Investigation into the Regularities of Hydrogen Fluoride Collection by the Developed Fibrous Ion-Exchange Material Under Dynamic and Static Conditions

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Abstract. Tests of respirators made of the developed material were conducted under dynamic and static conditions. Based on the methods of mathematical statistics and design of experiments, the authors determined the following dependences: of the dynamic activity of ion-exchanger on the sorbent layer height, of the sorption rate of hydrogen fluoride on the sorption time, of the effective protection time on the height of the layer of the material under investigation. The analysis of the results showed that the given fibrous ion-exchange material can be used as a sorption-filtering element of a respirator to ensure the required efficiency of protection against hydrogen fluoride.

1. Introduction
Nowadays, the construction sector is one of the key branches of industry in Russia, therefore enterprises involved in the manufacturing of engineering structures aimed at erecting residential and industrial buildings expand the production. Enterprises manufacturing reinforced concrete structures, where one of the production stages implies reinforcement bars cutting and welding of frames and grids, are an example of the above cases. The main problem of such industrial processes is heavy air pollution in the working zone. Due to the high temperature of welding arc, the procedure of welding of reinforcement bars into frames causes oxidation and evaporation of metals, fluxing agent, shielding gas, alloying elements, and leads to the formation of fine dust. The basic components of dust generated as a result of steel cutting and welding are the oxides of iron, manganese, silicon and other alloying elements. Nitrogen oxides, carbon monoxide and hydrogen fluoride (HF) belong to the most hazardous gases emitted during metal cutting and welding, given that HF causes mucous membrane irritation even at low concentrations. As a rule, local exhaust devices are used to improve the air quality in the working area of a welder, however the actual exhaust air rates do not often meet the requirements. The breathing zone of a welder performing manual operations contains hazardous substances in the amount that significantly exceeds both the background pollution level and the maximum permissible concentration for the working zone (MPCwz). Thus, the amount of solid particles in the working zone air is 5-6 MPCwz values, and the concentration of hydrogen fluoride exceeds the maximum permissible concentration (MPCwz) by 1,5-15 times. Ensuring the standard air purity in the working zone by means of local exhaust or general dilution ventilation is not possible in...
every instance. Therefore, it is necessary to use personal protective equipment for breathing organs, i.e. respirators [1].

A lot of respirators produced at the present time are perceived by the workers as an additional load and disturbance evoking the sensation of discomfort. When used under industrial conditions, lightweight framed respirators of “Snezhok” type proved themselves to be very efficient. Their development became possible only due to the use of a porous layer of fibrous ion-exchange materials as a filtering element.

It is the absence of nomenclature of textile materials with ion-exchange properties that substantially holds a large-scale implementation of the respirators of the given class.

Needle-punched fabrics are most commonly used as sorption-filtering materials in the respirators. They are manufactured through entangling the fibers of fabric applying specially designed needles.

2. Preparation of materials and investigation technique

For the purpose of welding aerosol collection, a needle-punched material has been developed, which contains two layers: the first layer is made of anion-exchange modified polycaproamide fibers; the second layer is made of hydrophilic modified cotton-like viscose fibers [2,3]. The proportion of the layers by mass is 1:(0,7-0,3), respectively. Fibers based on graft copolymer of polycaproamide and polydimethylaminoethyl methacrylate (KM-A1) are used as anion-exchange fibers [4].

The microporous structure of the nonwoven materials was investigated through the method of drying thermograms and the method of sorption – desorption isotherms. The macroporous structure was studied through the capillary rise method [2,4,5]. Based on the results of the investigations, differential and integral curves of pore size distribution were plotted. The integral curves characterize the cumulative absorptive capacity of the material macropores and the total volume of macropores in the material, while the differential curves determine the size range of macropores and the size of the most frequent pores in the ion-exchanger.

The analysis of the curves showed that the major part of the pore volume is formed by micropores of the size of (5…25)10^4 µm and macropores of the size of (250…630) µm. The material exhibits long effective protection time, considerable air permeability and water-absorbing capacity.

Among the physico-chemical properties of the sorption-filtering materials, the indices of sorption and air permeability are the most important. When they are used in respirators, the fitness of ion-exchange fiber materials for the purpose is first of all determined by their protective properties. They can be evaluated through particle breakthrough time, i.e. the occurrence of aerosol behind the sorbent layer, and the effective protection time (the time during which the aerosol concentration at the outlet from the adapter increases to 1MPC), as well as through the saturation time when the values of the gas concentration at the adapter inlet and its outlet become equal [5,6]. The essence of the method is the determination of the time interval until the occurrence of harmful substances in the amount detectable by an indicator behind the filtering element. The protective properties were tested under the following conditions: the temperature was 25°C, the velocity of gas-air mixture (GAM) was 3 cm/s, the concentration [HF] was 2,5mg/m^3, the GAM humidity was 65% [5].

3. Analysis of investigation results

The analyses of the given data demonstrates that the developed materials exhibit long effective protection time, and rather good indices of permeability. Introducing hydrophilic modified cotton-like viscose fibers into the sorbent composition enhances the protective and hygienic properties of ion-exchangers. It is probably explained by the fact that, when the hydrophilic fibers are introduced into the sorbent composition, the total moisture of the sorbent increases, additional swelling of ion-exchange fibers occurs, their specific surface area grows, thus expanding the contact surface with the gas to be sorbed. Consequently, the amount of the sorbed substance also increases, the effective protection time against the gas to be removed enhances, and the resistance of the filtering medium to aggressive environments improves [6-8]. Figure1 presents the dependence of ion-exchanger dynamic
activity (DA) on the height of the sorbent layer. Based on the analysis, it was revealed that, at first, the DA grows with an increase in the layer thickness but then remains practically constant.

Figure 1. The dependence of ion-exchanger dynamic activity (DA) on the height of the sorbent layer at the concentration of HF in gas-air mixture of 2,5 mg/m³, the GAM velocity of 3 cm/s, the GAM temperature of 25°C, the initial moister content of the sorbents of 5,5%.

Figure 2 presents the dependence of the rate of hydrogen fluoride sorption on the sorption time.

Figure 2. The dependence of the rate of hydrogen fluoride sorption on the sorption time.

The analysis of the dependence of effective protection time $\tau$ on the sorbent layer height $H$ in the process of hydrogen fluoride collection allowed concluding on the fact that the obtained dependence can be described by the existing Shilov equation of sorption dynamics [7,8], which has the following form for the case when $H>H_0$:

$$\tau = KH - \tau_0,$$

where $H_0$ – is the length of the functioning sorbent layer, cm; $\tau_0$ – is the loss of the effective protection time; $k$ – is the effective protection coefficient, $k=5,8$ (min/cm)
An isothermal model of adsorption was used for the description of the processes of HF sorption by the developed sorbent.

\[
\frac{\partial c}{\partial \tau} + u \frac{\partial c}{\partial x} + \left( \frac{1 - \varepsilon}{\varepsilon} \right) \frac{\partial a}{\partial \tau} = 0
\]  

(2)

\[
\frac{\partial a}{\partial \tau} = \beta_0 \left[ C - C_{bal}(a) \right]
\]  

(3)

\[ a = f(C) \tau. \]  

(4)

When the layer is initially not filled, the boundary and initial conditions of the mathematical model are the following:

\[
at \tau = 0 \quad C(0,x)=0, \quad a(0,x)=0
\]  

(5)

\[
at \tau > 0 \quad C(\tau,0)=C_0, \quad a(\tau,0)=f(\tau), x=0
\]  

(6)

In order to solve the system of equations under consideration, let us introduce a variable:

\[ z = x - \lambda \tau, \]  

(7)

where \( \lambda \) – is the velocity of the sorption boundary motion, m/s.

The solution of the equations (3-5) has the form:

\[
C_H = C_0 - \frac{\partial G}{\partial \tau} \frac{H \sigma}{\varepsilon F(u - \lambda)m_s}; \tag{8}
\]

\[
\beta_0 = \frac{\varepsilon}{\varepsilon - 1} \frac{(U - \lambda)}{H}; \tag{9}
\]

\[
\lambda = U \frac{C_0}{C_0 + a_0}. \tag{10}
\]

The value of \( a_0 \) was found by the formula:

\[
a_0 = C_0 \cdot (kU_n - 1) = C_0 \left( \frac{5.4893e^{-0.29x}}{G \cdot C_0} - 1 \right), \tag{11}
\]

where \( k \) – is the effective protection coefficient determined from the equation

\[
k = \frac{DA}{G \cdot C_0} = \frac{5.4893e^{-0.29x}}{G \cdot C_0}; \tag{12}
\]

where \( G \) – is the flowrate of gas-air mixture.

The velocity \( U_n \) can be determined from Darcy equation:
\[ U_n = \frac{k \Delta P_{fab}}{\mu h_{ion}}. \]  

(13)

where \( U_n \) – is the velocity of gas in a porous medium channel, m/s; \( \Delta P_{fab} \) – is the differential pressure at a porous element segment, Pa; \( \mu \) – is the gas viscosity, Pa·s; \( h_{ion} \) - is the thickness of porous sorbing element, m; \( k \) – is the proportionality factor characterizing the absolute permeability of a medium. For the purpose of ideal calculation, \( k \) is taken to be equal to the following:

\[ k = \frac{n_e d_{med}^2}{32}, \]  

(14)

with respect to the material texture, its pore structure

\[ d_{med} = \left( \frac{32 \mu h_{ion} k \bar{V}}{\Delta P_{fab} n_e^2} \right)^{0.5} \]  

(15)

The gas sorption rate \( U_{nr} \) can be determined by the formula:

\[ U_{nr} = \frac{I}{t} = \frac{M_g}{M_{fab}} = \frac{V_{a} \cdot C \cdot F_{filt}}{F_{fab} \cdot \rho_{fab} \cdot h_{ion}}. \]  

(16)

where \( M_g \) – is the mass of the sorbed gas, \( M_{fab} \) – is the mass of pure sorbent.

Taking into account the porosity and the specific surface area, the gas velocity specified by the adsorption process is calculated according to the formula:

\[ V_a = \frac{4U_{nr} F_{fab} \rho_{fab}}{\pi CS_{sp} k_d^2}. \]  

(17)

Then the velocity of the gas determined for the time \( t \) and specified by the adsorption process can be found by the formula:

\[ \bar{V}_a = \frac{4m_{fab} \Delta P_{fab}}{\pi CS_{sp} d_v^2 \cdot t_k} \int_{0}^{t_{fab}} U_{nr}(t, a) dt = \frac{4F_{fab} \rho_{fab}}{\pi CS_{sp} k_d^2} \int_{0}^{t_{fab}} 5,4893 \cdot e^{-0.29x} \, dx = \frac{20F_{fab} \rho_{fab}}{\pi CS_{sp} k_d^2} \left( e^{-0.29x} - 1 \right) \]  

(18)

For the purpose of optimization of the structure and properties of the filtering material, an experiment was conducted according to \( B_3 \) experiment design, for three factors (\( B_3 \)). The design matrix is graphically represented by a cube in which the cube corners contain center points. The matrix of a \( 2^3 \) full factorial design is taken for the experiment. “Star points” with the axial distance of \( \alpha = 1 \) are added to the center points. The axial distance is chosen according to the condition of maximization of the information matrix determinant [5]. With a small number of runs (\( N = 14 \)), the \( B_3 \) experimental design exhibits good statistical characteristics: the information matrix determinant \( |M| = 4.53 \times 10^4 \), the average variance \( d = 5.83 \), the maximum variance \( d_{max} = 11.2 \) [7,8,10]. In terms of the properties, the \( B_3 \) design is close to D-optimum designs ensuring the maximum accuracy of regression coefficients estimation, but it needs fewer runs [5]. The following criteria were chosen as optimization parameters: \( Y_1 \) – the effective protection time against HF, (hour), \( Y_2 \) – air permeability, (dm\(^3\)/m\(^2\)·s) [11].
The following varying factors were taken: \( X_1(N) \) – the content of high-modulus modified cotton-like viscose fibers, \%; \( X_2(n) \) – the number of work shifts prior to filtering element replacement; \( X_3(h) \) – the thickness of the filtering layer, mm.

As a result of the experiment implementation and the data processing, the authors obtained adequate equations (the check for adequacy was conducted through Fisher’s criterion). Taking into account the significant factors (the significance of the factors was evaluated through the Student’s t-test) they have the following form in the coded values:

\[
Y_1 = 29.01 + 11.22x_3 - 4.54x_3^2
\]

\[
Y_2 = 427.57 + 14.57x_2 - 172.07x_3 - 32.38x_1x_2 - 31.66x_2x_3 + 55.66x_2^2
\]

and in the named values:

\[
Y_1 = 29.01 + 11.22\left(\frac{h-4}{2}\right) - 4.54\left(\frac{h-4}{2}\right)^2 = -11.61 + 14.7h - 11.3h^2
\]

\[
Y_2 = 427.57 + 14.57\left(\frac{n-14}{4}\right) - 172.07\left(\frac{h-4}{2}\right) - 32.38\left(\frac{N-50}{20}\right)x
\]

\[
\times(\frac{n-14}{4}) - 31.66(\frac{n-14}{4})(\frac{h-4}{2}) + 55.66(\frac{n-14}{4})^2
\]

Based on the analysis of the obtained regularities, it is possible to draw a conclusion that the efficiency of hydrogen fluoride collection is influenced by all the factors under consideration, while the air permeability is primarily influenced by the proportion of the material layers. The optimization of the structure and properties of the developed material has been conducted through the superposition method for cross-sections of response surfaces. The optimal parameters has been found: the concentration of hydrogen fluoride in the gas-air mixture is 5 mg/m³, the proportion by mass of the layers of anion-exchange modified polycaproamide fibers and hydrophilic modified cotton-like viscose fibers is 1:(0.7÷0.3), the number of workshifts prior to regeneration is 15.

4. Conclusions
1. In order to improve the efficiency of collection of acid gas emissions from construction industry enterprises, a sorption-filtering material has been developed for the sorption-filtering element of a respirator. The authors have carried out experimental investigations of the regularities in hydrogen fluoride collection by the developed material under dynamic and static conditions.
2. The authors have refined the mathematical model for the description of the process of hydrogen fluoride sorption by the sorption-filtering element of the respirator represented by nonwoven needle-punched material made of ion-exchange polycaproamide fibers and high-modulus modified cotton-like viscose fibers.

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