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Abstract

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STUDY OF THE KINETICS OF HYDRATION OF PORTLAND-CEMENT CLINKER MINERALS DURING HYDROTHERMAL TREATMENT

The study of the kinetics of hydration of Portland cement at temperatures not exceeding 100° is of great importance, since hydrothermal treatment in this temperature range is the most widespread technological method for accelerating the hardening of reinforced-concrete products.

Despite this, the kinetics of hydration during hydrothermal treatment in the indicated temperature range has been studied in less detail than during normal hardening ($^{1-6}$) and during autoclave treatment ($^{7-11}$). In (^{8}), selective data are given characterizing the strength of clinker minerals under a combined hardening regime; in (^{3}), mixtures of clinker minerals with asbestos were investigated; in (^{14}), the maximum experimental temperature was 65°, while the data given in (^{12}) and (^{13}) refer to factory cements, which makes it difficult to compare them with the results of other studies. The limited nature of the literature data and, especially, the absence of a unified method for their evaluation make it difficult to compare research results because of differences in experimental conditions. These include differences in the conditions of synthesis of the starting materials and in their particle-size composition, as well as in the methods for determining the rate of hydration. Individual attempts at such systematization are found in the literature. Thus, in (^{5}) an equation was proposed for the rate of hydration of Portland cements at normal temperature

$$-\frac{dC_t}{d\tau} = \frac{DF}{\delta}(C_0 - C_t); \qquad (1)$$

where δ is the thickness of the layer of newly formed products; F is the surface area of the reacting cement particles; D is the diffusion coefficient. However, the processing by the authors of (^{5}) of various data, carried out with allowance for very rough approximations (constancy of F and δ), showed poor agreement of the experimental data with equation (1), as a result of which this equation was no longer used. In (^{4}), an equation was proposed for the rate of hydration of C_3S at 20°:

Figure 1

Figure 1: Figure 1

$$-\frac{dC}{d\tau} = KC^{1/2}. \tag{2}$$

But from the data given in (^{4}) it is evident that the values of K within a single experiment varied almost threefold, which likewise predetermines the unsuitability of this equation for processing experimental data. In (^{16}), theoretical equations were proposed for the dependence of the rate of hydration of gypsum and clinker minerals on the degree of supersaturation created during dissolution of the initial binders. However, the complexity of these equations, the need to carry out additional experiments to determine solubility values, and the difficulty of determining the degree of supersaturation under real conditions of cement-stone hardening, especially at elevated temperatures, limit their practical use.

The purpose of the present work was to study the kinetics of hydration of binders during hydrothermal treatment and to determine the possibility of its quantitative evaluation. For comparison with the literature data, the kinetics of hydration at 20° was also studied. The objects of investigation were the principal minerals of Portland-cement clinker: $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. The clinker minerals were synthesized according to the procedure described in (15). They had characteristic crystallographic and X-ray diffraction indices. Before mixing with water, the materials were ground until they passed completely through sieve No. 008. The samples for investigation were prepared from a paste of normal consistency.

Fig. 1. Hydration kinetics of silicate minerals at various temperatures. Solid lines—$3CaO \cdot SiO_2$: 1—20°; 2—50°; 3—70°; 4—90°; dashed lines—$2CaO \cdot SiO_2$: 5—20°; 6—50°; 7—90°

To carry out the hydrothermal treatment, the molds with samples were placed in a water thermostat of the TS-15M type. Hydration was stopped by treating the material with absolute alcohol. After this treatment the material was dried at 105° to constant weight. The quantity determined was the degree of hydration of the material under study. It was calculated from the results of quantitative X-ray diffraction analysis of the unhydrated phase* using the formula

$$L = 100 - A/100 + mA, \tag{3}$$

where L is the degree of hydration, A is the content of the unhydrated phase, and m is the stoichiometric coefficient accounting for the amount of bound water in the completely hydrated material.

Figure 2

Figure 2: Figure 2

X-ray diffraction patterns were recorded on a URS-50 diffractometer using CuK_α radiation. To determine the intensity, reflections characterized by the following values were selected.

Mineral	C_3S	C_2S	C_3A	C_4AF
d/n, Å	2.78*	2.77	2.69	2.64
d/n, Å	1.77**			

* Individual phase.
** Alite phase in cement.

The line intensity was determined as the average of three measurements. X-ray diffraction patterns were recorded with an external standard, for which the corresponding unhydrated material was used.

Fig. 2. Hydration kinetics of alumina-containing minerals. Solid lines—C_4AF: 1—20°; 2—50°; 3—90°; dashed lines—C_3A: 4—20°; 5—50°; 6—90°

Figures 1 and 2 present experimental data on the degree of hydration of the silicate minerals $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$, and on the degree of hydration of $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. As a result of processing the experimental data, an empirical relationship was obtained for the degree of hydration of the minerals as a function of hardening time:

$$L = K \lg \tau - B, \tag{4}$$

where τ is time, and K and B are constants.

* We express our gratitude to O. S. Volkov for consultation on the method of recording X-ray diffraction patterns and for analysis of some of the samples.

As can be seen from the figures, this equation is applicable for describing the hydration kinetics of the main mass (20-80%) of clinker minerals, i.e., in the interval of formation of the strength of cement stone.

Table 1

Effect of temperature on the value of K during hydration of clinker minerals

Mineral	Temperature, °C	Temperature, °C	Temperature, °C	Temperature, °C	Temperature, °C	$\frac{K_{t+10}}{K_t}$, mean
	20	50	70	90	98	
C_3S	48	95	65	–	120	1.19
C_2S	43	57	–	47	–	1.10
C_3A	26	38	–	33	–	1.15
C_4AF	18	38	–	77	–	1.46

Table 2

Values of K during hydration of a mixture of clinkers and the alite phase in Portland cement

Mineral	Temperature, °C	Temperature, °C	Temperature, °C	Temperature, °C
	20	50	70	90
Mixture + C_3S (90%)	–	–	67	–
Mixture + C_3A (10%)	–	–	41	–
Alite phase in Portland cement	43	31	–	85

From the data presented it is also evident that a change in temperature does not affect the character of the general relationship, but affects only the values of K (Table 1) and B (Fig. 1).

As can be seen from the data of Table 1, raising the temperature by 10° causes an increase in K for different minerals within the range of 10–46%. Similar data on the effect of temperature on the kinetics of formation of hydrosilicate phases are given in (11). Fig. 3 presents data on the degree of hydration of C_3S and C_3A in mixtures of clinker minerals and of the alite phase in Portland cement. It is clear from the figure that the general relationship described by equation (4) is preserved in this case as well, and only the value of K changes, as follows from the data given in Table 2.

As the treatment of literature data has shown, experimental material obtained in other works is satisfactorily described by the relationship found. As can be seen from the structure of equation (4), if on the ordinate axis, instead of L, one

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

plots the quantity proportional to it, $\frac{L}{K}$, and shifts the graph along the ordinate axis by the amount B, then the data described by equation (4) should lie on the bisector of the coordinate angle. The corresponding data are presented in Fig. 4. Table 3 gives the values of K obtained in processing literature data according to equation (4).

Table 3

Values of K obtained in processing literature data according to equation (4)

Mineral	Source	Source	Source	Source	Source	Source
	(1)	(2)	(3)	(7)	(14)*	(14)**
C_3S	33	18	32	27	32	23
C_2S	15	28	60	40	48	19
C_3A	6	–	7	–	–	–

* Temperature 20°.
** Temperature 50°.

Thus, equation (4) satisfactorily describes the hydration kinetics of individual clinker minerals, of the mixtures of them that were studied, and also of the alite phase in Portland cement; the experimental conditions are taken into account in summary form by the value K.

The constant B, which enters the equation, is proportional to the duration of the induction period of the hydration process. The causes of the induction period during hydration of one of the minerals, $3CaO \cdot SiO_2$, have been discussed in (17, 18). The use of equation (4), which is comparatively simple in structure, makes it possible substantially to reduce the number of experiments necessary for studying the hydration kinetics of cements under the action of various factors, and the temperature dependence found for the rate of hydration can, as a first approximation, be used for estimating

the influence of different hydrothermal-treatment regimes on the kinetics of hydration processes.

It also follows from the analysis of the experimental data that hydrothermal treatment does not have a negative effect on the hydration kinetics of the bulk of all the materials studied at the selected finenesses.

Fig. 3. Hydration kinetics of C_3S and C_3A in mixtures of clinker minerals and of the alite phase in Portland cement. Solid lines—mixture of composition

C_3S (90%) + C_3A (10%) at 70°: 1—C_3S, 2—C_3A; dashed lines—the alite phase in Portland cement: 3—20°, 4—50°, 5—90°.

Fig. 4. Processing of experimental data from various authors by equation (4). The source is indicated in parentheses.
a—C_3S, 20° (3), b—C_2S, 20° (1); c—C_2S, 65° (14); g—C_3A (in a mixture with C_3S), 20° (3); d—C_2S, 90° (our data); e—C_3S, 70° (our data); zh—the alite phase in Portland cement, 50° (our data).

The question of the rate of hydration of binders under a combined hardening regime (short-term hydrothermal treatment followed by hardening at room temperature) is the subject of further studies.

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