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Fig. 1

Figure 1: Fig. 1

Abstract

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CRYSTALLIZATION STRUCTURE FORMATION IN SUSPENSIONS OF TRICALCIUM ALUMINATE

The features of the processes of structure formation in aqueous suspensions of portland cement during the first hours after their preparation are determined mainly by the aluminate minerals and, above all, by tricalcium aluminate ([1,2]).

The study of these processes is of special interest, since it is precisely at this stage that one can influence the cement-water system and thus control the structure of cement stone. To establish the general laws of crystallization structure formation of the aluminate component, we studied in detail structure formation in a suspension of an individual clinker mineral—tricalcium aluminate $3CaO \cdot Al_2O_3$ (C_3A).

Fig. 1. Increase in plastic strength P_m after destruction of the crystallization structure of hydroaluminate at various stages of its formation in a suspension of 5% C_3A + 95% finely ground quartz sand + 33% H_2O based on the dry mixture: **1**—initial suspension (mixed during preparation for 45 sec.); **2, 3, 4, 5**—suspensions were remixed a second time until complete destruction of the structure, respectively, after 10, 30 min. and after 1 and 2-3 hours after preparation (the arrow indicates the moment of repeated mixing); **6**—systems **1-5**, mixed after 6 hours.

Mixtures of finely ground powders were investigated—from 1 to 5% tricalcium aluminate and 99-95% quartz sand. The processes of structure formation in such a suspension are determined exclusively by the tricalcium aluminate, while the large amount of inert filler facilitates the study of these systems ([3]) and brings the conditions of hydration of C_3A closer to those found in cement paste. The processes of structure formation were characterized by us, as previously ([1,3]), by the kinetics of increase in plastic strength, measured with the aid of a conical plastometer. After preparation, the suspension samples were placed in special vessels for measurements and stored in a desiccator over water.

In Fig. 1, for a suspension with 5% C_3A and 33% water based on the dry

Fig. 2

Figure 2: Fig. 2

mixture, the kinetics of increase in plastic strength under repeated remixing at various stages of formation of the crystallization structure of hydroaluminate are presented. In contrast to the suspensions of hemihydrate gypsum investigated by us ([3]), in suspensions of tricalcium aluminate, even at its low content and with a large amount of water, the first stage, preceding the appearance in the system of a crystallization structure,

is so short-lived that it is difficult to detect (Fig. 1, 1). Mixing the crystallization structure during its development leads to a sharp decrease in strength (Fig. 1, 2-6), while mixing after 1-2 hours practically prevents further development of the crystallization structure.

Measurements of the kinetics of the increase in plastic strength and of the chemical binding of water in suspensions of C_3A (Fig. 2) showed that both processes proceed in parallel ([3], [4]) and, at a temperature of 18-20°, are essentially completed 5-6 hours after preparation of the suspension. During the subsequent 1-2 days only a slight increase in strength is observed, accompanied by an equally slight increase in the amount of chemically bound water.

Fig. 2. Kinetics of crystallization structure formation and hydration of C_3A in the system: 5% C_3A + 95% ground quartz sand + 43% H_2O based on dry mixture. W —amount of chemically bound water, in percent of the C_3A charge.

A further increase in the strength of the crystallization structure that has formed, by approximately a factor of 2, can be achieved by drying the specimen. Subsequent moistening of the dried crystallization structure again lowers its strength to the initial value, which is explained by the effect of an adsorption decrease in strength ([5]), which in such structures with a developed internal surface should be manifested very clearly. If, however, the crystallization structure of the hydroaluminate is kept for a long time under moist conditions, then, after reaching its maximum value, its strength begins gradually to fall. This is especially pronounced in structures containing a large amount of water. Thus, in suspensions with 5% C_3A and 70-100% water based on the dry mixture, the crystallization structure, reaching a plastic strength of 1-2 kg/cm^2, proves after 20 days from preparation to be completely destroyed (the residual strength, of the order of 0.1 kg/cm^2, corresponds to a coagulation structure of free hydroaluminate crystals and sand). By analogy with the crystallization structure of calcium sulfate dihydrate ([6]), these phenomena are explained by the gradual dissolution of thermodynamically nonequilibrium crystallization contacts formed between hydroaluminate crystals during the emergence and development of the crystallization structure. In accordance with the lower solubility of the hydroaluminate in comparison with calcium sulfate dihydrate, in the crystallization structure of the hydroaluminate the dissolution of contacts and recrystallization proceed

considerably more slowly. These processes are accelerated when the temperature is raised, when, along with ordinary recrystallization, transformation of the hexagonal form of the hydroaluminate into the cubic form occurs.

In recent years, a plasticizing additive—sulfite-alcohol stillage (SAS)—has come into wide use in construction practice. Its effect on cement paste is determined mainly by adsorption interaction with the aluminate component of cement clinker ([1], [2]). In this connection it was important to investigate the effect of SAS additions on structure formation in suspensions of tricalcium aluminate. These investigations showed that the SAS additive, adsorbing on the surface of C_3A particles, on the one hand slows the processes of structure formation and hydration, as well as the crystallization of new formations, and on the other hand, ···

causing adsorption peptization and dispersion of the initial C_3A particles, accelerates these processes. In addition, an SSB additive, like any organic surfactant, adsorbing on the surface of the newly formed phases, blocks sites of possible contacts and thus lowers the strength of the crystallization structure. The overall influence of the additive on the strength of the crystallization structure depends on which of the indicated factors proves predominant at a given concentration of the additive.

Table 1 presents the kinetics of the increase in plastic strength and of the chemical binding of water in a suspension with 5% C_3A. The SSB additive was introduced with the mixing water. As can be seen from Table 1, SSB additives up to 1% retard the kinetics of strength increase and of chemical binding of water, and also reduce the final strength of the crystallization structure of hydroaluminate.

Table 1

Increase in plastic strength P_m and chemical binding of water W in a suspension containing 5% C_3A and 43% water per dry mixture (during preparation the mixture was ground for 45 sec.)

Time from the start of the experiment	0	0.5	1	3	5	8
Concentration of SSB, % of solid phase I. P_m in kg/cm^2	**0**	**0.5**	**1**	**3**	**5**	**8**
1 min.	0.004	0.002	0.002	0.002	0.002	0.002
5 min.	0.37	0.12	0.40	0.002	0.002	0.002
10 min.	1.4	0.14	0.70	0.66	0.002	0.002
30 min.	4.7	0.16	0.74	7.0	15.0	4.2
1 hour	6.0	0.19	0.85	10.0	27.5	41.0
3 hours	7.4	0.22	1.0	14.0	40.0	58.0
6 hours	7.8	0.27	1.2	16.0	48.0	72.0
1 day	8.0	0.40	2.0	20.0	55.0	82.0
3 days	8.0	0.65	2.4	20.0	56.0	82.0
5 days	8.0	2.1	3.6	20.0	55.0	81.0
10 days	8.0	4.0	4.2	20.0	56.0	80.0

Time from the start of the experiment	0	0.5	1.0	3.0
Concentration of SSB, % of solid phase	**0**	**0.5**	**1.0**	**3.0**

Figure 3: Microphotographs of C_3A suspensions

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Time from the start of the experiment	0	0.5	1.0	3.0
II. W **in % on** C_3A*				
30 min.	26.6	18.5	21.4	18.7
1 hour	31.0	21.5	23.6	21.4
2 hours	31.5	24.5	28.3	30.0
4 hours	36.0	26.7	32.4	35.6
8 hours	41.0	29.6	33.5	38.4
1 day	41.5	32.0	35.7	39.8
2 days	41.6	36.7	36.5	–
3 days	41.9	36.7	39.9	41.5
5 days	41.3	38.5	39.7	41.8
10 days	41.0	42.2	40.5	–

* According to the formula $C_3A \cdot 6\,aq$, $W \approx 40\%$.

Microscopic observations carried out on C_3A suspensions (Fig. 3) showed that at small additions of SSB a retardation of hydration is indeed observed, and this ultimately leads to the formation of larger hydroaluminate crystals than in the absence of the additive.

Fig. 3. Microphotographs of suspensions of C_3A (400×): **a, b** –0.7% suspension in water; **c, d** –the same in a 0.01% CCB solution; **e, f** –5% suspension in a 10% CCB solution. Photographs **a, c, e** relate to samples taken from the suspensions immediately after preparation (30 sec of stirring); photographs **b, d, f** were taken after 3 days. Hydration of C_3A took place in a microcuvette made from a slide and cover glass, into which the suspension sample was placed 30 min after preparation.

(Fig. 3e). The decrease in the strength of the crystallization structure is apparently explained by the fact that, when hydration is slowed, the probability of formation of thermodynamically nonequilibrium contacts decreases and, consequently, that part of the strength which is due to these contacts is reduced. The adsorption-blocking action of the additive also contributes to the reduction in strength.

With increasing concentration of the surface-active additive, both the retardation of hydration caused by it and its dispersing effect on the initial particles

of C_3A increase (Fig. 3d). The retardation of the growth of nuclei of the new phase—that is, of crystallization—caused by adsorption layers leads to the appearance of a distinct induction period of structure formation, which is the longer the greater the amount of CCB additive introduced. Special experiments showed that the amount of chemically bound water during the induction period is practically equal to zero. Intensive hydration, and in parallel with it the increase in plastic strength, begin after the end of the induction period and lead to the appearance in the system of a crystallization structure of hydroaluminate with very high strength. Stabilization of the nuclei by adsorption layers of the additive slows crystallization and prevents the formation of protective coatings of hydrate neoformations on the surface of the primary C_3A particles. All this ensures the occurrence, during the induction period, of high supersaturation, creating favorable conditions for the formation of a large number of crystallization contacts and for the creation of high strength in the resulting crystallization structure. At large CCB additions the strength of the crystallization structure of hydroaluminate may increase 8-10 times in comparison with the strength without additive. At the same time, an unusually strong refinement of the crystallites of the hydroaluminate being formed is observed (Fig. 3e): individual hydroaluminate crystallites cannot be distinguished even in an electron microscope at a magnification of 40,000. This is also indicated by adsorption measurements in dilute C_3A suspensions. The greatest adsorption of CCB after the completion of hydration reaches 4.5 g of CCB per 1 g of C_3A.

With a still greater increase in the concentration of the additive, the strength of the crystallization structure of hydroaluminate decreases, since the effect of stabilization and blocking of possible contact sites due to adsorption of CCB becomes predominant.

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