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# Theory of Chemical Processing Using Pulsed Precipitators\*

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#### Abstract

A theoretical analysis is given, using methods of gaseous electronics and plasma chemistry, of the removal of SO<sub>2</sub> and nitrogen oxides from flue gases by use of pulsed electrical corona. Calculations indicate that the rate coefficients in a typical flue gas for the electron dissociation of nitrogen, oxygen and water vapour 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 these data indicate that SO<sub>2</sub> is removed by conversion to sulphuric acid by reactions with OH radicals, and that oxides of nitrogen are removed largely by reduction from N atoms. To attain these high values of E/N, it is necessary to use pulsed voltages of pulse width  $\sim 1 \mu s$  in order to avoid electrical breakdown. The maximum pulse widths allowable to avoid breakdown is estimated by requiring the total energy input to be less than that which heats the gas by  $10^4$  K.

#### 1. Introduction

A topic of current interest in the field of gaseous electronics is the use of non-thermal gas discharges, such as corona, for chemical processing. Corona discharges have been used commercially for a long time to produce ozone from oxygen (Siemens 1857). Recently it has been discovered empirically that pulsed corona discharges can be used to remove, or at least partially remove, SO<sub>2</sub> and the oxides of nitrogen from flue gases of power stations (Masuda and Nakao 1990). These chemical changes are achieved through the action of initiating electrons of density no more than  $10^{14}$  cm<sup>-3</sup> in a background gas at atmospheric pressure and thus of density  $10^{19}$  cm<sup>-3</sup>. Furthermore, the reactions occur with the gas at ambient temperature, so that the processes should be energy efficient, unlike thermal plasma processing in an electric arc, where the temperature of all plasma particles is raised to the order of 15000 K. A recent study committee of MITI in Japan (Masuda 1993) has concluded that the pulsed plasma process using corona to remove oxides of sulphur and nitrogen from flue gases is feasible, economic and technically simple compared with two other technologies, namely (1) the conventional gypsum and ammonia-catalytic chemical process and (2) electron beam methods.

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The question now arises as to the detailed processes that occur. Are SO<sub>2</sub> and the oxides of nitrogen removed by (a) electron dissociation of these molecules, (b) oxidation by O atoms to higher oxides and thus to the formation of sulphuric and nitric acid through reacting with water vapour that is always present in a flue gas, (c) dissociative recombination of ions such as NO<sup>+</sup>, (d) oxidation reactions through the reactive species O<sup>-</sup>, (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 important, not only to understand how to improve the efficiency of the process, but also to determine whether non-thermal chemical processing can be used in other applications to eliminate other minority constituents, such as carcinogenic dioxins or ozone destructive fluorocarbons.

In the present paper, the methods of gaseous electronics are used to investigate these questions (Huxley and Crompton 1974). Previous investigations have used solutions of the Boltzmann transport equation to derive electron energy distributions as a function of the electric field. Then, by comparison of measured and derived transport coefficients obtained from these energy distributions, electron collision cross sections have been derived for individual electron collision processes for most common gases (e.g. Frost and Phelps 1962).

We have used these cross sections to derive rate coefficients for air and a particular flue gas mixture for the important processes of the plasma chemistry, i.e. the dissociation of nitrogen and oxygen into atoms, the attachment of electrons to form  $O_2^-$  and  $O^-$ , the dissociative attachment of electrons to water vapour to form OH, and the formation of important excited states such as  $O(^1D)$ , which reacts with water vapour to produce OH. These rate coefficients have then been used to elucidate the principal channels of the processes that reduce the concentrations of oxides of sulphur and nitrogen. The full analysis involves 96 reactions and is presented in Lowke and Morrow (1995).

#### 2. Theory

We consider only 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 per cm<sup>3</sup> in a uniform field corresponding to an E/Nof 150 Td for  $0.1 \ \mu s$  followed by an E/N of 40 Td ( $1 \text{ Td} \equiv 10^{-17} \text{ V cm}^2$ ). The E/N of 150 Td corresponds at 1 bar to a field of 37 kV cm<sup>-1</sup>. Rate coefficients for reactions between neutral species have been taken from various compilations (Eliasson and Kogelschatz 1986; DeMore 1990; Matzing 1991; Kossyi *et al.* 1992).

However, the important initiating reactions in the corona discharge are due to the collisions of electrons of the electrical discharge with the component constituents. Such reactions produce the neutral species O, N and OH which have a central role in removing  $NO_x$  and  $SO_x$  species long 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 air and in a flue gas mixture by a solution of the Boltzmann transport equation and thus 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 (e.g. Lawton and Phelps 1978; Pitchford and Phelps 1982). 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 (Lowke *et al.* 1973). Once the energy distribution is determined for a given flue gas mixture and electric field, individual rate coefficients can be obtained for the various electron collision processes.



Fig. 1. Rate coefficients calculated from cross sections and solution of the Boltzmann equation.

#### 3. Results

#### (3a) 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<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O 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  $O(^{1}D)$  atoms and  $N_{2}(A)$  states, which are also used in our rate equations.

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 the removal of oxides of nitrogen and sulphur, i.e. reactions leading to the formation of O, N, OH, O(<sup>1</sup>D) and N<sub>2</sub>(A) species. It is seen that for normal average electric fields of about 5 kV cm<sup>-1</sup> such processes are negligible.

### (3b) Pulse Widths

It is found experimentally that it is only through the application of voltage pulses with pulse widths of less than the order of  $1 \ \mu s$ , that significant reductions of  $SO_2$  and nitrogen oxides occur (Masuda and Nakao 1990). It is proposed that these small pulse widths are necessary to be able to attain the required high values of E/N, without the discharge becoming an arc. It is possible to attain values of E/N of 100 Td or more, without heating effects causing the discharge to become an arc, by having a sufficiently small pulse width. For an estimate of this limiting pulse width, we calculate the time interval  $\Delta t$  for the discharge to heat the gas by 10<sup>4</sup> K. We evaluate this time interval from  $\Delta t = \rho C_p \Delta T / jE$  where  $\rho = 0.001 \text{ g cm}^{-3}$  is the density of air at room temperature,  $C_p = 1 \text{ J/g K}$  is the specific heat of air, j is the current density, E is the electric field strength and  $\Delta T = 10^4$  K is the increment in temperature. By using  $j = n_e eW$  and an electron density value of  $n_e = 10^{15} \text{ cm}^{-3}$  from the equilibrium electron density, the drift velocity,  $W = 10^7 \text{ cm s}^{-1}$ , for 150 Td and electronic charge  $e = 1.6 \times 10^{-19} \text{ C}$ , we obtain  $j = 1000 \text{ A cm}^{-2}$ . Then using  $E = 4 \times 10^4 \text{ V cm}^{-1}$  for 150 Td at 1 bar, we obtain  $\Delta t = 1/8 \ \mu s$ , which is an estimate of the time for the temperature to increase by  $\Delta T = 10^4$  K. The curves in 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.

## (3c) Principal Chemical Reactions for Destruction of $NO_x$ and $SO_x$

The relative role of the various reactions has been determined by doing calculations of particle concentrations as a function of time for many different combinations of reactions (Lowke and Morrow 1994). 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:

$$O + SO_2 + N_2 \rightarrow SO_3 + N_2; \ k = 1 \cdot 4 \times 10^{-33},$$
 (1)

$$O + NO + N_2 \rightarrow NO_2 + N_2; \ k = 9 \cdot 0 \times 10^{-32},$$
 (2)

$$O + NO_2 + N_2 \rightarrow NO_3 + N_2; \ k = 9 \cdot 0 \times 10^{-32}.$$
 (3)

The rate coefficients k are given in units of  $\text{cm}^6 \text{s}^{-1}$  for three-body reactions and in units of  $\text{cm}^3 \text{s}^{-1}$  for two-body reactions. However, O also causes reduction of SO<sub>3</sub> and NO<sub>2</sub> through the following reactions:



Fig. 2. 'Efficiency' curve giving the calculated percentage of total input power for reactions leading to the removal of  $NO_x$  and  $SO_x$ . The curve marked 'Pulse width' gives the calculated time for the discharge to increase in temperature by  $10^4$  K and thus become an arc.

$$O + SO_3 + N_2 \rightarrow SO_2 + O_2 + N_2; \ k = 8 \cdot 0 \times 10^{-30},$$
 (4)

$$O + NO_2 \rightarrow NO + O_2; \ k = 1 \cdot 0 \times 10^{-11}.$$
 (5)

The rate coefficients of these last two reactions are large. The net effect is that there is little removal of  $SO_2$  and only a limited reduction in the total 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:

$$OH + SO_2 \to HSO_3; \ k = 7 \cdot 5 \times 10^{-12}, \tag{6}$$

$$OH + HSO_3 \to H_2SO_4; \ k = 1 \cdot 0 \times 10^{-12},$$
(7)

$$OH + NO_2 \rightarrow HNO_3; \ k = 1 \cdot 0 \times 10^{-11}, \tag{8}$$

$$OH + NO \rightarrow HNO_2; \ k = 6 \cdot 6 \times 10^{-12}, \tag{9}$$

$$OH + HNO_2 \rightarrow NO_2 + H_2O; \ k = 0.5 \times 10^{-11}.$$
 (10)

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:

$$N + NO \rightarrow N_2 + O; \ k = 5 \cdot 9 \times 10^{-11},$$
 (11)

$$N + NO_2 \rightarrow 2NO; \ k = 9 \cdot 0 \times 10^{-12}.$$
 (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, which considers 96 chemical reactions (Lowke and Morrow 1995), we make the following generalisations.

(a) The reaction rate for the spontaneous thermal oxidation of NO to NO<sub>2</sub> by molecular oxygen is very low  $(3 \cdot 3 \times 10^{-39} \text{ cm}^6 \text{ s}^{-1})$  and involves two NO radicals which are minority components, so that this reaction is very slow compared with the effect of reduction of NO<sub>2</sub> by N to NO.

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

(c) The production of OH radicals is achieved principally by the reaction

$$O(^{1}D) + H_{2}O \rightarrow 2OH; \ k = 2 \cdot 2 \times 10^{-10},$$
 (13)

rather than by the electron dissociation of  $H_2O$  into OH and H. Thus there are far more OH radicals than H radicals and we expect that the reduction effects of H radicals will be much less than for OH radicals, although we have not investigated these effects.

(d) There are many ion molecule reactions, for example charge transfer reactions of  $O_2^+$  with NO and NO<sub>2</sub> to produce NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup>. Subsequent dissociative recombination reactions

$$NO_2^+ + e \to NO + O; \ k = 3 \cdot 0 \times 10^{-7},$$
 (14)

$$NO^+ + e \to N + O; \ k = 7 \cdot 0 \times 10^{-7},$$
 (15)

also have the effect of reducing oxides of nitrogen.

(e) Also  $O^-$  reacts with NO and  $SO_2$  to produce  $NO_2$  and  $SO_3$ . However, we find that despite mechanisms (d) and (e), 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  $SO_2$ .

We have also investigated the production of  $N_2O$  by the corona discharge, for example by

$$N + NO_2 \rightarrow N_2O + O; \ k = 3.0 \times 10^{-12}.$$
 (16)

Despite reactions with  $O(^{1}D)$  and  $N_{2}(A)$ , which destroy  $N_{2}O$ , we find that about 20% of the NO<sub>2</sub> is effectively converted to nitrous oxide. Nitrous oxide is an inert gas compared with NO and NO<sub>2</sub>, but is an undesirable greenhouse gas in large quantities.

#### 4. Conclusion

Rate coefficients have been calculated as a function of electric field for the basic electronic processes occurring in air and flue gases in a pulsed electric discharge. These rate coefficients have then been used, together with published rate coefficients for neutral species, to elucidate the principal processes by which SO<sub>2</sub> and oxides of nitrogen are removed in a pulsed corona discharge. It is concluded that the principal process for the removal of SO<sub>2</sub> is through reactions with OH radicals to produce  $H_2SO_4$ . Nitrogen oxides are reduced principally by reduction from N atoms produced from the dissociation of nitrogen molecules by the discharge. For these reactions to occur, values of E/N of 100 Td or more are required within the discharge. At these values a discharge normally becomes an arc, although the detailed space time variations of a corona discharge are complex (Lowke and Morrow 1994). However, if the discharge is pulsed, our calculations show that it is possible to attain these high values of E/N.

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