The Influence of Calcium Chloride on Structure-Formation Processes in Aqueous Suspensions of Tricalcium Aluminate

1958

SovietRxiv

Abstract

Full Text

Physical Chemistry

E. P. Andreeva, E. E. Segalova, and E. E. Volynets

The Influence of Calcium Chloride on Structure-Formation Processes in Aqueous Suspensions of Tricalcium Aluminate

(Presented by Academician P. A. Rebinder, 4.VIII.1958)

The mechanism of the influence of calcium chloride on the processes of setting and hardening of cement, despite numerous studies (^{1}), has not been definitively clarified. A number of authors have shown that calcium chloride enters into chemical interaction with the aluminate component of cement clinker during hydration, with the formation of calcium hydrochloroaluminate (^{2}). However, until recently it has remained unclear how the formation of this compound affects the initial stage of structure-formation processes.

It has been suggested that this influence is associated with the chemical dispersion of the solid phase as a result of tensile stresses arising during the formation of hydrochloroaluminate (^{3}). This dispersion accelerates setting and hardening owing to the increase in the specific surface area of the cement. However, it can hardly be assumed that dispersion is the sole cause of such a sharp acceleration of the setting and hardening processes as is observed when sufficiently large additions of calcium chloride are introduced. Moreover, it does not explain why, in the presence of small and medium amounts of calcium chloride additions, not an acceleration but, on the contrary, a retardation of the setting processes is observed.

To elucidate the mechanism of the influence of calcium chloride on Portland cement, it is first of all necessary to study its influence on structure-formation processes in suspensions of tricalcium aluminate (C_3A)—an individual mineral of cement clinker that determines the character of structure-formation processes in the first stages of the interaction of cement with water. For this purpose, the kinetics of structure formation and chemical interaction were investigated in suspensions of C_3A and its hydrate $C_3A \cdot \mathrm{aq}$ ($3\mathrm{CaO} \cdot \mathrm{Al_2O_3} \cdot 6\mathrm{H_2O}$), gauged with calcium chloride solutions of various concentrations.

Experience has shown that, for studies of this kind, the most rational approach is to use mixtures containing from 2 to 10% binder and 98-90% inert filler –ground quartz sand or calcite (^{4}). Concentrated suspensions were prepared from these mixtures by impregnating the appropriate mixture, which prevented the possibility of destroying the crystallization structure that arises in the suspension immediately after it is gauged. The specimens were kept over water

Fig. 1. Kinetics of chemical binding of calcium chloride in suspensions of tricalcium aluminate and its hexahydrate.

Figure 1: Fig. 1. Kinetics of chemical binding of calcium chloride in suspensions of tricalcium aluminate and its hexahydrate.

and over the corresponding calcium chloride solutions. The structure-formation processes in the suspensions were characterized by the kinetics of increase in plastic strength (^{5}). The results of these experiments are presented in Figs. 1-3.

The final amount of bound calcium chloride (Fig. 1) is the same in all the suspensions investigated and amounts to 0.75 mol $CaCl_2$ per 1 mol C_3A. X-ray diffraction and thermographic studies showed that,

in all suspensions in which the amount of calcium chloride is sufficient to bind all the C_3A or its hydrate, one and the same compound is formed. The Debyegrams and thermograms of the product formed correspond to those given in the literature for the monochloride form of hydrochloroaluminate and to those that we also obtained for calcium hydrochloroaluminate synthesized by Fore' s method (^{2}).

The kinetics of the chemical binding of calcium chloride depend strongly on the composition of the suspension and especially on the concentration of the calcium chloride solutions. In suspensions of hydroaluminate, the chemical interaction initially proceeds more slowly than in a suspension of C_3A, owing to the lower solubility and

Fig. 1. Kinetics of the chemical binding of calcium chloride in suspensions of tricalcium aluminate and its hexahydrate, containing 3% $C_3A + 97\%$ finely ground quartz sand +35 ml of calcium chloride solution per 100 g of dry mixture (A), and 4.2% $C_3A \cdot aq + 95.8\%$ finely ground quartz sand +33 ml of calcium chloride solution per 100 g of dry mixture (B).
1–0.31 N $\mathrm{CaCl_2}$ solution, $n = 0.5$ (A); 2–1.58 N, $n = 2.5$ (A); 3–6.35 N, $n = 10$ (A); 4–0.31 N, $n = 0.47$ (B); 5–1.58 N, $n = 2.35$ (B); 6–3.17 N, $n = 4.7$ (B); 7–6.34 N, $n = 9.4$ (B).

the lower rate of dissolution of the hydrate in comparison with the anhydrous compound (^{6}), but subsequently the rate of binding increases and in all cases is already completed by the second day. In C_3A suspensions, in which, owing to the high rate of dissolution of C_3A and its increased solubility, higher supersaturations with respect to calcium hydrochloroaluminate may arise, the formation of hydrochloroaluminate at first proceeds very rapidly, but then, at medium additions of $\mathrm{CaCl_2}$, the process slows down and, for example, in suspensions with a molecular ratio of $\mathrm{CaCl_2}$ to C_3A, n, equal to 2.5, is completed only after 5-10 days. By analogy with the conditions of formation of hydrosulfoaluminate (^{7}), this can be explained by the retarding influence of microcrystals of hydrochloroaluminate that have arisen at high supersaturations and formed protective films

Figure 2. Kinetics of structure formation in suspensions of tricalcium aluminate containing 3% C_3A + 97% finely ground quartz sand + 35 ml of calcium chloride solution per 100 g of dry mixture. 1—H_2O; 2—0.31 N $CaCl_2$ solution, $n = 0.5$; 3—1.58 N, $n = 2.5$; 4—3.17 N, $n = 5.0$; 5—6.34 N, $n = 10.0$.

Figure 2: Figure 2. Kinetics of structure formation in suspensions of tricalcium aluminate containing 3% C_3A + 97% finely ground quartz sand + 35 ml of calcium chloride solution per 100 g of dry mixture. 1—H_2O; 2—0.31 N $CaCl_2$ solution, $n = 0.5$; 3—1.58 N, $n = 2.5$; 4—3.17 N, $n = 5.0$; 5—6.34 N, $n = 10.0$.

on the surfaces of the initial C_3A particles, which slows their dissolution. In suspensions of C_3A gauged with highly concentrated calcium chloride solutions,

($n = 5$ and 10), the formation of hydrochloraluminate proceeds extremely rapidly and is almost completely finished already after 30 min.

The kinetic features of the interaction of C_3A and its hydrate with calcium chloride also determine the features of the structure-formation processes occurring in these suspensions (Figs. 2 and 3). Although in all suspensions in which $n > 1$ the amount of hydrochloraluminate formed is the same, the strength of the hardening structures that arise is different, which indicates a strong dependence of the strength of the crystallization structure on the conditions of its formation.

Fig. 2. Kinetics of structure formation in suspensions of tricalcium aluminate containing 3% C_3A + 97% finely ground quartz sand + 35 ml of calcium chloride solution per 100 g of dry mixture.
1—H_2O; 2—0.31 N $CaCl_2$ solution, $n = 0.5$; 3—1.58 N, $n = 2.5$; 4—3.17 N, $n = 5.0$; 5—6.34 N, $n = 10.0$.

In suspensions of C_3A containing small additions of calcium chloride ($n < 1$), the increase in strength continues even after all the calcium chloride has been bound, which indicates subsequent crystallization of hydroaluminate. The crystallization structure of hydrochloraluminate that forms initially in this suspension has very low strength, apparently owing to the strong refinement of the hydrochloraluminate crystals arising at high supersaturations. The retarding effect of calcium chloride on the structure-formation process of C_3A is thus reduced to the fact that, instead of a sufficiently strong crystallization structure of hydroaluminate, a weak fine-crystalline structure of hydrochloraluminate arises in the suspensions, easily destroyed by mechanical action. The same weak structure arises in a suspension contain-

containing a large addition of calcium chloride ($n = 2.5$). The strength of this structure 3 hours after mixing is only 750 g/cm^2, although by this time the reaction of formation of hydrochloraluminate has already proceeded by approximately 40%. Subsequently, in the course of the slower crystallization of hydrochloraluminate and the overgrowth of the initially formed framework (^{8}), the strength of this structure increases and by the end of the process proves to be higher than in the C_3A suspension mixed with water.

Fig. 3. Kinetics of structure formation in suspensions of six-water tricalcium hydroaluminate containing 4.2% $C_3A \cdot aq$ + 95.8% finely ground quartz sand + 33 ml of calcium chloride solution per 100 g of dry mixture.
1 –0.31 N $CaCl_2$ solution, $n = 0.47$; 2 –1.58 N, $n = 2.35$; 3 –3.17 N, $n = 4.7$; 4 –6.34 N, $n = 9.4$

In the presence of large additions of calcium chloride ($n = 5$ and 10), when the reaction of hydrochloraluminate formation proceeds very intensively, a rapid increase in strength occurs in the suspensions; after reaching its maximum value, the strength begins to decrease (Figs. 2, 4 and 5; Fig. 3, 4). The drop in strength is connected in this case with a considerable expansion of the system. The increase in volume due to expansion in suspensions with $n = 10$ reaches 20%.

Department of Colloid Chemistry
Moscow State University
named after M. V. Lomonosov

Received
10 VII 1958

REFERENCES CITED

1. A. A. Baikov, *Collected Works*, **5**, 1948; V. M. Moskvin, *Additives–Accelerators of Concrete Hardening*, 1938; R. H. Bogue, *The Chemistry of Portland Cement*, N. Y., 1955.

2. L. S. Wells, J. Res. Nat. Bur. Stand., **1**, 4, 951 (1928); J. Foret, *Recherches sur les combinaisons entre les sels de calcium et les aluminates de calcium*, Paris, 1935; R. Nacken, R. Mosebach, Zs. anorg. u. allgem. Chem., **228**, 19 (1936).

3. Yu. A. Savvina, N. N. Serb-Serbina, *Stroit. prom.*, **9**, 6 (1954); N. N. Serb-Serbina, Yu. A. Savvina, *Cement*, No. 2, 3 (1955); N. N. Serb-Serbina, Yu. A. Savvina, V. S. Zhurina, DAN, **111**, No. 3, 659 (1956); V. V. Kind, E. V. Lavrinovich, R. E. Litvinova, *Cement*, No. 3, 7 (1955).

4. E. E. Segalova, E. S. Solov' eva, P. A. Rebinder, DAN, **113**, No. 1, 134 (1957).

5. E. E. Segalova, P. A. Rebinder, O. I. Luk' yanova, *Vestn. MGU*, No. 2 (1954); P. A. Rebinder, E. E. Segalova, *Priroda*, No. 12 (1952).

6. E. E. Segalova, E. S. Solov' eva, P. A. Rebinder, DAN, **117**, No. 5, 841 (1957).

7. E. E. Segalova, P. A. Rebinder, Abstracts of Reports, 4th All-Union Conference on Colloid Chemistry, Tbilisi, 1958, p. 130.

8. Du Yu-zhu, ibid., p. 133.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.