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Corresponding Member of the Academy of Sciences of the USSR B. V. DERYAGIN, M. A. AL' TSHULER

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Abstract

Full Text

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ON THE INFLUENCE OF THE PHYSICO-CHEMICAL PROPERTIES OF ENTRAPPED GASES ON THE IMPREGNATION OF POROUS BODIES

In paper ([1]), capillary impregnation of blind pores was considered. The impregnation of blind capillaries, as well as of bodies with through pores, if these bodies are completely immersed in a liquid, is determined by the pressure of the gas entrapped in the pores. If the gas does not dissolve in the liquid, impregnation ceases when the pressure of the entrapped gas becomes equal to the sum of the atmospheric and capillary pressures.

Below an attempt is made to describe the process of impregnation of blind capillaries with allowance for dissolution and diffusion of the entrapped gases in the liquids impregnating the capillary. Of course, the concepts developed here are also applicable to the impregnation of porous bodies with through pores that are completely immersed in a liquid.

Of special interest here is an assessment of the influence on the process of gases that are very slightly soluble (for example, air in water) and highly soluble (NH_3 or HCl in water, hydrocarbon gases in oil), since, on the one hand, removal of air from pores when construction materials are wetted adversely affects their durability ([4]), and, on the other hand, in processes for extracting valuable substances contained in porous materials, acceleration of impregnation due to increased gas solubility may prove useful ([1,3]). It is also known that, in experiments to determine porosity, the specimen is first saturated with a readily soluble gas, which accelerates impregnation of the specimen.

Let us further note that the impregnation of porous bodies with open pores, even if they are not completely immersed in a liquid, is usually retarded by the entrapment of individual gas bubbles. Of course, the solubility of the gas also plays a definite role in this case.

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Capillary impregnation of blind pores without allowance for dissolution of entrapped gases is described by the equations ([1])

$$t = -\frac{4\alpha\eta l_0^2}{r\sigma\cos\theta}\left\{\frac{1}{2}\varphi^2 + (1-\alpha)\left[-\alpha_1'\ln\frac{\alpha-\varphi}{\alpha} - \varphi\right]\right\} \tag{1}$$

and, at the initial stage, approximately by

$$l^2 \simeq \frac{r\sigma\cos\theta}{2\eta}t; \tag{2}$$

where t is the duration of impregnation, l is the depth of impregnation, l_0 is the full length of the capillary, $\varphi = l/l_0$ is the dimensionless depth of impregnation; σ is the surface tension; θ is the wetting angle; η is the viscosity of the liquid; $\alpha = 2\sigma\cos\theta/(rP_a + 2\sigma\cos\theta)$; P_a is atmospheric pressure; r is the radius of the capillary.

Expression (2) describes most accurately the capillary impregnation of a horizontal through capillary ([2]).

The rate of capillary impregnation of blind capillaries is

$$\frac{dl}{dt} = \frac{r^2}{8\eta l}\left(\frac{2\sigma}{r}\cos\theta + P_a - P_a\frac{l_0}{l_0 - l_i}\right). \tag{3}$$

The pressure of an insoluble gas entrapped in the liquid is equal to $P_a\dfrac{l_0}{l_0 - l}$. Impregnation in the presence of insoluble entrapped gases ceases under the condition

$$P_k + P_a - P_a'\frac{l_0}{l_0 - l_\infty} = 0, \tag{4}$$

where l_∞ is the limiting depth of capillary impregnation, $P_k = \dfrac{2\sigma}{r}\cos\theta$ is the capillary pressure. If the entrapped gas is capable of dissolving, then···

its pressure at any given moment will be below this value, and the rate of impregnation will be greater than that calculated by formula (3), and will never be equal to zero, right up to the end of impregnation.

The pressure of the trapped gas P_t, in turn, depends on the amount of gas that has diffused and on the depth of impregnation.

The process of motion of the liquid in a capillary and of dissolution and diffusion of the gas trapped in it is described by the equations

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$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x_1^2} + \frac{dl}{dt}\frac{\partial c}{\partial x_1}; \tag{5}$$

$$\frac{dl}{dt} = \frac{r^2}{8\eta l}\left(\frac{2\sigma}{r}\cos\theta + P_a - P_t\right), \tag{6}$$

where c is the concentration of the trapped gas in the liquid impregnating the capillary, and D is the diffusion coefficient of this gas in the liquid.

Since, as we noted earlier, the analysis of impregnation in the presence of very poorly soluble and highly soluble gases is of greatest interest, we shall confine ourselves to an approximate consideration of these cases.

Let us write the equation of convective diffusion in the "meniscus" system, i.e., in a system whose origin of coordinates is fixed relative to the meniscus; then the convective term in expression (5) vanishes, since the velocity of motion of the liquid in it is equal to zero,

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}. \tag{7}$$

Considering the case of impregnation in the presence of a very poorly soluble gas, we shall assume that during the time in which the meniscus moves to the depth l_∞, where the pressure of the trapped gas is close to the sum of the capillary and atmospheric pressures, such a small amount of gas has dissolved that it may be neglected. The gas dissolved in the liquid will be considered to obey Henry' s law $c = kP$, where k is Henry' s constant.

The boundary condition at the meniscus will have the form

$$x = 0, \qquad c = kP_t, \tag{8}$$

and at the mouth of the capillary

$$x = \infty, \qquad c = kP_a. \tag{9}$$

In condition (8), instead of $x = f(t)$ we have taken $x = \infty$; however, while simplifying the solution, this does not affect its validity. Since the rates of displacement of the meniscus in the stage limited by the rate of dissolution of a poorly soluble gas are very small, the pressure losses caused by viscous resistance to the motion of the liquid are also very small. Therefore it may be assumed that, in the case under consideration, the pressure of the trapped poorly soluble gas is maintained constant and equal to $P_k + P_a$ up to the complete filling of the capillary with liquid:

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$$P_t = P_k + P_a, \qquad \frac{dP_t}{dt} = 0. \tag{10}$$

Then, instead of condition (8), we write

$$x = 0, \qquad c = k(P_k + P_a). \tag{11}$$

We seek the solution of (7) satisfying conditions (9) and (11) in the form

$$c(x,t) = A \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) + B, \tag{12}$$

where

$$\operatorname{erf} y = \frac{2}{\sqrt{\pi}} \int_0^y e^{-t^2}\,dt$$

is the probability integral.

We find the values of the constants:

$$A = -kP_k, \qquad B = k(P_k + P_a).$$

The solution obtained is

$$c(x,t) = -kP_k \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) + k(P_k + P_a). \tag{13}$$

we use to find the concentration gradient of the dissolved gas at the meniscus:

$$\left.\frac{\partial c}{\partial x}\right|_{x=0} = -\frac{kP_\mathrm{k}}{\sqrt{\pi Dt}}. \tag{14}$$

As for replacing in (8) the condition $x = f(t)$ by $x = \infty$, its admissibility is clear from the fact that if $\operatorname{erf}(\infty) = 1$, then $\operatorname{erf}(3) = 0.9973$, i.e., practically equal to $\operatorname{erf}(\infty)$, and moreover $\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.9973$ for $t \sim 10^2$ sec at, for normal values of diffusion coefficients, distances x of the order of 10^{-3} cm. Therefore distances exceeding this value may, in the present problem, be regarded as infinitely large.

The gas trapped in the capillary occupies a volume $\pi r^2(l_0 - l)$. The mass of the trapped gas, which is under the pressure $P_\mathrm{k} + P_\mathrm{a}$, is

$$m = \frac{\pi R^2 (P_\mathrm{k} + P_\mathrm{a})(l_0 - l)}{RT}. \tag{15}$$

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The loss of trapped gas due to dissolution and diffusion is accompanied by displacement of the meniscus

$$\frac{dm}{dt} = -\frac{(P_\mathrm{k} + P_\mathrm{a})\pi r^2}{RT}\frac{dl}{dt}. \tag{16}$$

On the other hand, according to Fick' s first law,

$$\frac{dm}{dt} = DS\,\frac{\partial c}{\partial x}\bigg|_{x=0} = -\frac{\pi r^2 DkP_\mathrm{k}}{\sqrt{\pi Dt}}. \tag{17}$$

Equating (16) and (17), we obtain the expression

$$\frac{dl}{dt} = \frac{\alpha kDRT}{\sqrt{\pi Dt}}, \tag{18}$$

which, upon integration, gives an expression analogous to (2), but with another coefficient of proportionality,

$$\Delta l^2 = 4\left(\frac{\alpha kDRT}{\sqrt{\pi D}}\right)^2 t. \tag{19}$$

As is seen from (18) and (19), impregnation due to dissolution and diffusion is determined also by the capillary properties of the system and, in particular, by the solubility of the gas, since the diffusion coefficients of different gases differ comparatively little from one another (7).

Using known values of the diffusion coefficients and Henry's constant for nitrogen and ammonia in water, we find (at $T = 293^\circ$) for nitrogen

$$\frac{dl}{dt_{\mathrm{N2}}} = \frac{5 \cdot 10^{-5}\alpha}{\sqrt{t}} \tag{20}$$

and for ammonia

$$\frac{dl}{dt_{\mathrm{NH3}}} = \frac{1.08\,\alpha}{\sqrt{t}}, \tag{21}$$

from which we obtain, respectively,

$$(\Delta l_{\mathrm{N2}})^2 = 10^{-8}\alpha^2 t, \tag{22}$$

$$(\Delta l_{\mathrm{NH3}})^2 = 4.65\,\alpha^2 t. \tag{23}$$

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Below are given the results of calculations of the duration of capillary impregnation of blind capillaries 1 cm long and with different radii. Table 1 gives the time t_1 after which the capillary is impregnated to a depth equal to 0.99α (recall that the limiting depth of capillary impregnation of blind capillaries is equal to α). Also given here are the duration t_2 of complete impregnation of a through horizontal capillary, and also the duration of dissolution of the trapped gas: nitrogen t_3 and ammonia t_4.

Analysis of the calculation results given in Table 1 shows that, in the case of trapping of poorly soluble gases, the slowest sta-

···is the stage of dissolution and diffusion of the dissolved gas, and it determines the time of final filling of the capillary. Therefore the process should be calculated by formula (18).

When readily soluble gases are trapped, dissolution and diffusion proceed so rapidly that the trapped gas does not have time to be compressed, and its pressure remains practically at the initial level and, consequently, does not impede capillary impregnation. In this case the "blind-endedness" of the pores cannot

Table 1

	$r = 10^{-3}$ cm	$r = 10^{-4}$ cm	$r = 10^{-5}$ cm	
α	0.129	0.595	0.935	
$1 - \alpha$	0.871	0.405	0.065	
t_1, sec	$2.9 \cdot 10^{-2}$	3.4	33	Calculated by (1)
t_2, sec	0.276	2.76	27.6	» » (2)
t_3, sec	$4.4 \cdot 10^{9}$	$4.64 \cdot 10^{7}$	$4.83 \cdot 10^{5}$	» » (22)
t_4, sec	9.45	0.1	$1.04 \cdot 10^{-3}$	» » (23)

affect the kinetics of impregnation, and the process can be calculated by formula (2). The filling time of the capillaries increases with decreasing radius and in all cases is much less than the filling time of capillaries containing sparingly soluble gases; for example, in (3) a 600-fold increase in the rate of impregnation is described when the air in the pores of a material is replaced by ammonia.

It is interesting to note that the time for final filling of blind-ended capillaries containing a sparingly soluble gas decreases with decreasing capillary radius, whereas the duration of capillary impregnation proper increases; a dependence of this kind was observed in work (6).

The impregnation kinetics of pores with trapped nitrogen, calculated by formula (22), were compared with the experimental data of work (4), which gives the results of studying the impregnation of brick specimens over 20 days. At first there is rapid capillary impregnation, during which the main volume of pores is filled. Then the impregnation becomes slow and, beginning from 2 days, the

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experimental data satisfactorily fall on a straight line in coordinates with a proportionality coefficient corresponding to the diffusion stage of impregnation.

The mean pore radius found from formula (22), equal to 0.3 μ, corresponds to the information known about this material. Thus, according to data obtained on a low-pressure mercury porosimeter, pores with radii of 0.034–0.395 μ occupy 45.5% in plastic-molded brick, and 46% of the total pore volume in semi-dry pressed brick (5).

It also deserves attention that the duration of displacement of air from capillaries of radius 0.1 μ is on the order of several days, and from capillaries of radius 1 μ —more than a year. From the standpoint of frost resistance, this makes coarse-porous building materials preferable, since in such materials the preservation of air cushions in the pores, weakening the destructive action of ice, is more likely.

From the same standpoint, the use of organosilicon substances also becomes more understandable; treatment with them is not always accompanied by the formation of obtuse contact angles. An increase in the contact angle even within the limits of 90° reduces the capillary pressure and, consequently, also the pressure of the trapped air, which, in turn, increases the lifetime of the air cushion.

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