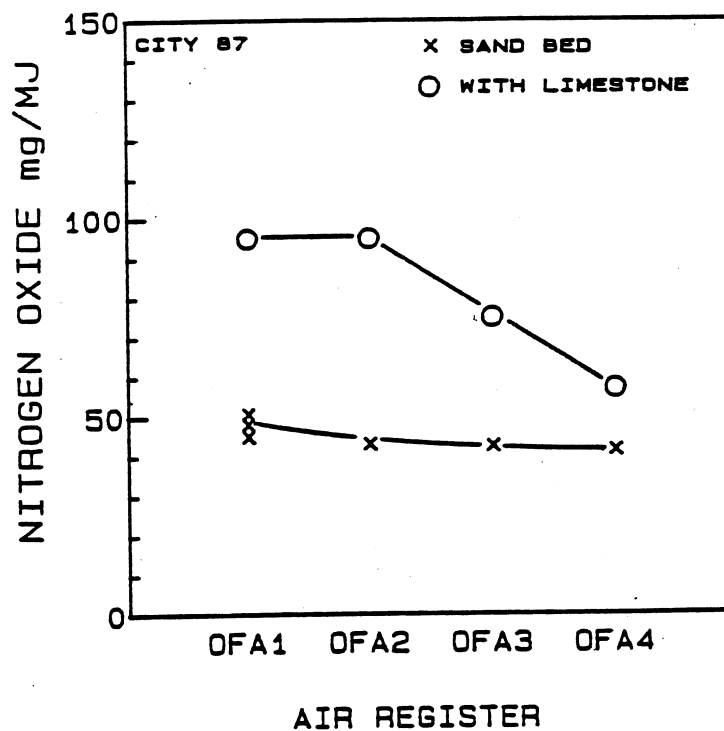


Figure 8. The NO emission when the secondary air is introduced through one of the four air registers in the 8 MW boiler. Comparison between sand bed and a bed with limestone addition, Ca/S=5. Note that the total excess air ratios are somewhat different.

	Sand bed	Lime bed
Bed temperature	843±2°C	840±4°C
Primary stoichiometry	0.76±0.03	0.73±0.06
Excess air ratio	1.22±0.02	1.40±0.05

less than 2 is probably the result of the less active (Lee 1987)  $\text{CaSO}_4$  surface predominating before the sulphur capture is complete. In both cases the increase of the NO emission should be caused by oxidation of ammonia according to the fast reaction 5 of Table 3.

Since the reaction 5 is an oxidation reaction, the obvious remedy for the deleterious effect of lime is to add as much of the air as possible when the ammonia is already decomposed to nitrogen and hydrogen. Although the fuel was present in the entire combustion chamber of the small 8 MW boiler, the bottom portion is more oxygen-starved than other parts. Furthermore, a pre-dominant devolatilization occurs in the bottom part of the combustion chamber where the fuel is fed. In this case the staged combustion should work to some extent. Figure 8 shows the result of adding secondary air through the different OFA registers compared with similar tests with a sand bed (Figure 6).

The comparison in Figure 8 is made at somewhat different total excess air ratios but it confirms the influence of the position of the secondary air register. At OFA 3 a marked decrease of the lime effect is achieved. At OFA 4 the emission level is almost back to the value without limestone addition.

For some reason the limestone effect is not as strong in the 8 MW boiler, Figure 9, as in the 40 MW boiler, Figure 7, in spite of the high dosage of limestone employed,  $\text{Ca/S}=5$ .

The work to decrease the negative influence of the limestone addition has only just started, but it is already seen that there are more possibilities to explore.

## CONCLUSIONS

Much remains to be learned about the factors influencing the nitrogen oxide emissions from fluidized bed boilers, but some conclusions can be drawn:

- A reduction in the bed temperature and in the total excess air ratio, as far as this can be accepted from a combustion point of view, decreases the emission of nitrogen oxides.
- Staged combustion plays an important role when the fuel is present in an air-deficient zone. Nitrogen oxide reduction by staged combustion is easier to accomplish in a stationary fluidized bed boiler than in

a circulating fluidized bed boiler, where the fuel tends to be present in the entire reactor.

The catalytic activity of the bed material plays an extremely important role. A bed which contains calcium oxide surfaces gives substantially increased emissions compared with a bed of silica sand. The negative influence of lime can be counteracted by adding the air to the combustion chamber in a suitable way and by avoiding very high sulphur retentions.

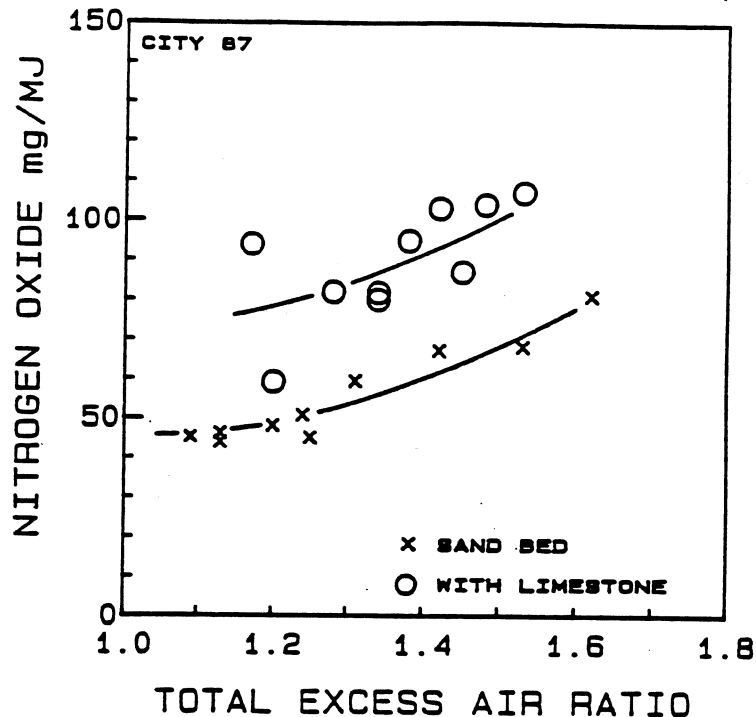


Figure 9. The NO emission from the 8 MW boiler as a function of the total excess air ratio. Comparison between sand bed and a bed with limestone addition,  $\text{Ca/S} \approx 5$ .

	Sand bed	Lime bed
Bed temperature	$842 \pm 5^\circ\text{C}$	$840 \pm 4^\circ\text{C}$
Primary stoichiometry	$0.75 \pm 0.05$	$0.74 \pm 0.03$
Air register	OFA 1	OFA 1

#### ACKNOWLEDGEMENT

This work has been financially supported by the Swedish National Energy Administration and Götaverken Energy. The following persons from the Department of Energy Conversion have contributed substantially to the work: Lennart Darell, Sten Johansson, Maria Karlsson and Rudolf Zimmermann. Kazimiera Puramäki from the Department of Inorganic Chemistry has made the analyses. The helpful assistance of the personnel of Götaverken Energy is also gratefully acknowledged.

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