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ON METASTABLE SOLUTIONS OF CALCIUM SILICATES

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Classical physicochemical studies of the system $CaO–SiO_2–H_2O$ and of the hydration processes of anhydrous calcium silicates β-Ca_2SiO_4 (β-C_2S) and Ca_3SiO_5–(C_3S) ([1-5]) leave open the question of the conditions of formation and the properties of metastable solutions that arise as an intermediate stage in the interaction of these compounds with water.

The works of P. A. Rehbinder and co-workers ([6-9]) showed that the physicochemical basis of the hardening processes of inorganic binders is the formation of dispersed crystallization structures that arise and develop in a medium supersaturated with respect to the hydration products of anhydrous binders. In this process the decisive role belongs to the magnitude and kinetics of the change in the concentration of supersaturated solutions. In the present work the formation of supersaturated solutions during the hydration of β-C_2S and C_3S was investigated, and the metastable solubility of these silicates was established as a function of the concentration of $Ca(OH)_2$ liberated as a result of their interaction with water. The change in the composition of the aqueous phase during the hydration of silicates was studied under conditions protected from CO_2 in the air, using dilute suspensions (0.04-2.0% silicates), by direct measurements of the concentrations of Ca and silicate ions (conventionally SiO_2) at a sufficiently high stirring rate. The anhydrous silicates were synthesized at 1500° from chemically pure oxides and contained: β-C_2S, 96%, and C_3S, 90% of the principal mineral, with an admixture of low-basicity silicates and with complete absence of free CaO. SiO_2 determinations were carried out by the colorimetric method using the blue silicomolybdate complex; Ca, by the complexometric method.

Determination of the composition of the aqueous phase during the hydration of calcium silicates at 20 and 30° (β-C_2S–Fig. 1*a*, C_3S–Fig. 1*b*) showed that the concentration of silicate ions passes through a maximum, the time required to reach it decreasing with increasing concentration of the suspensions and fineness of the anhydrous silicates, as well as in going from β-C_2S to C_3S under otherwise equal conditions. In the same order there occurs a gradual decrease in the SiO_2 concentration to practically 0. At the same time the concentration of Ca^{++} continues to increase, amounting to 8-10 mmol/l with almost complete

Fig. 1

Figure 1: Fig. 1

disappearance of SiO_2 from the solution.

The maximum concentrations of SiO_2 (C_m), or the equivalent amounts of silicates in solution, are invariant only in a first approximation and, unlike nonhydrolyzing binders, in particular gypsum, the period of their existence in the suspension is very short. The apparent absence of a prolonged period of high concentrations of supersaturated solution, especially noticeable with increasing concentration of the anhydrous silicate already within the range of dilute suspensions, may lead to the erroneous conclusion that supersaturation plays an insignificant role as a structure-forming factor in the case of calcium silicates. As will be seen below, all these features are explained by the dependence of the solubility of silicates on the concentration of $Ca(OH)_2$ liberated during hydrolysis. For the same reason, the solubility of β-C_2S and C_3S in water, determined by an indirect method ([10]), cannot be attained under the real conditions of silicate hardening. It is natural to assume that, like the equilibrium solubility of hydrosilicates,

it decreases as the concentration of $Ca(OH)_2$ released in this case during the hydrolysis of anhydrous silicates increases.

Comparison of the concentrations of Ca and SiO_2 in the aqueous phase of suspensions of β-C_2S and C_3S shows that, when C_{max} is reached, an excess of $Ca(OH)_2$ has already formed in the solution relative to the stoichiometric value of the $Ca(OH)_2$ concentration. Thus, for example, at 30°, by the time C_{max} is reached—1.05 mmol/l for β-C_2S and 1.07 mmol/l for C_3S—the CaO/SiO_2 ratio in solution increases from the initial value of 2 to 3 for C_2S and from 3 to 3.8 for C_3S. Thus, the concentrations C_{max} determined by us already correspond to solutions of $Ca(OH)_2$ of definite concentration, which is not the same for β-C_2S and C_3S.

Fig. 1. Kinetics of formation of supersaturated solutions of calcium silicates. **a**—β-C_2S (30°): 1—0.08; 2—0.2; 3—0.4; 4—0.8% silicate. **b**—C_3S (20°): 1—0.04; 2—0.08; 3—0.2; 4—0.4% silicate.

In this connection it is of interest to consider the results obtained in the form $SiO_2 = f(CaO)$, used in studying the system $CaO–SiO_2–H_2O$. In Fig. 2, which shows this dependence for β-C_2S at 30°, three regions can be distinguished, corresponding to three stages in the formation of supersaturated solutions of calcium silicates. The left-hand part of the graph reflects the process of dissolution of anhydrous silicates, which, as the dissolution of an ionic crystal lattice, is the transfer of the constituent ions into solution in stoichiometric ratios and, since these compounds are unstable with respect to water, is accompanied by the formation of supersaturated solutions. The molar ratio in the solution corresponding to the composition of the anhydrous silicate is shown in the graph by

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

the dashed straight line.

Fig. 2. Composition diagram of a supersaturated β-C_2S solution during its formation: **a**—suspension in water; **b**—in $Ca(OH)_2$ solution, 2 mmol/l; **c**—the same, 4 mmol/l.

Further, crystallization of a low-basicity hydrosilicate is superimposed on the dissolution process; this is expressed by the deviation of the experimental points from the straight line as a result of a change in the CaO/SiO_2 molar ratio in the solution. As a result of hydrolysis of SiO_4^{4-}, after its transfer into solution, the CaO/SiO_2 ratio in the hydrosilicate precipitate is smaller than that of the initial anhydrous silicate, which leads to accumulation in the solution of an excess of $Ca(OH)_2$. The solid hydrate formed under these conditions, both in the case of β-C_2S and of C_3S, is monocalcium hydrosilicate, which agrees with the literature data.

The right-hand part of Fig. 2 shows the decrease in SiO_2 (silicate) concentration with an increase in the total CaO content in the solution. This part of the curve does not depend on the concentration of the suspension. However, additional introduction of $Ca(OH)_2$ into the suspension lowers C_{max} and the subsequent SiO_2 concentrations to a greater extent than is required by the dependence of the SiO_2 concentration on the total calcium content in the solution.

It is more appropriate to express the dependence of the concentration of SiO_2 on the excess of Ca in comparison with the stoichiometric amount for the given silicate, or, what is the same, on the amount of $Ca(OH)_2$ released as a result of hydrolysis. The curves reflecting this dependence (Fig. 3) do not depend, within the limits of experimental error, on the concentration of β-C_2S or C_3S in the suspension, or on the initial content of $Ca(OH)_2$ in the solution (curve 1), and show the dependence of the concentration of $Ca(OH)_2$ on the metastable solubility of anhydrous silicates, which is reached after passing through C_{max} in the course of silicate hydration. Hydrolysis of the silicates with liberation of monocalcium hydrosilicate and accumulation of $Ca(OH)_2$ begins before the metastable solubility has been reached. Therefore, under real conditions of hydration of calcium silicates, their metastable solubility is always lower than the solubility in pure water.

Fig. 3. Dependence of the metastable solubility of calcium silicates on the concentration of $Ca(OH)_2$ in the solution, released during hydrolysis or introduced as an additive (30°). 1—β-C_2S: a—$Ca(OH)_2$ released during hydrolysis; b

–2 mmol/l; c–4 mmol/l $Ca(OH)_2$ introduced additionally into the suspension; 2–C_3S; 3–equilibrium solubility of hydrosilicate (11).

Comparison of the metastable solubility of silicates (C) with the equilibrium solubility (C_0) at identical concentrations of $Ca(OH)_2$ (Fig. 3, 3; data of Roller and Ervin (11)) reveals, to a first approximation, constancy of the ratios C/C_0, especially evident for β-C_2S over the entire interval of $Ca(OH)_2$ concentrations where the SiO_2 concentration can be measured. The magnitude of this ratio (4.4 for β-C_2S) may conventionally be regarded as the relative supersaturation, the constancy of which is a consequence of the identical or very similar dependence of the metastable and equilibrium solubilities of SiO_2 (silicates) on the excess of $Ca(OH)_2$.

Thus, the experimentally observed decrease in the concentration of supersaturated solutions of β-C_2S and C_3S after passing through $C_{\max}$ in the process of hydration still does not indicate a decrease in the relative supersaturation in the aqueous phase of the suspensions, but only reflects the dependence of the metastable solubility on the concentration of $Ca(OH)_2$. The period of high supersaturations during hydration of calcium silicates apparently continues even after the concentration of the saturated $Ca(OH)_2$ solution has been reached.

The invariance we have found of the concentration of supersaturated solutions with respect to the concentration of the suspension, as well as the fact that monocalcium hydrosilicate is isomorphous with the more highly basic hydrosilicates formed during hydration in concentrated suspensions (pastes), give grounds for believing that the regularities found in this work are also valid in the case of concentrated suspensions.

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