

# CHEMICAL KINETICS MODEL FOR NO REDUCTION FROM FLUE GAS EXCITED BY PULSED CORONA DISCHARGE

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## **Abstract:**

This paper is devoted to the development of chemical kinetics model coupled with electrical model for study the charged particle transport and particle model for determination of the basic transport and rate coefficients. This hybrid model is used to analyse the NO removal from flue gas excited by excited pulsed corona discharge. Then for a given discharge and gas composition, the main channels for NO removal and formation are detected and emphasised.

## **I. Introduction:**

As is known, flue gases (including  $N_2$ ,  $O_2$ ,  $H_2O$ ,  $CO_2$  and a few ppm of various oxides such as  $NO_x$  or  $SO_2$ ) can be stressed by pulsed corona discharges which produce energetic electrons. These free electrons are able to ionise, excite and dissociate molecules of flue gases. Some of radicals thus produced (as e.g. O, OH) in ionised channels left behind the successive streamers crossing the flue gas can favour, following complex kinetics schemes, the transformation of polluting agents (such as NO) in acids and then into salts when  $NH_3$  is added in flue gas in a stoichiometric ratio.

In this communication, we are interested by the evolution of the different chemical species (electrons, ions, excited species, radicals, oxides, neutrals, ...) involved in the transformation of polluting agents. So, we have developed a chemical kinetics model for NO reduction from typical flue gases including a few ppm of NO. But before, a multi-dimensional electrical fluid model is used to study the dynamics of charged particles thus giving in particular the initial conditions (concentration of charged particles and certain radicals inside the streamer channels) needed for the chemical kinetics model. Then, a particle model for charged particles is used to determine the

electron and ion transport coefficients needed for electrical model and also a part of reaction coefficients (of electron-molecule and ion-molecule interactions) needed for chemical kinetics model ; the specific profiles of charged particles due to non-thermal and non-equilibrium effects in gas are also given by the particle model. Gas dynamics model is also needed to obtain in particular the temperature profile of neutral gas. So the results obtained from the coupling of chemical kinetics model which must includes vibrational relaxation, electrical model and particle model are analysed as a function of discharge parameters and the main reactions involved in NO removal are emphasised.

**II. Hybrid model involving chemical kinetics model:**

In order to contribute to optimise the NO removal from a given flue gas, a complete model which involves the gas discharge phase followed by the gas dynamics phase coupled to the external electrical circuit is useful to analyse the NO removal efficiency as a function of different parameters of the plasma control pollution device (e.g. electrode geometry and separation, pulsed voltage: rise time voltage, voltage height, etc., flue gas composition, etc.). This model is described by the flowchart:

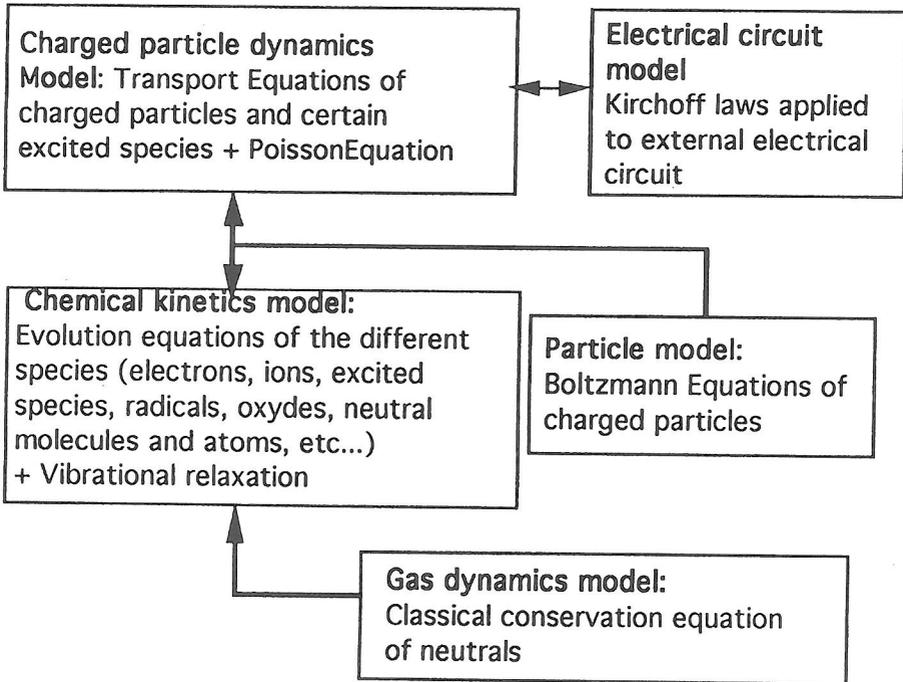


Figure 1: Flowchart of complete models for plasma simulation device for NO removal

As it can be observed in this flowchart, the different models are strongly coupled:

- the electrical model is based on conservation equation of charged particles, main excited particles and photons and coupled to Poisson equation. The aim is to determine the electrical behaviour of the discharge such as charge space electric field, current densities, densities of charged particles, the streamer dynamics and morphology, etc. The geometrical electric field is obtained from Kirchoff laws applied to external electrical circuit. So, we have developed a powerful electric model for charged particle dynamics analysis in wire-cylinder configuration in 2D cylindrical geometry corresponding to typical pulsed corona discharge configuration for flue gas treatment. (see e.g. Yousfi et al [1] and [2])
- the particle model based on Boltzmann equation solutions of electrons and ions. The aim is to determine the distribution functions of electrons and ions and also the electron-molecule and ion-molecule collision cross sections not available in literature, the transport coefficients needed for electrical model and also certain reaction coefficients needed for chemical kinetics model. For instance, by using a swarm unfolding technique for cross sections fitting we have determined the complete set of collision cross sections for the first time in the literature for several electron-molecules and ion-molecule systems such e.g. electron - H<sub>2</sub>O or electron-NH<sub>3</sub> and also ion-molecule sets : N<sup>+</sup>/N<sub>2</sub>, N<sub>2</sub><sup>+</sup>/N<sub>2</sub>, O<sup>-</sup>/O<sub>2</sub>, O<sub>2</sub><sup>-</sup>/O<sub>2</sub>, O<sup>+</sup>/O<sub>2</sub>, O<sub>2</sub><sup>+</sup>/O<sub>2</sub>, etc.(see e.g. Yousfi et al [2] and [3] )
- the hydrodynamic model based on classical conservation equations of neutrals. Such a model enables to study the gas dynamics effects which considerably affect the chemical kinetics. The neutral dynamics is due to Joule energy dissipation which causes a growth of gas temperature and pressure inside the streamer channel followed by its radial expansion.
- the chemical kinetics model is based on evolution equations of main chemical species involved directly or indirectly in removal of NO reactions. It is also necessary to develop the vibrational relaxation model which is based on evolution equations of main vibrational species (N<sub>2</sub>, O<sub>2</sub>) and whose the aim is to take into account the energy stored by these excited levels before dissociation of molecules,

The chemical kinetics model which is developed for NO removal involves 39 species undergoing 287 reactions. The different species are first those considered in the simplified flue gas composition before the discharge (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O and a few

ppm of NO) and then those created by the discharge when the streamer crosses the wire-cylinder gap (electrons, positive ions:  $N_2^+$ ,  $O_2^+$ ,  $H^+$ ,  $OH^+$ ,  $H_2O^+$ ,  $CO_2^+$ , negative ions:  $O^-$ ,  $O_2^-$ , excited species  $O(^1D)$ ,  $O_2(a^1\Delta_g)$ ,  $N_2(A^3\Sigma^+)$ ,  $N_2(a^1\Delta_u)$  and primary radicals:  $OH$ ,  $O$ ,  $N$ ,  $H$ ): these species are mainly created by electron-molecule impacts and constitute the initial conditions for the chemical kinetics model. Their concentrations are obtained from a coupling between electrical and particle models. Then, these different species and more particularly primary ( $OH$ ,  $O$ ,  $N$ ,  $H$ ) and secondary ( $O_3$ ,  $HO_2$ ) radicals interact with  $NO$  to create acid ( $HNO_3$ ). The chemical kinetics model take into account such interactions which can be summarised as following according an increasing time scale:

- the electron-molecule reaction during the discharge phase,
- the ionic recombination, charge transfer and ionic conversion,
- the reactions between excited and neutral species,
- the reactions of thermal dissociation and recombination.

Therefore, the chemical kinetics model involves 39 master equations which describes the time evolution of the 39 species considered. These ordinary differential equations of the first order are very stiff because the source terms involve terms which can differ by several orders of magnitude corresponding to the difference between the reaction coefficients of e.g. electron-molecule and molecule-molecule interactions. The stiffness of the obtained linear system of the 39 equations with the 39 unknowns (concentrations of each species) is taken into account by using an appropriate and powerful numerical scheme based on backward difference formulae.

### III. Results and discussion:

The different reactions of  $NO$  removal and creation are can be summarised as following [4]:

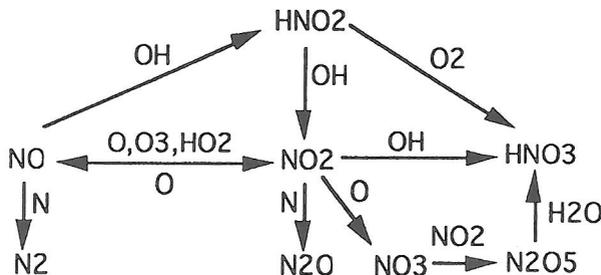


Figure 2: Simplified scheme of reactions involved in  $NO$  removal and formation

Figures 3 and 4 show as an example the time evolution of the concentrations of some important radicals (OH, O3 and HO2) and acid (HNO3) and also the NO concentration.

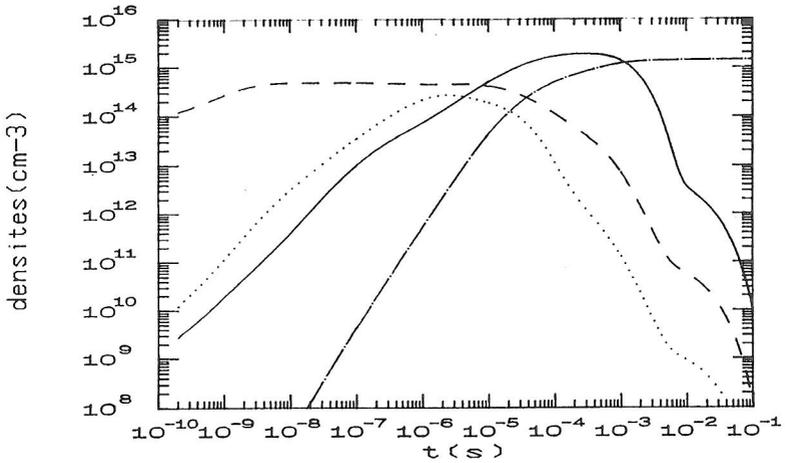


Figure 3: Evolution of O3 (---), OH (---), HO2 (.....) and HNO3 (---) concentration

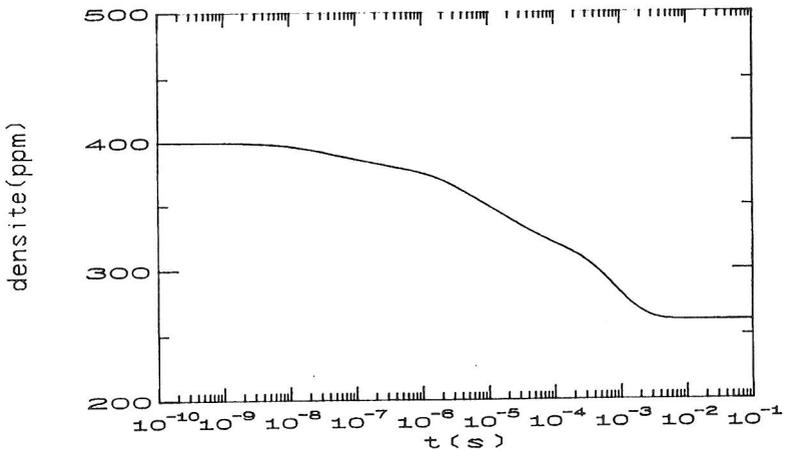


Figure 4 : Evolution of NO concentration

We observe on figure 3, the time scale of the different phases previously described before NO removal: i.e. the first phase corresponding to the formation of the primary and secondary radicals (O, OH, O<sub>3</sub> and HO<sub>2</sub>), followed by the phase of acid formation which corresponds in the same time to NO removal phase. It can be observed, under the discharge parameters chosen for these calculations, that NO concentration decreases from its initial value (400 ppm) down to about 260 ppm. Furthermore, a parametric study from our model has shown that the main channel of NO removal are the oxidation channel via  $\text{NO} + \text{O}_3 \rightarrow \text{O}_2 + \text{NO}_2$  or  $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$  reactions and the reduction channel via  $\text{NO} + \text{N} \rightarrow \text{N}_2 + \text{O}$  reaction. It is also observed that the channel:  $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$  is an important reaction for NO formation thus reducing of 50% the NO removal efficiency of the plasma device.

## VI. Conclusion:

From our hybrid model based on a simplified set of reactions and using a coupling between electrical-particle and chemical kinetics model, the time evolution and the behaviour of the main chemical species concentration are obtained and analysed. In the same time, the main reactions involved in NO removal and formation are also emphasised. So from present model and a parametric study, it is possible to judiciously choose the discharge and electrical circuit parameters to optimise the NO removal efficiency of the plasma device. In the next step, the present model will be completed by following the time evolution of the different species up to salt formation by adding NH<sub>3</sub> in the flue gas mixture and the effects of kinetics of vibrational molecule and neutral gas dynamics will be included and analysed.

## References:

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