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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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Solubility of Tricalcium Silicate in Calcium Chloride Solutions

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Calcium chloride accelerates the processes of hydration and structure formation in aqueous suspensions of tricalcium silicate, without entering into chemical interaction with calcium hydrosilicates ([1]). To elucidate the mechanism of its action, it is necessary to study the influence of calcium chloride on the solubility of tricalcium silicate (C_3S).

The process of silicate dissolution was studied in dilute suspensions under vigorous stirring, ensuring that the process proceeded in the kinetic region. Specially designed experiments showed that the invariance of the results (the independence of the dissolution kinetics from the rate of stirring of the solution) in calcium chloride solutions ($C \leqslant 0.1\ N$) is observed at a considerably higher stirring rate than in water. This indicates that the elementary act of transfer of silicate from the solid phase into the liquid takes place in weak calcium chloride solutions more rapidly than in water.

Fig. 1. a –kinetics of dissolution of tricalcium silicate in a 0.1 N calcium chloride solution at different initial silicate charges: 1 –0.05 g in 100 ml of solution; 2 –0.1 g; 3 –0.15 g; 4 –0.5 g; **b** –change in CaO_{excess} during dissolution of tricalcium silicate under the conditions of Fig. 1a

The determination of the concentration of silicon ions in the liquid phase of the silicate suspension was based on the reaction forming the yellow silicomolybdenum complex $H_2[Si(Mo_2O_7)_6]$, since it was shown in ([2]) that the presence in silicate solutions of chlorides of alkaline-earth metals, even in appreciable quantities, does not interfere with the determination of silicon by means of this reaction. The content of the complex was determined colorimetrically by the procedure described in ([2]).

For a complete characterization of the silicate dissolution process, it is necessary to know not only the content of silicon ions in the solution, but also the amount of calcium ions that has passed into solution during silicate dissolution.

Fig. 2. Metastable solubility of tricalcium silicate in calcium chloride solutions of different concentrations: 1 —water, 2 —$1 \cdot 10^{-2}\,N$ calcium chloride solution, 3 —$1 \cdot 10^{-1}\,N$, 4 —$3\,N$.

Figure 2: Fig. 2. Metastable solubility of tricalcium silicate in calcium chloride solutions of different concentrations: 1 —water, 2 —$1 \cdot 10^{-2}\,N$ calcium chloride solution, 3 —$1 \cdot 10^{-1}\,N$, 4 —$3\,N$.

Determination of this quantity in calcium chloride solutions from the change in the concentration of calcium ions is impossible because of the low solubility of the silicate; therefore, the concentration of these ions was determined by titra-

of a filtered sample of the suspension with hydrochloric acid (0.1 N). Such determinations during dissolution of the silicate in water gave results fully coinciding with the trilonometrical determination of calcium. The values of $[Ca^{+2}]$ obtained by the indicated method characterize the content in the solution of calcium ions in combination with silicate and hydroxyl ions. Recalculated as CaO g/l, they are denoted by us as total CaO. The difference between the total CaO content in the solution and the CaO bound to silicate ions in the stoichiometric ratio corresponding to tricalcium silicate corresponds to the excess concentration of CaO in the solution.

The metastable solubility of monomineral binding substances, as is known, is characterized by the presence in the solution, during the hydration process, of a time-constant level of supersaturation independent of the magnitude of the initial charge of the binder ([3]). However, as was shown in the study of the solubility of calcium silicates in water ([4]), as a result of their hydrolysis and the liberation of $Ca(OH)_2$, there occurs a continuous decrease in the solubility of the silicate and a lowering of the $[SiO_2]$ content in the solution. In this case, on the curve characterizing the kinetics of the change in the concentration of SiO_2 in the liquid phase of the silicate suspension, there is no horizontal segment associated with a constant, time-invariant solubility of the initial binder.

Fig. 2. Metastable solubility of tricalcium silicate in calcium chloride solutions of different concentrations: 1 —water, 2 —$1 \cdot 10^{-2}\,N$ calcium chloride solution, 3 —$1 \cdot 10^{-1}\,N$, 4 —$3\,N$.

When tricalcium silicate is dissolved in calcium chloride solutions, as is evident from Fig. 1a, the concentration of SiO_2 in the liquid phase of the suspension likewise does not remain constant with time: the curves in Fig. 1 have a clearly expressed maximum. In addition, the values of the maximum concentration decrease strongly with increasing charge, i.e., with increasing concentration of the suspension. Thus, a false impression may be created that, during dissolution of tricalcium silicate in calcium chloride solutions, the supersaturation arising in the liquid phase depends on the charge. In reality, what is observed here is the same dependence of the metastable solubility of silicates on the content of excess lime in the solution as in the absence of calcium chloride. On comparing

the curves characterizing the kinetics of silicate dissolution and the change in the concentration of excess CaO in the liquid phase of the suspension (Fig. 1), it is seen that the decrease in $[SiO_2]$ occurs during the period of the most intense increase in the CaO content in the solution. Dissolution of the silicate under conditions in which a hydrate less basic than the initial silicate is crystallizing out occurs not in pure calcium chloride solutions, but in solutions with a gradually increasing content of calcium hydroxide. An increase in the $Ca(OH)_2$ content in the solution leads to a decrease in the metastable solubility of tricalcium silicate. Indeed, if the experimental data obtained on the kinetics of dissolution of tricalcium silicate in a 0.1 *N* calcium chloride solution are represented as the dependence of the content of dissolved silicate on the concentration of excess calcium hydroxide in it, then the points from the descending branches of all the curves shown in Fig. 1a form, in the indicated coordinates, a single straight line, independently of the concentration of the suspension. The curve obtained characterizes the dependence of the metastable solubility of tricalcium silicate on the concentration

excess CaO in a 0.1 N calcium chloride solution (Fig. 2). The curves of the metastable solubility of tricalcium silicate in 0.01 N and 3 N calcium chloride solutions shown in Fig. 2 were constructed from analogous experimental data. It is evident from Fig. 2 that calcium chloride greatly reduces the metastable solubility of tricalcium silicate. It must be noted, however, that this decrease is considerably less abrupt than the decrease in the metastable solubility of silicate with increasing concentration of calcium hydroxide.

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