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KINETIC FEATURES OF THE HYDRATION HARDENING OF SULFATES

The study of the hydration hardening of sulfates with various cations is of particular interest. Constituting a single group of mineral binders according to the classification of Zhuravlev—Moshchanskii ([1],[2]), with a common chemism of interaction with water, sulfates make it possible to vary widely the conditions of crystallization structure formation. They exhibit differences in the crystal structures of the hydrates, in the solubility of these hydrates and of the initial anhydrous salts, and in their ability to form stable supersaturated solutions under the conditions of concentrated suspensions.

As shown by the work of E. E. Segalova and co-workers ([3]–[5]), the strength of dispersed crystallization structures of hardening is not a simple, single-valued function of the chemical composition and structure of the new solid phases, but is determined mainly by the kinetics of formation of these phases. The most important kinetic characteristics in this case are the duration of the induction period of crystallization and the rate of crystallization of the hydrates. These characteristics were obtained by us for concentrated suspensions of nine sulfates, by studying the kinetics of heat evolution during hydration of partially or completely dehydrated salts, the kinetics of their dissolution, structure formation in suspensions, and concurrently performed microscopic observations. The research methods have been described by us earlier ([6]–[8]).

In accordance with the type of the kinetic curves of hydration and hardening, all the salts studied may be divided into at least two groups, taking as the basis the duration of the induction period of crystallization τ_i and the ratio between this quantity and the time of complete hydration of the salt τ_h.

The features of each of these groups are clearly revealed when studying the effect on the hydration kinetics of such factors as the dispersity of the initial salt and the concentration of the suspension, i.e., the water/solid phase ratio (W/S). Figure 1 shows two limiting cases of the influence of the initial dispersity on the hydration kinetics of sulfates: $CdSO_4 \cdot H_2O$ and Na_2SO_4. The first of them has a clearly expressed induction period of crystallization of the hydrate $CdSO_4 \cdot 8/3H_2O$, stable at 20°, which decreases as the dispersity of the initial salt increases. In this case τ_h (the corresponding level of heat evolution is shown

Fig. 1

Figure 1: Fig. 1

by a simple dashed line) exceeds τ_i by only 2.5-3 times. The same type of hydration kinetic curve, with an analogous dependence on dispersity, is possessed, as is known, by calcium sulfate—anhydrous or hemihydrate gypsum. An entirely different character of the kinetic curve is given under these conditions by sodium sulfate; $\tau_i \approx 0$, and the phenomenon of hydration retardation is expressed the more strongly, the lower the dispersity of the initial salt. Thus, for a salt with a conventional specific surface $S = 3000$ cm^2/g (according to Tovarov), 50% hydration is reached only after 3 hr of interaction with water ($\tau_h = 1$ day). Observations with a polarizing microscope, even at small magnifications (400×), make it possible to establish the cause of the sharp⋯

the retardation of hydration—the formation on the surface of the crystals of the initial salt of a layer of tightly intergrown crystals of the decahydrate. Similar phenomena have so far been found only for sparingly soluble substances with a small diffusion coefficient. This phenomenon, and the directly proportional relation associated with it between the value of the conventional specific surface and the amount of salt hydrating during the first 3–5 min, would be incorrectly attributed to the hydration of the anhydrous salt without prior dissolution. Direct measurements of the concentration of sodium sulfate in the aqueous phase of the suspension, with intensive stirring and sufficiently large W/S ratios, make it possible to detect supersaturations corresponding to the tabulated values of the metastable solubility of the anhydrous salt at the given temperature. The formation of hydrate crystallites immediately at or on the surface of the initial salt is therefore caused by high rates of formation of crystallization nuclei and of their growth, as compared with the rate of diffusion of salt ions into the solution.

Intermediate positions, in terms of the type of the kinetic curves of hydration (and hardening), are occupied by the sulfates of Mg, Zn, Cu, Co, and Fe^II (monohydrates), which have a small τ_i (1-3 min) and weakly expressed retardation of hydration.

Fig. 1. **A** –Kinetics of heat evolution during hydration of $CdSO_4 \cdot H_2O$, W/S = 0.21: 1 –S = 2400, 2 –S = 4700, 3 –S = 7100 cm^2/g, and Na_2SO_4, W/S = 1.20; 4 –S = 500, 5 –S = 2800, 6 –S = 5100, 7 –S = 7200 cm^2/g. **B** – Dependence of Q after the end of the induction period (in percent of the heat of complete hydration) on the dispersity (S) of the initial salt.

To explain the differences in the kinetics of hydration of sulfates with different cations, it seems appropriate to us to bring in modern concepts of the theory of the structure of electrolyte solutions (^{9}) and data on the structure of the crystalline hydrates of the salts studied. It is known that in concentrated solutions of many hydrating salts the structure of the coordination sphere of the cation

Figure 2

Figure 2: Figure 2

is identical with its structure in crystalline hydrates. Such correspondence between the structure of solutions and crystalline hydrates, among the sulfates we studied, occurs for the salts of Na, Mg, Zn, Co, Ni, and Fe^II, whereas the sulfates of Cd and Ca show in their stable crystalline hydrates a lower coordination number (c.n.) of the cation with respect to water (for Ca, 2; for Cd, <3) than is usually observed for these cations in salt solutions (for Ca, 4.6; for Cd, 6). It may be assumed that the work of formation of crystallization nuclei, and consequently also the stability of the supersaturated solutions formed during salt hydration, decreases as the correspondence between the structure of the solution and of the crystallohydrate precipitating from it increases. An analogous phenomenon is encountered in crystallization from the melt of substances for which a difference in the structures of the melt and the solid compound has been reliably established (salicylic acid ethers), which is expressed by a larger value of τ_i. The formation of the most stable supersaturated solutions was observed for the sulfates of Sr and Ba. For example, for strontium sulfate hundredfold relative supersaturations were obtained at τ_i equal to several minutes (10). In this case the change in the c.n. of the cation with respect to water must be very sharp—from 6 or 4 to 0.

In seeming contradiction to the statement expressed here is nickel sulfate, whose hydration from the monohydrate to the 7-hydrate proceeds with a large τ_i. However, as measurements of concentration during the dissolution of this salt and of the kinetics of heat evolution during hydration at different W/S ratios have shown (Fig. 2), the long induction period is caused by slow dissolution of the salt: after a constant solution concentration is reached (with a heat of dissolution of 30 cal per 1 g H_2O), heat evolution accelerates sharply. This effect, corresponding to the onset of hydrate crystallization, is attained at relative supersaturations $C/C_0 = 1.09$, which indicates their low stability. Thus, nickel sulfate may be assigned to the same kinetic group as the sulfates of Mg, Zn, and Na. It should be noted that sodium sulfate apparently should occupy a special place in this classification, since for it the structure of the cation coordination sphere corresponds not only to the structure of its concentrated solution, but also to the quasi-crystalline structure of water (coordination number 4), which apparently is also the reason for its crystallization under conditions of concentrated suspensions without a noticeable induction period.

Fig. 2. Kinetics of heat evolution during hydration of $NiSO_4 \cdot H_2O$. 1 –W/S = 0.65, 2 –W/S = 1.00, 3 –W/S = 1.40

The different nature of the induction period in salts—representatives of different kinetic groups—nickel and cadmium sulfates—appears when their monohydrates are mixed with saturated solutions of the corresponding salts. As is seen from Fig. 3, in the case of cadmium sulfate, mixing with a saturated solution sub-

Figure 3

Figure 3: Figure 3

stantially does not change the kinetics of hydration of the salt, removing only the effect of the heat of dissolution. Only by reducing the work of formation of crystallization nuclei, in this case by introducing a crystalline seed, can a reduction of the τ_i period be induced and brought practically to zero (Fig. 3, 3, 4). Nickel sulfate, which does not form stable supersaturations under conditions of concentrated suspensions, already when mixed with a saturated solution hydrates without an induction period (Fig. 3, 5, 6).

Fig. 3. Kinetics of heat evolution during hydration of $CdSO_4 \cdot H_2O$ (1-4) and $NiSO_4 \cdot H_2O$ (5, 6), mixed with water –1, 5; with a saturated solution of the corresponding salts –2, 6; with a saturated solution containing additions of crystalline hydrate –3 (20%) and 4 (60% of the weight of the initial salt)

All the salts studied, when interacting with water under conditions of concentrated suspensions, give during hardening strong crystallization structures at relatively high W/S ratios—both individually and in mixtures with an inert filler (ground sand), which we introduced to prevent sedimentation at large W/S ratios.

From Table 1 it is evident that sodium sulfate belongs to the salts capable of hydration hardening, which had previously been denied. However, this property appears only when the mixing with water is carried out by impregnation, without mechanical stirring, which is due to the very small τ_i.

Table 1 also gives strength values for coagulation structures that arise after mechanical destruction of the initial crystallization structures and that have strengths an order of magnitude lower than the latter. This proves that the strength of crystallization structures in the present case is not a consequence only of the sharp decrease in W/S during hydration of most of the salts studied.

Table 1

Strength of dispersed structures during hydration hardening of sulfates

Salt	S, cm^2/g	W/S	Salt/water	p_m, kg/cm^2 cryst.	p_m, kg/cm^2 coag.
Na_2SO_4	1200	1.2	1:5	13.3	–
Na_2SO_4	500	1.2	1:5	5.7	0.3
$ZnSO_4$	2400	0.7	1:1	140	0.8
$NiSO_4$	8000	1.0	1:3	25.6	0.5
$CdSO_4$	2400	0.2	1:0	166	0.8
$CdSO_4$	7300	0.3	1:1	170	–

The proposed addition to the classification of binders according to the principle of correspondence between the structures of solutions and the products of hydration is applicable only to substances that form true crystalline hydrates upon interaction with water, i.e., to compounds into which water enters in molecular form. Such binders cannot include, for example, calcium silicates, whose products of interaction with water are not simple crystalline hydrates. The inversion of binding properties in the transition from silicates and their analogues in Mendeleev’ s periodic system to sulfates (1) is apparently associated with the fact that sulfates are characterized by the incorporation of water in molecular form into the coordination sphere of the cation. This gives rise to binding properties when the cation radius decreases within a single subgroup of the periodic system. Hydration of silicates, however, is expressed primarily in a change in the structure of the anion, and in the case of its enlargement the binding properties should increase as the cation radius increases, which is indeed observed.

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