Theoretical and experimental investigation of the component content of active particles generated by barrier discharge in dry and wet air in the remote chamber

I.A. Soloshenko[1], V.V. Tsiolko[1], V.Yu. Bazhenov[1], A.G. Terentyeva[1], A.I. Shchedrin[1], A.V. Ryabtsev[1], A.I. Kuzmichev[2]

[1]Dept. Gas Electronics, Institute of Physics of National Academy of Sciences of Ukraine, Kiev, Ukraine
[2]Dept. Electron Device, National Technical University of Ukraine "Kiev Polytechnical Institute", Kiev, Ukraine

Abstract

In the present work detailed theoretical and experimental studies of the plasma-chemical reactor, which consists of two parts: 1) generator of active particles based on volume barrier discharges; 2) work chamber, are accomplished for widely used plasma generating medium – dry and wet air. It is shown that the essential amount of active molecules, such as O_3, H_2O_2, N_2O_5, HNO_3, HNO_2, NO_3, is possible in work chamber volume with concentrations depending on flow rate and water vapor percentage.

1. Introduction

In the last ten years nonthermal discharges at one atmosphere pressure find more and more applications in the technology. Particularly, possibilities of the use of corona and barrier discharges for efficient cleaning of industrial gases from nitrogen oxides NO_x and N_xO_y, sterilization of medical articles, in modification of surface features of polymer materials and chemical warfare agent decontamination were demonstrated. For solving the last three tasks the most optimal is the use of plasma-chemical reactor, which consists of two parts: 1) generator of active particles based on one or several discharges; 2) – work chamber with relatively big volume containing articles or materials to be processed. Such design enables elimination of the influence of processed articles on the discharge operation regime and, consequently, on the component content of active particles.

Purpose of the present work consists in theoretical and experimental investigation of the component content and concentration of active particles in work chamber of developed by us reactor of the type mentioned above at the use of ambient air with various humidity as working medium. Calculations were performed both for the discharge gap, where formation and decomposition of radicals and molecules occurred under action of electrons, and for the chamber, where only chemical reactions between the particles formed in the discharge took place.

2. Experimental setup and methods of measurements

Generation of active particles was performed in sixteen volume barrier discharges placed evenly on top wall of work chamber made of polymethylmethacrylate with 80 liters volume (430x430x430 mm). Internal chamber walls were covered by glass plates for diminishing losses of active particles. The active particles formed in the discharges came to the chamber, where articles to be processed were placed, and then left the chamber via the system of filters through the hole placed in a center of the chamber bottom plane. Air was supplied to the discharges via the system for moistening/desiccation, which enabled relative humidity (RH) variation in 20-90% range at temperature 20-22^{0}C. Volume rate of air purge could be adjusted in range 1-8 l/min (at that transient time of working medium in barrier discharge volume changed in range 5÷0.6 s, and linear velocity of particles at entrance to the chamber – in range 1.5÷12 cm/s). For performing optical measurements of the component content windows made of KU-1 quartz were placed at side walls of the chamber at distances of 65, 215 and 365 mm from top chamber wall. For powering the discharges high-voltage AC source with 15 kV maximum amplitude and 400 Hz frequency was used. Total active power introduced into the discharges comprised 120 W, and specific power value was 1.5 W/cm^3.

For researches of mixture component content in the chamber absorption spectroscopy method was implemented with the use of hardware-software complex based on monochromator MDR-23 (having 0.1 nm spectral resolution). Detection of light beams was performed by means of photomultiplier tube (PMT) FEU-100. For measuring digitized values of PMT electric signal specially developed hardware-software complex with 16-bit conversion and 11025 Hz sampling rate was used. NO_3 concentration was calculated

from measurements of absorption by this component at wavelengths $\lambda = 662$ nm and 623 nm. Component concentrations of O_3, NO_3, N_2O_5, HNO_3, HNO_2, H_2O_2, HO_2NO_2 were calculated from measurements of total absorption curve in wavelength range 200-300 nm. For that purpose values of component densities were chosen by means of automatic curve fitting software, so that resulting absorption curve would coincide with measured one. Use of such method was possible due to fact that characters of spectrum dependencies of absorption cross sections for studied components in wavelength range 200-300 nm are essentially different. For validation the method, O_3 concentration values obtained by procedure described above were compared with results on O_3 concentration measurements by its absorption at 296.5 nm wavelength, when it was possible to neglect absorption contributed by the other components. O_3 concentration values obtained by two those methods coincided with precision of concentration measurement (that is, scatter values for different measurements). Precision of the measurements was not worse than 5% for ozone, and 10-15% for the other components. Absorption cross sections for O_3, NO_3, N_2O_5, HNO_3, HNO_2, HO_2NO_2, H_2O_2 were taken from references given in [1].

3. Methods of numeric modeling the plasma component content in barrier discharge and work chamber

As it was already noted in the introduction, the most optimal plasma-chemical reactor for many technological tasks is one consisting from two independent parts – generator of active particles based on the discharges at atmosphere pressure and work chamber intended for placement of articles to be processed. Such design leads to significant complication of the calculations, because it is necessary at first to calculate component content of active particles in the discharge space, and then to take into account changes of content and concentrations of particles immediately in the chamber only due to chemical reactions. The second complexity of the calculations results immediately from specificity of barrier discharge, which represents a set of filamentary micro-discharges stochastically spread in space and time between the electrodes, so that each of micro-discharges has $\sim 10^{-8}$ s duration and ~ 0.1 mm diameter. Normally [2], at determining concentrations of particles in discharge, initially plasma kinetics is calculated in separate current channels of micro-discharges, and then after time of the order of diffusion time value ($\sim 10^{-3}$ s) averaging of concentrations of all components over the whole discharge space is performed. In such approach there exists a set of parameters (dimensions, density per discharge electrode square unit and rate of formation the current channels) that are not well known and essentially depend on design of the discharge space and gas type. Such parameters are usually fitting ones.

Calculations represented in the present work are based on another approach, in which power introduced into the discharge is immediately averaged over the discharge volume. In such approach valid consideration is assured for the processes, that are linear on specific power, and also for non-linear processes with typical reaction time longer than diffusion time ($\tau > 10^{-3}$ s). This condition is fulfilled good enough in the system under study, because typical durations of chemical reactions between dissociation products in current channels normally exceed 10^{-2} s. Advantage of such approach consists in the absence of free parameters, and thus exactly this approach was used in our calculations. At performing the calculations, processes at barrier discharge electrodes and those at work chamber walls were not taken into consideration.

In calculations of the plasma component content and concentrations of molecules and radicals formed in barrier discharge volume, kinetic equation were used as follows:

$$\frac{dN_i}{dt} = S_{ei} + \sum_j k_j N_j + \sum_{j,l} k_{jl} N_j N_l + \dots \tag{1}$$

Here N_i are concentrations of molecules and radicals; k_j, k_{jl} are rate constants of molecular processes; S_{ei} is rate of formation of the products of electron-molecular reactions, which was calculated from the equation:

$$S_{ei} = \frac{W}{V} \frac{1}{\varepsilon_{ei}} \frac{W_{ei}}{\sum_j W_{ej} + \sum_j W_j} . \tag{2}$$

W is power introduced into barrier discharge; V is barrier discharge volume. W_{ej} is specific power spent for electron-molecular process of non-elastic scattering with threshold energy ε_{ej}:

$$W_{ei} = \sqrt{\frac{2q}{m}} n_e N_i \varepsilon_{ei} \int_0^\infty \varepsilon Q_{ei}(\varepsilon) f(\varepsilon) d\varepsilon , \tag{3}$$

where $q = 1.602 \cdot 10^{-12}$ Erg/eV; m and n_e are electron mass and concentration; Q_{ei} is cross section of respective non-elastic process; $f(\varepsilon)$ is electron energy distribution function (it was calculated from Boltzman equation). W_i is specific power spent for heating the gas:

$$W_i = \frac{2m}{M_i} \sqrt{\frac{2q}{m}} n_e N_i \int_0^\infty \varepsilon^2 Q_i(\varepsilon) f(\varepsilon) d\varepsilon , \tag{4}$$

where M_i is mass of respective type of molecules, Q_i is transport scattering cross section.

Electron distribution function was calculated from Boltzman equation in two-term approximation [3].

$$\frac{1}{n_e N} \left(\frac{m}{2e}\right)^{1/2} \varepsilon^{1/2} \frac{\partial(n_e f_0)}{\partial t} - \frac{1}{3}\left(\frac{E}{N}\right)^2 \frac{\partial}{\partial \varepsilon}\left(\frac{\varepsilon}{\sum_i \frac{N_i}{N} Q_i} \frac{\partial f_0}{\partial \varepsilon}\right) - $$

$$- \frac{\partial}{\partial \varepsilon}\left[2 \sum_i \frac{m}{M_i} \frac{N_i}{N} Q_i \varepsilon^2 \left(f_0 + T \frac{\partial f_0}{\partial \varepsilon}\right)\right] = S_{eN} \tag{5}$$

where ε is energy (eV); T is gas temperature (eV); e is electron charge; E is electric field strength; N is total concentration of the molecules; N_i is concentration of respective type of the molecules; m is electron mass; S_{eN} and S_{ee} are integrals of non-elastic collisions of electrons with neutral particles and electrons, respectively.

The integral of non-elastic collisions of electrons with gas molecules was chosen in form

$$S_{eN} = \sum_i \frac{N_j}{N}\left[(\varepsilon - \varepsilon_i)Q_{ei}(\varepsilon + \varepsilon_i)f_0(\varepsilon + \varepsilon_i) - \varepsilon Q_i(\varepsilon_i)f_0(\varepsilon)\right], \tag{6}$$

Q_{ei} are cross sections of excitation and ionization of O_2 and N_2 molecules with threshold energy ε_j.

Electron-electron scattering was not taken in consideration, because, as it was shown by our test calculations, at fulfilling inequality $n_e/N \leq 10^{-6}$ e-e scattering does not have significant effect on rate constants of electron-molecular processes. Absence of e-e scattering integral in equation (5) leads to fact that stationary electron distribution function becomes independent on electron concentration. For that reason, for determining densities of neutral plasma components there is no necessity to solve kinetic equations for electrons and ions. It was assumed in the calculations that electric field in the discharge did not change in space and time, and it was taken to be equal 20 kV/cm, which is mean field value in barrier discharge on air, as it follows from [4]. At solving equations (1) 105 elementary processes were taken in consideration. Equations (1) were solved together with Boltzman equation by numerical techniques analogous to [3].

At second stage of the calculations it was assumed that the whole mixture acquired in barrier discharge volume (excluding charged plasma components) comes to work chamber in spatially uniform way with rates:

$$S_{ir} = \frac{N_{i\tau}}{\tau_r} \frac{V_r}{V_a} , \tag{7}$$

where τ_r and V_r are pump-through time and volume of barrier discharge space, respectively, $N_{i\tau}$ are concentrations of particular components of the mixture in time point τ_r, V_a is work chamber volume.

Calculation of concentrations of molecules and radicals in work chamber was performed on a basis of equations:

$$\frac{dN_i}{dt} = S_{ir} - S_{ia} + \sum_j k_j N_j + \sum_{j,l} k_{jl} N_j N_l + ... \tag{8}$$

Here $S_{ia} = \dfrac{N_i}{\tau_a}$ is rate of coming the plasma components out of work chamber due to gas purge, τ_a is time of gas purge through work chamber.

4. Results of numeric modeling of the component content of active particles in work chamber volume

In Fig.1 calculated values of concentrations of gas mixture components in work chamber with dry (20% RH, light bars) and wet (80% RH, black bars) air for pu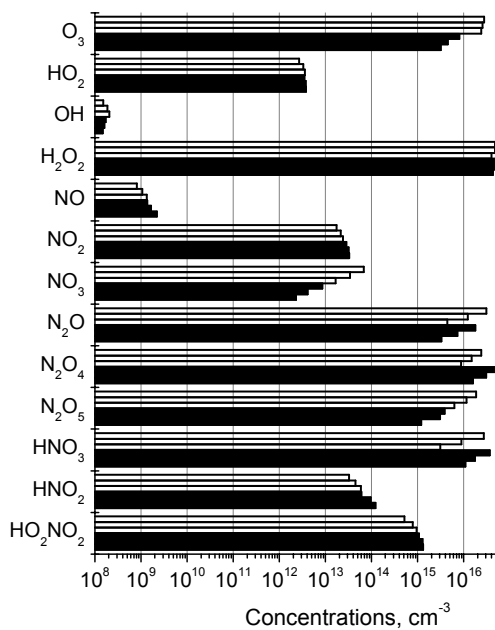rge rates of 2, 4 and 8 l/min. Such purge rates correspond to average time of mixture presence in the chamber of 40, 20 and 10 minutes, and average time of mixture presence in barrier discharge volume of 2.5, 1.25 and 0.5 s, respectively. As one can see from Fig.1, concentrations of particular components of the mixture possess different dependencies on purge rate. For that reason, by varying purge rate one can change ratio between concentrations of particular components in rather wide range.

In Fig.2 temporal dependencies of the component concentrations of gas mixture in work chamber with dry (20% humidity) air for 8 l/min purge rate are presented. Mentioned concentrations have practically linear dependence on time in the interval before approximately 1 minute. It is due to fact that the rate of their coming from the discharge does not change in time, and chemical reactions in the chamber volume do not have enough time to change ratios between concentrations of the components. Thus, only after big enough time interval ($\tau \gg 1$ min) quasi-stationary values of the component concentrations are reached, that gives evidence to steady in time income of these components, that is, the income is determined by processes of carrying the molecules out of barrier discharge volume. Ozone concentration reaches its

Fig.1. Calculated quasi-stationary concentration values of gas mixture components in work chamber in dry (20% RH, light bars) and wet (80% RH, black bars) air at purge rates 2, 4 and 8 l/min (purge rate increases from top to bottom).
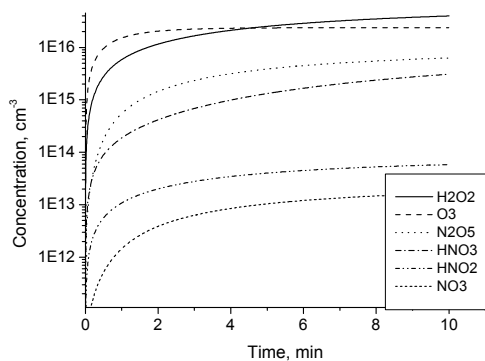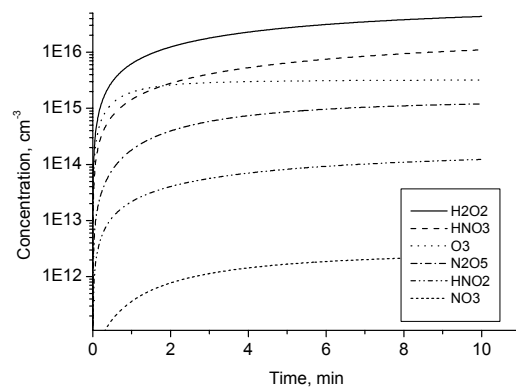

Fig.2. Calculated dependencies of component concentrations of H_2O_2, O_3, N_2O_5, HNO_3, HNO_2, NO_3 in work chamber on time at 8 l/min purge rate of dry air (20% RH)

Fig.3. Calculated dependencies of component concentrations of H_2O_2, O_3, N_2O_5, HNO_3, HNO_2, NO_3 in work chamber on time at 8 l/min purge rate of wet air (80% RH).

quasi-stationary value for the time of about $100 - 250$ s. Hydrogen peroxide concentration is practically independent on time, because in our calculations it is limited by value of saturated vapor concentration.

At increase of air humidity (Fig.3) concentrations of acid components (HNO_3, HNO_2) grow up due to increase of concentration of hydrogen-containing molecules in the mixture. At that ozone concentration decreases by about one order of magnitude due to fact that in barrier discharge volume increase of ozone decomposition at collisions with OH and HO_2 molecules occurs. For the same reason NO_3 concentration decreases in wet air, and since main channel of N_2O_5 formation is represented by reactions with NO_3 participation, N_2O_5 concentration is respectively decreased.

5. Experimental results for dry air (RH≈25%)

Measurements of component concentrations of O_3, NO_3, N_2O_5, HNO_3, HNO_2, H_2O_2, HO_2NO_2 in the chamber were performed at three volume rates of the purge (8, 4 and 2 l/min) at distances of 65, 215 and 365 mm from top wall of the chamber. HO_2NO_2 was not detected in any operation regime of the setup. It agrees with fact that calculated values of HO_2NO_2 concentration do not exceed $1 \cdot 10^{15}$ cm^{-3}, and sensitivity threshold of measuring technique does not exceed that value. The experiments have shown that characters of the dependencies of quasi-stationary concentrations of O_3, N_2O_5, HNO_3, HNO_2, NO_3 in the chamber on purge rate are in good agreement with calculated ones: concentrations of O_3, NO_3, N_2O_5, HNO_3 grew up with decrease of purge rate, and HNO_2 concentration decreased at that. However, for correct comparison of experimental results with calculated ones, one should determine, to which extent an assumption about uniform distribution of active particles in work chamber volume is fulfilled. Measurements of concentrations of active particles in three cross sections of the chamber have demonstrated the following. Heterogeneity of the distribution of measured densities of the particles on the chamber height is minimum at 8 l/min supply rate (minimum scatter about 10% was observed for O_3, and maximum about 30-40% - for HNO_2), and increases essentially with the rate decrease, reaching 200-300% for NO_3 and N_2O_5 at 2 l/min supply rate. As it was shown by experiments with smoke supply to gas route, such character of the dependence of homogeneity of particle distribution in the chamber volume on purge rate, first of all, is due to peculiarities of the process of mixing active particles coming from the discharges with air in the chamber. It was determined that at low rates of air supply (1-2 l/min) process of filling the chamber by active medium in the first approximation can be imagined as motion of gas "plunger" from top to bottom. That is, mixing of active particles with air occurred only in top part of the chamber, and then formed mixture moved downward and extruded residual air out of the chamber. But in case of volume supply rate of 8 l/min flows of active particles passed through the whole chamber due to higher initial velocity, then they were reflected from the bottom and returned to the chamber, thus providing good mixing of active particles with air present in the chamber volume. Thus, one can see that the most correct comparison of calculated and experimentally measured concentration values is possible at high purge rate.

Fig.4 exhibits dependencies of averaged over chamber height densities of O_3, NO_3, N_2O_5, HNO_3, HNO_2 on time for 8 l/min purge rate. (Starting values of component concentrations in Figs. 4 and 5 correspond to sensitivity thresholds of measuring technique.) One can see from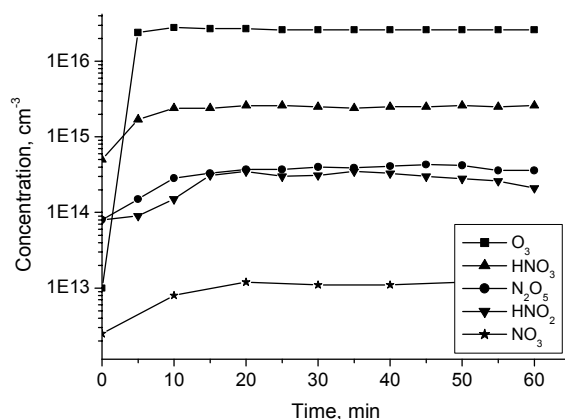 the figure that, as in case of calculations (see Fig.2), concentrations of all components practically reach quasi-stationary values in short time. Concentrations of O_3 and HNO_3 comprise $2.6 \cdot 10^{16}$ cm^{-3} and $2.6 \cdot 10^{15}$ cm^{-3}, respectively, and are essentially higher than densities of other components. Comparison of experimental data with calculated ones at 10-th minute shows that discrepancies between theoretical and experimental concentration values do not exceed 5% for O_3 and 25-100% for HNO_3, NO_3, HNO_2. In case of N_2O_5, the difference is essentially greater - experimentally measured concentrations are lower than calculated ones approximately by factor of 20. The most probable reason of the discrepancy between theory and experiment may consist in intensive precipitation of N_2O_5 at surfaces of the chamber walls, because their temperature is lower than that of dinitrogen pentoxide sublimation (32.4^0C). Another

Fig.4. Dependencies of experimentally measured concentrations of O_3, HNO_3, N_2O_5, HNO_2, NO_3 averaged over the chamber volume on time at 8 l/s purge rate of dry air (RH≈ 25%).

essential difference between experimental results and the theory is the absence of H_2O_2 in the chamber, although calculated values of hydrogen peroxide concentration are $\geq 5 \cdot 10^{16}$ cm^{-3}, which is almost one order of magnitude higher than sensitivity threshold of used measuring technique.

6. Experimental results for wet air (RH ≈ 80 %).

As in the case of dry air, heterogeneity of distribution of component concentrations of O_3, NO_3, N_2O_5, HNO_3, HNO_2 on chamber height is minimum at 8 l/min and increases essentially at rate decrease down to 2 l/min. However, homogeneity degree is worse than in previous case. Particularly, for the rate of 8 l/min maximum difference in concentration values of NO_3, N_2O_5, HNO_3, HNO_2 measured at top and middle windows comprised about 100% (at that homogeneity of O_3 distribution remained high enough – concentration difference in those cross-sections 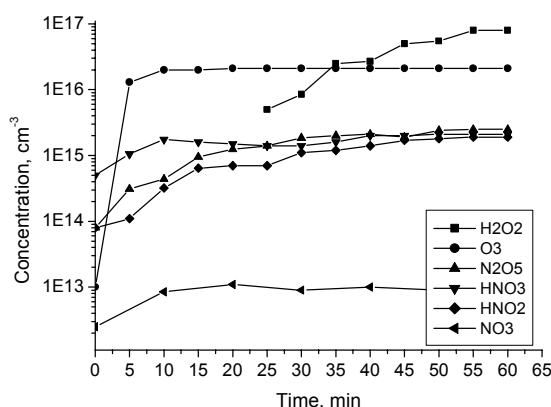did not exceed 10%). Unlike previous case, at the use of wet air and purge rates of 8 and 4 l/min hydrogen peroxide was also detected. In Fig.5 the dependencies of averaged over top part of the chamber (only measurements at top and middle windows were considered) component concentrations of O_3, NO_3, N_2O_5, HNO_3, HNO_2, H_2O_2 on time for 8 l/min purge rate are given. One can see from the figure that component concentrations of O_3, HNO_3, NO_3, N_2O_5, HNO_2 reach their quasi-stationary values till 10-20 minutes of filling the chamber. Hydrogen peroxide concentration reaches quasi-stationary value $\approx 8 \cdot 10^{16}$ cm^{-3} only at 55-60 min after the start of chamber filling. Comparison of theoretical and experimental data at 10-th minute shows that agreement between calculated and measured component concentration values of O_3, NO_3, N_2O_5, HNO_3, HNO_2 in case of wet air is essentially worse than that in case of dry air. Whereas theoretical and calculated concentrations of N_2O_5, HNO_2 and NO_3 differ approximately twice, in case of O_3 and HNO_3 this difference is significantly more. Particularly, theoretical values of O_3 concentration are about 6 times less than experimental ones. As to HNO_3, on the contrary, theoretically obtained concentration values are 6-7 times higher than measured ones. The most possible reason for such effect may be increased HNO_3 exit out of the chamber volume at air humidity growth due to solving nitrogen acid molecules in water layer at chamber walls.

Fig.5. Dependencies of experimentally measured concentrations of H_2O_2, O_3, N_2O_5, HNO_3, HNO_2, NO_3 averaged over volume of upper half of the chamber on time at 8 l/s purge rate of wet air (RH≈80%).

7. Conclusions

Accomplished comparison of calculated and experimentally measured concentrations of O_3, NO_3, N_2O_5, HNO_3, HNO_2, H_2O_2 in the work chamber at different air humidity shows that proposed by us approach to calculation of concentration of the particles in most cases gives good agreement between the theory and the experiment. Noticeable discrepancies observed in certain cases may be reasonably explained by factors that can not be correctly taken into account in the theory. The most important of those is the influence of discharge electrode surfaces and work chamber walls, and inhomogeneity of component distribution in the chamber.

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