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Abstract

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On the Formation of Metastable Hydrates in the Process of Hydration of Tricalcium Silicate in Water and in Solutions of Calcium Chloride

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The work carried out during the last decade by Brunauer and coworkers (^{1}), Bernal (^{2}), Taylor (^{3}), Krasil' nikov (^{4}), and others was devoted mainly to the study of the hydration processes of calcium silicates and to investigation of the chemical nature of the products obtained thereby. In these works the relation between the processes of hydration and hardening was not studied. Investigations undertaken in our laboratory in this direction (^{5}) showed that the hardening of calcium silicates, like that of other inorganic binders, is connected with the formation of dispersed crystallized structures in the process of crystallization of newly formed products (hydrosilicates) from a supersaturated solution.

In the present work we give the results of long-term measurements of the increase in plastic strength (P_m) (^{6}) and of the amount of chemically bound water in suspensions of tricalcium silicate (C_3S) gauged with water and with solutions of calcium chloride.

To investigate the hardening processes, suspensions were taken that contained a mixture of C_3S and finely ground calcite used as a filler ($S_1 = 5200$ cm^2/g)* at $W/S = 0.29$. In determining the amount of chemically bound water, suspensions without filler were used, the ratio H_2O/C_3S in them being kept the same as in the hardening suspensions containing filler.

Determination of the amount of water chemically bound by the silicates was carried out on the basis of methods developed by Copeland (^{7}) and Taylor (^{3}). The pastes were dried for 3–4 hours at $t = 20°$ in a vacuum oven at $p =$ 8-10 mm Hg. After drying, the specimens were kept for 5 days over anhydrone ($P_{H_2O} = 5 \cdot 10^{-4}$ mm Hg) and were again subjected to drying in a vacuum oven at 80° and $p =$ 8-10 mm Hg for 4-5 hours. If, during repeated storage over anhydrone, the weight of the specimens did not change over the course of a day, the drying was considered complete.

Specimens gauged with solutions of calcium chloride, before determination of the amount of chemically bound water, were first washed with alcohol until a negative reaction for chloride ion in the wash waters was obtained.

Figure 1. Kinetics of structure formation in suspensions of C_3S mixed with water and calcium chloride solutions. Suspension composition: 3% C_3S + 97% $CaCO_3$ + 29 ml H_2O per 100 g dry mixture. $S_1 = 3$ m^2/g (BET). a –H_2O, b –0.5 N $CaCl_2$ solution, v –1 N, g –6 N, d –3 N $CaCl_2$ solution.

Figure 1: Figure 1. Kinetics of structure formation in suspensions of C_3S mixed with water and calcium chloride solutions. Suspension composition: 3% C_3S + 97% $CaCO_3$ + 29 ml H_2O per 100 g dry mixture. $S_1 = 3$ m^2/g (BET). a –H_2O, b –0.5 N $CaCl_2$ solution, v –1 N, g –6 N, d –3 N $CaCl_2$ solution.

Analyses of these suspensions for chemically bound chloride ion confirmed the conclusion of the preceding work ([8]) that calcium chloride does not enter into chemical interaction with calcium hydrosilicates. The hardening specimens were periodically subjected to X-ray diffraction analysis, which made it possible to judge the completion of hydration from the disappearance of the lines of anhydrous tricalcium silicate. For the experiments a highly dispersed silicate with a specific surface $S_1 = 3$ m^2/g by BET was used.

The results obtained show that the increase in strength in C_3S suspensions proceeds nonuniformly (Fig. 1); moreover, from comparison of the data of Fig. 1 and Table 1 it is seen that a noticeable increase in strength continues after the amount of chemically bound water ceases to change–

* By the air-permeability method.

increases, reaching its maximum value. This maximum value corresponds to the theoretical value calculated from the Brunauer equation (0.238 g H_2O per 1 g C_3S); therefore it might be supposed that it indicates the completion of hydration of C_3S. However, X-ray diffraction studies showed that a constant value of chemically bound water does not indicate the complete conversion of tricalcium silicate into hydrosilicate. Thus, by 20 days in the case of water and by 5–10 days in the case of 3 N and 6 N calcium chloride solutions, the complete set of lines characteristic of C_3S is still very clearly delineated on the Debyegrams.

Fig. 1. Kinetics of structure formation in suspensions of C_3S mixed with water and calcium chloride solutions. Suspension composition: 3% C_3S + 97% $CaCO_3$ + 29 ml H_2O per 100 g dry mixture. $S_1 = 3$ m^2/g (BET).
a –H_2O, *b* –0.5 N $CaCl_2$ solution, *v* –1 N, *g* –6 N, *d* –3 N $CaCl_2$ solution.

set of lines characteristic of C_3S. Taking into account that an unchanged content of chemically bound water is observed with a continuous

Table 1

Kinetics of chemical binding of water (g H_2O per 1 g C_3S) during the hydration of tricalcium silicate in water and in calcium chloride solutions, $B/T = 2.9$

Time after mixing	$CaCl_2$ content, g-eq/l	$CaCl_2$ content, g-eq/l	$CaCl_2$ content, g-eq/l	Time after mixing	$CaCl_2$ content, g-eq/l	$CaCl_2$ content, g-eq/l	$CaCl_2$ content, g-eq/l
	0	3	6		0	3	6
3 hours	0.018	0.142	0.108	30 days	0.238	0.237	0.240
1 day	0.153	0.192	0.164	45 ”	0.235	0.238	0.238
5 days	–	0.238	0.266	60 ”	0.222	0.237	0.238
10 ”	0.222	–	–	90 ”	–	0.240	–
15 ”	–	0.235	0.236				

decrease of the initial silicate, it can be explained only by the fact that at the beginning of hydration a metastable, more highly hydrated hydrate is formed, which then transforms into a stable, less hydrated one, while the water released in this process is absorbed by the hydrating silicate. In those cases where, during the hydration of a binder, a metastable hydrate forms, hardening may also occur after the completion of hydration as a result of recrystallization of the more soluble metastable hydrate into a less soluble and more stable one. In the present case, the metastable

hydrate plays the role of the initial binder, maintaining the supersaturations necessary for the formation of the hardening structure. Such posthydration hardening is clearly observed in suspensions of C_3S mixed with calcium chloride solutions, in which by 45 days the lines of C_3S are completely absent from the diffractograms, but a noticeable increase in strength continues for 3-4 months. When silicate is mixed with water, posthydration hardening was observed by Bogom (9). The hypothesis of the formation of metastable compounds in the course of hydration of tricalcium silicate under conditions of concentrated suspensions agrees with the results of Brunauer’ s latest work (10), in which it was shown that at the beginning of the process of silicate hydration more highly basic tobermorites are formed than the sesquicalcium hydrosilicate.

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