UV EMISSION AND CHEMICAL KINETICS OF POSITIVE CORONAS AS ENVISAGED FOR FLUE GAS TREATMENT

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Abstract. We have investigated the effect of positive streamer coronas on NO concentrations in $N_2/O_2/NO$ gas mixtures. The energetic electrons of the streamer corona produce active radicals that lead to the removal of NO. The work presented here is also aimed at gaining some insight into the early chemical processes occurring in the discharge. The early processes in a repetitive positive streamer discharge in $N_2/O_2/NO$ mixtures have been studied by measurements of specific light emissions, using time-correlated single photon counting. The time averaged NOγ emission ($A^2\Sigma^+ \dashrightarrow X^2\Pi$) serves as an indicator of the remaining NO concentration in the gas mixture. The evolution of particular species in the discharge is simulated by using a time dependent non-equilibrium plasma chemistry code.

1. Introduction

Streamer coronas are gaining interest in the area of combustion flue gas treatment because of their ability to produce energetic electrons which, through dissociation and ionization processes, generate active species that react with the toxic nitrogen oxide molecules. Emissions from a $N_2/O_2/NO$ gas mixture have here been studied and excited states of N_2, N_2^+, and NO have been identified as suitable candidates for optical detection [1]. The chemical reactions subsequent to energetic electron generation play a very important role in NO removal. In order to understand the early chemical processes occurring in a discharge intended for flue gas treatment, the light emission from a repetitive positive streamer corona in mixtures of $N_2/O_2/NO$ has been studied, varying the concentration of the minor components (O_2 and NO). For the range of conditions considered here, the mean NOγ emission proves to be roughly proportional to NO concentration (see Fig. 1), thus for a closed-off system it can indicate the success or failure of NO conversion versus integrated power input. Hence our efforts here are focused on the measurement of the mean intensity of NOγ emission which, as has been mentioned above, gives information on the remaining NO concentration in the gas mixture in the course of treatment.

Furthermore, to understand the process of corona induced plasma chemistry, we simulated the time dependent non-equilibrium plasma chemistry for sub-atmospheric pressure $N_2/O_2/NO$ gas mixtures. The simulation of species evolvement supports the assumptions about important early processes in the gas mixture considered here.

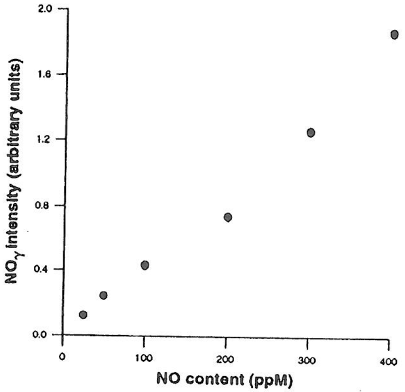

Fig. 1 $NO\gamma$ intensity vs. NO concentration for 25-400 ppM of NO in 365 mb N_2 and 2 mb O_2.

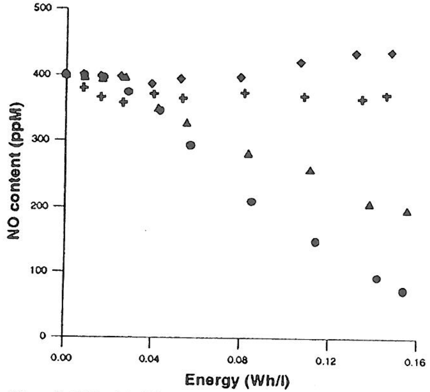

Fig. 2 NO (A-X) emission as a measure of remaining NO concentration in dependence upon specific electrical energy input, normalized to the known initial NO concentration of 400 ppM in 365 mb N_2. Oxygen contents of 2 (●), 4 (▲), 12 (✚) and 24 mb (◆) at 25° C.

2. Experimental Procedure

The discharge used here is a repetitive positive point-plane streamer discharge with a DC high voltage source. The positive electrode has a hemispherical platinum point of 0.1 mm radius which is mounted on the axis of a tubular vessel of borosilicate glass of 7.3 litre volume. The discharge originating from this platinum point faces a monel mesh at a spacing of 15 mm, is supplied via a series resistor from a 0-15 kV *constant current* source typically set to 250 μA, and this produces discharge repetition at a few kHz. Light from along the discharge filament is focused axially on to the entrance slit of a 250 mm Czerney-Turner monochromator. For the detection of monochromatic radiation, time-correlated single photon counting is employed. The light detector is a fast-focused photomultiplier operated in the single-photon counting mode. The standard time-correlation set-up [2] utilizes the sharp initial rise in discharge current to start the time-to-amplitude converter (TAC). A fixed time window of 1 μs duration is used here to maintain a correlation with the bulk of the photon emission associated with each streamer discharge. For recording the light intensity of a particular emission ($NO\gamma$ emission here), the TAC "valid start" and "valid stop" pulses are taken to analogue ratemeter, the linear outputs of which are fed directly to a potentiometric recorder. The present series of measurements is based on a gradual build-up of a standard flue gas (ESP II: 6% O_2, 8% H_2O, 13% CO_2, and balance N_2 with varied NO content(25 - 400 ppM here)) to 500 mb total pressure at 25°C. To a base concentration of N_2 (365 mb), varying amounts of O_2 and NO are added in order to assess to influence of these minor components on NO removal efficiency. Finally the gas composition (especially NO and NO_2 content), is checked after a fixed treatment time by means of FT-IR absorption analysis in a 11.25 m gas cell. The gas sample drawn from the corona discharge reactor produces a pressure of about 60 Torr in the FT-IR measurement cell. This gas is subsequently diluted with N_2 to a total pressure of 750 Torr. Quantitative analysis was carried out by means of simple spectra subtraction.

3. Measurements of NOγ mean emission intensity

The proportionality of NO concentration and NO (A - X) emission (Fig. 1) from a gas of high N_2 content offers a relatively simple way to follow the evolution of NO concentration in the course of discharge treatment in a closed-off system. The results of a series of such measurements are shown in Fig. 2. For the simple dry gas investigated here (400 ppM NO in 365 mb N_2 with 2/4/12/24 mb O_2), the NO removal at 250 μA mean discharge current is most successful at the lowest oxygen content of 2 and 4 mb (lowermost points in Fig. 2). The removal efficiencies achieved are about 2130 ppM·l/Wh with 2 mb O_2 and 1400 ppM·l/Wh with 4 mb O_2. This is understandable as the main removal process for NO here would be the reaction with atomic nitrogen; the competing reaction of NO is oxidation by atomic oxygen forming NO_2 which becomes more and more important as the oxygen concentration is increased. NO_2 in turn reacts with atomic oxygen, re-forming NO. With increasing oxygen content, the re-cycling of NO involves an increasing percentage of the NO present until eventually the rate of new formation of NO in other reactions in the discharge becomes greater than the removal rate, as is observed with a 24 mb (6%)

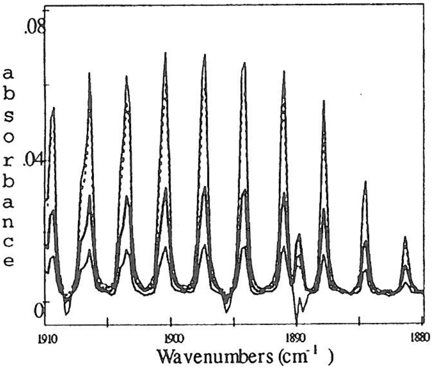

Fig. 3 IR absorption spectrum representative of residual NO content after electrical energy injection of about 0.15 Wh/l , for different oxygen content of 0.5, 1, 3 and 6 % from bottom to top.

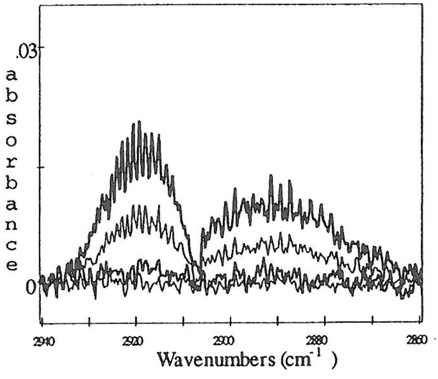

Fig. 4 IR absorption spectrum representative of residual NO_2 content after electrical energy injection of about 0.15 Wh/l , for different oxygen content of 0.5, 1, 3 and 6 % from bottom to top.

oxygen content (uppermost points in Fig. 2). The treatment results given in Fig. 2 for an energy investment of about 0.15 Wh/l have been roughly confirmed by FT-IR absorption measurements which also indicate minimal NO (Fig. 3, lower curves) and NO_2 (Fig. 4, lower curves) final concentrations at 2 and 4 mb oxygen. With higher oxygen content (12 and 24 mb corresponding to 3 and 6 %), the FT-IR measurements indicate considerable generation of NO_2 (Fig. 4, upper curves), while NO removal is unsuccessful. Overall NO_x (NO + NO_2) increases by 25 % with 0.15 Wh/l energy input. The failure of NO removal at 3 and 6% oxygen content in our dry gas mixture is due to the NO cycling mentioned, combined with the new generation of NO.

4. Plasma chemistry simulation

In order to understand the process of corona induced plasma chemistry more completely, we simulated the time dependent non-equilibrium plasma chemistry for sub-atmospheric pressure $N_2/O_2/NO$ gas mixtures. For this simulation we used the plasma chemistry code KINEMA [3], coupled with the electron Boltzmann solver, ELENDIF [4]. The plasma chemistry code is a time dependent chemical kinetics code, which solves the set of coupled rate equations. The kinetics code is coupled with the Boltzmann code, to compute the concentrations of all the chemical species involved as a function of time. A relatively complete set of chemical reactions [5] of the species involved is fed to the chemistry code along with their reaction rate coefficients. The Boltzmann code reads all the elastic and inelastic cross sections as input and generates the electron energy distribution. The electron rate constants corresponding to the calculated electron energy distribution and the mean electron temperature are also produced and fed into the chemistry code.

Fig. 5 shows the species evolution of a $N_2/O_2/NO$ gas discharge excited by a nanosecond time scale Gaussian pulse with a pulse width of 75 nanoseconds and a peak E/N of 180 Townsend. The fast decay of NO at early times can be explained by the following excited state reactions of N_2 with NO:

$$(1) \quad N_2(A^3\Sigma_u^+) + NO \text{ ----> } N_2 + N + O \quad [6]$$
$$(2) \quad N_2(a'^1\Sigma_u^-) + NO \text{ ----> } N_2 + N + O \quad [7]$$
$$(3) \quad N_2(A^3\Sigma_u^+) + NO \text{ ----> } NO(A\,^2\Sigma^+) + N_2 \quad [8]$$

The amount of O_2 in the discharge has a strong influence on the intensity of NO(A-X) emission as NO(A $^2\Sigma^+$) is quenched by oxygen [9][10]. However, reaction (3) is of particular interest in our measurements, as it serves as an indication of the NO content in the gas mixture. Thus for comparing absolute NO concentrations in different gas mixtures, the strong quenching of NO(A $^2\Sigma^+$) by O_2 has to be taken into account. At long times the dominant reaction that leads here to the removal of NO is:

$$(4) \quad N + NO \text{ ----> } N_2 + O \quad [11]$$

The dotted curve in Fig. 5 shows the N_2 regenerated via this reaction path. In the discharge, generation of NO can also take place. For instance the oxygen atoms produced in the discharge react with NO_2 to produce NO via reaction,

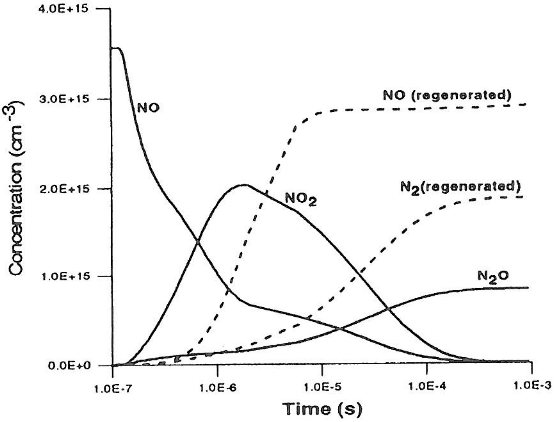

Fig. 5 Species evolution in a mixture of 365 mb N_2 with 400 ppM NO and 12 mb O_2.

(5) $O + NO_2 \text{ ----> } NO + O_2$ [12]

This is shown in Fig. 5 by the dotted curve labelled NO (regenerated). NO_2 also reacts with atomic nitrogen to produce N_2O [11], which is an important reaction for the removal of NO_2. The other reaction that contributes to N_2O formation is the reaction of $N_2(A^3\Sigma_u^+)$ with O_2 [13].

5. Conclusions

In a closed-off system which does not offer an efficient removal process for NO_2, the predominant final decomposition of NO has to be N_2 plus a modest quantity of N_2O probably originating from the reaction of NO_2 with N atoms. With high oxygen content the *oxidation* path becomes more dominant and thus enhances the recirculation of NO until eventually - due to new formation of NO from other discharge products - NO removal can no longer be achieved. Thus the decomposition of NO to N_2 is brought about when oxygen concentrations are low.

By optimizing the discharge for relatively less energy injection into late stages of streamer development, it will certainly be possible to obtain better NO/NO_x removal efficiencies than those reported here, even for the same process as those considered here. Chemical kinetics based simulations of the species evolvement can help to understand the important reaction paths.

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