On the boundary, from Eq. (16) we have

$$c(0,\ t) = \frac{4\Delta c}{\sqrt{\pi}} \Phi\left(\frac{u\sqrt{t}}{2D}\right) + \frac{\Delta c u \sqrt{t}}{2\sqrt{D}} \exp\left(-\frac{9u^2 t}{4D}\right) - \frac{\Delta c}{3} \Phi\left(\frac{3u\sqrt{t}}{2\sqrt{D}}\right) + \frac{3u^2 \Delta c t}{2D}\left[1 + \Phi\left(\frac{3u\sqrt{t}}{2\sqrt{D}}\right)\right].$$

From this it is simple to see that as $t \to \infty$ the quantity

$$c(0,\ t) \to \frac{3u^2\Delta c}{D} t.$$

Thus, the gas concentration on the phase boundary for constant velocity of crystallization-front motion grows proportionally to time t and to the square of this velocity. Thus, in principle, after a certain period of time homogeneous gas-bubble formation should begin.

In the case considered here the effect of diffusion separation of gas components ahead of the crystallization front will appear to a still higher degree.

In conclusion, we note that solutions of problems analogous to those considered above but with other crystallization-front displacement velocities are obviously quite difficult to achieve. The solutions obtained above offer definite descriptions of the character of ice-structure formation in the water-crystallization process.

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EFFECT OF ULTRASOUND ON THE PROCESS OF MASS TRANSFER IN CEMENT MORTAR AND CONCRETE

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We present new results in the investigation of the depth and rate of impregnation of cement mortar and concrete. We show the effect of ultrasound on the process of mass transfer in concrete. We establish the possibility of using ultrasound for accelerating the impregnation of concrete and also of other capillary-porous materials.

The most important materials for the industrial production of structural elements of buildings and industrial installations are concrete and cement–sand mortar. Both of these materials belong to the category of capillary-porous substances, whose distinguishing feature is their capacity for actively absorbing moisture and gases from the surrounding medium. This phenomenon is due to the chemical properties of the cement stone and its micropore structure.

The absorptive and capillary intake by the concrete or the mortar of substances which are harmful to the cement stone leads to a reduction of strength, an increase in deformability, and a change in the heat-engineering characteristics of structural elements. These phenomena are more often observable at chemical-industry enterprises [1-4], where there is always a high concentration of aggressive reagents in the surrounding medium.

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The most widespread method of protection against corrosion is painting the external surface with chemically stable varnishes and paints based on polymer materials [5]. The main advantage of this method is that the protective covering is monolithic and can be applied by simple techniques. Because the paint is very viscous and the solvent evaporates rapidly, there is a limit to the depth of impregnation of the concrete by the protective substance. As a rule, the thickness of the protective-covering layer is between 1 and 3 mm.

The thickness of the protective layer can be increased by impregnating the structural elements with polymer materials in autoclaves in high temperature and pressure. A significant disadvantage of this method is the high cost of the autoclaves and the long duration of the impregnation process. This method cannot be introduced into industrial practice until detailed economic calculations have been carried out.

One of the possible ways to increase the depth of impregnation of the concrete and speed up this process is the use of the ultrasound and heating of the impregnating material [6-9]. E. G. Konovalov established that under the action of ultrasonic vibrations a liquid will rise much higher in capillary channels and will go up much faster than under the action of capillary forces. This effect may be intensified by preliminary heating of the liquid.

In order to study the effect of ultrasound on the variation of the kinetics of the mass-transfer process and the possibility of using this effect for the desired impregnation, special investigations were carried out on specimens of cement mortar and concrete.

The installation on which these investigations were carried out consists of two assemblies. The first assembly is a system consisting of two subsystems A and B and closed with respect to mass exchange with the surrounding medium. Such a formulation of the tests meets the main requirements of the theory of similarity, the mass-transfer differential equations, and therefore the first assembly may be regarded as a mathematical model of a known problem in thermophysics concerning the propagation of heat or another substance along a semibounded body whose lateral surface is appropriately insulated [18]. Thus, in the first assembly we simulate the field of mass transfer when there is directed action of a field of ultrasonic vibrations on the liquid.

The second assembly is an auxiliary system recording the progress of the mass-transfer process both in time and in space. The second assembly is connected to the first by special sensors set up in the specimen being investigated. The sensor used is based on the known fact that the resistance of cement stone or other capillary-porous material to electric current varies when there is a slight change in humidity. This property is widely used in technology as a basis for designing instruments for the rapid determination of the moisture content of materials [12-16].

The observations made during the ongoing process are recorded on a diagram with a constant time scale; with this system there can be a single independent variable, namely, time from the beginning of the test, and it is in terms of this time that we express two quantities which are different in their physical nature – the mass of liquid entering the specimen through the plane of contact between the two media and the path traversed by the liquid along the specimen. This makes it possible to avoid the problems (very difficult to solve analytically or experimentally) of describing those physicochemical processes which take place in the specimen when the penetrating liquid interacts with the multicomponent system of the cement stone.

During the experiment, the mass content was acted upon by ultrasonic and gravitational fields.

In order to determine the effect of the ultrasound on the mass-transfer process, we prepared specimens with dimensions of d = 54 mm, h = 70 mm, and h = 140 mm. The specimens were shaped in separable metal forms. A block of forms was used, making it possible to shape six identical specimens at the same time. The specimens were made of cement mortar with a composition of 1:1, 1:2, 1:3, and 1:4 (ratio of cement to sand). In all cases the water–cement ratio (W:C) was taken to be 0.5. The specimens were made with unscreened quartz sand with grain size ranging from 0.5 to 1 mm and "200" brand cement.

The mortar was packed in the form on a standard laboratory vibration table. Afterwards the specimens were subjected to 8 h of thermomoisture treatment in a steam chamber. After this the specimens were stored under room conditions for an additional 18-20 days until they reached an equilibrium state. Only after the entire treatment cycle was completed did we subject the specimens to the main tests to investigate the mass-transfer phenomenon.

In order to exclude any possible leakage of liquid through the pores opening onto the surface of the specimen, the lateral surface of the specimen was subjected to special treatment. This treatment consisted in covering the surface with a layer of waterproof varnish and then wrapping it in a polyethylene sheet.

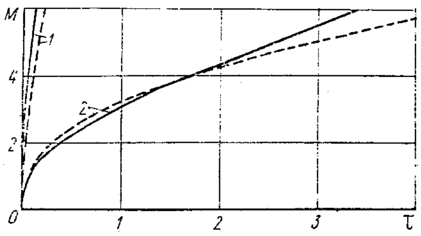

Fig. 1

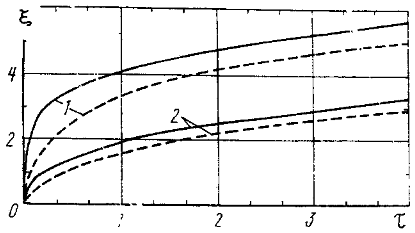

Fig. 2

Fig. 1. Variation of the total amount of water absorbed through the contact surface as a function of time: 1) for a 1:2 mortar; 2) for a 1:4 mortar. M in grams; τ in hours.

Fig. 2. Motion of the water front along the specimen: 1) for a 1:2 mortar; 2) for a 1:4 mortar.

During the experiment, at the same time as we filled subsystem A with the liquid, we applied vibrations with a frequency of $\nu = 40$ kHz from an ultrasound source. The penetrating medium used in our investigation was ordinary water. The initial additional hydrostatic head was equal to $h_0 = 42$ cm of water. The temperature of the water, the specimen, and the surrounding medium was 18°C. The age of the specimen until the time the experiment was performed was $\tau = 18$ days, counted from the time at which the specimen was removed from the thermomoisture treatment.

The observations were recorded on a roll of paper with millimeter markings, sufficiently long to record tests lasting prolonged periods. The recorder paper moved at a rate of 6 mm/min. The values recorded on the diagram were not digital but varied continuously.

The amount of liquid entering the specimen was measured with a burette with scale divisions of 0.1 cm^3. The readings were recorded on the diagram at constant intervals of 0.5 cm^3. This recording made it possible to calculate in a simple manner the mass of liquid entering the specimen during a fixed period of time.

Since all the sensors were positioned along the height of the specimen at a constant interval of $\Delta\xi = 0.5$ cm, this made it possible to determine the ξ-coordinate of the moving liquid at any instant of time.

The results obtained by analyzing the diagrams of the experiments for specimens made of cement mortar with a composition of 1:2 and 1:4 are shown in the form of two graphs: the variation of the total absorbed mass of liquid M entering the specimen as a function of time τ (Fig. 1) and a graph showing the motion of the water front along the specimen (Fig. 2). These two graphs are related to the same independent variable τ – the time measured from the moment of contact between the two media.

Obviously, such quantities as F, the area of contact (the cross section of the specimen); ν, the frequency of the ultrasonic vibrations; A, the chemical properties of the liquid (affinity); t^0_α, the temperature of the liquid; B, the cement–sand ratio of the specimen; τ_b, the age of the specimen; and t^0_b, the temperature of the specimen, are regime parameters of the process under investigation and remain constant during the test. The effect of each of these parameters on the development of the mass-transfer process can be determined by means of a special investigation.

In order to determine the effect of the ultrasound on the mass-transfer process, parallel with the main experiment we set up a second experiment without ultrasound, using a duplicate specimen with identical regime parameters. Obviously, the second experiment is a control for the first. In this case we investigate the effect of transfer in what might be called the "pure form."

The results of the investigations are shown in the form of graphs on which the values for the first test are shown by solid curves and the values for the second are shown by dashed curves. This treatment of the observation results makes it possible to show more completely and visibly the effect of the ultrasound on the process investigated.

Analyzing Figs. 1 and 2, we note that as the mass-transfer process develops with increasing time, three characteristic regions can be distinguished.

In the region $0 \le \tau \le 3$-5 min we observe an almost linear variation with time both for the amount of liquid absorbed by the specimen and for the motion of the liquid front along the axis of the specimen.

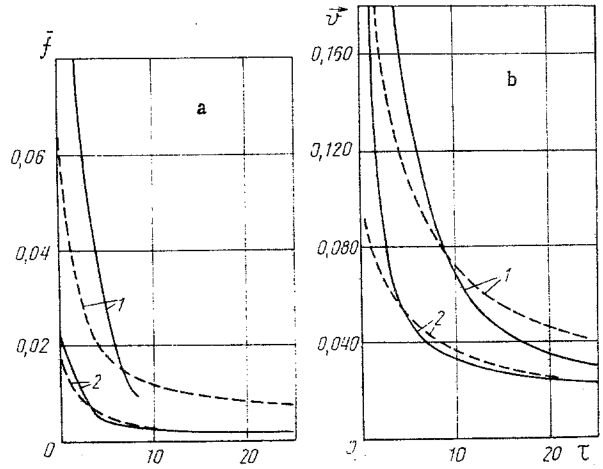

Fig. 3. Variation of the flow density (a) and velocity (b) with respect to time: 1) composition 1:2, 2) composition 1:4.

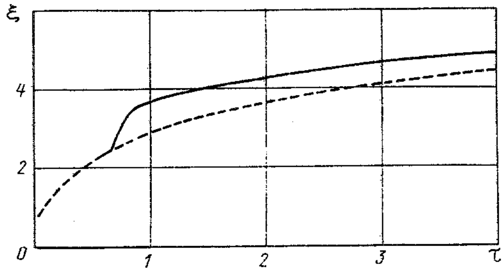

Fig. 4. Motion of the water front in a specimen when the ultrasound was applied 30 min after the moment of contact between the two media. ξ in centimeters.

For the region 3-5 $\le \tau \le$ 40-50 min we have a marked nonlinearity in the behavior of these quantities as functions of time. The process almost comes to a halt.

In the region $\tau > 1$ h we observe monotonic asymptotic damping of the process.

This can be explained [11, 12, 17] by the physical nature of the forces under whose action the motion of the liquid takes place. In the first region the motion of the liquid along the specimen takes place under the action of capillary forces.

The motion of the liquid (water) in the second region is determined primarily by adsorption forces and concentration diffusion resulting from the dissolution of individual components of the cement stone during the time when the liquid moves within the first region.

For the third region the determining process is molecular diffusion of the substance.

In order to verify these conclusions, we took two specially selected specimens with a composition of 1:2 which had a large number of large pores, measuring 2-4 mm, opening onto their lateral surfaces. The lateral surface of the specimens was not covered with a layer of varnish but was closely wrapped in two layers of transparent film. Examining these specimens after the test, we found that only in the first zone, 20-25 mm from the surface of contact with the water, were the pores filled with a viscous colloidal mass. Below this zone we observed only "sweating" of the inner surface of the film, and the space in the pores themselves was not filled with liquid. In the third zone we observed only the color variation characteristic of moist cement mortar. No "sweating" of the transparent film was observed.

The dimensions of the first two regions are significantly effected by the amount of cement stone contained in a unit volume of the specimen. The larger the cement-stone content per unit volume, the more intensive is the process and the deeper the substance penetrates.

As can be seen from the graphs, the ultrasound has the most significant effect on the intensification of the mass-transfer process within the limits of the first and second regions, as was also observed in the investigations of Konovalov and other authors [6-9]. In the third region this effect is gradually damped out. It should be noted that the ultrasound has a greater effect on the depth of penetration of the substance into the specimen than on the mass **transferred.**

The initial effect of the ultrasound on the depth of penetration of the substance may be estimated as a provisional increase in the amount of cement stone per unit volume by a factor of 1.5-2.5; after 1 h this effect may be estimated as an increase of only 0.25.

Figures 1 and 2 are the fundamental data of the investigations carried out and give a general quantitative estimate for the development of the mass-transfer process in space and time when the process is subjected to a directed ultrasonic field.

A detailed description of the physical process taking place can be obtained only when we investigate the variation of the local transfer parameters: the density of the stream of material, the rate of transfer, and the density of the moving medium in space and time.

In order to study the variation of these local parameters of the process, we make use of the fundamental relations of the theory of heat and mass transfer [18, 19].

As is known, the density of the stream of material $\vec{J}$ (the mass velocity) is given by the relation

$$\vec{j} = \vec{1}_n \frac{1}{F} \cdot \frac{dM}{d\tau}, \tag{1}$$

and the rate of transfer is given by

$$\vec{v} = \vec{1}_n \frac{d\xi}{d\tau}. \tag{2}$$

The density of flow of the material may be written in another form:

$$\vec{j} = \rho\vec{v}, \tag{3}$$

from which the density of the moving medium is

$$\rho = \frac{\vec{j}}{\vec{v}}. \tag{4}$$

The flow density, the transfer velocity, and the density of the moving medium, given by relations (2)-(4), are the average statistical values of these quantities. The averaging of these quantities takes place automatically during the transfer process itself and is due to the fact that in addition to the main axial motion of the liquid along the specimen, there is also a radial displacement due to the inhomogeneity of the structure of the cement mortar [19]. The front of the liquid moving in this specimen is always plane. This is confirmed by longitudinal splitting of the specimens after the test.

Since the results of the experiment are shown in the form of graphs and not in the form of an analytic relationship expressed by a function of the main independent variable τ, the differentiation can be carried out only approximately, by a numerical method.

The results of the calculation according to formulas (1) and (2) are shown in the form of graphs of $\vec{J} = f(\tau)$ and $\vec{v} = \varphi(\tau)$ in Fig. 3, where the main experiment is shown by a solid curve and the control experiment is shown by a dashed curve. As was to be expected [6-19], the directed ultrasonic vibrations caused a sharp increase in the density of flow and the transfer velocity in comparison with the control experiment.

In Fig. 3 we can observe that the imposition of an ultrasonic field has a significant effect on the variation of the local mass-transfer parameters only during the first 15-30 min after the start of the process. During this time there takes place in the specimen a volumetric displacement of the liquid along the capillaries within the limits of the first region, while film adsorption of the liquid takes place in the second region. As the process goes into the region of molecular-diffusion transfer, this effect is practically damped out.

It should be noted that the ultrasound produces a stronger effect on the variation of the initial transfer velocity than on the variation of the initial flow density. This indicates that there is very little change in the cross-sectional dimensions of the capillaries during the transfer process.

Thus, the imposition of a directed field of ultrasound on the mass-transfer process leads to an increase in the kinetic energy of the moving medium , i.e., in the present case the well-known Curie principle is observed [18].

As a result of the increase in the kinetic energy of the flow of the moving medium, there is a blurring of the capillary walls and a displacement of fine particles of cement stone by the liquid. Because of this, at some depth from the contact surface between the two media, where the transfer velocity has become less than a fixed quantity, there is a flooding of the capillaries. This flooding of the capillaries retards the volumetric motion of the liquid and brings the transfer process into the molecular-diffusion region. The existence of retardation regions is confirmed by Fig. 3. In the region of capillary flooding the flow and the transfer velocity in the main test become less than the corresponding values in the control test.

An examination of the specimens after the test showed that at a depth of 25-30 mm from the contact surface there is a region of denser structure. This region is more clearly marked on specimens made of cement with ratios of 1:1 and 1:2.

In order to explain the effect of ultrasound on the mass transfer in the molecular-diffusion region, we set up an experiment in which the application of the sound was delayed 30 min after the time of contact between the two media. The graph showing the motion of the liquid front for this test is given in Fig. 4.

The specimen was made of a cement mortar with a composition of 1:2, the water–cement ratio was taken to be 0.5, and the age up to the time the experiment was conducted was taken to be 90 days. The test showed that in this region as well, the application of ultrasound has a significant effect on the development of the mass-transfer process. The initial effect for this region is considerably less and shows up with some retardation after the time when the ultrasound is applied.

There is reason to suppose that by the periodic application of ultrasound during the first hour of the mass-transfer process we can increase the depth of penetration of the liquid and simultaneously establish in the specimen a zone of increased density of the basic material.

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INFLUENCE OF MOISTURE WITH DIFFERENT FORMS OF BONDING IN VISCOSE THREADS ON THE KINETICS OF THREAD DEFORMATION DURING DRYING

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Shrinkage effects in viscose threads during drying are shown to be governed principally by the form of bonding in the water being eliminated, and the stabilization of the pore structure of the threads is shown to be governed principally by the number of times they are repeatedly wetted and dried.

Drying is one of the most important operations in the process of viscose-thread production. A swollen viscose thread being dried from a moisture content of almost 200% of its absolute dry weight shrinks by more than 10% of its initial volume during drying, causing marked changes in the thread structure and affecting its physicomechanical indices, capacity for dye absorption, capacity for deformation, etc. In this connection, investigations into the influence of the form of moisture bonding in viscose threads on the kinetics of their deformation during drying can be used to provide a sound basis for selecting drying conditions to produce a high-quality material.

The investigations are made on No. 60 viscose textile threads produced in the Kiev Artificial Fiber Combine by the centrifugal method of spinning.

Thermographic [1] and sorption [2] measurements of the aqueous properties of the threads under investigation, which characterize the state of moisture in them according to the form of bonding, are shown in Table 1.

The viscose threads under investigation belong to the group of colloidal capillary-porous bodies [3], and, as can be seen from Table 1, they possess a fairly well-developed macroporous (with pores more than 10^{-7} m in radius) and microporous (with pores less than 10^{-7} m in radius) structure.

The influence of moisture on the deformation of viscose threads during drying is investigated on an apparatus providing for the automatic tracing of the curve of thread weight loss, the curve of linear thread deformation, and the curves of ambient temperature and moisture during experiments onto the tape of a recording potentiometer.

A bunch of 50 threads with an initial length of $(110\text{-}115)\cdot 10^{-3}$ m is used in all the drying experiments. The threads for the bunch are unrolled from a wet coil which has not been dried. Before the experiment the bunch is wetted as much as possible with distilled water. The drying experiments are made with the following parameters for heat-transfer agents: relative moisture content of the air 30% and temperatures of 313, 353, and 393°K. Curves of the dependence of the relative deformation of the threads ε on the moisture content W of the bunch and curves of the rate of drying and rate of deformation are plotted from the experimental results.

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