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ON CAPILLARY CONTRACTION DURING DRYING IN FILM-LAYERS OF GELS AND POROUS DISPERSE BODIES

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The modern doctrine of the influence of a liquid medium on the properties of a solid body ([1],[2]) has been fruitfully used in elucidating the mechanism of the setting and hardening of cement, which has led to the discovery of the possibility of regulating these processes ([3–5]).

In the light of these concepts, a phenomenon no less important for practice is now being considered: the corrosion of concretes. It has turned out that in this complex phenomenon, under isothermal conditions and in the absence of chemically aggressive agents, adsorption and solvation layers also play a decisive role. Their action is manifested especially sharply under frequent alternation of wetting and drying of concretes and many natural and artificial materials similar to them.

The influence on solids of water and of substances dissolved in it is known as the adsorption lowering of strength (the Rebinder effect) ([1]), consisting in the weakening of intermolecular bonds in the structure, in its loosening and swelling as a result of interaction with the surrounding liquid medium. When passing from wetting to drying, capillary forces arise and gradually increase, acting at the water-air interface. Their action is directed toward compaction (compression) of the hydrophilic drying body, which is indirectly confirmed, for example, by the decrease in the volume of disperse bodies such as concretes during drying, despite the considerable strength of the structure. Also in favor of such a conception of the role of capillary forces is the well-known method of obtaining xerogels (aerogels) from hydrogels by replacing the polar medium with a nonpolar one through a series of intermediate media. However, these forces, which cause shrinkage, cracking, warping, the occurrence of stresses, the formation of voids—internal ruptures during the drying of gels—and other important phenomena, have until now not been studied directly. Recently their role in the formation of the active surface of certain adsorbents ([6]) and catalysts ([7]) has been shown.

We have detected and are quantitatively studying, by a direct, although integral, method the indicated forces, called **forces of capillary contraction** (F_σ), on

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

drying films of high-molecular and disperse systems under dynamic conditions. The kinetics of their development in the drying process has been investigated.

It should be noted that, while recognizing in the phenomena studied the full importance of the role of capillary forces acting at the liquid–air interface, it is also necessary to take into account the cohesive interaction between particles of the solid phase or macromolecules. It is already manifested through liquid molecular layers under conditions of very narrow gaps, pores, and microcracks, where the properties of the liquid at the surface of the solid body change, causing a corresponding increase in the forces of capillary contraction. To a certain extent, forces of coagulation attraction are also manifested here. Gradual—

but, as the liquid residues are removed, the influence of the surface of the solid phase is manifested to an ever greater degree. Upon absolute drying the capillary forces disappear and what remains is the action of intermolecular (cohesive) forces in pure form. Consequently, the capillary-contraction forces under study are a complex quantity, requiring further comprehensive investigation.

Measurements in the study of various high-polymer films and disperse systems are carried out by us with an instrument that makes it possible to determine F_{σ} throughout the entire drying process while preventing shrinkage in the direction of action of the forces being determined. Specimens in the form of strips

Fig. 1. *a*—curing for 22 hours; —161 hours; ′—rapid fall of F_{σ} under the action of water vapor

Fig. 2. Dependence on the time of preliminary hardening: *A*—maximum values of capillary-contraction forces; —strength; 28 days—the standard period of hardening to design strength

were prepared, for example, from cement powder with a small admixture of ground fibrous asbestos (1.3%) as a micro-reinforcing agent preventing accidental ruptures and therefore greatly increasing the reproducibility of the results. Pure asbestos itself, when dried in the dispersed state, exhibits almost no capillary-contraction forces.

In Fig. 1 the rising curves show the development of capillary-contraction forces during drying of two cement specimens previously kept for hardening in a moist environment for different periods. Comparing the two curves, one can see the influence of cement hardening time on the capillary-contraction forces. It was also established that, when cement is dried before it has set, these forces are manifested very weakly.

The dependence of F_{σ} on the time of preliminary hardening of cement specimens was studied in detail. The experimental results obtained for specimens with different hardening periods over an interval of more than 1000 hours are presented in Fig. 2, *A*. For comparison, curve is given, showing the increase in strength of specimens—cubes with an edge of 3 cm, made from cement mortar. The similarity in the course of both curves confirms our considerations ([8]) that the development and strengthening of the structure increases F_σ. The true value of F_σ increases continuously with the development of the microstructure, but at the same time the resistance of the structure to the compressive action of the forces under study also increases. Obviously, the quantity determined is essentially the difference between these two opposing forces. In this difference, the capillary-contraction forces initially have the predominant value. After the maximum is reached, the relation of the forces changes. Curve *A*, with considerable continuation, i.e. with further growth of the strength of the structure, should turn downward as a result of the disappearance of the menisci.

Hence it is easy to understand the inversion in the position of the terminal portions of the curves in Fig. 2.

In experiments with all specimens, at any stage of drying up to the maximum F_σ, the magnitude of this force, under the action of water vapor in isothermal conditions, rapidly decreased to zero. Such a decrease is shown in Fig. 1 by the dashed descending branch b'. Water adsorbing and capillary-condensing from the vapor, filling the narrowest parts of the microcracks and causing a lowering of the strength of the structure (in the general sense), reduces the forces of capillary contraction, and in some regions eliminates them altogether. Stresses in the structure may relax to zero. If the same specimen is again subjected to drying, then F_σ rises to its former maximum values. This occurs noticeably faster than the first time, which indicates the absence of a reserve of moisture in the deep layers of the specimen.

Alternation of drying with exposure to water vapor can be repeated many times. In cement this is reflected in the same way as a loosening alternating external mechanical action, accompanied by the gradual accumulation in the structure of irreversible changes, a drop in strength, and an irreversible increase in volume (7). This is completed by the appearance and development of cracks. Hence the role of capillary-contraction forces in the processes of corrosion of concretes is evident.

The concept of the surface mechanism of action of the forces under study and of the possibility of controlling them is convincingly confirmed by the experimental data given in Fig. 3. The ascending portions of the curves reflect the growth of F_σ during drying of one specimen, as in Fig. 1; the descending dashed portions show the fall under the action of vapors of water or other liquids. Curve *A* shows the course of the dependence under study in the second cycle (drying—moistening), where the fall of F_σ is caused by the action of water vapor with an admixture of phenol (5% in the liquid phase). The effect of phenol consists in lowering the surface tension on the surface of the contracting water menisci—the bridges between neighboring structural elements, possibly in some hydrophobization of the surface of the solid phase and in an additional adsorp-

Fig. 3

Figure 2: Fig. 3

tion lowering of the strength of the structure. This effect is revealed during the following drying (curve), when the maximum proves to be considerably lowered.

Fig. 3. Influence of a change in the molecular nature of the liquid medium on F_σ. A—ascending branch for the second drying; descending—fall of F_σ under the influence of vapors of a 5% aqueous solution of phenol; —the maximum value of F_σ during the third drying is lowered by the action of sorption layers of phenol; the descending branch shows the fall of F_σ under the action of benzene vapor; —the maximum is reduced still more under the influence of adsorption layers of phenol and benzene; the fall of F_σ under the action of pure water vapor is greatly slowed owing to wetting hysteresis; —last drying.

An even greater decrease in the maximum value of F_σ was obtained upon subsequent action on the same specimen by benzene vapor (Fig. 3,). However, this combined effect of phenol and benzene proved to be very unstable, since after ordinary overnight holding of the specimen in an atmosphere of water vapor, F_σ during the next drying rises again, approaching the former maximum values. The action of water vapor in cycle proceeds somewhat more slowly owing to the considerable hysteresis of wetting of the surface occupied by benzene and phenol residues. The growth of F_σ is also slowed in the process of the subsequent (last) drying . The results considered allow—

make it possible to speak with confidence about the possibility of successfully combating the destructive action of capillary-contraction forces by using stable hydrophobizing sorbents.

It must be borne in mind that, in drying processes, a simultaneous complex combination is possible in one and the same system of the action of capillary-contraction forces and of the strength-reducing action of adsorption-hydrate layers. This occurs especially intensively under conditions of rapid drying, when, with considerable capillary-contraction forces and large moisture gradients in the surface layers of the structure, high stresses arise and "pre-destruction zones" (Rebinder) develop. Here, in embryonic regions of microcracks along newly formed surfaces, molecular layers of water and substances dissolved in it rapidly penetrate from deeper, wetter layers, exerting a destructive action. Therefore, alternation of drying and moistening acts the more aggressively, the sharper the transitions between the mutually replacing opposite processes.

Summarizing all the results presented here and earlier, it may be said that, under atmospheric conditions, when there are abrupt changes in the moisture content of the surface layers of cement, as well as of other inorganic and organic hydrophilic materials, there occurs a continuous and very complex interplay of oppositely directed but inseparably connected molecular-surface forces of capillary contraction and of adsorption-hydrate layers that reduce strength. The action of these forces is the cause not only of corrosion of concrete, but also of many other phenomena in nature and in technology.

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Note: Figure translations are in progress. See original paper for figures.