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QUESTION OF THE MOVEMENT OF WATER IN CONCRETE WHEN IT FREEZES

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We determine the dimensions of capillaries capable of removing the excess water from a freezing pore when there are no destructive processes taking place.

Cement concrete is a capillary–porous solid. In the overall volume of its porosity we generally distinguish two main types of pores and capillaries: cement-gel pores, whose radii vary from $2 \cdot 10^{-9}$ to $2 \cdot 10^{-8}$ m, and capillaries, which have a radius greater than 10^{-7} m [1]. The relation between these types of porosity and the distribution of pores along the radii depends on a number of technological factors and is determined mainly by the composition of the concrete: by the amount of water used and the water-to-cement ratio (w/c). When the concrete freezes, the water in the pores of the gel does not freeze above 233°K [1, 2], but in the capillary pores it freezes at higher temperatures; as a result of the increase in its specific volume, in this phase transition, excess pressures arise in the pore system of the concrete. The stresses in the structure of the concrete which result from these pressures may lead to its failure. The capability of withstanding a specified number of cycles of alternating freezing and thawing while its loss of strength remains within a prescribed limit is called the frost resistance of the water-saturated concrete. The introduction of air-entraining or gas-producing additives into the concrete mix creates in the concrete closed air bubbles with radii of $5 \cdot 10^{-6}$-$2 \cdot 10^{-4}$ m, which are surrounded by the cement gel, do not fill up with water under ordinary conditions, and are connected to the general capillary–porous structure by the pores in the gel [3]. It is known that such bubbles in the concrete help to increase its frost resistance [2, 3]. The greater the number of bubbles and the smaller the distances between them, the greater will be the increase in the frost resistance of the concrete [1-3]. Most investigators – e.g., [1-3] – attribute this to the fact that the air bubbles are compensating volumes into which the excess water can go when the water freezes in the capillaries.

Figure 1 shows a simplified scheme of the structure under consideration. A water-filled cylindrical pore of radius R_p and length l_p is closed at the bottom and surrounded by cement stone containing air bubbles connected with the pore by water-filled capillaries. The connecting capillaries are represented by straight cylindrical channels with an orientation perpendicular to the surface of the filled pore and having an average length and variable radius r_i. In the freezing process the heat is removed from the upper part of the specimen.

If the time required for the freezing of the water in the pore is much longer than the time required to stabilize the freezing rate [4], we can assume that the plane crystallization front moves along the pore axis at constant velocity v_s. The thermal conductivity of the mass surrounding the pore is disregarded, since the supercooling of the water is enough to absorb the heat that is generated. In this case the value of Q, the volumetric flow rate of the water from the water-filled pore, required to prevent an intensive increase in pressure is determined as follows:

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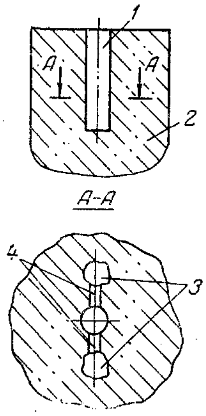

Fig. 1. Scheme of the structure: 1) water-filled cylindrical pore; 2) surrounding medium containing air pores and connecting capillaries; 3) air pores (for convenience, we have shown only two); 4) connecting capillaries.

$$Q = S_p v_s \left(\frac{\rho_w - \rho_s}{\rho_w}\right). \tag{1}$$

Starting from the dimensions of the pores and capillaries in the concrete [1-3] and also from the results of the investigations in [5], the movement of water in the connecting capillaries can be considered laminar and inertialess, and the pressure gradient can be determined by the action of the viscous forces alone. At each instant of time the pressure along the entire length of the water-filled pore is the same. The counter-pressure at the capillary outlets is also considered constant. Then the movement of the water in the connecting capillary is Poiseuille flow, and the flow rate in the capillary [6] is

$$Q_i = \frac{\pi r_i^4}{8\mu}\frac{dP}{dl_c}, \tag{2}$$

where dP/dl_c is the pressure gradient in a capillary of minimum radius, forming the pressure in the pore at each instant of time.

The flow rate of the water through the surface of the pore S_p, which varies with time t, will be the following when the water freezes:

$$Q = \sum_i n_i Q_i, \tag{3}$$

where n_i is the number of capillaries of a given radius.

Since the length of the capillaries surrounding the pore is small, the porosity can be defined approximately as the ratio of the area of the cross sections of these capillaries to the surface area of the pore, $\Pi \approx \sum_i \pi r_i^2/S$. Then

$$n_i = \frac{S\Pi_i}{\pi r_i^2}, \tag{4}$$

$$S = \pi [R_p^2 + R_p(l_p - v_s t)]. \tag{5}$$

After substituting (2), (4), and (5) into (3), we obtain

$$Q = \frac{\pi}{8\mu}[R_p^2 + R_p^2(l_p - v_s t)]\frac{dP}{dl_c}\sum_i r_i^2 \Pi_i. \tag{6}$$

Equating (1) to (6) yields an expression for the pressure gradient in the capillary of minimal radius, forming the pressure in the pore:

$$\frac{dP}{dl_c} = \frac{8\mu R_p^2 v_s(\rho_w - \rho_s)}{\rho_w [R_p^2 + R_p(l_p - v_s t)]\sum_i r_i^2 \Pi_i}.$$

This expression was obtained for the case in which all of the excess water passes through the surface of the pore in unit time, and there is no change in the pore volume (no deformation of the pore) resulting from the pressure. In addition, the counterpressure due to the compression of the air in the air pore may be disregarded. This latter assumption is permissible, because the volumes of the water-saturated and the air-filled pores are approximately equal, and the water displaced does not exceed 10% of the volume, so that the increase in pressure due to the compression of the air is negligible in comparison with the pressure required to overcome the viscous forces.

After integrating along the length of the capillary, we find that the excess pressure for the case of Poiseuille flow is equal to

$$P_1 = \frac{8\mu R_p^2 v_s (\rho_p - \rho_s) l_c}{\rho_w [R_p^2 + R_p(l_p - v_s t)] \sum_i r_i^2 \Pi_i}.$$

From the expression obtained above it can be seen that the pressure in the pore increases with time. When t = 0, there is no excess pressure, since $v_s = 0$. Using the total time of the process $t_{max} = l_p/v_s$, we can determine the maximum value of the pressure in the pore:

$$P_{1max} = \frac{8\mu v_s (\rho_w - \rho_s) l_c}{\rho_w \sum_i r_i^2 \Pi_i}. \qquad (7)$$

Since in actuality the movement of the liquid in the capillary is accelerated, we find that the excess pressure causing the acceleration is $P_{2i} = \rho_w v_i^2$, where v_i is the velocity of the water in the capillary. From (2) it follows that $v_i = r_i^2 P_1/8\mu l_k$.

The total water pressure in the pore that is required to ensure a given flow rate is $P = P_1 + P_2$. Here P_1 and P_2 are the excess pressure values required to overcome the viscous-friction forces and to produce the acceleration of the liquid, respectively. However, for the given flow rates, P_2 is negligibly small, so that $P = P_1$. The maximum pressure in the pore is independent of the pore length and radius (7).

Considering the cement stone surrounding the pore shown in Fig. 1 in the form of an annular layer of thickness l_c, we can estimate (the estimate is somewhat high) the maximum stresses in it that are caused by the increase of pressure in the pore, using the expression for the definition of the maximum equivalent stress in a thick-walled cylindrical shell [7]. Since $l_c >> R_p$, it follows that $\sigma_t = 2P_{max}$. The material surrounding the pore will withstand the resulting pressure if the stresses caused by the pressure do not exceed the tensile strength of the material.

On the basis of the expressions obtained, we carry out the calculation for the cement stone, some properties and parameters of whose structure can be taken from [1-3]: for w/c = 0.4, 0.6, and 0.8, the compressive ultimate strength will be σ_{bco} = 20-45 MPa; the tensile ultimate strength will be σ_{bt} = 3.0-5.0 Mpa; $R_p = 10^{-5}, 10^{-6}, 10^{-7}$ m; $l_p = 8R_p$; the total porosity of the cement stone for the indicated w/c values and a degree of hydration equal to 0.6 will be 0.3, 0.45, and 0.55, respectively, and the porosity resulting from the capillaries with radii of 10^{-5} to 10^{-7} m is equal to 0.138, 0.326, and 0.444; $l_c = 0.15 \cdot 10^{-3}$ m.

In the case of cement stone without appropriate additives forming air or gas bubbles, at the minimum considered value of w/c = 0.4, the frost resistance does not exceed 150 cycles and decreases as w/c increases.

The possible initial supercooling of the water upon freezing is 5°K [8]. On the basis of the calculation of the rate of motion of the crystallization front from [4, 9] and the data of [10], we take v_s = 0.15 m/sec. The determination of the time required for stabilization of the rate of freezing [4] showed that its value is much smaller (by one order of magnitude) than the time for the entire process.

Variational calculation of the possible maximum pressure in the pore according to the expression (7) was carried out for different radii of the capillaries r_i, according to the indicated porosity. The smallest possible dimension of the capillary forming the pressure in the pore which does not cause stresses exceeding the ultimate strength was found to be $r = 2.8 \cdot 10^{-7}$ m, where $P_{max} \leqslant 2.5$ MPa. At these pressures the anomalous phenomena noted in [11] will not take place in our case. The flow rate for the capillaries of the smallest radius will be insignificantly small at this pressure. Comparing the necessary pressure gradients from Poiseuille's law for capillaries with $r = 5 \cdot 10^{-9}$ and $r = 2.8 \cdot 10^{-7}$ m. we can conclude that at a pressure of 2.5 MPa in the pore, smaller capillaries, in spite of the fact that there are more of them, carry no more than 1% of the given flow rate. Moreover, the anomalous behavior of the water in capillaries with radius $r < 10^{-8}$ m, caused by the surface tension from the capillary walls [11], reduces the flow rate even further.

Our analysis shows that the necessary removal of water from the freezing pore can be ensured only by capillaries of large radius ($r \geqslant 2.8 \cdot 10^{-7}$ m) for a porosity $\Pi \geqslant 0.138$ resulting from them. Since the air bubbles are connected with the general capillary–pore structure of the cement rock by capillaries of much smaller radius, the freezing of the water in the filled capillary pores must result in the development of a destructive process associated with the breakdown of the pore walls, because the water freezes in the large connecting capillaries as well. The fact that the air bubbles surrounded by the nonfreezing capillaries of the cement gel have a positive effect on the frost resistance of the concrete is due to a different mechanism, not to the forcing out of the excess water when it freezes. Probably, this positive effect is manifested because the air bubbles introduced into the concrete increase its microcrack resistance, i.e., reduce the length of the cracks that arise as a result of the destruction and prevent them from developing further, and in addition they increase the limiting tensility of the system.

NOTATION

Q, flow rate; ρ, density; S, area of cross section and lateral surface of a pore; R, $\dot{r}$, radii; t, time; v, velocity; P, pressure; l, length; σ, stress; n, number of capillaries; μ, dynamic viscosity or water; Π, porosity. Subscripts: w, liquid phase of water; s, solid phase of water (ice); i, indication for one of a set of quantities; c, capillary; p, pore, cross section; co, compression; t, tension; b, ultimate strength.

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