COEFFICIENT OF RESISTANCE TO THE DIFFUSION OF GASES IN POROUS BODIES

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A method is proposed for calculating the diffusion resistance coefficient for porous materials having a structure with interpenetrating components and for granular systems.

In the study of the diffusion of gases in porous bodies, it is customary to use the concept of the diffusion resistance coefficient μ as a characteristic of diffusive transfer. This coefficient is equal to the ratio of the diffusion coefficient of a gas in open space to its diffusion coefficient in the porous body:

$$\mu = \frac{D}{D_{\text{por}}}. \tag{1}$$

The coefficient μ depends both on the porosity of the material m and on its structural characteristics, particularly on the sinuousness τ and the opening δ of the pores. Different relations have been presented in various studies to determine μ.

Kreisher [1] introduced μ as a structural factor characterizing the structure of the material and determined by the expression

$$\mu = \mu_l \mu_s, \tag{2}$$

where the quantities μ_l and μ_s are reliably determined from the following formulas for materials with a relatively uniform structure

$$\mu_l = \tau, \quad \mu_s = \frac{1}{m}. \tag{3}$$

Thus, Eq. (1) takes the form

$$\mu = \frac{\tau}{m}. \tag{4}$$

It was reported in [2] that Bird had found the following empirical relation:

$$\mu = \frac{1}{0{,}58m}. \tag{5}$$

The same study presented a formula found by Brabbit and Hertis for μ in relation to porosity, opening, and sinuousness:

$$\mu = \frac{\tau^2}{m\delta}. \tag{6}$$

Taking the most likely value $\delta = 0.75$, while $1 < \tau < 1.3$, they obtained

$$\mu = \frac{1}{0{,}57m}. \tag{7}$$

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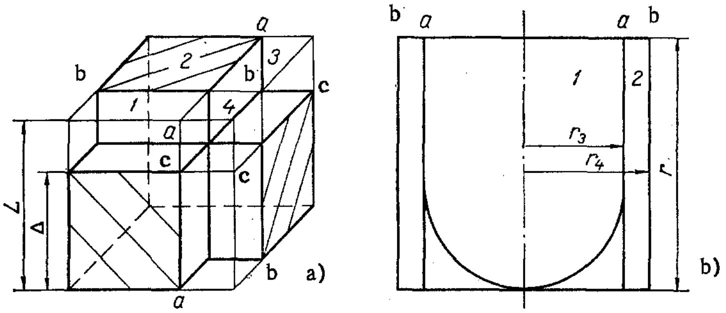

Fig. 1. Model representation of porous materials: a) 1/8 of a unit cell of a structure with interpenetrating components; b) averaged element of the structure of a granular material.

Equations (5)-(7) do not have an asymptote at m = 1, at which μ should be equal to unity. Also, there was no consideration of the dependence of τ and δ on m.

Here, we propose a method of calculating μ for granular systems and for materials having a structure with interpenetrating components, i.e., the skeleton and the pore space. Using electrical resistance as an analogy, we introduce the diffusion resistance $R = L/DS$ of a rectilinear channel of length L and cross-sectional area S, and we express the parameter μ through this resistance. The flow of gas J_{por} through the porous body:

$$J_{\text{por}} = D\frac{1}{\tau}\left|\frac{dn}{dx}\right| S_{\text{por}},$$

where $\left|\frac{dn}{dx}\right|$ is the absolute value of the concentration gradient; S_{por} is the area of the midsection of the pores.

When we replace the actual pore space by an effective rectilinear pore channel of length L, $\tau = 1$, and cross-sectional area S and we introduce a certain effective diffusion coefficient D_{por}, we obtain the following for the gas flow

$$J_{\text{por}} = D_{\text{por}}\left|\frac{dn}{dx}\right| S_{\text{por}}.$$

Using the last two expressions and considering the relationsip between the thickness L of the effective rectilinear pore channel, the sinuousness of the pore τ, the length of the pore $l = \tau L$, and Eq. (1), we obtain an expression for μ:

$$\mu = \frac{D}{D_{\text{por}}} = \tau\frac{S}{S_{\text{por}}} = \frac{L\tau}{DS_{\text{por}}}\,\frac{SD}{L} = \frac{R_{\text{por}}}{R}, \quad R_{\text{por}} = \frac{L\tau}{DS_{\text{por}}}, \tag{8}$$

where R_{por} is the diffusion resistance of the porous body.

We will analyze the diffusion process in 1/8 of a unit cell of a structure with interpenetrating components (Fig. 1a). The adiabatic planes a—a and b—b, parallel to the general direction of flow of the diffusing gas and the side walls of the cell, are subdivided by the walls into four individual, parallel-connected sections 1, 2, 3, and 4. Since sections 1, 2, and 3 are impermeable to the diffusing gas, the expression for the diffusion resistance of the unit cell will have the form

$$R_{\text{por}} = \frac{L}{D(1-c)^2L^2}, \tag{9}$$

where the parameter $c = \Delta/L$ is determined from the solution of the cubic equation [3]:

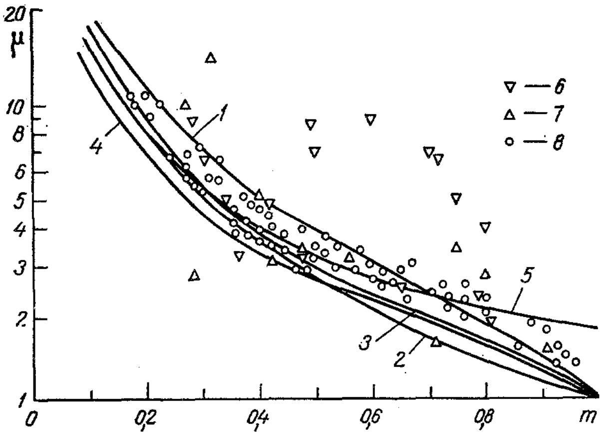

Fig. 2. Dependence of the diffusion resistance coefficient μ on porosity for different materials: 1, 2, 3, 4, 5) calculation with formulas (12), (13), (14), (18), (7); 6, 7, 8) experimental data [1], [2], [4].

$$m = 2c^3 - 3c^2 + 1. \tag{10}$$

The diffusion resistance of the same volume in open space is equal to:

$$R = \frac{L}{DL^2}. \tag{11}$$

Using (9) and (11) and allowing for (8), we obtain a formula to find μ in the case of adiabatic fragmentation of the unit cell

$$\mu_a = \frac{1}{(1-c)^2}. \tag{12}$$

Proceeding in a similar manner, we can obtain expressions for the diffusion resistance coefficient in the cases of isothermal and combination fragmentation.

In the case of isothermal fragmentation, we draw the isopotential plane c–c perpendicular to the mean diffusion flow. As a result, the expression for μ_i takes the form:

$$\mu_i = \frac{c}{(1-c)^2} + \frac{1}{1+c}. \tag{13}$$

Another possible variant of subdivision of the unit cell is combination (adiabatic–isothermal) fragmentation. Here, the a–a plane is taken to be impermeable for the streamline, while the c–c plane is taken to be isothermal. In this case, the diffusion resistance coefficient will be determined by the expression:

$$\mu_c = 1 + \frac{c}{(1-c)^2}. \tag{14}$$

Let us determine the coefficient μ for granular systems. In examining the process of heat transfer in granular materials, we isolate an average element (Fig. 1b) with the geometric parameters [3]:

$$y_3 = \frac{r_3}{r} = \frac{2\sqrt{N_c - 1}}{N_c}, \quad y_4 = \frac{r_4}{r} = \frac{y_3}{\sqrt[3]{1-m}},$$
$$N_c = \frac{m + 3 + \sqrt{m^2 - 10m + 9}}{2m}. \tag{15}$$

For simplicity, we assume that the particles are in point contact with one another. We subdivide the average element by adiabatic cylindrical surfaces a–a and b–b, parallel to the direction of flow of the diffusing gas (surface b–b coincides with the side wall of the element), thus obtaining two individual, parallel-connected sections 1 and 2. Considering that section 1 is impermeable to the gas, we write the expression for the diffusion resistance of the average element:

$$R_{\text{por}}=\frac{r}{\pi D\left(r_4^2-r_3^2\right)}. \tag{16}$$

The diffusion resistance R is determined as follows:

$$R=\frac{r}{\pi D r_4^2}. \tag{17}$$

Using (8), (16), and (17), we finally obtain a formula to determine μ for a granular system:

$$\mu_g=\frac{y_4^2}{y_4^2-y_3^2}. \tag{18}$$

Figure 2 shows theoretical relations and experimental data for μ for different materials [1, 2, 4]. Calculations with the formulas for adiabatic and isothermal subdivision of the unit cell (relations 1 and 2) establish the upper and lower boundaries of the theoretical values of μ. The combination subdivision (relation 3) gives results intermediate between μ_a and μ_i. The values of μ_g (relation 4) obtained from Eq. (18) for granular systems are close to the values of μ_c.

It is evident that a fairly large group of materials is described well by the theoretical relations. At the same time, the theoretical results differ markedly from the experimental data for a number of materials (this is especially true of chromium and half-chromium leather, coffee grounds, chocolate pudding, cardboard, and several other materials). This can be attributed to differences in the structures of the given materials and the structures of systems with interpenetrating components in the sense that the sinuousness of these materials τ is not equal to unity (in the model, $\tau = 1$). Other reasons for the discrepancy may be the presence of open porosity, the small number of through pores (many "dead ends" and clusters in the pore space), and the presence of narrow bridges of material between the pores. This is turn means that additional information is needed on the structure of the material. Accordingly, it will be necessary to conduct further studies to develop a method suitable for calculating the diffusion resistance coefficient μ.

Equation (14) can be recommended for evaluating μ for granular systems and for materials having a structure similar to that of systems with interpenetrating components (skeleton and pore space).

NOTATION

μ, gas diffusion resistance coefficient for a porous body; μ_a, μ_i, μ_c, μ_g, diffusion resistance coefficients in a unit cell with different methods of subdivision (adiabatic, isothermal, combination) and in an average element for granular systems; D, D_{por}, diffusion coefficients in open space and in the porous body, m²/sec; m, porosity of the material; δ, opening of the pores; τ, sinuousness of the pores; R, R_{por}, diffusion resistance of an isolated section in open space and in the porous body, sec/m³; L, Δ, geometric parameters of a unit cell, m; c, relative dimension of an edge of the unit cell; S, S_{por}, cross-sectional area of the isolated section, pore, m²; n, concentration of gas, kg/m³; J_{por}, flow of gas through the porous body, kg/sec; r, r_3, r_4, geometric parameters of the average element, m; N_c, coordination number.

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STEADY-STATE TWO-DIMENSIONAL DIFFUSION OF A RADIOACTIVE IMPURITY IN A CHANNEL WITH SORBING WALLS

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We consider the analytical solution of the problem of steady-state diffusion of a radioactive impurity in a gas-filled channel of finite length with sorbing walls, with allowance for surface diffusion. The conditions under which the two-dimensional problem becomes one-dimensional are found.

The study of diffusion of impurity components in gas-filled porous media is of great importance in developing a whole range of technologies associated with processes of drying, absorption, desorption, and heterogeneous catalysis, as well as in solving radioecological problems. The simplest model of capillary-porous media in the form of a set of cylindrical capillaries allows the discussion to be confined to diffusion in a single capillary. Further analysis is carried out, as a rule, on the assumption that the bulk and adsorption phases are in equilibrium in each cross section of the capillary, which allows the problem to be reduced to a one-dimensional formulation with the introduction of an effective diffusion coefficient, which makes allowance for the effect which both absorption and diffusion on the surface of the capillary have on the total diffusion flux [1-3]. In the case of steady-state diffusion of a radioactive impurity as well as in the case of unsteady-state diffusion of a stable impurity, however, the local equilibrium in an element of length of the channel may be disrupted substantially and as a result the contributions of volume and surface diffusion to the total diffusion flux through the capillary are redistributed considerably. In our study we find the parameter that specifies the degree of such nonequilibrium in the case of steady-state diffusion of a radioactive impurity and examine the conditions for the transition to the one-dimensional formulation.

Let us consider a cylindrical channel of length L and radius r_0, filled with a motionless inert gas. Suppose that the concentration of the radioactive impurity is maintained at c_0 at the beginning of the channel and is zero at the end of the channel. In accordance with the geometry of the problem we chose a cylindrical coordinate system, directing the z axis along the axis of the channel. Then steady-state diffusion of this impurity in the channel, complicated by adsorption on the channel walls and diffusion along the channel surface, can be described by the system of equations

$$\varepsilon \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial c}{\partial \rho} - gc(x, \rho) = 0, \tag{1}$$

$$\varepsilon \frac{d^2 c_s}{dx^2} - pc_s(x) - s \left(\frac{\partial c}{\partial \rho} \right)_{\rho=1} = 0, \tag{2}$$

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