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## Abstract

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# ON DIFFERENCES IN THE TIMES OF COMPLETION OF HYDRATION AND OF ATTAINMENT OF THE GREATEST STRENGTH OF THE CRYSTALLIZATION STRUCTURE IN SUSPENSIONS OF HEMIHYDRATE GYPSUM

It is often assumed ($^1$) that hydration in the process of hardening of mineral binders should end earlier than the maximum strength of the hardening material is reached. This is in accord with the views of A. A. Baikov on hardening processes, according to which the formation of stone is the result of recrystallization of a gel into a polycrystalline intergrowth. However, parallel measurements of the kinetics of hardening and hydration of various specimens of hemihydrate gypsum, carried out by O. V. Kuntsevich, Ya. L. Zabezhinskii, V. B. Ratinov, and others ($^{2-4}$), as well as by P. A. Rebinder and co-workers ($^{5,6}$), showed that the endings of these processes practically coincide in time, and the prolonged hardening of gypsum specimens is in fact explained by an increase in the strength of the crystallization structure of gypsum during drying.

A more detailed study of this question, carried out by us for suspensions of $\alpha$- and $\beta$-hemihydrate gypsum of different dispersities at different values of the water–solid ratio ($W/S$), showed that, in the general case, the increase in strength ends before hydration is completed, and the difference between the durations of hydration and hardening depends on the experimental conditions. The investigations were carried out on suspensions whose solid phase consisted of 30% hemihydrate gypsum and 70% finely ground quartz sand with a conventional specific surface, determined on a Tovarov apparatus, of 3600 cm$^2$/g.

The kinetics of structure formation was studied with the aid of a conical plastometer ($^7$). The study of hydration kinetics was carried out on the same suspensions in a calorimeter with an automatically regulated adiabatic jacket ($^8$).

In Fig. 1, as an example, the results of these experiments are given, obtained for $\alpha$-hemihydrate gypsum of two different dispersities. It is seen from Fig. 1 that the maximum strength of the crystallization structure is attained considerably earlier than hydration of the hemihydrate gypsum ends. The increase in strength, associated with crystallization of the principal part of the dihydrate, is replaced by a halt in the growth of strength (Fig. 1a), and, at high dispersity of the initial hemihydrate, even by a decrease in strength before the end of hydration (Fig. 1b).

The noncoincidence in the times of completion of hydration and structure formation is characterized by a relative decrease in the time at which the structure attains the greatest strength, $t_m$, in comparison with the time of complete hydration, $\tau_H$:

$$h = \frac{\tau_H - \tau_m}{\tau_H}.$$

The greater $h$, the earlier (if time is considered in fractions of the time of complete hydration), in the process of crystallization of the newly formed products, the increase in strength ceases or even its decrease is observed. It should be noted that the presence of a decrease is especially sharply manifested···

of strength in the process of crystallization of newly formed products appears in suspensions of calcium oxide during its hydration hardening ([9]).

These phenomena are explained by partial destruction of the crystallization structure in its weakest sections under the influence of stresses arising in the process of directed growth of crystals, which are joined to one another by strong intergrowth contacts and form the framework of the crystallization structure ([10,11]). The growth of such a framework leads, on the one hand, to strengthening of the structure through an increase in the size of the crystals composing it, and, on the other hand, to the appearance of internal tensile stresses, which cause destruction of the structure and a decrease in its strength. These two processes—strengthening and destruction—proceed simultaneously and overlap one another. Depending on which process predominates, one may observe a continuous increase in strength up to the end of hydration, as occurred in the works mentioned above ([2–4]), a cessation of strength increase (Fig. 1a), or even its drop (Fig. 1b) before the end of hydration.

**Fig. 1.** Kinetics of structure formation ($P_m$) and kinetics of hydration ($q$) by heat evolution for suspensions of $\alpha$-hemihydrate gypsum at $B/T = 0.4$, $t = 18$°C. Conditional specific surface of the initial hemihydrate: $a$—3000 cm$^2$/g; $b$—9700 cm$^2$/g.

Since internal stresses are associated with the growth of the crystals composing the hardening structure, they should be stronger and should manifest themselves earlier the lower the fineness of the initial hemihydrate, when high supersaturations—at which the crystallization framework is formed—are maintained for a relatively shorter time in the system and are restored more slowly. In this case, more favorable conditions are created for the growth of the crystals composing this framework. Therefore the tensile stresses should be more sharply expressed at

**Fig. 2.** Dependence of the magnitude of relative linear expansions of specimens of $\alpha$-hemihydrate gypsum on: $a$—the fineness of the initial hemihydrate ($B/T = 0.4$), $b$—the magnitude of $B/T$ ($S_1 = 3900\ \text{cm}^2/\text{g}$), $t = 22°\text{C}$. Composition of the solid phase of the suspension: 30% hemihydrate gypsum and 70% ground quartz sand.

**Fig. 3.** Dependence

$$h = \frac{\tau_H - \tau_m}{\tau_H}$$

for suspensions of $\alpha$-hemihydrate gypsum on: $a$—the fineness of the initial hemihydrate ($B/T = 0.4$), $b$—the magnitude of $B/T$ ($S_1 = 3900\ \text{cm}^2/\text{g}$), $t = 18°\text{C}$.

at lower dispersities of the initial binder. The magnitude $B/T$ should have an analogous effect on the magnitude of the stresses, since with a decrease in $B/T$ the porosity of the structure decreases and greater obstacles are created to the free growth of crystals. The external manifestation of the internal stresses developing in the structure during its formation is expansion, which always, to a greater or lesser degree, accompanies the hardening of binders. Expansion increases with increasing internal stresses, and therefore it should increase with decreasing initial specific surface of the binder and $B/T$. Indeed, our study of the linear expansions of specimens of $\alpha$-hemihydrate gypsum at different specific surfaces of the initial hemihydrate and different $B/T$ showed that the relative magnitude of these expansions is inversely dependent on the indicated quantities (Fig. 2).

**Table 1**

| $S_1$, cm$^2$/g | $\frac{(P_m)_H - (P_m)_3}{(P_m)_H}$, $B/T = 0.4$ | $\frac{(P_m)_H - (P_m)_3}{(P_m)_H}$, $B/T = 0.6$ |
|---:|---:|---:|
| 3000 | 0.09 | 0.31 |
| 3900 | 0.12 | 0.37 |
| 7700 | 0.13 | 0.44 |
| 9700 | 0.14 | 0.46 |

**Note.** $(P_m)_H$ is the strength of the structure by the end of hydration; $(P_m)_3$ is the strength of the structure at 3 days.

The observed discrepancy between the time of completion of hydration and the attainment by the structure of its greatest strength is also the result of the action of tensile stresses. Therefore the value $h$, characterizing this discrepancy, should depend on the initial specific surface and $B/T$ in the same way as expansion. This is confirmed by the data presented in Fig. 3.

It is necessary to distinguish the arrest in the increase of strength, or the decrease of strength, occurring in the process of crystallization of newly formed phases, from the decrease in strength occurring after the end of hydration as a result of recrystallization processes, which lead to the dissolution of thermodynamically nonequilibrium crystallization contacts. In the specimens we studied, a decrease in strength due to dissolution of contacts also takes place, but it appears only in a more prolonged study of the strength of specimens stored under humid conditions. In contrast to the phenomena considered above, the decrease in strength due to dissolution of crystallization contacts occurs the more strongly, the higher the dispersity of the initial binder and the higher $B/T$ (Table 1), which agrees with previously published works [10,12].

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