EFFECT OF SPATIAL ORIENTATION ON THE KINETICS OF CAPILLARY ABSORPTION INTO POROUS MATERIALS

A. I. Rabinovich and V. N. Antsiferov

UDC 532.685

Results are presented from the comparison of predictions and experimental data for the effect of the gravitational field on the kinetics of capillary absorption into porous materials.

The analysis of studies devoted to the effect of the gravitational field on the processes of capillary impregnation of porous materials and cylindrical capillaries reveals that the experimental data obtained are disjointed and in many cases disagree with theoretical results.

It is universally adopted to base the predictions of capillary rise and absorption rates on the Poiseuille equation for viscous flow and on the expression for capillary pressure of the meniscus. For straight cylindrical capillaries oriented at an angle φ to the horizon, the equation of the liquid front motion in the gravitational field is written in the form [1, 2]:

$$\omega = \frac{dL}{d\tau} = \frac{R^2}{8\mu}\left(\frac{2\sigma\cos\Theta_d}{RL} - \rho g\sin\varphi\right). \tag{1}$$

An analogous equation describing the velocity of the liquid motion in a heteroporous wick is obtained in [3]:

$$\omega = \frac{K}{\mu\Pi}\left(\frac{\Delta P}{L} - \rho g\sin\varphi\right). \tag{2}$$

If the capillary pressure in Eq. (2) is assumed unchangeable throughout the impregnation process, which corresponds to $\Theta_d = \Theta_0 = \text{const}$ for cylindrical capillaries (the possibility of making such an assumption will be discussed below, yet we would like to note that, according to the hydrodynamic solutions carried out for complete wetting conditions, noticeable differences of Θ_d from statistical values may be anticipated, for example, for water only when $\omega \geq 10$ mm/sec [4], which exceeds the velocities of menisci motion by the action of capillary forces), ΔP may expressed in terms of the height of the liquid column L_0 held by this pressure: $\Delta P = \rho g L_0$. For Eq. (1), this corresponds to $2\sigma\cos\Theta_0/R = \rho g L_0$.

Then Eqs. (1) and (2) may be written as

$$\omega = \frac{dL}{d\tau} = a\left(\frac{L_0}{L} - \sin\varphi\right), \tag{3}$$

where $a = R^2\rho g/8\mu$ for Eq. (1) and $a = K\rho g/\mu\Pi$ for Eq. (2).

For samples in the horizontal position ($\sin\varphi = 0$), from Eq. (3) we obtain

$$\omega = \frac{dL}{d\tau} = a\frac{L_0}{L},$$

then $LdL = aL_0 d\tau$ and after integration we arrive at

$$\tau_h = \frac{L^2}{2aL_0}, \quad L(\tau) = \sqrt{2aL_0\tau} = k\sqrt{\tau}, \tag{4}$$

where $k = (2aL_0)^{1/2}$

Republican Engineering-Technical Center of Powder Metallurgy, Perm. Translated from Inzhenerno-fizicheskii Zhurnal, Vol. 64, No. 1, pp. 5-11, January, 1993. Original article submitted November 1, 1991.

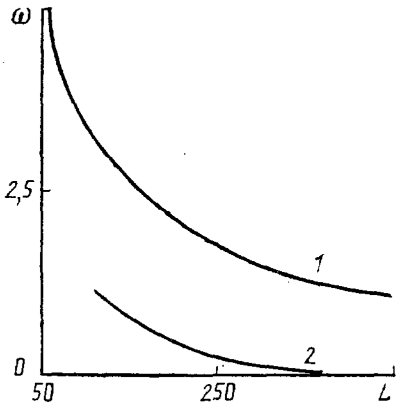

Fig. 1. Velocity of water front motion ω (mm/sec) in metal felt with a maximum impregnation height of about 500 mm at a porosity of 79%; 1) $\varphi = 0°$, 2) $\varphi = 90°$ [3, 7]. L, mm.

With samples in the vertical position and an ascending impregnation, it is also possible to derive from Eq. (3) the expression for the time of capillary rise τ_a to the height L [1, 5]:

$$\tau_a = \frac{L_0}{a}\left[-\frac{L}{L_0} - \ln\left(1 - \frac{L}{L_0}\right)\right]. \quad (5)$$

Study [6] compared experimental data for the water-impregnation of quartz capillaries with a molecularly-smooth surface and predictions from Eq. (5). It was established that, up to the height of the order of $0.65L_0$, $L \sim \sqrt{\tau}$ (the nonlinearity degree of the predicted curve $L(\tau)$ in the coordinates $[L, \sqrt{\tau}]$ will be shown below), the experimental values of L are markedly smaller than follows from Eq. (5). The authors of [6] have related the differences between the theoretical and the experimental data to the variation of a dynamic wetting angle Θ_d from Θ_0, derived in the same study. Because of high values of Θ_d at the initial stage of ascent when the absorption rates are high, the experimental curves $L(\tau)$ pass lower than the theoretical ones, predicted at $\Theta_0 =$ const without corrections for dynamic effects.

The interpretation suggested cannot be valid for two reasons:

1) the relations $\Theta_d(\omega)$ are obtained by substituting the experimental values of $\omega(L)$ into the initial Eq. (1), and, naturally, such a procedure could not have led to another result;

2) it is necessary to explain whether the experimental relations $L(\tau)$ in the coordinates $[L, \sqrt{\tau}]$ were accidentally linear and how to treat the data of [2], which has shown that, in a glycerine absorption into vertically positioned glass capillaries, $L(\tau)$ is also proportional to $\sqrt{\tau}$ up to the height $0.8L_0$. Here, in conformity with [1], dynamic effects on high-viscous fluids (oils, glycerine), readily wetting the capillaries, are insignificant.

Studies [3, 7] investigated the influence of spatial orientation of wicks made of cuprum metal felt on the rate of water absorption into a dry structure. Having demonstrated theoretically that the relationship between the velocity of an impregnating water front and the length of an impregnated part under the gravitational field conditions corresponds to Eq. (2), the authors have not, unfortunately, compared predictions with experimental data (Fig. 1) but merely ascribed the great difference between the absorption rates to the effect of a hydrostatic uplift pressure.

However, there may be an alternative interpretation stemming from the structure of the experimental rig employed in this study, where, with a horizontal position of a porous sample of thickness 2 mm, the fluid was supplied from a buret to the sample end continually and, most important, excessively. This was bound to lead to the formation, on a bottom surface of the wick, of an excess fluid layer of thickness 0.5-1.0 mm held by capillary forces. As a consequence, the fluid arriving from the buret moved over the sample not only due to the capillary absorption into the porous structure but also due to the excess layer. Apparently, this is what caused an appreciable rise in the impregnation rate.

In elucidating the regularities of the impregnation of porous netlike materials with alcohol, study [5] considered a porous body model consisting of a pile of cylindrical capillaries of various diameters, connected by horizontal channels. Good

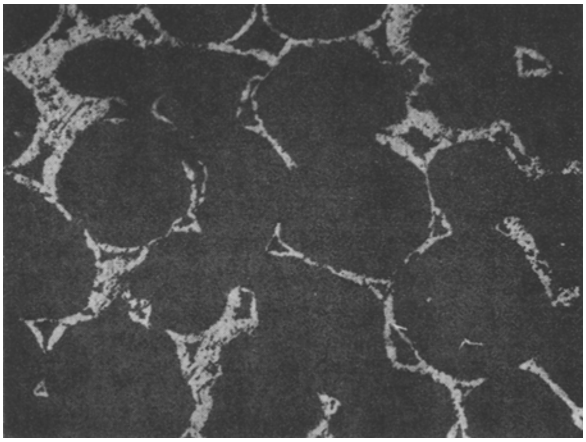

Fig. 2. HPCM microstructure. ×50.

agreement between the experimental and theoretical results was obtained. However, because of many assumptions and the inconsistency between the measured and predicted values, for example, for the maximum impregnation height, the validity of the proposed model and the prediction procedure per se is questionable.

In the late 1970s a new class of porous materials appeared, namely, high-porous permeable cellular materials (HPCM) [8]. They are distinguished from the familiar ones in that, apart from the main cellular porosity constituting 86-92%, their structure includes a channel porosity, formed at the site of the foam polyurethane skeleton removed by thermal destruction [9]. The channels make up a unified three-dimensional network penetrating the entire HPCM structure. Besides cellular voids and channels, the HPCM structure also has micropores resulting both from dispersity of the initial materials and from sintering conditions (Fig. 2). The voidage, forming the channels and micropores, is as large as 3-8%. Mechanical, gasdynamic, and thermophysical characteristics of these materials as functions of the mesh size and density have been studied in [8-11]. However, capillary-transport properties of the HPCM have not been investigated. Therefore, we set out to find general rules of the impregnation for elementary cylindrical capillaries and porous bodies, to study the wetting kinetics for HPCM samples, and to compare it both with the predictions and with the impregnation kinetics for known porous metals and for cylindrical capillaries.

The investigation was concerned with HPCM samples based on a 50% Cu + 50% Ni alloy of size 580 × 25 × 3 mm, porosity 89%, and mesh diameter 0.9 ± 0.1 mm, which were cut from a deformed plate of initial thickness 12 mm, as well as with filter paper samples measuring 1000 × 30 × 0.12 mm.

Distilled water and 96% ethyl alcohol were used as the working fluid. Immediately prior to impregnation the samples were acidulated to improve water-wettability of the HPCM.

The distance travelled by the impregnating fluid front was determined in the filter paper samples visually and in the HPCM samples using the setup and the technique described in [3, 7]. However, with a horizontal position, the sample was L-shaped rather than plane, which eliminated the fluid filtration over cellular voids on the horizontal working section. The height of the vertical part was equal to 60 mm in this case. In the filter paper samples, where the kinetics of the descending impregnation was investigated, the length of the initial part of the absorption zone was equal to 27-30 mm. In all cases, the distance travelled by the front was reckoned from the level of the fluid that filled the vessel.

We consider the linearity degree of relation (5) in the coordinates $[L, \sqrt{\tau}]$. For this end, having expanded $\ln(1 - L/L_0)$ in a power series and having taken its first three terms, we transform Eq. (5) to the form

$$\tau_a = \frac{L_0}{a}\left[-\frac{L}{L_0} + \frac{L}{L_0} + \frac{1}{2}\left(\frac{L}{L_0}\right)^2 + \frac{1}{3}\left(\frac{L}{L_0}\right)^3 + \dots\right] = \\ = \frac{L_0}{2a}\left(\frac{L}{L_0}\right)^2 + \frac{L_0}{3a}\left(\frac{L}{L_0}\right)^3 = \frac{L^2}{2aL_0} + \frac{L^3}{3aL_0^2}. \qquad (6)$$

It follows from Eq. (6) that $L(\tau) \sim \sqrt{\tau}$ as long as $L^2/(2aL_0) >> L^3/(3aL^2_0)$ or $1.5L_0 >> L$, that is, when $L \ll 0.15L_0$.

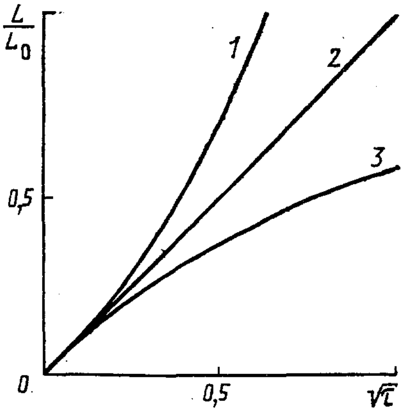

Fig. 3. Predicted dependences of the length of the wetted zone on the impregnation time: 1) with a descending impregnation; 2) with a horizontal impregnation; 3) with an ascending impregnation.

The relationship between the impregnation time and the length of the wetted zone for the descending impregnation is written in the form

$$\tau_d = \frac{L_0}{a}\left[\frac{L}{L_0} - \ln\left(1 + \frac{L}{L_0}\right)\right]. \tag{7}$$

Correspondingly, having expanded Eq. (7) in a power series, we derive

$$\tau_d = \frac{L^2}{2aL_0} - \frac{L^3}{3aL_0^2}, \tag{8}$$

i.e., in this case $L(\tau) \sim \sqrt{\tau}$ also, as long as $L << 0.15L_0$.

At large values of L the pattern becomes more complicated. Figure 3 shows predictions for relations (4), (5), and (7) at k equal numerically to 1. Clearly, the curves $L(\tau_a)$ and $L(\tau_d)$ are proportional to $\sqrt{\tau}$ only on the initial section of the absorption, and with increasing L the relation $L(\tau_a)$ departs from the straight line $L(\tau_h) = \sqrt{\tau}$ faster than $L(\tau_d)$.

Figure 4 gives time dependences of the distances travelled by water and alcohol fronts in the HPCM and filter paper samples with different spatial orientations.

It is seen that the impregnation kinetics for the filter paper is proportional to $\sqrt{\tau}$ within the experimental error, independently of the orientation. In this case, a kink on curves 5 and 7 for the ascending impregnation both with water and alcohol is associated with an abrupt variation in the quantity of pores participating in the fluid transport. Initially, the absorption proceeds by the pores of an interfiber space of the paper, and after heights of 400 mm for water and 170 mm for alcohol have been attained, the fluids start rising through the pores in cellulose fibers. With the descending impregnation, the kinetics is governed solely by the interfiber pores, and a little kink in the beginning of the process is linked with the presence, in the samples considered, of starting sites, where the impregnating fluids are directed oppositely to the gravity force.

In the horizontally positioned HPCM sample, the length of the impregnated zone is proportional to $\sqrt{\tau}$, except the initial section, wherein the rise occurs through the cellular porosity (Fig. 4, curve 1). With the ascending impregnation (Fig. 4, curve 2), the kinetics remains for the most part unchanged; i.e., up to a height of 80 mm, just as in the horizontal case a fast water absorption through the cellular pores proceeds. Further on, up to a height of 500 mm, an increase in the length of the wetted part of the sample is proportional to $\sqrt{\tau}$, whereas at the final stage the ascent slows down because of an increasing influence of the return pressure.

It ensues from Fig. 4 that with the same length of the impregnated zone,

$$\frac{\omega(L_a)}{\omega(L_h)} = \left(\frac{k_a}{k_h}\right)^2 = \mathrm{const},$$

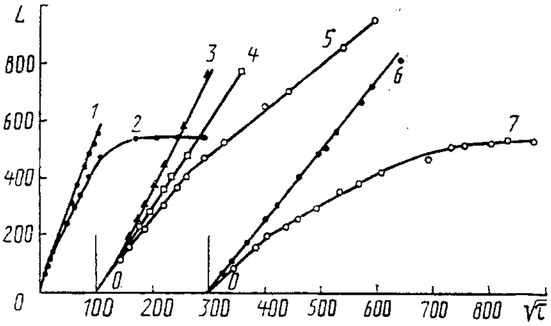

Fig. 4. The distance L (mm) travelled by the liquid front in the HPCM (1, 2) and in the filter paper (3-7) as a function of the time $\sqrt{\tau}$ (sec$^{0.5}$): 1, 4) $\varphi = 0°$; 2, 5, 7) 90°; 3, 6) $-90°$; wetting liquids: 1-5) water; 6, 7) alcohol.

where k_h and k_a are inclination angles of the rectilinear sections. This ratio for the HPCM is equal to 0.71 up to a height $0.9L_0$ and, for the filter paper, to 0.66 up to a height of about 400 mm.

The results obtained differ radically from those presented in [3, 7] (see Fig. 1), where the ratio $\omega(L_a)/\omega(L_h)$ with the impregnation up to a height $0.5L_0$ varied smoothly from 0.4 to 0.01.

It is impossible to attribute the proportionality of the impregnation kinetics $\sqrt{\tau}$ for different spatial orientations of the samples to dynamic variations in the wetting angle, as is done in [1, 6] for the ascending impregnation case. Should such assumptions be valid, then the lengths of the impregnated part of the samples in a horizontal and especially in the descending position would increase quicker than by the $\sqrt{\tau}$ law, which is not observed experimentally.

The authors propose a hypothesis for discussion capable, to their mind, of explaining the majority of familiar experimental facts and of fitting them to predictions.*

The linear dependence of the kinetics in the coordinates $[L, \sqrt{\tau}]$ for the ascending and descending impregnation suggests that a force, counterbalancing the increasing hydrostatic pressure, arises in these cases. Its origination may be connected with the emergence of an additional, relative to the horizontal position, deflection of the meniscus under the effect of the hydrostatic pressure. Here, with increasing length of the impregnated zone, the radius of the meniscus curvature will be reduced during the ascending impregnation and be enlarged during the descending impregnation. Such a variation in the meniscus shape will compensate for the increasing hydrostatic pressure, and, therefore, the impregnation kinetics in the coordinates $[L, \sqrt{\tau}]$ will be linear, as is the case with the horizontal position.

However, such a compensation to infinity is impossible. In the ascending impregnation case, on the fluid column attaining a certain height, the proportional relationship between the additional deflection and the increasing hydrostatic pressure is upset, the wetting angle approaches Θ_0, and the variation law of $L(\tau)$ begins to correspond to Eq. (5). The existence of such a point is established in practice for all capillary bodies. Its position in each individual case is specified by the impregnating fluid characteristics, by the wetting processes, and by the structure of a porous space of the capillary bodies. In cylindrical capillaries, these points for the impregnation with water are located at a height $L = 0.7\text{-}0.8L_0$ [6], with glycerine, at a height $0.8\text{-}0.9L_0$ [2], for water in the HPCM, at a height $0.8\text{-}0.9L_0$, for alcohol in cellular materials, at a height $0.5L_0$ [12], and for alcohol in titanium-based powdered materials at a height $0.5\text{-}0.6L_0$ [13].

It follows from the data presented that the kinetics of the HPCM impregnation is close to the kinetics of the fluid motion in cylindrical capillaries. Porous cellular and powdered materials have a smaller range of linearity of the kinetics $L(\tau) = k\sqrt{\tau}a$ in view of drying processes developing therein [3].

With the descending impregnation, a disturbance of linearity of the kinetics $L(\tau) = k\sqrt{\tau}$ must, apparently, occur at appreciably larger sizes of the fluid column and, therefore, it was not registered because of insufficient sizes of the experimental setup.

---

*The advanced hypothesis might be validated by experimental measurements of the meniscus curvature radius or of the wetting angle during the impregnation of cylindrical capillaries. However, the methods for such measurements have not yet been worked out.

CONCLUSIONS

1. With an ascending impregnation, in the HPCM samples $L \sim \sqrt{\tau}$ up to $0.9L_0$, which indicates similarity of the impregnation processes of these materials and of cylindrical capillaries.

2. At the initial stage of wetting of capillary-porous bodies, independently of their spatial arrangement, the impregnation kinetics follows the law $L(\tau) = k(\tau)$. Here, on the samples having been brought from one position to another, a variation in the impregnation rate with the same length of the wetted zone does not exceed 40%.

3. It may be assumed that the retention of the linear dependence of L on $\sqrt{\tau}$ at a vertical position of the samples is due to the additional deflection of the meniscus by the action of the hydrostatic pressure, rather than due to dynamic variations in the wetting angle.

NOTATION

ω, velocity of the impregnating fluid, m/sec; L, the length of the impregnated part, m; τ, impregnation time, sec; R, capillary radius, m; μ, fluid viscosity, N·sec/m^2; σ, surface tension, N/m; Θ_d, dynamic wetting angle, deg; ρ, density, kg/m^3; g, acceleration by gravity, m/sec^2; φ, angle of inclination of the sample axis to the horizon, deg; K, penetration factor, m^2; Π, porosity; ΔP, available capillary pressure, Pa; L_0, maximum height of the impregnation, m; τ_a, τ_d, τ_h, wetting time for the ascending, descending, and horizontal impregnation, sec.

REFERENCES

1. N. V. Churaev, Physicochemistry of Mass Transfer Processes in Porous Bodies [in Russian], Moscow (1990).
2. A. P. Porkhaev, Kolloidn. Zh., **11**, No. 5, 346-353 (1949).
3. M. G. Semena, A. N. Gershuni, and V. K. Zaripov, Heat Pipes with Metal-Fiber Capillary Structures [in Russian], Kiev (1984).
4. V. M. Starov, N. V. Churaev, and A. G. Khvorostyanov, Kolloidn. Zh., **39**, No. 1, 201-205 (1977).
5. S. V. Belov and Yu. M. Novikov, Inzh.-fiz. Zh., **43**, No. 1, 91-95 (1982).
6. V. V. Berezkin and N. V. Churaev, Kolloidn. Zh., **44**, No. 3, 417-423 (1982).
7. M. G. Semena, A. G. Kostornov, A. N. Gershuni, et al., Inzh.-fiz. Zh., **27**,, No. 6, 1009-1014 (1974).
8. V. N. Antsiferov, V. D. Khramtsov, D. M. Pitirimov, et al., Poroshk. Metall., No. 12, 20-24 (1980).
9. S. V. Belov (ed.). Porous Permeable Materials: Reference Book [in Russian], Moscow (1987).
10. Z. Kamidze and K. Tani, Kamikaru and Ziniyaringu (Japan), **26**, No. 10, 746-754 (1981).
11. V. M. Kiseev, A. I. Rabinovich, N. P. Pogorelov, et al., Inzh.-fiz. Zh., **58**, No. 1, 68-72 (1990).
12. S. V. Belov, A. A. Ivanchuk, and D. M. Karinos, Poroshk. Metall., No. 5, 63-65 (1981).
13. A. G. Kostornav, N. É. Skrynskaya, and S. M. Agayan, Poroshk. Metall., No. 5, 32-47 (1990).