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Secondary effects in sampling ammonia during measurements in a circulating fluidised-bed combustor

H KASSMAN*, L-E ÅMAND** and B LECKNER**

A previous paper presented the results of measuring the ammonia (NH_3) concentration in the combustion chamber of a circulating fluidised-bed (CFB) boiler. Two sampling techniques were used: a gas-quenching (GQ) probe where the sample is quenched directly in the probe tip by a circulating trapper solution, and a gas-sampling probe connected to a Fourier-transform infra-red (FTIR) instrument. In this paper, an attempt is made to estimate the influence of potential secondary reactions with NH_3 in the GQ probe tip by means of a plug-flow model. The calculations showed that heterogeneous and homogeneous reactions could be of importance to the accuracy of the measurement. This contradicts the almost identical results relative to the parallel FTIR measurement, and the conversion of NH_3 is probably overestimated by the model. In addition, transients obtained during the FTIR measurement were used to study the accuracy of the gas-sampling probe.

1 Introduction

This paper is a sequel to a paper by Åmand *et al*[1], which presented the results of measuring the ammonia (NH_3) and ethene concentration profiles in the combustion chamber of a circulating fluidised-bed (CFB) boiler. The boiler was operated in three air-staging conditions, with peat as a fuel and with the addition of lime. Two sampling techniques[1] were used for analysing ammonia: a gas-quenching (GQ) probe[2] where the sample was quenched directly in the probe tip by a circulating trapper solution, and a gas-sampling probe connected to a Fourier-transform infra-red (FTIR) instrument.

A comparison of the concentration profiles of NH_3 measured by the two sampling procedures showed strikingly similar results (Fig.7 in Reference 1). This could be explained in two ways: either the measurement was correct for both methods, or they were influenced equally by secondary reactions. It is not likely, however, that two probes with different sampling procedures are influenced by the same secondary reactions during operation under various air-staging conditions. Nevertheless, this paper deals with potential secondary reactions and measurement errors from the use of two sampling probes in measuring NH_3 in a CFB boiler. The influence of potential secondary reactions with NH_3 in the GQ probe tip was estimated by means of available kinetics[3,4] and a simple plug-flow model. The theory for the model is presented below. The accuracy of the gas sampling probe was evaluated by the study of transients during the FTIR measurements, since this method allows the storage of data every 30 seconds.

2 Theory

2.1 The model

It was assumed that the GQ probe tip could be described by three ideal plug-flow reactors in series (Fig.1) representing a filter-cake (F), the uncooled quartz filter (Q), and homogeneous reactions (H) in an uncooled section before NH_3 in the sampled gas was quenched. In F and Q there were only heterogeneous reactions, and in H only homogeneous ones. The reaction rate r in a plug-flow reactor, assuming a first-order rate expression, is:

$$r = -\mathrm{d}C/\mathrm{d}t = k * C \qquad (1)$$

which on integration gives:

$$C_t/C_O = \exp(-k * t) \qquad (2)$$

where C_t is the concentration after the time t (s), C_O is the original concentration and k (s^{-1}) represents the first-order rate constant. Based on catalyst mass, the unit of the rate constant k becomes ($m^3\ s^{-1}\ kg^{-1}$) and that of the space time τ' ($m^{-3}\ s^1\ kg^1$). The rate constant can be calculated from the Arrhenius equation:

$$k = A * \exp(-E_a/RT) \qquad (3)$$

where E_a is the activation energy, A is the pre-exponential factor and T is the temperature (K).

The NH_3 concentration in the combustor is C_O, and C_F after passing the filter-cake, C_Q after passing the quartz filter, and finally the concentration becomes C_H before being quenched by the trapper solution. The rate expressions for F and Q are based on the masses of the filter-cake and the quartz filter, where k_F and k_Q are the rate constants, and τ'_F and τ'_Q are the space times. The reactor H was divided into small plug-flow reactors in series to describe the temperature fall, with a different rate expression for each drop in temperature T_i. The rate constant k_{Hi} can be inserted into Eqn (2) together with the residence time τ_i for each plug-flow reactor.

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*Department of Environmental Inorganic Chemistry, Chalmers University of Technology and University of Gothenburg, S-412 96 Gothenburg.
**Department of Energy Conversion, Chalmers University of Technology, S-412 96 Gothenburg.

Table 1 Important reactions for NH_3 at FBC temperatures.

Heterogeneous reactions[3]	Catalyst[x]	Rate constant at 1100 K ($m^3\ s^{-1}\ kg^{-1}$)
R1: Decomposition of NH_3	calcined limestone[5+]	2.5 E-2
	sulphated limestone[5+]	2.5 E-2 → 2.0 E-3
	quartz sand[6]	8.5 E-3
	char[6]	0
R2 and R3 R2: Oxidation of NH_3 to NO R3: Oxidation of NH_3 to N_2	calcined limestone[7]	5 → 7
	sulphated limestone[7+]	5 → 5 E-3
	quartz sand[8]	8.0 E-3
	char[9]	3
R4: Reduction of NO with NH_3	calcined limestone[10]	4.0 →7.0 E-2
	sulphated limestone[10+]	4.0 E-2 →2.5 E-3
	quartz sand[6]	3.0 E-3
	char[9]	0.9
Homogeneous reactions[4]	Reaction rate expression (r) ($kmol\ m^{-3}\ s^{-1}$)	Parameters[xx]
R5: Oxidation of NH_3 to NO	$r_{NH3} = k * C_{NH3}$	$k_0 = 2.2\ E14$ $E/R = 35\ 230$
R6: Reduction of NO with NH_3	$r_{NH3} = -2/3\ r_{NO}$ $r_{NO} = k * C_{NO} * C_{NH3}$ $r_{NH3} = k' * C_{NH3}$	$k_0 = C_{NO} * 2.45\ E17$ $E/R = 27\ 680$

x = Original kinetic data recalculated by Johnsson[3], only reference number in the present paper given in the column.
xx = Kinetic data in Reference 4 was adapted from Duo *et al*[11].
+ The rate constant varies due to the degree of sulphation for the limestone.
In R4, the rate constants presented in Reference 3 are for NO instead of NH_3.
In R6, a C_{NO} of 200 ppm was used in the calculations of k'.

2.2 NH_3 kinetics at FBC temperatures

Heterogeneous and homogeneous reactions with NH_3 have been investigated by several researchers under conditions of fluidised-bed combustion (FBC). The rate constants of the heterogeneous reactions with NH_3 over different bed materials have been compared by Johnsson[3] in terms of first-order or pseudo-first-order reaction rate constants based on the mass of catalyst. In general, char and calcined limestone have a high catalytic activity. The activity of limestone falls with sulphation, and both sulphated limestone and quartz sand have low activity.

These rate constants, together with those of homogeneous reactions, Table 1, and an appropriate reactor model, can determine whether secondary reactions at the GQ probe tip could have influenced the result of the NH_3 measurement. The heterogeneous reactions, Table 1, are: decomposition of NH_3 (R1); oxidation of NH_3 to NO (R2), or N_2 (R3); reduction of NO with NH_3 (R4). The predominant homogeneous reactions, Table 1, are: oxidation of NH_3 to NO (R5); reduction of NO with NH_3 (R6). The reactions R1 to R6 were assumed to proceed parallel with each other.

3 Results

3.1 The gas-quenching probe

The rate constants used as input data for the three id plug-flow reactors representing the GQ probe tip had to determined before any model calculations could be ma In the following sections are presented the methods us for estimating the catalytic activity for the filter-cake quartz filter, and for obtaining the temperatures of homogeneous reactions. Finally, model calculations performed for two possible conditions at the probe tip.

3.1.1 Characterisation of the filter-cake

The catalytic activity of the filter-cake is unknown, bu can be estimated. Unlike the situation with other fu there was no filter-cake on the probe tip during com tion of wood chips in the boiler. During combustion of NH_3 was measured as a transient from the start of the li stone addition. NH_3 fell initially, but after a couple of h the concentration was similar to the original value be the start of lime addition; this indicates that when the li stone particles became sulphated, the activity for oxida of NH_3 dropped. The added limestone particles believed to react quickly enough with SO_2 to make influence from pure CaO negligible. During change measurement port, any filter-cake on the probe tip c be observed and collected. The amount of filter-cake i measurement during peat combustion varied with

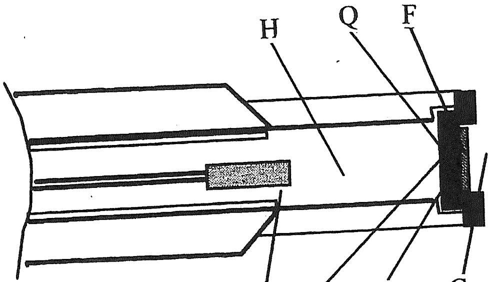

Fig.1 The tip of the gas-quenching (GQ) probe; F, filter-cake; Q, quartz filter; H, geneous reactions in an uncooled section. The NH_3 concentration in the combustor and C_F after passing the filter-cake, C_Q after passing the quartz filter, and finally C_H

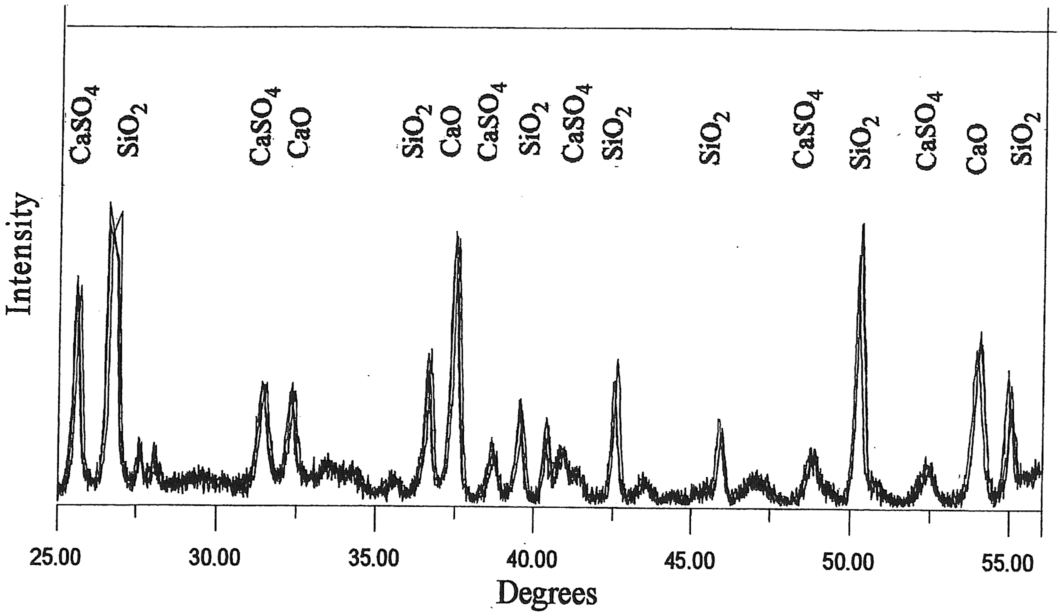

Fig.2 X-ray powder diffraction from three different filter-cakes taken from measurement ports H2, H4 and H9 in the combustion chamber during operation under reversed air-staging conditions. Note that there are three different but almost identical XRD traces on the same graph.

stone addition, height above the nozzles and air-staging conditions. However, the appearance of the filter-cakes was similar; they were much thicker at the top part of the quartz filter than the lower part.

Selected filter-cakes were analysed by X-ray powder diffraction (XRD). The sample preparation included grinding, and therefore the result shows the components in the bulk of the material. Fig.2 presents a comparison of XRD results from three filter-cakes taken from the measurement ports H2, H4 and H9 in the combustion chamber[1] during operation under reversed staging conditions. The heights of the major peaks SiO_2, CaO and $CaSO_4$ have the same relationship to each other, and consequently the same concentration, independent of measurement position in the combustor. Note, however, that XRD analysis does not give the composition on the particle surfaces in the filter-cake; and non-crystalline phases, such as char, cannot be detected. For this reason, other analytical methods were applied for the analysis of the composition. The amounts of calcium (Ca) and sulphur (S) were obtained from analysis of total Ca and S, and SiO_2 is the remaining component after burning off the char content.

3.1.2 Heterogeneous reactions F and Q

The following assumptions were made in the model for the filter-cake, F: it consisted of quartz sand, partly sulphated limestone and char; no pure CaO was present in the filter-cake; the filter-cake was evenly distributed; NH_3 kinetics was based on char from combustion of coal instead of peat; pseudo-first-order rate constants were used when necessary; NH_3 kinetics in reaction R4 was based on rate constants for the reduction of NO.

Table 2 gives the kinetic data of the reactions included in the model for F. The relative importance of each reaction is expressed as a rate constant multiplied by the mass fraction of the component, (k_i * m_i). Oxidation of NH_3 over char is the most important reaction in the model. However, the rate constants for char are of poor quality; they were estimated from coal data because of the lack of experimental data on the NH_3 kinetics of peat combustion. The total rate constant k_F of the nine reactions is $\Sigma\, k_{Fi} * m_i$ and can be inserted in Eqn (2) together with the space time τ'_F, which is calculated from the mass of each mm of filter-cake, its density and the gas flow through the filter-cake.

Table 2 Rate constants for heterogeneous reactions in F and Q adapted from Reference 3.

Reaction	Catalyst[x]	Rate constant (k_i), ($m^3\,s^{-1}\,kg^{-1}$)	Mass fraction[xx] (m_i)	m_i *k_i *1000 ($m^3\,s^{-1}\,kg^{-1}$)
R1	Limestone[5]+	8.0 E-3	0.365	2.9
R1	Quartz sand[6]	8.5 E-3	0.630	5.4
R1	Char[6]	-	0.005	0
R2, R3	Limestone[7]+	1.0 E-2	0.365	3.6
R2, R3	Quartz sand[8]	8.0 E-3	0.630	5.0
R2, R3	Char[9]	3	0.005	15.0
R4	Limestone[10]+	7.0 E-3	0.365	2.6
R4	Quartz sand[6]	3.0 E-3	0.630	1.9
R4	Char[9]	0.9	0.005	4.5

x = Original kinetic data recalculated by Johnsson[3], only reference number in the present paper given in the column.
xx = Calculated mass fraction for limestone and quartz from analysis of total S and Ca, analysed mass fraction for char.
\+ = Partly sulphated limestone, the degree of sulphation estimated from Tables 4, 5 and 6 in Reference 3.
− = Decomposition of NH_3 over char has not been observed[6].

Table 3 Primary data for homogeneous gas phase reactions used in Fig.3.

Flow reactor C_Q-C_H	Temp.(K)	$k_{Hi}(s^{-1})$	Case 1 τ (ms)	$C_{(NH3)i}$ case 1 C_Q=1.0	Case 2 τ (ms)	$C_{(NH3)i}$ case 2 C_Q=1.0
C_Q-C_1	1120	11.19	0.25	0.997	2.5	0.971
C_1-C_2	1110	8.74	0.25	0.995	2.5	0.951
C_2-C_3	1100	6.79	0.25	0.993	2.5	0.935
C_3-C_4	1090	5.26	0.25	0.992	2.5	0.923
C_4-C_5	1075	3.56	1.00	0.988	2.5	0.915
C_5-C_H	1050	1.82	13.0	0.965	2.5	0.910

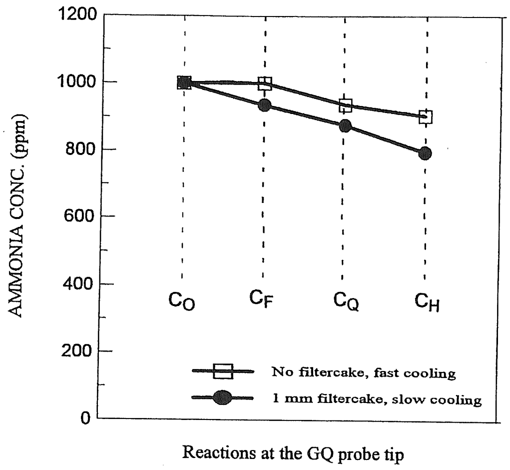

Fig.3 Conversion of NH_3 from two possible conditions at the probe tip. The inlet concentration C_O was assumed to be 1000 ppm, either passing the quartz filter without a filter-cake and finally being quenched with cooling, case 1 (C_F = 1000 ppm, C_Q = 937 ppm and C_H = 904 ppm), or passing 1 mm filter-cake, the quartz filter and quenched with cooling case 2 (C_F = 935 ppm, C_Q = 876 ppm and C_H = 797 ppm). For details see Section 3.1.4.

The catalytic activity of the quartz filter Q was estimated by means of the rate constants for quartz sand in Table 1. Most of the investigations quoted were performed over quartz sand instead of the less active pure quartz, which was used in the filter; the NH_3 conversion was therefore slightly overestimated in Q. The total rate constant k_Q ($\Sigma\, k_{Qi}$) of the three reactions can be inserted into Eqn (2) together with the space time τ'_Q, which is calculated from the mass of the filter and the gas flow through it.

3.1.3 Homogeneous reactions, H

The gas temperature in the reactor H was assumed to fall gradually until the reactions are quenched by the trapper solution. H was divided into six plug-flow reactors in a series (H1 to H6). The rate constants for R5 and R6 were calculated for each drop in temperature, using kinetic data from Table 1. The rate constant k_{Hi} is $k_{R5i} + k_{R6i}$ and can be inserted into Eqn (2) together with the residence time τ_i for each temperature, which is calculated from the volume of H and the gas flow through H. The total conversion of NH_3 in H can then be expressed as:

$$C_{(NH3)Q} / C_{(NH3)H} = \exp\left(-\sum_{n=1}^{6} k_{(Hn)} * \tau_n\right) \qquad (4)$$

3.1.4 Model calculations

Fig.3 compares the results from model calculations with two possible conditions at the probe tip. The sampled gas passed the quartz filter Q, either with or without a filter-cake, followed by two hypothetical cooling cases. In cooling case 1 the residence time was short at high temperatures, and in case 2 the temperature drop was slower and linear. The inlet concentration C_O was assumed to be 1000 ppm, either passing the quartz filter without a filter-cake and finally being quenched with cooling case 1 (C_F = 1000 ppm, C_Q = 937 ppm and C_H = 904 ppm), or passing 1 mm filter-cake, the quartz filter and quenched with cooling case 2 (C_F = 935 ppm, C_Q = 876 ppm and C_H = 797 ppm). The primary data used for F were: $k_F = 40.9\ E{-3}\ m^3\ s^{-1}\ kg^{-1}$, $\tau'_F = 1.64\ m^{-3}\ s^1\ kg^1$ per mm filter-cake. The primary data used for Q were: $k_Q = 19.5\ E{-3}\ m^3\ s^{-1}\ kg^{-1}$, $\tau'_Q = 3.32\ m^{-3}\ s^1\ kg^1$. The primary data used for H can be found in Table 3.

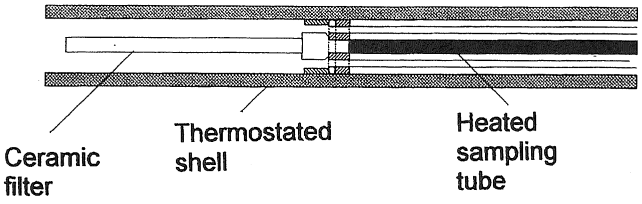

Fig.4 Front part of the gas sampling probe adapted from Fig.2b in Åmand *et al*[1].

The model calculations showed that secondary reactions with NH_3 could take place both in a filter-cake F and in the quartz filter Q, as well as homogeneously in H. Together, these reactions could be of importance for the accuracy of the GQ probe measurement. This simple model also gives some suggestions for future improvements and design of probes. It is important to have residence times as short as possible in hot and uncooled sections like H, Fig. 1, to avoid homogeneous reactions with NH_3. Possible reactions over the quartz filter can also be reduced by the use of pure and less active filter materials. Finally, it is important to design a probe in such a way that formation of a thick filter-cake is avoided.

3.2 The gas-sampling probe

It is more complicated to apply the model to the tip of the gas-sampling probe, Fig.4. The reason is that the flow pattern is unknown and therefore a simple plug-flow assumption is not suitable. However, the transients can be studied during the measurement, since the FTIR store data every 30 seconds. This technique was used below to estimate the importance of secondary reactions in a possible filter-cake or in the filter. Adsorption on surfaces in the sampling line of Teflon before reaching the FTIR analyser was also investigated by means of the transient technique.

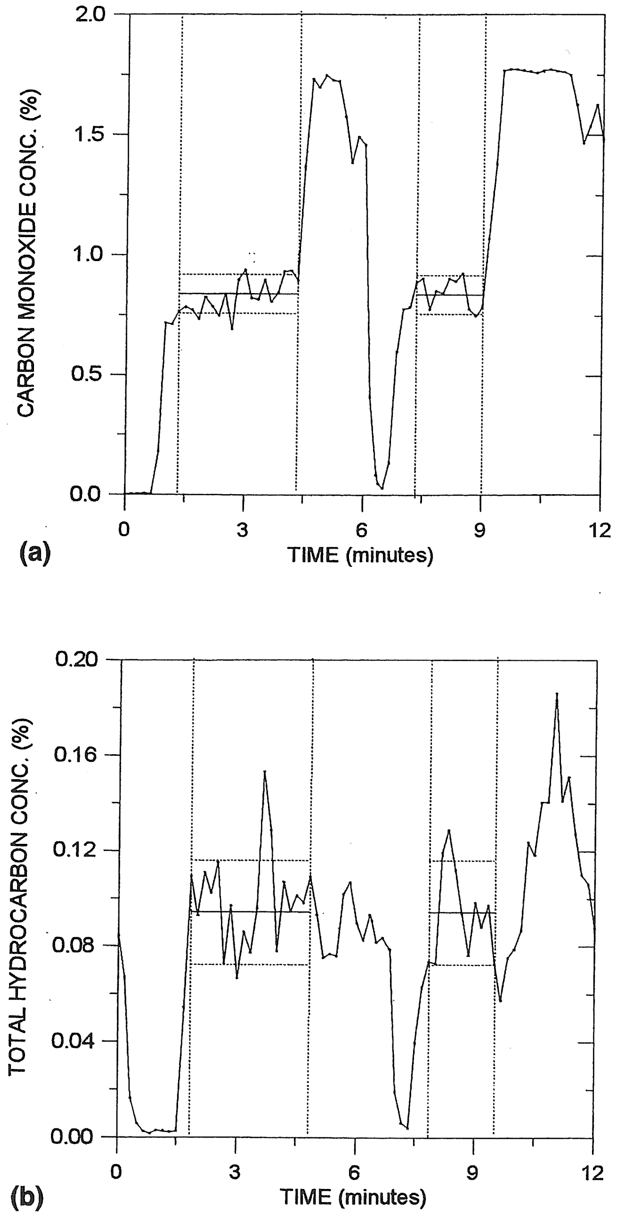

Fig.5a,b Concentration profiles of CO and total HC from measurement periods indicated with vertical dotted lines. After the measurement period the probe is first plugged with bed material (CO rises) and then backflushed (CO falls). Mean values and mean ± one standard deviation are indicated with horizontal (solid and dotted) lines.

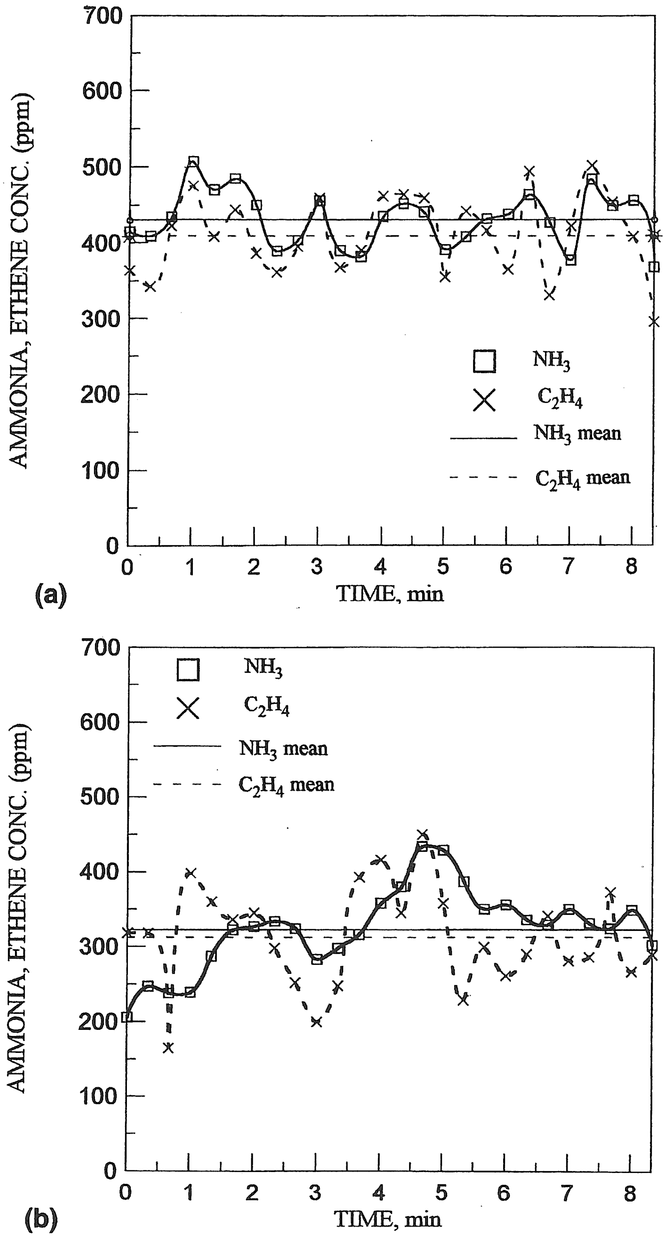

Fig.6a,b Concentration profile of NH_3 and C_2H_4 from measurements in port H2 (0.65 m from the bottom), Fig 6a and port H13 (11 m from the bottom), Fig.6b The mean values are indicated as solid and dotted lines.

3.2.1 Reactions in a filter-cake

A possible filter-cake would consist of silica sand, ashes and (partly devolatilised) char. In a previous measurement during coal combustion, the formation of a filter-cake resulted in higher levels of CO and hydrocarbons over a period of time until the quartz filter was back-flushed, as shown in Fig.5. The transient in Fig.6 is taken from the present measurements, and was obtained by evaluation of all the individual spectra (27 spectra) forming the mean values indicated. No trends similar to those observed in Fig.5 can be seen in Figs.6a and b for NH_3 and C_2H_4 in measurement position H2, close to the dense bed, or in H13 in the exit of the combustion chamber. This is a strong indication that measured gas concentrations are not affected by the formation of a filter-cake. Bed material that enters the probe is believed to stay on the bottom of the cooling shield, and sampled gas probably passes the top part where the pressure-drop is lower.

3.2.2 Adsorption of NH_3 in the sampling lines

NH_3 could also possibly be adsorbed somewhere in the gas sampling probe, its filters, pump or at the walls of the heated Teflon sampling tubing. Fig.7 shows the transient of NH_3, NO and CO from a previous test with NH_3 injection to the exit of the cyclone duct, where an on-line gas sampling infra-red spectrometer[12] (MCS 100, Perkin Elmer Bodenseewerk) was used temporarily for analysing hot flue gases. Fig.7 can be divided into three periods: a) start of NH_3 injection; b) connecting of sampling tubing to wash bottles for a period of 66 minutes; c) end of NH_3 injection. Both the starting and stopping of the NH_3 injection led to very long transients of the NH_3 signal from the instrument relative to the fast response in the NO and CO signals. A fast response of all three signals NH_3, CO and NO can be seen in the beginning of period 2 when air was suddenly passed directly into the sample cell of the instrument. Reconnecting the sample tubing at the end of period 2 also led to a fast response of the three signals, which implies that the probe, filter and tubing were saturated with adsorbed NH_3, since gas was flushed continuously through into the wash-bottles during period 2.

For the FTIR system, Fig.8 (where a plot similar to Fig.7 of each NH_3 spectrum was taken every 30 seconds) shows a different picture. In Fig.8, three NH_3 / NO molar ratios were tested, beginning with the highest ratio 7.1, reducing it to 2.8 and finally to 1.0. The concentration levels (NH_3 peaks at 966 and 930 cm^{-1}) respond directly to any changes of the flow rate of injected NH_3; this was especially clear when the NH_3 injection was started, where only 2 minutes elapsed (four spectra) before the average NH_3 level was reached (compared with 2 hours in Fig. 7). It was also clear when the valve for injection of NH_3 was accidentally opened instead of closed for a short period on the occasion when the flow rate was adjusted from a molar ratio of 2.8 to 1.0. This incident can be closely followed as 'spikes' in the NH_3 peaks in Fig.8.

The behaviour with long transients of the MCS 100 system is probably linked to the use of a probe filter made of sintered stainless steel, since the heated Teflon tubing and pump are identical with those used in the present FTIR instrument. The gas-sampling probe, Fig.4, is instead equipped with a ceramic filter (Kellundite: Ferro Corporation), which minimised the adsorption problem. The transient behaviour of the FTIR system means that no adsorption effects exist such as those observed when a probe with a sintered stainless-steel filter unsuitable for NH_3 measurements was used.

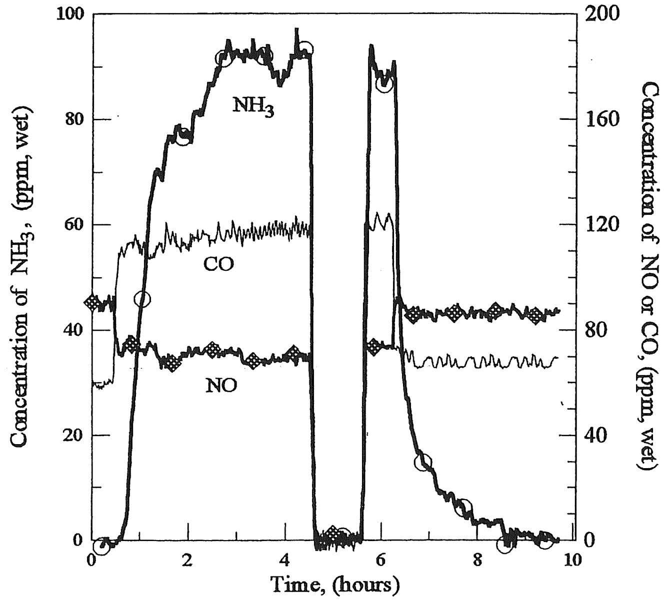

Fig.7 Concentration of CO, NO and N_2O (as measured) in the flue-gas duct from the CFB boiler during a previous test with NH_3 injection into the exit duct of the hot cyclone. NH_3 injection between t = 0.5 and 6.23 h. Sample tube bypassing instrument between t = 4.5 and 5.6 h.

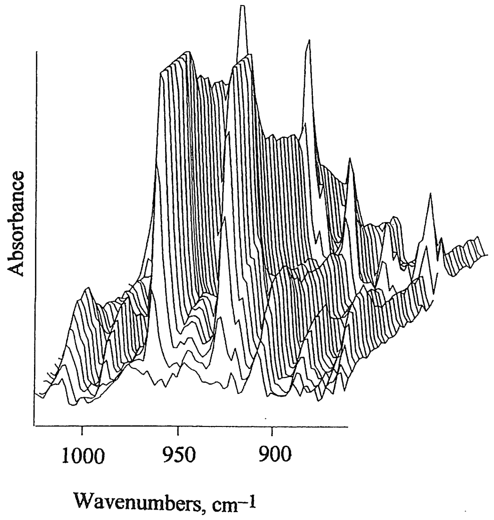

Fig.8 Spectra of the wet flue gas collected during the NH_3 injection to the exit duct of the hot cyclone. Spectral range expanded to the interval used for the determination of NH_3 (NH_3 - peaks at 966 and 930 cm^{-1}). The time elapsed between two spectra is 30 seconds. The highest NH_3/NO molar ratio of 7.1 viewed after 4 spectra. Note the 'spikes' in NH_3 absorbance when changing from a NH_3/NO molar ratio of 2.8 to 1.0.

4 Discussion and conclusions

The model calculations showed that secondary reactions with NH_3 could be of importance for the accuracy of the GQ probe measurement. This contradicts the almost identical results in the comparison with the parallel FTIR measurement[1], where almost identical NH_3 concentrations were measured. The reason for this difference between the calculation and this measured result could be an overestimation of the conversion of NH_3 by the model. The dominant reaction in the model is oxidation over char.

According to measurements carried out in the same boiler[13], NH_3 and oxygen are not well mixed and therefore not normally present at the same time in the probe. If this is the case, the influence of oxidation reactions becomes overestimated by the model. The assumption of an evenly distributed filter-cake on the quartz filter could also lead to a high influence of the filter-cake, since if it were unevenly distributed the sampled gas would probably pass through the thinnest part of it, where the pressure-drop is lower. Because of these imperfections, the model should be regarded primarily as a tool for simple estimation of measurement errors and for design of probes. It is important to design a probe in such a way that formation of a thick filter-cake is avoided. Possible reactions over filters can be reduced by the use of pure and less active filter materials. Finally, homogeneous reactions can be avoided by having residence times as short as possible in hot and uncooled sections. In addition, more accurate calculations of measurement errors would be possible, if the quality of the input data concerning the kinetics in the model were improved.

Transients taken from FTIR showed that the accuracy of the NH_3 measurement with the gas-sampling probe is not affected by the formation of a filter-cake or by adsorption in the sampling lines. The study of transients is not possible in the GQ probe measurement, since each test was carried out for 15 minutes. The mean value from two reliable double samples in each port was used instead in the evaluation.

5 Acknowledgement

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