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THE INITIAL STAGE IN CAPILLARY IMPREGNATION

A. V. Kuz'min, P. A. Novikov, and V. I. Novikova UDC 532.68

The impregnation kinetics are considered during the initial stage of capillary rise. A formula is derived describing the nonstationary impregnation with allowance for inertia, friction, and change in wetting angle.

Porous materials are widely used in space technology, particularly in devices that transport energy and mass (thermal tubes, porous evaporative heat exchangers, etc.), which gives considerable interest to liquid flow in capillaries and porous bodies, while the results are of practical significance.

The static theory of capillary impregnation is reflected in a large number of theoretical and experimental papers, but there has been inadequate research on impregnation kinetics in the initial stages. We therefore analyze the initial stage in the movement of a liquid through a capillary, which plays an important part in starting up and shutting down heat-engineering devices.

The theory of capillary impregnation is based on equation describing the nonstationary laminar flow in a cylindrical capillary [1]:

$$\frac{d^2l}{dt^2}+\frac{1}{l}\left(\frac{dl}{dt}\right)^2+\frac{8\eta}{r^2\rho}\frac{dl}{dt}-\frac{2\sigma\cos\theta}{r\rho l}+g\sin\alpha=0. \tag{1}$$

In solving (1), one often [1-5] neglects the first two terms, which incorporate the inertial force, which in practical cases are less by an order of magnitude than the other terms, i.e., one assumes that

$$\frac{1}{l}\left(\frac{dl}{dt}\right)^2\approx 0,\quad \frac{d^2l}{dt^2}\approx 0 \tag{2}$$

and thus reduces the solution of (1) to the following relation for a horizontal capillary:

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$$l = \left(\frac{\sigma r \cos \theta}{2\eta} \right)^{\frac{1}{2}} t^{\frac{1}{2}}. \quad (3)$$

On the whole, (3) agrees well with experiment for sufficiently large times [1, 6, 7] and is frequently used to calculate $\ell = f(t)$ for a liquid flowing in capillaries, or in a somewhat modified form for porous bodies [6, 7]. However, in the initial stage, where the meniscus is high, there are substantial differences between measurements and calculations from (3) [8-11]. One reason is that the inertial forces have been neglected in solving (1). In [11], a numerical solution to (1) was compared with the solution neglecting the inertial forces, which showed that neglecting the first two terms distorts the physical picture in the initial stages.

We compare the capillary impregnation curves calculated in [12] from the formula of [13]

$$l = \left\{ \frac{\sigma r \cos \Theta}{2\eta} t + \frac{\sigma r^3 \rho \cos \Theta}{16\eta} \left[\exp \left(-\frac{8\eta}{r^2 \rho} t \right) - 1 \right] \right\}^{\frac{1}{2}}, \quad (4)$$

obtained by solving (1) for the case of a horizontal capillary with the initial condition $t = 0$ and $\ell = 0$, where the comparison with experiment shows that (4) also gives over-estimates. The discrepancy occurs because the wetting angle Θ is assumed constant in solving (1) and equal to the equilibrium value Θ_e. There is virtually no doubt that (1) itself is correct, so the assumption that the wetting angle is constant is incorrect and has to be abandoned.

In [2-4] and elsewhere, it has been found that the dynamic wetting angle is dependent on the speed of the meniscus, although not much is known about the details. In [4], it was suggested that in general the relationship can be determined only by experiment, while a mathematical approximation to the experimental data was proposed for speeds $d\ell/dt \leq 3 \cdot 10^{-4}$ m/sec. In a subsequent paper [14], the molecular kinetic theory of interaction between liquids and solids was used in deriving a physical basis for the $\Theta = f(d\ell/dt)$ dependence near the contact line, but no explicit expression for this function was obtained.

Dynamic wetting angles may be dependent on the speed [5] if the external forces substantially exeed the capillary pressure, which is the driving force. In the initial stage, where the wetting angle varies in time, it decreases from $\Theta = 90°$ (instant of contact with the capillary) and tends in the limit to Θ_e, while the capillary pressure p_c increases, which is responsible for an increase in the impregnation rate. In that case, one almost always has obedience to the condition that the external gravitational forces are negligible by comparison with the capillary pressure, and therefore the dependence of Θ on $d\ell/dt$ may be considered as minor, while $p_c = f(t)$ is major [5], being determined by the rate of decrease in the wetting angle $d \cos \Theta / dt$, i.e., by the wetting kinetics [15-17].

For $\Theta \leq 90°$, one can describe the wetting kinetics satisfactorily by means of an equation of relaxation [5, 18, 19]:

$$\cos \Theta = \cos \Theta_e \left[1 - \exp \left(-\frac{t}{\tau_r} \right) \right], \quad (5)$$

which is widely used for capillary impregnation. In [15-17, 20, 21], we find a physical basis for this relationship. The relaxation τ_r appearing is the time for the attainment of 0.75 of the equilibrium wetting angle, and in general it is dependent on the properties of the liquid and of the solid surface, on the wetting perimeter, and so on [5, 16, 19]. In some cases, τ_r is taken as 0.5-1 sec.

In [5], the dependence of (5) was incorporated in solving (1) with condition (2) also for $t \ll \tau_r$ (initial stage), which gave the expression

$$l = \left(\frac{\sigma r \cos \Theta_e}{2\eta} \right)^{\frac{1}{2}} \left(\frac{1}{2\tau_r} \right)^{\frac{1}{2}} t. \quad (6)$$

Formula (6), which has been derived neglecting the inertial terms, also deviates from experiment.

To obtain a fuller picture of the initial stage, it is necessary to incorporate the inertial and frictional forces as well as the time dependence of the wetting angle, i.e., it is necessary to solve (1) with (5).

We introduce the symbol $z = \ell^2$ for a horizontal capillary and convert (1) to

$$\frac{d^2z}{dt^2} + \frac{8\eta}{r^2\rho}\frac{dz}{dt} = \frac{4\sigma\cos\Theta_e}{r\rho}\left[1 - \exp\left(-\frac{t}{\tau_r}\right)\right]. \tag{7}$$

We introduce the symbols

$$\frac{dz}{dt} = x, \quad \frac{8\eta}{r^2\rho} = \frac{1}{\tau_0}, \quad \frac{4\sigma\cos\Theta_r}{r\rho} = a, \tag{8}$$

to get

$$\frac{dx}{dt} + \frac{1}{\tau_0}x = a\left[1 - \exp\left(-\frac{t}{\tau_r}\right)\right]. \tag{9}$$

We seek the solution to (9) as

$$x = y\exp\left(-\frac{t}{\tau_0}\right), \tag{10}$$

where y = y(t) is some unknown function of time. We substitute (10) into (9) to get

$$\frac{dy}{dt} = a\left[1 - \exp\left(-\frac{t}{\tau_r}\right)\right]\exp\frac{t}{\tau_0}$$

and integrate with the initial condition t = 0, y = 0 to get

$$y = a\tau_0\left\{\left[1 - \frac{\tau_r}{\tau_r - \tau_0}\exp\left(-\frac{t}{\tau_r}\right)\right]\exp\frac{t}{\tau_0} + \frac{\tau_0}{\tau_r - \tau_0}\right\}.$$

Then

$$x = a\tau_0\left[1 - \frac{\tau_r}{\tau_r - \tau_0}\exp\left(-\frac{t}{\tau_r}\right) + \frac{\tau_0}{\tau_r - \tau_0}\exp\left(-\frac{t}{\tau_0}\right)\right]. \tag{11}$$

The solution to (11) with (8) is

$$z = a\tau_0\left[t + \frac{\tau_r^2}{\tau_r - \tau_0}\exp\left(-\frac{t}{\tau_r}\right) - \frac{\tau_0^2}{\tau_r - \tau_0}\exp\left(-\frac{t}{\tau_0}\right)\right] - a\tau_0(\tau_r + \tau_0). \tag{12}$$

After certain transformations of (12), the law for the meniscus motion along the capillary is

$$l = \left\{a\tau_0\left\{t - \tau_r - \tau_0 + \frac{1}{\tau_r - \tau_0}\left[\tau_r^2\exp\left(-\frac{t}{\tau_r}\right) - \tau_0^2\exp\left(-\frac{t}{\tau_0}\right)\right]\right\}\right\}^{\frac{1}{2}}. \tag{13}$$

Figure 1 shows capillary-impregnation curves calculated from (3), (4), (6), and (13) for capillaries with r = 0.35 and 0.75 mm and those derived from experiment by cinephotography of the meniscus for water in glass capillaries for the same radii in the strictly horizontal position [22]. The relaxation time for water entering a glass capillary was taken as one second [5].

The figure $\ell = f(t)$ as calculated from (13) gives a good description of the behavior of water in capillaries. For capillaries with r = 0.75 mm, a curve constructed from this formula for times of 0-1 sec essentially coincides with the experimental curve. There is also satisfactory agreement with experiment for 1-15 sec. A calculation from all the formulas for the wide range 0-15 sec shows that (6) (curve 3) agrees satisfactorily with

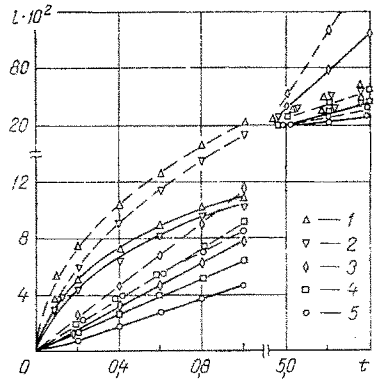

Fig. 1

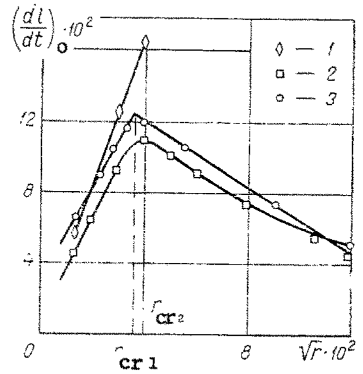

Fig. 2

Fig. 1. Capillary impregnation kinetics for water; calculation from the following formulas: 1) (3); 2) (4); 3) (6); 4) (13); 5) experimental data of [22]. The solid lines are for $r = 0.35 \times 10^{-3}$ and the dashed ones for $r = 0.75 \times 10^{-3}$ m; ℓ in m and t in sec.

Fig. 2. Dependence of the water entry rate in the initial stage on capillary radius calculated from the following formulas: 1) (6); 2) (13); 3) experimental data of [5]; $(d\ell/dt)_i$ in m/sec, $r^{\frac{1}{2}}$ in $m^{\frac{1}{2}}$.

experiment for t < 1 sec, while (3) and (4) (curves 1 and 2) do so for t > 5 sec. On the other hand, formula (13) (curve 4), which we have derived, not only describes $\ell = f(t)$ well in the initial period but is also closer to the experimental values than are (3), (4) and (6) throughout the time interval.

Figure 2 shows the impregnation rate for water in the initial stage as a function of capillary radius derived from (13); there is a certain critical radius $r_{cr2} = 1.6 \cdot 10^{-3}$ m at which the entry rate is maximal, being 11×10^{-2} m/sec, which is very close to the measured value of [5]: $r_{cr1} = 1.2 \cdot 10^{-3}$ m and $(d\ell/dt)_e = 12.5 \cdot 10^{-2}$ m/sec. Formulas (3), (4), and (6) do not imply this critical radius. For example, (6) gives a linear relation between the impregnation rate in the initial stage and $r^{\frac{1}{2}}$ (Fig. 2).

Therefore, our model is the most accuracte of the models for describing impregnation kinetics in the initial stage, where the wetting angle is variable and one cannot neglect the inertial forces. The model enables one to derive the critical radius previously observed by experiment.

NOTATION

r, capillary radius; r_{cr}, critical capillary radius; ℓ, column length in capillary at time t; η, σ, and ρ, kinematic viscosity, surface tension, and density, respectively; Θ and Θ_e, contact angle and equilibrium contact angle; g, acceleration due to gravity; α, slope towards horizon; τ_e, wetting relaxation time; $(d\ell/dt)_i$, initial capillary impregnation rate.

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