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Abstract

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ON THE INDUCTION PERIOD OF STRUCTURE FORMATION DURING THE HARDENING OF HEMIHYDRATE GYPSUM

Studies of the processes of hydration and crystallization structure formation (hardening) in suspensions of β-hemihydrate gypsum have shown that both of these processes proceed with a pronounced induction period, the duration of which depends on the experimental conditions (the concentration of the hardening suspension, the quality of the initial hemihydrate gypsum and the content of dihydrate in it, the type of filler, etc.) ([1]).

The induction period of hydration is connected with the fact that, under the supersaturation that is created in a suspension of hemihydrate gypsum, the emergence of nuclei of new formations occurs comparatively slowly, which accounts for the low initial rate of crystallization of dihydrate gypsum. As nuclei accumulate, grow, and the total surface area of the new formations increases in connection with this, the crystallization rate increases. The end of the induction period of crystallization or hydration in a suspension of hemihydrate gypsum usually coincides with a sharp increase in strength; this indicates the end of the induction period of structure formation. The induction period of structure formation is taken to be the interval of time from the moment the binder is mixed with water to the moment of a sharp increase in strength, during which a continuous framework of the crystallization structure is built up. Before this framework appears, the suspension contains a coagulation structure of particles of the original binder, filler, and crystallites of the new formations. The strength of this structure, like that of any moistened coagulation structure, is very small ([2]) and during the induction period increases slowly as a result of an increase in the number of particles through the formation of microcrystallites of the new formations and the chemical binding of part of the mixing water.

The emergence of a continuous structural framework causes not only a sharp increase in strength, but also the appearance of expansion, which accompanies the entire process of formation of the hardening structure and replaces the decrease in volume due to contraction observed in the induction period of

Fig. 1

Figure 1: Fig. 1

structure formation. The duration of the induction period both of crystallization and of structure formation is determined primarily by the magnitude of the supersaturation created in the liquid phase of the hardening suspension. If this supersaturation exceeds the region of existence of metastable hydrate solutions, crystallization begins at an appreciable rate even before the solubility of the initial binder is reached and practically without an induction period. The induction period of structure formation is likewise practically absent, since the sizes of the crystallites that arise are very small and only a very small amount of hydrate is required to create a continuous framework of the hardening structure. Examples of binders of this type may be tricalcium aluminate ([3]) and calcium oxide ([4]).

With a decrease in supersaturation, the induction period of crystallization, as well as of structure formation, increases, since the larger the size of the crystallites that arise, the greater the amount of hydrate required to create a framework capable of reinforcing the entire suspension.

These regularities are clearly revealed in a comparative study of the processes of hydration and structure formation in suspensions of α- and β-hemihydrate gypsum at different temperatures. Figure 1 presents the results of such experiments for suspensions of β-hemihydrate gypsum at 20° (solubility of the initial hemihydrate $C_p = 8$ g/l), α-hemihydrate at 20° ($C_p = 6$ g/l), and α-hemihydrate gypsum at 60° ($C_p = 3.5$ g/l) ([5]). The composition of all the suspensions is the same. As can be seen from Fig. 1, in a suspension of hemihydrate gypsum the processes of hydration and crystallization structure formation proceed with a noticeable induction period, whose duration is the greater the lower the solubility of the initial hemihydrate, i.e., the smaller the supersaturation arising in the liquid phase of the suspension. The solubility of dihydrate gypsum changes very little with increasing temperature ([1,5]).

Fig. 1. Kinetics of structure formation (1), hydration (2), and dependence of the final strength of the structure on the time of repeated mixing (3) in hardening suspensions of α- and β-hemihydrate gypsum. Composition of the solid phase of the suspension: 30% hemihydrate and 70% ground quartz sand.
a $-\beta$-hemihydrate gypsum, $W/S = 0.4$, $t = 20°$;
b $-\alpha$-hemihydrate gypsum, $W/S = 0.4$, $t = 20°$;
v $-\alpha$-hemihydrate gypsum, $W/S = 0.4$, $t = 60°$.

With decreasing solubility of the initial binder, the induction period of structure formation increases rather sharply not only in time, but also in the amount of substance hydrated within it. Thus, in the case of α-hemihydrate gypsum hardening at 60°, during the induction period of structure formation about 30% of the binder hydrates, while for β-hemihydrate hardening at room temperature this value is 10%. Such an increase in the amount of substance hydrated during the induction period of structure formation leads to the fact that mechanical action on the hardening suspension, even during the induction period of structure formation, causes a sharp decrease in the strength of the hardening structure that subsequently forms. In Fig. 1, curve 3 characterizes the ability of the hardening structure to regain its strength after mechanical action causing complete destruction of the structure. The abscissa axis gives the time elapsed from the beginning of hardening to the moment of mechanical destruction of the structure, and the ordinate axis gives the final strength of the structure arising in the suspension after such destruction.

It was previously assumed that mechanical action on the hardening structure—for example, additional mixing of the suspension during the induction period of structure formation—does not cause a decrease in the strength of the structure ([6]). However, as can be seen from Fig. 1, such a statement is valid only for suspensions of β-hemihydrate gypsum, for which the induction periods of hydration and structure formation practically coincide in time. In the case of α-hemihydrate gypsum, repeated mixing of the suspension during the induction period of structure formation leads to a sharp decrease in the final strength of the structure (Fig. 1b, v).

This shows that, before the formation of a continuous framework of the hardening structure, in the induction period of structure formation the suspension already contains separate elements of the future hardening structure that are not yet connected with one another; mechanical action on these elements leads to irreversible destruction of the crystallization contacts of coalescence present in them. Subsequently, these structural elements coalesce and intertwine with one another, producing a continuous framework of the crystallization structure, whose strengthening in the course of structure formation leads to a sharp increase in strength.

These conclusions are consistent with the ideas on the mechanism of the initial formation of the hardening structure put forward in the work of P. P. Budnikov and I. V. Kravchenko ([7]).

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