Chapter 2

Flue Gas Emissions from Fluidized Bed Combustion.

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2.1. INTRODUCTION

During the past decades fluidized bed coal combustion was developed as a technology for burning coal in an effective way meeting the standards for pollution control. During the earlier years of research on fluidized bed combustion, the potential for limiting the SO_2 emission by adding limestone to the bed was investigated extensively. In later years there was an increasing awareness of the role of NO_x in the acid rain problematic and also standards for NO_x where introduced, which initiate more research on this subject.

The present standards for SO_2 and NO_x in the Netherlands are given in table 1.

TABLE 1
Present standards in the Netherlands (mg/nm^3 - 7 % oxygen)

	< 300 MW_{th}	>300 MW_{th}
SO_2	700	400 and > 85 % desulphurisation
NO_x	500	400

To meet the present and future standards, a comprehensive research project was executed at the Twente University and at TNO Organisation for Applied Scientific Research on different subjects of emission reduction in fluidized beds for coal combustion, the results of which are reported in this chapter.

The influence of different process parameters on the emissions are discussed for both unstaged combustion as well for staged combustion conditions. The research work concerning the combustion characteristics of coal and the emissions in the TNO 4 MW_{th} AFBB is reported by Bijvoet [1]

The results presented here are from research work done in the 1 MW_{th} fluidized bed combustor at the Twente University and the 4 MW_{th} fluidized bed combustor at TNO. The two installations are described by Valk [2].

The emission values presented in this chapter are given as mg/nm^3, dry flue gases with 7 % oxygen, measured downstream the freeboard cooler.

2.2. FORMATION AND RETENTION OF SULPHUR DIOXIDE

The sulphur content of coal varies widely from less than 1 % to about 10 % by weight, although in most cases the sulphur content is between 1 and 3 wt.%.
The sulphur in the coal can be divided in two groups:

- Inorganic sulphur
- Organic sulphur

The inorganic sulphur mainly appears as iron disulphide (FeS_2) in two crystalline forms, the pyrite (cubic) and the marcasite (rhombic). Most of the disulphide appears as pyrite and are found in small discrete particles within the coal. The pyrite can be removed from the coal by washing or by other mechanical separation methods.
The amount of sulphate sulphur is for most coal types in the order of 0.1 wt.% and is not discussed here.

The organic sulphur is bound in the hydrocarbon matrix of the coal and is in the form of, thiophenes (aromatic sulphur), mercaptans (R-S-H) , disulphide (R-S-S-R), etc. This sulphur cannot be removed from the coal without changing the chemical structure of the coal.

During combustion sulphur in coal is oxidized to sulphur dioxide. The inorganic sulphur is oxidized by the combustion of the remaining char after devolatilisation; the organic sulphur by combustion of both volatiles and char.
The release of hydrogen sulphide is of minor importance during combustion in an oxidizing environment.

In a fluidized bed combustor the sulphur released from coal as sulphur dioxide (SO_2) can be removed by adding alkali compounds like limestone to the combustion process.
In atmospheric fluidized bed combustors limestone will be calcinated in situ. The calcination reaction is endothermic and produces CaO and CO_2 by the following

reaction

$CaCO_3$ ——> $CaO + CO_2$ - 183 KJ/gmol

The equilibrium partial pressure of carbon dioxide for this reaction is a function of the bed temperature only.

The formed calcium oxide can react within the bed with sulphur dioxide and oxygen producing gypsum by the following exothermic so called sulphation reaction:

$CaO + SO_2 + 1/2\,O_2$ ——> $CaSO_4$ + 486 KJ/gmol

The equilibrium partial pressure of SO_2 depends on the oxygen concentration and bed temperature.

In figure 2.1 the partial pressures of SO_2 and CO_2 are plotted versus temperature. This figure shows that under typical AFBC conditions of 850 °C and with a CO_2 concentration of 0.15 bar, the calcination can be complete and the thermodynamics of the sulphation reaction allows very low SO_2 concentrations in the flue gases.

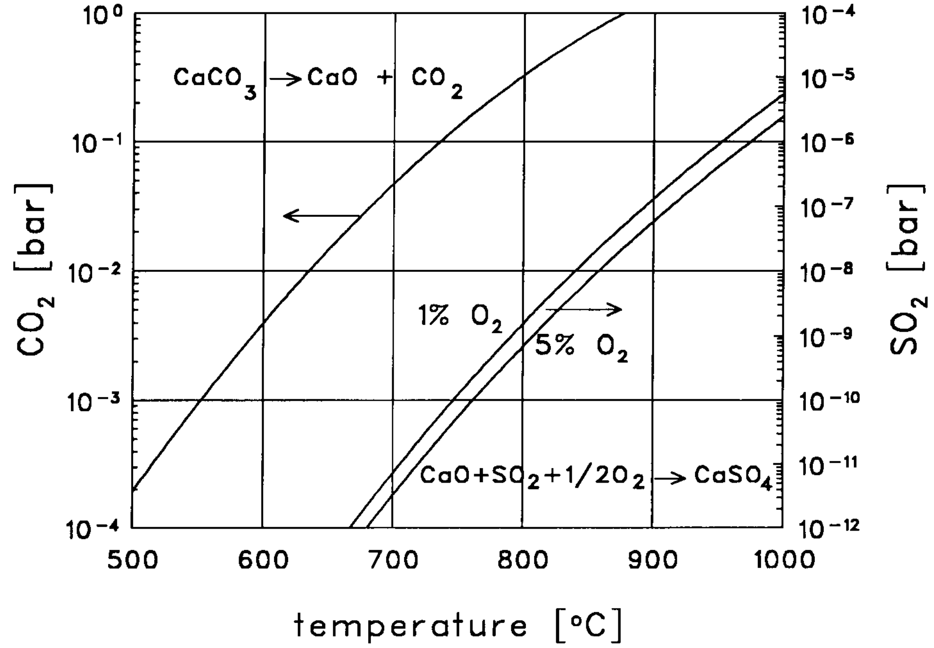

figure 2.1 The equilibrium partial pressures of CO_2 and SO_2.

2.3. FORMATION AND REDUCTION OF NITROGEN OXIDES

Burning fossil fuel, there are three main routes producing nitrogen oxides (NO_x):

- thermal NO_x
- prompt NO_x
- fuel NO_x

The thermal NO_x is produced by the reaction of atmospheric nitrogen with oxygen atoms especially at higher temperatures (T > 1000 °C):

$$\begin{aligned} &O + N_2 \longrightarrow NO + N \\ &N + O \longrightarrow NO + O \end{aligned}$$

Prompt NO_x is produced also at higher temperatures and is induced by fuel radicals under fuel-rich conditions:

$$\begin{aligned} &CH + N_2 \longrightarrow CHN + N \\ &N + O_2 \longrightarrow NO + O \end{aligned}$$

For fluidized bed combustion, at typical temperature range of 800 to 900 °C, the formation of thermal and prompt NO_x is less than 5% of the total NO_x emitted [3] and only of minor importance.

The fuel NO_x originates from oxidation of nitrogen compounds chemically bound in the fuel. Coal typically contains 0.5 to 1.5 wt.% of chemical bound nitrogen in the form of pyridines(C_5H_5N-), quinolines, isoquinolines (C_9H_6RN), amines (R_3N), indoles (C_8H_6RN) and carbazolen ($C_{12}H_9N$) [4].

During devolatilisation the fuel nitrogen is converted into two fractions: volatile nitrogen (mainly HCN and NH_3) and char bound nitrogen. The relative amount of the volatile nitrogen released from coal depends on devolatilisation temperature, heating rate and coal type.

Nitric oxide is generated during the combustion of both the volatiles and the char. Simultaneous with the production of NO, also NO reduction to N_2 can occur in the combustion process. The NO can be reduced by gas-solid reactions, gas-solid catalytic reactions and homogeneous gas phase reactions.

Nitric oxide is reduced to nitrogen by the reaction on the char surface:

Char as reactant:

$$\begin{aligned} &C + 2NO \longrightarrow N_2 + CO_2 \\ &C + NO \longrightarrow 1/2N_2 + CO \end{aligned}$$

Under more reducing conditions where carbon monoxide and hydrogen are present the char even works as a catalyst for the reduction of nitric oxide with these species, with C_f as a free carbon site:

Char as catalyst:

$$C_f + NO \longrightarrow 1/2N_2 + C(O)$$
$$C(O) + CO \longrightarrow CO_2 + C_f$$
$$C(O) \longrightarrow CO$$

Volatile nitrogen compounds can react to either NO or atmospheric nitrogen (N_2):

Homogeneous gas phase reactions:

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$
$$RCN + O_2 \longrightarrow NO + RCO$$
$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$$
$$4NH_3 + 6NO \longrightarrow 5N_2 + 6H_2O$$

The first reaction, oxidation of ammonia to NO, can be catalysed by calcium oxide [5]

2.4. EMISSIONS OF SO_2 AND NO_x

This paragraph deals with the research on the emissions of SO_2 and NO_x both under unstaged combustion conditions as well as under staged combustion conditions. The influence of the different process parameters will be discussed.

2.4.1. Unstaged combustion

- Influence of bed temperature.

The bed temperature is one of the most sensitive parameters for sulphur capture in a fluidized bed combustor. The typical influence of the bed temperature measured at the Twente University is shown in figure 2.2.

Optimal sulphur capture is obtained at about 850 °C. The limestone fed to the bed will be calcined before the sulphur dioxide capture reaction with calcium oxide can take place:

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SO_2 + 1/2\ O_2 \longrightarrow CaSO_4$$

Calcination at acceptable rates is obtained at temperatures over 800 °C, so at lower temperatures the calcination reaction is the rate controlling step for sulphur capture. Increasing the bed temperature, the rate of the sulphation reaction is increased also resulting in a better sulphur capture. At higher temperature (>875 °C) the sulphation reaction is that fast that the SO_2 will react at the entrance of the pores and will block these pores resulting in a lower utilization of the limestone particles. At higher bed temperatures also more sintering of limestone particles occurs. This will decrease the active internal surface of the particles. Decomposition of the formed $CaSO_4$ can also occur at higher temperatures: $CaSO_4 \longrightarrow CaO + SO_2 + 1/2O_2$

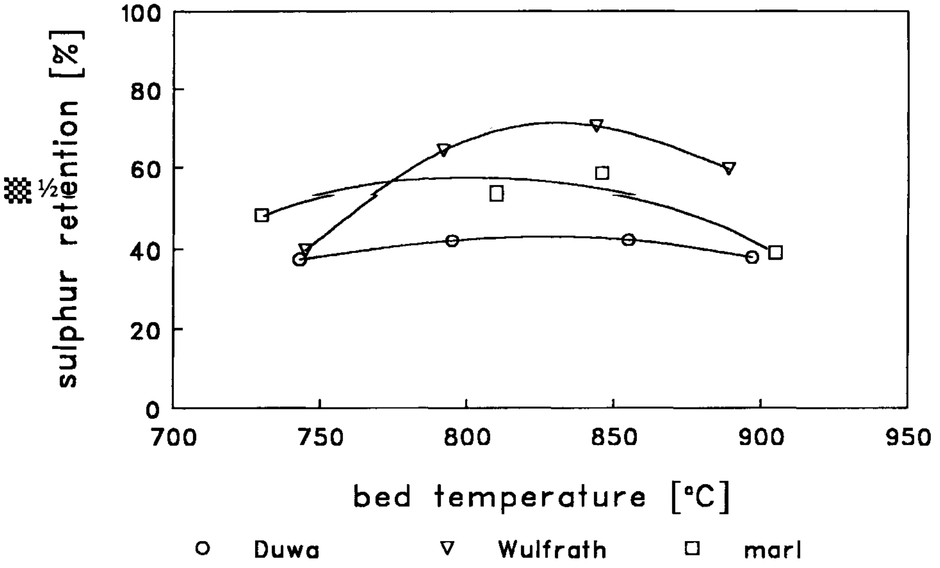

figure 2.2 Influence of the bed temperature on the SO_2 emission, Virginia coal, air ratio = 1.2, Ca/S = 3 R/C = 0, TU

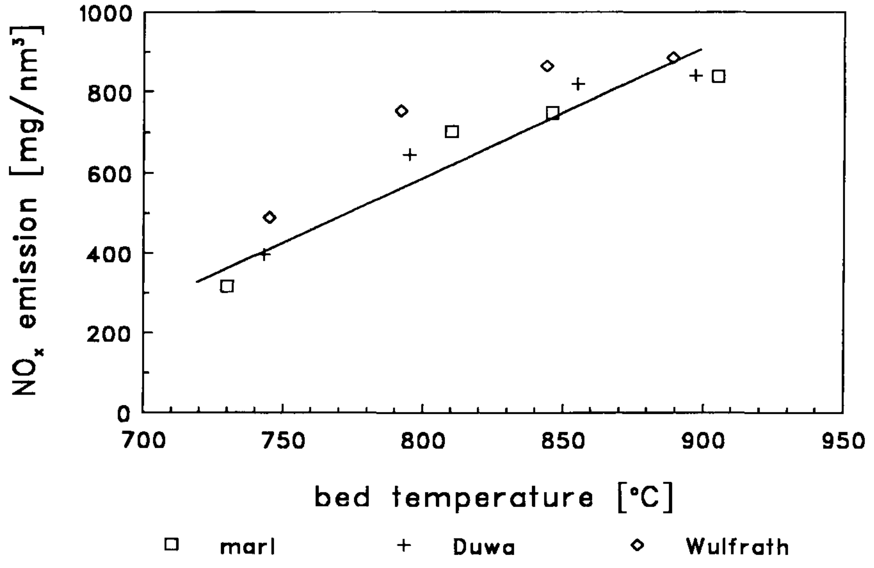

figure 2.3 Influence of the bed temperature on the NO_x emission, Virginia coal, air ratio = 1.2, Ca/S = 3 R/C = 0, for three different limestone types, TU.

The bed temperature is also an important parameter influencing the NO_x emission. The NO_x emission as a function of bed temperature is given in figure 2.3.

As can be seen from figure 2.3 the NO_x emission increases sharply when the bed temperature is raised, caused by the increase of the volatile production and an enhancement of the ammonia oxidation rate to NO_x at higher temperatures. The NO_x emission increases with a rate of about 3 mg/nm^3 per deg. C.

- Influence of the freeboard temperature

A comparative NO_x emission research with different sizes of fluidized bed combustors was carried out within the framework of an EC-project. Beside the size of the bed section of the combustors the design of the freeboard section for the combustors has also been different. The whole research work and the different combustors are described by Braun et al [6]. The measured freeboard temperature profiles of the boilers for similar process conditions are shown in figure 2.4 (same: coal type, feed system and air ratio).

In the EBV combustor (bed section 2.3 x 2.3 m) the freeboard is not equipped with a freeboard cooler. The freeboard temperature increases from 850 to about 890 °C at the end of the freeboard. In the RWTH boiler (bed section 2 x 3.6 m) the flue gases are almost immediately cooled down to about 600 °C. In the combustor of the Twente University (bed section 0.6 x 0.6 m) the flue gases are cooled by the thermal losses of the combustor walls along the freeboard before entering the freeboard cooler.

For the different combustors the NO_x concentration profiles are measured along the freeboard. The NO_x profiles versus the height above the distributor plate are plotted in figure 2.5. As can be seen, near the bed surface in the three combustors (1 m above the distributor plate) almost the same NO_x emission level is measured. This indicates that the size of the bed section did not influence the NO_x formation within the bed.

The NO_x concentration profiles along the freeboard are quite different for the three combustors. In the RWTH combustor in which the flue gases are immediately cooled down, the NO_x emission remains almost at a constant level along the freeboard. In the Twente combustor, a small reduction in the freeboard section is shown. In the EBV combustor with the highest freeboard temperature a remarkable reduction of the NO_x in the freeboard is shown. In the freeboard of this combustor the NO_x concentration drops from 1000 mg/nm^3 just above the bed to 500 mg/nm^3 at the end of the freeboard. At higher freeboard temperatures the reduction rates of NO_x by char and gaseous components are enhanced.

These results show clearly that the freeboard can be very effective in reducing the NO_x emission.

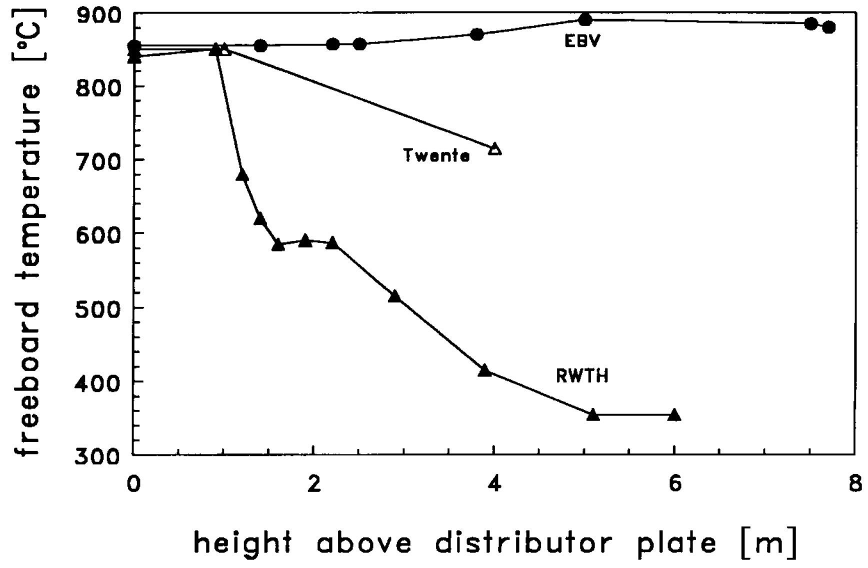

figure 2.4 The freeboard temperature profiles of the different combustors [6]

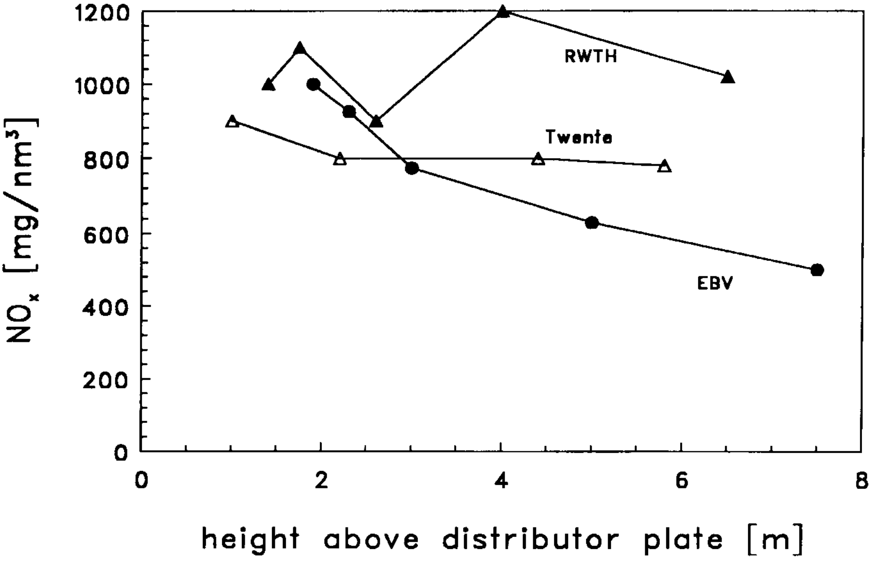

figure 2.5 The freeboard NO_x profiles of the different combustors [6]

- Influence of limestone addition.

Based on the stoichiometry of the sulphur capture reaction with calcium oxide a theoretical limestone feed of one mole calcium per mole of sulphur would be enough for complete sulphur capture. However the molar volume of $CaSO_4$ is larger compared to the molar volume of calcium carbonate and therefore complete conversion of the limestone particle is impossible. Besides, the fast sulphation reaction can produce a layer of $CaSO_4$ at the entrance of the pores, blocking this pores for further reaction. Due to these blocking of the pores, the utilisation of the limestone is decreased further. This incomplete conversion to $CaSO_4$ increases the limestone consumption and so the costs for the limestone and for the disposal of the ashes.

In figure 2.6 and 2.7 the measured SO_2 emissions are plotted versus the calcium over sulphur molar ratio (Ca/S) for the fluidized bed combustors of the Twente University and TNO.

Both combustors show the same trend. The sulphur capture is increased when the calcium over sulphur mole ratio (Ca/S) is raised. Up to 95 % retention can be achieved at Ca/S ratios of 2 to 3.

The NO_x emissions tend to increase at higher calcium to sulphur ratios as shown in figure 2.8. Calcined limestone acts as a catalyst on the ammonia oxidation reaction.

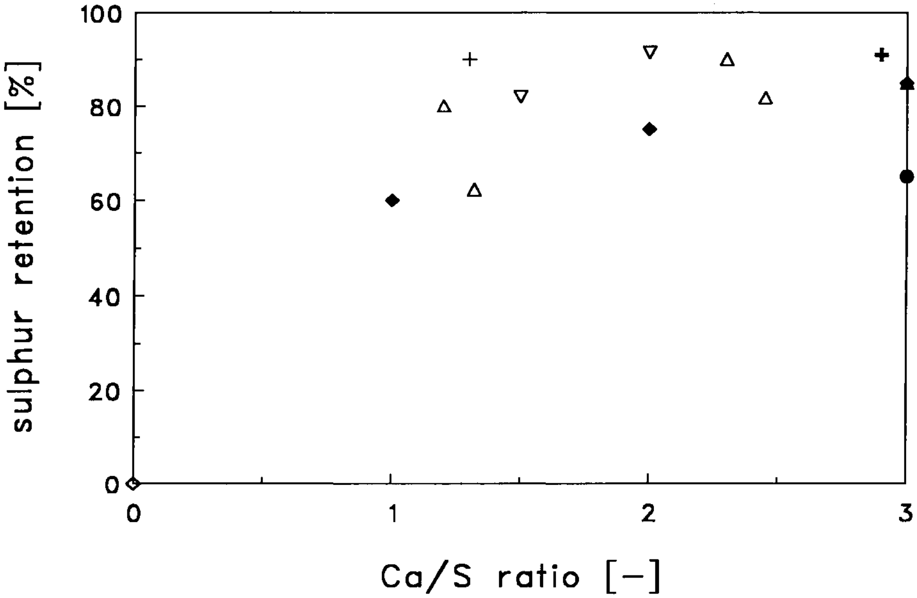

figure 2.6 The influence of the Ca/S ratio on the sulphur retention for different limestone and coal types, T_{BED} = 850 °C, air ratio = 1.2, R/C = 1, TU

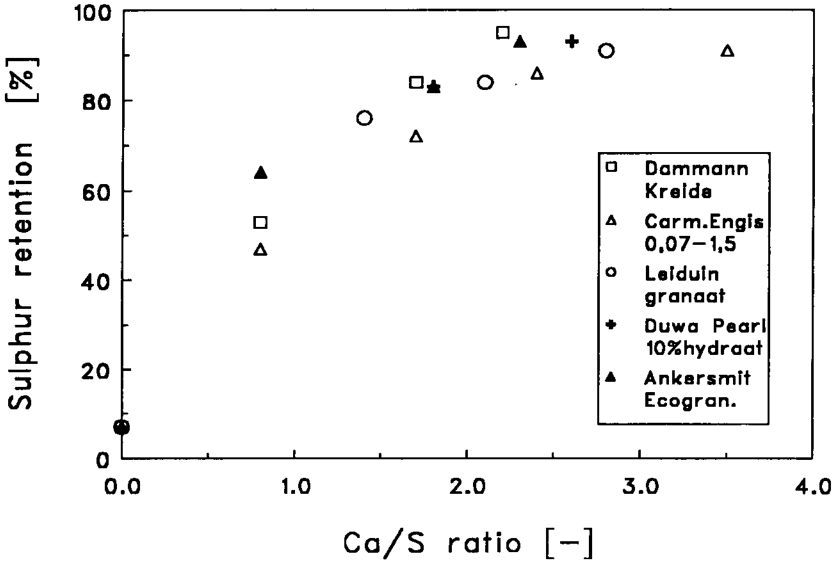

figure 2.7 Influence of the Ca/S ratio on the SO_2 emission for different limestone types, Kentuckky coal, T_{BED} = 850 °C, air ratio 1.1, R/C = 1, TNO

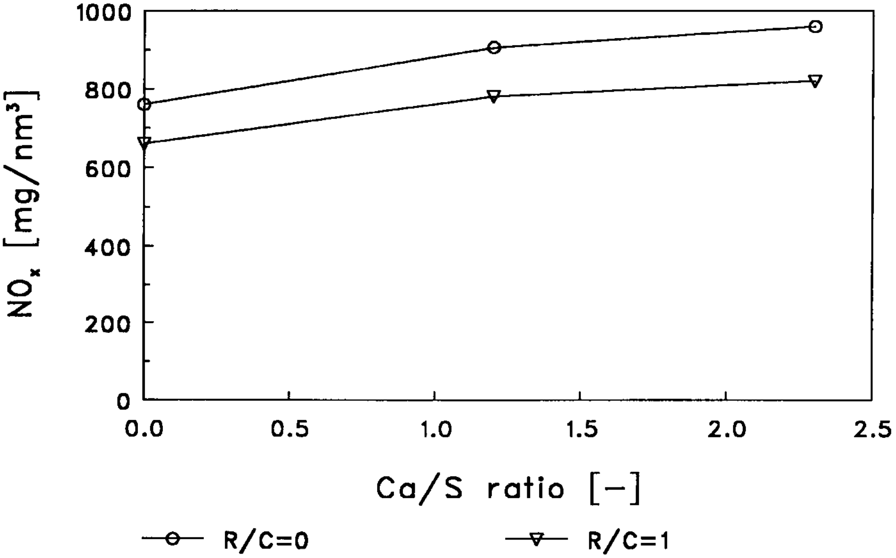

figure 2.8 Influence of the Ca/S ratio on the NO_x emission, Rietspruijt coal, T_{BED} = 850 °C, air ratio = 1.2, TU

- influence of limestone type

In the TNO boiler a comparative test program has been carried out with respect to the sulphur capture of different limestone types. The results of this test program with Kentucky coal (2% sulphur) are shown in figure 2.7.

From this plot we can see that soft marl types like Dammann Kreide are very active for sulphur capture.

Also laboratory experiments have been performed with thermogravimetric analyzing (TGA), scanning electroscopy and sulphur X-ray mapping to screen the limestone types. Qualitative tests have been carried out with respect to the mechanical strength of the limestone particles and the resistance to thermal shock.

The results of the thermogravimetric analysis are presented in figure 2.9.

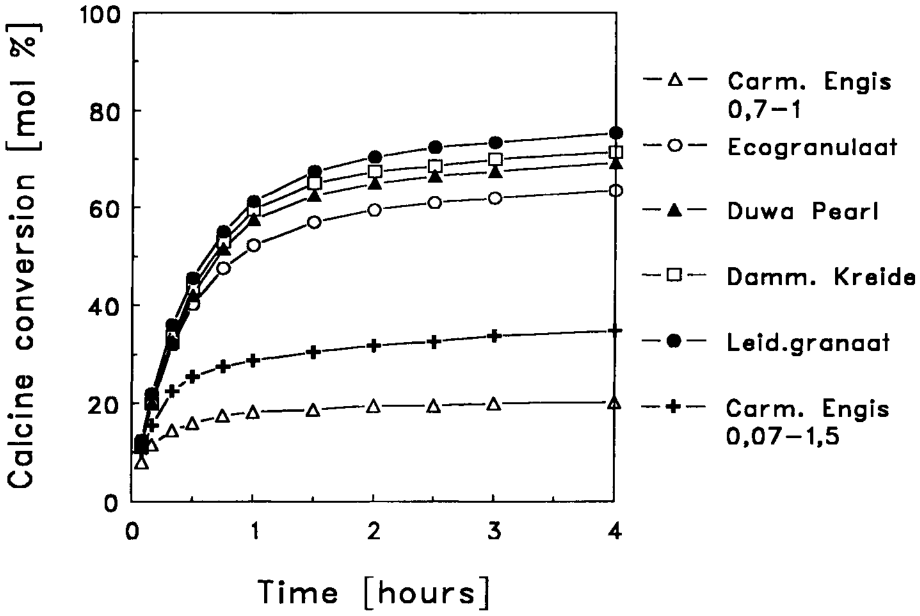

figure 2.9 Thermogravimetric analysis of the sulphation proces of different limestone types, TNO

Comparison of the results of the figures 2.7 and 2.9 shows that the thermogravimetrically measured limestone conversion does correspond to the results of the fluidized bed boiler experiments, except for Carmeuse Engis. In the case of Carmeuse Engis the sulphation reaction is restricted largely to the external surface while the sulphur capture of the other limestone types takes place within the pores. This has been confirmed by scanning electron microscopy and sulphur X-ray mapping of the sulphated limestones. The unexpected high sulphur retention of the Carmeuse Engis under fluidized bed boiler conditions compared to the TGA results, can be explained by attrition of the surface layer of the particle.

-Influence of sorbent particle size

Figure 2.10 shows the results from tests with Carmeuse Engis limestone used in the TNO boiler with different limestone sizes. For the fine limestone the retention is about 10 % better compared to the coarse limestone. The coarse limestone has a reduced surface area resulting in a lower utilisation of the limestone. Münzner et al [7] showed by their laboratory test that the best results are obtained with either extremely fine limestone particles (large surface area) or with limestone particles with a diameter just above the elutriation size (lower surface area but a longer residence time).

No influence was found of the limestone type and the particle size of the limestone on the NO_x emission.

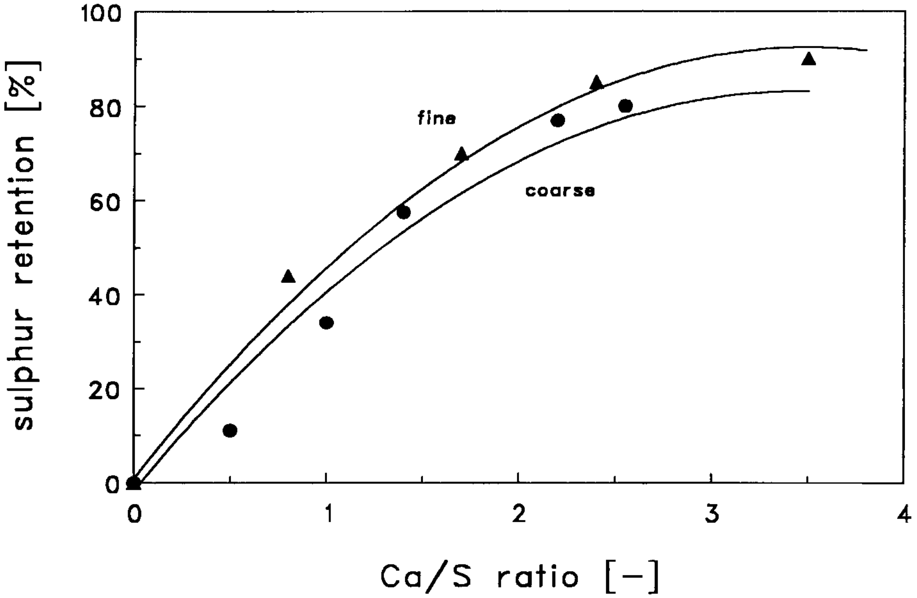

figure 2.10 Sulphur retention versus Ca/S ratio for two sorbent particle sizes of Carmeuse Engis, TNO

- Influence of coal type

It is clear that the sulphur content of the different coal types is in direct relation to the required amount of limestone added to the bed for good sulphur retention. Not only the sulphur content of the coal, but also the calcium content of the coal itself plays an important role for sulphur retention. During the past years different coal types with various "natural" Ca/S mole ratios are investigated. In figure 2.11 the "natural" sulphur retention is plotted versus the natural Ca/S ratio without additional limestone. This figure shows that the calcium within the coal is very effective in reducing the SO_2 emission. For the German browncoal ($Ca_N/S=2$) emission levels down to 100 mg/nm^3 (90 % retention) were achieved without adding limestone.

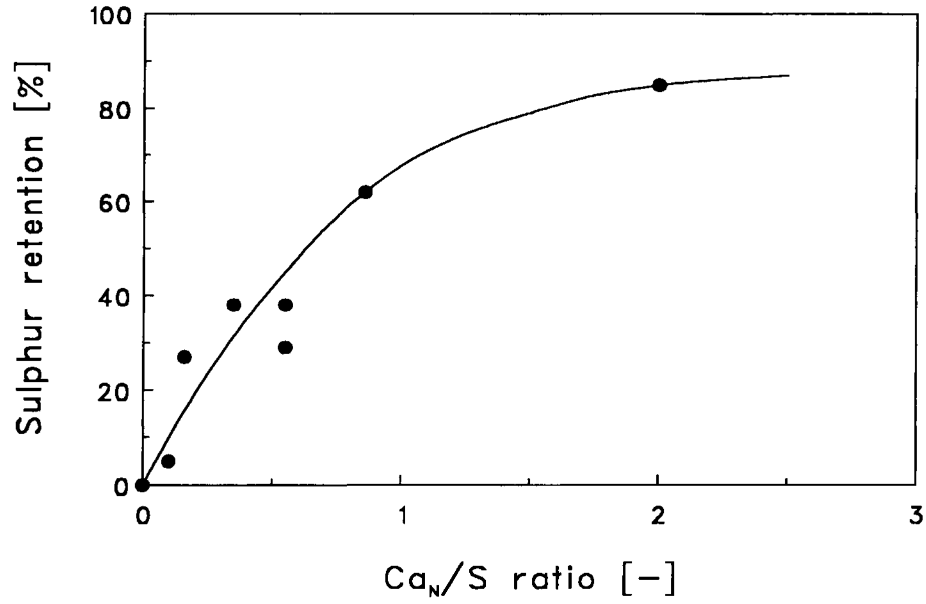

figure 2.11 Natural sulphur retention versus the Ca$_N$/S, T_B = 850 °C, air ratio = 1.2, R/C = 0, no limestone addition,TU

The nitric oxides are mainly formed from fuel nitrogen in fluidized beds so that with an increasing nitrogen content in the coal, higher nitric oxide emissions could be expected. Nitrogen oxide emissions depending on the nitrogen content in the coal were not confirmed by the NO_x measurements for different coal types.

- Influence of fly ash recycling

Recycling of fly ash is a relatively simple measure to increase the combustion efficiency especially for less reactive coal types [2]. Attendant benefits of fly ash recycling are a better sulphur retention and lower emissions of NO_x.

In figure 2.12 the NO_x and SO_2 emissions are plotted versus the recycle ratio. The recycle ratio is defined as the ratio of the mass flow rate of the recycled fly ash to the mass flow rate of the coal supplied.

This better sulphur retention is a consequence of the increased residence time of limestone particles, as the elutriated particles which are not or only partial converted are recycled. Especially when fine limestone particles are used a large influence of fly ash recycling on the SO_2 emission is expected.

The lower NO_x emissions at higher recycle ratios can be caused by :
- increase of carbon content in the bed and freeboard
- lower oxygen concentration due to better combustion

- higher reduction rates in the freeboard by an increase of the freeboard temperature
- more carbon monoxide in the bed and the freeboard enhancing the NO_x reduction.

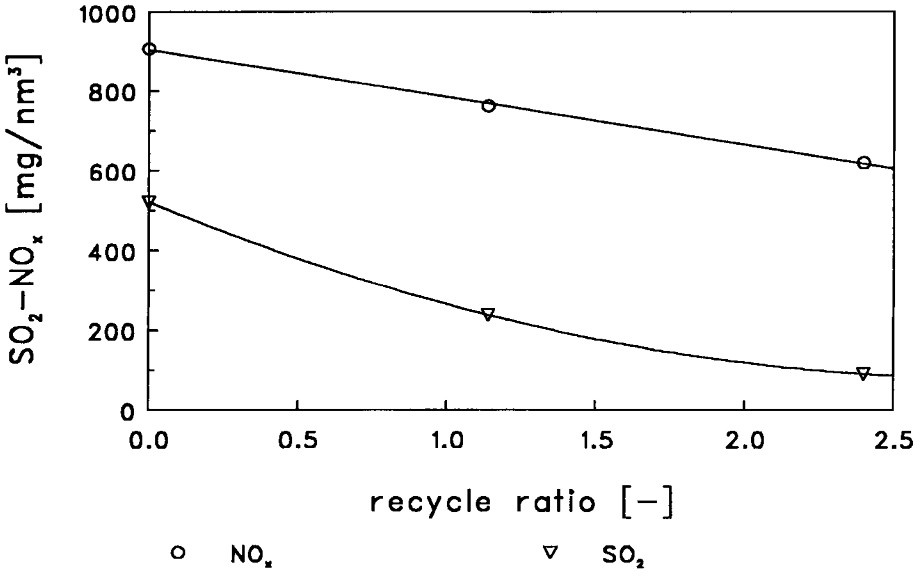

figure 2.12 NO_x and SO_2 emissions versus the recycle ratio, Rietspruijt coal, T_B = 850 °C, air ratio = 1.2, Ca/S = 1.2, Carmeuse Engis limestone, TU

Some concluding remarks concerning the emissions of SO_2 and NO_x under unstaged combustion conditions:

- Optimal temperature for sulphur retention lies between 825 and 850 °C.
- Increasing the bed temperature results in higher NO_x emissions.
- The freeboard is very effective in reducing NO_x emissions.
- By limestone addition the SO_2 emission can be controlled at a desired value, however the NO_x emission is increased slightly by adding limestone.
- Soft limestone types, like marl show the best sulphur retention.
- The calcium within the coal is very effective for sulphur retention.
- Beside increasing the combustion efficiency recycling of fly ash is also able to lower the emissions of SO_2 and NO_x.

2.4.2 Staged combustion conditions

In the middle of the 1980th it became clear that the standards for nitric oxide emissions would become more severe: NO_x < 200 mg/nm^3. Fluidized bed combustion under oxidizing conditions is not capable to reach NO_x levels meeting this new standards.

Lower NO_x emissions in a fluidized bed can be achieved by means of staged combustion [8,9].

Staged combustion means splitting the air in two separated streams, the primary air through the air distributor plate and the bed, the secondary air supplied as overfire air in the freeboard above the bed. When the total excess air is kept constant the availability of oxygen in the bed section will be lowered. Lowering the oxygen concentration in the bed will decrease the NO_x formation from char and volatile nitrogen and increase the formation of NO_x reducing components.

NO_x formed by oxidation of fuel nitrogen can be reduced by either gaseous or solid reducing components. Staged combustion will enhance the availability of these reducing species.

At the Twente University a test program was performed to study the impact of staged combustion on the emissions of SO_2 and NO_x and the influence of different process parameters on the emissions. Later on the optimal conditions found at the Twente University were tested in the 4 MW combustor at TNO.

- Influence of the primary air ratio.

The influence of the primary air ratio on the emissions of SO_2 and NO_x was tested with and without an additional freeboard cooler. The additional freeboard cooler was installed about 1.5 m. above the bed section. Without the additional freeboard cooler the temperature of the freeboard was about 50 °C higher compared to the bed temperature and with the additional freeboard cooler about 70 °C lower than the bed temperature..

The in-bed air ratio was varied between 0.6 and 1.1 by varying the coal flow to the bed. That means that the fluidizing velocity is controlled at a fixed value and the total air ratio was set on 1.1. The bed temperature was kept constant by changing the amount of heat transfer area in the bed section. The emission of NO_x from these experimental runs are shown in figure 2.13.

These test runs show that lowering the primary air ratio is an effective way to reduce the NO_x emission. The NO_x emission was reduced by 30 to 50 percent when the primary air ratio decreased from 1.1 to 0.6. NO_x emission levels down to 250 mg/nm^3 can be reached by staged combustion.

The freeboard temperature has a relative large effect on the NO_x emission. Installation of the second freeboard cooler doubled the NO_x emission level for some process conditions. At higher freeboard temperatures the combustion will be more complete in the freeboard section resulting in lower oxygen concentrations, the higher freeboard temperature will also increase the rate of the NO_x reduction reactions.

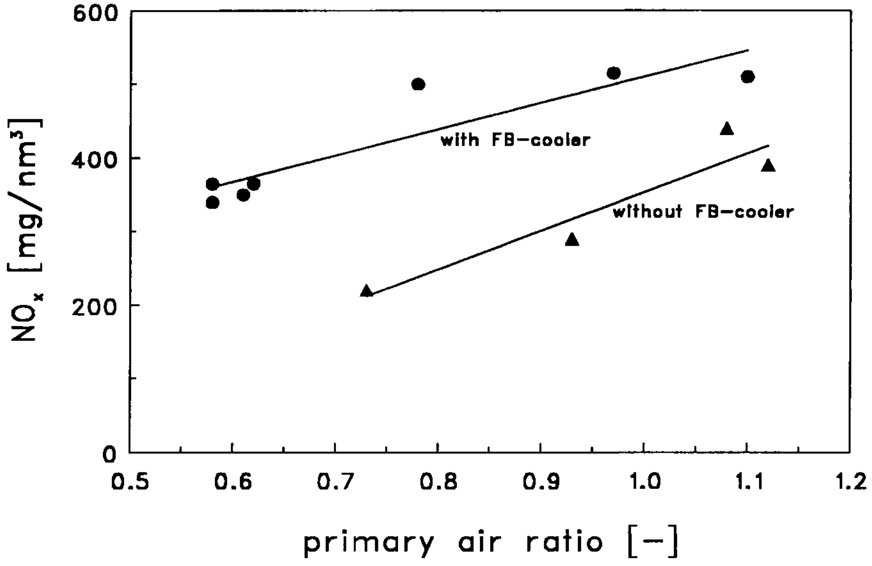

figure 2.13 NO_x emission versus primary air ratio, Marine coal, total air ratio = 1.2, T_B = 850 °C, R/C = 1.5, TU

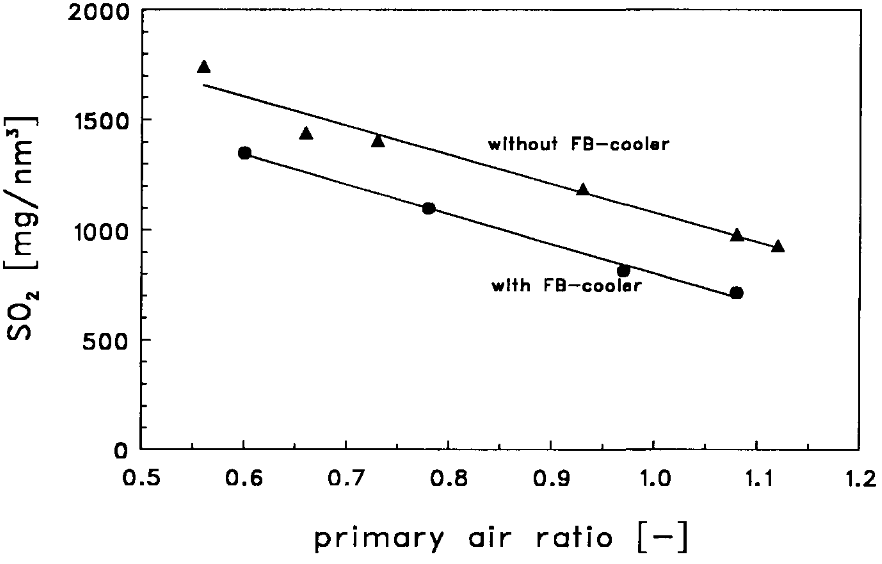

figure 2.14 SO_2 emission versus primary air ratio, Marine coal,total air ratio = 1.2, T_B = 850 °C, R/C = 1.5, Ca/S = 1.5, TU

In spite of a lower NO_x emission level the SO_2 emission increases when the primary air ratio is lowered. Under the same process conditions the SO_2 emission level doubled when the primary air ratio is reduced from 1.1 to 0.6. The sulphur capture drops dramatically, SO_2 emissions up to 1600 mg/nm^3 are measured. In figure 2.14 the influence of the primary air ratio on the sulphur dioxide emission is shown.

Also here an influence of the second freeboard cooler is observed, however with a reverse effect.

- Influence of the bed temperature.

Under staged combustion conditions the influence of bed temperature and related to it the freeboard temperature, on the emissions of SO_2 and NO_x are investigated. At an in bed air ratio of 0.6 the bed temperature was varied from 790 to 880 °C, figure 2.15.

In contrast with unstaged combustion the NO_x emission decreases with an increase of the bed temperature. At higher temperatures under staged combustion conditions the NO_x reduction reactions are more enhanced than the reactions forming NO_x. The SO_2 emission increases sharply when the bed temperature is raised.

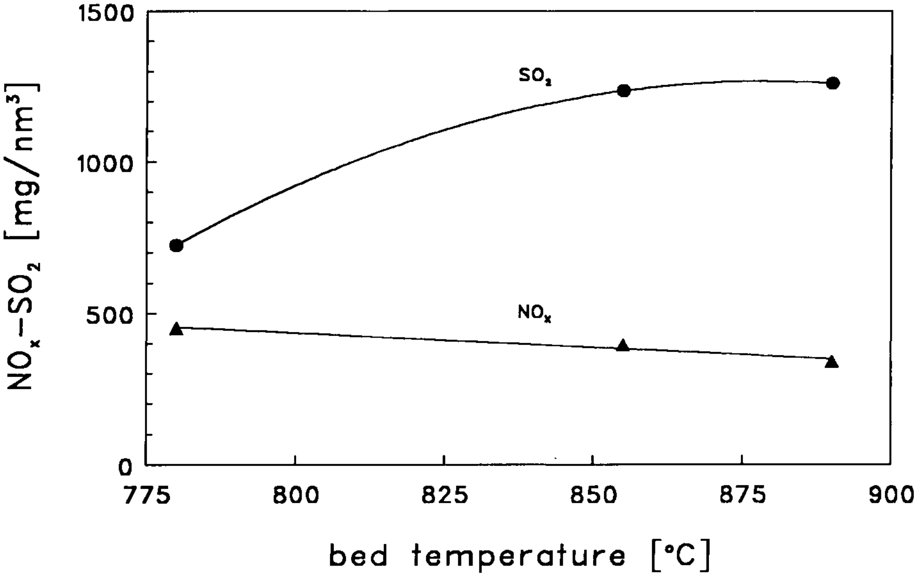

figure 2.15 SO_2 and NO_x versus bed temperature, Marine coal, primary air ratio = 0.6, total air ratio = 1.2, R/C = 1.5, Ca/S = 1.5, TU

The higher SO_2 emission under reducing conditions (fig.2.14) especially at higher temperatures (fig.2.15) can be explained by two possible mechanisms. First the increase of SO_2 might be caused by a lower in bed oxygen partial pressure during staged combustion, so the oxygen consuming sulphation reaction is not favoured.

$$CaO + SO_2 + 1/2\, O_2 \longrightarrow CaSO_4$$

Another explanation could be the decomposition of $CaSO_4$ under reducing conditions. The experimental results presented in figure 2.16 indicate that this mechanism can occur during staged combustion. In this unsteady state experiment the bed temperature is raised from 840 to 890 °C at an in-bed air ratio of 0.75. When the bed temperature is raised the SO_2 concentration increases to values higher than the theoretical possible SO_2 concentration (maximum SO_2 concentration by sulphur in the coal). A negative sulphur retention was measured of about 100 % at a bed temperature of 890 °C. This negative sulphur retention can only be explained by decomposition of the $CaSO_4$ already present in the bed material.

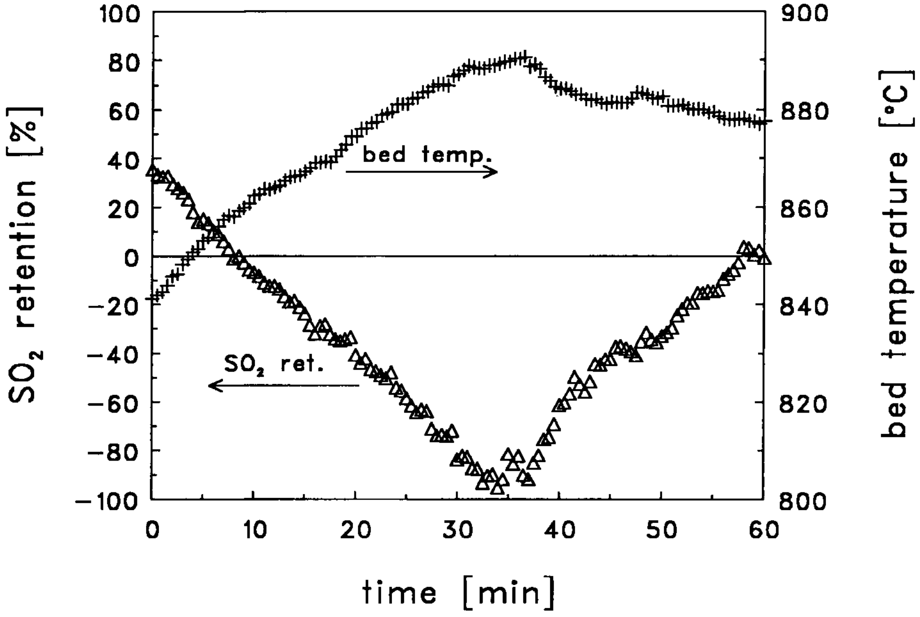

figure 2.16 The SO_2 retention and bed temperature versus time, total air ratio = 1.1, primary air ratio = 0.7, R/C = 2, Ca/S =2, Marine coal (unsteady state), TU

Possible reactions involved in the decomposition of $CaSO_4$ are:

$$CaSO_4 + CO \longrightarrow CaO + SO_2 + CO_2$$

$$CaSO_4 + 4CO \longrightarrow CaS + 4CO_2$$

$$3CaSO_4 + CaS \longrightarrow 4CaO + 4SO_2$$

In these reactions carbon monoxide is the reducing agent but also hydrogen (H_2) or carbon (C) can cause a reduction of $CaSO_4$.

The equilibrium partial pressure of SO_2 for the above reactions are calculated by thermodynamic data and are plotted in figure 2.17. From this figure it can be seen that regeneration of $CaSO_4$ to SO_2 and CaO is thermodynamically possible in the presence of reducing components and at temperatures between 800 and 900 °C. Decomposition in an oxidizing atmosphere only occurs at bed temperatures above 1000 °C.

Experiments in a fixed bed reactor confirm the possibility of $CaSO_4$ decomposition under reducing conditions at relevant temperatures [10].

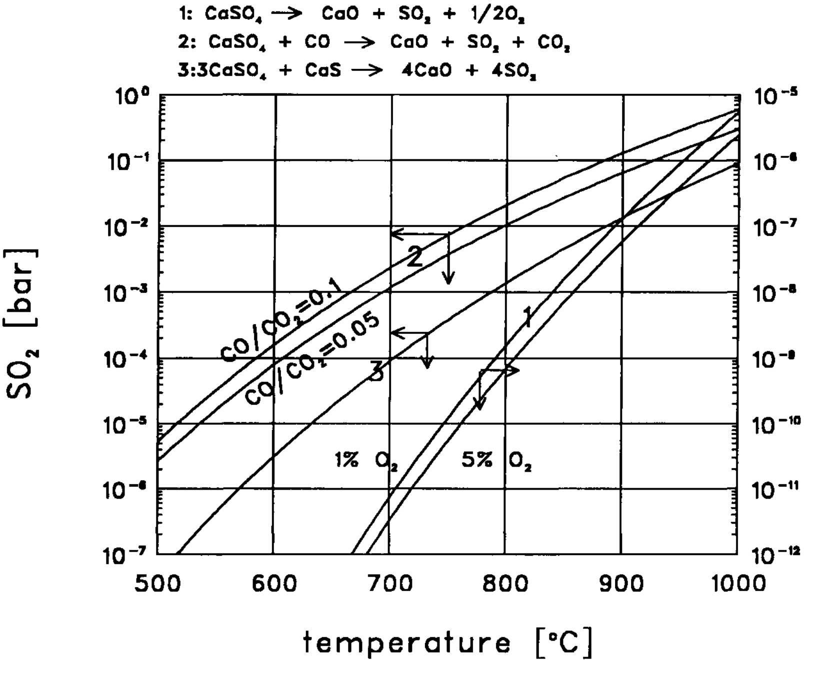

figure 2.17 Equilibrium partial pressures of SO_2 for the different reactions versus temperature

- Influence of bed material particle size

The effect of bed material particle size on the emissions of SO_2 and NO_x is investigated. Two experimental runs are carried out, one with coarse bed material (d_p mean = 1.6) and one with fine bed material (d_p mean = 0.7 mm). For these two mean sizes of bed material the primary air ratio is varied from 1.2 to 0.8 at a constant bed temperature. The NO_x emission versus the primary air ratio for the two bed materials is shown in figure 2.18.

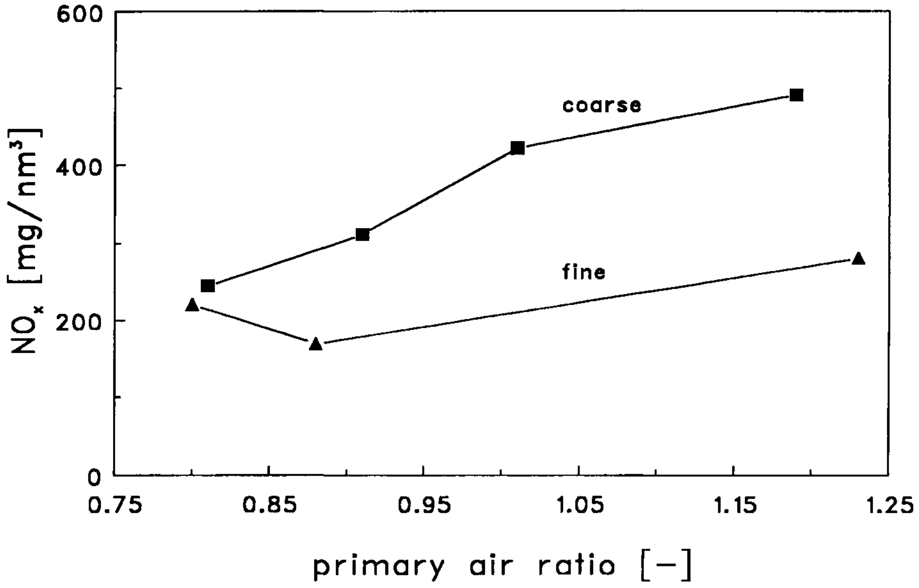

figure 2.18 Effect of bed material particle size on the NO$_x$ emission, T_B = 850 °C, R/C = 1.5, Ca/S = 1.5, total air ratio = 1.2, TU

The mean diameter of the bed particles has a strong relation to the emissions of NO$_x$ (fig.2.18). In the unstaged mode (primary air ratio of 1.2) the emission of NO$_x$ is about 50 % lowered by using fine bed material compared to the use of coarse bed material. With the fine bed material a 30 % reduction in the NO$_x$ emission was achieved by lowering the primary air ratio from 1.2 to 0.9. At a lower primary air ratio of 0.8 the NO$_x$ emission increases, probably caused by the slip of volatile nitrogen (NH_3 and HCN) to the freeboard were it is oxidized to nitrogen oxide.

The influence of the bed particle size on the NO$_x$ emission can be caused by different mechanisms.

First the bubble regime of fluidization is of interest. Calculation show that for fine bed material the gas flow through the bed is best described as a two-phase flow and for coarse bed material as a one-phase plug flow.

The superficial gas velocity (U_{df}) in the dense phase is given as [11]:

$$U_{df} = (U_{mf} + 1/3(\ U_{fl}\ -\ U_{mf}))/\epsilon$$

For a superficial fluidizing velocity (U_{fl}) of 1.8 m/s the gas velocity in the dense phase (U_{df}) is 1.71 m/s for fine bed material and 2.75 m/s for coarse bed material. (U_{mf} = minimum fluidizing velocity, ϵ = dense phase porosity)

For tube containing beds the maximum bubble size is in the order of 1.2 times the pitch of the tube bundle [12]. In our case a maximum bubble size of 0.12 m. The rising velocity of these bubbles (U_b) is calculated according to Davidson [13]:

$$U_b = U_{fl} - U_{mf} + U_b^{\infty}$$

with $U_b^{\infty} = 0.71 \times (g \times d_b)^{0.5}$

In figure 2.19 the ratio of the bubble rise velocity and the velocity in the dense phase is given as a function of the particle size of the bed material. As can be seen the bubble rise velocity for fine bed material is higher than the gas velocity in the dense phase of the bed. This results in a two-phase flow through the bed. For coarse bed material we find slow bubbles resulting in a plug flow of the gas through the bed. The two-phase flow will create an oxygen slip within the bubbles through the bed. This leads to less oxygen available for combustion in the dense phase of the bed. The lower oxygen concentration decreases the NO_x formation from fuel nitrogen and increases the concentration of NO_x reducing components like carbon and CO within the bed.

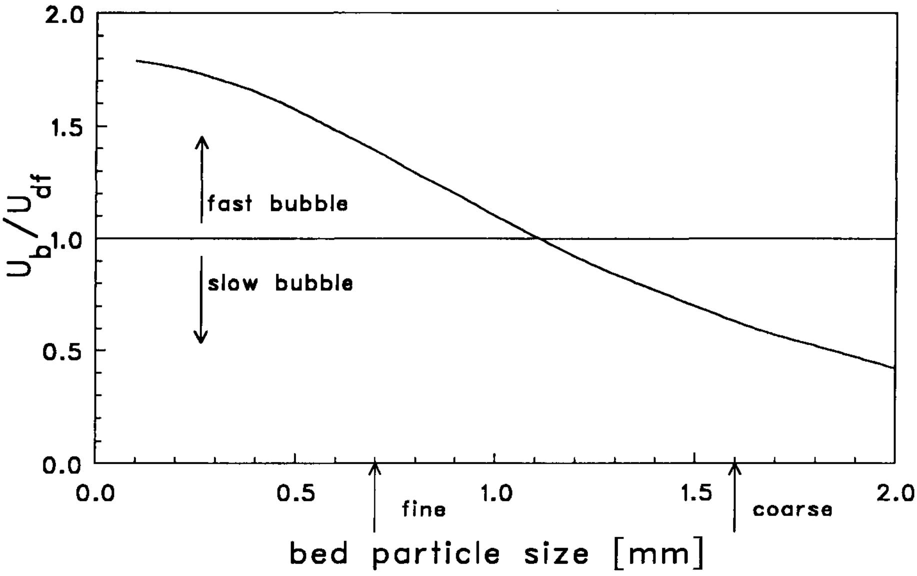

figure 2.19 The ratio of the bubble rise velocity and the velocity in the dense phase versus the bed particle size, U_{fl}= 1.8 m/s, d_b= 0.12 m

The particle size of the bed material effects also the mass and heat transfer between the dense phase and a burning coal or char particle. Prins [14] has measured the mass and heat transfer coefficients to freely moving spheres in fluidized beds. This research work shows that the heat transfer increases with decreasing particle size of the bed material, see also chapter 1 of this book. The mass transfer is decreasing for finer bed particles. These two phenomena will result in a lower combustion rate of coal and char particles and cause a higher carbon content in the bed which favours the NO_x reduction.

The particle size of the bed material has almost no influence on the SO_2 emission under oxidizing and moderate staged combustion conditions, figure 2.20. At a primary air ratio of 0.8 we can see a clear difference in the sulphur capture between fine and coarse bed material. The more reducing conditions for the fine bed material is probably the reason for the high SO_2 emissions at lower primary air ratios while also decomposition of $CaSO_4$ can occur.

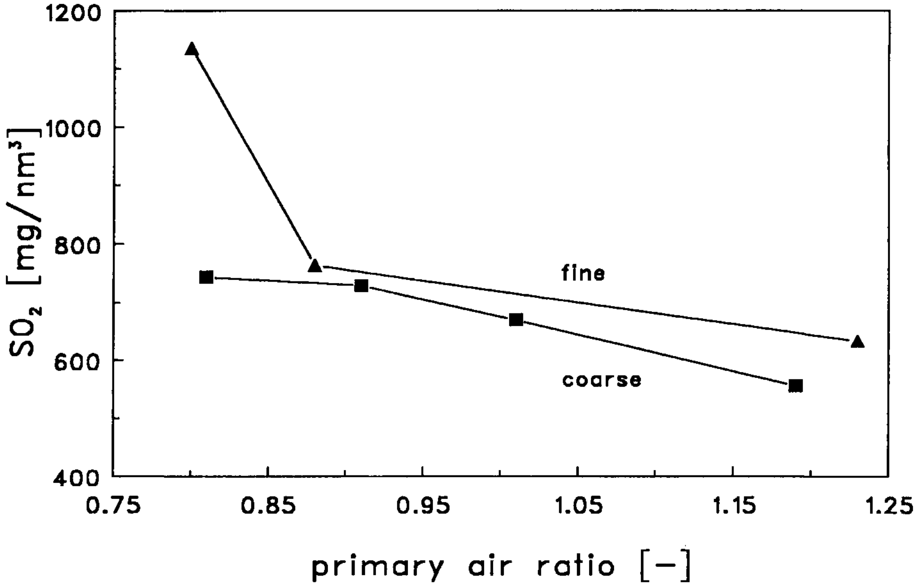

figure 2.20 Effect of particle size of the bed material on the SO_2 emission, T_{bed} = 850 °C, R/C=1.5, Ca/S = 1.5, total air ratio = 1.2, Polish coal, TU

- Optimization of the emissions of NO_x and SO_2

Above we have seen that using fine bed material the NO_x can be lowered to levels below 200 mg/nm^3 at a primary air ratio of about 0.9. At this primary air ratio the SO_2 emission is increased only to small extend. Using fine bed material the emissions of NO_x and SO_2 are further optimized by varying the bed temperature, recycle ratio and the calcium over sulphur ratio.

In figure 2.21 and 2.22 the NO_x and SO_2 emissions are given as a function of the bed temperature for three different primary air ratios.

The NO_x emission decreases about 30 % when the bed temperature is lowered from 875 to 800 °C. The general level of the SO_2 emission decreases with 50 % when the bed temperature is lowered from 875 to 825 °C. There is no significant influence of the primary air ratio and the bed temperature on the combustion efficiency [15], so a bed temperature of about 825 °C and moderate staged combustion (primary air ratio = 0.9) shows to be optimal for low SO_2 and NO_x emissions.

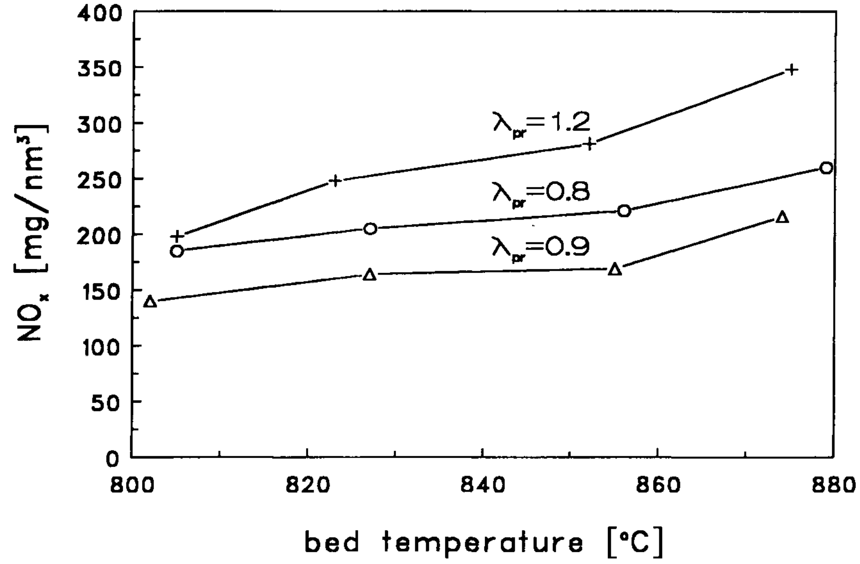

figure 2.21 NO$_x$ emission versus bed temperature for three different primary air ratio, R/C = 1.5, Ca/S = 1.5, total air ratio = 1.2, Polish coal, TU

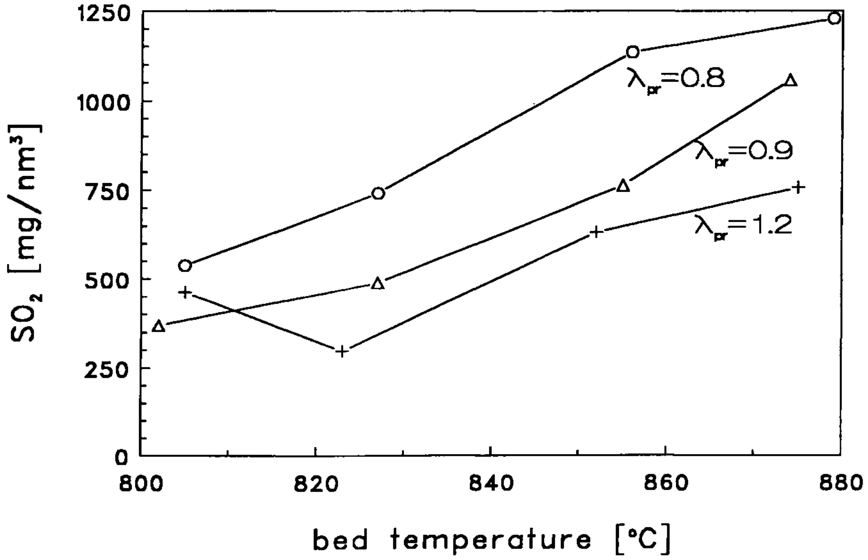

figure 2.22 SO$_2$ emission versus bed temperature for three different primary air ratios, R/C = 1.5, Ca/S = 1.5, total air ratio = 1.2, Polish coal, TU

At optimal process conditions for Polish coal (bed temperature = 825°C, primary air ratio = 0.9) the influence of limestone addition is investigated. The Ca/S ratio is varied from 0 to 4.5. The emissions of SO_2 and NO_x are given in figure 2.23. Even under staged combustion conditions the SO_2 emissions can be reduced to low levels by increasing the limestone supply. The SO_2 decreases from about 1000 to 50 mg/nm^3 by increasing the Ca/S ratio from about 0 to 4.5.

The NO_x emission increases slightly from 160 to 225 mg/nm^3 under these conditions. The catalytic effect of calcined limestone on the formation of NO from NH_3 occurs also at staged combustion conditions.

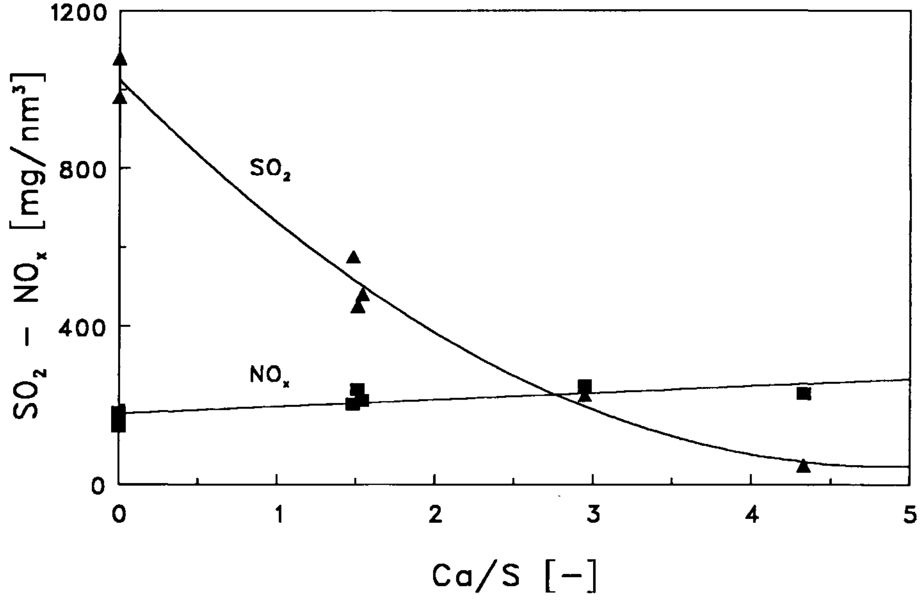

figure 2.23 SO_2 and NO_x versus the Ca/S ratio, primary air ratio = 0.9, total air ratio = 1.2, R/C = 1.5, T_{bed} = 825 °C, Polish coal, TU

The last step in the optimization program was to study the influence of the recycle ratio on the emissions. The recycle ratio (R/C) was varied from 0 to about 2, the results are shown in figure 2.24.

By increasing the recycle ratio under these conditions the SO_2 emissions can be reduced to very low levels. The SO_2 decreased from 50 to values less than 5 mg/nm^3 by increasing the recycle ratio from 0 to 2.2.

The NO_x emission also drops by increasing the recycle ratio, from 400 to about 250 mg/nm^3 under these conditions.

Recycling of fly ash is not only decreasing the emissions of SO_2 and NO_x but at the same time the combustion efficiency is increasing at higher recycle ratios [15].

Only the results for Polish coal are shown here, but also for other coal types the same trends are observed.

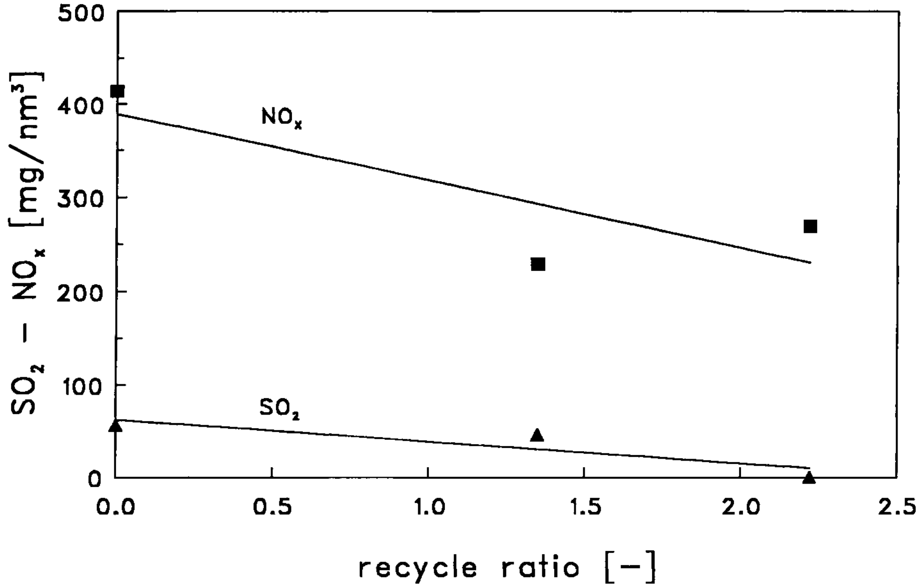

figure 2.24 SO_2 and NO_x versus the R/C ratio, primary air ratio = 0.9, total air ratio = 1.2, Ca/S = 4.5, T_{bed} = 825 °C, Polish coal, TU

Optimal staged combustion conditions found at the Twente University are:
* fine bed material
* moderate staged combustion (primary air ratio ≈ 0.9)
* bed temperature around 825 °C

2.4.3 Staged combustion results from the 4 MW combustor at TNO

To confirm the results from the test work done at Twente University the 4 MW combustor at TNO has been modified for staged combustion experiments.

In this combustor also the position of the secondary air injection port can be varied. In figure 2.25 the different configurations of the secondary air nozzles are shown. The D- nozzles are mounted horizontally at 0.6 meters above the bed level and the A-nozzles are mounted slightly inclined at about 1.6 meters above the bed level.

In this combustor the influences of different process parameters on NO_x and SO_2 emissions are investigated: particle size of the bed material, primary air ratio, nozzle position, bed temperature etc. Some of the experimental results are shown is this section.

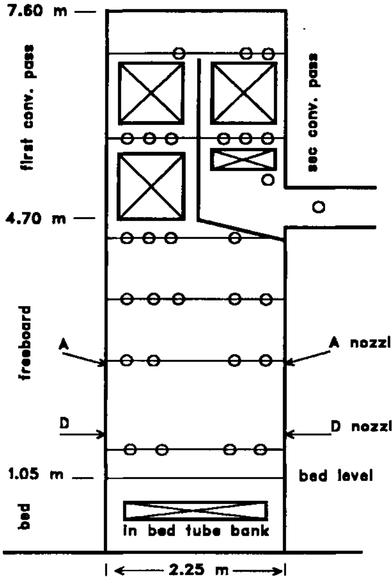

figure 2.25 Freeboard dimensions with secondary nozzle positions and sample ports, TNO

The results of the first test series are shown in the figures 2.26 and 2.27. For the staged combustion experiments fine bed material is used. The emission levels for the unstaged combustion experiments with coarse bed material are shown in the figures as striped zones. A remarkable difference is shown (about 200 to 300 mg/nm^3) between the unstaged combustion experiments with coarse bed material compared to the staged combustion experiments with fine bed material at almost the same primary air ratio. This effect is caused by the use of fine bed material. NO_x emission levels below 200 mg/nm^3 are obtained at a primary air ratio of about 1.1 with fine bed material. The NO_x is lowered to about 100 mg/nm^3 when the primary air ratio decreases to 0.9. These levels are below the most stringent present standards.

The SO_2 emission versus the primary air ratio is plotted in figure 2.27. In the TNO combustor also the diminished sulphur capture is shown at a lower primary air ratio. In this figure also the results from three experiments at different bed temperatures are given. We can see clearly that under staged combustion conditions the sulphur capture is very sensitive to the bed temperature. The SO_2 emission increased from 150 to 500 mg/nm^3 caused by the decomposition of formed $CaSO_4$ to CaO and SO_2, when only the bed temperature was raised from 800 to 850 °C. Low SO_2 emission levels can be obtained at primary air ratios down to about 0.9 and bed temperatures below 825 °C.

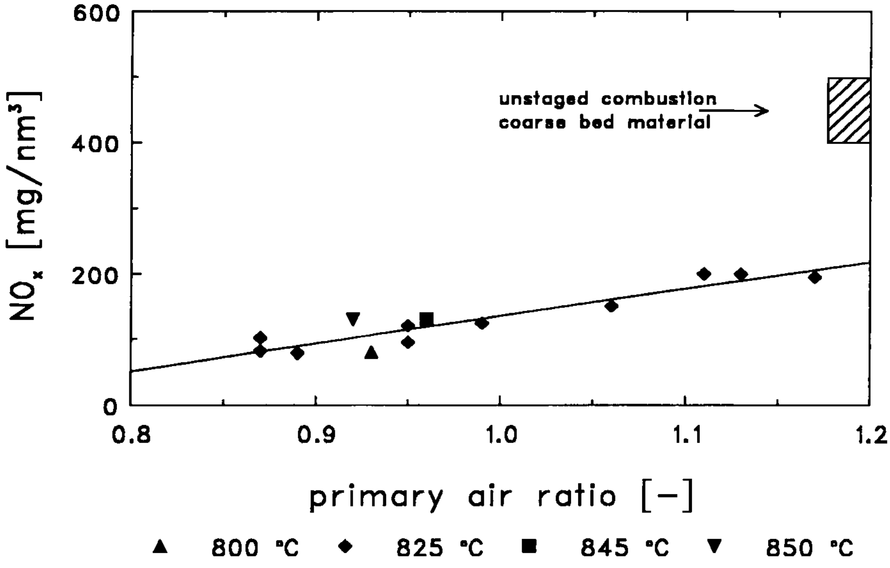

figure 2.26 NO$_x$ emission versus the primary air ratio, total air ratio = 1.2, R/C = 2 Ca/S = 2, Polish coal, TNO

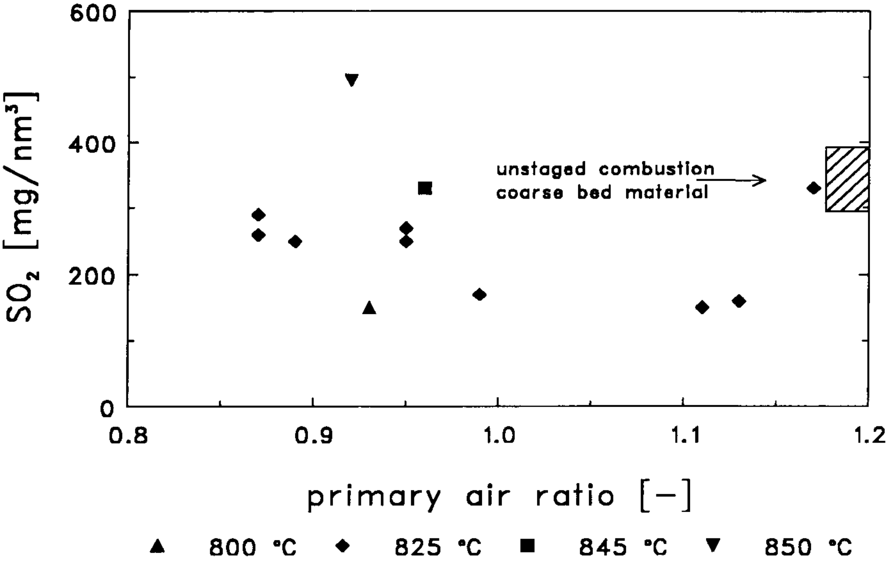

figure 2.27 SO$_2$ emission versus the primary air ratio , total air ratio = 1.2, R/C = 2 Ca/S = 2, Polish coal, TNO

The influence of the height above the air distributor plate of the secondary air injection is shown in figure 2.28. With the horizontal mounted and lower placed D-nozzles, higher NO_x emission levels are obtained than with the A-nozzles. This can be caused by the interaction of the secondary air with the splash zone of the fluidized bed. Here the reducing atmosphere in the upper part of the bed is diminished, resulting in an increased NO_x emission.

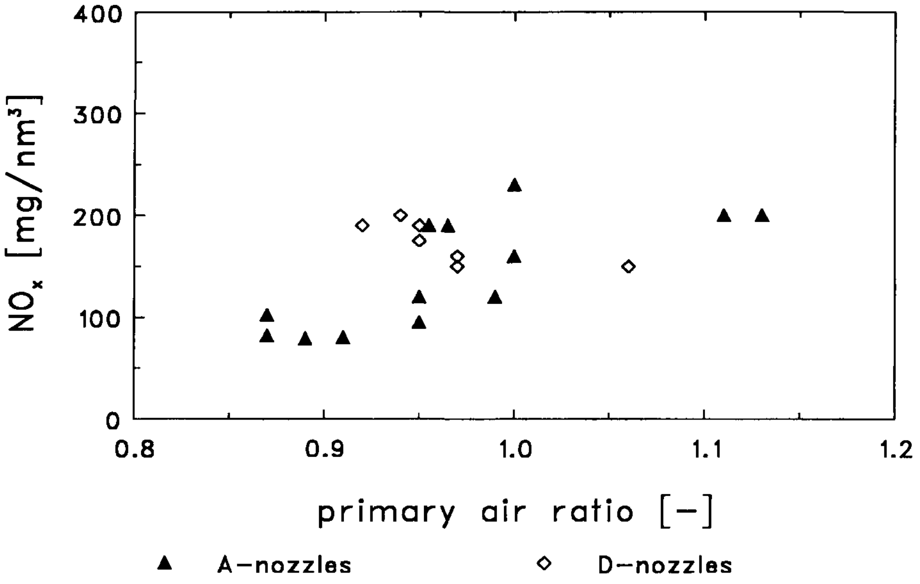

figure 2.28 NO_x emission as a function of the primary air ratio for two the nozzle positions total air ratio = 1.2, R/C = 2, T_{bed} = 825 °C, Polish coal, TNO

The measured NO_x concentration profile along the freeboard height of the TNO combustor is shown in figure 2.29. Also at staged combustion conditions the freeboard is effective for NO_x reduction.

For the A-nozzle at 1.6 m above the expanded bed level the NO_x concentration is reduced from about 330 to 120 mg/nm³ at the end of the freeboard (65 % reduction).

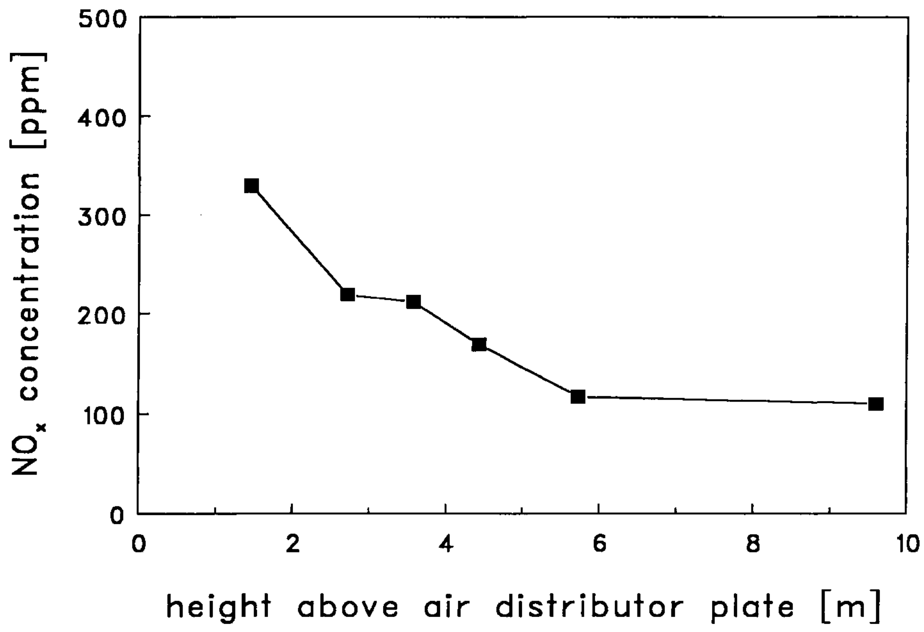

figure 2.29 NO$_x$ concentration profiles along the freeboard, A-nozzles, staged combustion, concentrations corrected for dilution by secondary air, TNO

Some comcluding remarks concerning the emissions under staged combustion conditions:

- Staged combustion is an effective measure to lower the NO$_x$ emission.
- Staged combustion is not promoting the sulphur capture.
- Increasing the bed temperature under staged combustion increases the SO$_2$ emissions sharply.
- The drop in sulphur capture at staged combustion is probably caused by decomposition of CaSO$_4$.
- The use of finer bed particles can reduce the NO$_x$ emission.
- The SO$_2$ and NO$_x$ emissions can be lowered by increasing the recycle ratio.
- Very low SO$_2$ emission levels can be obtained at higher Ca/S ratios, even under staged combustion conditions.
- The freeboard of the combustor is effective in reducing the NO$_x$ emission.

2.5. UREA INJECTION

2.5.1 Introduction

Instead of applying the staged combustion mode the NO_x emission can also be lowered by the use of suitable reagents in the freeboard of the combustor. This way of NO_x reduction is a so called secondary measure.

Among these measures in combustion techniques, the method of selective non-catalytic reduction of NO_x employing Exxon's "Thermal DeNOx" process is most widespread [16]. This method of selective reduction relies on the injection of NH_3 into fuel-lean combustion zones at about 950 °C. The effectiveness of the thermal reduction of NO_x by NH_3 in the presence of O_2 has been demonstrated in flow reactor experiments with premixed gases [17-18] and experiments with burners fired with methane, oil and coal [19,20]. In trying to get low NO_x emissions at fluidized bed combustion, the method has also been investigated at a pilot-scale FBC with injection of NH_3 in the freeboard by Hampartsoumian and Gibbs [21], by Åmand and Leckner [22]. These authors showed that the extent of reduction is mainly influenced by the location of the injection ports, the amount of excess air present and the NH_3/NO_x molar ratio. These parameters were also found to be most important in flow reactor studies mentioned above. Maximum reductions up to 75% were possible. So the "Thermal DeNOx" seems to be promising in the FBC application.

However a main disadvantage of this reduction method is that NH_3 injection needs careful attention for security as it is a very toxic and corrosive gas. Therefore a more safe and simple reducing agent is preferred.

The objective of the research at the Twente University was to investigate the use of urea instead of NH_3 as reagent for the selective non-catalytic reduction of NO_x in the FBC application. Urea is a cheap non-toxic, non-corrosive bulk chemical that is easy to handle.

In some patents [23,24] the use of urea as NO_x reducing agent is described, but only in relation with gas fired boilers. In this application often a special reaction unit is needed to created the optimal reaction conditions for the "Thermal DeNOx Process". In the FBC application, however, the freeboard seems to be an ideal reactor for the selective non-catalytic reduction of NO_x with regard to temperature and residence time and also with sufficient turbulence.

When urea is heated up, it will dissociate. Some dissociation reactions given in literature are [25]:

$$3\ H_2N\text{-}CO\text{-}NH_2 \longrightarrow C_3N_3(OH)_3 + 3\ NH_3 \qquad (180 < T < 280\ ^\circ C)$$

$$6\ H_2N\text{-}CO\text{-}NH_2 \longrightarrow C_3N_3(NH_2)_3 + 6\ NH_3 + 3CO_2 \qquad (T \approx 380\ ^\circ C)$$

As seen in the these reaction equations ammonia is produced among other dissociation products, so urea can be used in the "Thermal DeNOx process".

In this paragraph pilot scale FBC experiments with urea are described and discussed.

2.5.2 Experimental

Experimental Equipment.

The experiments were carried out in the 1 MW_{th} fluidized bed combustor of the Twente University.

The urea was used in the form of an aqueous solution (10 wt.%), which was found to be most effective for the NO_x reduction as at this concentration the urea could be uniformly distributed within the effluent gas. The urea solution was injected horizontally into the freeboard by a tubing pump and an air cooled injector made of stainless steel (figure 2.30), which dispersed the urea solution into a spray of fine droplets. This is an important step in the urea reduction process, because it enables uniform mixing of the urea with the effluent and sufficient penetration of the urea in the freeboard.

A cooled injector system is necessary to prevent an early evaporation of the urea solution and the decomposition of urea on steel surfaces prior to injection into the FBC.

The flue gases from the fluidized bed boiler were continuously analyzed for concentrations of CO_2 ,CO, SO_2 (infrared analyzers), NO_x (chemiluminescence analyzer), C_xH_y (flame ionisation detector) and O_2 (paramagnetic analyzer). The NH_3 concentration was sampled discontinuously by absorbing it in acidified water. The absorbed ammonium ions were determined by spectrophotometry (Berthollet's reaction).

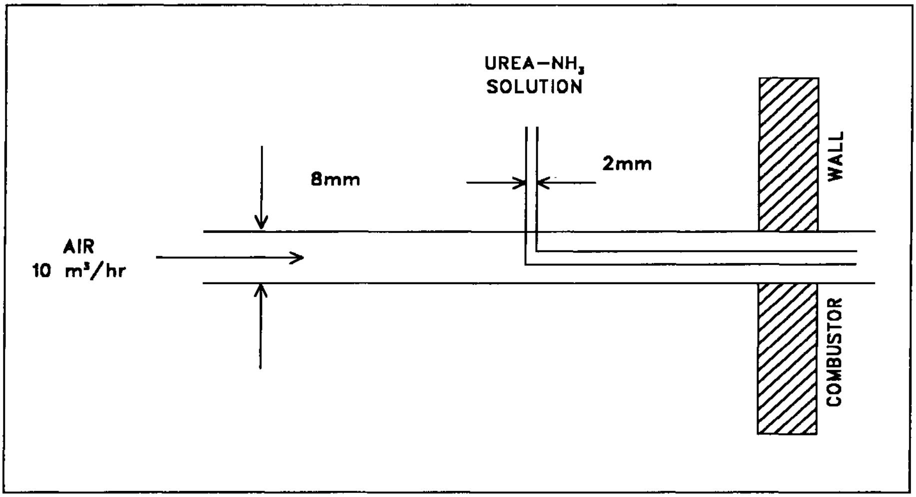

figure 2.30 The injector system

Experimental conditions.

The experiments were carried out under the process conditions shown in table 2. The bed material was silica sand. The fly ash from the cyclone is partially reinjected into the bed, the recycled mass flow rate of which was controlled at 1.5 times the flow rate of the coal supplied.

Although a temperature of 950 °C is commonly used in applying the "Thermal DeNOx process" a freeboard temperature of 900 °C was chosen because Wittler et al [26] showed that this was the optimal working temperature in the FBC application. They postulated that the temperature characteristics were altered by heterogeneous reactions on the surfaces of particles elutriated from the bed into the freeboard. Furthermore the urea injection port was situated at such a height that the residence time was at least 1.5 s, which was considered to be long enough for the selective NO_x reduction reaction [26].

TABLE 2
Experimental conditions urea injection, TU

Fluidizing velocity	1.8 (± 0.2)	[m/s]
Bed temperature	875	[°C]
Freeboard temperature	900	[°C]
d_p bed material	0.4 - 0.8	[mm]
Bed height (expanded)	0.95	[m]
Ca/S mol ratio	1.5	[-]
Coal type	Polish	
Limestone	Duwa-95	

Experimental program.

The NO_x reduction was measured as a function of the urea/NO_x molar ratio, the oxygen concentration and the height of the injecting point of the urea solution above the distributor plate on the NO_x reduction is investigated. Some experiments carried out with an ammonia solution to compare the NO_x reduction capacity of urea with that of ammonia. Finally it was investigated which urea/NO_x and NH_3/NO_x molar ratio gave rise to a slip of NH_3. The experimental program is given in table 3.

Remark: The urea/NO_x and the NH_3/NO_x molar ratio are related to the NO_x concentration in the flue gases 1 m above the distributor plate measured without urea or NH_3 injection for all experiments of table 3. The NO_x emission reduction is calculated from the emission level when no urea or ammonia is injected in the freeboard.

TABLE 3
Experimental program

Run	Reagent	Mol ratio	Injection height [m]	O_2 [vol.%]
1	urea	0 - 10	1	2.8
2	urea	4	0.5 - 1 - 2	2.8
3	urea	4	1	0.9 - 4
4	ammonia	0 - 4	1	2.8

2.5.3 Results and discussion

In figure 2.31 the measured NO_x emission is given as a function of the urea/NO_x ratio, fore urea injection 1 m above the distributor plate. These experimental results show that NO_x emission can be reduced from about 400 to 90 mg/m^3 (78%) by injection of an urea spray with a molar ratio urea/NO_x = 10, while the emission value of 200 mg/m^3 is reached at a molar ratio urea/NO_x = 2.

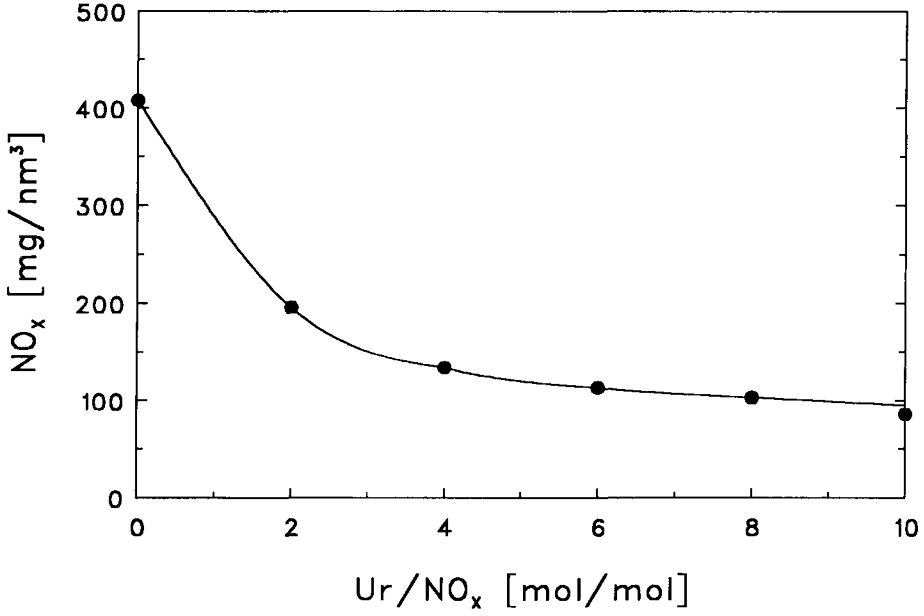

figure 2.31 NO_x emission as a function of the urea over NO_x molar ratio, Run 1, TU

Figure 2.32 shows the influence of the injection height of the urea spray on the NO_x reduction. As can be seen in this figure the injection of the urea spray at the height of 0.50 m above the distributor plate, so in the bed, gives much smaller reduction in the NO_x concentration than injection just above the bed. The best results, however, are achieved by injection at 2 m above the distributor plate, resulting in a reduction of 72.5 % of the NO_x emission at a molar ratio urea/NO_x = 4.

When the urea is injected in the bed, it will partly oxidize to NO_x which accounts for the smaller reduction of the NO_x emission.

The higher NO_x-reduction achieved by the injection at 2 m above the distributor plate can be explained by the lower NO_x concentration at the injection port caused by the reduction capacity of the freeboard itself (volatiles and char). The local urea/NO_x ratio is higher and subsequently the NO_x reduction is better. As is shown in figure 2.32, a ratio of urea/NO_x = 1.5 will be enough to achieve a NO_x emission level of 200 mg/nm^3.

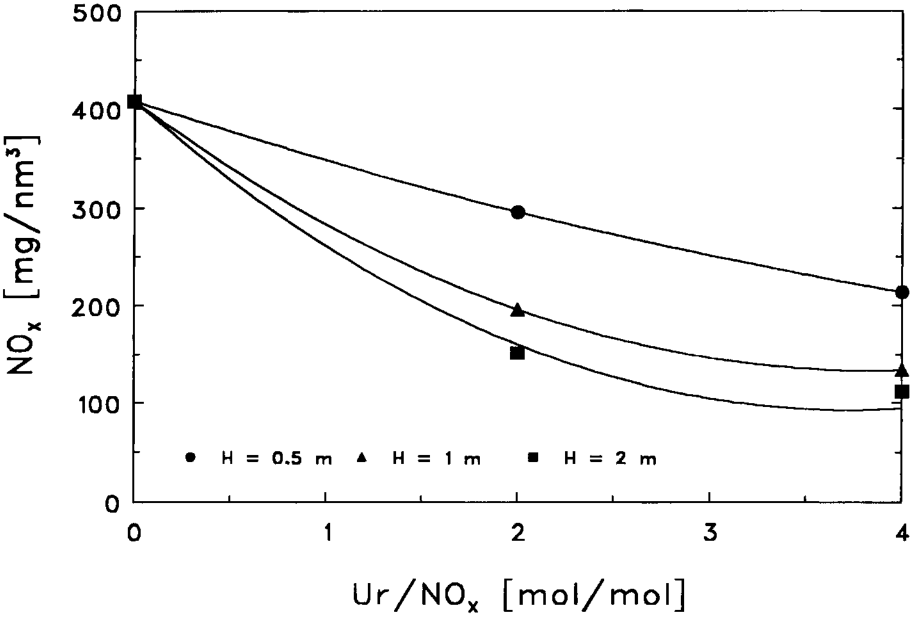

figure 2.32 NO_x emission as a function of the urea over NO_x molar ratio, for different heights of urea injection, Run 2, TU

The influence of the oxygen concentration on the NO_x reduction by urea is investigated at a molar urea/NO_x ratio of 4 and an injecting height of 1 m above the distributor plate. This influence on the NO_x reduction is significant (see fig. 2.33). This shows that at 0.9 % oxygen a 71 % reduction of the NO_x emission is reached (100 mg/m^3), while at 4 % oxygen a NO_x reduction of 65 % is achieved (135 mg/m^3).

A higher oxygen concentration probably gives rise to a higher formation of NO_x due to a higher degree of urea oxidation. The reduction of the NO_x emission at 4 %

O_2 is notable.

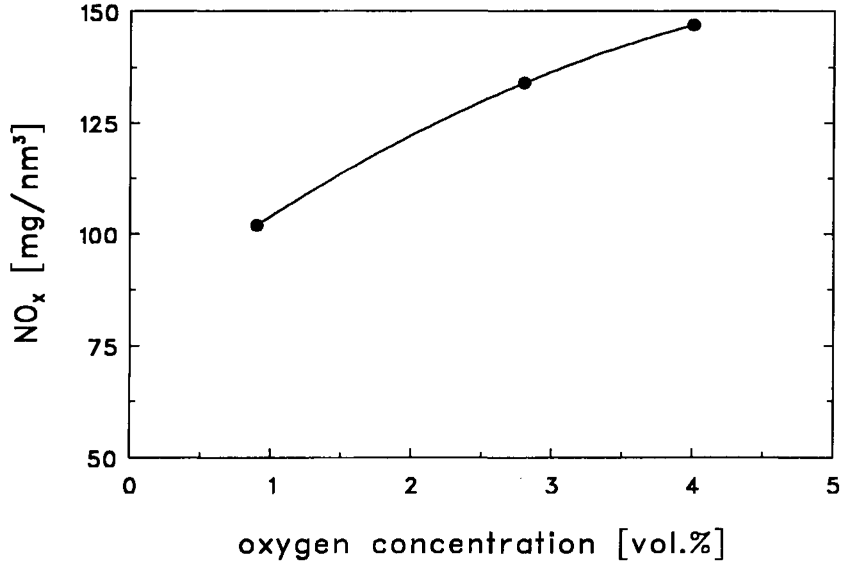

figure 2.33 Influence of the O_2 concentration on the NO_x reduction, urea over NO_x ratio = 4, run 3, TU

On comparing the NO_x reduction capacity of urea with that of ammonia, figure 2.34 shows that urea is at least as active as ammonia. This is an important result because urea is preferable to ammonia as a reducing agent.

Besides a reduction of the NO_x emission by injection of urea, we also found that above a molar ratio urea/NO_x = 4, the SO_2 emission was greatly reduced. The reason for this can be the overshoot of NH_3 in the freeboard resulting in a NH_3 slip through the freeboard. When there is NH_3 in the freeboard SO_2 can react with it resulting in the formation of $(NH_4)_2SO_4$ (ammonium sulphate). This will reduce the SO_2 concentration. Figure 2.35 shows that there is indeed a relation between the NH_3 concentration and the SO_2 reduction.

In trying to obtain evidence for this mechanism, we analyzed the ashes for ammonium ions. However, there were none present. So more research on this phenomenon is required.

An important fact is that urea has a much greater effect on the SO_2 reduction than ammonia. This is probably due to the higher concentration of NH_2 radicals formed by thermal dissociation of the urea. Another important fact is that when the molar ratio of urea/NO_x is smaller than 4, only the concentration of NO_x seems to be reduced, while the SO_2 concentration remains unchanged. Due to the fact that the NO_x emission of 200 mg/m^3 can be easily obtained on applying a molar ratio urea/NO_x = 2 the 'thermal selective reduction 'of NO_x by urea will only slightly affect the SO_2 emission level, without the formation of the corrosive ammonium sulphate salt.

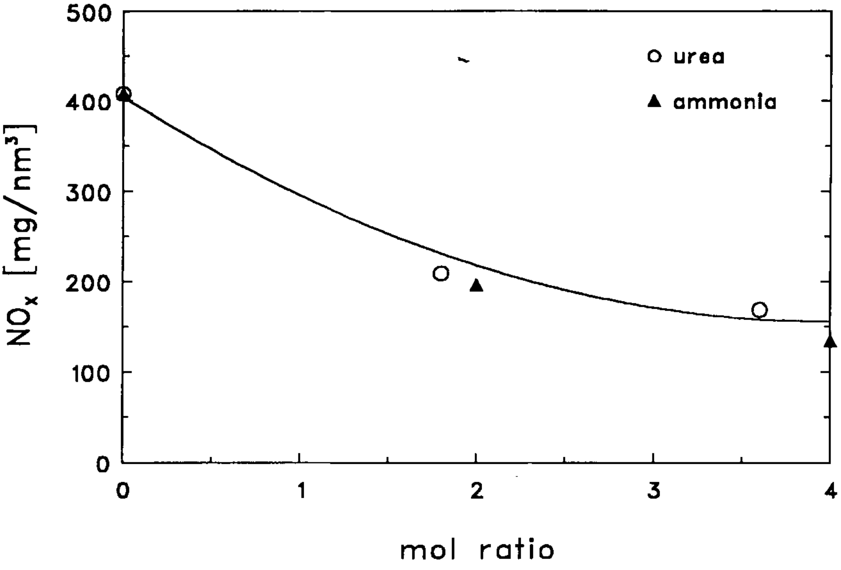

figure 2.34 The NO$_x$ reduction by the addition urea and ammonia, run 4, TU

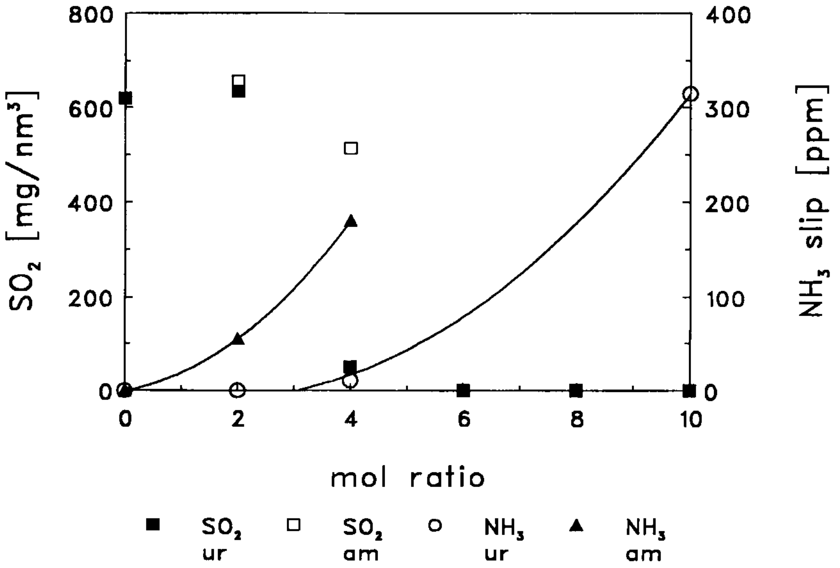

figure 2.35 SO$_2$ and NH$_3$ concentration as a function of the urea or ammonia over NO$_x$ ratio, run 1 and 4, TU

Later on urea injection was also tested during staged combustion experiments. During these tests pelletized carbonaceous material was used as fuel in the combustor. In figure 2.36 the NO_x is plotted versus the urea/NO_x ratio for unstaged as well as for staged combustion conditions. As we can see the urea is remarkable more effective in the NO_x reduction during staged combustion. Without staged combustion the NO_x decreases from about 700 to 350 mg/nm^3 (50 %) and during staged combustion from about 650 to 100 mg/nm^3 (85 %) at a urea/NO_x = 3.

The higher NO_x reduction efficiency at staged combustion conditions can be caused by improved mixing in the freeboard when secondary air in the freeboard is injected.

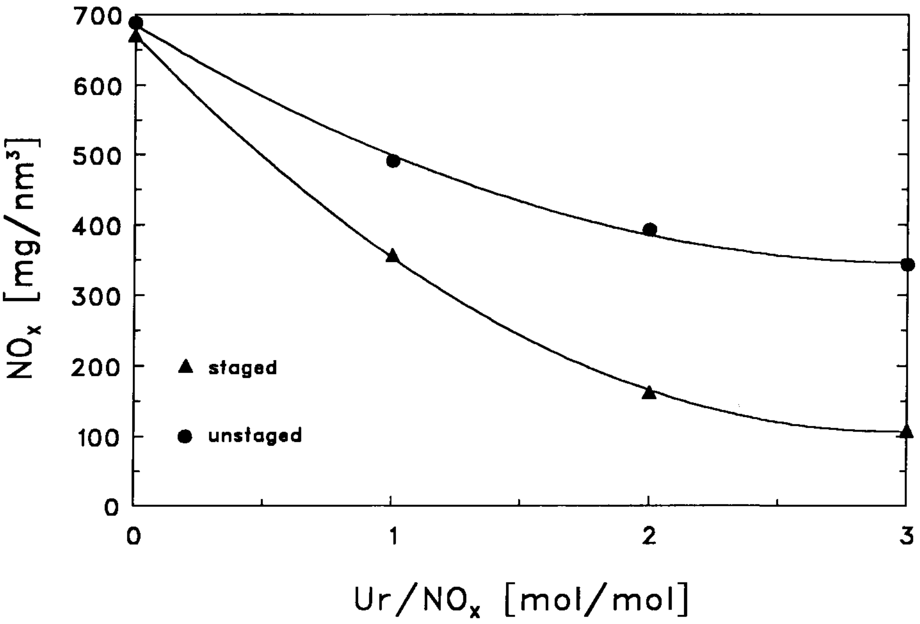

figure 2.36 NO_x emission versus urea/ NO_x molar ratio for staged as well as unstaged combustion,TU

2.5.4 Conclusions urea injection

- Thermal selective reduction is an effective measure to reduce the NO_x emission for FBC applications
- The freeboard of a AFBC has appropriate reaction conditions for the NO_x reduction by injection of urea or ammonia
- Urea is as effective as ammonia for the reduction of NO_x
- NO_x emission levels far below 200 mg/nm^3 are achievable by urea injection
- Formation of ammonium sulphate salt can occur for high urea/NO_x ratios
- Mixing in freeboard is very important for a satisfying NO_x reduction

2.6. EMISSIONS OF NITROUS OXIDE

2.6.1 Introduction

In the last years more attention is given to the emission of nitrous oxide (N_2O) from fossil fuel combustion. Nitrous oxide has two effects in the atmosphere. First, as a trace gas it contributes to the greenhouse effect and second it is an agent which can destruct the ozone layer in the stratosphere.

Due to the low combustion temperature FBC yields low NO_x emissions. However this low temperature results in remarkable amounts of N_2O in the off gases from fluidized bed combustors. N_2O emissions up to 500 mg/nm^3 are measured [27,28].

N_2O can be produced during combustion from the volatile nitrogen as well from the char nitrogen [29]. In figure 2.37 a simplified reaction scheme of the N_2O production and reduction is given. In the homogeneous gas phase (volatile combustion) HCN is an important intermedium for N_2O production. HCN reacts in the gas phase to give NCO which can react with NO producing N_2O. The most important destruction reactions for N_2O in the gas phase are the reactions with H and OH radicals.

During the combustion of char, N_2O can be produced from the char nitrogen, directly on the char surface or via HCN as intermedium. Additional N_2O can be produced by the reduction of NO on the char surface. The produced nitrous oxide can also be reduced on the same char surface, forming N_2. From literature it is not clear up to now which are the important reactions producing and reducing the nitrous oxide, it is also not known whether the volatiles, the char or both are important.

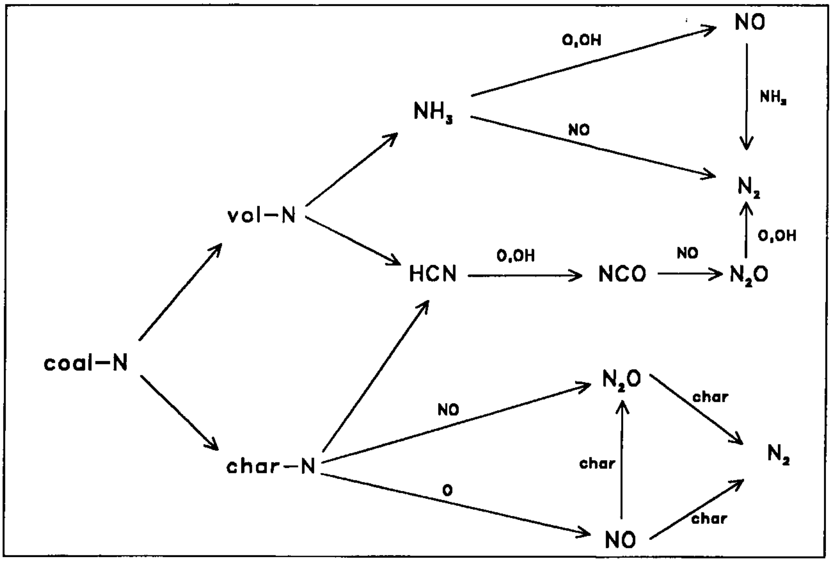

figure 2.37 Simplified reation scheme for N_2O production and reduction

In this section firstly a for this purpose developed continuous infrared measuring system for N_2O is presented. Secondly results from experimental research at TU and TNO is reported about the influence of the following process parameters:

- bed temperature
- staged combustion
- recycle ratio

2.6.2 N_2O Measurement

When measuring N_2O by grab sampling, some N_2O can be produced over time in the sample bags when SO_2, NO_x and condensed water is present [30]. For this reason we have tried to measure the N_2O on-line by a variable wavelength infrared spectrometer (Wilks, Miran-80). The analyzer is equipped with an adjustable long-path gas cell (0.75-20 meters), volume 5.4 litre. Before the sample gas flows through the analyzer it is dried first by an ice bath cooler and then completely dried by $CaCl_2$. The residence time in the sampling system is about 1.5 s. The analyzing and sampling system for N_2O measurement is shown in figure 2.38.

The most sensitive wavelengths for N_2O analysis are 4.5 and 7.8 μm. Unfortunately at these wavelengths other flue gas components can interfere, CO_2, CO at 4.5 μm and NO_2, SO_2 at 7.8 μm. For measurements at these wavelengths the interfering components must be removed by scrubbing or measured separately and calculated for their interfering effect. Scanning the N_2O spectra we found also absorption at 3.79 μm. At this wavelength the absorption is weak, but there is almost no interference from other flue gas components.

At this analytical wavelength of N_2O (3.79μm) the instrument was evaluated for interference from NO, SO_2 CH_4, CO and CO_2 at various concentrations. In figure 2.39 the interference from the different flue gas components are shown. This figure shows that only CH_4 gives significant error in the N_2O measurements at higher CH_4 concentrations. Normally the C_xH_y emission at fluidized bed combustion conditions is lower than 100 ppm so the CH_4 will not influence the N_2O measurement for FBC application.

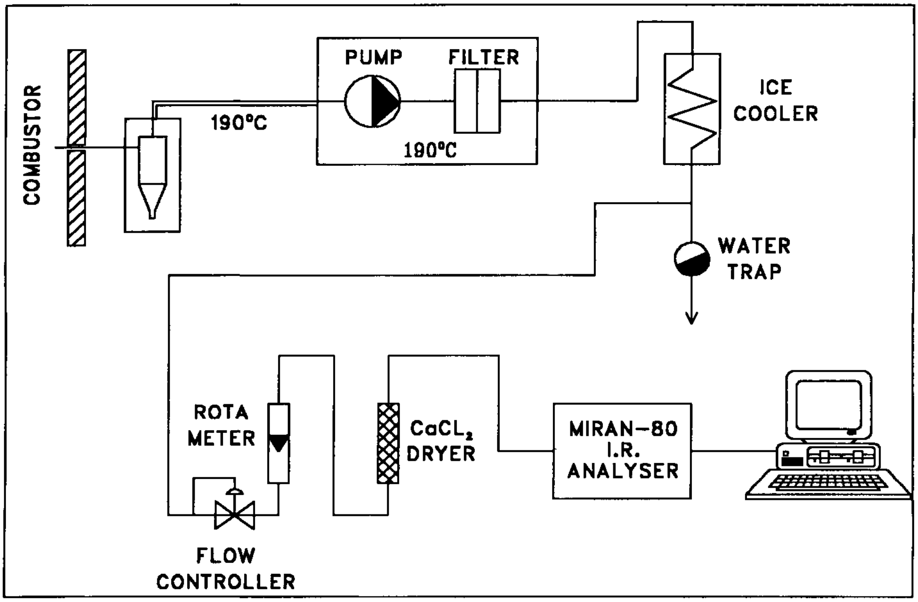

figure 2.38 N_2O sample preparation and measuring system, TU

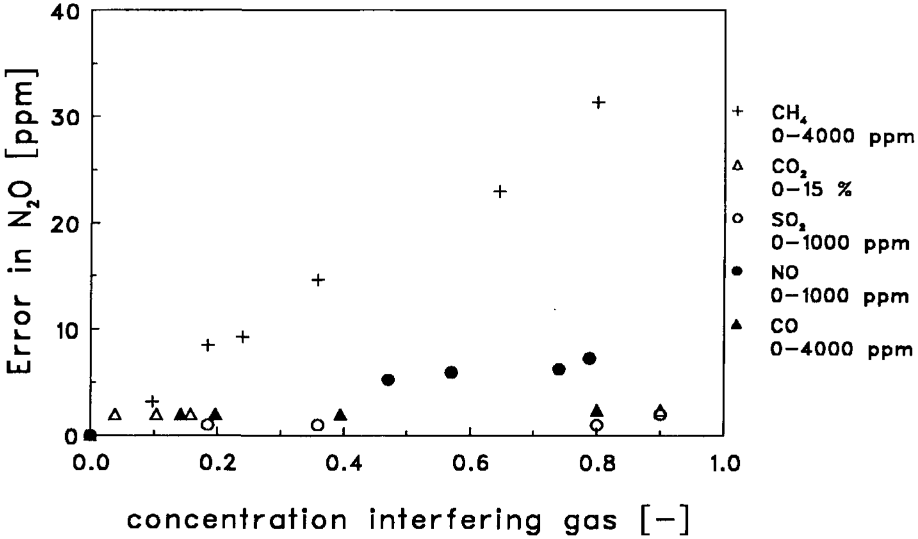

figure 2.39 Interference from other flue gas components at the analytical wavelength of N_2O (3.79μm). TU

2.6.3 Experimental program.

In the 1 MW_{th} fluidized bed combustor two experimental runs are carried out. The first one with a high volatile and the second one with a medium volatile coal, both with addition of limestone. For each coal type the influences of bed temperature, primary air ratio and recycle ratio on the emissions of N_2O are investigated. When changing one parameter all the others are kept constant. Table 4 shows the operating conditions.

TABLE 4
Experimental conditions

Constant process conditions:

fluidizing velocity = 2 [m/s]
bed height (expan.) = 1 [m]
air ratio = 1.2 [-]
mean particle size bed material = 0.7 [m]
Ca/S ratio = 1.5 [-]

Experimental variation:

				standard condition	
bed temperature	775	825	875	825	[° C]
primary air ratio	0.8	0.95	1.2	1.2	[-]
recycle ratio	0	0.75	1.5	0.75	[-]

2.6.4 Experimental results

The reported emissions of NO_x and N_2O are converted values in mg/nm^3 at 7% oxygen in the flue gases. The N_2O emission levels are given as N_2O and the NO_x emission as NO_2.

- Influence of bed temperature:

In figure 2.40 the N_2O and NO_x emissions are plotted versus bed temperature for the two different coal types. It can be seen that the bed temperature has an opposite effect on the emissions of N_2O compared to NO_x. Significant amounts of N_2O can be emitted by fluidized bed combustion especially at lower temperatures. At lower temperatures the emission of N_2O is at the same or even a higher level than the emission level of NO_x. These results are in agreement with other investigations, [27,28]. From the literature [28,31] it is known that coal types with higher volatile content emit less nitrous oxide. For the different coal types used here (volatile content: 19 % for the Illawara coal and 32.8 % for the El-Cerrejon coal) we can't see a clear difference in N_2O emission.

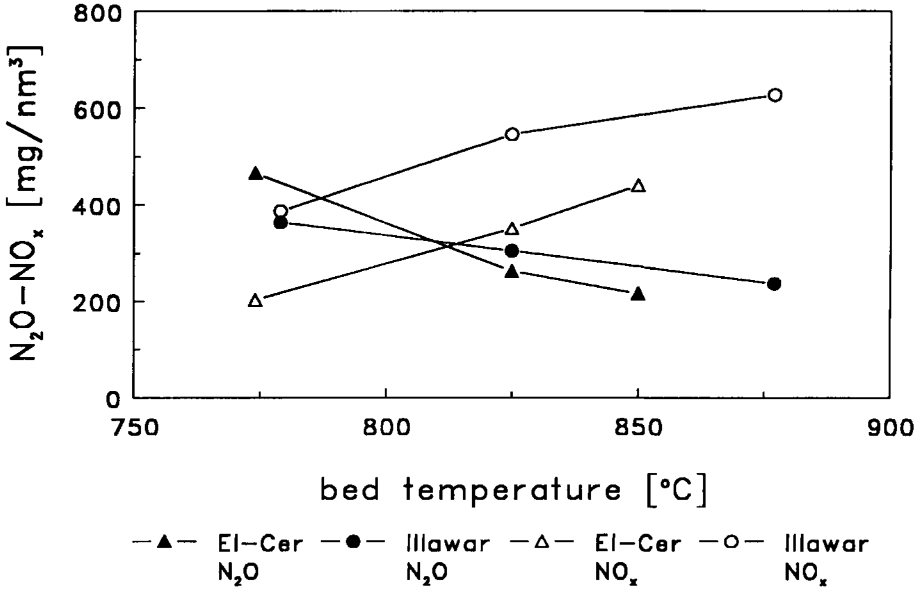

figure 2.40 The NO_x and N_2O emission versus bed temperature, R/C = 0.75, Ca/S = 1.5, air ratio = 1.2, TU

- Influence of the recycle ratio:

During some experiments the recycle ratio (R/C = recycled cyclone ash mass flow/coal mass flow) is varied, the results are plotted in figure 2.41. Due to the higher char content in the bed and freeboard section by increasing the recycle ratio, the NO_x emission is reduced. The N_2O emission however is increased by increasing the recycle ratio. The increase in N_2O at higher recycle ratios can partially be caused by the reaction of NO_x over char in the bed and freeboard producing nitrous oxide. This suggestion is supported by the results from concentration measurements in the freeboard, figure 2.42. In this figure the NO_x and N_2O concentrations at two different heights in the freeboard are plotted for three recycle ratios. Increasing the recycle ratio results in a higher freeboard NO_x reduction but at the same time a higher N_2O production. At higher recycle ratios the freeboard temperature becomes higher, this increase in freeboard temperature has probably an opposite effect on the N_2O production in the freeboard as shown by the TNO experiments presented below.

One of the trends discussed here, an increase of the N_2O and a decrease of the NO concentration with freeboard height was found in a circulating fluidized bed by Moritomi [28].

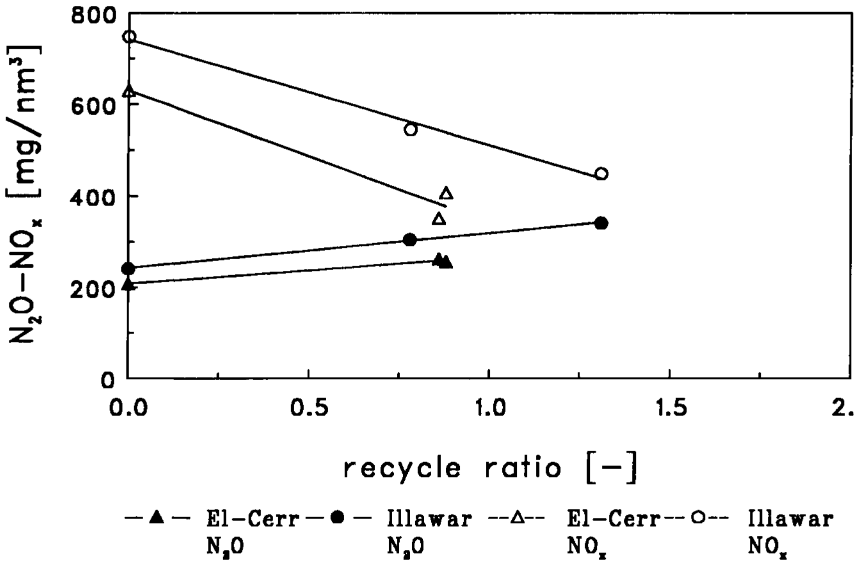

figure 2.41 The NO$_x$ and N$_2$O emission versus the recycle ratio, air ratio = 1.2, T_{BED} = 825 °C, Ca/S = 1.5, TU

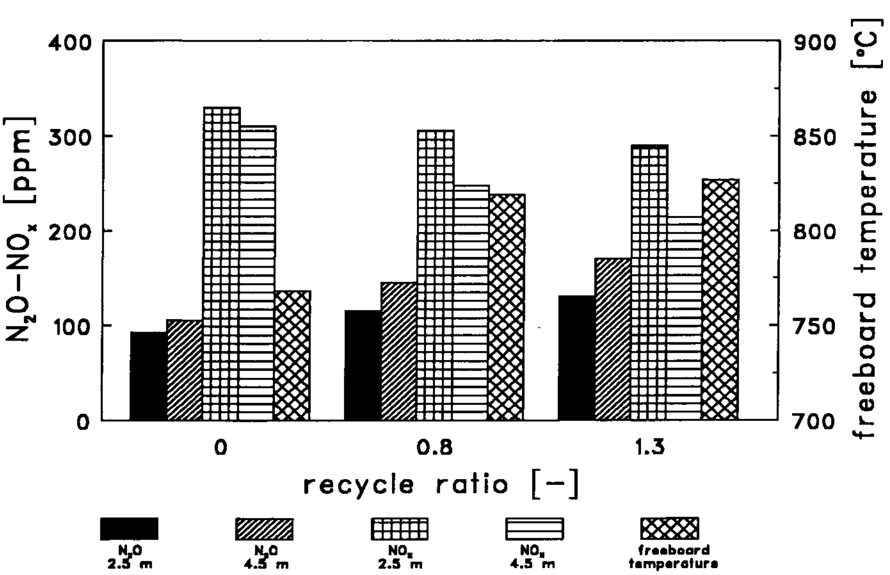

figure 2.42 The NO$_x$ and N$_2$O concentration at different heights in the freeboard and the freeboard temperature for three R/C ratios, El-Cerrejon coal, TU

Experiments in the TNO combustor show the opposite effect of recycle on the N_2O emission. These experiments are executed under staged combustion conditions and the freeboard temperature is higher compared to the experiments done at the Twente University. At these higher freeboard temperatures the thermal decomposition of N_2O causes probably the lower N_2O emission.

In figure 2.43 the N_2O emission is given as a function of the freeboard temperature, the freeboard temperature is however not an independent parameter but correlated with the recycle ratio as given in this figure.

The N_2O emission decreased with an increase of freeboard temperature and recycle ratio.

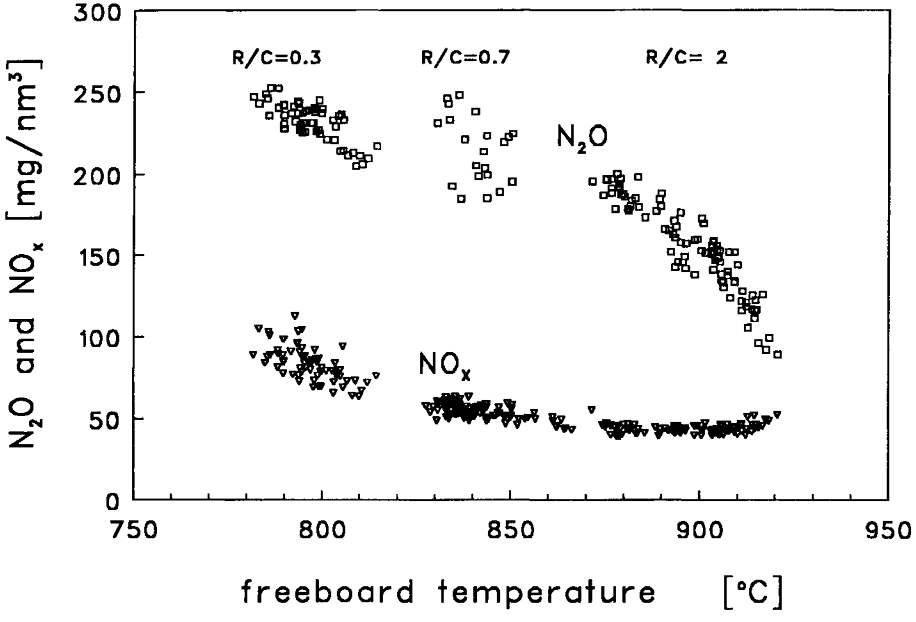

figure 2.43 The NO_x and N_2O emission versus freeboard temperature Venezuela coal, T_{BED} = 820 °C, staged combustion, TNO

Influence of the primary air ratio

The emissions of N_2O and NO_x versus the primary air ratio are given in figure 2.44. This figure shows that staged combustion lowers both emissions of N_2O and NO_x. The NO_x emission decreases from 550 to 375 mg/nm³ by decreasing the primary air ratio from 1.2 to 0.8 for the Illawara coal and from 325 to 200 mg/nm³ by increasing the primary air ratio from 1.2 to 0.85 for the El-Cerrejon coal. The NO_x emission from the high volatile El-Cerrejon coal is significant lower than the NO_x emission for the medium volatile Illawara coal.

The N_2O emission decreases from 310 to 230 mg/nm³ for the Illawara coal and from 270 to 240 mg/nm^3 for the El-Cerrejon coal for the same variation of the primary air ratio. At staged combustion the concentration of char and volatiles in the bed and the freeboard increases. These components are probably promoting the N_2O reduction.

Under staged combustion conditions the N_2O reduces in the freeboard as opposite to unstaged combustion. Here we find a production of N_2O in the freeboard. The freeboard temperature decreases for lower primary air ratios, see figure 2.45.

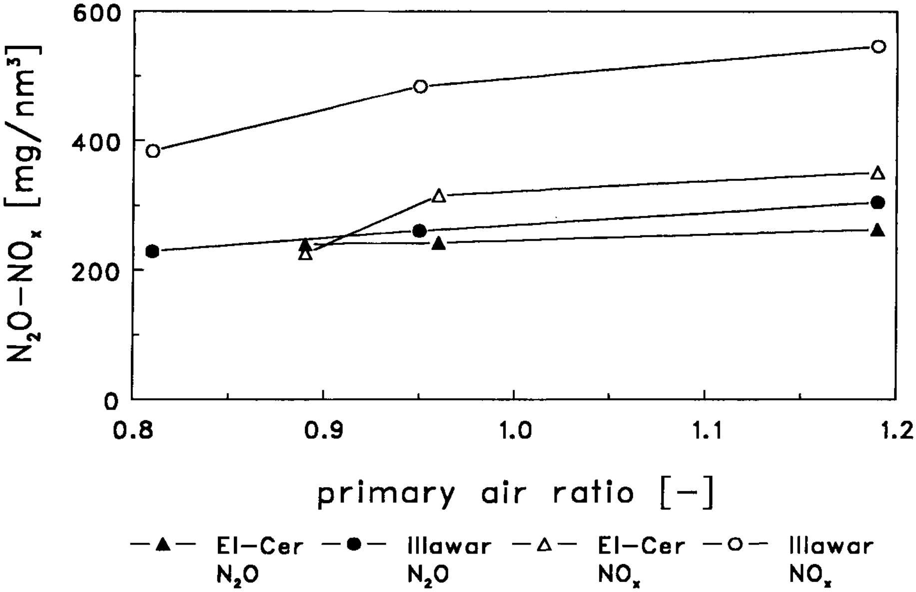

figure 2.44 The NO_x and N_2O emission versus the primary air ratio, total air ratio = 1.2, T_{BED} = 825 °C, R/C = 0.75, TU

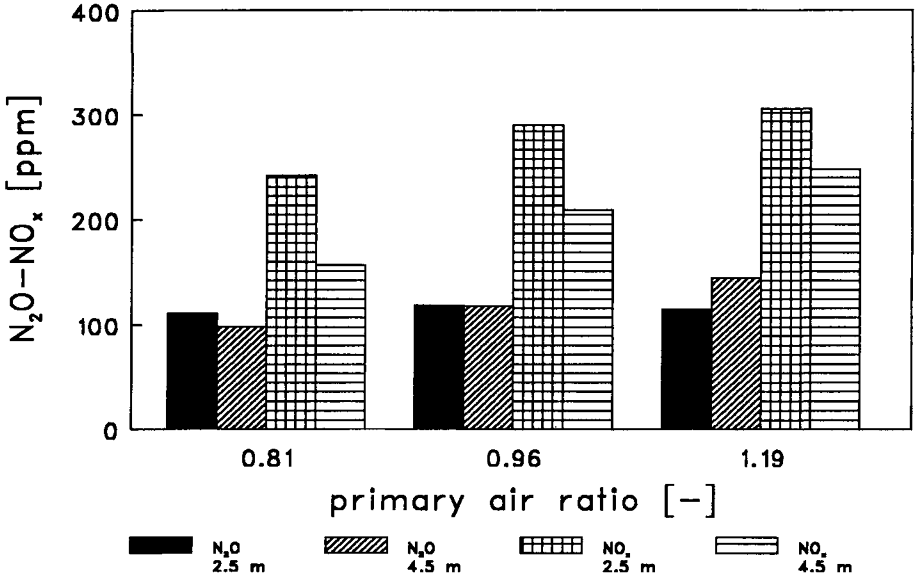

figure 2.45 NO_x and N_2O concentrations at different heights in the freeboard for three primary air ratios, El-Cerrejon coal, T_B = 825 °C, R/C = 0.7, TU

2.6.5. Conclusions nitrous oxide emissions

- At fluidized bed combustion, significant amounts of N_2O can be emitted, 400-500 mg/nm^3 N_2O are measured.
- At higher bed temperature the N_2O emission decreases and the NO_x emission increases
- Staged combustion lowers both emissions of N_2O and NO_x

2.7. EMISSIONS OF CO, HCl, HF, and PAH

2.7.1. Carbon monoxide

For combustion plants the carbon monoxide emission is not yet restricted by standards in the Netherlands. In the near future however a standard for CO of < 250 mg/nm^3 is expected, the same value as the present standard in the Federal Republic of Germany.

The emission values for carbon monoxide are measured under different process conditions in the TNO combustor, some of the results are presented here.

Under unstaged combustion conditions the carbon monoxide emission is in the range of 200 to 500 mg/nm^3. In figure 2.46 the carbon monoxide emission is given versus the recycle ratio. The carbon monoxide emission is increased from about 200 without recycling to 400 mg/nm^3 with recycling of fly ash. The recycled fly ash burns mainly in the freeboard of the combustor [2], this freeboard combustion produces additional carbon monoxide which is not completely converted to carbon dioxide. At higher recycle ratios the freeboard temperature increases resulting in lower carbon monoxide emissions.

Under staged combustion condition the carbon monoxide emission is significant higher compared to unstaged combustion conditions as shown in figure 2.47. Higher bed temperatures, consequently also higher freeboard temperatures, can lower the carbon monoxide emission, 1000 mg/nm^3 at 800 °C to 600 mg/nm^3 at about 850 °C.

The values measured in the TNO combustor are rather high compared to the German standards. Freeboard temperature, residence time in the freeboard and the degree of gas mixing in the freeboard will be the main parameters for lowering the carbon monoxide emission. The size of combustor has a great influence on these parameters. An increase of the bed area to wall area ratio improves the freeboard mixing and increases the freeboard temperature. Carbon monoxide emission values from the 90 MW$_{th}$ boiler at AKZO, similar design as the TNO combustor, shows these scale effects. In this boiler a 2 years average value of 115 mg/nm^3 is measured [32].

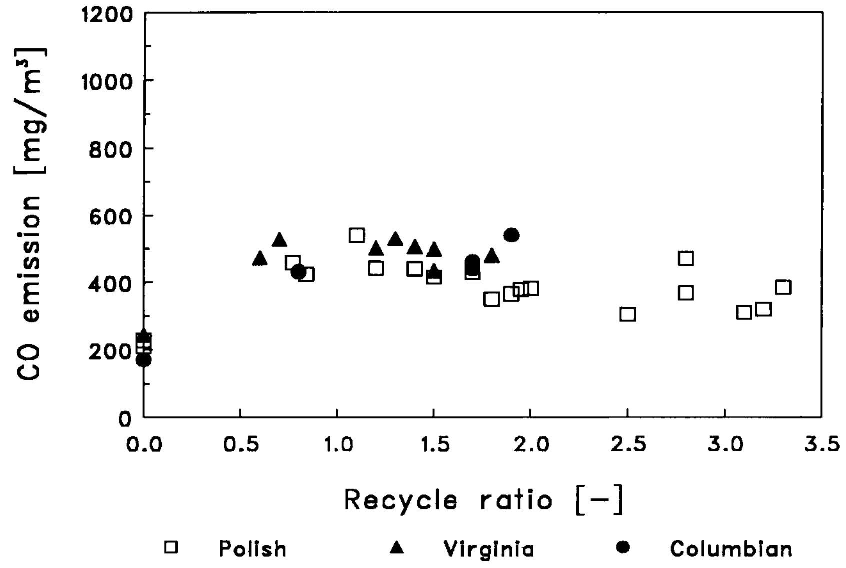

Figure 2.46 The CO emission versus the recycle ratio, air ratio =- 1.2, T_{BED} = 850 °C, TNO

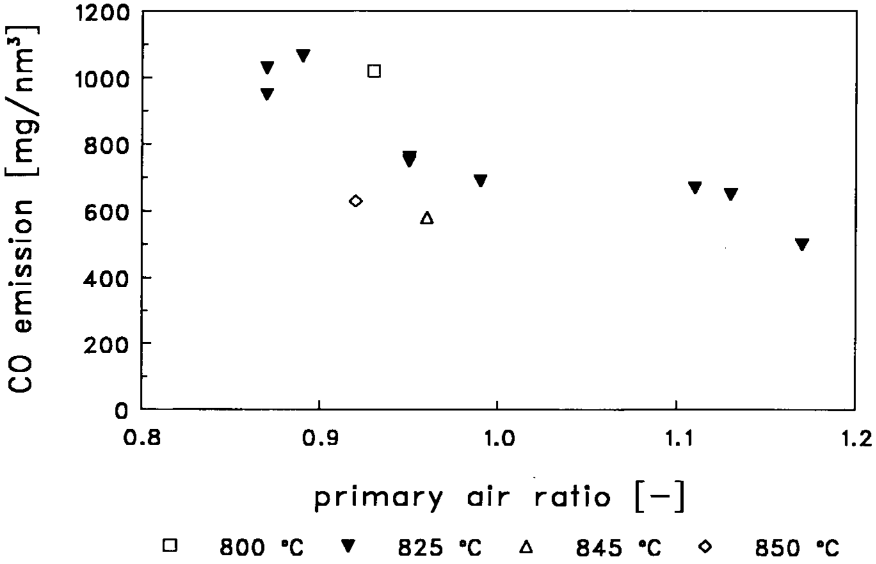

Figure 2.47 The CO emission versus primary air ratio, Polish coal, R/C = 2, TNO

2.7.2. HCl and HF emissions

Beside sulphur dioxide and nitrogen oxide also the acidic gases hydrogen chloride and hydrogen fluoride can be formed during the combustion of coal. The typical halogen content of coal is: 0.1 wt.% chloride and 0.01 wt.% fluoride.

The halogens are present in the mineral matter of the coal and are transformed to HCl and HF by pyrohydrolysis [33]:

$$CaCl \quad + \quad H_2O \quad \text{——>} \quad 2HCl \quad + \quad CaO$$

$$CaF_2 \quad + \quad H_2O \quad \text{——>} \quad 2HF \quad + \quad CaO$$

The equilibrium concentrations of HCl and HF related to the reactions with CaO are given in figure 2.48. The equilibrium partial pressures are depending on temperature and water content. Under fluidized bed combustion conditions (850 °C and 5 % H_2O) the equilibrium partial pressures are about 100 ppmV for HF and about 2000 ppm for HCl. This means that the capture of these halogens components can not occur within the bed section. HCl and HF can only react with CaO downstream the freeboard where the flue gases are cooled down. In most cases the reaction time in this section is short.

At TNO experimental research was done on the halogens capture by limestone. A Polish coal was used with a simulated high chloride content of 0.35 wt.%, which was achieved by adding sodium chloride to the coal. Two limestone types are used, Carmeuse Engis and Dammann Kreide. Both have been added under bed as well as over bed. In figure 2.49 the HCl retention is plotted versus the calcium over chloride molar ratio (Ca/2Cl). With the less reactive Carmeuse Engis (also less reactive for sulphur capture) a HCl retention of 80 % was achieved when the Ca/2Cl ratio was increased to 25 and for the more reactive Dammann Kreide 77 % retention at a Ca/2Cl ratio of 18. These amounts of limestone correspond to Ca/S = 5.6 and Ca/S = 4.1 respectively when considered for sulphur capture. The amount of limestone is rather high related to the sulphur capture, which is in agreement with laboratory experiments of Münzner et. al [33]. Experimental results from Münzner showed also that fluorine capture is much better than chlorine capture.

There was no significant difference in chlorine capture between in-bed and over-bed feeding of limestone.

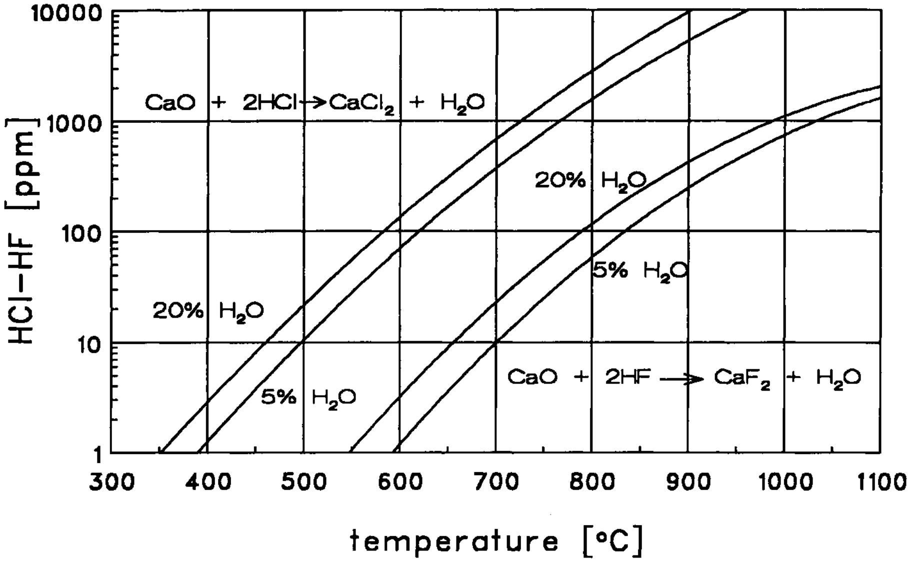

Figure 2.48 The equlibrium concentrations of HCl and HF versus temperature

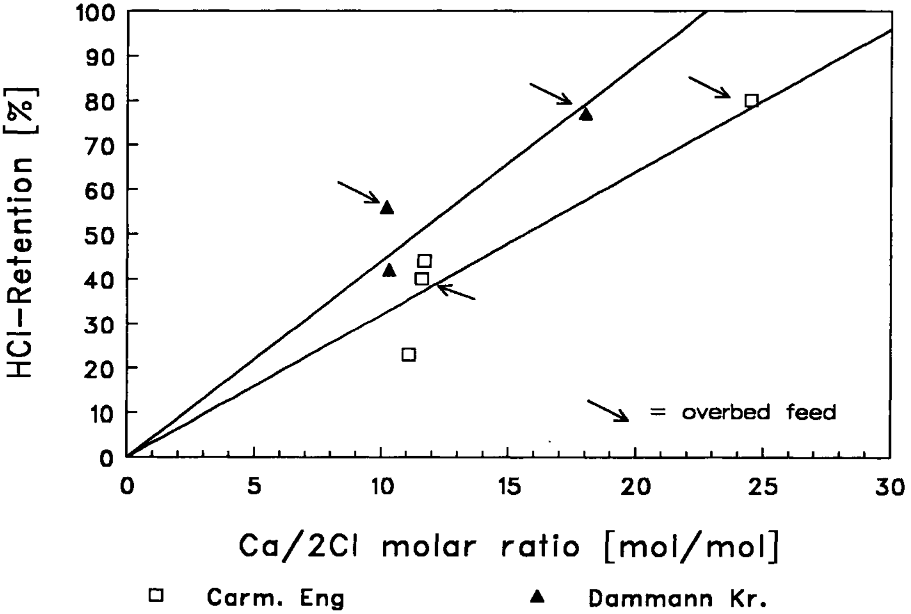

Figure 2.49 The HCl retention versus the molar Ca/2Cl ratio, Polish coal, T_{BED} = 820 °C, TNO

2.7.3 PAH Emissions

Polycyclic Aromatic Hydrocarbons (PAH) emissions were measured in the TNO combustor under unstaged combustion conditions [34]. The PAH emission values where between 100 and 720 ng/nm^3, with a mean value of 340 ng/nm^3. The measured emission values of Benzo(a)pyrene varied between 0.3 and 3μg/GJ with a mean value of 0. 7 μg/GJ. The emission levels under staged combustion conditions are almost of the same order as under unstaged combustion conditions. The PAH emissions from fluidized combustion are about five times lower compared to conventional coal fired power plants [35,36]

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