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THERMAL CONDUCTIVITY OF COLLOIDAL CAPILLARY POROUS BODIES
IN THE PROCESS OF STRUCTURE FORMATION

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The article presents the results of the experimental investigation of the thermal conductivity of a solidifying system in the process of formation of a capillary porous structure.

The thermophysical processes occurring in colloidal capillary porous bodies have a substantial effect on structure formation and on the eventual physicomechanical properties of materials. For instance, the structure formation of binder-based disperse systems is directly connected with the regularities of heat and moisture transfer in them. Investigation of the thermal conductivity of such systems in the process of their solidification in the course of a long time is therefore very important for the study of problems of the interrelation between the structural, thermal, and strength characteristics of binders.

The present work represents the first investigation of the thermal properties in the process of formation of a capillary porous structure of the solidification of a modeling monomer binder, viz., gypsum.

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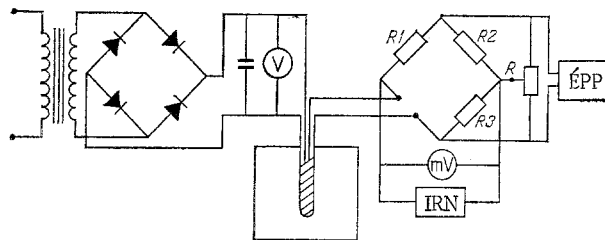


Fig. 1. Arrangement for measuring the thermal conductivity of gypsum specimens.

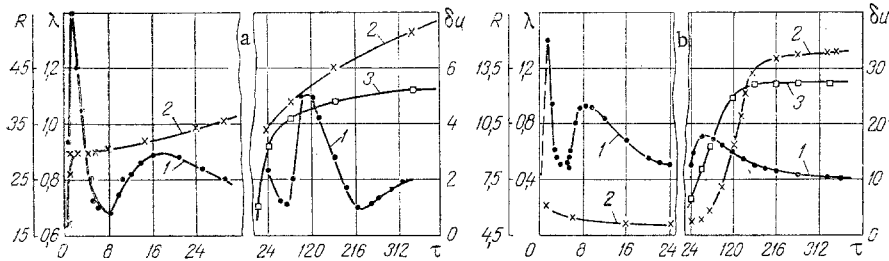


Fig. 2. Dependence of thermal conductivity (1), of strength under compression (2), of decrease of moisture (3) on time for a gypsum system: a) formed under pressure; b) with standard solidification. λ , W/m·deg; R, MPa; δu , %; τ , h.

For investigating the thermal conductivity of specimens the non-steady-state method of a cylindrical probe with constant power [1-3] was used. With the ratio of the working length of the probe L to its diameter $2r_0$ of the order of magnitude of 30, the probe may be regarded as an unbounded cylindrical source of heat.

The mathematical problem for a temperature field, produced by the probe heater in the medium, was formulated and solved in [1-3].

The formula for calculating λ has the form

$$\theta_1(\tau_2) - \theta_1(\tau_1) = A \ln \frac{\tau_2}{\tau_1} = \frac{K_1}{\lambda} \ln \frac{\tau_2}{\tau_1},$$

and hence

$$\lambda = \frac{K_1 \ln(\tau_2/\tau_1)}{\theta_1(\tau_2) - \theta_1(\tau_1)},$$

where $K_1 = q/4\pi$.

The probing sensor used in the experiments consisted of two bifilar, electrically insulated windings: the heater of manganin wire with 10^{-4} m diameter, and the temperature sensor, a resistance thermometer made of copper wire with $5 \cdot 10^{-5}$ m diameter. The length of the probe was $3 \cdot 10^{-2}$ m, its diameter $7 \cdot 10^{-4}$ m.

The measuring arrangement of the instrument for determining the thermal conductivity of gypsum specimens by the "probe" method consisted of a bridge circuit, a source of electric power, a millivoltmeter, an electronic recording potentiometer ÉPP-09MZ that records the excess temperature of the probe (Fig. 1). The probing sensor was placed in the center of the specimen of rectangular shape, $7 \times 7 \times 28 \cdot 10^{-2}$ m in size.

The specimens were made by mixing gypsum binder with water in accordance with GOST 125-70 and by the method of [4] using compression with removal of the excess liquid phase at the stage of coagulation structure formation. The experiments were carried out at a temperature of 298°K of the medium. Overheating of the specimen in the region of the probe did not exceed 276-278°K; this could not cause a noticeable effect of heat and moisture conductivity. According to [3] and the experimental conditions, the specific weight of the heat transfer factor, determined by mass transfer, amounted in the investigated material to less than 10% of the full effect of heat transfer. The error in determining λ did not exceed 8%.

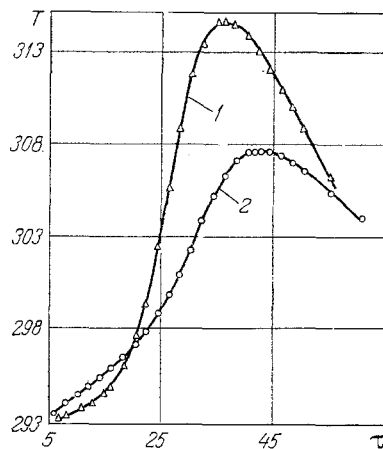


Fig. 3. Change of the temperature T ($^{\circ}\text{K}$) during the process of solidification of the system gypsum-water with time τ (min): 1) system formed under pressure; 2) system of standard solidification.

Together with the thermal properties of the system gypsum-water, we also investigated the time-dependent increase of strength under compression, the degree of hydration of the initial solid phase, decrease of moisture in the system, formation of the capillary porous structure of solidification, and linear deformation.

The investigations showed that during the first few days of solidification there occurs an abrupt change of thermal conductivity of the systems under study (Fig. 2). In the first 1.5 h after the beginning of the formation of the systems, thermal conductivity increases in consequence of the chemical and physical bonding of a considerable amount of liquid medium in the process of crystallization of highly disperse hydrated formations and on account of the liberation of heat in the systems at this stage. In the graphs of change of strength of the specimens with time, intensive increase of strength corresponds to this period. The decrease of thermal conductivity at the subsequent stage of solidification is connected with the drop of temperature in the systems (Fig. 3) and with the process of recrystallization of small crystals into larger ones (which is thermodynamically inevitable if the system contains free water). This is accompanied by partial loss of crystallization contacts and consequently by an increase of contact resistance of the systems. That the process of recrystallization occurs at this period is testified to by the incipient shrinkage of the specimens and the abrupt decrease in the rate of their hardening (see Fig. 2) [5]. With decreasing amount of free water in the system and as a result of natural drying, recrystallization gradually ceases, and processes leading to the strengthening of the structure become prevalent. In a system of gypsum-water formed under pressure, recrystallization is concluded approximately 8 h after mixing has begun (see Fig. 2a). From this instant on, up to the age of one day the thermal conductivity of this system increases. Especially in this period more than half of all the free water is removed from it. The loss of free water, together with the continuing process of hydration, leads to the formation of a strong spatial solidification structure which is characterized by conditioned-coagulative and crystallizational bonds between the crystals. However, the process of structure formation, which on the one hand causes increased strength of the solidifying system, is on the other hand the cause of internal stresses gradually arising in it, and these internal stresses lead in most cases to the formation of microcracks. This is apparently also the cause of the regular drop in thermal conductivity of a system formed under pressure when between one and two days old. After the age of two days the process of growth of the crystals practically ceases. The degree of hydration of the system attains 98%. Further evaporation of moisture from the material, causing some slight supersaturation ($\alpha = 1.2$) of the liquid phase to be maintained, leads to contact formation in the system because of the preferential crystallization of contact nuclei under such conditions (nuclei in the gap between two surfaces) in comparison with volume and surface nuclei whose boundary of lability is much higher. This was confirmed by electron-microscopic investigations of the structure carried out by the method of self-

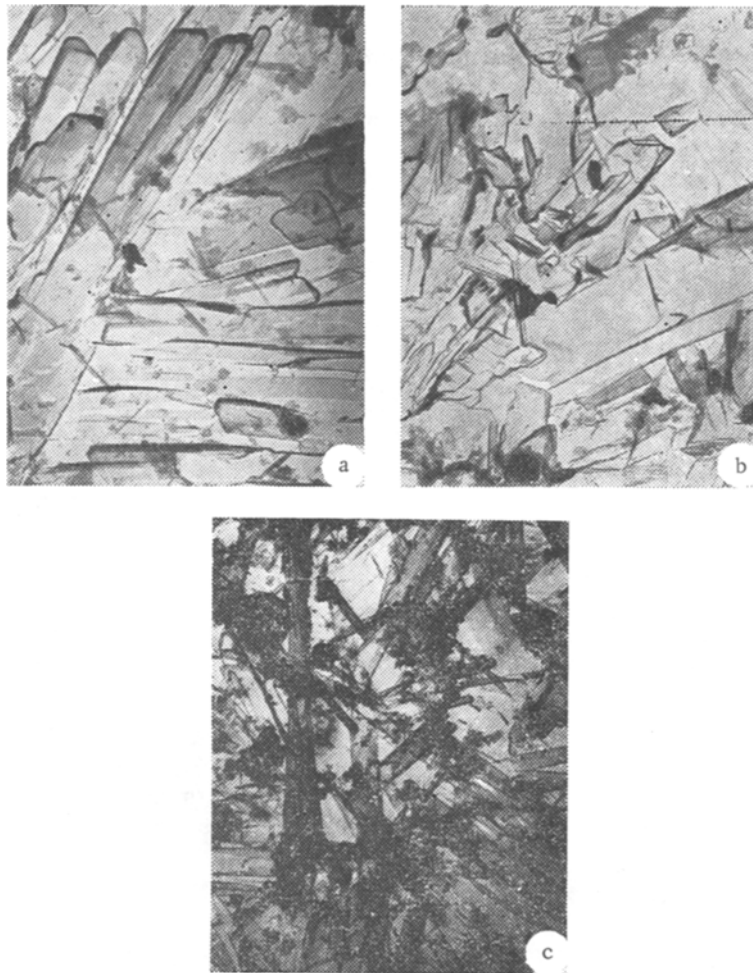


Fig. 4. Photographs of the microstructure of the cleavage face of a gypsum stone. 6200 \times : a) pressed stone aged 1 day; b) pressed gypsum stone aged 3 days; c) gypsum stone of standard solidification aged 1 day.

preshadowed carbon replicas. Photographs of the microstructure of the cleavage face of specimens, aged from three days onward, show clearly how separate crystals grow together (Fig. 4a, b). The result is that the increase of strength of the system continues and that thermal conductivity at this stage increases. The drop in thermal conductivity on the section from five to nine days is connected with the increased contact resistance of the system because the moisture in the pores of the material is practically completely replaced by air. On this section the evaporation of moisture from the material ceases, and a state of equilibrium between the specimen and the environment is attained. After that, up to the age of half a year, the strength of the system increases, and its thermal conductivity increases evenly because of the increase of the cross-sectional area of the phase contacts between the crystalline hydrates.

In specimens with standard solidification the first minimum on the curve of change of thermal conductivity, connected with the return of the temperature of the system to its initial values and with the beginning process of recrystallization, occurs sooner (4 h after the beginning of mixing) than in specimens formed under pressure (Fig. 2b). The absolute value of λ , corresponding to the extreme on this section of the curve, is much lower than the corresponding value of λ of specimens formed under pressure. This is due to the difference in the rate and duration of the processes of hydration of the investigated systems (Fig. 3).

Whereas in specimens formed under pressure the process of recrystallization practically ceases 8 h after the beginning of mixing, and then processes leading to the formation of a spatial structure of solidification with prevalent crystallization bonds between the crystals

predominate, in specimens of standard solidification the process of recrystallization lasts perceptibly up to the age of one day. In this period the curve of the change in strength vs. time shows a drop in strength of the system caused by the process of recrystallization. Investigations by electron microscope of the geometry of the solid phase confirm that the process of recrystallization takes place at this period, and this is also indicated by the lack of distinct crystallographic faces of the crystals (Fig. 4c). The change in thermal conductivity in this time interval (amounting in sum to a drop) is also due to recrystallization. On the section from 4 to 8 h thermal conductivity increases; this is due to the decrease of the equilibrium interlayer of the liquid disperse medium and to the increase of the cohesive force between particles of crystalline hydrate as a result of loss of moisture by the system due to natural drying. Cessation of recrystallization toward the age of one day and further evaporation of moisture from the material lead to strengthening of the structure (rise of the curve $R = f(\tau)$ in consequence of the transition of the coagulation bonds into conditionally coagulation and partly crystallization bonds). The subsequent drop in thermal conductivity on the section of 4-8 days, like in specimens formed under pressure, is due to the practically complete replacement of moisture in the pores of the material by air. A distinguishing feature of the entire subsequent period of investigation of the system with standard solidification is the stabilization of its thermal and strength properties.

Thus the results of the investigations express the qualitative interrelation between the processes of heat and moisture transfer found in a solidifying system based on monomineral binder substances and the process of formation of a disperse capillary porous structure in it.

NOTATION

θ_2 , excess temperature of the external medium; θ_1 , excess temperature of the probe; τ , time; λ , thermal conductivity of the external medium; q , specific heat flux of the heater per unit length; R , strength.

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