E. A. SHABANOVA, E. E. SEGALOVA, Academician P. A. REBINDER

1965

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

E. A. SHABANOVA, E. E. SEGALOVA, Academician P. A. REBINDER

THE INFLUENCE OF ELECTROLYTES ON THE PROCESS OF CRYSTALLIZATION STRUCTURE FORMATION (HARDENING) IN SUSPENSIONS OF HEMIHYDRATE GYPSUM

The question of the mechanism by which electrolytes influence the process of crystallization structure formation (hardening) of mineral binders is of great importance, since electrolytes are widely used in practice as accelerators and retarders of hardening. Many investigators believe that their influence is reduced mainly to a change in the supersaturation arising during hydration of the binder ([1]). V. B. Ratinov, Ya. L. Zabezhinskii, and T. I. Rozenberg ([2]) proposed a semi-empirical equation that makes it possible to describe quantitatively the kinetics of hydration of hemihydrate gypsum in the presence of various electrolytes, if the influence of these electrolytes on the solubility of hemihydrate and dihydrate gypsum is known.

However, the literature contains no systematic physicochemical studies of the mechanism by which electrolytes influence the process of the appearance and development of the crystallization structure of hardening. Brief results of such a study are presented in this paper.

For the experiments, suspensions of α-hemihydrate gypsum were used in a mixture with an inert filler—quartz sand, previously washed with a hydrochloric-acid solution and then with water until the reaction for chloride ion disappeared. As additives, KCl was used as an electrolyte containing no ions in common with gypsum, and K_2SO_4 and $CaCl_2$, containing an ion in common with gypsum. K_2SO_4 and $CaCl_2$ increase the relative supersaturation arising during hydration of hemihydrate gypsum, while KCl, practically without changing the relative supersaturation, increases the difference between the solubilities of hemihydrate and dihydrate gypsum ([2]). The electrolytes were introduced into the mixing water in concentrations that exclude the formation of double salts.

A parallel study of the kinetics of hydration and structure formation in sus-

Fig. 1. Dependence of the plastic strength of hardening structures on the degree of hydration of the binder in suspensions of α-hemihydrate gypsum ($S_1 = 3000$ cm^2/g), mixed with KCl solutions of different concentrations: 1—0; 2—0.1 N; 3—0.25 N; 4—1.0 N. a—W/S = 0.8; b—W/S = 0.4, t = 20°

Figure 1: Fig. 1. Dependence of the plastic strength of hardening structures on the degree of hydration of the binder in suspensions of α-hemihydrate gypsum ($S_1 = 3000$ cm^2/g), mixed with KCl solutions of different concentrations: 1—0; 2—0.1 N; 3—0.25 N; 4—1.0 N. a—W/S = 0.8; b—W/S = 0.4, t = 20°

pensions of α-hemihydrate gypsum in the presence of the indicated electrolytes revealed a sharp acceleration of these processes; moreover, KCl and K_2SO_4, at equivalent concentrations, produce practically the same acceleration, while $CaCl_2$ produces a somewhat smaller one. Usually such acceleration was explained by an increase in supersaturation in the presence of electrolytes, especially those having an ion in common with gypsum. However, microscopic studies carried out by us showed that all the electrolytes investigated cause the formation of larger crystals of dihydrate gypsum. Similar results were also obtained in the work of Ridge (^{3}). This shows that, despite the increase in supersaturation, the presence in the solution of foreign electrolytes hinders the formation of nuclei of the new phase, which has a decisive influence on the entire crystallization process. Consequently, the magnitudes of supersaturation in water and in electrolyte solutions cannot be quantitatively compared.

It should be noted that, in investigating the effect of electrolytes on the rate of hydration, their effect on the rate of dissolution of the initial compound was not taken into account. Meanwhile, special experiments have shown that the dissolution of hemihydrate gypsum, occurring under intensive stirring (i.e., in the kinetic region), is considerably accelerated in electrolyte solutions; moreover, KCl and K_2SO_4, at equivalent concentrations, produce a considerably stronger acceleration than $CaCl_2$. This increase in the rate of dissolution of the hemihydrate in the presence of electrolytes should lead to an acceleration of the processes of hydration and hardening (^{4}).

Fig. 1. Dependence of the plastic strength of hardening structures on the degree of hydration of the binder in suspensions of α-hemihydrate gypsum ($S_1 =$ 3000 cm^2/g), mixed with KCl solutions of different concentrations: 1—0; 2—0.1 N; 3—0.25 N; 4—1.0 N. **a**—W/S = 0.8; **b**—W/S = 0.4, $t = 20°$.

The kinetic curves of strength increase and the course of hydration still say nothing about the nature of the process of structure formation, all the more so because the final strengths of the hardening structures that arise at low electrolyte concentrations are quite close to the strength of the structure obtained in the absence of electrolyte. Only comparison of the strength of the forming structure with the amount of hydrate responsible for this strength makes it possible to judge the changes introduced by the presence of electrolytes into the process of formation of the crystallization structure.

It is evident from Fig. 1 that, in the presence of KCl, the amount of substance required to build the initial framework of the hardening structure increases considerably. The presence of electrolytes as it were worsens the conditions for the formation of crystallization contacts, and in order to obtain a hardening structure of a given strength in the presence of an electrolyte, a substantially larger amount of dihydrate gypsum is required.

This negative action of the electrolyte is manifested most strongly at the beginning of hydration, when the strength of the forming hardening structure is determined mainly by the number of intergrowth contacts arising between the crystals of the newly formed phases.

A decrease in the number of crystallization contacts leads to a reduction of internal stresses. Therefore, toward the end of hydration, when in a suspension of hemihydrate gypsum containing no electrolyte additive the increase in strength slows down (Fig. 1a) or ceases altogether (Fig. 1b), in a suspension containing KCl the strength continues to increase intensively. In the presence of a small addition of KCl in a sufficiently dense suspension (Fig. 1b, curve 2), the increase in strength due to the reduction of internal stresses proves greater than its decrease due to the reduction in the number of crystallization contacts, and the final strength of the hardening structure is higher in the suspension containing the electrolyte additive.

However, in most cases in suspensions of hemihydrate gypsum, the decrease in strength due to a reduction in the number of crystallization contacts plays the decisive role and ultimately leads to a decrease in the final strength of the structure developing in the presence of electrolytes. As can be seen from Fig. 1, this decrease is the greater, the larger the electrolyte addition and the lower the internal stresses accompanying the hardening process, i.e., the greater the W/S.

In the presence of K_2SO_4 and $CaCl_2$, at all concentrations investigated (0.05-0.5 N), a decrease in the final strength of the hardening structure was observed.

Moscow State University
named after M. V. Lomonosov

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
1 X 1964

REFERENCES CITED

[1] P. P. Budnikov, *Gypsum, Its Study and Application*, 1943; H. V. Weiser, G. Moreland, *J. Phys. Chem.*, **36**, 1 (1936); *J. Am. Chem. Soc.*, **59**, 1456 (1937); **58**, 1261 (1938). [2] V. B. Ratinov, Ya. L. Zabezhinskii, T. I. Rozenberg, in: *Proceedings of the All-Union Scientific-Research Institute of Railway Transport*,

No. 1 (3), 1957. [3] M. J. Ridge, *Austr. J. Appl. Sci.*, **10**, 218 (1959); M. J. Ridge, H. Surkevicius, *J. Appl. Chem.*, **12**, 246 (1962). [4] K. Schiller, *J. Appl. Chem.*, **12**, 135 (1962).

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