Physical Chemistry

E. E. Segalova, E. S. Solov’ eva, and Academician P. A. Rehbinder

1957

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Physical Chemistry

E. E. Segalova, E. S. Solov' eva, and Academician P. A. Rehbinder

Determination of the Magnitude of Supersaturation in the Aqueous Medium of Suspensions of Tricalcium Aluminate and the Kinetics of Its Change

Supersaturations arising in suspensions of mineral binders are of decisive importance for the processes of crystallization structure formation (hardening), since the magnitude and duration of the existence of supersaturation largely determine the conditions necessary for the appearance of crystallization contacts, as was shown in previous works of our laboratory ([1–3]).

The literature gives measurements of the magnitudes of supersaturation in suspensions of individual binders; however, only for hemihydrate gypsum has a maximum stable supersaturation been firmly established, i.e., a definite value that is conventionally regarded as the "solubility" of hemihydrate gypsum ([4]). For individual minerals of alumina and portland-cement clinker, data are available indicating the formation of supersaturated solutions in their suspensions ([5]), but systematic investigations of the magnitude of the supersaturations and of the kinetics of their change are lacking.

Fig. 1. Kinetics of the specific electrical conductivity in suspensions containing 150 ml of water. 1—1.0 g C_3A; 2—1.5 g C_3A; 3—2.0 g C_3A; 4—4.0 g C_3A; 5—6.0 g C_3A; 6—4.0 g of C_3A hydrate.

The aim of the present work was such an investigation, carried out on suspensions of tricalcium aluminate (C_3A), the structure-formation processes in which we had studied in detail ([3]). The change in the kinetics of supersaturation in C_3A suspensions was carried out by the conductometric method at the optimum stirring speed (400 rpm) ([2,6]). To protect the suspensions from carbonation, all measurements were carried out in an atmosphere of nitrogen.

Figure 1 presents the change in specific electrical conductivity in C_3A suspensions of various concentrations at 20°. First of all, it should be noted that in all sufficiently concentrated suspensions a constant level of electrical conductivity

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

is established, corresponding to the maximum supersaturation—a quantity that may conventionally be regarded as a kind of “solubility” of the initial compound, i.e., the anhydrous binder.

Unlike suspensions of hemihydrate gypsum, in which the maximum level of electrical conductivity was reached practically instantaneously (20-30 sec), in suspensions of C_3A the constant level of supersaturation is reached comparatively slowly, and the rate at which it is reached increases sharply with increasing suspension concentration. At small suspension concentrations, two regions are readily distinguished on the electrical-conductivity kinetic curve. At first the electrical conductivity increases very rapidly, but at $\varkappa = 3.2 \cdot 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ a break is observed, followed by a weakly sloping region, the more pronounced the smaller the content of the dispersed solid phase in the suspension. After this break, the electrical conductivity increases much more slowly than at the beginning. The moment of the break in the curve corresponds to the appearance in the suspension of newly formed, very small crystals of hydroaluminate, which is readily detected by the strong turbidity of the diluted suspension.

The kinetics described can be explained as follows. Upon contact with water, C_3A begins to dissolve rapidly, but, in

Fig. 2. Kinetics of specific electrical conductivity in a suspension containing 1.5 g of C_3A in 150 ml of water in the presence of an added hydroaluminate in the amount: 1—0 g; 2—0.5 g; 3—2 g; 4—6 g

Fig. 3. Kinetics of specific electrical conductivity in a suspension containing 1 g of C_3A in 150 ml of water or aqueous solutions of SSB. 1—water; 2—0.05% SSB solution; 3—0.5% SSB solution

contrast to suspensions of hemihydrate gypsum, at supersaturations still far from the maximum, nuclei of a new phase—microcrystals of hydroaluminate—begin to appear in the suspension. These microcrystals settle on the surfaces of the initial C_3A particles, covering them as though with a protective film and slowing further dissolution. The slowing of the growth of electrical conductivity is associated both with this slowing of dissolution and with the fact that part of the substance passing into solution separates out in the form of hydroaluminate, without increasing the supersaturation of the solution.

The assumption that shielding protective shells of newly formed material are formed on the surfaces of C_3A particles should be checked in the following way:

1) Introducing into the C_3A suspension crystals of previously prepared hydroaluminate should create conditions under which the probability of formation of new hydroaluminate nuclei will be greatly reduced, since the substance that has passed into solution will crystallize on the hydroaluminate crystals already present in the suspension.
2) Introducing small additions of surface-active substances, which are adsorbed on the initial C_3A particles, should, on the one hand, slow dissolution and, on the other, prevent the settling of hydroaluminate microcrystals on the surfaces of particles already covered by an adsorption layer of the additive.

Figure 2 presents the kinetics of electrical conductivity in suspensions of C_3A in the presence of various additions of prepared hydroaluminate, and Fig. 3 shows the same kinetics in the presence of small additions of sulfite-alcohol stillage (SAS).

As can be seen from Fig. 2, additions of hydroaluminate greatly accelerate the process of concentration increase in the solution.

Since the rate of dissolution of C_3A cannot increase in the presence of hydroaluminate, and the increase in electrical conductivity should have slowed as a result of the increased rate of crystallization of hydroaluminate on preexisting centers, the acceleration of solution saturation can be explained only by the fact that, in the presence of hydroaluminate, no coating of its crystallites is formed that blocks the surface of the original C_3A particles, and thus no slowing of its dissolution occurs.

The larger the addition of hydroaluminate, the lower the probability of formation of hydroaluminate microcrystallites on the surface of the original C_3A particles and the higher the rate of its dissolution. As the addition increases, the rate of crystallization also increases, so that with a large addition of hydroaluminate the upper level of supersaturation is no longer reached (Figs. 2, 4).

Figure 3 shows that small additions of SAS, which are completely adsorbed by the original C_3A particles ([3]), do not change the maximum level of electrical conductivity, but substantially affect the kinetics of the process: the initial rate of dissolution of C_3A before the appearance of nuclei of a new phase is noticeably reduced in the presence of 0.5% SAS. However, in the presence of an SAS addition, as in the presence of hydroaluminate additions, no break is observed in the curve of electrical-conductivity increase, and the maximum value of electrical conductivity is reached in the presence of the addition much more rapidly than without it.

With larger additions of SAS its retarding effect on the initial rate of dissolution of C_3A becomes still more noticeable; but at the same time, owing to the presence of SAS in the liquid phase of the suspension, the electrical-conductivity values change, and the measurement data become incomparable with the preceding ones.

These results can be explained only by the fact that, although adsorption of SAS on the surface of C_3A particles does lead to some slowing of its dissolution, the predominant effect is the prevention of the formation of armored shells of hydroaluminate on the surface of the original particles. As a result, the rate of solution saturation in the presence of small additions of SAS is greatly accelerated.

To determine the magnitude of the maximum stable supersaturation arising in C_3A suspensions, it was necessary to separate the liquid phase of the suspension and determine its content of CaO and Al_2O_3.

An attempt to filter or centrifuge the C_3A suspension after the maximum supersaturation had been reached in it gave no positive results. The resulting hydroaluminate crystallites are so small that they practically did not settle in an ordinary centrifuge, while during filtration they clogged the pores of the filter; the liquid was filtered so slowly that any supersaturation in it had time to fall to zero.

As is known (^{3}), in the presence of small additions of SAS, larger hydroaluminate crystallites are formed, while the magnitude of the maximum supersaturation does not change. Therefore determination of the magnitude of the maximum supersaturation was carried out in suspensions containing very small additions of SAS (0.01–0.05% SAS in the solution).

In this way it was possible for the first time to establish the magnitudes of maximum stable supersaturation in C_3A suspensions. At 20° it proved equal to 1.428 g C_3A per 1 liter of solution, which corresponds to concentrations of CaO 0.888 g/liter and Al_2O_3 0.540 g/liter, $CaO : Al_2O_3 = 2.99$. The determination of CaO and Al_2O_3 was carried out–

was carried out by the weight method. The data presented are the average of 7 determinations. The solubility of hydroaluminate, determined by the same method both in pure water and in weak sucrose solutions, proved to be equal to 0.412 g/l CaO and 0.260 g/l $\mathrm{Al_2O_3}$, which is in good agreement with the literature data (^{7}).

Moscow State University
named after M. V. Lomonosov

Received
19 VII 1957

CITED LITERATURE

[1] E. E. Segalova, V. N. Izmailova, P. A. Rebinder, *DAN*, 110, No. 5 (1956). [2] E. E. Segalova, V. N. Izmailova, P. A. Rebinder, *DAN*, 114, No. 3 (1957). [3] E. E. Segalova, E. S. Solov' eva, P. A. Rebinder, *DAN*, 113, No. 1 (1957). [4] P. P. Budnikov, *Gypsum, Its Study and Its Application*, 1943; P. F. Konovalov, E. I. Morozov, *Cement*, No. 5 (1956); Ya. L. Zabezhinskii, V. B. Ratinov, T. I.

Rozenberg, *DAN*, 108, No. 6 (1956); V. B. Ratinov, Ya. L. Zabezhinskii, T. I. Rozenberg, *DAN*, 109, No. 5 (1956). [5] R. H. Bogue, *The Chemistry of Portland Cement*, N. Y., 1947; J. Brocard, *Chemie et industrie*, 59, No. 5 (1948); A. M. Kuznetsov, A. I. Sosnina, *Izv. Estestvenno-nauchn. inst. pri Permsk. gos. univ. im. A. M. Gor' kogo*, 13, No. 6 (1952). [6] B. Ya. Yampol' skii, E. S. Solov' eva, *Proceedings of the 3rd All-Union Conference on Colloid Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1956. [7] V. M. Moskvin, T. V. Rubetskaya, *Research of the All-Union Scientific Research Institute for Construction*, *Concretes and Binders*, Moscow, 1955; T. V. Rubetskaya, ibid.; R. Nacken, *Zement*, 34, 565 (1936); 35, 583 (1936).

* **CORRECTION**

In the article by E. E. Segalova, V. N. Izmailova, and P. A. Rebinder, "Study of the kinetics of supersaturation in connection with the development of crystallization structures during the hardening of gypsum," published in *DAN*, vol. 114, No. 3, 1957, the caption to Fig. 3 should read:

Kinetics of structure formation in a suspension containing 30% hemihydrate gypsum and various amounts of sand and dihydrate gypsum, W/G = 0.5:

Curves	1	2	3	4	5	6	7
Sand, %	70	68	65	60	50	20	0
Dihydrate gypsum, %	0	2	5	10	20	50	70

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.