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Abstract

Full Text

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PHYSICAL CHEMISTRY

E. E. SEGALOVA, Z. I. MARKINA, and Academician P. A. REBINDER

ON THE MECHANISM OF THE EFFECT OF SMALL ADDITIONS OF ELECTROLYTES ON THE STRENGTH OF THE CRYSTALLIZATION STRUCTURE OF HARDENING

Many investigators have studied the effect of electrolytes on the rate of hydration and the strength of structures arising during the hardening of hemihydrate gypsum; moreover, as a rule, the effectiveness of their action on the setting time of gypsum was taken as the basis for classifying additives (¹). Electrolytes are, for the most part, accelerators, although among them there are also some that retard the process of setting and hardening.

Recently, the question of the influence of electrolytes on the hydration kinetics of hemihydrate gypsum was considered in detail in the works of Ya. L. Zabezhinskii, V. B. Ratinov, and T. I. Rozenberg (²). These authors showed that, knowing the solubility of hemihydrate and dihydrate gypsum in a solution of a given electrolyte, it is possible quantitatively to describe the rate of hydration of the hemihydrate in the presence of this electrolyte. This, to a considerable degree, enabled them to explain the action of electrolytes as retarders and accelerators of hydration.

However, these concepts still do not make it possible to explain the influence of electrolytes on the strength of the crystallization structure, primarily because the question of the role of the magnitude of supersaturation in the formation of the hardening structure has not yet been clarified; moreover, in these works the influence of the electrolyte on the rate of dissolution of hemihydrate gypsum is entirely disregarded. The rate of dissolution of the initial binder, as was shown by the work of our laboratory (³), substantially affects the strength of the hardening structure that forms, even at an unchanged value of the maximum supersaturation arising during hydration.

The influence of an electrolyte on the rate of dissolution of the initial binder and, in connection with this, on the strength of the structure that arises is best studied in the presence of sufficiently small additions of electrolytes, when their influence on the magnitude of supersaturation can be neglected. For this purpose we selected KCl as an electrolyte that has no common ion with CaSO₄,

Figure 1

Figure 1: Figure 1

Figures 2 and 3

Figure 2: Figures 2 and 3

does not enter into chemical interaction with it, and in small additions (0.05 g-equiv/l) changes only very slightly the supersaturation in suspensions of hemihydrate gypsum (4).

It is seen from Fig. 1 that a small addition of KCl sharply accelerates the process of structure formation in suspensions of hemihydrate gypsum and, at low dispersion of the initial binder, increases the strength of the hardening structure that forms, while at high dispersion it decreases it. This agrees with the data obtained in work (4).

It follows from Fig. 2 that a small addition of KCl increases the strength of the hardening structure in the case when the dispersion of the initial gypsum (or the rate of its dissolution in water) was below the optimum, and decreases it if the rate of dissolution of the initial hemihydrate, owing to its high dispersion, was above the optimum. In the presence of KCl, the entire curve of the dependence of the final strength of the structure on the dispersion of the initial

gypsum turns out to be shifted, as it were, which indicates a higher rate of dissolution of hemihydrate gypsum in a 0.05 N KCl solution in comparison with the rate of its dissolution in pure water.

This assumption was confirmed by a direct comparison of the dissolution rate of α -hemihydrate gypsum in water and in a 0.05 N KCl solution, for which the conductometric method (3) was used. Since the absolute

Fig. 1. Kinetics of structure formation in suspensions of β -hemihydrate gypsum in water (1) and in a 0.05 N KCl solution (2). Dispersity of the initial hemihydrate gypsum:

$$a - S = 0.34 \text{ m}^2/\text{g};$$

$$b - S = 1.65 \text{ m}^2/\text{g}$$

values of the maximum electrical conductivity during dissolution of hemihydrate gypsum in water and in KCl solution are different, in Fig. 3 the values of specific electrical conductivity are presented as fractions of its maximum value, corresponding to saturation of the liquid phase of the suspension with respect to

Fig. 2. Dependence of the final strength of the crystallization structure of dihydrate gypsum P_m on the dispersity of the initial hemihydrate S , gauged with water (1) and with a 0.05 N KCl solution (2)

Fig. 3. Kinetics of specific electrical conductivity in suspensions of α -hemihydrate gypsum in water (1) and in a 0.05 N KCl solution (2)

$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. All measurements were carried out under conditions of sufficiently high stirring rates, eliminating the limiting role of diffusion. Under these conditions, the dissolution rate no longer changes with a further increase in the stirring rate.

It is evident from Fig. 3 that the dissolution rate of hemihydrate gypsum increases sharply in the presence of KCl. Thus, for the suspension studied, the maximum electrical conductivity in pure water is reached after 12 min, whereas in a 0.05 N KCl solution it is reached after 5 min. Thus, the results obtained show that the effect of small additions of KCl on the strength of the hardening structure of hemihydrate gypsum is always associated with a considerable increase in the dissolution rate of the hemihydrate in the presence of an electrolyte. It may be assumed-

to suppose that the action of electrolyte additions is reduced to a change in the structure (a decrease in the thickness) of the ionic double layer on the surface of the hemihydrate gypsum crystals.

Moscow State University
named after M. V. Lomonosov

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

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