

SECONDARY EFFECTS IN SAMPLING AMMONIA IN THE COMBUSTION CHAMBER OF A CFB BOILER

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Abstract

The characterisation of the concentration profiles of NH_3 and HCN is of great importance for increasing the knowledge of the formation and destruction pathways of NO and N_2O in a fluidized bed boiler (FBB). The dependence of air-staging conditions on the NH_3 and HCN levels in the combustion chamber of an FBB burning coal was previously investigated by means of two independent sampling methods. A comparison of the results concerning NH_3 for the sampling methods revealed a measurement error, which was especially apparent during oxidising conditions in the furnace. In this paper, a more thorough investigation into the measurement errors due to materials in particle filters is presented. NH_3 was measured in a position in the combustion chamber of the same FBB by means of a gas-sampling probe connected to a Fourier Transform Infra Red (FTIR) instrument. Selected were two new and two old filters of materials previously used. The filters consisted of sintered quartz and a ceramic material made of fused alumina particles. A significantly lower level of NH_3 was measured with an old quartz filter in the probe tip compared to all the other materials. The possible explanations for this measurement error are discussed in depth. The occurrence of catalytic oxidation of NH_3 on impurities consisting of entrained bed material in an old quartz filter is suggested.

1 Background

This paper is a sequel to a paper by Kassman *et al*¹, where the influence of air-staging on the concentration profiles of ammonia (NH_3) and hydrogen cyanide (HCN) was studied in the combustion chamber of a CFB boiler burning coal. The measurements were carried out by means of two sampling techniques already applied in the same boiler^{2,3}. These were a gas-sampling (GS) probe connected to an FTIR analyser and a gas-quenching (GQ) probe in which the sample is quenched directly in the probe tip by a trapper solution. The results from these techniques were only in the same range under certain air-staging conditions. The inaccuracy was especially apparent in

the measurements of NH_3 by means of FTIR during oxidising conditions (no air-staging) in the combustion chamber. This inaccuracy was not always of the same magnitude from one day to the next during the same air-staging conditions (Figure 1).

In a previous measurement, a comparison of the two sampling techniques showed almost identical results for NH_3 during three air-staging cases². The NH_3 concentration profile was also compared to that of ethene (C_2H_4). Each change in NH_3 was followed by an identical change in ethene. Consequently, if NH_3 and C_2H_4 do not follow each other, this indicates a measurement error.

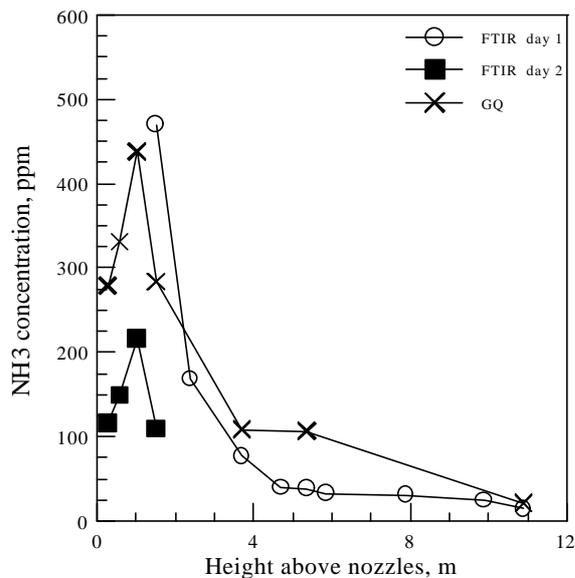


Figure 1. Comparison of the measurements of ammonia with both the gas-quenching probe and the gas-sampling probe during no air-staging (Adopted from Ref. 1)

The possible secondary reactions and measurement errors in sampling ammonia with the two sampling probes have previously been investigated in a model calculation⁴. Kassman *et al*⁴ found that the passing of a particle filter in the probe tip was especially critical for the accuracy. Here, secondary reactions could occur both in a possible filtercake and in the filter material itself.

The arrangement of the particle filter in the GS probe tip was similar to that of the GQ probe¹. The filter material was sintered quartz in both sampling techniques. It is probable that a measurement error due to a filtercake would be of the same magnitude in both sampling techniques and also to the same extent from one day to the next during the same air-staging conditions. The quartz filter in the GQ probe was regularly replaced with a new one but the filter in the GS probe tip was only replaced when a visual inspection indicated a breakdown. It was speculated whether the use of old quartz filters could explain the inaccuracy in the results from the gas-sampling probe¹.

This paper presents a more thorough investigation into the possible measurement

errors related to the selection of filter materials. NH_3 and C_2H_4 were measured in one position in the combustion chamber of the same boiler during oxidising conditions.

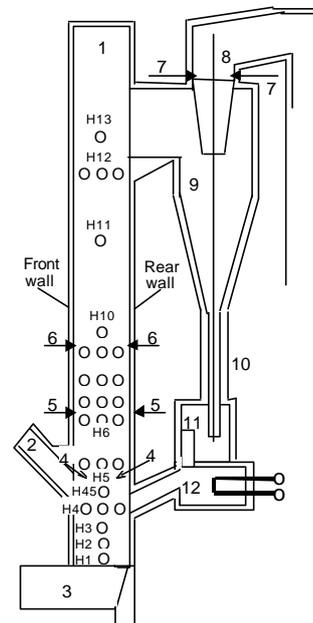


Figure 2. The 12 MW_{th} CFB boiler at Chalmers University of Technology (1) combustion chamber; (2) fuel feed chute; (3) air plenum; (4) secondary air inlet at 2.1m; (5) secondary air inlet at 3.7m; (6) secondary air inlet at 5.4m; (7) secondary air inlet into cyclone exit duct; (8) cyclone exit duct; (9) cyclone; (10) particle return leg; (11) particle seal; (12) heat exchanger. Measurement ports (H1 to H13) on the right boiler wall are indicated

2 Experimental

Operating conditions

The tests were performed in the 12 MW_{th} CFB boiler at Chalmers University of Technology^{1,2,3}. The measurement ports on the wall of the combustion chamber enable the sampling of gas inside the combustor and a more detailed characterisation of the combustion behaviour. In this particular measurement, all sampling was carried out in measurement port H2 (Figure 2).

The fuel was a bituminous coal from Katowice in Poland, the properties of which are given in Ref. 5. The properties were

similar to that in Ref. 1. Limestone was supplied at a molar ratio of 1.8 – 2.0 for sulphur capture. The temperature in the bottom of the combustion chamber was held at approximately 850°C. The excess air-ratio (λ_c) was kept constant at 1.23. The boiler was operated at *no air-staging*: no secondary air, all air added to the bottom of the combustion chamber except a small amount for fluidisation of the particle seal and particle cooler. The conditions were significantly more oxidising in the lower part of the combustion chamber compared to the other air-staging cases in Ref. 1.

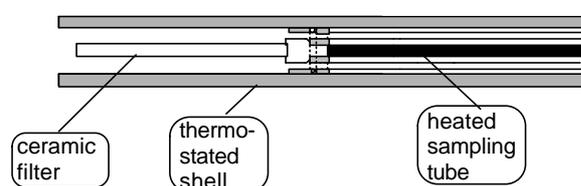


Figure 3a. Front part of the gas-sampling probe as arranged in Åmand *et al*²

Gas-sampling probe and FTIR analysis

The previous arrangement^{2,3} of the gas-sampling probe with a shielded filter tube in the front is shown in Figure 3a. The front part has been reconstructed in order to prevent bed material from being accumulated at the inlet of the filter-tube.

In the present arrangement¹ (Figure 3b), a particle filter is attached to the probe tip in a similar way to that already used in the GQ probe. The filter unit is replaceable enabling a simple change of filter materials. The hot combustion gas passed the filter and was then transported through the centre-pipe, which was electrically heated to 200°C. Downstream of the probe, the combustion gas was transported to the FTIR analyser through heated gas lines (200°C).

The FTIR analyser is a Bomem MB9100 with a 2 dm³ quartz glass cell with an optical path-length of 6.4 metres. The instrument is equipped with a DTGS detector. The maximum resolution 1 cm⁻¹

was used in all tests. The gas cell is heated to 174 °C. The Grams 32 software package is used for evaluation and control of the spectrometer. During the present tests, spectra were collected in a continuous mode where 12 mirror scans, approximately five seconds in length, were sampled for each single-beam spectrum stored. This corresponds to a measurement time of about 1 minute for each single-beam spectrum. An absorbance spectrum was produced from the ratio of this average spectrum and a reference spectrum (100% nitrogen), which was collected immediately before the sampling of the single-beam spectra.

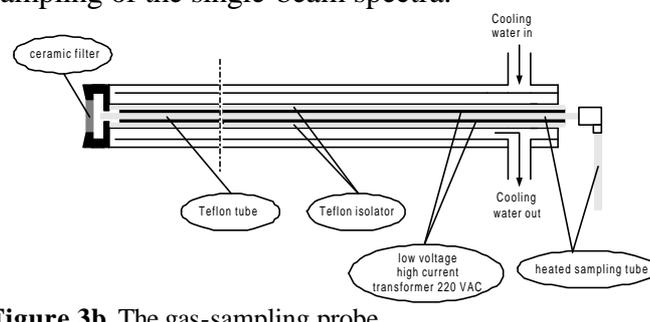


Figure 3b. The gas-sampling probe

In Karlsson and Åmand⁶, a comparison of three procedures for spectral evaluation was made, one of which was selected for this project i.e. a multiple variable analysis method known as partial least square (PLS). The PLS software has been improved since Ref. 6 by means of producing a rest spectrum, which could be visualised, facilitating a judgement of the quality of the prediction.

3 Filter materials

Two new and two old filters were selected from materials previously used in the gas-sampling probe or in the GQ probe. The filters were made of a ceramic material and sintered quartz. The ceramic filter was made of fused alumina particles bonded with a complex alumina borosilicate glass. Made by the Ferro Corporation, it is commercially available under the name of Kellundite.

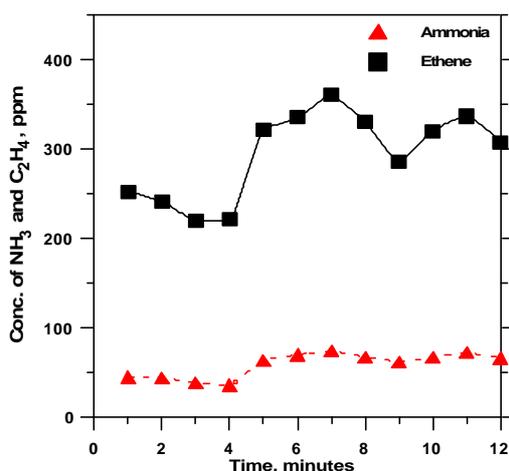


Figure 4. Measurement of ammonia and ethene in measurement port H2 with a new ceramic filter in the probe tip during no air staging

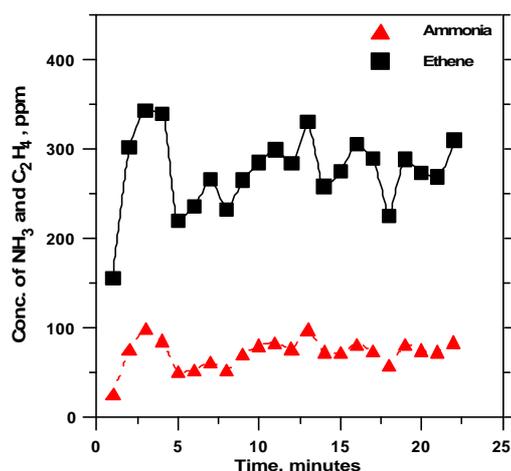


Figure 5. Measurement of ammonia and ethene in measurement port H2 with an old ceramic filter in the probe tip during no air staging

4 Results

A ceramic filter

Figure 4 shows the concentration of ammonia and ethene in measurement port H2 with a new ceramic filter in the probe tip. The changes in the levels of NH_3 and C_2H_4 follow each other indicating that they are due to variations in the furnace over a period of time. The new ceramic filter was then replaced with an old previously used ceramic filter.

In Figure 5 the concentration of NH_3 and C_2H_4 with an old ceramic filter is shown. Also here the changes in the levels of NH_3 and C_2H_4 follow each other in the furnace. It can be observed in Figures 4 and 5, that NH_3 is in the same magnitude (40 to 80 ppm), irrespective of whether the ceramic filter is new or old. The C_2H_4 concentration is between 200 and 350 ppm, regardless of the age of the filter. There are no indications of a measurement error due to secondary reactions with NH_3 .

A quartz filter

Long-term tests were carried out with the quartz filters to investigate the inaccuracies previously found¹. Figure 6 illustrates the

concentrations of ammonia and ethene with a new quartz filter in the probe tip. The changes in the levels of NH_3 and C_2H_4 follow each other in the furnace. No signs of secondary reactions with NH_3 are seen, although the test was carried out for almost two hours. NH_3 was approximately 80 – 120 ppm and C_2H_4 300 to 400 ppm. The NH_3 and C_2H_4 concentrations were somewhat higher to than those using a ceramic filter in the tip of the gas-sampling probe.

The new filter was then replaced with an old quartz filter. Figure 7 displays ammonia and ethene with an old quartz filter. A clear decreasing trend in the NH_3 concentration was observed. The changes in the levels of NH_3 and C_2H_4 no longer follow the same pattern in the furnace. The NH_3 concentration decreased from an initial value of approximately 100 ppm to only 10 ppm, while the long-term decrease of C_2H_4 was less dramatic. A significantly lower level of both NH_3 and C_2H_4 was measured with an old quartz filter in the probe tip compared to all the other filter materials. Figure 8 presents a comparison between the NH_3 results using a new and an old quartz filter and in Figure 9 the same comparison is made for C_2H_4 .

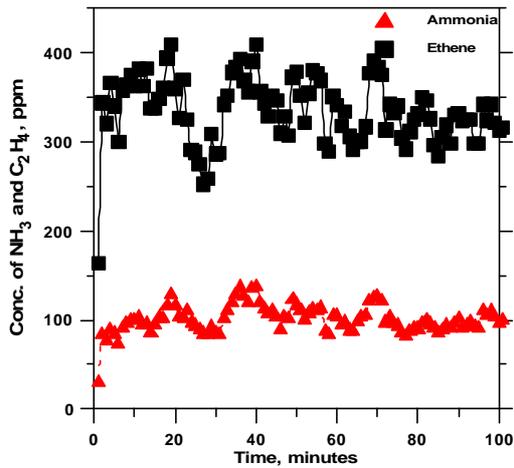


Figure 6. Measurement of ammonia and ethene in measurement port H2 with a new quartz filter in the probe tip during no air staging

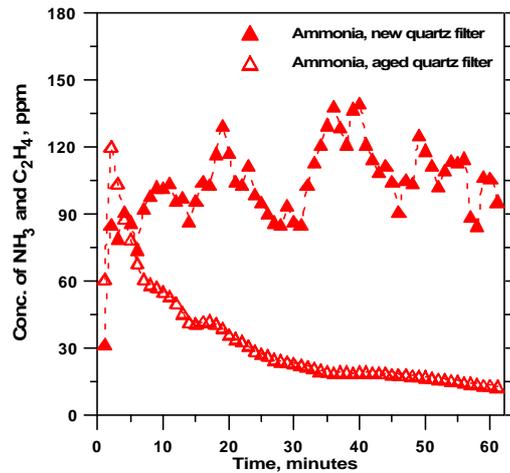


Figure 8. A comparison of the results for ammonia using a new and an old quartz filter in the probe tip during no air staging

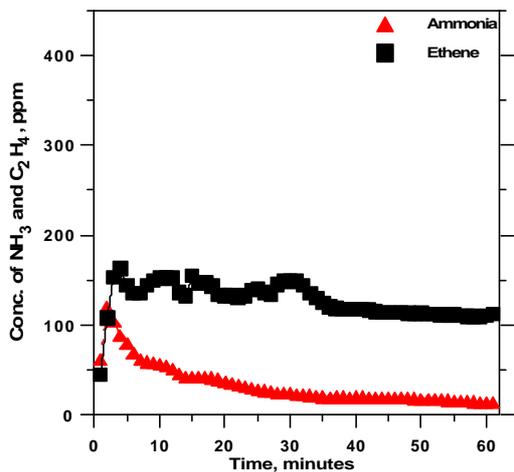


Figure 7. Measurement of ammonia and ethene in measurement port H2 with an old quartz filter in the probe tip during no air staging

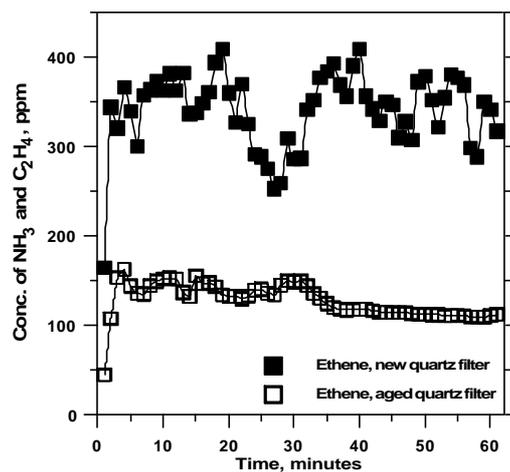


Figure 9. A comparison of the results for ethene using a new and an old quartz filter in the probe tip during no air staging

5 Discussion

The temperature in the combustion chamber of a CFB boiler is approximately 850°C. The temperature together with the presence of particles and the complexity of the gas composition, make a measurement of the true gas concentration of NH_3 with a sampling probe a challenge. Important heterogeneous NH_3 reactions at FBC temperatures are⁴: decomposition of NH_3 (R1); oxidation of NH_3 to NO (R2) or N_2 (R3); reduction of NO with NH_3 (R4). The inaccuracies¹ were especially apparent during oxidising conditions, which favours

oxidation of NH_3 , according to R2 or R3. The model calculations⁴ revealed the passing of the particle filter as especially critical for the accuracy in such a measurement. Here, secondary reactions could occur both in a possible filtercake composed of bed material and in the filter material itself.

The filter consisted of sintered quartz or a ceramic, which are rather inert materials⁴. The bed material during burning of coal mainly consists of limestone, char, silica sand and fuel ash. Secondary reactions in a

filtercake would, however, be irrespective of the age of the filter. The filter is probably self-cleaned with the present arrangement in the probe making the impact from secondary reactions in a filtercake less critical. Visual inspection of old filters showed that this self-cleaning caused a rough and uneven surface with pits from erosion on sintered quartz filters but not on the harder ceramic ones. NH_3 oxidation on impurities of entrained bed material in the uneven surface of an old quartz filter is a possible explanation for the measurement errors using an old quartz filter.

These impurities must then consist of bed material with a high catalytic activity. Calcined or partly sulphated limestone, char and also certain metal oxides, which can be found in fuel ashes, are active materials. Åmand *et al*⁷ performed a step response test with excess supply of lime in a full-scale CFB boiler and observed a rapid increase of NO. One explanation is that NH_3 in the combustion chamber was catalytically oxidised by CaO to NO. A similar rapid increase in NO was observed during another step response test in the same boiler with addition of iron oxide (Fe_3O_4). The presence of iron oxides in the fuel ashes would favour heterogeneous oxidation of NH_3 . Reactions between NH_3 in the combustion gas and calcined limestone, char, or Fe_3O_4 could occur in an old quartz filter in the presence of impurities of entrained bed material.

6 Conclusion

- A similar concentration of ammonia was measured with a new quartz filter and ceramic filters regardless of their age.
- Oxidation of ammonia occurred in an old quartz filter in the presence of impurities of catalytically active bed material. This caused a significant error during measurements in the combustion chamber during oxidising conditions.

7 Acknowledgement

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8 References

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