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E. E. Segalova, V. N. Izmailova, and Academician P. A. Rebinder

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Abstract

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Study of the Kinetics of Supersaturation in Connection with the Development of Crystallization Structures during the Hardening of Gypsum

In disperse systems, the formation of two types of structures is possible—coagulation and crystallization structures ([1]). One of the widespread varieties of the latter are structures that arise during the hydration hardening of mineral binding substances. The strength of hardening structures is due to the formation, between individual crystallites of hydrates crystallizing out of supersaturated solutions, of strong crystallization contacts, i.e., sites of direct intergrowth. Such crystallization contacts are thermodynamically nonequilibrium formations ([2]), and their occurrence under ordinary conditions is possible only in the presence of sufficient supersaturations.

Mechanical destruction of the crystallization structure in the course of its formation is irreversible even when hydration is still far from complete ([1]). Continued hydration and the associated crystallization of the dihydrate do not then lead to the formation of a crystallization structure. This can be explained only by the fact that in this case there are no favorable conditions for the formation of crystallization contacts between individual crystallites of calcium sulfate dihydrate. Apparently, this is due to the large amount of dihydrate accumulated in the suspension.

The magnitude of supersaturation and the kinetics of its change in suspensions of hemihydrate gypsum can conveniently be observed conductometrically. In the experiments, β-hemihydrate with a nominal specific surface area $S = 3060$ cm^2/g was used. Figure 1 presents the change with time of the specific electrical conductivity, which determines the concentration of calcium sulfate or the degree of supersaturation, in suspensions with different contents of hemihydrate gypsum at a temperature of 25°. The electrical conductivity was measured by the usual method using alternating current.

First of all, it must be noted that in all suspensions of hemihydrate gypsum prepared on the basis of more than 8 g of $CaSO_4$ per 1 l, the same maximum supersaturation is observed ([3],[4]), corresponding to a $CaSO_4$ concentration of 8.0 g/l in the liquid phase of the suspension, which corresponds to the value conventionally taken as the "solubility" of the hemihydrate. This stable high supersaturation is maintained in the aqueous medium of the suspension as long

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

as the rate of entry of Ca^{++} and SO_4^{--} ions into solution compensates for the rate of their removal from solution as a result of crystallization of the dihydrate. As can be seen from Fig. 1, the higher the concentration of the suspension, the earlier the decrease in supersaturation begins and the more rapidly it proceeds.

Figure 2 shows the change with time of the specific electrical conductivity in suspensions of hemihydrate gypsum at different contents of dihydrate added during preparation of the suspension. Crystallites of calcium sulfate dihydrate, which are ready-made crystallization centers, accelerate the process of gypsum crystallization. This leads to the fact that a dihydrate content of up to 30% in the solid phase of the suspension shortens the time during which supersaturation ...

···rapidly arising, remains constant. When more than 30% dihydrate is introduced into the solid mixture, the rate of crystallization of the new phase becomes so great that the upper level of supersaturation does not have time to be reached, and a sharp decrease in supersaturation begins immediately in the suspension. The content of gypsum dihydrate in the system at which the upper level of supersaturation will no longer be reached should increase as the dispersion of the dihydrate decreases and as the dispersion of the initial hemihydrate gypsum increases.

Fig. 1. Kinetics of specific electrical conductivity in suspensions containing, in 500 ml of water: 1 –6 g; 2 –10 g; 3 –25 g; 4 –50 g; 5 –150 g of $CaSO_4 \cdot 0.5H_2O$

The dependence of the magnitude of supersaturation on the content of gypsum dihydrate in the suspension explains the effect of additions of the finished new formation—the hydrate—on the strength of the hardening structure. Fig. 3 shows the kinetics of structure formation from the increase in plastic strength ([5],[1] ,[2]) in a paste consisting of 30% hemihydrate gypsum and 70% filler (a mixture of ground quartz sand and gypsum dihydrate).

Fig. 2. Kinetics of specific electrical conductivity in a suspension of 25 g $CaSO_4 \cdot 0.5H_2O$ in 500 ml of water when dihydrate is added: 1 –0; 2 –1 g; 3 –3 g; 4 –10 g; 5 –20 g; 6 –25 g; 7 –50 g; 8 –75 g; 9 –100 g $CaSO_4 \cdot 2H_2O$

Curve 1 corresponds to the initial suspension without addition of dihydrate, and curve 2 to a suspension containing a small addition of gypsum dihydrate. This addition causes a shortening of the induction period of structure formation ([5],[1]), i.e., an acceleration of hardening, but does not affect the final strength of the structure.

Fig. 3. Kinetics of structure formation in systems containing 30% $CaSO_4 \cdot 0.5H_2O$ and 70% filler (different amounts of sand and dihydrate in the solid mixture). W/S = 0.5

Figure 3: Fig. 3. Kinetics of structure formation in systems containing 30% $CaSO_4 \cdot 0.5H_2O$ and 70% filler (different amounts of sand and dihydrate in the solid mixture). W/S = 0.5

The subsequent curves of Fig. 3, corresponding to increasing dihydrate content, show an even greater acceleration of hardening, but with an increasingly decreasing maximum level of strength.

When half or all of the sand is replaced by dihydrate (curves 6, 7), the strength of the crystallization structure decreases by a factor of 30-60 in comparison⋯

with the normal strength of gypsum stone with sand without the addition of dihydrate. It should be noted that the hydration of hemihydrate gypsum in all cases was complete, and the kinetics of hydration fully corresponded to the kinetics of structure formation (^{1}).

The decrease in the greatest strength of the crystallization structure of gypsum observed in these experiments is explained by a decrease in the maximum level of supersaturation attained in the presence of additions of dihydrate (Fig. 2). A decrease in supersaturation (the short duration of its existence) reduces the probability of intergrowth of crystallites, i.e., of the formation of crystallization contacts. With a high content of dihydrate in the suspension, only slight supersaturations arise, persisting for a short time. Under these conditions crystallization contacts practically do not arise at all, and consequently no hardening structure is formed.

Fig. 3. Kinetics of structure formation in systems containing 30% $CaSO_4 \cdot 0.5H_2O$ and 70% filler (different amounts of sand and dihydrate in the solid mixture). W/S = 0.5

It is precisely for this reason that, when a sufficient amount of the new formation —dihydrate—has accumulated in the suspension, further hydration hardening is prevented after the destruction of the crystallization structure that has not yet been completely formed.

From this point of view it is clear that in suspensions of highly dispersed calcium sulfate dihydrate, proposed by some authors as a kind of binder material (^{6}), crystallization hardening is impossible under ordinary conditions: those supersaturations which might arise in the suspension due to the colloidal fraction formed during fine grinding cannot be realized because of the enormous amount of calcium sulfate dihydrate, and recrystallization of particles of colloidal size will not lead to intergrowth of crystallites, but only to their free growth.

The strength in such systems, when their density is sufficiently high, as in the case of clays, is due to the removal of water during drying and the consequent strengthening of coagulation contacts between crystallites upon their closest approach. As is known, such structures, in contrast to crystallization structures, are extremely non-water-resistant, i.e., upon

upon moistening, completely lose strength as a result of the reversibility of the strength of coagulation contacts when the thickness of the interlayers of the aqueous medium between particles changes (7).

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