THEORETICAL ANALYSIS OF REMOVAL OF OXIDES OF SULPHUR AND NITROGEN IN PULSED CORONA

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Abstract

The plasma chemistry has been examined for reactions occurring in pulsed electrostatic precipitators. Calculations have been made of the rate coefficients in air and a typical flue gas for the electron dissociation of nitrogen, oxygen and water vapour. These rates are found to only become appreciable for values of E/N greater than about 80 Td; E is electric field strength and N the gas number density. Chemical calculations using this data indicate that SO_2 is removed by conversion to sulphuric acid by reactions with OH radicals, and that oxides of nitrogen are removed largely by reduction by N atoms. To attain these high values of E/N,it is necessary to use pulsed voltages of puse width ~ 1 μs to avoid electrical breakdown.

Introduction

Recently it has been discovered empirically that pulsed corona discharges can be used to remove, or at least partially remove, SO_2 and the oxides of nitrogen from flue gases of power stations [1]. Questions then arise as to the detailed chemical processes that occur: Are SO_2 and the oxides of nitrogen removed by (a) electron dissociation of these molecules, (b) oxidation by O atoms and then further reactions with water vapour that is always present in a flue gas leading to the formation of sulphuric and nitric acid, (c) dissociative recombination of ions such as NO^+, (d) oxidation reactions through the reactive species O^-, (e) oxidation through the OH radical produced from water vapour, or (f) reduction processes from N atoms? Furthermore why is it necessary to pulse the discharge? These questions are examined in this paper and are important, not only in understanding how to improve the efficiency of the process, but also in determining whether non-thermal chemical processing can be used in other applications to eliminate other minority constituents, such as carcinogenic dioxins or ozone destructive chloro and fluorocarbons.

Theory

We consider a uniform electric field for a uniform plasma and no attempt is made to explain the experimental finding that chemical processing is far more efficient for positive corona, possibly due to the presence of streamers, than for negative corona. In order to simulate the high field region of the streamer head generated by the high voltage pulses, we calculate the time dependence of various species starting with 1 electron/cc in a uniform field corresponding to an *E/N* of 150 Td for 0.1 ms followed by an *E/N* of 40 Td; 1 Td = 10^{-17} Vcm^2. The *E/N* of 150 Td corresponds at 1 bar to a field of 37 kV/cm. Rate coefficients for ~ 90 reactions between species have been taken from various compilations [2-4]. However, the important initiating reactions in the corona discharge are due to the collisions of electrons of the discharge with the component constituents. Such reactions can produce the neutral species O, N and OH which can have a central role in removing NO_x and SO_x species for some time after the initiating electrons of a corona pulse have been removed from the discharge. The rate coefficients of reactions involving electrons depend on the energy of the electrons which is determined by the energy balance between energy gained from the local electric field and the energy losses due to collisions with the gas molecules. Thus the rate coefficients depend on the electric field.

We calculate the energy distribution of electrons in a flue gas mixture using the methods of gaseous electronics [5-6] by obtaining a solution of the Boltzmann transport equation. We can then calculate rate coefficients for the various reactions as a function of the local electric field. Literature values of electron collision cross-sections, as a function of energy, have been used to account for all collision processes contributing to electron energy losses [7-9]. A total of 62 inelastic processes were considered. The method and computer code used for this calculation were those used in an earlier calculation to obtain similar energy distributions for various mixtures of gases used in CO_2 lasers [8]. Once the energy distribution is determined for a given flue gas mixture, individual rate coefficients can be obtained for the various electron collision processes.

Results

(1) Rate Coefficients.

We have calculated the rate coefficients for various electron processes as a function of

E/N for a flue gas mixture of N_2, O_2, CO_2 and H_2O in the ratio 0.741 : 0.033 : 0.143 : 0.083, which is the calculated ratio obtained from burning coal from the Bayswater Colliery in NSW, Australia. Rate coefficients for the processes which dissociate oxygen, nitrogen and water vapour into O, N, H and OH radicals, shown in Fig. 1, are particularly important. Also shown are production rates for $O(^1D)$ atoms and $N_2(A)$ states, which are also used in our rate equations.

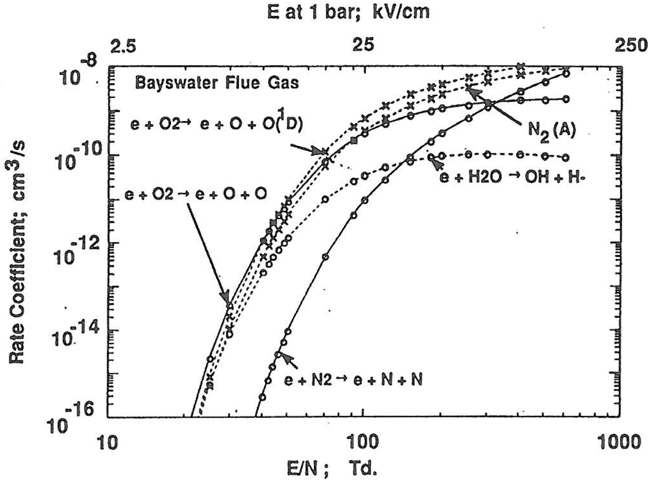

Fig. 1 Calculated rate coefficients from cross sections using the Boltzmann equation.

It is only at values of *E/N* of 80 Td or more that these processes are significant. This is seen in Fig. 2, where the plot marked 'efficiency' is the percentage of electric power spent in exciting electron collision processes aiding in the removal of oxides of nitrogen and sulphur, i.e. reactions leading to the formation of O, N, OH, $O(^1D)$ and $N_2(A)$ species. It is seen that for normal average electric fields of about 5 kV/cm, such processes are negligible.

(2) Pulse Widths.

It is only through the application of voltage pulses with periods of less than the order of 1 μs that it is possible to attain values of *E/N* of 100 Td or more without heating effects causing the discharge to become an arc. For an estimate of this limiting pulse width, we calculate the time interval Δt for the discharge to heat the gas by 10 000 K after attaining equilibrium conditions. We evaluate this time interval from $\Delta t = \rho C_p \Delta T/(jE)$ where ρ =

0.001 g cm^{-3} is the density of air at room temperature, $C_p = 1$ J/(g K) is the specific heat of air, j is the current density, E is the electric field strength and $\Delta T = 10000$ K is the increment in temperature. By using $j = n_e e W$, we obtain $j = 1000$ A/cm^2 with $n_e = 10^{15}$ cm^{-3} from the equilibrium electron density obtained by balancing ionization with recombination and attachment, the drift velocity, $W = 10^7$cm/s, for 150 Td and electronic charge, $e = 1.6\ 10^{-19}$ C. Then using $E = 40\ 000$ V/cm for 150 Td at 1 bar, we obtain $\Delta t = 1/8$ µs as an estimate of the time for the temperature to increase by $\Delta T = 10\ 000$ K. The curves of Fig. 2 indicate that the efficiency of such processes increases for values of E/N up to 200 Td, for which a pulse width of 1 ns would be necessary.

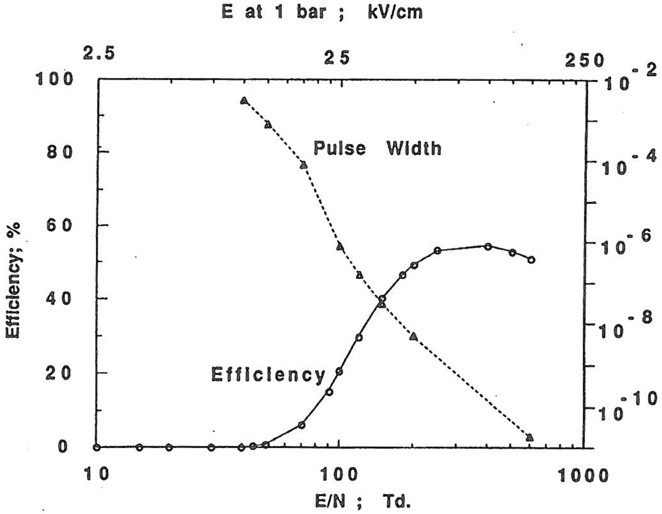

Fig. 2 Calculated Pulse Widths to prevent arc formation and "Efficiency" for the removal of SO_x and NO_x.

(3) Principal Chemical Reactions for destruction of NO_x and SO_x.

The relative role of the various reactions has been determined by calculating particle concentrations as a function of time for many different combinations of reactions [10]. Over 90 reactions have been considered. It might be thought that the production of O radicals through the electron dissociation of oxygen would have a major role in the oxidation of SO_2, NO and NO_2 to higher oxides because of the following reactions

$$O + SO_2 + N_2 \rightarrow SO_3 + N_2 \; ; \; a = 1.4 \; 10^{-33}$$

$$O + NO + N_2 \rightarrow NO_2 + N_2 \; ; \; a = 9.0 \; 10^{-32}$$

$$O + NO_2 + N_2 \rightarrow NO_3 + N_2 \; ; \; a = 9.0 \; 10^{-32}.$$

The rate coefficients *a*, are given in units of $cm^6 \; s^{-1}$ for three body reactions and in units of $cm^3 \; s^{-1}$ for two body reactions. However, O also reduces SO_3 and NO_2 through the reactions

$$O + SO_3 + N_2 \rightarrow SO_2 + O_2 + N_2 \; ; \; a = 8.0 \; 10^{-30}$$

$$O + NO_2 \rightarrow NO + O_2 \; ; \; a = 1.0 \; 10^{-11}$$

The rate coefficients of these last two reactions are large. The net effect is that there is no removal of SO_2 and only a small reduction in the oxides of nitrogen.

The OH radical from water vapour can convert SO_2 into sulphuric acid and nitrogen oxides into nitric acid. These acids are assumed to be removed from flue gases because of their solubility in moisture which is always present in the flue stack. The following reactions involving the OH radical contribute to acid formation.

$$OH + SO_2 \rightarrow HSO_3 \; ; \; a = 7.5 \; 10^{-12}$$

$$OH + HSO_3 \rightarrow H_2SO_4 \; ; \; a = 1.0 \; 10^{-12}$$

$$OH + NO_2 \rightarrow HNO_3 \; ; \; a = 1.0 \; 10^{-11}$$

$$OH + NO \rightarrow HNO_2 \; ; \; a = 6.6 \; 10^{-12}$$

$$OH + HNO_2 \rightarrow NO_2 + H_2O \; ; \; a = 0.5 \; 10^{-11}$$

Our calculations show that OH has the major role in the removal of SO_2 and some role in the removal of oxides of nitrogen at 150 Td.

The N atoms produced by electron dissociation of molecules of nitrogen have an influence on the reduction of oxides of nitrogen because they can chemically reduce them to nitrogen through the following reactions.

$$N + NO \rightarrow N_2 + O \; ; \; a = 5.9 \; 10^{-11}$$

$$N + NO_2 \rightarrow 2\,NO \; ; \; a = 9.0 \; 10^{-12}$$

Our calculations indicate that these reactions have the major role in reducing the concentrations of nitrogen oxides at 150 Td.

From our more detailed study [10], we make the further generalisations

(a) Reactions caused by direct electron impact with SO_2 and nitrogen oxides have little effect, because electrons and the oxides are minority components.

(b) Ion molecule reactions such as charge transfer reactions of O_2^+ with NO and NO_2 produce NO^+ and NO_2^+. Subsequent recombination reactions

$$NO_2^+ + e \rightarrow NO + O \; ; \; a = 3.0\ 10^{-7}$$

$$NO^+ + e \rightarrow N + O \; ; \; a = 7.0\ 10^{-7}$$

have the effect of reducing oxides of nitrogen. Furthermore O^- reacts with NO and SO_2 to produce NO_2 and SO_3 also reducing oxides of sulphur and nitrogen. However, we find that the reduction effect of N atoms is still dominant in the removal of nitrogen oxides and reactions involving OH are dominant for the removal of SO_2.

(c) Production of nitrous oxide. We have also investigated the production of nitrous oxide (N_2O) by the corona discharge, for example by

$$N + NO_2 \rightarrow N_2O + O \; ; \; a = 3.0\ 10^{-12}.$$

Despite reactions with $O(^1D)$ and $N_2(A)$, which destroy N_2O, we find that about 20% of the NO_2 is effectively converted to nitrous oxide. Nitrous oxide is relatively inert gas, but it is a greenhouse gas so its production in large quantities is undesirable.

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