RESEARCHING OF OZONE DECAY DINAMICS IN DIFFERENT TECHNOLOGICAL CONDITIONS

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The ozone decay dynamics in the working camera, previously filled with an ozone-air mixture, is studied experimentally and theoretically. For different initial concentration at the inlet to the camera and the experimental conditions, several cases were considered: with empty camera, filled with polystyrene foam by 30% and filled with metal by 30 and 50%. The dependence of ozone concentration in the camera on time and experimental parameters, taking into account its internal surface area is obtained. It is shown that the rate of ozone decay in the working camera is affected both by the mechanism of its destruction in the gas, and by the decay on the inner surface of the camera, as well as by the material of the camera filling.
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INTRODUCTION

Ozone is an air environment component. It is a simple substance consisting of three oxygen atoms. The natural ozone concentrations in the ambient air usually vary from 0.002 to 0.02 mg/m^3.

Various methods allow synthesize ozone from oxygen-containing substance. In particular, ozone can be obtained by chemical methods, by means of ultraviolet radiation, using radioactive radiation in the electrical discharge. The last method is the most preferable [1].

Ozone is a very active chemical substance, effectively interacts with many toxic and unpleasant smelling chemical compounds, microbes, bacteria, etc. The excess ozone amounts are quickly converted into molecular oxygen as a result of reactions with environment molecules. In particular, ozone disinfection does not require subsequent treatment – products washing or degassing. Exactly these features determine the perspective of ozone technologies using.

Ozone drastically reduces bactericidal contamination of surfaces. The ozone use is the most effective in the treatment of surfaces that are unstable to temperature treatment, as well as destroyed by acids or alkalis [2].

It should be noted that studies that were carried out by the Electric Power Research Institute (EPRI, USA) on order U.S. The Food and Drug Administration (FDA) obtained that food products, treated by ozone, do not produce any substances that have a mutagenic or carcinogenic effect. That's why the FDA certified the ozone substance as a disinfectant and sanitizer suitable for using without any restrictions in the US food industry. It means that ozone is granted the status of "Generally Recognized as Safe" (GRAS), which opens up wide opportunities for the use of environmentally friendly gas mixture that contains ozone, in production [3].

The majority of technological processes with ozone using occur in closed chamber, therefore, it is important to study the ozone decay dynamics in this chamber, which is the purpose of the research in this paper.

THEORY

The ozone decay can be represented in terms of the simple atomic mechanism [4, 5]:

$$O_3 + M \underset{k_r^M}{\overset{k_f^M}{\rightleftharpoons}} O_2 + O + M, \quad (1)$$

$$O_3 + O \overset{k_f^O}{\Longrightarrow} 2O_2,$$
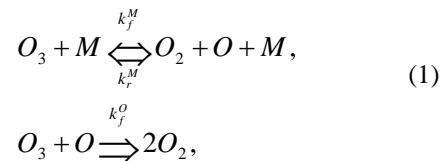
where M = {N_2, O_2, H_2O, O_3, CO_2, He, Ar, N_2O, including surface interaction}. In the equations (1) k_f^M and k_r^M are the rate constants of the forward and reverse reactions and they are different for different M, k_f^O is the rate constant of the second forward reaction. All rate constants depend on the temperature T.

From the system of equations describing the ozone decay mechanism, it is easy to get the equation for O_3 concentration by using the method of steady-state concentrations for O [7, 8]:

$$\frac{dC_{O_3}}{dt} = -2\frac{k_f^O \sum_M k_f^M C_M}{C_{O_2} \sum_M k_r^M C_M + k_f^O C_{O_3}} C_{O_3}^2, \quad (2)$$

here C_M is a concentration of M.

The equation (2) shows that in general case the O_3 decay is described by equations of first or second order, depending on the experiment parameters. If $k_f^O C_{O_3} \gg C_{O_2} \sum_M k_r^M C_M$, then the reaction of ozone decay becomes the reaction of first order: $dC_{O_3}/dt = -2C_{O_3} \sum_M k_f^M C_M$. Otherwise, if $k_f^O C_{O_3} \ll C_{O_2} \sum_M k_r^M C_M$, the O_3 decay is described by reactions of second order:

$$\frac{dC_{O_3}}{dt} = -2\frac{k_f^O \sum_M k_f^M C_M}{C_{O_2} \sum_M k_r^M C_M} C_{O_3}^2. \quad (3)$$

The numerical estimations of expressions $\sum_M k_f^M(T)C_M(t)$ and $\sum_M k_r^M(T)C_M(t)$ show that they do not depend on time and are defined by the initial bulk densities of reagents [6]. For experiment parame-

ters the reactions, described ozone decay, are the second order. The equation (3) can be integrated:

$$C_{O_3} = \frac{C_{O_3}^{in}}{1 + 2kC_{O_3}^{in}t}, \qquad (4)$$

where

$$k = k_f^O \sum_M k_f^M C_M / C_{O_2} \sum_M k_r^M C_M,$$

$C_{O_3}(t=0) = C_{O_3}^{in}$ is an initial concentration. It corresponds to the following ozone decay scheme: $2O_3 \overset{k}{\Longrightarrow} 3O_2$, where the effective «reaction rate constant» k depends on the initial densities of nitrogen, water and oxygen as well as on the reaction rate constants which are included in the equations (1).

The ozone decay on the surface can be included in the equation (3) by integrated the continuity equations over the volume. After the integration over the container surface and by introducing the probability of the particle decay on the surface γ_{O_3}, the equation (3) can be presented in the following way:

$$\frac{dC_{O_3}}{dt} = -2\frac{k_f^O \sum_M k_f^M C_M}{C_{O_2} \sum_M k_r^M C_M + k_f^O C_{O_3}} C_{O_3}^2 - \alpha\gamma_{O_3}v_{O_3}\frac{S}{V}C_{O_3}, \quad (5)$$

where V is a vessel volume where ozone decay takes place, S is a surface limiting the volume V, v_{O_3} is particle velocity and α is a coefficient considering the problem geometry.

For the case of ozone-air mixture by integrating the equation (5) the solution for $C_{O_3}(t)$ can be obtained in the following way:

$$\frac{C_{O_3}(t)}{C_{O_3}^{in}} = \frac{\exp(-at)}{1 + \frac{bC_{O_3}^{in}}{a}[1 - \exp(-at)]}. \qquad (6)$$

Here $a = \alpha\gamma_{O_3}v_{O_3}\frac{S}{V}, b = 2K$, where

$$K = k_f^O \sum_M k_f^M C_M / C_{O_2} \sum_M k_r^M C_M + k_f^O C_{O_3}$$

does not depend on time and is defined by the initial concentration of reagents. The decay on the walls is considered by the multiplier $\exp(-at)$.

If assume that $bC_{O_3}^{in} / a \gg 1$, what means large initial ozone concentrations or small surface areas in relation to the volume, or both at the same time, than the expression (6) cannot be applied, as it considers that K does not depend on time and is defined by the initial concentrations of reagents. Therefore it should be solved numerically. The case $bC_{O_3}^{in} / a \ll 1$ means small initial ozone concentrations or large surface areas in relation to the volume, or both at the same time and expression (6) can be rewritten as: $C_{O_3}(t) / C_{O_3}^{in} \approx \exp(-at)$.

Consider the case $a \ll 1$ taking into consideration that K does not depend on time, $\exp(-at)$ may be expanded:

$$\frac{C_{O_3}(t)}{C_{O_3}^{in}} \approx \frac{1}{1 + bC_{O_3}^{in}t} - \frac{at}{1 + bC_{O_3}^{in}t}. \qquad (7)$$

The first term in the right part in expression (6) is the solution (5) for the ozone decay in the chamber volume, and the second term defines an influence of the wall.

Thus, there are two limiting modes of ozone decay in the chamber. The first mode can be called the surface dominated ozone decay mode. In this case, ozone concentration decreased in accordance with the exponential law: $C_{O_3}(t) \approx C_{O_3}^{in} \exp(-\delta t)$, where the exponent is determined by the surface $\delta = \beta S / V$. The second mode can be called the volume dominated ozone decay mode with $C_{O_3}(t) \approx C_{O_3}^{in} / (1 + \sigma t)$, and the ozone decay is determined by the decay in the volume.

EXPERIMENT

To study the ozone decay dynamics in the camera, a stand was designed and manufactured. The experimental stand, schematically presented on Fig. 1, consisted of: Onyx Oxygen Generator (USA) with a capacity up to 0.6 m³/h with an integrated rotameter, an ozonator station "StreamOzone", consisting of three ozonizers (total production capacity up to 20 g/h), the ozone meter Teledyne Instruments (USA) model 454H with an ozone concentration measuring range 0.1…100 g/m³ and a laboratory camera made from galvanized iron with volume 320 liters. Also, the gas temperature in the camera was monitored with an electronic thermometer TPM-10.
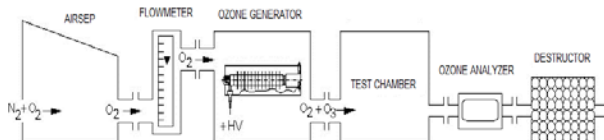

Fig. 1. Experimental stand

To carry out the experiments, a gas mixture, containing ozone, with different concentrations (10 and 20 g/m³) was fed into the camera. The pumping rate gas mixture through the camera was 0.30 m³/h. The filling time was determined by the output of the ozone concentration in the camera to the stationary level. Then, the ozone-oxygen mixture feeding from the ozonizers was switched off and every 30 minutes the ozone concentration in the experimental camera was measured. The results of experimental studies and theoretical calculations of the ozone decay dynamics in an empty camera are shown on Fig. 2. The asymptotic ozone concentration in the camera with inlet concentration 20 g/m³ was 13 g/m³, and with input concentration 10 g/m³ it was 7.7 g/m³. The time of reaching the asymptotic concentration in the camera was 2h. The theoretical curve was calculated by the formula (4).

From the graph it can be concluded that the ozone concentration change in the camera has an exponential character. The rate of ozone decay depends on its initial concentration. The difference between the theoretical and experimental curves is related with the fact that the calculation did not take into account the ozone decay on the camera walls.
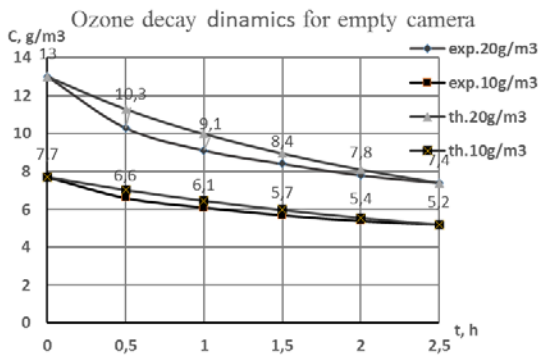
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Fig. 2. Ozone decay dynamics in empty camera

For the next experiment, a 30% volume camera was filled with polystyrene foam, then closed and filled with an ozone-air mixture at various concentrations (10 and 20 g/m^3). The asymptotic concentration in the camera with the inlet concentration 20 g/m^3 was 7 g/m^3, and with the input concentration 10 g/m^3 it was 3.5 g/m^3. The camera filling time was 2 h. Theoretical calculation of the ozone concentration change dynamics in a camera filled with polystyrene foam was carried out taking into account the ozone decay on the surface and was made using the formula (6). The results of the study are shown in Fig. 3.
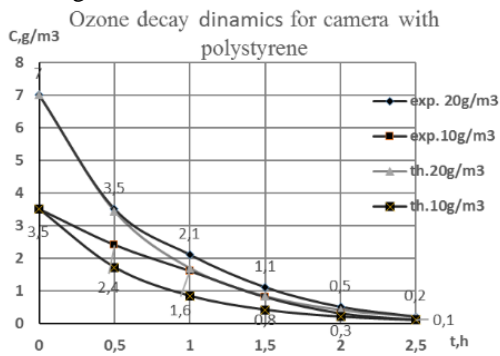

Fig. 3. Ozone decay dynamics for the camera with polystyrene foam

As can be seen from the graph the presence of polystyrene foam in the experimental camera reduces the initial concentration in volume twice.

For the next experiment, the camera volume was filled with metal by 30 and 50%. The ozone concentration in the gas mixture at the camera inlet was 20 g/m^3. The asymptotic ozone concentration in the camera with 30% filling in was 2.5 g/m^3, with 50% − 1.5 g/m^3. The camera filling time was 2h. The experimental results of the ozone concentration change in the camera from time are presented in Fig. 4.
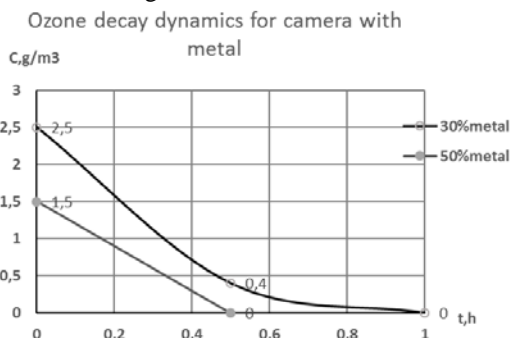

Fig. 4. Ozone decay dynamics for the camera with metal

The theoretical calculation for this case is complicated because of the complex geometry of the ozone disintegration surface.

As can be seen from the graph, the presence of metal significantly increases the surface of ozone decay. This involves the interaction mechanism of ozone with iron, which greatly accelerates the decay process.

On the following graph (Fig. 5) the experimental results of ozone decay in the empty camera, in the camera filled with expanded polystyrene foam by 30% and in the camera filled with metal by 30% are presented.
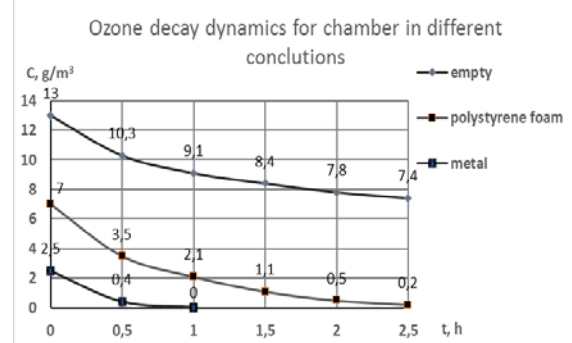

Fig. 5. Ozone decay curves for empty camera, camera with polystyrene foam and metal

From the analysis of the data presented on the graph, it can be concluded that the presence of the developed surface in the working camera significantly (more than 5 times) increases the ozone decay rate.

In the next experiment, the ozone decay dynamics at different temperatures (10 and 20°C) was studied. The ozone concentration in the gas mixture at the camera inlet was 20 g/m^3. The asymptotic concentration in the camera at 10°C was 13 g/m^3, and at 20°C it was 8.5 g/m^3. The camera filling time was 2h. The experimental results of the ozone concentration change in the camera from time and the calculated curves are shown in Fig. 6.
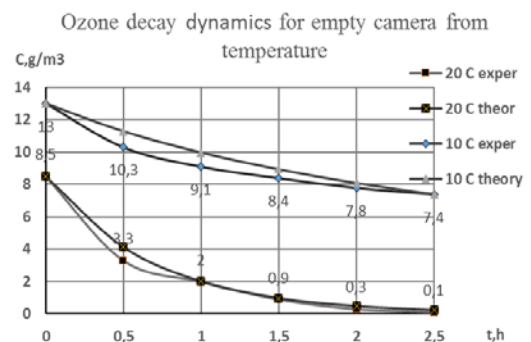

Fig. 6. Ozone decay dynamics at different temperature

From the graph it can be concluded that the higher is the temperature in the experimental camera, the faster ozone decays.

CONCLUSIONS

The results of theoretical and experimental study of the ozone decay dynamics in the experimental chamber previously filled with the ozone-air mixture are presented. Assuming that ozone decay takes place in a volume and is described by first-order kinetics, an analytical expression for the dependence of the ozone concentration in the camera on time and the problem parameters,

such as the feeding rate of ozone-air mixture to the camera inlet, the ozone concentration at the camera inlet, the camera volume and the area of its internal surface is obtained.

The ozone decay dynamics in the camera was experimentally studied with the ozone-air mixture pumping rate 0.3 m^3/h for various ozone concentrations at the inlet (10 and 20 g/m^3). It is shown that the rate of ozone decay depends on the area of the working camera inner surface and the objects material placed inside. In this case, the asymptotic ozone concentration that is generated in the camera also significantly depends on the area of the camera inner surface and the filling material.

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ИССЛЕДОВАНИЯ ДИНАМИКИ РАСПАДА ОЗОНА ПРИ РАЗЛИЧНЫХ ТЕХНОЛОГИЧЕСКИХ УСЛОВИЯХ

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Экспериментально и теоретически исследована динамика распада озона в рабочей камере, предварительно заполненной озоно-воздушной смесью. Для различных значений начальной концентрации на входе в камеру и условий эксперимента были рассмотрены несколько случаев: с пустой камерой, заполненной пенополистиролом на 30% и заполненной металлической стружкой на 30 и 50%. Получена зависимость концентрации озона в камере от времени и параметров эксперимента, учитывая ее площадь внутренней поверхности. Показано, что на скорость распада озона в рабочей камере влияют как механизм его деструкции в газе, так и распад на внутренней поверхности камеры, а также материал заполнения камеры.

ДОСЛІДЖЕННЯ КІНЕТИКИ РОЗПАДУ ОЗОНУ В РІЗНИХ ТЕХНОЛОГІЧНИХ УМОВАХ

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Експериментально і теоретично досліджена динаміка розпаду озону в робочій камері, яка попередньо була заповнена озоно-повітряною сумішшю. Для різних значень початкової концентрації на вході в камеру і умов експерименту були розглянуті кілька випадків: з порожньою камерою, заповненою пінополістиролом на 30% і заповненою металевою стружкою на 30 і 50%. Отримано залежність концентрації озону в камері від часу і параметрів експерименту, враховуючи її площу внутрішньої поверхні. Показано, що на швидкість розпаду озону в робочій камері впливають як механізм його деструкції в газі, так і розпад на внутрішній поверхні камери, а також матеріал заповнення камери.