Component Content of Active Particles in Plasma-Chemical Reactor Based on a Volume Barrier Discharge

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Abstract. In this proceeding the results of theoretical and experimental studies of the component content of active particles formed in plasma-chemical reactor composed of multiple-cell generator of active particles based on volume barrier discharge, and working chamber are presented. For calculation of the content of uncharged plasma components an approach is proposed which is based on averaging of introduced power over the entire volume. Advantages of such approach consist in absence of fitting parameters, such as dimensions of microdischarges, their surface density, and rate of breakdowns. The calculation and the experiment were accomplished with the use of dry air (20% relative humidity) as plasma generating medium. Concentrations of O_3, HNO_3, HNO_2, N_2O_5, and NO_3 were measured experimentally in the discharge volume and working chamber for transient time of the particles on the discharge of 0.3 s and more, and the discharge specific power of 1.5 W/cm^3. It has been determined that the best agreement between the calculation and the experiment occurs at calculated gas medium temperature in the discharge plasma of about 400÷425 K, which corresponds to experimentally measured rotational temperature of nitrogen. In the most cases calculated concentrations of O_3, HNO_3, HNO_2, N_2O_5, and NO_3 for barrier discharge and working chamber are in a good agreement with respective measured values.

Keywords: barrier discharge, microdischarge, component content.
PACS: 82.33Xj

INTRODUCTION

In the last decade non-thermal discharges at one atmosphere pressure attain more and more applications in technology. Particularly, possibilities of the use of corona and barrier discharges were demonstrated for efficient removal of nitrogen oxides NO_x and N_xO_y from industrial gases, sterilization of medical articles, modification of surface features of polymer materials and cleaning the surfaces contaminated in result of chemical weapon action. For solving the last three tasks, the most optimum is the use of plasma-chemical reactor composed of two parts - 1) generator of active particles with one ore several gas discharge cells; 2) working chamber having relatively large volume for placement of processed articles or materials. Such design allows minimum influence of processed articles on the discharge and, consequently, on the component content of active particles in it.

Purpose of the present work consists in theoretical and experimental study of the component content of active particles and its dependence on different factors of the concentrations, both in volume barrier discharge, and in working chamber of the reactor developed by us, with the use of ambient air with ≈ 20% relative humidity as working medium.

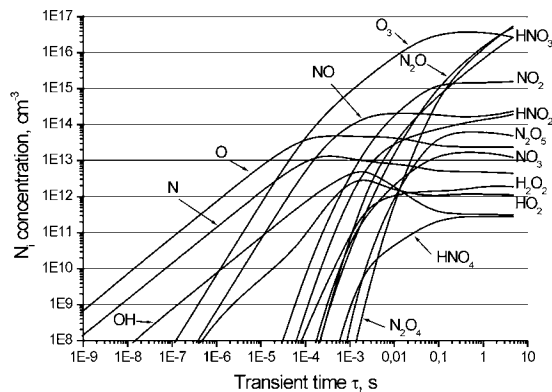## EXPERIMENTAL SETUP AND METHODS OF MEASUREMENTS

The plasma-chemical reactor consisted from working chamber made of polymethylmethacrylate having 80 liters volume (430x430x430 mm) and sixteen volume barrier discharge cells which were evenly located at top wall of the chamber. Active particles formed in the discharges were supplied to the chamber, and after that left the chamber by

passing to deactivation system via opening located at the chamber bottom. Air was supplied to the discharge cells through wetting/desiccation system which enabled relative humidity (RH) variations in range of 20-90% at 20-22^{0}C temperature. Volume pumping rate through each of the discharge gaps was varied from 1 cm^3/s up to 8 cm^3/s (at that volume rates of pumping through the chamber comprised 1÷8 liters per minute). These volume rates corresponded to mean transient time values in the discharge gap $\tau = 2.4÷0.3$ s (Mean transient time of the particles in the discharge is $\tau = V/2\upsilon$, where V is the discharge volume). Alternating current source with voltage up to 15 kV and 400 Hz frequency was used for powering of the discharges.

NO$_3$ concentration was calculated on a basis of the lamp radiation absorption at wavelength $\lambda = 662$ nm and 623 nm. Densities of O$_3$, HNO$_3$, HNO$_2$, N$_2$O$_5$, H$_2$O$_2$ were calculated with the use of curve of integral absorption by these particles in 200÷300 nm wavelength range by means of automated fitting routine. The routine performed selection of concentration values for the particles until reaching coincidence of experimental and calculated curves with pre-determined precision. Possibility of use of such method is based on fact that in 200÷300 nm wavelength range spectrum dependencies of absorption cross sections for these particles are essentially different. At calculations of concentrations of the particles, cross section values taken from [1] were used.

RESULTS OF NUMERICAL MODELING OF COMPONENT CONTENT OF THE PARTICLES IN BARRIER DISCHARGE VOLUME AND IN WORKING CHAMBER

As it is known, barrier discharge represents an assembly of filamentary microdischarges each having $\approx 10÷100$ ns duration and ~ 0.1 mm diameter which are stochastically spread in time and in the discharge volume. Commonly [2] at determining concentrations of particles in the discharge, plasma kinetics in separate current channels of the microdischarges is calculated at first, and after that in time of an order of diffusion one ($\sim 10^{-3}$ s) averaging of concentrations of all components over the entire discharge volume is performed. With such approach there exists a set of parameters that are poorly known and essentially depend on design of the discharge cell and kind of gas, such as rates of occurrence of current channels, their dimensions and surface density at the discharge electrodes. Those parameters are commonly fitting ones.
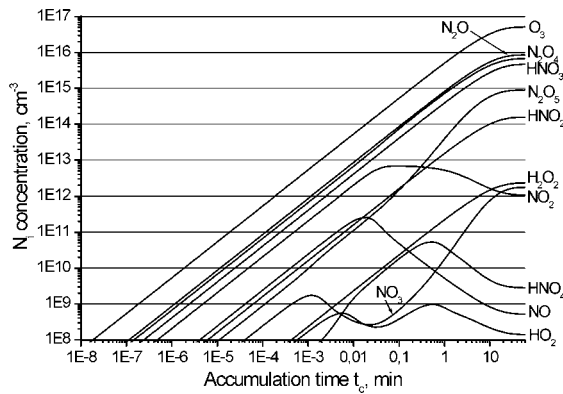
Calculation presented in the present paper is based on another approach, at which power introduced into the discharge is immediately averaged over the discharge volume. With such approach, correct description is provided for processes with linear dependence on electron density, as well as for nonlinear ones with typical time of reaction being longer than the diffusion time ($t > 10^{-3}$ s). Since typical duration of chemical reactions between dissociation products in current channels does not exceed 10^{-2} s, approach used by us is valid. Besides, an advantage of this approach consists in the absence of fitting parameters.

FIGURE 1. Calculated dependencies of concentrations of different neutral particles in barrier discharge volume on their transient time in the discharge gap τ. $W_d = 1.5$ W/cm^3. Gas temperature $T_d = 425$ K, air RH 20%.

Calculations of component content of the particles in the discharge gap and working chamber were performed at specific power in the discharge $W_d = 1.5$ W/cm^3, transient time of gas mixture in the discharge gap up to 4.8 s, and gas mixture temperature in the discharge gap $T_d = 300, 375, 400, 425$ and 500 K. (In case of necessity, known experimental temperature dependencies of reaction rates in range of 200÷450 K were extrapolated to 500 K). Relative humidity of air supplied to the discharge gap comprised 20% at 20^{0}C. In Fig.1 calculated dependencies of concentrations of neutral components of barrier discharge plasma on transient time of gas mixture in the discharge gap τ are presented for gas mixture temperature $T_d = 425$ K. (It was assumed in the calculations that the particles are permanently present in the discharge gap for time duration τ, and only after that are ejected outside it). Concentrations of H, HNO and O(d) components are not shown in the figure due to their smallness (Ni $\leq 10^8$ cm^{-3}). One can see from the figure that at initial stages of the discharge development (before $\sim 10^{-4}÷10^{-1}$ s) concentrations of all components exhibit practically linear growth in time, and after that either reach saturation (H$_2$O$_2$, NO$_2$, NO, N, O, OH, HO$_2$), or start to decrease (O$_3$, NO$_3$, N$_2$O$_5$), or continue to grow with smaller rate (N$_2$O$_4$, N$_2$O, HN0$_3$, HNO$_2$).

One can also see from the figure that: 1) maximum quasi-stationary concentration values $\approx (1 \div 5) \cdot 10^{16}$ cm^{-3} are exhibited by O_3, N_2O, N_2O_4 and HNO_3 components; 2) HNO_2, NO and NO_2 concentrations reach values of $10^{14} \div 10^{15}$ cm^{-3}; 3) at $\tau > 10^{-2}$ s concentrations of majority of the components possess weak dependence on transient time of gas mixture in the discharge; 4) only N_2O_4, HNO_3 and N_2O concentrations essentially depend on transient time τ – at its increase from 0.3 to 2.4 s their concentrations grow up by practically an order of magnitude.

In Fig.2 calculated dependencies of concentrations of the particles in working chamber on accumulation time of the particles t_c are presented for transient time of gas mixture in the discharge gap $\tau = 0.3$ s, and temperature of gas mixture in the discharge and working chamber $T_d = 425$ K and $T_c = 300$ K, respectively. First of all, it should be noted that unlike the case of the discharge volume, concentrations of N, O and OH components in working chamber do not exceed 10^8 cm^{-3} (respective curves are not shown in Fig.2). It is due to fact that the reactions leading to formation of these particles are practically absent in working chamber volume, and the particles coming from barrier discharge volume quickly "burn out" forming more stable molecules. In time interval $t_c \approx (10^{-8} \div 10)$ minutes, linear growth of concentration with time is inherent for majority of the particles, thus giving evidence to uniform in time coming of these particles, that is, their coming to the chamber is determined by processes of their carrying out of the discharge volume. NO_3 concentration linearly grows for t_c up to $\sim 10^{-3}$ s; after that it starts its decrease, and than after passing the minimum starts the increase again reaching its quasi-stationary value in a time of about 10 minutes. Temporal dependence of HO_2 concentration exhibits more complex behavior – initially linear dependence is replaced by oscillating one at $t \sim 5 \cdot 10^{-3}$ minutes. Concentrations of NO, NO_2 and HNO_4 reach their maximum values in time from 0.01 to 0.5 minutes, and after that they start their decrease due to influence of death processes. Concentrations of O_3, HNO3, HNO_2 and N_2O_5 components linearly increase up to quasi-stationary values for $10 \div 20$ minutes.

FIGURE 2. Calculated dependencies of concentrations of the particles in working chamber on accumulation time t_c at $\tau = 0.3$ s, $W_d = 1.5$ W/cm^3. $T_d = 425$ K, $T_c = 300$ K; air RH 20%.

Comparison of Figures 1 and 2 shows that: 1) quasi-stationary values of O_3, HNO_3, HNO_2, N_2O, N_2O_4, H_2O_2 and N_2O_5 concentrations in the chamber exceed the densities of these components in the discharge thus giving evidence to their accumulation in working chamber. However, while in case of O_3, HNO_3, HNO_2, N_2O, N_2O_4, H_2O_2 components this increase comprises a factor of $1.5 \div 2$, N_2O_5 density in the chamber increases by factor of ≈ 15. This effect is, first of all, due to strong decrease of decomposition rate for this component at injection of the mixture from the discharge with temperature $T_d = 425$ K to the chamber with temperature $T_c = 300$ K; 2) on the contrary to mentioned above components, NO_3, HNO_4, NO_2, HO_2, and NO concentrations in the chamber are less than those in the discharge by factor of $(5 \div 10^6)$, first of all, due to their "burn-out".
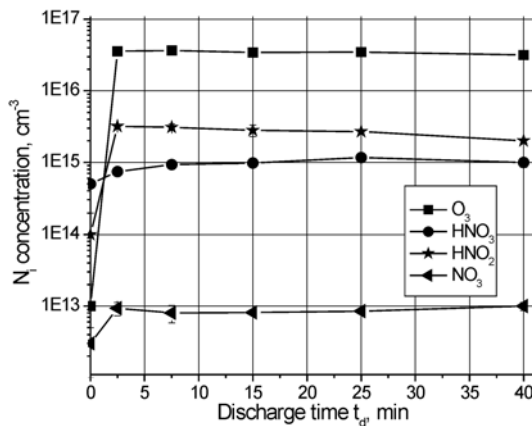
RESULTS OF EXPERIMENTAL STUDIES OF CONCENTRATIONS OF PARTICLES IN DISCHARGE VOLUME AND WORKING CHAMBER

The rates of many reactions essentially depend on temperature of the particles. Thus, for correct comparison of the results of calculations and experiments it is necessary to know gas mixture temperature. It has been shown in [3] that rotational temperature of nitrogen molecules T_{rot} is close to the temperature of translational movement. For determining rotational temperature, 0-0 transition of SPS of nitrogen was used in the present work. Measurements of dependency of rotational temperature on the discharge glowing time for $\tau = 0.3$ s and $W_d = 1.5$ W/cm^3 have shown that T_{rot} reaches its quasi-stationary value of 400 ± 12 K approximately at $15 \div 20$ minute of the discharge glowing.

It should be noted that we did not succeed in measurement of N_2O_5 and H_2O_2 concentrations in the discharge gap and H_2O_2 in the working chamber. It gives evidence to fact that concentrations of these particles in the discharge are lower than sensitivity thresholds of used method of measurements which comprise $\approx 10^{14}$ and 10^{15} cm^{-3}, respectively.
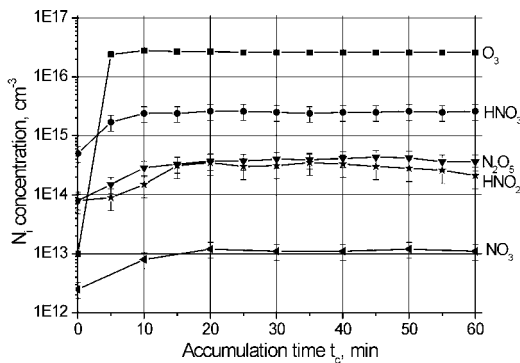
In Fig.3 experimentally obtained dependencies of O_3, HNO_3, HNO_2, NO_3 concentrations in the discharge gap on the discharge glowing time t_d are presented for $\tau = 0.3$ s and $W_d = 1.5$ W/cm^3 (discharge glowing time t_d is one measured from the point of turning on the discharge powering voltage till the point of its turning off). Each point at the figure represents data averaged for $3 \div 4$ measurements

Comparison of Figs.1 and 3 shows that calculated values of O_3 and NO_3 concentrations exceed respective experimental values by factor of about $1.5 \div 2$. In case of HNO_3 this ratio is somewhat higher and comprises about 2.5. The largest discrepancy between the experiment and the calculation is observed for HNO_2 – calculated concentration values are less than experimentally measured ones by more than one order of magnitude.

The measurements of concentration of O_3, HNO_3, N_2O_5, HNO_2, H_2O_2 and NO_3 components in the chamber were performed at transient time $\tau = 0.3$ s (it corresponded to 8 liters per minute volume rate of blowing the mixture through the chamber), $W_d = 1.5$ W/cm^3 at distances 65, 215 and 365 mm from top wall of the chamber. Spread of measured densities of the particles along the chamber height is minimum one for O_3 comprising $\approx 10\%$, and maximum one for HNO_2 being about 30-40%.

In Fig.4 the dependencies of O_3, NO_3, N_2O_5, HNO_3, HNO_2 concentrations averaged over the chamber height on accumulation time in the chamber t_c are presented (each point in the figure represents data averaged for $6 \div 9$ measurements). Comparison of measured concentration values for

FIGURE 3. Experimentally measured dependencies of O_3, HNO_3, HNO_2, NO_3 concentrations in the discharge volume on time of the discharge glowing t_d at $\tau = 0.3$ s. $W_d = 1.5$ W/cm^3, air RH is about 25%.

particles in the chamber with the calculations (Fig.2) shows that: 1) calculated values of O_3, HNO_3 and N_2O_5 concentrations exceed their measured values by factor of about two; 2) in cases of NO_3 and HNO_2 the contrary situation is observed – calculated values of the concentrations are about twice less than those measured in the experiment.

One can see from figures 1-4 that in cases of O_3, HNO_3 and N_2O_5 behavior of changes of their concentrations at gas mixture injection from the discharge to the chamber is the same both in the calculations and the experiments, at that: 1) O_3 concentrations in the discharge and the chamber are practically equal; 2) HNO_3 and N_2O_5 concentrations increase by factors of about $(2 \div 3)$ and $(10 \div 15)$, respectively.

As to NO_3 and HNO_2 components, the following mismatch between the calculation and the experiment is observed: 1) theoretically calculated NO_3 concentration in the discharge exceeds that in the chamber by factor of about five, whereas measured concentrations of these particles are practically equal; 2) calculated values of HNO_2 concentrations in the discharge and the chamber are practically the same, whereas in the experiment concentration of these particles in the chamber is less by almost one order of magnitude

FIGURE 4. Experimentally measured dependencies of O_3, HNO_3, N_2O_5, HNO_2 and NO_3 concentrations in the chamber on accumulation time t_c at $\tau = 0.3$ s. $W_d = 1.5$ W/cm^3, air RH is about 25%.

than that in the discharge volume.

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