

COEFFICIENTS OF CAPILLARY MASS TRANSFER
OF POROUS SOLIDS BASED ON CURVES OF
PORE DISTRIBUTION

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The coefficients of capillary conductivity, capillary diffusion, and thermal diffusion of a liquid are determined for porous ceramic and quartz sand using differential curves of pore distribution obtained experimentally.

The mechanism of transfer of an absorbed liquid in a porous solid and the transfer coefficients reflecting the mechanism depend on the geometry of the porous space of the solid and degree of filling of the pores with liquid.

There are several works devoted to the study of the mass transfer coefficients of porous solids taking into account the properties of their porous structure.

Expressions for the capillary transfer coefficients of a liquid were obtained theoretically by A. V. Lykov [1, 2] for a model solid whose porous space is formed by a system of cylindrical capillaries of different radii not interconnected:

$$k_{\psi} = \frac{\rho^3}{8\eta} \int_{r_0}^r r^2 f(r) dr, \quad (1)$$

$$a_n^{\psi} = \frac{\sigma \cos \theta}{4\eta r^2 f(r)} \int_{r_0}^r r^2 f(r) dr, \quad (2)$$

$$a_T^{\psi} = \frac{\rho \cos \theta}{4\eta \rho_0 r} \frac{d\sigma}{dT} \int_{r_0}^r r^2 f(r) dr. \quad (3)$$

The filtration sizes of the pores, which determine the resistance to the flow of a viscous liquid in a porous solid through its separate continuous capillaries, and the differential size distribution function of the filtration pores play the main role in Eqs. (1)-(3). The equations for the coefficients of internal mass transfer obtained by A. V. Lykov based on the model of a porous body which he developed are applicable for calculating the corresponding coefficients of real solids with mass contents higher than the hygroscopic state of the absorbed liquid. The limit of applicability of Eqs. (1)-(3) is approached upon the removal of the liquid from the finest continuous capillary passing through the specimen studied.

Analytical expressions for the coefficients of isothermal mass transfer of a model solid composed of spherical nonporous particles of the same diameter were obtained by N. V. Churaev [3]. In this report the total porosity of the system, determined through the diameter of the particles and their mode of packing, is considered. The equations obtained by N. V. Churaev are suitable for the calculation of mass transfer coefficients in the case of the predominance of the diffusional and film mechanism of liquid transfer, i. e., when the mass contents of the system are not high.

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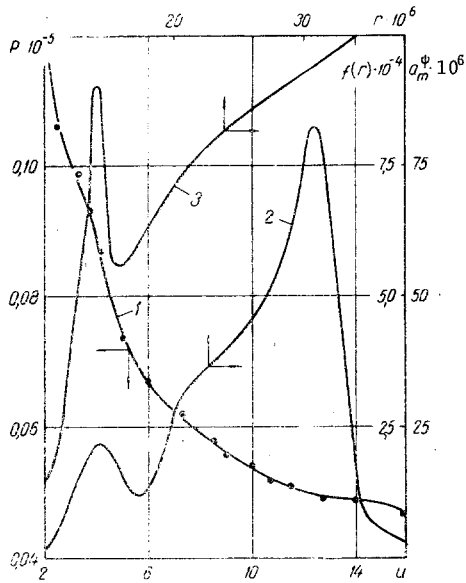


Fig. 1. Porous ceramic: 1) experimental dependence of excess air pressure P (N/m^2) on moisture content u (%); 2) differential curve $f(r)$ (m^{-1}) of pore distribution with respect to radius r (m); 3) dependence of coefficient of capillary diffusion of water a_m^ψ (m^2/sec) on pore radius.

In view of the absence of experimental works employing the basic parameters of the porous structure of a solid (pore sizes, total porosity, size distribution of pores, and others), in order to determine the mass transfer coefficients it is necessary first of all to determine the coefficients of capillary conductivity, capillary diffusion, and thermal diffusion of a liquid for real porous bodies based on Eqs. (1)–(3) of A. V. Lykov. In these equations the properties of the porous structure of the solid are taken into account by the differential function of pore distribution and by the pore sizes. Therefore the second aspect of the problem comes down to the development of a method of determining the differential pore distribution function from the effective radii with an accuracy sufficient for the use of the function in quantitative calculations of the coefficients under consideration.

The dependence of the mass content at different cross sections of a column containing the experimental specimen on the capillary pressure of the absorbed liquid is the reference experimental dependence for obtaining the differential pore distribution function in the solid. The capillary pressure of the liquid in the solid was measured by means of its compensation by the excess air pressure. This made it possible to measure the mass content of the solid at one cross section of the column and to reduce the height of the column to 10–20 mm.

In the course of the experiment the liquid absorbed by the solid was gradually expelled from it by increasing the excess air pressure. A certain value of the mass content of the solid corresponded to each value of the excess air pressure. The changing mass content at a given cross section of the solid in the course of the experiment was measured by the method of gammascopy. The method of conducting the experiments is described in detail in [4].

From the given $P(u)$ the integral distribution of pores in the solid with respect to their effective radii is constructed as the ratio of the area of the capillaries filled with liquid at the given cross section of the solid at the given excess air pressure to the area of all the capillaries at the same cross section which are filled with liquid at atmospheric pressure (the maximum mass content of the solid):

$$F(r) = \frac{S(r)}{S_{\max}}$$

The areas $S(r)$ and S_{\max} are easily related to the specific mass content of the solid

$$u = \frac{S(r) h \rho}{\pi R^2 h \rho_0},$$

from which

$$S(r) = u \pi R^2 \frac{\rho_0}{\rho}.$$

Similarly,

$$S_{\max} = u_{\max} \pi R^2 \frac{\rho_0}{\rho}.$$

With allowance for the latter two equations we finally find the integral pore distribution in the form

$$F(r) = \frac{u}{u_{\max}}. \quad (4)$$

The position of the cross section of the specimen at which the mass content is measured during the experiment does not affect the nature of the integral pore distribution.

The Laplace equation for capillary pressure is used together with the experimental dependence $P(u)$ to determine the effective radii of the pores.

The differential pore distribution function with respect to the effective radii is found as the derivative of the integral distribution

$$f(r) = \frac{dF(r)}{dr}. \quad (5)$$

The equations of discrete differentiation of [5, 6], which make it possible to find the derivative from tabular values, are used for its determination.

The error in determining the function $f(r)$ consists of the error in measuring the mass content of the solid and the error in the discrete differentiation. The methods of calculating each of the components of the total error in $f(r)$ are presented in [7] and [6], respectively.

Porous ceramic and quartz sand, moistened with water, are taken as the experimental systems.

The porous ceramic is used as a filter for the spinning solution in the production of chemical filaments. The ceramic has a rigid porous structure and the density of the dry material is 1480 kg/m^3 .

The quartz sand, baked and washed with acids and distilled water, was screened in the form of three fractions with grain sizes of 0.063-0.16, 0.2-0.25, and 0.75-0.8 mm. These specimens simulate macroporous solids whose porous structure contains only open continuous pores.

In Fig. 1 the experimental dependence of the excess air pressure on the moisture content (curve 1) and the differential porosity distribution function calculated by the method indicated above (curve 2) are shown for porous ceramic.

It is seen from Fig. 1 that in the ceramic the effective radii of the filtering pores encompassed by curve 2 lie in the interval from 10 to 40μ . The distribution of porosity with respect to radius is complicated: two maxima are observed on curve 2. This indicates the heterogeneity of the porous structure of the ceramic studied. The larger maximum of the $f(r)$ curve occurs for pores of 31μ radius, from which it follows that pores of this size are encountered most often in the ceramic (most probable radius).

The differential curves of pore distribution in each of the three fractions of quartz sand are obtained similarly. The distribution curves smoothly cover the range of pores with radii from 10 to 170μ . Within a single fraction the pore distribution in sand is close to the normal distribution from the nature of the curve.

Thus, the subjects of the study represent a group of capillary-porous solids with a constant porous structure in a wide range of effective macropore radii.

The amount of micropores in the solids studied is very small. Consequently, the amounts of adsorbed moisture are also small. This permits one to make no correction to the filtering sizes of the pores for the thickness of the adsorbed film.

The distribution function $f(r)$ obtained were used to calculate the coefficients of capillary transfer of water for the solids studied in accordance with Eqs. (1)-(3). In the calculations it was assumed that $\cos \theta = 1$ since the extraction of water from solids moistened to the maximum extent took place in the experiments. The experiments were conducted at a temperature of 20°C . The approximate integration was carried out according to Simpson's equation transformed for the case of integration with a variable upper limit.

The coefficients of capillary conductivity of water as functions of the moisture content of the solid are presented in Fig. 2a, for porous ceramic (curve 1) and quartz sands of fractions 0.063-0.16 mm (curve 2), 0.2-0.25 mm (curve 3), and 0.75-0.8 mm (curve 4).

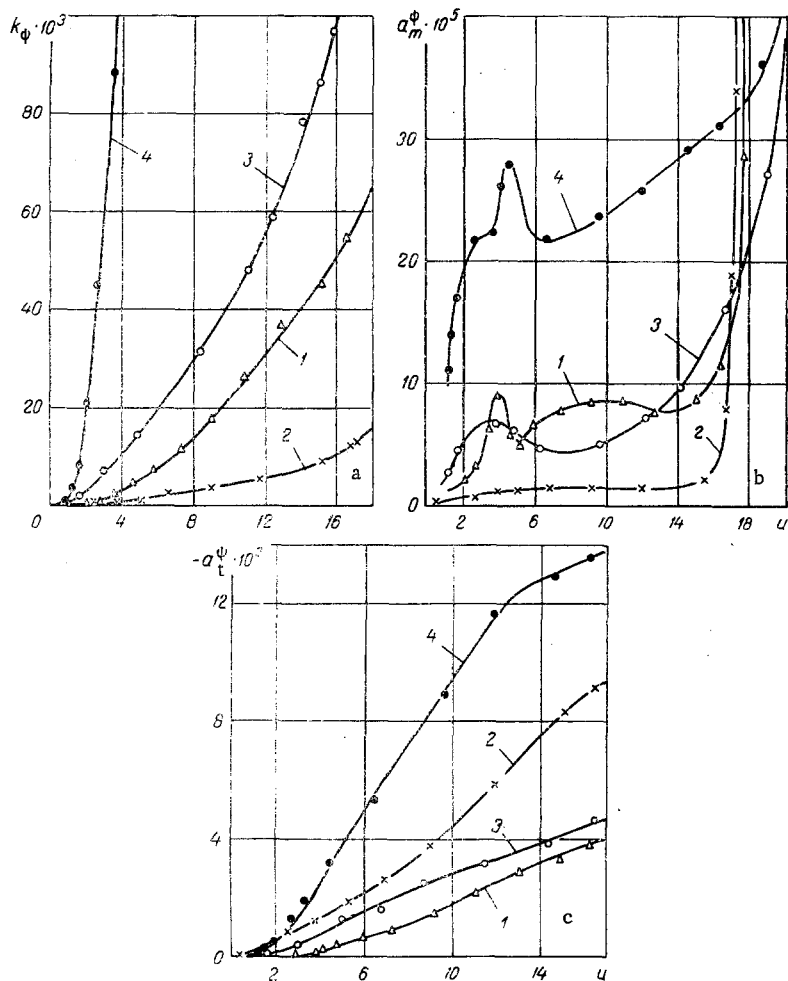


Fig. 2. Dependence on moisture content u (%) of coefficients of capillary conductivity of water k_{ψ} ($\text{kg} \cdot \text{sec}/\text{m}^3$) (a), of capillary diffusion of water a_m^{ψ} (m^2/sec) (b), and of capillary thermal diffusion of water a_t^{ψ} ($\text{m}^2/\text{sec} \cdot \text{deg}$) (c): 1) porous ceramic; quartz sand of fraction. 2) 0.063-0.16 mm; 3) 0.2-0.25 mm; 4) 0.75- 0.8 mm.

As is seen from Fig. 2a, the coefficients of capillary conductivity of water increase monotonically for all the specimens with an increase in their moisture content. This dependence is explained by a decrease in the hydraulic resistance to the flow of water through the capillaries since an increase in moisture content of the solids under consideration means the filling of pores of increasing radii with water. This dependence is displayed especially sharply with a stepwise change in pore radii from one specimen to another at a fixed moisture content. The greater the pore radii in the solid, the more sharply the coefficient k_{ψ} increases with an increase in moisture content.

Thus, the coefficient of capillary conductivity of porous solids depends strongly on the porosity of the solid and its moisture content.

The dependence of the coefficient of capillary diffusion of moisture on the moisture content for porous ceramic and quartz sand of different particle fractions is shown in Fig. 2b (curve 1: ceramic; 2: quartz sand of fraction 0.063-0.16 mm; 3: 0.2-0.25 mm; 4: 0.75-0.8 mm).

The dependences $a_m^{\psi}(u)$ presented in Fig. 2b have a complicated nature reflecting the specifics of the porous structure of the solid and the state of the absorbed moisture in the pores.

The coefficients of capillary diffusion of quartz sands of different particle sizes increase with an increase in moisture content. For the ceramic and for the sand of large fractions (0.2-0.25 and 0.75-0.8 mm) $a_m^{\psi}(u)$ passes through a maximum at a moisture content of 3-4.5% (curves 1, 3, and 4 of Fig. 2b),

while minima are observed on these curves when a moisture content of 5.5-7% is reached. Further saturation of the solid with water leads to a sharp increase in the coefficient of capillary diffusion.

The indicated ranges of moisture content for quartz sand of large particles are critical from the point of view of the forms of association and the states of the moisture in the capillaries of the solid. The meniscus (junction) state of moisture in the pores of quartz sand with particle sizes of 0.5-0.75 mm corresponds to a moisture content of 2.5% [8], while for particles of 0.5-1.0 mm it corresponds to 3.67% [9]. The film-meniscus state of moisture in quartz sand (0.5-0.75 mm) starts at a moisture content of 6.4% [8].

Thus, the extremal nature of the function $a_m^\psi(u)$ calculated from Eq. (2) for the macroporous quartz sand-water system is observed only with low moisture contents when the water forms separate menisci in the sand around the particle junctions (maximum) and when it joins the menisci with liquid films over the surface of the particles (minimum). A further increase in the moisture content converts the moisture to the capillary state (filling of the space between the particles), from which the mobility of the water and the rate of capillary diffusion increase sharply. The sharpest increase in $a_m^\psi(u)$ is observed in all the solids when the water fills the pores of most probable radius (in the ceramic $r_p = 31 \mu$ and the corresponding $u = 14.5\%$; in quartz sand of 0.20-0.25 mm $r_p = 39 \mu$ and $u = 10\%$). We note that on the curve of the dependence of the coefficient a_m^ψ on the pore radius (curve 3 of Fig. 1 for the ceramic) no sharp increase in the coefficient is observed near $r = r_p$.

The results obtained for the coefficient of capillary diffusion of moisture for quartz sand and ceramic agree well qualitatively in nature of the $a_m^\psi(u)$ curve with the theoretical calculations and physical interpretation of the coefficient of moisture diffusion carried out by N. V. Churaev for the quartz-water model system [3]. Clearly, quartz sand with a narrow fraction of particle sizes well reflects both models of a porous solid mentioned at the start of the article.

On curve 2 (Fig. 2b), obtained for fine-grain quartz sand (0.063-0.16 mm), no minimum is observed in the dependence $a_m^\psi(u)$. The absence of a minimum is probably explained by the comparatively rapid transition of the water through the film-meniscus state to the capillary state owing to the small pore sizes.

In addition, for this sand the coefficient a_m^ψ is practically independent of the moisture content in the range of moisture content from 4 to 14%. This is explained by the fact that with the existing granulometric composition of the sand particles the pore radii vary insignificantly in the given interval and as a consequence the coefficient a_m^ψ remains constant.

Thus, in determining the coefficients of internal mass transfer and studying the mechanism of transfer of a liquid in a porous solid one must know both the states and forms of the association of the moisture with the solid and the differential size distribution of pores in the solid.

In calculating from Eq. (3) the coefficient of capillary thermal diffusion of the solids studied it was assumed that the derivative $d\sigma/dT$ is constant and equal to $-1.68 \cdot 10^{-4}$ N/m · deg. For water this assumption is valid in the temperature range from 20 to 100°C [8].

Curves 1-4 (Fig. 2c) represent the dependence of the coefficient of capillary thermal diffusion of water on the moisture content for porous ceramic and for quartz sands of particle fractions 0.063-0.16, 0.2-0.25, and 0.65-0.8 mm, respectively. For small moisture contents the coefficient a_t^ψ for the solids examined is close to zero, and then it increases monotonically with an increase in moisture content. A tendency toward a decrease in the coefficient of capillary thermal diffusion is noted in the region of high saturations of the sand with water.

The porometric method considered for the determination of the coefficients of mass transfer for porous solids contains in its basis the assumption that material is transported only in the liquid form, and evaporation of the liquid within the body is ignored.

The coefficient of capillary diffusion of water for quartz sand calculated from Eq. (2) is much larger than the coefficient of diffusion of moisture determined for quartz sand in the process of drying by the kinetic method [10] and by other methods examined in the monograph [1]. The reason for the disagreement of these results probably consists in the fact that Eq. (2) provides for the molar filtration flow of liquid moisture through the capillaries of the solid whereas the diffusional transfer of moisture in the liquid and vapor form occurs in the drying processes.

The total error in determining the coefficients of capillary mass transfer for the solids studied in the present work does not exceed 16%.

NOTATION

k_{ψ} , a_m^{ψ} , a_t^{ψ}	are the coefficients of capillary conductivity, capillary diffusion, and thermal diffusion, respectively;
r	is the effective radius of pores, varying from the minimum r_0 to r_{\max} ;
r_p	is the most probable effective radius of pores;
$f(r)$	is the differential pore distribution function with respect to radius;
σ and η	are the surface tension and viscosity of liquid absorbed by solid;
ρ and ρ_0	are the density of liquid and of absolutely dry solid;
θ	is the wetting angle;
T	is the temperature of system;
$F(r)$	is the integral pore distribution function with respect to radius;
u	is the mass content of solid;
$S(r)$ and S_{\max}	are the area of pores filled with liquid and total area of all pores in a cross section of the solid;
R	is the cross-sectional radius of solid;
h	is the height of solid;
P	is the excess of air pressure above atmospheric pressure.

LITERATURE CITED

1. A. V. Lykov, Transport Phenomena in Capillary-Porous Solids [in Russian], Gos. Izd-vo Tekhn. i Teor. Lit., Moscow (1954).
2. A. V. Lykov, Heat and Mass Exchange [in Russian], Énergiya, Moscow (1972).
3. N. V. Churaev, Inzh.-Fiz. Zh., 23, No. 5 (1972).
4. D. P. Litevchuk, M. F. Kazanskii, and P. P. Lutsik, *ibid.*, 19, No. 6, 1031 (1970).
5. C. Lanczos, Applied Analysis, Prentice Hall, Englewood Cliffs, N.J. (1961).
6. A. G. Temkin, in: Study of Nonstationary Heat and Mass Exchange [in Russian], Minsk (1966), p. 184.
7. P. P. Lutsik, Legka Promislovist', No. 4 (1967).
8. M. F. Kazanskii, Inzh.-Fiz. Zh., 4, 53 (1961).
9. A. A. Rode, Principles of the Study of Ground Moisture [in Russian], Vol. 1, Gidrometeoizdat (1965).
10. P. P. Lutsik, E. A. Strashkevich, and M. F. Kazanskii, in: Thermophysics and Heat Technology [in Russian] (1972), No. 22.