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## INFLUENCE OF AIR SUPPLY ON THE EMISSIONS OF NO AND N<sub>2</sub>O FROM A CIRCULATING FLUIDIZED BED BOILER

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The air supply to a circulating fluidized bed (CFB) boiler is divided between primary air supplied to the bottom of the combustion chamber and secondary air supplied further up in the furnace. This arrangement creates a nominally substoichiometric zone in the bottom of the combustion chamber. The length of this zone and the stoichiometry above the zone have dramatic effects on the emission of N<sub>2</sub>O compared with the effects on the NO emission. This is shown in a test program carried out in a 12 MW CFB boiler where the secondary air was supplied to air registers located at different levels. Changes of the overall stoichiometry were also made, and it was shown that the excess air ratio influences both the N<sub>2</sub>O and the NO emissions from the boiler.

### Introduction

Fluidized bed combustion (FBC) is a convenient way of burning solid fuels of different ranks, from wood to anthracite. Due to the low combustion temperatures (800 °C–900 °C), the emissions of nitrogen oxides (NO<sub>x</sub>) are low compared to other combustion technologies such as pulverized coal combustion. By adding limestone to the bed, sulphur can be captured as well, and very low emissions of sulphur dioxide (SO<sub>2</sub>) can be achieved. However, if coal is used as a fuel, the low emissions of NO and SO<sub>2</sub> are generally accompanied by large emissions of nitrous oxide (N<sub>2</sub>O) (Åmand *et al.*<sup>1</sup>). N<sub>2</sub>O is one of the greenhouse gases and it is also believed to contribute to the ozone depletion in the stratosphere (Ramanathan *et al.*<sup>2</sup> and Crutzen & Howard<sup>3</sup>). It is known that considerable quantities of N<sub>2</sub>O are emitted only from combustors which burn nitrogen-containing fuels at temperatures below 1000° C. This fact has brought the N<sub>2</sub>O emissions from FBC into focus and great efforts are being made to learn more about the formation and reduction of N<sub>2</sub>O in FBC, as shown by ref. 4 to 24. From these investigations it is known that the N<sub>2</sub>O emission from FBC decreases as the bed temperature increases (Åmand & Leckner,<sup>5</sup> Leckner *et al.*,<sup>23</sup> Hiltunen *et al.*,<sup>7</sup> Brown & Muzio,<sup>11</sup> Mjörnell *et al.*,<sup>22</sup> Braun *et al.*,<sup>10</sup> Shimizu *et al.*,<sup>8</sup> Moritomi *et al.*<sup>16</sup>). The emission decreases with decreasing rank of the fuel (Åmand & Leckner,<sup>5</sup> Hiltunen *et al.*,<sup>7</sup> Moritomi *et al.*,<sup>16</sup> Shimizu *et al.*,<sup>8</sup> Wójtowicz *et al.*,<sup>17</sup> Mjörnell *et al.*<sup>23</sup>). Lime supply to the bed for sulphur capture also decreases the N<sub>2</sub>O emission

somewhat compared to a bed without lime (Mjörnell *et al.*,<sup>22</sup> Hiltunen *et al.*,<sup>7</sup> Leckner *et al.*,<sup>23</sup> Åmand *et al.*<sup>1</sup>).

The influence of lime on the reduction of N<sub>2</sub>O has been investigated in laboratory reactors by Miettinen *et al.*,<sup>15</sup> Moritomi *et al.*,<sup>16</sup> Iisa *et al.*<sup>18</sup> and Wójtowicz *et al.*<sup>20</sup> The influence of air supply has been studied by Shimizu *et al.*<sup>8</sup> and Bramer & Valk<sup>9</sup> in stationary fluidized beds (SFB), while in the results from circulating fluidized bed (CFB) boilers (Åmand & Leckner,<sup>5</sup> Hiltunen *et al.*<sup>7</sup> and Brown & Muzio<sup>11</sup>) the influence of air supply has been affected by a simultaneous influence from a variation in the bed temperature. In order to fill in the gap in knowledge of the influence of the air supply on the N<sub>2</sub>O emission from CFB boilers, a special test program has been carried out on the 12 MW CFB boiler at Chalmers University of Technology.

The full-scale experiments presented have the advantage of providing a realistic environment for studying the influence of the air supply. The results obtained from the global measurements (flue gas concentrations) do not directly reveal the detailed processes in the combustion chamber, but considering the very recent discovery of N<sub>2</sub>O as a potentially harmful pollutant from CFB combustion, knowledge of the general behaviour of the N<sub>2</sub>O emission is essential as a starting point for more detailed studies. At present, information is lacking for modelling of the processes involved but the existing knowledge on the formation and destruction of N<sub>2</sub>O can be used for a tentative interpretation of the results.

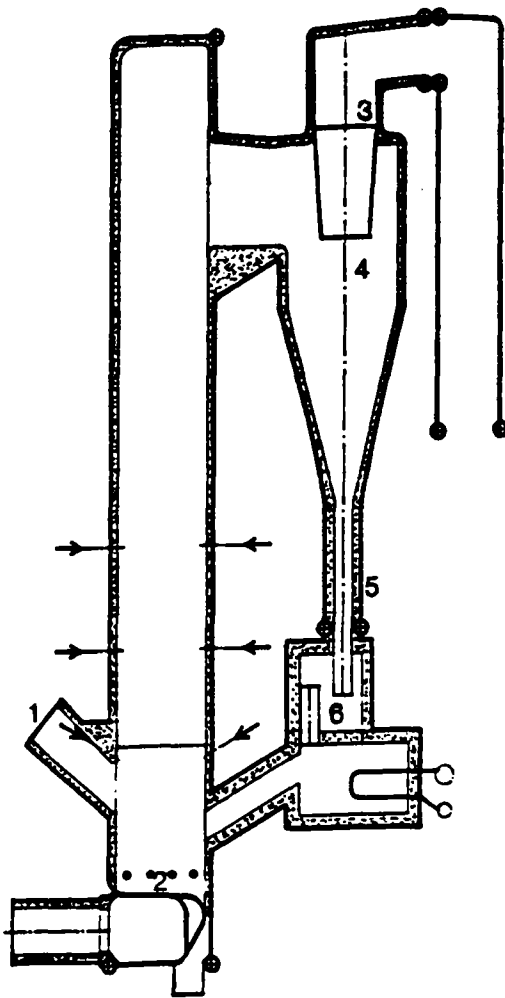


FIG. 1. The 12MW CFB boiler at Chalmers University of Technology.

1. Fuel feed chute.
2. Bottom plate.
3. Air register in cyclone outlet channel.
4. Cyclone.
5. Particle return leg.
6. Particle seal.

### Experimental

#### The Boiler:

The 12 MW CFB research plant is built in the form of a commercial boiler, Fig. 1. The height of the combustion chamber is 13.5 m and the square cross-section is about 2.9 m<sup>2</sup>. Fuel is fed to the bottom of the combustion chamber through a fuel chute (1). Primary air is introduced through nozzles in the bottom plate (2) and secondary air can be

injected through several registers located along the height of the combustion chamber as indicated by the arrows in Fig. 1. It is also possible to supply air to the outlet of the cyclone (3) and thereby operate both the boiler and the cyclone at the stoichiometric condition desired. Entrained bed material is captured in the hot, refractory-lined cyclone (4) and returned to the combustion chamber through the return leg (5) and particle seal (6).

The equipment for fly ash recirculation is not shown in Fig. 1. This equipment consists of a secondary cyclone located before the baghouse filter and a fly-ash bin which serves the purpose of maintaining a stable recycling flow of fly ash back to the bottom of the combustion chamber. This system has been used in all tests in the present program.

Also not shown in Fig. 1 is the flue-gas recycling system, which supplies flue gas to the combustion chamber through the bottom plate in order to control the temperature of the boiler.

Apart from the instrumentation used for normal operation of the boiler, the research plant is equipped with on-line gas analyzers for continuous monitoring of O<sub>2</sub>, CO, SO<sub>2</sub>, NO and N<sub>2</sub>O on cold and dry gases. The N<sub>2</sub>O instrument is an infra-red analyzer (Spectran 647 from Perkin Elmer) which is cross-sensitive towards water and SO<sub>2</sub>. Water is removed in a refrigerator located ahead of the gas analyzers and SO<sub>2</sub> is only a problem at concentrations higher than 500 ppm. This amount was not reached during the present tests. For a check, some samples of dry flue gas were collected in Tedlar bags for subsequent N<sub>2</sub>O analysis on a gas chromatograph. No difference was found in the results from the N<sub>2</sub>O analyzer and the gas chromatograph.

Finally, a data acquisition system was used for collection and storage of data from the boiler.

The properties of the bituminous coal used as a fuel are the following:

- Content of ash, moisture and combustibles: 7.1%, 7.4% and 85.5% analysed as delivered;
- The elementary analysis yields C, H, O, S and N: 83.8%, 4.9%, 9.1%, 0.8% and 1.4% analysed on a moisture and ash-free (maf) basis.
- The volatile content was 35.7% on maf basis.
- The size of the coal was 0–30 mm with a mean size of 14.4 mm and 5% of the fuel had a size less than 1 mm.

Silica sand was used as a bed material.

#### The Tests:

A reference case was defined, corresponding to a bed temperature at the bottom of the combustion chamber of 850°C, a total excess air ratio of 1.2, a primary air stoichiometry of 0.75, and the secondary air supply at the lowest secondary air register. With these operating conditions, temperatures at

the top of the combustion chamber of 860°C and at the outlet of the hot cyclone of 810°C were achieved. The reference case has a fluidizing velocity of about 6 m/s at the top of the combustion chamber. The recycling of fly ash from the secondary cyclone was held at a ratio of 0.5, measured as the ratio of recycled flow of fly ash to fuel flow. In order to avoid interference from the sulphur capture process on the NO/N<sub>2</sub>O chemistry (such as reported by Åmand *et al.*<sup>1</sup>), no limestone was used. The load of the boiler was kept constant during the tests, except for some cases mentioned in the text.

The three parameters, excess air ratio, primary air stoichiometry and secondary air level, were varied around the reference condition, one at a time while keeping the two others constant, thus defining three test series. The excess air ratio series also included a comparison of the strategies used for changing the excess air ratio. There are two principal methods: the excess air ratio can be changed either by changing the fuel flow or the total air flow to the boiler. The change in excess air ratio affects the whole combustion chamber unless adjustments of the ratio of secondary to primary air are made to keep the primary air stoichiometry constant and to change only the stoichiometry above the secondary air level. So, for each of the principal methods another two alternatives arise: either the primary air stoichiometry is maintained or it is adjusted. Thus, there are in all four alternative procedures for changing the excess air ratio.

The operating conditions for each test series are given in Table I, together with the standard deviations. Each test consists of a transient period, dur-

ing which the desired conditions were attained, followed by a steady state period of 90–120 minutes.

## Results

The results are given as concentrations normalized to a flue gas with an oxygen concentration of 6%.

The results from the primary air stoichiometry series are given in Fig. 2. For both NO and N<sub>2</sub>O only a weak dependence of the primary air stoichiometry was found. This is in agreement with the results from previous tests in another boiler (Åmand & Leckner<sup>3</sup>). The reason for the small dependence is probably the relatively short primary air zone. The effect of increasing the primary air zone by moving the secondary air supply to air registers located at higher levels is shown in Fig. 3. An increased primary air zone led to a large reduction of the N<sub>2</sub>O emission. The NO emission, however, only decreased when the secondary air was moved from the level at 2.2 metres to 3.8 metres above the bottom. Moving the secondary air further up to 5.5 metres led to a small increase of the NO emission again. In an additional test, not shown in Fig. 3, the secondary air was divided between the air register at 5.5 metres and the air register located at the outlet of the cyclone. This resulted in a sub-stoichiometric zone corresponding to a primary air stoichiometry of 0.73 up to the 5.5-metre level where the first part of secondary air raised the stoichiometry to 0.93, which was retained in the remaining part of the combustion chamber as well as in the cyclone. At the exit of the cyclone the stoi-

TABLE I

Operating conditions. Mean values and standard deviation. Active changes are shown with an arrow

Parameter	Fig. 2	Figs. 3 & 4	Fig. 5,A	Fig. 5,B	Fig. 5,C	Fig. 5,D
Load (MW)	9.1 ± 0.1	9.1 ± 0.0	8.2 → 10.2	8.2 → 10.2	9.2 ± 0.1	9.2 ± 0.2
Temperatures, °C						
–bottom bed	850 ± 1	850 ± 1	850 ± 0	850 ± 1	850 ± 1	850 ± 1
–furnace top	866 ± 1	862 ± 2	862 ± 5	860 ± 4	864 ± 1	863 ± 2
–after cyclone	816 ± 5	819 ± 2	817 ± 11	819 ± 10	813 ± 0	814 ± 1
Excess air ratio	1.22 ± 0.00	1.21 ± 0.01	1.11 → 1.33	1.11 → 1.33	1.11 → 1.37	1.12 → 1.35
Primary air stoichiometry	0.52 → 1.14	0.73 ± 0.01	0.74 ± 0.01	0.67 → 0.82	0.74 ± 0.00	0.69 → 0.80
Ash recirculation ratio	0.50 ± 0.01	0.55 ± 0.02	0.54 ± 0.01	0.53 ± 0.01	0.51 ± 0.02	0.50 ± 0.02
Pressure difference, kPa						
–reactor	6.4 ± 1.2	5.9 ± 0.2	5.5 ± 0.1	5.6 ± 0.2	5.5 ± 0.2	5.7 ± 0.4
–bottom < 2 m	3.0 ± 1.0	2.8 ± 0.2	2.5 ± 0.4	2.4 ± 0.2	2.5 ± 0.3	2.5 ± 0.3
Fluidization velocity, m/s	6.3 ± 0.3	6.3 ± 0.4	6.5 ± 0.4	6.6 ± 0.4	6.0 → 7.2	6.1 → 7.1

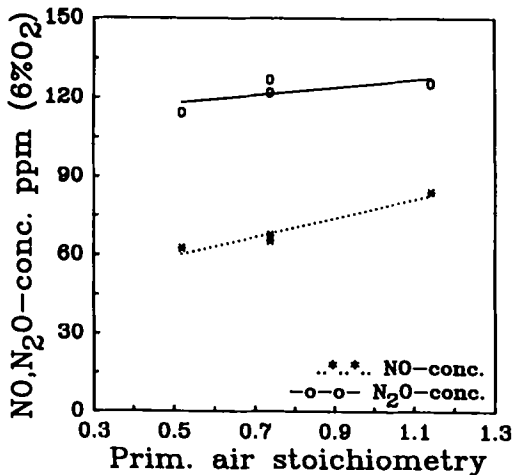


FIG. 2. Normalized concentrations of NO and N<sub>2</sub>O in the outlet of the boiler as a function of the primary air stoichiometry. Operating conditions: See Table I: ...\*... NO concentration normalized to 6% oxygen; —○—○— N<sub>2</sub>O concentration normalized to 6% oxygen.

chiometry was further raised up to the total excess air ratio of 1.2. The result of this test is reported as a transient in Fig. 4. It is evident from Fig. 4 that this strangling of the air supply to the boiler had an immediate and dramatic effect on the N<sub>2</sub>O emission from the boiler. A decrease of N<sub>2</sub>O from 90 ppm down to only 32 ppm occurred at the same

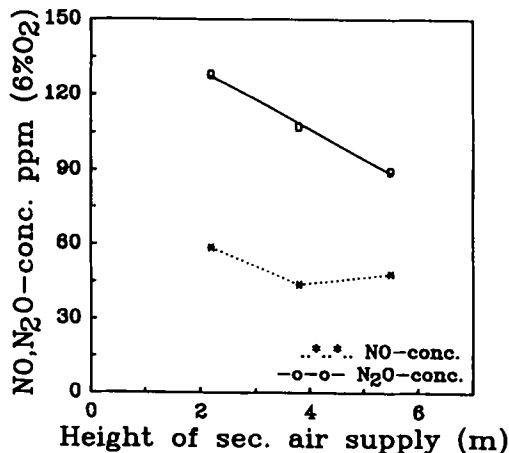


FIG. 3. Normalized concentrations of NO and N<sub>2</sub>O in the outlet of the boiler as a function of the location of the secondary air supply. Operating conditions: See Table I: ...\*... NO concentration normalized to 6% oxygen; —○—○— N<sub>2</sub>O concentration normalized to 6% oxygen.

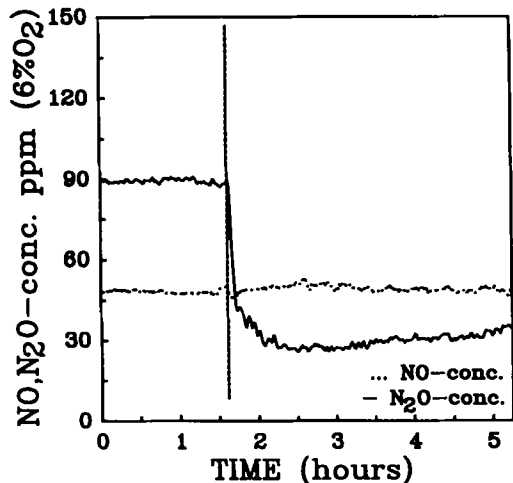


FIG. 4. Transient response test. At  $t = 1.61$ , 50% of the air supplied to the air register at 5.5 meters was conducted to the cyclone outlet duct. Operating conditions: See Table I: ..... NO concentration normalized to 6% oxygen; — N<sub>2</sub>O concentration normalized to 6% oxygen

time as the NO level remained constant at 48 ppm (Fig. 4). Starting from the N<sub>2</sub>O level of the reference case (128 ppm) a total reduction of the N<sub>2</sub>O emission of 75% was achieved by gradually reducing the oxygen supply to the boiler.

The last series to report is the one showing the influence of over-all excess air. In Fig. 5, the results of all four strategies used for changing the excess air ratio are given. The NO and N<sub>2</sub>O emissions are both seen to be strongly dependent on the excess air ratio, but N<sub>2</sub>O is more affected than NO. The strategy used for changing the excess air ratio did not influence the results. In previous tests on an 8 MW CFB boiler reported by Åmand and Leckner,<sup>5</sup> on the other hand, the NO emission was influenced by the strategy used for changing the excess air ratio. This difference between the two boilers might be caused by differently designed secondary air ports. Also, during the present tests, the load of the boiler was higher, and this led to a smaller influence of changes in the excess air ratio on the temperatures at the top of the furnace than in the case of the 8 MW boiler.

#### Formation and Destruction of NO and N<sub>2</sub>O

The formation and reduction of NO and N<sub>2</sub>O in a combustion chamber of a CFB boiler are not well understood.

An attempt by Åmand and Leckner<sup>5</sup> to show schematically the NO/N<sub>2</sub>O chemistry under FBC

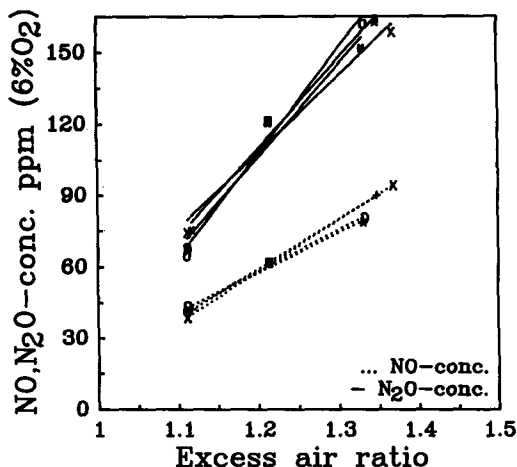


FIG. 5. Normalized concentrations of the NO and  $N_2O$  in the outlet of the boiler as a function of the excess air ratio. Operating conditions: See Table I: ..... NO concentration normalized to 6% oxygen; —  $N_2O$  concentration normalized to 6% oxygen. The strategies used for obtaining the different excess air ratios are represented by the following symbols: \* A: Total air constant. Change of fuel feed.  $\lambda$  prim. = constant; O B: Total air constant. Change of fuel feed.  $\lambda$  prim. = not constant; x C: Fuel flow constant. Change of total air.  $\lambda$  prim. = constant; + D: Fuel flow constant. Change of total air.  $\lambda$  prim. = not constant. ( $\lambda_{\text{prim}}$  is primary air stoichiometry.)

conditions was continued by the same researchers,<sup>21</sup> and has been followed up by others (Cabrita *et al.*,<sup>13</sup> Moritomi *et al.*,<sup>16</sup> Wójtowicz *et al.*<sup>17</sup>). The homogeneous reactions involving formation and destruction of  $N_2O$  was first treated for fluidized bed conditions by Kilpinen and Hupa,<sup>6</sup> and some of the important findings from the model calculations, for example that HCN, which originates from the volatiles of the fuel, can form  $N_2O$ , were shown by laboratory tests by Hulgaard and co-workers.<sup>14</sup> However, at present, no tests in the laboratory or in CFB boilers have been able to show if this homogeneous formation route with HCN as a precursor may play an important role in the heterogeneous environment of a CFB boiler.

This should be compared with the SFB boiler, where tests by Bramer and Valk<sup>9</sup> show large differences in  $N_2O$  emission when a bituminous coal burned, compared to a similar case when only the devolatilized char was used and the  $N_2O$  emitted (calculated as fuel-nitrogen conversion to  $N_2O$ ) was only one-third of that from the bituminous coal. Bramer and Valk<sup>9</sup> also tested addition of acetonitrile ( $CH_3CN$ ), a cyanic compound which was effectively converted to  $N_2O$  in their SFB test unit.

The difference in  $N_2O$  level between bituminous coal and the corresponding char in an SFB application has also been shown by Wójtowicz *et al.*<sup>17</sup> It is quite clear that gas phase reactions play a considerable role in the SFB boiler.

The homogenous reduction of  $N_2O$  at fluidized bed temperatures has been studied experimentally in laboratory reactors by Hulgaard *et al.*<sup>14</sup> and Iisa *et al.*<sup>18</sup> They found that the reduction at fluidized bed temperatures (800°C–900°C) is rather slow, but if radicals such as H and OH are present the rate of reduction of  $N_2O$  is considerably increased. Also for these laboratory findings no verifying tests have been carried out so far for the heterogeneous environment of a CFB where quenching of important radicals could be expected.

Apart from the homogeneous reduction of  $N_2O$  by radicals, de Soete<sup>24</sup> has shown that  $N_2O$  can be reduced heterogeneously on char surfaces as well.

Finally, Åmand and Leckner<sup>21</sup> proposed, supported by tests in the present 12 MW boiler, that a possible formation route for  $N_2O$  is through the reduction of NO on char surfaces or by oxidation of char nitrogen directly to  $N_2O$ . No laboratory investigations are available so far to support the proposal of formation through reduction of NO on char.

## Discussion

Before starting the discussion it should be concluded that the three test series concerning the air supply to the boiler are not affected by the well-known temperature dependence of the  $N_2O$  emission. This is seen from Table I, where the standard deviation of the temperature of the combustion chamber never exceeds 5°C. Changing temperatures has been a problem earlier in our own measurements in the 8 MW CFB boiler, reported by Åmand & Leckner,<sup>5</sup> as well as in tests carried out by others (Hiltunen *et al.*<sup>7</sup>). The large changes in emissions found in the present results must then be explained by other factors.

Another comment concerns the air-fuel ratio in the combustion chamber (including the cyclone). If imperfect mixing is disregarded, the primary air stoichiometry and the over-all excess air ratio are the two most important quantities which define the air-fuel situation in the combustion chamber. The excess air ratio expresses the over-all stoichiometry and is evaluated from the air and fuel supply to the boiler or from the flue gas oxygen concentration. The significance of the excess air ratio is easily conceived. The concept of primary air stoichiometry might, however, lead to erroneous interpretations of the air-fuel situation in the bottom zone. The primary air stoichiometry is calculated from the total fuel and primary air flows, implying that all oxygen is consumed in the bottom zone. This is a

reasonable estimate in an SFB where the solid fuel is contained in the bubbling bed and in the splash zone, and the secondary air provides additional air for final burn-out. In the CFB application, on the other hand, the fuel might well to a large extent burn above the secondary air injection level, especially if this is only 2 m from the bottom. In such a case the primary zone might be over-stoichiometric in spite of a primary air stoichiometry of less than one, and most of the fuel burns under over-stoichiometric conditions as well in the primary as in the secondary zone. However, if the level of injection of secondary air is raised, thus extending the primary zone, this zone may gradually become truly sub-stoichiometric since more fuel has the possibility to burn there.

With this discussion about the stoichiometries of the bottom zone and of the entire combustion chamber, the results from the three test series can be analysed in the light of the theory presented in the previous section. In view of the lack of verification of both the homogeneous formation and destruction of  $N_2O$  in a CFB environment only a tentative explanation can be made based on the assumption that the availability of oxygen in the combustion chamber influences homogeneous reactions primarily.

Two important sets of reactions involved are formation of  $N_2O$  from HCN and reduction of  $N_2O$  by radicals.

In order to produce  $N_2O$ , HCN has to be oxidized to NCO, and thereafter NCO reacts with NO to form  $N_2O$ . If HCN is not oxidized to NCO due to reducing conditions, then HCN could be hydrated to  $NH_3$  instead, and  $NH_3$  could later oxidize to  $N_2$  or NO catalyzed by the char surfaces. This would take place when a deficit of oxygen develops as the secondary air level is moved upwards, as seen in Fig. 3 and in the extreme case when most of the combustion chamber is sub-stoichiometric, like in Fig. 4. This extreme case should be closest to the SFB tests presented by Shimizu,<sup>8</sup> and Bramer & Valk<sup>9</sup> where considerable effects of the primary air stoichiometry were found.

At the same time as there was a considerable reduction of the  $N_2O$  emission, the effect of secondary air on the NO emission was small (Fig. 3) or non-existent (Fig. 4).

A reduction of the air supply should improve the NO reduction capacity of the boiler, since the rate of combustion is reduced, which increases the concentration of reducing species, important for the NO reduction, such as CO and  $H_2$ , and the catalytic char surface. However, it is possible that an additional formation of NO from the  $NH_3$ , mentioned above, could counterbalance the positive effects caused by the increased concentrations of CO,  $H_2$  and char. This could result in an almost constant NO level.

In the excess air series, on the other hand, the lowest secondary air level is used and the conditions in the combustion chamber are on the average over-stoichiometric, with a change in the excess air from 10% to 30%. Here it can be suspected that the radicals (such as H and OH), which are present also at sub-stoichiometric conditions, gradually decrease in concentration as the excess air ratio increases. This should be the primary reason for the increase in  $N_2O$  seen in Fig. 5, while the formation of  $N_2O$  from HCN again takes place at over-stoichiometric conditions and the reduction of NO by CO or  $H_2$  on char surfaces dominates the NO emission in accordance with what is shown in Fig. 5.

### Conclusions

- The creation of sub-stoichiometric zones in the combustion chamber of a CFB boiler has a dramatic effect on the  $N_2O$  emission, which can be reduced by 75% from that of normal operating conditions.
- The NO emission is almost unaffected by the same change in operating conditions.
- The excess air ratio is the only boiler parameter known so far which decreases both the  $N_2O$  and the NO emission. A decrease of the excess air from 1.3 to 1.1 decreases both the  $N_2O$  emission and the NO emission by about 50%.
- The NO and  $N_2O$  emissions were only affected to a small extent when the primary air stoichiometry was changed. The reason for this is probably that the test was carried out with a secondary air register which was located too close to the bottom of the bed.
- The results from the secondary air level series and excess air ratio series can be explained on the basis of homogeneous formation and destruction of  $N_2O$ . These reactions have been reported in the literature but they have not been verified in a heterogeneous environment characteristic of a CFB boiler.
- More laboratory investigations, as well as detailed measurements inside the combustor of a CFB boiler, are needed in order to learn more about the formation and reduction of NO and  $N_2O$  in real CFB boilers.

### Acknowledgements

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## COMMENTS

*Dr. B. C. Young, University of North Dakota, USA.* Would you care to speculate further on the homogeneous and heterogeneous formation and destruction mechanisms for N<sub>2</sub>O in CFBC systems?

*Author's Reply.* This question was discussed during the recent 5th Int'l. Workshop on N<sub>2</sub>O emissions, NIRE/IFP/EPA/SCEJ, Tsukuba, July 1992,

where it was stated that gas phase chemistry plays a significant role, at least for the formation of N<sub>2</sub>O. This was not accepted by many of the participants, who pointed out that the large amount of particle surface in a fluidized bed certainly influences the reaction mechanisms. However, an experiment consisting of injection of NO into a fluidized bed combustor led to a rise in the N<sub>2</sub>O emission. Al-



though the subject is not well known, one interpretation is that the rise in  $N_2O$  is a consequence of the reaction  $NCO + NO \rightarrow N_2O + CO$  which would indicate that the gas phase chemistry is essential for the formation of  $N_2O$ . The lower  $N_2O$  emission observed when moving the secondary air to higher levels in the combustion chamber or when decreasing the excess air could also be a conse-

quence of homogeneous gas phase reactions,  $HCN \xrightarrow{+O} NCO \xrightarrow{+NO} N_2O$ , where the  $N_2O$  production is affected by a higher probability of existence of oxygen-deficient zones in the combustor as the oxygen supply to the combustion chamber is reduced. At present the complex behaviour of circulating fluidized bed combustion chambers is not sufficiently known to avoid speculation.