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Abstract

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ON THE FORMATION OF THE α-HYDRATE OF DICALCIUM SILICATE

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α-$2CaO \cdot SiO_2 \cdot H_2O$ is a synthetic hydrosilicate formed in the reaction between CaO and SiO_2 under hydrothermal conditions (1); it may be present in lime-sand building materials and cements treated in an autoclave (2). Its negative effect on the strength of these products is known (3). Nevertheless, the properties of the α-hydrate itself have by no means been studied. A preliminary, very incomplete, analysis of its structure (4) cannot explain the peculiarities of its behavior under hydrothermal conditions.

We studied the process of formation of α-$2CaO \cdot SiO_2 \cdot H_2O$ from mixtures of calcium oxide and crystalline silica at 170–175°, which corresponded to a pressure in the autoclave equal to 8 atm. CaO was obtained by calcining natural calcite at 1000°. Finely ground rock crystal was used as crystalline SiO_2. The ratio $CaO : SiO_2$ in all the mixtures studied was 2:1. The amount of liquid phase exceeded the solid phase by a factor of 20. The duration of treatment ranged from 2 hr (2, 4, 6, etc., up to 24) to several days (2, 3, 5, 10, 15, 20). After the required holding time, the autoclaves containing the samples were quenched in water. The study was carried out by differential-thermal analysis, X-ray, and chemical methods. Special attention was devoted to microscopic study of the preparations in immersion.

The results of the investigation made it possible first of all to present the possible course of formation of α-$2CaO \cdot SiO_2 \cdot H_2O$. The precursor of the α-hydrate is, in our opinion, a finely dispersed, isotropic hydrosilicate, almost amorphous to X-rays, which we designated X and which has a $CaO : SiO_2$ ratio below 2.

A clear picture of the transformation of hydrosilicate X into the α-hydrate was provided by microscopic study. Thus, after 6-hour treatment, the sample contained, along with birefringent $Ca(OH)_2$, a fine-grained, extremely weakly birefringent mass with an average refractive index of 1.57. The differential-thermal analysis curves in Fig. 1 show an endothermic reaction at approximately 500-520° (curves 1-6, 8, 11), characteristic of calcium hydroxide, and, in the range 700–800°, one probably characteristic of hydrosilicate X, since no other phases capable of giving such a halt were found. Increasing the holding time to 8 hr led

Figure 2. Microphotographs of the products of hydrothermal synthesis after 8 (1), 10 (2), 12 (3), 16 (4), and 24 (5) hours of treatment in crossed nicols. 450×

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Fig. 1. Curves of differential thermal analysis of the products of hydrothermal synthesis

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to coarsening of the grains of hydrosilicate X (Fig. 2, 1), some of which acquired birefringence and increased their refractive index to 1.64–1.65. Finally, after 10-hour synthesis, the sample consisted almost entirely of birefringent plates (Fig. 2, 2) of α-$2CaO \cdot SiO_2 \cdot H_2O$ ($N_g = 1.633$; $N_p = 1.614$).

A reliable indication of the α-hydrate is an endothermic reaction below 500° (Fig. 1, 3–12). According to chemical-analysis data, the amount of $Ca(OH)_2$ in the sample not bound in hydrosilicate proved to be minimal. Analysis of the ionization curves of intensity (Fig. 3) and calculations showed that only two lines, 3.02 Å and 1.82 Å, are characteristic of hydrosilicate X. On

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on the X-ray diffraction patterns of the specimens after 6- and 8-hour synthesis, the lines 3.02 and 1.82 are the strongest. As the α-hydrate forms, the intensity of these lines decreases appreciably (Figs. 3, 3). At the same time, the amount of free $Ca(OH)_2$ also decreases. The change in the relative amounts of hydrosilicate X and α-hydrate can be followed by comparing the intensities of the principal maxima, marked on the X-ray patterns as X and α, respectively.

Further study of mixtures obtained after longer syntheses revealed special features in the behavior of the α-hydrate. Thus, the specimen after a 12-hour holding period (Figs. 2, 3) presented an unexpected picture: most of the α-hydrate crystals proved to be destroyed, comminuted, and in part to have lost their birefringence. The amount of free $Ca(OH)_2$ increased. The intensity of the lines 3.02 and 1.82 increased to strong (Figs. 3, 4, 5).

Subsequently, α-hydrate crystallizes again. The amount of free $Ca(OH)_2$ decreases (in the specimen after 16-hour synthesis) until it disappears completely (18-hour synthesis). The line 3.02 on the X-ray pattern of this specimen acquired a diffuse character, while the line 1.82 almost disappeared (Fig. 3, 6). The X-ray pattern corresponds to
α-$2CaO \cdot SiO_2 \cdot H_2O$.

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Fig. 3. Ionization intensity curves of the products of hydrothermal synthesis

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hydrothermal synthesis

The periodicity in the assimilation of calcium hydroxide is also manifested at longer holding times. Thus, an insignificant amount of free $Ca(OH)_2$ appears in the specimens after 22-hour synthesis (Fig. 1, 8) and even after 15-day synthesis (Fig. 1, 11). Synthesis for 20 days led to the formation of a fibrous hydrosilicate, $\beta\text{-}2CaO \cdot SiO_2 \cdot H_2O$, which we identify with hillebrandite.

The reason for the destruction of the α-hydrate with a simultaneous increase in the content of free $Ca(OH)_2$ and hydrosilicate X in the specimen, in our opinion, is as follows.

The formation of the structure of the α-hydrate apparently occurs through the addition of calcium hydroxide to hydrosilicate X. In this case, in the initial stage of the process, a disordered joint crystallization of $\alpha\text{-}2CaO \cdot SiO_2 \cdot H_2O$ with $Ca(OH)_2$ is possible.

The tendency toward easy decomposition of aggregates of α-hydrate with hydroxide, with detachment of the latter, follows from preliminary structural considerations, namely: there is nothing in common between the structure of α-hydrate and $Ca(OH)_2$. Subsequently, under conditions favorable for the existence of the α-hydrate, well-formed crystals of this compound grow (Fig. 2, 5).

Since the hydrothermal synthesis conditions are not ideal for the growth of perfect crystals, defective crystals of the α-hydrate, or separate regions of them, which undergo destruction, may also subsequently form. This is why a small amount of free $Ca(OH)_2$ appears periodically.

Fig. 3. Ionization intensity curves of the products of hydrothermal synthesis

Under the microscope, the decomposing α-hydrate has pitted edges; some plates are strongly corroded (Fig. 2, 4). At times the corrosion proceeds so deeply that the crystals lose birefringence. In this case their refractive index decreases and varies from 1.57 to 1.6. The loss of birefringence is associated with possible partial amorphization. Nevertheless, the plates retain the habit of the α-hydrate, forming pseudomorphs.

The ability of the α-hydrate to take up calcium hydroxide and to split off the latter is the reason for the nonconstancy of the composition proposed by Kalousek (1) in the form $1.5—2.4\ CaO \cdot SiO_2 \cdot 1—1.25\ H_2O$, and may partly explain the cyclic variation in the strength (5) of autoclaved building materials.

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