EMISSIONS OF NITROUS OXIDE (N2O) FROM FLUIDIZED BED BOILERS

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Proceedings of the

1989 INTERNATIONAL CONFERENCE ON FLUIDIZED BED COMBUSTION

FBC — TECHNOLOGY FOR TODAY

10TH

Volume One

held in
SAN FRANCISCO, CALIFORNIA
APRIL 30—MAY 3, 1989

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

edited by
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EMISSIONS OF NITROUS OXIDE (N_2O) FROM FLUIDIZED BED BOILERS

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ABSTRACT

Measurements of emissions of nitrous oxide (N_2O) have been carried out on two kind of fluidized bed boilers. One of them, a circulating fluidized bed boiler has been run with three kind of fuels at different operating conditions. The results of the measurements show that the emission of N_2O depends on bed temperature and fuel. The temperature dependence is explained by the strong influence of temperature on the rate of destruction of nitrous oxide by radicals in the gas phase.

INTRODUCTION

Nitrous oxide (N_2O) is created from natural and anthropogenic processes, one of which is combustion. The deleterious effect of the N_2O emissions has only recently been considered. For this reason N_2O has not been investigated as thoroughly as NO and NO_2. A description of the environmental effects as well as results from different combustion facilities have been presented at three workshops on N_2O (EPA Workshop ..., 1986, EPA/NOAA ..., 1988, European Workshop, 1988). At the last workshop, it was concluded that the emission level from a coal—fired fluidized bed boiler (FBB) is 50—200 ppm, but it is only 1—20 ppm in boilers equipped with other types of combustion devices. For this reason, it is worthwhile to investigate the emissions from FB boilers more thoroughly. The present work is a first step in that direction.

FORMATION AND DESTRUCTION OF N_2O

The formation and destruction of N_2O are not well understood. For gas flames, where the chemical reactions are homogeneous, there are reaction schemes available which give reasonable guidance (Kramlich et al., 1988), but the knowledge of the heterogeneous processes, such as may occur in pulverized coal flames or in fluidized beds, is poor. In a fluidized bed there is not only coal present but also sand and limestone, making interpretation even more difficult.

It has been shown (Bowman, 1988) that HCN is an important compound for production of N_2O. HCN originates from the devotilization of the fuel and so it exists in solid fuel combustion systems. In a flame, N_2O is produced from HCN in the fuel—rich, high temperature zone, but it is almost immediately removed due to the fast reactions between N_2O and hydrogen radicals. This reduction of N_2O depends largely on temperature.

The heterogeneous reactions involving N_2O are:
- N_2O reduction on char surfaces
- N_2O formation through reaction of NO with char nitrogen
- N_2O formation from the char nitrogen during combustion.

Kramlich et al. (1988) have investigated the two last ones for post—flame conditions. His conclusion is that they give insignificant contributions to the N_2O

emission. It is not obvious whether this conclusion can be extrapolated into the temperature range typical of fluidized beds. However, this temperature range has been covered by de Soete (1989). He concludes that all three reactions are important. In addition, his results show that N_2O and NO are formed from the char nitrogen during combustion at a rate proportional to the rate of combustion.

EXPERIMENTAL

In order to investigate the N_2O emissions from commercial—scale fluidized bed boilers, two test series were carried out, one in a circulating fluidized bed boiler (CFBB) and one in a stationary fluidized bed boiler (SFBB). The boilers were run with different fuels under different operating conditions.
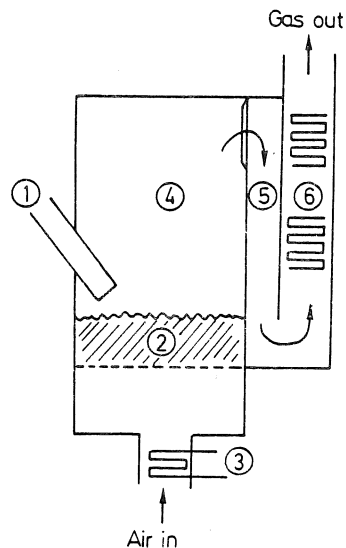
The Boilers

Most of the tests were run in an 8 MW CFBB designed and built by Götaverken Energy in 1981. The features of the boiler are shown in Fig.1a.
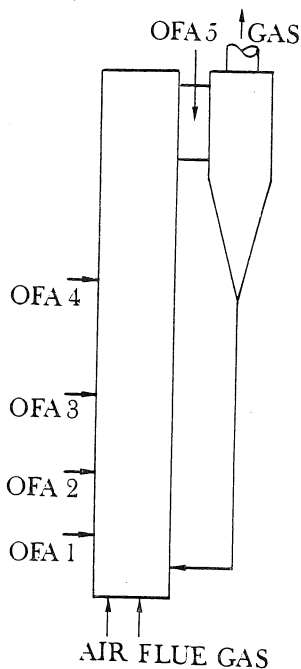
The height of the combustion chamber is 8.5 m and the cross—section is about 1.8 m². The fluidizing velocity is normally in the range of 3 to 6 m/s. The fuel is fed with a screw at the bottom of the combustion chamber. Particles are recirculated by a hot cyclone to the combustion chamber. Secondary air can be supplied through four registers, but only the lowest one was used during the present tests. The bed temperature is controlled by recirculation of flue gases to the bottom of the combustion chamber. Silica sand was used as a bed material and no limestone was added during the N_2O program.

A few tests were run in the 16 MW SFBB at Chalmers University. The features of this boiler are shown in Fig.1b. The characteristic data are: cross—section 10 m², bed depth 1 m, height of freeboard 4 m, fluidizing velocity 1.5 m/s. The fuel is fed on to the surface of the bed through an inclined fuel duct. Except for one test run, an old bed of lime containing CaO and $CaSO_4$ was used, which may have influenced the conversion of fuel nitrogen to nitrous oxide, but this needs further investigation.

1	Fuel feed chute
2	Fluidized bed
3	Steam air—preheater
4	Freeboard
5	Empty gas pass
6	Convection gas pass

a)   Götaverken   b)   Chalmers

Fig. 1   Schematic picture of the boilers.

The Fuels

Three fuels were used: a brown coal from the German Democratic Republic, a bituminous coal from Pennsylvania (USA) and a petroleum coke from a Dutch oil refinery. The fuel characteristics are listed in Table 1. During the runs with the SFBB the brown coal was not available.

The Tests

In the CFBB a parameter study of the influence of bed temperature, primary air stoichiometry and excess air ratio was carried out during constant load of the boiler. A reference case is defined by a bed temperature of 850^0C, a primary air stoichiometry of 0.75, and an excess air ratio of 1.2. Each parameter was changed around this reference case while keeping the two others constant, if needed, by means of flue gas recirculation. In addition, a closer study on the bituminous coal included:

a) measurement of the concentration of gases in the combustion chamber as well as at the exit of the boiler,
b) addition of nitric oxide to the fluidizing air,
c) addition of ammonia to the fluidizing air and to the inlet of the cyclone.

In the SFBB the reference case was run with bituminous coal. Additional tests involved change of bed temperature and excess air ratio with petroleum coke as a fuel.

MEASUREMENT OF NITROUS OXIDE

In this project the N_2O samples were taken and analyzed in the following way:

The water vapor of the flue gas was removed by condensation and subsequently the gas was passed through a Perma—pure drier. After that the gas holds a water content corresponding to a saturation pressure of 4 Pa and it can therefore be considered to be dry.

The samples were then stored in bags made of aluminium foil, covered on both sides with two layers of plastic, the innermost of which is polyethylene. For practical reasons the time of storage was between 6 and 15 hours. The analyses were made by the Swedish Environmental Research Institute (IVL) on a Varian 3300 GC equipped with an EC detector and a 10 m Pora Plot Q fused silica column from Crompack, Middelburg, the Netherlands.

Table 1   The Fuels

Type	Brown coal	Bituminous coal	Petroleum coke
Size, mass mean, mm	*	6.5	7
% smaller than 1 mm	0	11	14
Volatiles % maf	57	35	14
Proximate analysis, %			
Combustibles	80	87	91
Ash	5	7	2
Moisture	15	6	7
Ultimate analysis, % maf (preliminary)			
C	70	85	92
H	5	6	4
O	23	6	0
S	0.8	1.6	1.8
N	1.3	2.1	1.7

*   The brown coal was supplied as uniform cylinders, diameter 60 mm, length 35 mm.

An important question is whether there was any transformation from NO to N_2O in the samples. It is known from the European Workshop on N_2O Emissions (1988) that the storage of moist gases which contain SO_2 and NO may result in a production of N_2O. However this may also occur during the storage of dry gases containing SO_2 and NO. De Soete (1988) has studied this problem with dry gas samples stored in stainless steel vessels. According to these investigations, no transformation to N_2O occurs in 65 ppm SO_2 if the NO concentration is less than 300 ppm, but a 2% transformation of NO can be expected in dry samples containing 600 ppm NO and 1000 ppm SO_2. In the worst case this would lead to a production of 8 ppm N_2O in the data presented below.

During the test program double samples were taken on some occasions. These samples gave the same results. Double tests were also made during the reference cases of the boiler on different days and N_2O samples were stored for different times with no difference in N_2O concentration. We therefore believe our measurements of N_2O to be safe enough to form a basis for a conclusion on N_2O levels and emission trends in fluidized bed combustors.
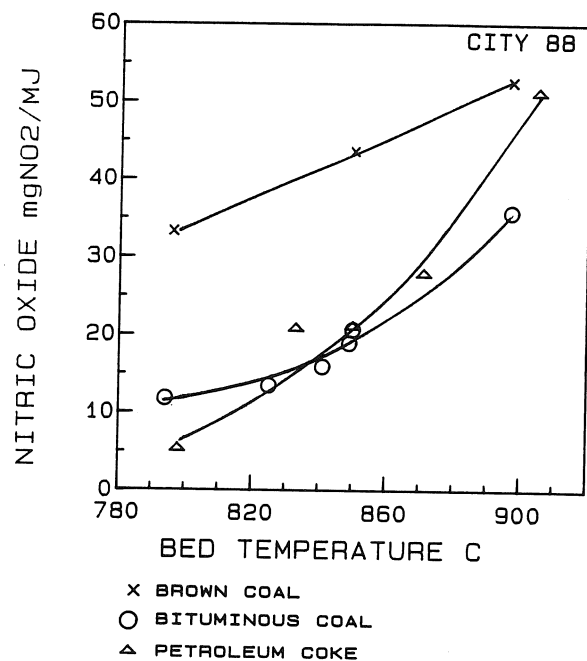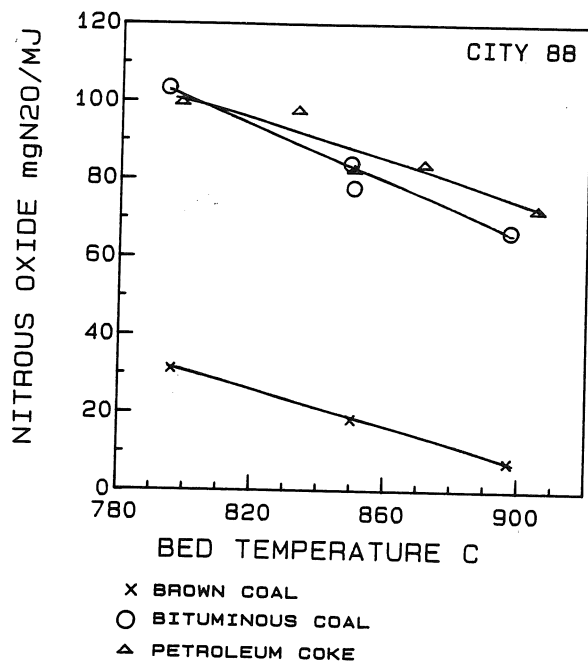
Fig. 2   Emissions of N_2O (mg N_2O/MJ) and NO (mg NO_2/MJ) versus bottom bed temperature in the CFBB. Excess air ratio: 1.2. Primary air stoichiometry: 0.75. (Note the different scales of the vertical axes).

RESULTS FROM THE CIRCULATING FBB

Influence of Fuel and Bed Temperature

Fig.2 shows the emissions of nitrous oxide (N_2O) and nitric oxide (NO) plotted versus bed temperature for the three fuels. The emission of nitric oxide is expressed as mg NO_2/MJ fuel supplied, and for nitrous oxide as mg N_2O/MJ fuel supplied. (1 mg N_2O/MJ $\longleftrightarrow$ 1.7 ppm N_2O at 6% O_2 and 1 mg NO_2/MJ $\longleftrightarrow$ 1.6 ppm NO at 6% O_2).

The following remarks can be made:

- The emission of nitrous oxide is always higher than the emission of nitric oxide, except in the case of brown coal.
- The influence of bed temperature on the emission of nitrous oxide is different from that of nitric oxide. This conclusion is valid for all fuels.

The conclusion is that the levels of emission, are in this case with a sand—ash bed:

- Below 50 mg NO_2/MJ for all fuels and the entire range of bed temperature;
- Between 10 and 30 mg N_2O/MJ for brown coal and 70 to 100 mg N_2O/MJ for bituminous and petroleum coke.
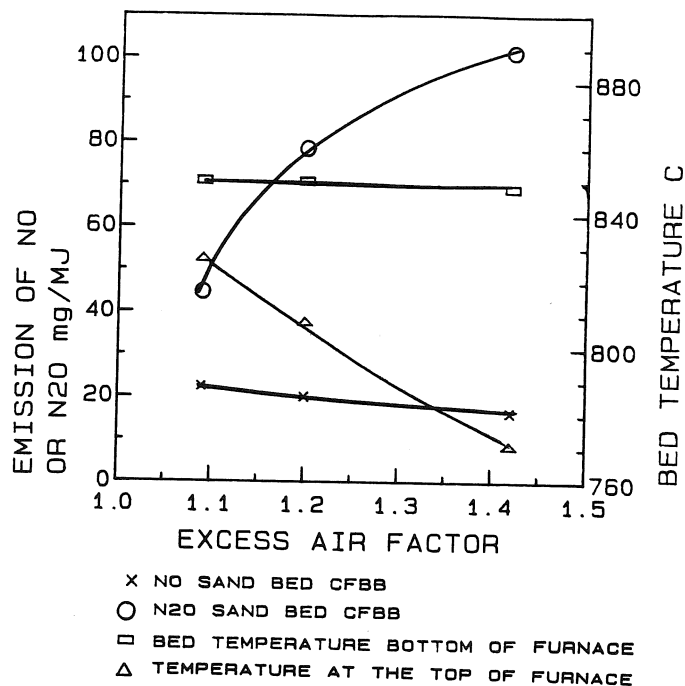

Fig. 3   Emissions of NO (mg NO_2/MJ) and N_2O (mg N_2O/MJ) versus excess air factor in the CFBB. Bottom and top temperatures are also shown. Fuel: Petroleum coke.

Influence of Excess Air Ratio and Primary Air Stoichiometry

In Fig.3 the influence of excess air ratio on the emission of NO and N_2O is given for the petroleum coke. N_2O rises sharply at higher excess air ratios, whereas the NO concentration is almost constant. It is seen from the figure that the bottom bed temperature has been kept constant but the top temperature declined in runs with higher excess air ratios. This drop in top temperature contributes to the rise in N_2O emissions in accordance with the temperature dependence already shown in Fig.2a. The problem with changing top temperatures is the same for all fuels. The conclusion is that the N_2O emission is very sensitive to changes of temperature in the entire combustion chamber (and probably also in the cyclone).

Concentrations of NO and N_2O in the Furnace

In Fig.4 the concentration of NO and N_2O is plotted versus the height above the primary air nozzles of the combustion chamber. The fuel used was bituminous coal and the boiler was operated at the reference case.

As can be seen, the NO and the N_2O gradients in the furnace are quite different. The NO concentration is high at the bottom, and decreases up through the furnace, whereas the N_2O concentration increases slightly. If the fact that secondary air is introduced at 1 to 2 meters above the bottom air—nozzles is taken into account, the ppm values in the lowermost part of the combustion chamber are not comparable to those higher up. If the measured ppm values are transformed to ppm based on the total air flow (or mg/MJ), the concentrations at the bottom become considerably lower than those shown in Fig.4, only 60% of the values presented. Thus the NO concentration does not decrease up through the furnace as much as is seen from the figure, but the N_2O increase becomes more marked.

Addition of Nitric Oxide to the Fluidizing Air

The tests with NO addition were performed during reference case operation of the boiler. Measurements of emissions were made before and during NO addition and the difference is presented in Fig.5, which shows the excess emission of NO and N_2O expressed as % of the NO added for the three runs. Two important observations can be made.

- Clearly detectible amounts of N_2O as a result of the NO addition are observed in all three runs.
- The amounts of N_2O produced are larger for the higher char loadings, as illustrated by the case of petroleum coke.
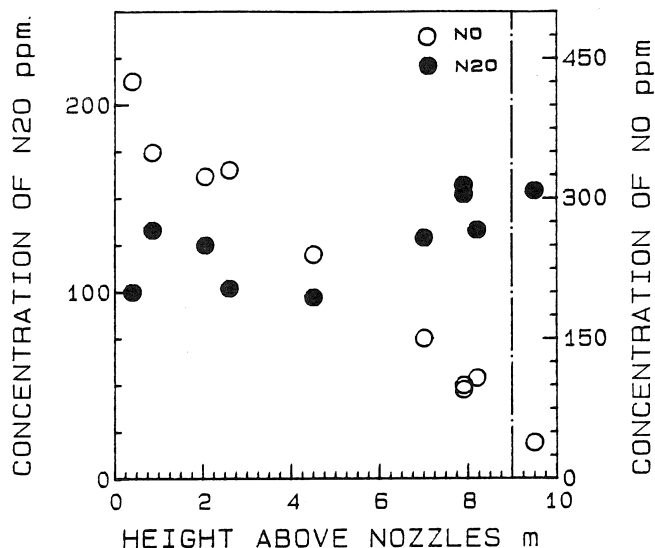
Fig. 4   Concentrations of NO and N_2O up along the gas path through the furnace of the CFBB. The entrance of the cyclone is indicated at 9 m. Fuel: Bituminous coal.
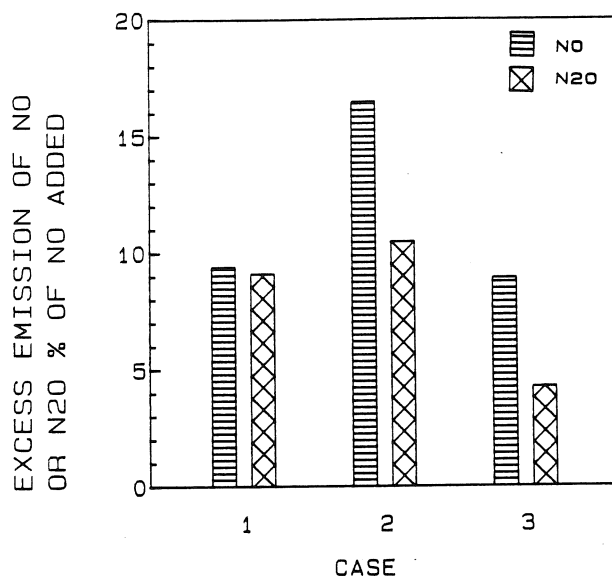
Fig. 5   Excess emission of NO and N_2O during NO injection into the primary air duct of the CFBB.

1.   Petroleum coke, 1200 ppm NO related to total air
2.   Petroleum coke, 2200 ppm NO related to total air
3.   Bituminous coal, 2200 ppm NO related to total air

Addition of Ammonia to the Combustion Chamber of the CFB

Ammonia was injected at one occation with a molar ratio, NH_3/NO_{exit}, larger than 10 and at a combustion chamber temperature of 800^0C, together with recirculated flue gas to provide sufficient momentum for jet penetration. There was no change in the N_2O emission in all cases when ammonia was supplied to the combustion chamber. This cannot be directly translated to the conditions of injection of ammonia into a homogeneous gas stream, since the ammonia is most likely broken down in contact with the particles of the fluidized bed.

RESULTS FROM THE STATIONARY FBB

Reference Case of a Bed of Silica Sand

Only one test run was carried out in the SFBB with bituminous coal as fuel. This run, the reference case with a bed of sand and ashes, gave the same emissions of N_2O as in the reference case with the CFBB: 74 mg N_2O/MJ for the SFBB compared to 77 mg N_2O/MJ for the CFBB.

X N2O LIMEBED SFBC
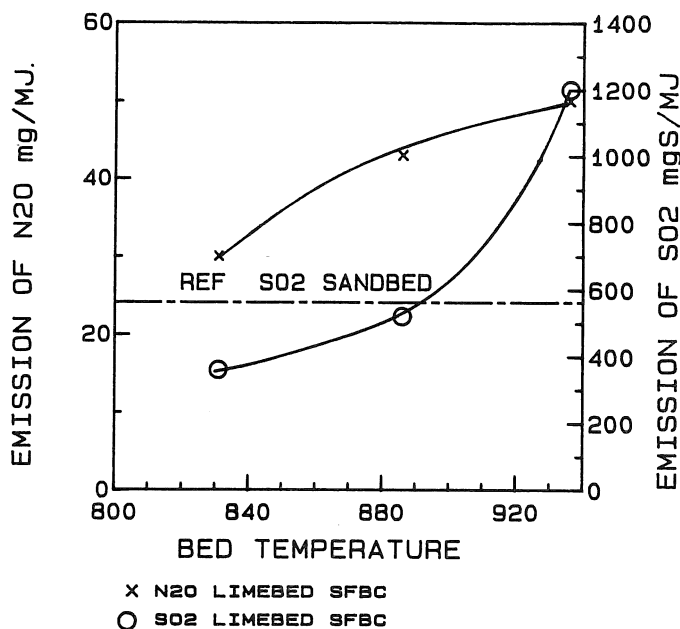O SO2 LIMEBED SFBC

Fig. 6   Emission of N_2O and SO_2 versus bed temperature during tests to prove the release of sulphur from $CaSO_4$ in the bed in the SFBB with a lime bed. The horizontal line represents the emission of SO_2 from a sand bed.
Fuel: Petroleum coke. Excess air ratio: 1.3—1.4. No secondary air.

Change of Bed Temperature in an Old Bed of Lime

A few samples were taken during a sulphur capture project reported by Lyngfelt and Leckner (1988). The bed of the SFBB was loaded before these test runs with 1000 kg $CaSO_4$, and when the bed temperature was raised the $CaSO_4$ was reduced by CO to CaO and possibly also to CaS. During this operation the N_2O increased with temperature as shown in Fig.6. This bed temperature dependence is completely different in the CFBB with a sand bed, where the N_2O emission decreases with increasing bed temperature, Fig. 2a. The NO emission of the lime bed is lower than that of corresponding runs with a sand bed, which to some extent may be caused by a reduction of NO into N_2O, as occurred in the NO injection tests on the CFBB. Such a reduction might take place on CaS surfaces in the bed, for example.

Change of Excess Air Ratio in an Old Bed of Lime

The results indicate a slight increase of the N_2O emission as the excess air ratio increases from 1.15 to 1.45.

DISCUSSION

The results of the measurements show that the emission of N_2O depends heavily on temperature and fuel. This is a consequence of the homogeneous and heterogeneous reaction mechanisms which form and remove N_2O.

Homogeneous Reactions

Studies of the homogeneous chemistry of formation and destruction of N_2O show that if HCN is evolved during devolatilization N_2O will be formed. They also show that the destruction step is dependent on temperature.

In order to investigate the sensitivity of this destruction process, a kinetic model was run at fluidized bed temperatures (Grimsberg 1988b). The model is based on 88 radical reactions which are valid in a homogeneous gas phase system. The rate constants are taken from the literature (Grimsberg 1988a). The model calculated the conversion of 3000 ppm HCN in 5% O_2, 7% H_2O, 11% CO_2 and 77% N_2 in a well mixed reactor at constant temperatures ranging from 1050 K to 1300 K. In this temperature range the maximum yield of N_2O formed is almost constant, between 45% and 50%. In Fig.7 it can be seen how much of this N_2O that is reduced to N_2 in two seconds. Although the results of this calculation are only qualitative, the conclusion is evident: the influence of temperature is
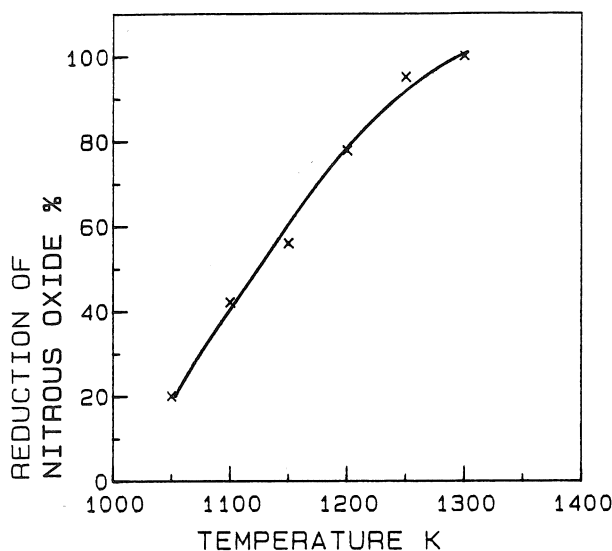
Fig. 7   Reduction of N_2O as a result of the
         homogeneous reaction scheme for different
         temperatures.

dramatic. This explains the temperature effect seen in
Fig.2a and Fig.3, and also the difference between
fluidized bed combustion and flame combustion.

Heterogeneous Reactions

De Soete (1989) found that the reduction of N_2O on a
char surface is faster than the reduction of NO. However,
the NO reduction rate is much more sensitive to the
concentration of CO than the rate of N_2O reduction is.
When the CO concentration increases, the NO reduction
rate increases while the N_2O reduction rate is unchanged.
In the bottom of the combustors the CO concentration is
very high, sometimes several percent. This is a con-
sequence of the staged combustion, the devolatilisation
and the low temperatures of a fluidized bed combustor.
The high CO concentration contributes to making the NO
reduction much faster than that of the N_2O, and the NO
concentration decreases up through the furnace, Fig.4,
whereas no decline in the N_2O concentration is seen.

Another finding of de Soete's is that a small part
of the char—bound nitrogen is oxidized to N_2O during
combustion ($\approx 5\%$), whereas 40–50% of the char nitrogen
produces NO. This explains the high NO concentrations at
the bottom of the combustion chamber. It also suggests
that some of the N_2O found in the bottom is formed this
way.

The results of de Soete and the present measure-
ments stress the importance of the distribution of the
release of volatiles, which volatiles are released, and
how much nitrogen remains in the char. Experiments
(Freihaut and Seery, 1981) show that coal heated up at an
intermediate rate up to 900°C releases half its nitrogen
as volatiles and only a small part as HCN (which is
regarded as a source of N_2O). This situation is different
from that in a flame, where much HCN is released.

To estimate the relative importance of each
reaction, more work is needed. However, it can be assumed
that the formation of N_2O is a combination of homogeneous
and heterogeneous reactions. The destruction of N_2O is
very temperature—dependent, which indicates that the
homogeneous reactions are important. Still, the hetero-
geneous reactions can not be excluded.

The SFBB Results

In the SFBB the emission of N_2O increases with
temperature, in contrast to the results from the CFBB and
the indications from the homogeneous reaction scheme.
Unfortunately the runs in the SFBB and CFBB also differed
in the composition of the beds, the former containing a
certain amount of CaO and $CaSO_4$.

CONCLUSIONS

Measurements of N_2O emissions together with NO
emissions have been carried out in a circulating and a
stationary fluidized bed boiler. The measurements show
that

- the N_2O emission is dependent on temperature,
  probably because of the strong temperature
  dependence of the N_2O destruction mechanism;
- the N_2O concentration increases up through
  the CFBB furnace, whereas the NO
  concentration decreases;
- N_2O is formed from NO to a small extent when NO
  is reduced;
- CFBB and SFBB have approximately the same
  emission level;
- the influence of limestone in the bed is not
  clear.

However, the chemistry is not well enough
understood to fully interpret all information, and no
definite model can yet be proposed.

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THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS.

TENTH INTERNATIONAL CONFERENCE ON FLUIDIZED BED COMBUSTION

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April 30 - May 3, 1989