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Abstract

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CALORIMETRIC STUDY OF THE HYDRATION OF SODIUM METASILICATE

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Anhydrous sodium metasilicate is the only Na silicate that forms a hydrate, $Na_2H_2SiO_4 \cdot 8H_2O$ (acid orthosilicate), which crystallizes well under ordinary conditions, whereas high-silica Na silicates are more characteristically vitrified as a consequence of the high-molecular nature of the anions ([1]-[3]). Crystalline metasilicate and its concentrated aqueous solutions also contain condensed silicate anions, which are, however, capable of reversible hydrolytic cleavage in dilute solutions ([3], [4]). It is of interest to determine to what extent metasilicate follows the general laws of hydration of inorganic binders ([6]-[8]), and what influence the presence of the condensed form of silica has on this process.

Table 1

Dependence of the heat of formation of supersaturated solutions on the Na_2SiO_3 content

Conc. p, % Na_2SiO_3	32.2	33.7	35.3	37.2	39.0	41.2	48.4	50.8
Q, cal/g Na_2SiO_3	76.4	77.6	74.6	71.8	67.8	66.5	54.6	50.0
Q, cal/g H_2O	35.9	39.5	40.8	42.4	43.3	46.5	51.2	53.5
Q_{H_2O}/p	1.12	1.17	1.15	1.14	1.11	1.13	1.06	1.05

The dissolution of anhydrous metasilicate and the crystallization of its hydrate are exothermic processes, which determines the use of the calorimetric method for studying these processes; the second of them, as the slower one, dictates the choice of a diathermic calorimeter with a constant rate of heat exchange ([5], [6]). The starting silicate used for preparing the solutions and the anhydrous Na_2SiO_3 was chemically pure nonahydrate (dehydrated at 5-7 mm with gradual heating).

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Preliminary experiments showed that anhydrous Na_2SiO_3 readily forms supersaturated solutions when mixed with a saturated solution of the hydrate or with H_2O; moreover, the metastable solutions of Na silicate are relatively stable. It has been shown previously that under such conditions it is possible to attain and determine the limiting concentration of the supersaturated solution of a salt —for example, sulfuric acid—or the metastable solubility of its dehydrated form ([7], [8]).

The calorimetric method can be applied for this purpose if it is assumed that the heat of formation of the supersaturated solution tends to a limit when the metastable solubility is reached with increasing salt concentration in the solution. We determined the heats of formation of supersaturated solutions in water as a function of the amount of anhydrous salt introduced, including systems whose composition corresponds to the melt of

$Na_2H_2SiO_4 \cdot 8H_2O$ (43.0% Na_2SiO_3) and with a high content of sodium metasilicate. The data given in Table 1 do not reveal a tendency toward a limit in the investigated concentration range and are described by a linear dependence, for example for Q, expressed in calories per gram of Na_2SiO_3,

$$Q = 54.6 - 1.34(p - 48.4),$$

where p is the percentage content of Na_2SiO_3.

It may therefore be assumed that the metastable solubility of Na_2SiO_3 is much higher than the content of anhydrous salt in the melt of the stable crystalline hydrate $Na_2H_2SiO_4 \cdot 8H_2O$. This conclusion is not contradicted by a rough estimate of the metastable solubility of Na_2SiO_3 by extrapolating to 20° the solubility curve of this salt at elevated temperatures, which gives $\approx 80\%$ Na_2SiO_3. Direct determination of this value could not be carried out because of the rapid vitrification of solutions of high concentrations (more than 50%). Thus, the relative stability of supersaturated solutions formed during the hydration of Na_2SiO_3, including the hydrate melt, is to a considerable extent due to the fact that the concentration of Na_2SiO_3 in these systems is always far from reaching the metastable solubility.

Fig. 1. Kinetics of heat evolution: 1 –40.4, 2 –41.3, 3 –41.6, 4 –42.6, 5 –43.2 Na_2SiO_3

Fig. 3

Figure 3: Fig. 3

Fig. 2. Dependence of heat evolution on the concentration of Na_2SiO_3: 1 —heat of formation of supersaturated solutions, 2 —thermal effects during crystallization of $Na_2H_2SiO_4 \cdot 8H_2O$, 3 —rate of heat evolution during crystallization

The kinetics of hydration and crystallization from supersaturated Na_2SiO_3 solutions close in composition to the hydrate melt has been studied, since it is of interest for the first time to compare the properties of supersaturated solutions of an inorganic binder with the properties of melts. By the calorimetric method the kinetics of these processes was determined for systems containing 40–43% Na_2SiO_3. Figure 1 shows the kinetics of heat evolution during hydration of anhydrous Na_2SiO_3 in a saturated hydrate solution; two types of kinetic curves can be distinguished. The first is characterized by rapid attainment of the limiting heat evolution, occurring in one stage and describing the hydration of the salt in the process of forming a supersaturated solution (curves 1 and 5). In curves of the second type, after a prolonged cessation or sharp slowing of heat evolution corresponding to the induction period of crystallization, a second stage of heat evolution is observed, describing the course of the crystallization process itself (curves 2–4). These two processes in individual cases overlap in time (curves 3, 4); however, as is seen from comparison with curves 1 and 5, this overlap is small, and the process of dissolu-

…in general ends before crystallization begins. In the hydration of sodium metasilicate there is practically no period of coexistence of the anhydrous salt and the hydrate. Heat evolution in the second stage describes only the crystallization process, in contrast to poorly soluble binders under conditions of concentrated suspensions, where it constitutes the sum of the thermal effects of dissolution and crystallization.

From Fig. 2 it is evident that heat evolution in the first stage increases linearly with the content of Na_2SiO_3 in the system, as do the previously described heats of dissolution of this salt in water (curve 1). By contrast, heat evolution due to crystallization of the hydrate passes through a sharply pronounced maximum at a content of Na_2SiO_3 in the system considerably lower than in the melt $Na_2H_2SiO_4 \cdot 8H_2O$. This is true both for the thermal effect Q (curve 2) and for the rate of heat evolution (curve 3). The existence of a maximum in the crystallization rate from supersaturated solutions close in composition to the melt corresponds to the well-known proposition of the theory of crystallization from a melt (^{9}). The shift of this maximum toward lower Na_2SiO_3 contents is evidently due to structural features of the supersaturated solutions associated with the presence of polysilicate anions.

Fig. 3. Kinetics of crystallization of $Na_2H_2SiO_4 \cdot 8H_2O$ with seed crystals: 1 —$Na_2H_2SiO_4 \cdot 8H_2O$ (29% Na_2SiO_3); 2, 3 —quartz (2 —25%, 3 —23.4% Na_2SiO_3

in solution)

The crystallizing hydrate is formed by hydrolyzed ions of orthosilicic acid, $H_2SiO_4^{2-}$, the content of which as a whole increases with the concentration of silicate in the solution. However, the condensation–decondensation equilibrium is thereby shifted increasingly toward the formation of polysilicate ions, which hinder crystallization. Thus, a content of 41.6% sodium metasilicate in the system corresponds to the optimum composition of the supersaturated solution, most consistent with the structure of the stable hydrate and determining the greatest rate of its crystallization.

The upper boundary of the region of rapid crystallization is also apparently associated with a decrease in the solutions of the content of $H_2SiO_4^{2-}$ ions and with the accumulation of metasilicate ions proper—of a condensed, chain form. A consequence of this is also the process of vitrification of concentrated solutions. The lower boundary of this region is mobile and is readily shifted into the region of lower concentrations by introducing crystalline seed crystals and inert fillers. This phenomenon was observed by us, in particular, in supersaturated solutions obtained by cooling and diluting the melt $Na_2H_2SiO_4 \cdot 8H_2O$ (Fig. 3) in the presence of additions of this hydrate (curve 1) and crystalline SiO_2 (quartz, $S_{\text{sp}} = 0.62$ m^2/g by BET, curves 2–3). Expansion of the region of rapid crystallization in this way toward high concentrations (into the vitrification region) was not observed.

Thus, the calorimetric study of the hydration of sodium metasilicate made it possible to reveal such general properties of this inorganic binder as the occurrence of stages of dissolution of anhydrous Na_2SiO_3 and crystallization of a stable hydrate, and the shortening of the induction period of crystallization under the action of fillers. The high rate of dissolution indicates that metasilicate chains of condensed anions of the solid silicate do not exert a substantial influence on the kinetics of dissolution, apparently because of rapid hydrolytic cleavage. Features of metasilicate were also noted that distinguish it from other binders and are associated with the presence of condensed···

of hydrated anions in solutions of high concentration; the high stability of supersaturated solutions with $C/C_0 = 2.5$ and higher at high relative concentrations –43% Na_2SiO_3, or 100% calculated as the crystalline hydrate; the possibility, as a consequence of this, of obtaining by dissolution of anhydrous Na_2SiO_3 concentrations corresponding to a melt of the hydrate; the shift of the maximum crystallization rate of this hydrate toward lower Na_2SiO_3 concentrations; and the fundamental unattainability of metastable solubility of Na_2SiO_3 owing to vitrification of concentrated solutions.

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