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Åmand, L. ; Leckner, B. (1988) "Ammonia Addition for NO_x Reduction in Fluidized Bed Boilers". Proceedings from the 1st International Conference on Industrial Furnaces and Boilers

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**AMMONIA ADDITION FOR NO_x REDUCTION IN
FLUIDIZED BED BOILERS**

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ABSTRACT

Ammonia is added to the gases in the combustion chamber of fluidized bed boilers in order to investigate its effect on the emission of nitrogen oxides. A stationary and a circulating fluidized bed boiler are used. In the stationary fluidized bed boiler an addition corresponding to a (NH₃/NO_{exit}) molar ratio of 3 gives a 50% reduction of the NO emission. Larger doses lead to escape of ammonia and other disadvantages. In the circulating fluidized bed boiler no effect from injection of ammonia into the combustion chamber is noted. The ammonia is decomposed. If NH₃ is to be used in circulating fluidized bed boilers it should be introduced in the particle-free gas after the particle separator.

KEYWORDS

Ammonia injection, reduction of nitrogen oxides, fluidized bed combustion, circulating fluidized bed boilers, stationary fluidized bed boilers.

INTRODUCTION

Ammonia addition into the flue gas pass of utility boilers is a method for lowering the emissions of nitrogen oxides. The method was invented by the Exxon Research and Engineering Co (Lyon, 1973) and it was already tested in Japan in 1974 (Hurst, 1985). Since nitrogen-containing compounds, such as ammonia originating from the devolatilization of coal, play an important role for NO_x reduction during combustion in fluidized beds, it was natural that the method was also tested in this application (Hampartsoumian, 1982; Tatebayashi and co-workers, 1980; Yamahata and co-workers, 1983). The investigations published so far have been carried out in small laboratory fluidized beds. For that reason it was of interest to make tests in commercial-type boilers. A 16 MW stationary fluidized bed boiler (SFBB) and an 8 MW circulating fluidized bed boiler (CFBB) are used for experiments with ammonia addition with the purpose of obtaining experience of the advantages and disadvantages of ammonia injection in relation to other methods to reduce the emissions of NO_x in fluidized bed boilers.

BOILERS AND TEST ARRANGEMENTS

A schematic view of the boilers is shown in Fig. 1 and the principal data are given in Table 1.

TABLE 1 Basic Boiler Characteristics

	SFBB	CFBB
Thermal power, MW	16	8
Height, m	5	8.5
Cross-section, m ²	10	1.8
Bed height at operation, m	0.8-1.2	8.5
Fluidization velocity m/s	2.3	3-6
Fuel feed point, number	1	1
Location of the secondary air registers	1.9m over bed bottom	OFA 1-4 Fig.1

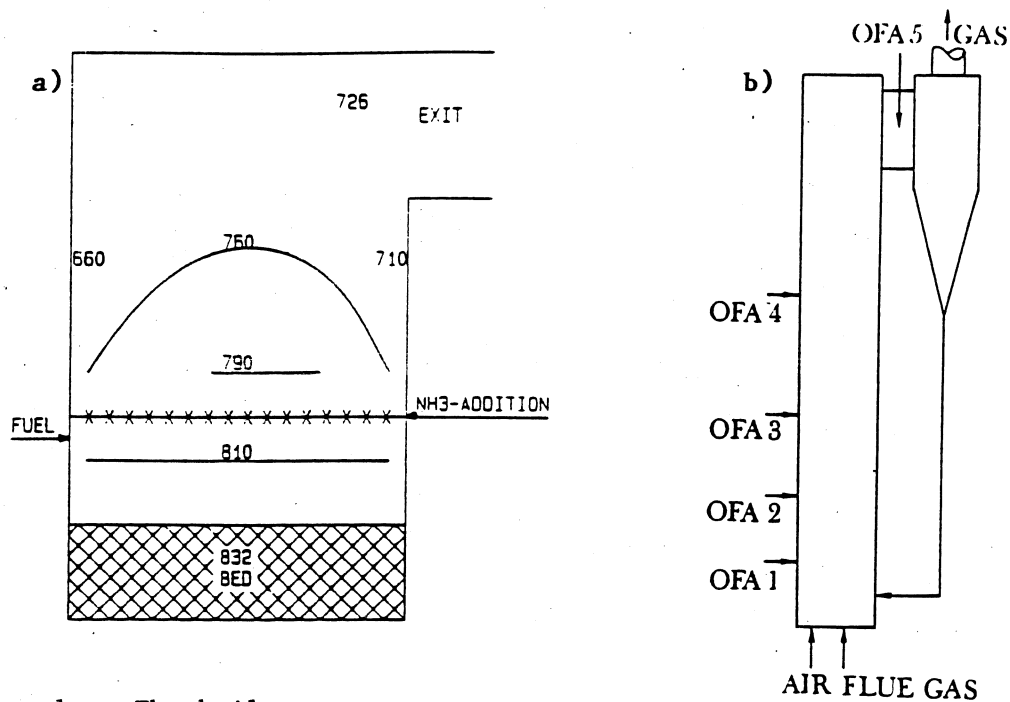


Fig. 1. The boilers.

- a) The stationary fluidized bed boiler at Chalmers.
Excess air ratio 1.3.
 - b) The circulating fluidized bed boiler of the design of Götaverken Energy at Cityvarvet.
Excess air ratio 1.2, bed temperature 840 to 850°C.
- The beds consist of silica sand and ashes.

The combustion chambers of the boilers have conventional water-cooled panel-tube walls. The lower part of the CFBB is refractory-lined, as is the hot cyclone which recirculates a flow of bed material 50 to 100 times larger than the fuel feed rate. In the SFBB there is a cold cyclone, but the rate of recirculation is insignificant.

The nozzle registers for secondary air injection surround the combustion chamber of the SFBB on three sides, Fig. 1a. In the present tests only the two lateral air registers are used. The registers can be fed with recirculated flue gases instead of air if desired.

In the CFBB, Fig. 1b, there is a similar arrangement, but the air or the flue gas can be added in four registers (OFA 1 to 4) situated at various heights of the combustion chamber. In addition, there is one register, OFA 5, just before the cyclone.

The ammonia is stored in large pressurized bottles in the form of liquid ammonia. It is vaporized in a heat exchanger before injection into the secondary air/recirculation gas ducts leading to the air registers. The flow of ammonia is determined by weighing the bottles before and after each run.

Several coals have been used. They are all bituminous coals with a volatile content around 40% and a nitrogen content around 2% on a moisture and ash free basis. They are single-screened with a maximum size of 30 mm.

The emission of nitrogen oxides is represented by measurements of the concentration of nitrogen oxide, NO. The measurement value in ppm is converted to mg NO₂/MJ. The reduction of NO by NH₃ injection is defined as:

$$\text{NO reduction (\%)} = \frac{\text{ppm NO without NH}_3 - \text{ppm NO with NH}_3}{\text{ppm NO without NH}_3} \cdot 100$$

The reduction is related to the amount of ammonia injected, expressed as the molar ratio NH₃/NO without NH₃. The concentration of NO is measured at the exit of the boiler. Actually, the concentration of NO at the place of injection is several times greater than that at the exit. For this reason the ratio NH₃/NO always appears to be large.

PREPARATORY TESTS

The temperature of the gases in the combustion chamber is important for the NO-NH₃ reaction. In the Exxon process there is a temperature window of 900 to 1000°C in which the reactions proceed as desired. In the CFBB heat release occurs in the entire combustion chamber. During the tests the bed temperature of the CFBB was around 845°C and decayed only a little along the combustion chamber. There was a slight increase in the cyclone due to after-burning. In the SFBB the gases are cooled in the freeboard and the temperature decreased from 830°C to 725°C in a typical run illustrated in Fig. 1a. The temperature was about 800°C at the point of the NH₃ injection.

The temperature field in the combustion chamber is important, but so is the mixing of the ammonia. The mixing of the ammonia was tested by increasing the momentum of the jets of injection until no further decrease of the NO concentration was observed. Then the momentum of the jets was further increased somewhat to be on the safe side.

MAIN TESTS

The results from ammonia injection into the freeboard of the SFBB with flue gas as a carrier gas are presented in Fig. 2.

The NO emission of 110 mg/MJ without ammonia injection is a representative value at a normal single-stage combustion operation of this boiler. It is seen that already at $\text{NH}_3/\text{NO} = 3$ a 50% reduction in the NO emission is obtained, at $\text{NH}_3/\text{NO} = 7$ the reduction is 75%, but further increase in the ammonia addition is not efficient. However, already at $\text{NH}_3/\text{NO} = 7$, a negative effect in the form of an increased CO emission is apparent from the curve in Fig. 2. The increased emission of carbon monoxide is probably caused by the ammonia which consumes all the OH radicals needed for the oxidation of CO to CO_2 . A high level of CO is often taken as a sign of incomplete combustion. In order to prove that the ammonia does not affect the burn-out of hydrocarbons, samples were taken of hydrocarbons in the range C_7 to C_{18} at different NH_3/NO molar ratios. As expected there is no connection between the ammonia addition and the combustion of hydrocarbons.

The main problem is the emission of ammonia. For instance, at $\text{NH}_3/\text{NO} = 7$, the level of emission of NH_3 and NO is about the same as the NO emission level without ammonia injection. The excess ammonia reacts with SO_2 and SO_3 in the flue gas to form salts of ammonia, which act as condensation nuclei for the moisture in the flue gas. The flue gas plume not only becomes visible but it also falls down close to the boiler house. The visible flue gas plume was observed as soon as the injection with a high dosage of ammonia started. An addition of $\text{NH}_3/\text{NO} = 3$ seems to be optimal in order to avoid the negative effects.

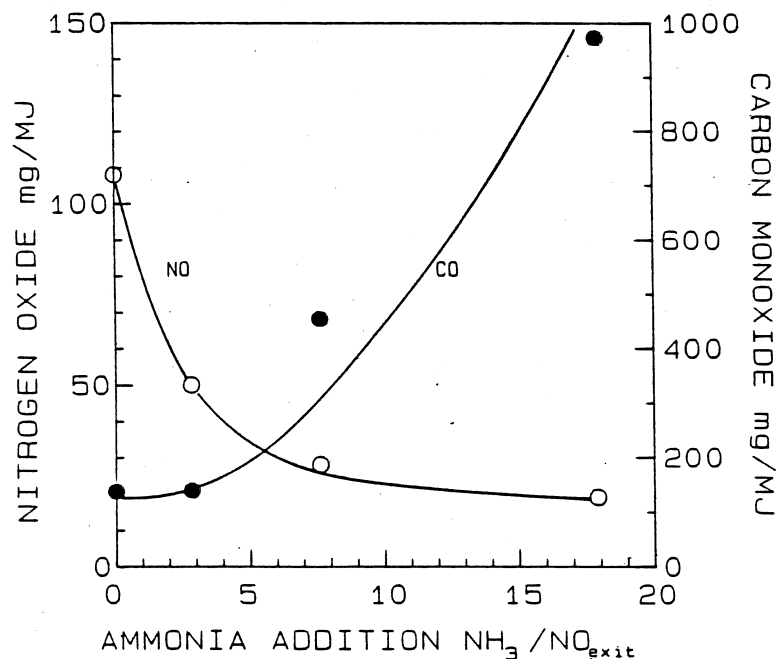


Fig. 2. NO and CO emissions at ammonia injection into the freeboard of the SFBB.

Without ammonia injection the NO emission of the SFBB is strongly dependent on the excess air ratio. Fig. 3 shows that the NO emission after ammonia injection (a rather large quantity in this case) becomes unaffected by the excess air ratio.

If secondary air is used as a carrier gas instead of recirculated flue gas at the same total excess air ratio of the boiler, the NO reduction is poor, Fig. 4. This is due to the low starting point (the NO emission at secondary air addition without ammonia) which is only 60 mg/MJ. Furthermore, the oxygen concentration is high at the injection point of ammonia and it is likely that part of the ammonia is oxidized to nitrogen oxide in agreement with the results of Hampartsoumian (1982). The oxidation of ammonia is most probably the reason for higher NO emission values, than those characteristic of injection with flue gas. Higher values were measured for $\text{NH}_3/\text{NO} > 5$, in spite of the low initial value of 60 mg/MJ.

THE TEMPERATURE DEPENDENCE

Fluidized beds usually operate in the range of 800 to 850°C and the temperature in a cooled freeboard is even lower, whereas the optimum range of NO reduction with ammonia is around a hundred degrees higher. In spite of this, the results are fairly good.

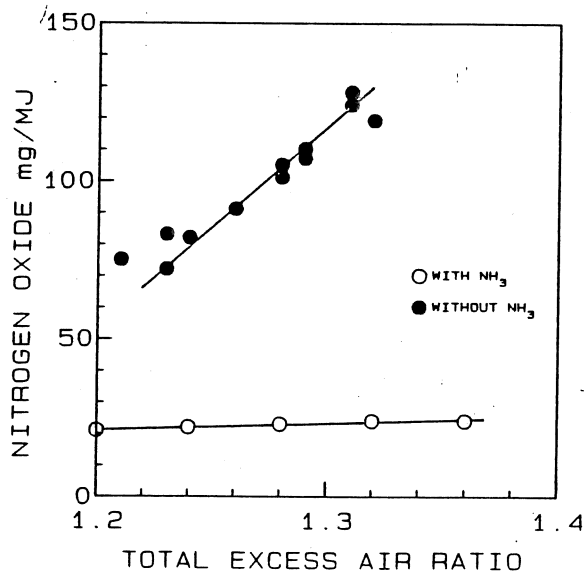


Fig. 3. Nitrogen oxide emission as a function of the excess air ratio with and without ammonia injection.

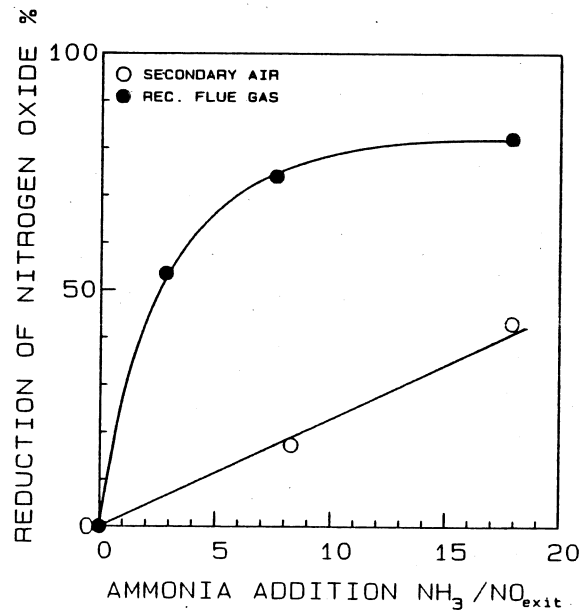


Fig. 4. Reduction of nitrogen oxide as a function of ammonia injection. Comparison between a case with secondary air as a carrier gas and a case with recirculated flue gas (Fig. 2).

Lyon (1979) has shown that simultaneous injection of hydrogen and ammonia will lower the boundary of the temperature window. Kimball-Linne and Hanson (1986) explain that below 920°C the production of OH radicals is too small to reduce NH_3 to NH_2 (which is the active component) in sufficient quantity for the reaction to continue. The injected hydrogen produces enough OH radicals and the boundary of the window is moved a few hundred degrees towards lower temperatures. A short test in the SFBB with hydrogen injection did not change the NO emission. However, the excess CO emission vanished, which confirms the presence of OH radicals.

It is most probable that the presence of burning hydrocarbons affects the temperature window in a favorable way. This has also been discussed by Hampartsoumian (1982). In order to test this further, mixtures of peat and coal or wood-chips and coal, in the proportion (related energy) peat/coal or wood/coal = 0.35, were used as a fuel. Fig.5 shows that the effect of adding a high volatile fuel was negligible.

It is known from, for instance, Azuhata and co-workers (1982) that hydrogen peroxide (H_2O_2) may lower the temperature window to about 500°C. This could be studied in a flue gas pass situated after the exit of the combustion chamber of Fig. 1a. Theoretical calculations by Cooper (1988) showed that an injection of ammonia and hydrogen peroxide at the exit of the combustion chamber would lead to a considerable reduction in the NO emission. Since H_2O_2 is a liquid, a nozzle duct was introduced in the gas path in order to spread the injected matter evenly over the gas path. However, no change in the nitrogen oxide emission was observed, possibly due to the difficulty of introducing the H_2O_2 . The conclusion of this experiment is that it is not convenient to spread a liquid substance evenly over a large cross-section of a boiler flue gas pass. Although gas injection may also have its limitations, it is certainly much easier to handle than liquid injection.

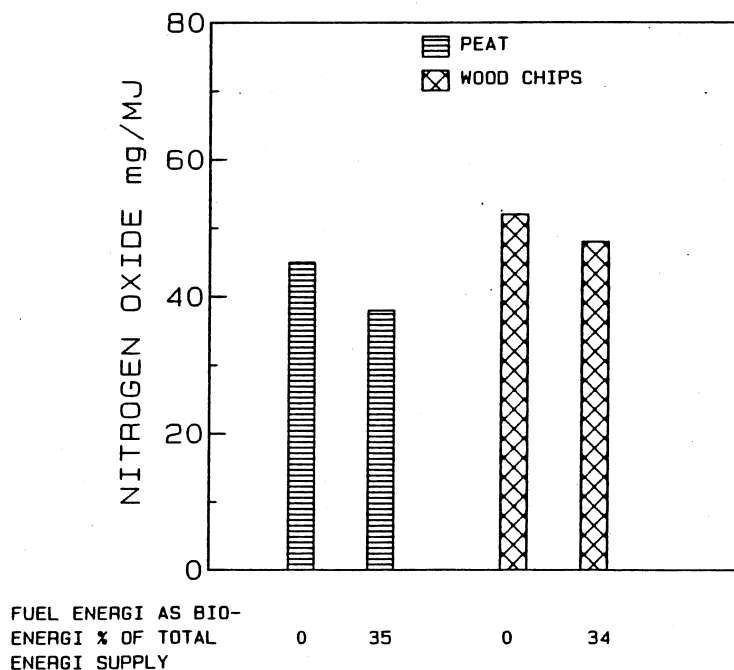


Fig. 5. The effect on the emission of nitrogen oxide of mixing wood-chips with coal during ammonia injection.

INJECTION INTO THE BED

Injection of ammonia in the air channel leading to the bed of the SFBB did not affect the NO emission. This is in agreement with previous experience (Tatebayashi and co-workers, 1980; Hampartsoumian, 1982). It is explained by the decomposition of the ammonia in the bed.

Similar experience was also found in the circulating fluidized bed boiler, where the bed material is present in the entire combustion chamber and cyclone. It was confirmed by injecting ammonia with flue gas through the OFA registers shown in Fig. 1b. In spite of a large variation in NH_3/NO no effect was found on the emissions except when injecting in the register close to the cyclone (OFA 5) where a slight reduction in the NO emission occurred. In this case, however, there was also an escape of NH_3 through the stack. The tests were made with a sand bed. With a bed of lime an increased NO emission may occur, since oxygen and bed material are in good contact in the CFBB and lime has a catalyzing effect on the oxidation of ammonia to nitrogen oxide. If NO reduction by ammonia injection is to be applied in a CFBB, the injection has to take place immediately after the particle separator (the cyclone). The arrangement will then be analogous to the Exxon process.

DISCUSSION AND CONCLUSION

A 50% reduction of the emission of nitrogen oxide is readily achieved when ammonia is injected into the freeboard of a stationary fluidized bed boiler. The amount of ammonia is then between 1 and 3, expressed as the NH_3/NO molar ratio.

Larger injections are not feasible, due to the increase in the emissions of unreacted ammonia, ammonium salts and carbon monoxide.

Ammonia injection in a circulating fluidized bed boiler has to be done in the particle-free flue gas after the particle separator. Injection in the combustion chamber is analogous to injection in the bed of a stationary fluidized bed boiler. The effect is nil, or even negative if some of the ammonia is oxidized as a consequence of the catalytic effect of certain bed materials.

It is possible to reduce the nitrogen oxide emission in fluidized bed boilers by modifying the combustion through design measures or through suitable choice of operating conditions, for instance, bed temperature and excess air (Leckner and Åmand, 1987; Åmand and Leckner, 1988). Therefore ammonia addition only needs to be considered in this application when the emission standards are very low, for instance below 50 mg/MJ.

ACKNOWLEDGEMENT

This work has been financially supported by the Swedish National Energy Administration.

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