SOME PROPERTIES OF GAS FLOW THROUGH WETTED POROUS BARRIERS

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The influence of the noncylindrical nature of the pores on gas flow through porous bodies filled with a wetting liquid is discussed. A method of calculating the size distribution of the pores is considered.

The wide application of porous materials in various technological processes as filters, phase separators, etc. necessitates the improvement of methods of studying their porous structure.

For filtering materials the most important characteristic is the distribution of the entire flow over the pores, as the size of which one takes the diameter at the narrowest part.

To estimate this distribution, one usually takes the dependence of the gas flow rate through a wetted specimen on the pressure. Two cases are distinguished: when the pores of the specimen are filled with liquid while there is none of it above the specimen [1] and when the specimen is wetted by the liquid while there is a layer of the same liquid above it [2]. In the first case the pressure dependence of the gas flow rate through the specimen will have the form of curve 2 in Fig. 1. Under pressure the largest pores start to be freed of liquid in accordance with the well-known equation of capillary pressure

$$P = 2\sigma \cos \Theta / R.$$

Since after a pore is freed of liquid the gas flow through it becomes the same as that through a dry pore at the same pressure, it is easy to obtain the fraction of the total liquid flow passing through pores having a narrowing radius $R \geq 2\sigma/P_i$ as the ratio $Q_2(P_i)/Q_1(P_i)$, where P_i is the gas pressure which opens pores with a radius R_i.

The first main defect of this method consists in the fact that, along with the expulsion of the liquid from the pores by the gas, the intense evaporation of this liquid also occurs, which grows sharply as the pores are freed. Attempts to accelerate the measurement can increase the delay in the opening of pores relative to the rise in pressure [3]. A second defect of the method is that it is practically impossible to fully realize the main condition of this method – the absence of liquid over the surface of the specimen. With an increase in pressure the liquid is displaced from the pore space of the specimen, covering its surface with a thin layer until this process is compensated for by the removal of liquid by the gas flow. The investigation which we performed on specimens of porous PNS-5 and FNS-2-3 stainless steel, porous titanium, and others showed that the behavior of the flow-rate characteristic curves in the initial stage fully coincides with their behavior for the same specimens but covered by a layer of the impregnating liquid. The length of this section depends on the properties of the liquid characterizing its removal and on the characteristics of the specimen itself.

If a layer of liquid is poured over the surface of the test specimen in order to prevent the evaporation effect, then the form of the pressure dependence of the gas flow rate becomes considerably different (curve 3 of Fig. 1). The procedure for calculating the distribution of the flow by pore size also becomes complicated. In this case the fraction of the flow taking place through pores with a radius $R \geq R_i$ can be found as the ratio of the tangent of the angle of slope of the characteristic curve at the pressure P_i to the tangent of the slope angle α for the dry membrane [2]. This method, while it does get rid of the evaporation of liquid in the pores, has important defects. First, the tangent of the slope angle is a differential characteristic, not measured directly, and finding it is associated with a considerable error. Second, this method, as shown below, works only in the case of cylindrical pores or pores with the smallest narrowing diameter located directly at the outer surface.

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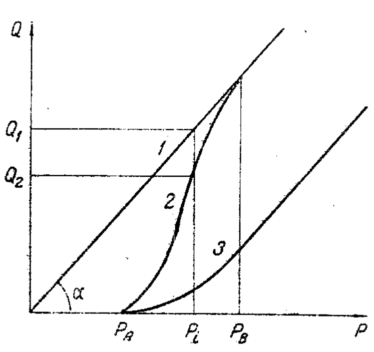

Fig. 1

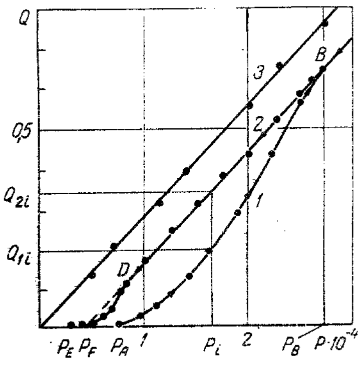

Fig. 2

Fig. 1. Theoretical form of pressure dependences of gas flow rate through the same porous material containing cylindrical pores: 1) dry material; 2) pores of material filled with alcohol, no liquid over the surface; 3) pores filled with alcohol, a layer of alcohol poured over the surface.

Fig. 2. Experimental pressure dependence of gas flow rate through a sheet of PNS-5 metal ceramic 0.75 mm thick with an area of 5 cm^2: 1) material impregnated with alcohol and a layer of alcohol poured over the surface, pressure grows (direct characteristic curve); 2) a layer of alcohol poured over the surface, pressure falls (reverse characteristic curve); 3) dry specimen. Dashed line) presumed behavior of reverse characteristic curve under the condition that the exit diameters of all the pores are the same and correspond to the mean capillary pressure at the surface of the specimen. Q, m/sec; $p \cdot 10^{-4}$, Pa.

In the investigation of a porous metal ceramic we encountered two difficulties. First, the form of the pressure dependence of the gas flow rate as the pressure increases (the direct characteristic curve) differs completely from the ideal form. The typical form of the actual dependence for the material PNS-5 is shown in Fig. 2 (curve 1). At high pressures ($P > P_B$) the slope of the direct characteristic curve coincides with the slope of the characteristic curve of a dry membrane (curve 3), but at $P < P_B$ there is a section in which the slope of the direct characteristic curve is considerably larger than the slope of the characteristic curve of a dry membrane. Therefore, the calculation of this characteristic curve by the standard method is impossible. Second, with a decrease in pressure hysteresis occurs. The loop does not tighten and disappear with an increase in its measurement time. A possible reason for the hysteresis in gas permeability may be hysteresis of the angle of wetting of the surface by the liquid during flow in and out. In our experiments, however, we used kerosene and ethyl alcohol, for which the angles of wetting the surface of the metal ceramic are very small, as the wetting liquid. Therefore, a difference in the wetting angles during inflow and outflow in the given case cannot lead to an appreciable hysteresis of the gas permeability.

Henceforth, for simplicity we will assume that $\cos \Theta = 1$. Therefore, the main reason for the hysteresis, in our view, is not a delay in the opening of pores and not a wetting hysteresis but the noncylindrical nature of the pores of the metal ceramic. If a pore has a narrowing, and the diameter of the exit opening is larger than the diameter of the narrowing, then to force the liquid meniscus through the pore it is necessary to overcome the capillary pressure P' in the narrowest part. Since the diameter of the opening is larger at the outer surface, the corresponding capillary pressure P'' will be lower. After the pore is opened under the action of the pressure P', the gas flow through it abruptly grows to that value for which the dynamic resistance of the pore to the gas flow becomes equal to the pressure difference $P' - P''$. With a further increase in pressure the gas flow rate will grow linearly, with the slope of the dependence being the same as that for a dry pore. With a decrease in pressure the closing of the pore takes place not at the opening pressure P' (as for a cylindrical pore) but at the pressure P'', i.e., hysteresis develops. Since the ratio between the outer diameter of a pore and its narrowing has a random character and may differ by several times, the size of the jump in pressure $P' - P''$ and in the corresponding gas flow rate can be very considerable.

Porous materials of the metal-ceramic type are obtained by sintering pressed powders, and each open pore through the entire thickness of the porous material is formed by a collection of "elementary pores" formed by the free space between neighboring grains. These elementary pores form a complicated intersecting structure in which each through pore consists of at least several tens of elementary pores.

The concepts presented allow a qualitative explanation of the pressure dependence of the gas flow rate through a metal ceramic under a layer of liquid. The opening of the largest pores, not having narrowings, begins when the value P_A is reached. Then as the pressure rises pores with smaller and smaller narrowings start to open. The probability that the smallest elementary pore is at the outer surface is very small, and one can practically assume that all the narrowings are located in the inner part of a pore. Consequently, when the liquid is forced down into the narrowest part of the pore they all give a jump in the gas flow rate. And the smaller the size of the narrowing, the larger the jump. And it is just this which explains the sharp rise in the direct characteristic curve in the section P_AB. When the pressure P_B is reached practically all the pores of the material are open and then the direct characteristic curve runs parallel to the flow-rate characteristic curve for a dry membrane with a shift by an amount P_F corresponding to the average capillary pressure at the surface of the membrane. With a decrease in pressure the reverse characteristic curve runs parallel to the flow-rate characteristic curve of a dry membrane down to the point D, which corresponds to the smallest value of the pore diameters at the surface of the material. With a further decrease in pressure the reverse characteristic curve drops abruptly at first and then tends toward the point P_E. This is explained as follows: when the pressure falls so much that there appear at the surface a considerable number of pores having a capillary pressure greater than the gas pressure, then the liquid starts to be drawn through them under the action of capillary forces, and since the pores intersect, by flowing through the narrowest capillaries this liquid can block an additional number of pores owing to the sticking of gas bubbles in their narrowings. At the point P_E the passage of gas through the specimen stops entirely. This pressure corresponds to the closing of the largest pores at the surface of the material. In the section DE under the conditions of return capillary suction of the liquid the process of gas flow through a porous specimen proves to be extremely complicated and is not subject to calculation. Therefore, we are confined to ascertaining the start of this process at point D. From this it becomes clear that the direct characteristic curve is determined both by the distribution of through pores with respect to narrowings and by their distribution with respect to the size of the exit diameter. Therefore, it cannot be used in the existing methods of determining the size distribution of the pores. Second, the reverse characteristic curve is determined mainly by the distribution of the exit openings of the pores, and if the influence of the mutual intersection is not too great (the dip in the characteristic curve in section P_ED is absent or slight) then this distribution can be obtained using the usual method. But if the influence of the intersection of pores is large and the total distribution of exit openings of the pores cannot be obtained in this way, from this characteristic curve it is still easy to obtain the largest pore size at the surface,

$$R''(\max) = 2\sigma/P_E,$$

the smallest,

$$R''(\min) = 2\sigma/P_D \quad ,$$

and the average pore size at the surface,

$$R''(\mathrm{av}) = 2\sigma/P_F.$$

Here it is interesting to determine how this averaging occurs. We assume that the gas flow rate Q_j through the individual j-th pore is directly proportional to the pressure P with a proportionality factor K_j. If part of the pressure is expended in overcoming the capillary pressure P'' at the exit from the pore, then the gas flow rate through the pore will be

$$Q_j = K_j(P - P''_j);$$

the total gas flow rate through a unit surface is

$$Q = \sum_1^n K_j(P - P''_j), \quad .$$

where n is the number of pores per unit surface.

The coefficient K_j characterizes the dynamic resistance of the j-th pore. As already noted, however, a through pore in a metal ceramic represents a random sequence of elementary pores, and therefore its exit radius is in no way connected with the total dynamic resistance of the pore (except for the rare cases when the narrowing of the pore falls at the exit). One can therefore assume that the dynamic resistance of all the pores is the same on the average, $K_j = K$. Then

$$Q = \sum_{1}^{n} K_j (P - P_j'') = nK (P - P''),$$

where P'' is the arithmetic-mean capillary pressure of the menisci of the exit openings of the pores, corresponding to the pressure P_F (Fig. 2).

The overall form of the direct and reverse characteristic curves allows one to determine the largest and smallest diameters of narrowing of the pores at once. The largest diameter will correspond to the pressure P_A and the smallest to the pressure P_B at which the direct and reverse characteristic curves diverge.

For filtering materials it is important to obtain the distribution of the entire flow over pores with different diameters of the narrowings. Let us attempt to find this distribution using the direct and reverse characteristic curves, as well as the concept of the pores of a metal ceramic as a collection of individual elementary pores, the size of each of which is a random value. In this case neither the diameter of the exit opening of a through pore nor the diameter of its narrowest section can by itself determine its dynamic resistance, since the length of an elementary pore is far less than the total length of the entire through pore, while the diameters of other elementary pores of the given through pore are random values. Therefore, it is reasonable to simply assume that the gas flow rate through each through pore is porportional to the pressure, while the proportionality factor is the same for all through pores and is a characteristic of the porous material.

Using this approach, let us first consider the direct and reverse characteristic curves in the pressure range from P_D to P_B, where the reverse characteristic curve is parallel to the characteristic curve of a dry specimen, i.e., the pores of the material are free of liquid. The fact that the characteristic curve of the dry specimen in section BD is parallel to the characteristic curve of the wetted specimen serves as a guarantee that at the pressures reached practically all the through pores are free of liquid. The point Q_{1i} of the direct characteristic curve shows the gas flow rate through all those pores whose radii of narrowing satisfy the condition

$$R > 2\sigma / P_i = R_i,$$

where P_i is the value of the pressure corresponding to the point Q_{1i}. On the reverse characteristic curve this pressure corresponds to a gas flow rate Q_{2i}. Since Q_{2i} is the gas flow rate through all the pores of the material at the pressure P_i while Q_{1i} is the gas flow rate under the same conditions but through pores with a narrowing radius $R > R_i$, it is obvious that the fraction of gas passing through pores with a narrowing radius $R > R_i$ equals Q_{1i}/Q_{2i}.

Thus, the distribution of gas flow over pores with the smallest narrowing radius $R > R_i$ in the pressure interval from P_D to P_B is found simply as the ratio of the corresponding values of the direct and reverse characteristic curves.

This cannot be done for pressures $P < P_D$, since here the reverse characteristic curve indicates the filling of the pores with liquid. One can escape the difficulty by taking all the exit openings of the through pores as the same, corresponding to the average capillary pressure at the exit from the pores, determined by the value P_F. Then the average value of the jump in the gas flow rate upon the opening of pores along the direct characteristic curve does not change, and the form of the direct characteristic curve will be the same (for the same distribution of pores with respect to narrowings). In this case the form of the reverse characteristic curve will correspond to the dashed line extending the line BD parallel to the characteristic curve of a dry specimen (Fig. 2). Then the distribution of flow over the pores does not change, and the fraction of the flow taking place through pores having a radius of narrowing $R > R_i$ can easily be found as the ratio Q_{1i}/Q_{2i}', where Q_{2i}' is the value of the gas flow rate taken along the dashed extension of the reverse characteristic curve (Fig. 2).

Thus, one can obtain the total distribution of the entire flow over pores having a radius of narrowing $R > R_i$ for all values of R_i.

Since we have assumed above that the dynamic resistances of all the pores can be taken as the same in general, regardless of the narrowing or the exit opening, the numerical distribution of pores with respect to the narrowing radii will be similar to the flow distribution over pores with different narrowing radii.

What was said above is also valid when a wetting liquid possessing a wetting hysteresis is used. In this case to obtain the sizes of the pore narrowings one must allow for the outflow factor cos Θ, while in estimating the sizes of pores at the surface one must allow for the equilibrium factor cos Θ.

To determine the total number of pores, one must draw upon additional data based on additional model considerations or microscopy data.

NOTATION

P	is the pressure;
σ	is the surface tension;
Θ	is the wetting angle;
R	is the capillary radius;
Q	is the gas flow rate through membrane;
Q_1	is the gas flow rate through wetted membrane during an increase in pressure;
Q_2	is the gas flow rate through wetted membrane during a decrease in pressure;
P'	is the capillary pressure in the narrowest part of the capillary;
P''	is the capillary pressure at the exit of the capillary at the surface.

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EVAPORATION OF SEVERAL SUBSTANCES FROM A POROUS BODY

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A system of equations of heat and mass transfer is derived and analyzed which describes evaporation of several volatile substances from a porous body.

Porous materials are widely heat treated in industry for the removal of volatile substances. One form of such a treatment is drying, where one substance (moisture) evaporates [1]. In some technological processes it is important to remove from a porous body not one but a group of various volatile substance (fillers) contained therein. In titanium production, e.g., the reactant mass is vacuum-heated for purification of the titanium sponge of magnesium and magnesium chloride [2]. When not one but several volatile substances are removed, there arise new patterns due to the effect which escaping of more volatile fillers has on the distribution of less volatile fillers in the porous body.

I. Mathematical Model. The system of transfer equations will be constructed on the following basic premises.

1. The condensate phase of volatile fillers is stationary relative to the "skeleton" of porous material. This is possible, e.g., when sublimation of solid fillers occurs during heat treatment. When some of the fillers are in the liquid state, however, then one assumes that they are adsorbed on the surface of the solid phase and not free to move under action of gravitational or capillary forces.

2. The fillers do not form solutions with one another or with the material of the porous body.

3. Transport of vapors through channels and pores is affected by the pressure gradient, according to Darcy's law, the role of diffusion being negligible. This also assumes a subsonic flow of vapor (Mach number smaller than unity), with vapor behaving like an incompressible fluid, and assumes the model of a continuous

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