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Leckner, B. ; Åmand, L. (1987) "Emissions from a circulating and a stationary fluidized bed boiler: A comparison". Proc of the 9th International Conference on Fluidized-Bed Combustion, vol. 2 pp. 891-897.

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Volume Two

# 1987 INTERNATIONAL CONFERENCE ON FLUIDIZED BED COMBUSTION

FBC COMES OF AGE

*held in*

BOSTON, MASSACHUSETTS  
MAY 3-7, 1987

*sponsored by*

THE AMERICAN SOCIETY OF MECHANICAL  
ENGINEERS — ADVANCED ENERGY  
SYSTEMS DIVISION  
ELECTRIC POWER RESEARCH INSTITUTE  
TENNESSEE VALLEY AUTHORITY

*edited by*

JOHN P. MUSTONEN

THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS  
United Engineering Center      345 East 47th Street      New York, N.Y. 10017

reprinted from

**1987 International Conference on Fluidized Bed Combustion-Volume Two 1987**

Editor: John P. Mustonen

(Book No. I0232B)

published by

THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS

345 East 47th Street, New York, N.Y. 10017

Printed in U.S.A.

## EMISSIONS FROM A CIRCULATING AND A STATIONARY FLUIDIZED BED BOILER: A COMPARISON

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### ABSTRACT

A comparison is presented of the emissions of sulphur dioxide and nitrogen oxide from a stationary fluidized bed boiler and a circulating fluidized bed boiler. The boilers used for the comparison were the 16 MW stationary bed boiler at Chalmers University and the 40 MW circulating bed boiler at Nyköping (Sweden).

In order to focus the comparison on the design of the boilers and to eliminate differences caused by fuel and sorbent, both boilers were run with the same coal and limestone.

The influence of the operating conditions on the emissions is studied. The main influencing parameters are: Limestone feed rate, bed temperature, and excess air ratio. One of these parameters was varied at a time while the others were kept constant.

The results show that both types of boiler can be run conveniently with low emissions of sulphur and nitrogen oxides. The sulphur absorption is superior in the circulating bed boiler, where an almost complete absorption is attained at a calcium-to-sulphur molar ratio of 2.

Without limestone addition, and at bed temperatures below 850°C, the nitrogen oxide emission from the circulating bed boiler is as low as is reasonable, achieving the equilibrium value of nitrogen oxide in oxygen and nitrogen. With limestone addition, however, considerably higher emission values are obtained in the circulating bed boiler, whereas the corresponding emission from the stationary bed boiler is not affected by limestone.

In addition to the studies of sulphur and nitrogen oxide emissions, the influence of limestone on the emissions of mercury, chloride, and fluoride was investigated.

### INTRODUCTION

A comparison is presented of the emissions from a stationary fluidized bed boiler and a circulating fluidized bed boiler.

In order to focus the comparison on the design of the boilers and to eliminate differences caused by fuel and bed material, both boilers were run with the same coal and limestone. The make-up bed material, silica sand, was of the same brand but of different sizes.

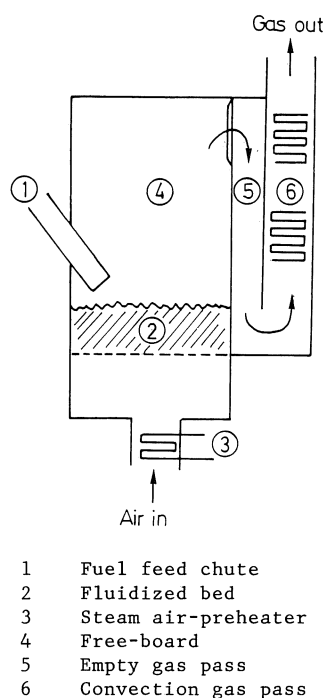
The purpose of the tests was, further, to study the influence of the operating conditions of the boilers on the emissions of sulphur and nitrogen oxides. In addition, the influence of limestone on some minor flue gas constituents was investigated. The main influencing parameters are: Limestone feed rate, bed temperature, and excess air ratio. These parameters were varied one at a time, with the other parameters being kept constant. Due to the limitations imposed by the heat balance of the bed, such a parameter variation cannot be carried out without changing other parameters which might have an influence. The parameters affected unintentionally are the fluidizing velocity (load) and the amount of bed material (bed height). The variations from one test to another are relatively small and they are deemed to be of minor importance. Possibly more important is the change in the ratio of primary to secondary air accompanying changes of the bed temperature in the circulating bed boiler.

Detailed results from the stationary bed boiler are reported by Åmand et al. [1] and from the circulating bed boiler by Leckner et al. [2]. In the following, these results will be compared.

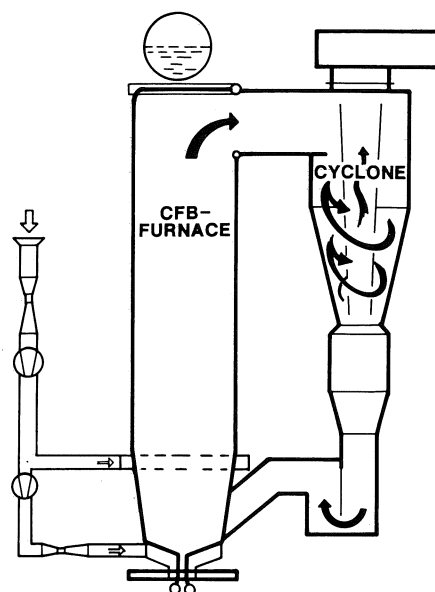
### BOILERS, FEED MATERIALS, AND TESTS

The two boilers used for the comparison were the 16 MW boiler at Chalmers University, Svensson et al. [3], and the 40 MW circulating bed boiler manufactured by Götaverken Energy Systems for the district heating system in Nyköping, Figure 1. Kullendorff [4] describes the principles of design of the latter boiler.

Both boilers have cross-sections about 10 m<sup>2</sup>. The stationary boiler has a bed depth of around 1 m and a height of the free-board of 4 m, whereas the



a) Chalmers



b) Nyköping

Fig. 1 Schematic picture of the boilers

vertical measure of the reactor of the circulating boiler is in the order of 15 m. The fluidization velocities are around 2 m/s and 4 to 6 m/s for the stationary and the circulating bed boilers. There is a very small recirculation of bed material from the flue gases to the bed in the stationary bed boiler. The recirculation ratio (recycled flow rate to fuel feed rate) is in the order of 0.2. The fuel as well as the limestone are fed onto the bed through inclined ducts ending just above the surface of the bed.

The coal is of North American origin. The size is less than 30 mm with 20% smaller than 1 mm and a mass mean size of 6.9 mm. Other characteristics are given in Table 1.

The accuracy of the sulphur content determination is important for judging the results. There is a certain variation from sample to sample. The coefficient of variation of the approximately one hundred analyses made is 10%, which leads to a corresponding uncertainty in the sulphur retentions calculated, especially at low values of sulphur retention.

The content of calcium in the fuel corresponds to a molar ratio of calcium to sulphur in the fuel,  $(Ca/S)_{fuel} = 0.2$  to 0.3.

The limestone is a soft and porous type of the name of Ignaberga. The stone is double-screened, 0.2 to 1.5 mm. In spite of this, there is a fraction of 10 to 15% less than 0.2 mm. The sulphur capture properties of this stone in comparison to other stones has been studied by Andersson et al. [5] and by Hamer [6]. Ignaberga was found to be among the better stones investigated in these laboratory studies.

Table 1 The coal characteristics

Ash (as received)	12 %
Moisture (as received)	13 %
Ultimate analysis:	
Carbon	85 %
Hydrogen	5 %
Oxygen	6 %
Nitrogen	2 %
Sulphur	2 %
	100 %
Volatile matter (a.m.f.)	36 %
Heating value (lower, a.m.f.)	33 MJ/kg

Silica sand is used as a make-up bed material.

The chemical analyses of the materials of the bed are given in Table 2.

About 30 principal runs were made with each boiler. In Chalmers another 30 runs were recorded during longer periods to ensure accurate mass balances. The measurements were registered during a period of one to two hours when the boiler was in thermally stable operation. Normally two tests were run during a day.

The sampling for gas analyses and for the evaluation of the gas concentrations was carried out after the flue gas filter before the stack.

Table 2 Composition of the bed materials, percent

	Limestone	Ash	Sand
CaO	51	6.8	0.02
SiO <sub>2</sub>	5	41.5	99.4
Al <sub>2</sub> O <sub>3</sub>	0.4	24.0	0.15
Fe <sub>2</sub> O <sub>3</sub>	0.2	14.0	0.10
MgO	0.5	2.5	*
MnO	< 0.1	0.12	*
K <sub>2</sub> O	0.2	1.6	0.07
Na <sub>2</sub> O	< 0.1	0.34	0.01
S	0.02	-	*
P	0.04	-	*
SO <sub>3</sub>	-	6.9	-

\* not analyzed

## SULPHUR RETENTION

The comparison of the sulphur retention efficiencies obtained in the two boilers is presented in Figures 2 and 3. The sulphur retention efficiency is defined as follows

$$\eta_s = \frac{\text{sulphur in with the fuel} - \text{sulphur out with the gas}}{\text{sulphur in with the fuel}}$$

The limestone feed rate is related to the sulphur feed rate through the molar ratio Ca/S. In publications, this ratio is sometimes expressed as

$$(\text{Ca/S})_{\text{total}} = (\text{Ca/S})_{\text{added}} + (\text{Ca/S})_{\text{fuel}}$$

and sometimes as  $(\text{Ca/S})_{\text{added}}$ . Here we use the latter option. The sulphur retention by the fuel ash, the self-absorption, is then found at  $(\text{Ca/S})_{\text{added}} = 0$  in Figure 2. The sulphur retention curves in Figure 2 are extended to the fictitious case of  $\eta_s = 0$  at  $(\text{Ca/S})_{\text{total}} = 0$ . This point is found at  $(\text{Ca/S})_{\text{added}} = -(\text{Ca/S})_{\text{fuel}}$ .

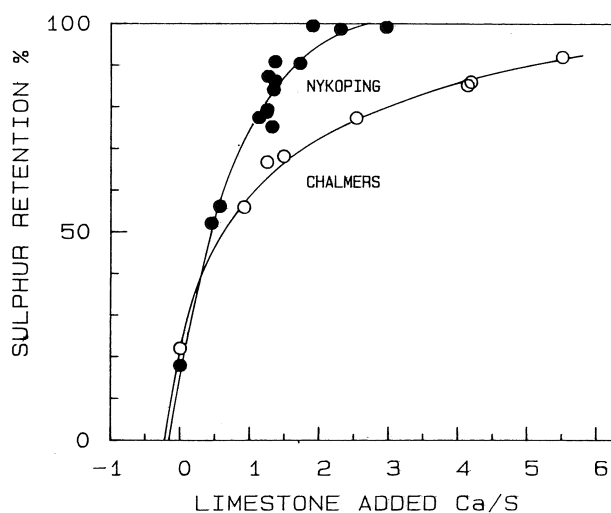


Fig. 2 Sulphur retention in the Nyköping and Chalmers boilers at optimum temperatures as a function of the limestone added.

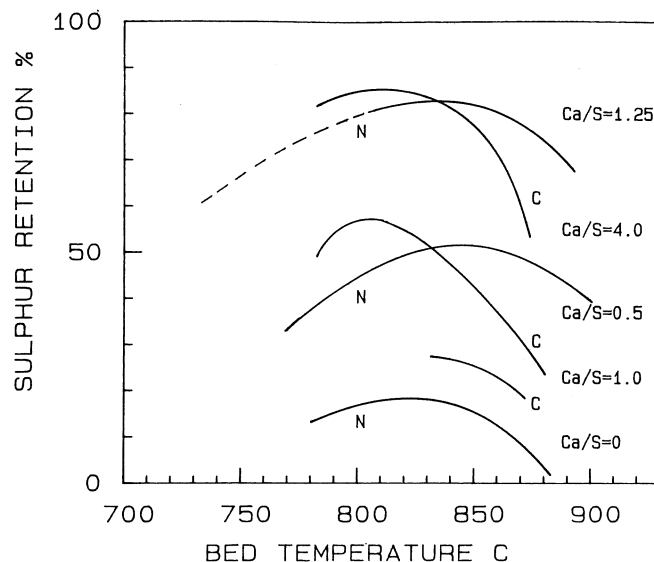


Fig. 3 Sulphur retention in the Nyköping (N) and Chalmers (C) boilers at various Ca/S molar ratios as a function of the bed temperature.

Figure 2 represents the sulphur capture at optimum temperatures. The sulphur retention is seen to be much better in the circulating bed boiler at Nyköping than in the stationary bed boiler.

The stationary bed boiler at Chalmers employs overbed feed of fuel. Furthermore, the recirculation ratio is very small. Tests conducted at TVA's 20 MW AFBC Pilot Plant [7, 8] have shown that increasing the recirculation of solid particles from the flue gas substantially improves the sulphur capture. In addition, underbed feed was found to give a better sulphur capture performance than overbed feed in the TVA plant [8]. Neglecting the possible differences caused by different limestones, it seems that, in spite of substantial improvements, the stationary bed boiler does not attain the high values of the circulating bed boiler shown in Figure 2.

The self-absorption of the fuel due to  $(\text{Ca/S})_{\text{fuel}}$  is an important factor when predicting the sulphur retention capacity of a certain installation or when comparing different installations. In the present case the self-absorption should be the same when the same fuel is used in beds with the same sand-ash mixture in both boilers. The values obtained are  $\eta_s = 0.18$  in the circulating bed and 0.24 in the stationary bed at 850°C. These values are both  $\eta_s = 0.2$  considering the accuracy of the measurement, as mentioned above. With a  $(\text{Ca/S})_{\text{fuel}} = 0.2$  to 0.3, the utilization of the calcium of the fuel ash is found to be almost complete.

Figure 3 shows, for both boilers at several calcium-to-sulphur ratios, the dependence of the sulphur retention on the temperature of the bed. The optimum temperature of the stationary bed boiler is a little above 800°C whereas in the circulating bed boiler the optimum is a little below 850°C. Due to the scatter of the data points and to the relatively few points at some conditions, the optima are not very well defined. However, the measurements are accurate enough to allow the following conclusion: In spite of using the same coal and the same limestone, the temperature optima of sulphur retention are different in the two beds. The reason for this difference is not known at present.

Tests have been run at total excess air ratios in the range of 1.05 to 1.45. Within these limits no dependence of the sulphur retention on the air ratio has been observed.

The following conclusions can be made:

- The sulphur retention of the circulating fluidized bed boiler is almost complete at a calcium-to-sulphur ratio of 2 with the present coal and limestone.
- The sulphur retention of the stationary bed boiler is lower than that of the circulating fluidized bed boiler at a given calcium-to-sulphur ratio. Complete absorption is not reached with the present coal and limestone. It is known from tests in other boilers that a considerable improvement is achieved with recirculation of particles from the flue gas to the bed.
- The temperature dependence of the sulphur retention is related not only to the coal and limestone but also to the design of the boiler.
- The self-absorption depends on the content of calcium in the fuel. It is also influenced by the bed temperature.
- The sulphur retention is independent of the total air ratio at least as long as this quantity is greater than one.

#### NITROGEN OXIDE

The flue gas concentration of nitrogen oxide (NO) is measured. This value is recalculated into  $\text{NO}_2$ . Considering the composition of the flue gas, the nitrogen oxide concentration is thus expressed as  $\text{mg NO}_2/\text{MJ}$  fuel supplied. (This unit is employed as a measure of the  $\text{NO}_x$  emission in some countries).

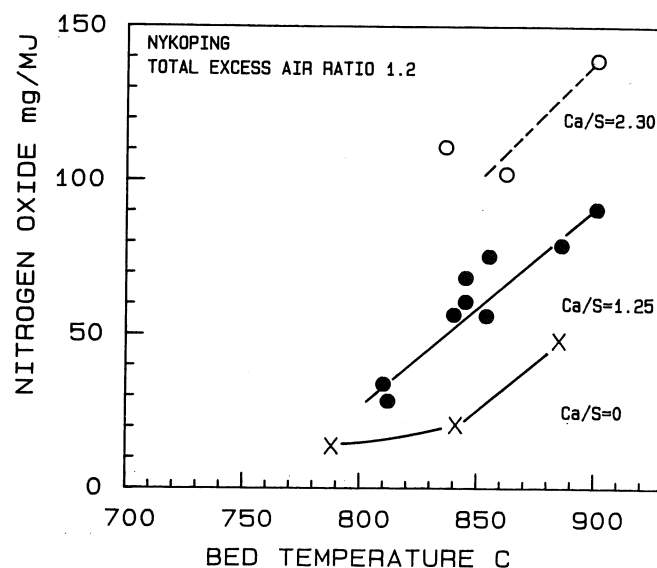
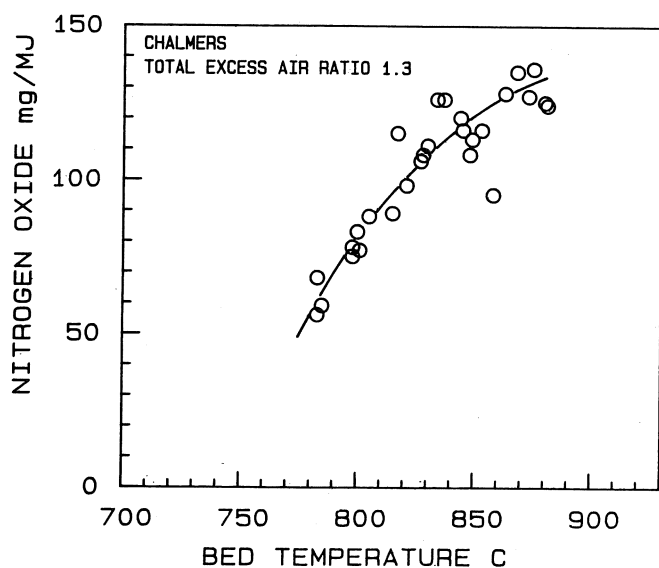
The temperature dependence of the nitrogen oxide emission, shown by the slope of the curves in Figure 4, is about the same in both boilers. The deviation from the straight line at lower temperatures in Figure 4b indicates an approach to the equilibrium concentration of NO in the presence of oxygen and nitrogen,

$$[\text{NO}]_{\text{eq}} = K \sqrt{[\text{N}_2][\text{O}_2]}$$

With values of the equilibrium constant  $K$  according to [9] and an estimate of the concentrations of nitrogen and oxygen  $[\text{N}_2] \approx 0.8$  and  $[\text{O}_2] \approx 0.03$ , the equilibrium concentrations of nitrogen oxide,  $[\text{NO}]_{\text{eq}}$ , expressed in the same units as the NO concentrations of Figure 4, becomes 17, 27 and 41 at the temperatures of 800, 850, and 900°C. This coincides approximately with the measured values of Figure 4 at bed temperatures below 850°C, i.e. in this temperature region the nitrogen oxide originating from the fuel nitrogen is eliminated as far as possible. At high temperatures there is another deviation from the straight line, seen at least in figure 4a. This may be caused by a more rapid course of the reduction reactions at higher temperatures.

Figure 4b, as well as figure 5b, shows that the addition of limestone increases the emission of nitrogen oxide in the circulating bed boiler. The difference between runs with and without limestone is clearly seen. One point, which represents an excessive limestone addition ( $\text{Ca/S} = 2.96$ ), gives rise to a very high emission of nitrogen oxide (232  $\text{mg}/\text{MJ}$ ). This value falls outside of Figure 4b. It should be remembered from Figure 2 that the sulphur capture is almost complete at  $\text{Ca/S} = 2$ .

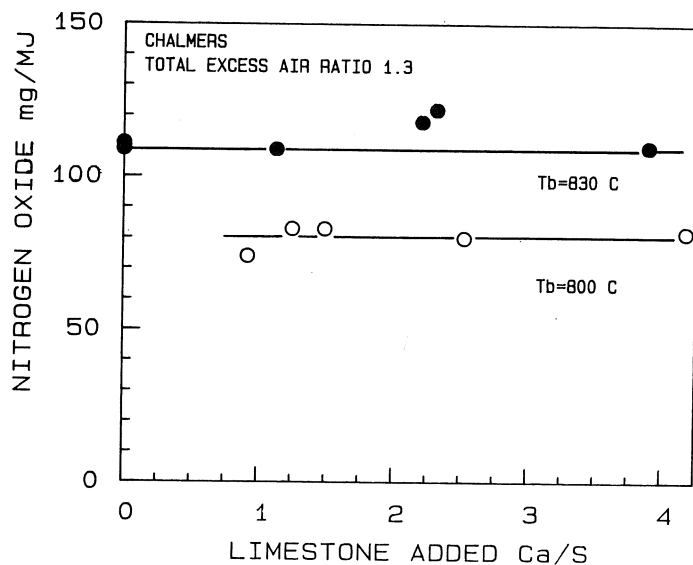
The data points of Figure 5b are represented by straight lines. The positions of the points suggest that the relationships may be more complicated. The surface of the calcium oxide particles catalyzes the conversion of the nitrogen-containing volatiles. The conversion follows different paths depending on the presence or the absence of oxygen. In the absence of oxygen, the calcium oxide may contribute to the reduction of nitrogen oxide [10]. In the presence of oxygen, on the other hand, the production of nitrogen oxide is enhanced [11, 12]. The latter situation may be the reason for the increase in the emission of nitrogen oxide when limestone is added to the circulating bed boiler where, particularly at excess limestone addition, a considerable amount of calcium oxide surface is contained in the reactor



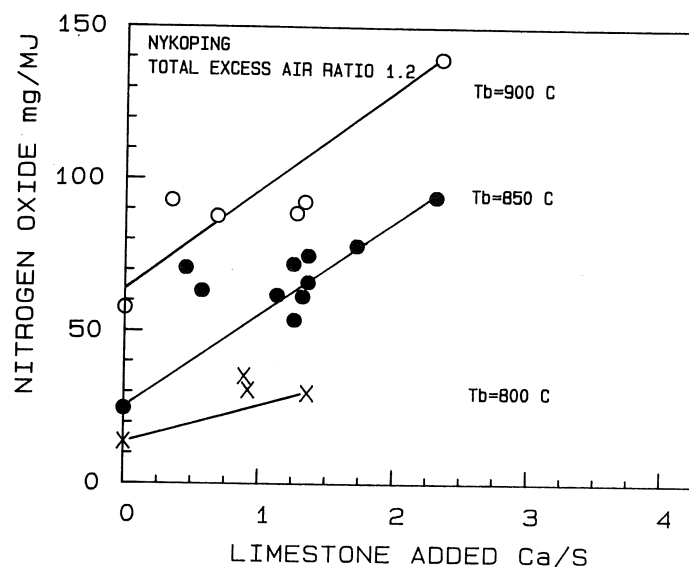
a) Chalmers

b) Nyköping

Fig. 4 The influence of the bed temperature on the nitrogen oxide emission at constant total excess air ratio. (In the Nyköping boiler the ratio primary/secondary air varies with temperature).

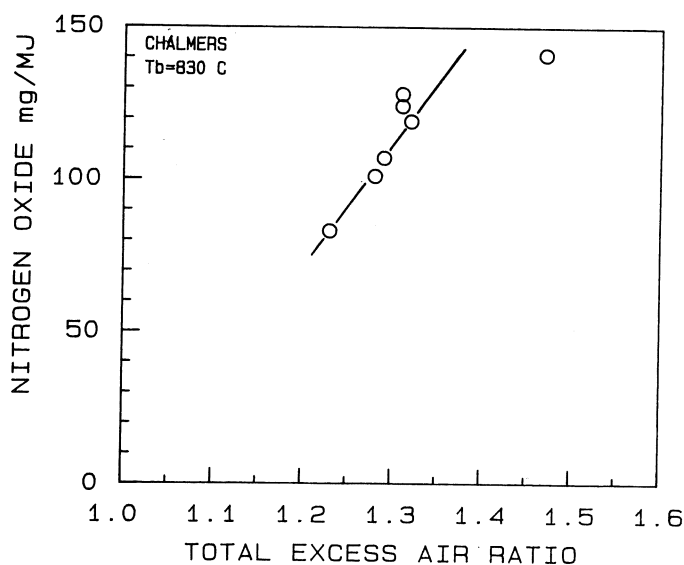


a) Chalmers

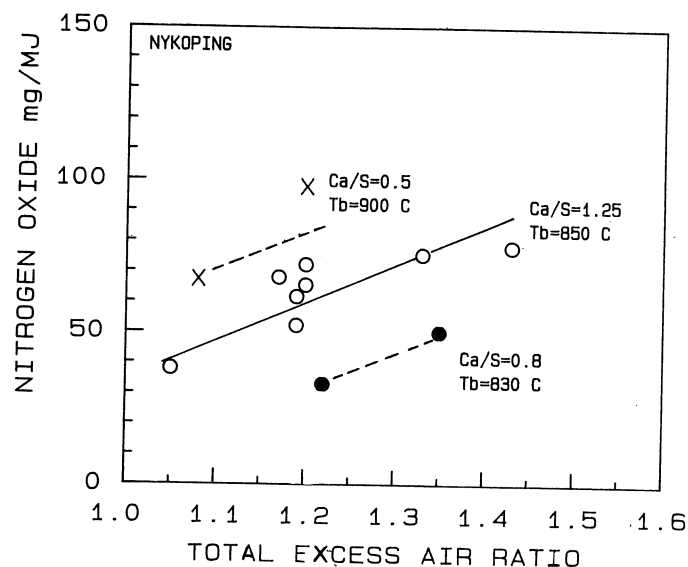


b) Nyköping

Fig. 5 The influence of the limestone addition on the nitrogen oxide emission at constant air ratio.



a) Chalmers



b) Nyköping

Fig. 6 The influence of total excess air

in contact with oxygen. The lack of influence of the limestone in the stationary bed boiler illustrated by Figure 5a is more difficult to explain. It may be the consequence of an insufficient contact between the lime contained in the particle phase of the bed and the volatiles of the fuel. Over-bed combustion of volatiles (corresponding to about 10% of the heating value of the fuel in a similar case [13]) certainly contributes to this lack of contact.

When comparing the absolute levels of the NO emissions in Figures 4a and b, it should be observed that the curves represent the excess air ratios of the design points of the boilers, 1.3 in the case of the stationary bed boiler, and 1.2 in the case of the circulating bed boiler. A comparison at the same total excess air ratio could be made according

to the values of Figures 6a and b, which show the influence on the nitrogen oxide emissions of the total excess air ratio.

In the above comparison staged air supply was used in the circulating but not in the stationary fluidized bed boiler. The effect of staged air supply on the emissions from the circulating fluidized boiler has not been determined. However, in the stationary bed boiler there is a considerable influence of secondary air addition. This is illustrated in Figure 7 when secondary air addition is compared with other methods to reduce the emission of nitrogen oxide. With 20-25% secondary air the NO emission is about 50 mg/MJ for the stationary bed boiler compared to 20-60 mg/MJ for the circulating bed. Further reductions of the nitrogen oxide emission are seen to



be possible. Figure 7 also illustrates the effect of ammonia injection in the freeboard. The ammonia injection results in still lower emissions of nitrogen oxides. Since the amount of ammonia in the present example is high, an emission of ammonia to the surroundings results also. Furthermore, the emission of carbon monoxide increases. At the present state of experience it seems that ammonia injection in fluidized bed boilers is not necessary, especially when the negative consequences are taken into consideration. In fluidized bed combustion the other methods of NO reduction are more profitable.

The following conclusions can be reached about the nitrogen oxide emission:

- The nitrogen oxide emission decreases with bed temperature at about the same rate for both boilers except for the region of operation mentioned in the following conclusion.
- Without limestone addition, the reduction of the fuel nitrogen oxides in the circulating bed boiler is as great as possible at temperatures below 850°C.
- With limestone addition, the nitrogen oxide emission increases considerably in the circulating bed boiler but not in the stationary bed boiler.
- With the present coal and limestone (and probably also with other coals and limestones) the optimum bed temperature with respect to sulphur retention and nitrogen oxide emission for both types of boiler is in the range of 810 to 840°C.

#### OTHER EMISSIONS

The influence of the limestone addition on the emissions of mercury, chloride, fluoride, and sulphur trioxide is shown in Table 3.

Table 3 gives data measured in the circulating bed boiler. The results from the stationary bed

Table 3 Emissions of minor gas constituents from the circulating fluidized bed boiler

Run nr**	Ca/S	Hg µg Hg/MJ	HCl mg Cl <sup>-</sup> /MJ	HF mg F <sup>-</sup> /MJ	SO <sub>3</sub> mg S/MJ
2	0	3.9	53.5	2.4	1.8
2	0	0.9	57.4	2.4	2.4
13	1.1	1.9	44.3	0.3	0.5
13	1.1	0.9	63.8	1.8	0.3
18	1.4	1.9	52.4	1.2	0.5
19	1.4	*	52.6	0.7	0.3
25	1.9	*	45.2	0.3	0.4
In fuel		4.6	61.3	3.4	638

\* not detected

\*\* refers to the runs in a series of 1 to 30 when the minor gas constituents were analyzed

boiler are similar, with the exception of the SO<sub>3</sub> measurements which are of the same magnitude but scattered with respect to the Ca/S ratio. With this exception the following conclusions are valid for both boilers:

- In agreement with other studies concerning atmospheric fluidized bed boilers, the SO<sub>3</sub> emission from both boilers was very small. In the circulating bed boiler it decreases with limestone addition. In the stationary bed boiler no significant influence of limestone addition was observed.
- The measurements of mercury in gaseous form, including the very small amount found on particles after the filter, are rather scattered. When completed with the mercury balance, however, a relatively safe conclusion can be drawn: About half of the mercury added with the fuel is found in the fly-ash and the other half is emitted. There is no evident influence from the limestone.
- The measurements of chloride and fluoride confirm the observation of Münzner and Schilling [14] that the limestone is active in absorbing the fluoride, at flow-rates of Ca/S > 1, whereas the chloride is emitted.

#### GENERAL CONCLUSION

Both types of boiler can be run conveniently with low emissions of sulphur dioxide and nitrogen oxides. The sulphur absorption is much better in the circulating bed boiler where an almost complete absorption is attained already at Ca/S = 2. While the sulphur absorption in the stationary bed boiler is inferior to that in the circulating bed boiler, other investigations have shown that it can be considerably improved by increasing the recirculation of particles from the flue gas to the bed.

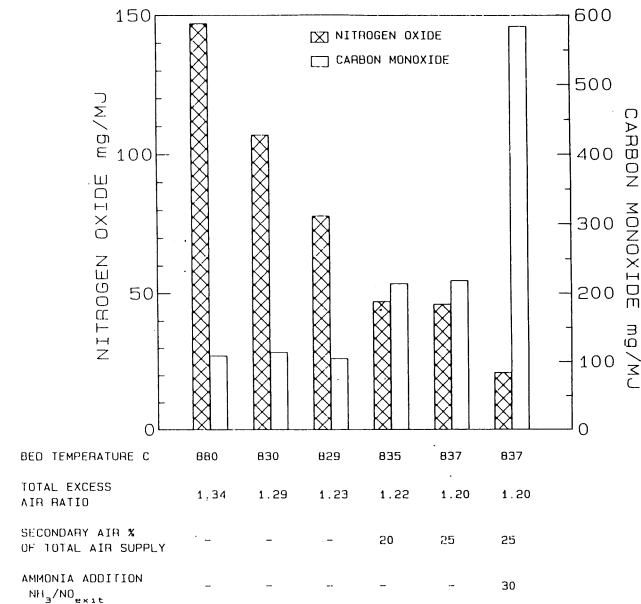


Fig. 7 Various possibilities to influence the nitrogen oxide emissions. Measurements from the stationary fluidized bed boiler at Chalmers.

Without limestone addition, and at bed temperatures below 850°C, the nitrogen oxide emissions from the circulating bed boiler approach the equilibrium value. Limestone addition leads to considerably higher emissions in the circulating bed boiler and the two types of boiler reach about the same emission level if properly optimized.

It is believed, however, that there are possibilities to counteract the deleterious influence of limestone in the circulating bed boiler. This subject needs to be further explored.

#### ACKNOWLEDGEMENTS

The work at the Department of Energy Conversion has been supported financially by the Swedish National Energy Administration.

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