

# Computer simulation of smoke gas purification

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A comprehensive nonstationary kinetic model of the  $N_2$ - $O_2$ - $H_2O$ - $CO_2$ - $SO_2$  mixture is constructed. Calculated results simulating the impact of a stationary electron beam on the mixture are presented, as well as their comparison with experimental data. Main mechanisms of removing pollutants from the mixture are revealed and the reasons of intensification of smoke gas purification are discussed.

The effect of ionizing radiation on the chemical composition of atmospheric air has been studied experimentally for a long time. The interest of investigators is mostly aimed at the study of the impact (possible impact) of human activity on the environment. Processes of pollution and purification of atmospheric air are under discussion. Electron beam (e-beam) irradiation of smoke gases is one of the efficient methods of removing sulfur and nitrogen oxides from them. One of the recent papers devoted to this issue is Ref. 1.

Numerous attempts were undertaken to treat, discuss, and simulate experimental results. However, there are no models taking into account a large number of components and solving a large number of kinetic equations. Simple mixtures like nitrogen-oxygen or oxygen-water (see, for example, Refs. 2-5) are usually considered. When dealing with complex mixtures and the actual atmosphere, only some explicit or experimentally confirmed processes can be discerned with confidence (see, for example, Ref. 6).

The aims of this work are, first, to test the kinetic model of the  $N_2$ - $O_2$ - $H_2O$ - $CO_2$ - $SO_2$  mixture and, second, to reveal the mechanisms of the e-beam effect on the modeled mixture. This work is facilitated by the fact that experiments are usually conducted with model mixtures and the detailed description of experimental conditions allows them to be reconstructed in a theoretical model. The only difficulty is that the model energy pumped by the e-beam into the mixture is to correspond to the actual energy, and the latter, in its turn, to the e-beam current density and the electron energy reported by experimenters.

## Description of the kinetic model of the $N_2$ - $O_2$ - $H_2O$ - $CO_2$ - $SO_2$ mixture

The kinetic model presented here was earlier used for purely theoretical estimates<sup>7,8</sup> with the PLASER suit of programs. By now it is complemented with a number of new plasma-chemical reactions for the  $N_2$ - $O_2$ - $H_2O$ - $CO_2$  mixture and extended due to reactions with participation of components of the  $SO_2$  admixture.

The PLASER program suit uses the input set of characteristics of plasma-chemical reactions and other needed parameters to form the model of relaxation of a selected medium pumped by a hard ionizer. The constructed model allows calculations of the ionic composition and populations of atomic, molecular, and ionic ( $N_i$ ) electronic states, as well as the electron  $T_e$  and gas  $T_g$  temperature under nonstationary conditions in accordance with the kinetic equations:

$$\begin{aligned} \frac{dN_i}{dt} = & \sum_k v_{ik} M_k + \sum_{m,l} a_{im} N_m N_l (M_k, N_e) - \\ & - \sum_l b_{li} N_i N_l (M_k, N_e), \\ \frac{d}{dt} \left( \frac{3}{2} N_e T_e \right) = & \sum_{i,k} v_{ik} M_k \Delta T_{ik} + \sum_{i,n} c_{in} N_i N_n \Delta T_{in} - \\ & - \sum_k \sigma_k v_e M_k N_e T_e, \end{aligned}$$

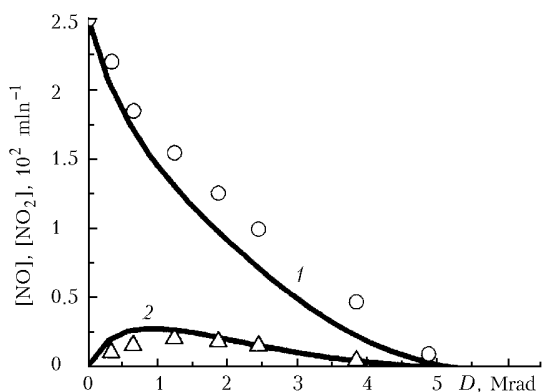
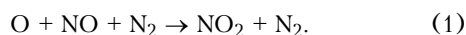
where  $M_k$  are neutral molecules of the mixture (nitrogen, oxygen, water vapor, carbon dioxide);  $v_{ik}$  are the frequencies of the processes of ionization and excitation of these molecules by an external source (e-beam in this case) that lead to accumulation of the ionized and excited mixture components  $N_i$ ;  $a_{im}$  are the rate constants of reactions generating  $N_i$  from the components  $N_m$  (transitions between excited states at inelastic collisions with neutral particles  $N_l$  and electrons  $N_l = N_e$ , conversion and dissociation of ions, dissociative and triple recombination of ions (factor  $M_k$  or  $N_e$  is added in case of three-particle reactions), ion-ion recombination, electron attachment to ( $N_l = N_e$ ) and detachment from gas particles, Penning reactions at neutral particles, reactions of ion re-charging at atoms and molecules, and others);  $b_{li}$  are the rate constants for reactions of withdrawal of the components  $N_i$  from the mixture at collisions with another particle  $N_l$  or electron  $N_e$ ;  $c_{in}$  are the rate constants of reactions with electron participation leading to a change in the Maxwell

temperature  $T_e$  of the latter;  $\Delta T_{ik}$  and  $\Delta T_{in}$  are, respectively, the energy acquired or lost by electrons in the processes of ionization, recombination, electron attachment (detachment), and others with participation of any other particle  $N_n$ , including an electron;  $\sigma_k$  are the cross sections of elastic collisions of electrons with molecules  $M_k$  that cool electrons;  $v_e$  is the electron speed in the Maxwell distribution. The electron concentration  $N_e$  is determined from the condition of quasi-neutrality of the generated plasma. The frequencies of ionization and excitation of mixture components  $\nu_{ik}$  are calculated based on the specific data on the e-beam parameters and the structure of the corresponding molecule.

The model was tested against the experimental results obtained in Japan for ten years with different mixtures starting from the simplest NO–N<sub>2</sub> mixture and ending with additives of hydrocarbons. This experimental works are reviewed in Ref. 2. A mixture was blown through a one-liter vessel irradiated by a continuous e-beam with the energy of 1.5 MeV and the current of 2 mA. The power of the energy pumped into the mixture was 0.29 Mrad/s (absorbed radiation dose).

### The NO(NO<sub>2</sub>)–N<sub>2</sub> mixture

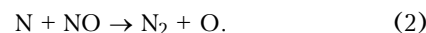
Our computations gave the following results. Figure 1 demonstrates the behavior of NO and NO<sub>2</sub> in the mixture of nitrogen with NO molecules (the experimental results from Ref. 2 are shown by signs in the figures, and the results of our computations are shown as curves, the admixture concentrations are in ppm, the initial concentration of NO molecules is 250 ppm, and the mixture temperature is  $T_g = 100^\circ\text{C}$ ). The decrease of the NO concentration and the initial increase of the NO<sub>2</sub> concentration are explained by association of NO molecules with atomic oxygen with participation of nitrogen as a third particle:



**Fig. 1.** Concentration of NO (1) and NO<sub>2</sub> (2) as a function of the absorbed dose  $D$  in the mixture NO–N<sub>2</sub> at the initial NO concentration  $[\text{NO}]_0 = 250$  ppm and the mixture temperature  $T_g = 100^\circ\text{C}$ : experiment (signs) and calculation (curves).

It is clear that NO molecules serve a source of oxygen atoms. The decisive reaction in destruction of

nitrogen monoxide and accumulation of atomic oxygen is the following:



Nitrogen atoms, in their turn, are produced from molecular nitrogen under the exposure to e-beam irradiation. As the radiation dose increases, the concentration of NO<sub>2</sub> decreases due to the following reactions:

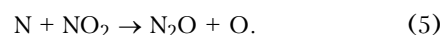
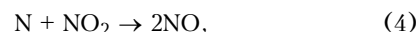
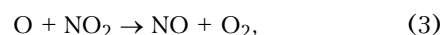
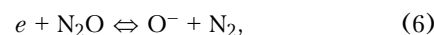
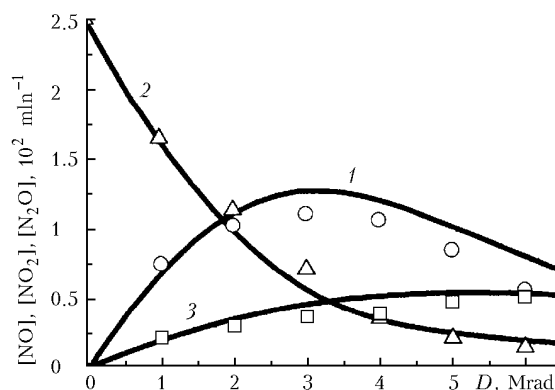


Figure 2 depicts the time behavior of three components of the NO<sub>2</sub>–N<sub>2</sub> mixture. Here the decrease of NO<sub>2</sub> molecules and the increase of [NO] occur in reactions (3) and (4), the further decrease of [NO] occurs in reactions (1) and (2), and N<sub>2</sub>O molecules are largely accumulated in reaction (5). At further impact of e-beam, [N<sub>2</sub>O] decreases due to reactions



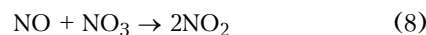
The electron concentration in the mixture during the e-beam irradiation exceeds  $10^{10}/\text{cm}^3$ .



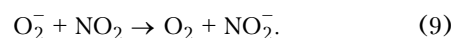
**Fig. 2.** Concentration of NO (1), NO<sub>2</sub> (2), and N<sub>2</sub>O (3) as a function of the absorbed dose  $D$  in the NO<sub>2</sub>–N<sub>2</sub> mixture ( $[\text{NO}_2]_0 = 250$  ppm,  $T_g = 100^\circ\text{C}$ ).

### The NO–N<sub>2</sub>–O<sub>2</sub> mixture

As oxygen is added to the mixture, the efficiency of removal of nitrogen monoxide decreases markedly, whereas at low initial NO concentrations it even accumulates. There arise extra channels of NO<sub>2</sub> transformation:

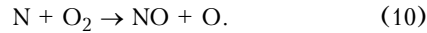


and



Just the presence of electronegative oxygen in the mixture leads to generation of NO<sub>3</sub> molecules and the increase of the role of negative ions in plasma kinetics

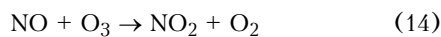
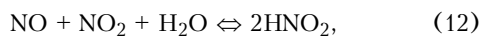
with simultaneous decrease of the electron concentration lower than  $5 \cdot 10^7 \text{ cm}^{-3}$ . The increase of  $[\text{NO}]$  after the appropriate decrease at low initial concentrations is also explained by the presence of oxygen and activation of the accumulation channel:



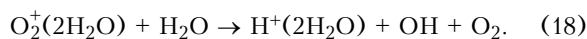
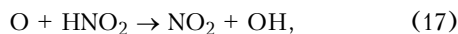
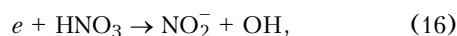
At high  $[\text{NO}]_0$  this channel is invisible against the background of intense channels (8), (9), (1), (4), (2), and (3).

### The NO–N<sub>2</sub>–O<sub>2</sub>–H<sub>2</sub>O mixture

Reference 2 also presents the results on exposure of wet mixtures containing 12% of oxygen to e-beam irradiation. Figure 3 shows the NO concentration as a function of the absorbed dose in dry and wet mixtures. The absence of experimental points for the dry mixture and the presence only of a curve are not explained in Ref. 2; the curve in Ref. 2 is similar to the curve obtained by us and depicted in Figure 3. As it can be seen, addition of water vapor increases the efficiency of removal of nitrogen monoxides from the mixture. It should be noted that no more than 100 ppm of NO<sub>2</sub> molecules is accumulated in the wet mixture. In connection with the presence of water vapor and 12% oxygen in the model mixture, the pattern of plasma-chemical reactions considerably changes. In addition to the above reactions, the following reactions take part in balancing different components of the mixture:



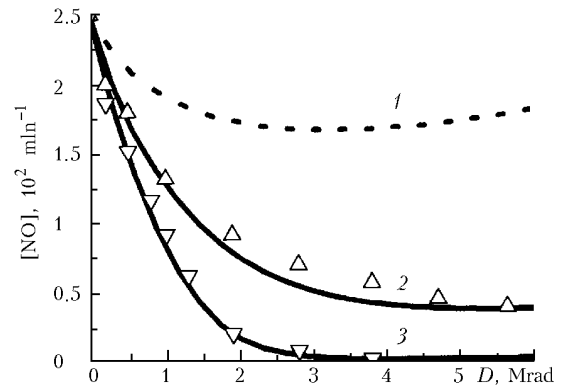
(M denotes any third particle), and reaction (2) remains the main actual channel of the NO removal. The main sources of OH radicals are, strange as it may seem at first glance, the following reactions earlier ignored in consideration of such problems:



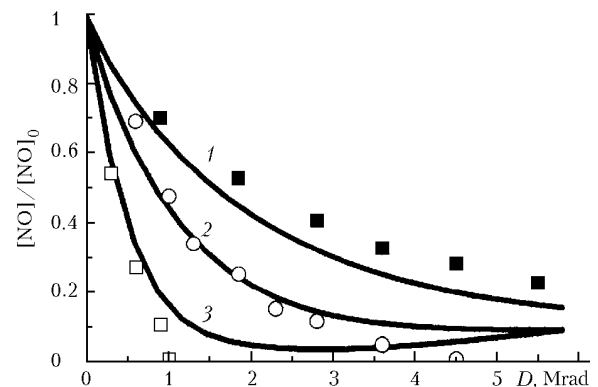
Just *plasma-chemical reactions* become most important here. Depending on the amount of water vapor these reactions change places in the sense of their significance. Reaction (14) becomes of importance just at so high electron concentrations, at which intense production of ozone starts.

Figure 4 depicts the ratio  $[\text{NO}]/[\text{NO}]_0$  at the fixed water vapor content in the mixture at different initial  $[\text{NO}]$ . Removal of nitrogen monoxide is more efficient at low initial content of NO. The point is that,

as was noticed in Ref. 2, the increase of the oxygen content in the mixture from 3 to 12% increases the degree of purification, and process (8) is responsible for this increase. “Fins” observed at the calculated curves for low  $[\text{NO}]_0$  are explained by reaction (10) of NO accumulation, which is likely compensated by something under actual conditions in the presence of water vapor in the mixture.



**Fig. 3.** Concentration of NO as a function of absorbed dose for  $[\text{NO}]_0 = 250 \text{ ppm}$  at different water vapor concentration: dry mixture (1),  $[\text{H}_2\text{O}] = 2.2\%$  (2),  $[\text{H}_2\text{O}] = 12.9\%$  (3); oxygen – 12%, nitrogen – from 75 to 88%,  $T_g = 120^\circ\text{C}$ .



**Fig. 4.** The ratio of the final (after exposure) to initial NO concentration as a function of  $D$  for different  $[\text{NO}]_0$ : 500 (curve 1), 250 (2), and 100 ppm (3) at the water content of 8.3%, oxygen content of 12%, and nitrogen content of 79.7%,  $T_g = 120^\circ\text{C}$ .

### The NO–N<sub>2</sub>–O<sub>2</sub>–H<sub>2</sub>O–CO mixture

Further Ref. 2 considers the effect of carbon monoxide and hydrogen additives on purification of smoke gases. Figure 5 demonstrates the qualitative effect of the presence of CO molecules in the mixture. Addition and increase of CO concentration accelerate the purification of the mixture from NO molecules, but increase the content of NO<sub>2</sub> molecules in it. Accumulation of NO<sub>2</sub> follows an interesting scheme (Fig. 6a): starting from NO<sub>3</sub> molecules, in cooperation with OH and HO<sub>2</sub> radicals, this chain closes at some equilibrium between NO<sub>2</sub> and HNO<sub>3</sub> molecules. This mechanism works both in the presence of CO and

without it. The difference is that if without CO the NO<sub>3</sub> production follows a simple channel of association of NO and O<sub>2</sub> molecules at participation of a third particle, then when CO is added to the mixture, another, more exotic and more powerful channel activates (Fig. 6b). Just this channel causes some insignificant difference in the [NO<sub>2</sub>] curves. As to Fig. 5, intensification of the process of NO removal with addition of CO molecules is likely connected with the increasing concentration of free OH and HO<sub>2</sub> radicals and others, but we still failed to reveal the mechanism of this process.

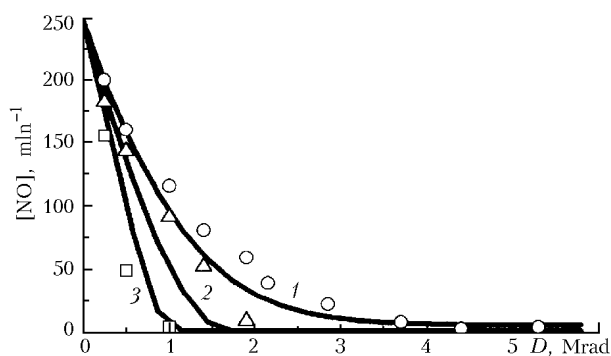


Fig. 5. Dependence of [NO] on  $D$  at  $[\text{NO}]_0 = 250$  ppm, O<sub>2</sub> (12%), H<sub>2</sub>O (8%), and N<sub>2</sub> (78.8–80%) for different CO content: 0% (curve 1, ○ – experiment), 0.29% (curve 2, △), 1.17% (3, □);  $T_g = 120^\circ\text{C}$ .

### The N<sub>2</sub>–O<sub>2</sub>–H<sub>2</sub>O–SO<sub>2</sub> mixture

Figure 7 shows the results of studying the effect of addition of water vapor on the SO<sub>2</sub> removal. At first glance, calculated and experimental results are not in close agreement, but the increase of significance of water vapor in the purification is qualitatively seen in the experimental data as well. The main channels of the SO<sub>2</sub> removal are the following:

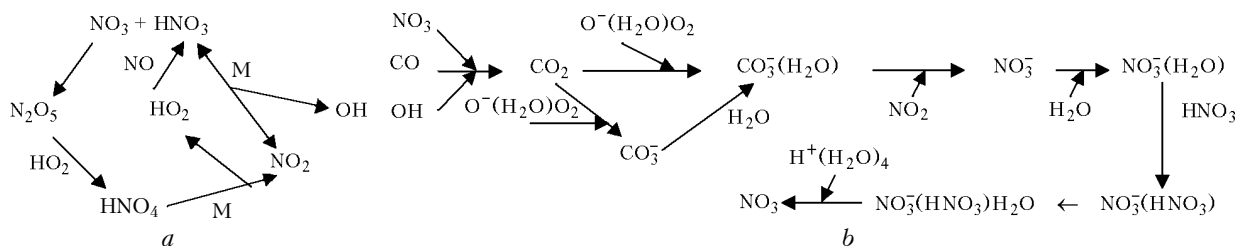
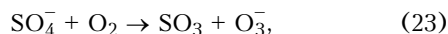
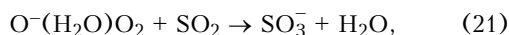


Fig. 6. Scheme of NO<sub>2</sub> accumulation in the mixture NO–N<sub>2</sub>–O<sub>2</sub>–H<sub>2</sub>O–CO (a) and NO<sub>3</sub> with participation of CO-cycle (b).

but SO<sub>3</sub> molecules can produce SO<sub>2</sub> molecules in reaction with atomic oxygen. It is clear that just water vapor plays the decisive role in removal of SO<sub>2</sub>, and the fact that this is not pronounced in the experiment can be explained by over-saturation of the model mixture with water vapor.

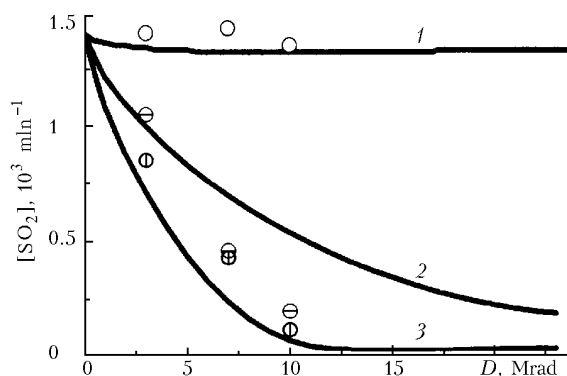


Fig. 7. Dependence of [SO<sub>2</sub>] on the absorbed dose at  $[\text{SO}_2]_0 = 1400$  ppm, O<sub>2</sub> (20%), N<sub>2</sub> (71.9–79.8%) for different content of H<sub>2</sub>O vapor: 0% (curve 1, ○), 0.26% (2, ⊙), 0.53% (3, ⊗);  $T_g = 100^\circ\text{C}$ .

### Conclusion

A comprehensive nonstationary kinetic model of atmospheric air in the N<sub>2</sub>–O<sub>2</sub>–H<sub>2</sub>O–CO<sub>2</sub>–SO<sub>2</sub> mixture was created. The model was tested by extended experimental data. A close agreement was obtained between the calculated and experimental results. The list of the processes playing the main role in purification of smoke gases from detrimental impurities under the action of the relativistic e-beam was refined and extended for different conditions in different mixtures. It was confirmed theoretically that the presence of water vapor, carbon monoxide, and large amounts of oxygen in the mixture significantly increases the efficiency of purification of smoke gases for NO, NO<sub>2</sub>, and SO<sub>2</sub>. It should be noted that the recent experiments<sup>1</sup> evidence the higher efficiency of smoke gas purification by pulsed e-beams as compared with continuous ones.

The constructed model can be successfully used to understand and predict the results of experiments on exposure of atmospheric air to hard ionizing radiation (not only pulsed and stationary e-beams, but also shortwave electromagnetic radiation and charged products of nuclear reactions).

### Acknowledgments

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