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Abstract

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STUDY OF THE KINETICS OF HYDRATION OF PORTLAND-CEMENT CLINKER MINERALS

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In papers ([1]) it was shown that the hardening of binders is the result of two interrelated processes: their dissolution and the crystallization of new formations from supersaturated solutions, the stages of dissolution and growth of the solid phase proceeding under diffusion control. In contrast to them, the stage of spontaneous formation of nuclei of the new phase proceeds in the kinetic region; the duration of this process is small, the mass of crystallization nuclei arising in this process is also small, and in the equation of material balance it may be neglected in the first approximation ([2], [3]). Knowledge of the laws governing dissolution of binders and crystallization of new formations enabled us to derive equations for the joint development of both processes. In doing so, a simplifying assumption was adopted concerning the monodispersity of both the initial and the final phases; this did not introduce any fundamental changes into the final conclusions.

Let us introduce the notation: let m_1 and m_2 be, respectively, the mass of the binder and of the new phase (calculated for the anhydrous substance) at an arbitrary time τ:

$$m_{1,2} = \gamma_{1,2} N_{1,2} \rho_{1,2} l_{1,2}^3. \tag{1}$$

Here and below $\gamma_{1,2}$ is the particle shape factor ($\gamma_1 \simeq \gamma_2$); $\rho_{1,2}$ is the density; $N_{1,2}$ is the number of particles; $l_{1,2}$ is their characteristic size; $m_{1,0}$ and $m_{2,0}$ are the masses of the binder and of the new phase at the initial time τ_0 ($\tau_0 \ll \tau$); $dm_1/d\tau \sim dl_1^3/d\tau$ is the dissolution rate of the binder; $dm_2/d\tau \sim dl_2^3/d\tau$ is the growth rate of the new phase; c_1 and c_2 are, respectively, the solubilities of the binder and of the new formation; c_τ is the concentration of the substance at an arbitrary time τ; D is the diffusion coefficient (in our case of dilute solutions, the value of D is practically independent of changes in the concentration of the solution); Nu is the Nusselt criterion; δ is the effective thickness of the diffusion boundary layer.

Fig. 1. Kinetics of change in the quantity $m_1^{1/3} - m_{1,0}^{1/3}$ for tricalcium silicate: 1 —without additives, and with addition of additives: 2-5 $NaNO_2$, 0.025, 0.05, 0.14, and 0.3 mol/l, respectively; 6-9 KCl, 0.01, 0.02, 0.03, and 0.04 mol/l, respectively; 10-13 K_2SO_4, 0.025, 0.05, 0.3, and 0.5 mol/l, respectively.

Figure 1: Fig. 1. Kinetics of change in the quantity $m_1^{1/3} - m_{1,0}^{1/3}$ for tricalcium silicate: 1—without additives, and with addition of additives: 2-5 $NaNO_2$, 0.025, 0.05, 0.14, and 0.3 mol/l, respectively; 6-9 KCl, 0.01, 0.02, 0.03, and 0.04 mol/l, respectively; 10-13 K_2SO_4, 0.025, 0.05, 0.3, and 0.5 mol/l, respectively.

From the general theory of V. G. Levich ([4]) it is known that, in the region of convective diffusion for spherical particles,

$$\delta \simeq \text{const} \cdot D^{1/3}. \tag{2}$$

The material-balance equation is

$$(m_1 - m_{1,0}) + (m_2 - m_{2,0}) + c_\tau = \text{const}. \tag{3}$$

We shall assume that the experiments are carried out without an externally introduced seed, and that the binder used is practically unhydrated, i.e.,

$$m_{2,0} = 0, \qquad (N_{2,0} = 0). \tag{4}$$

In papers ([1]) it was shown that the kinetics of hydration of clinker minerals and of cement paste in concrete can, to some extent conventionally, be divided into two stages: in the first (the early stage of hardening of binders, for clinker minerals on the order of 1-3 days), transport of matter is effected by convection and diffusion, since at this stage the influence of the preceding mixing of the cement paste and of the exothermic effect during hydration of its constituents is manifested.

At the second stage, which proceeds at a later stage of hardening of binders, after the formation of a rigid structural framework and under conditions of nonintensive heat evolution, mass transfer is close to purely molecular.

The fact of diffusion control over the hydration process of binders is also confirmed by the fact that, having accepted this assumption, A. F. Polak ([3]) derived an equation suitable for describing the kinetics of hydration of calcium sulfate hemihydrate.

Fig. 1. Kinetics of change in the quantity $m_1^{1/3} - m_{1,0}^{1/3}$ for tricalcium silicate: 1—without additives, and with addition of additives: 2-5 $NaNO_2$, 0.025, 0.05, 0.14, and 0.3 mol/l, respectively; 6-9 KCl, 0.01, 0.02, 0.03, and 0.04 mol/l, respectively; 10-13 K_2SO_4, 0.025, 0.05, 0.3, and 0.5 mol/l, respectively.

Let us examine in more detail the kinetics of hydration of binders in the region of convective diffusion.

The kinetics of dissolution of the initial phase for this early stage of the process is described by the equation

$$\frac{dl_1}{d\tau} = \frac{D}{\rho_1 \delta_1}(c_\tau - c_1), \tag{5}$$

or, taking equation (2) into account,

$$\frac{dl_1}{d\tau} = A_1 \rho_1^{-1} D^{2/3}(c_\tau - c_1). \tag{5a}$$

Similarly, the kinetics of growth of new formations will be written in the form

$$\frac{dl_2}{d\tau} = A_2 \rho_2^{-1} D^{2/3}(c_\tau - c_2). \tag{6}$$

We integrate equations (5a) and (6) for the case of a constant value of $A_{1,2}\rho_{1,2}^{-1}D^{2/3}$ and subtract one from the other, taking equation (1) into account; we obtain

$$\frac{1}{K_1}(m_1^{1/3} - m_{1,0}^{1/3}) - \frac{1}{K_2}(m_2^{1/3} - m_{2,0}^{1/3}) = -D^{2/3}(c_1 - c_2)\tau, \tag{7}$$

where

$$K_{1,2} = A_{1,2}\rho_{1,2}^{-1/3}\gamma_{1,2}^{1/3}N_{1,2}^{1/3} \simeq \text{const} \cdot N_{1,2}^{1/3}. \tag{8}$$

The kinetics of dissolution of the initial phase and growth of crystals of the new phase in the purely molecular region, as is known ([4]), is described by the equation

$$\frac{dl_{1,2}}{d\tau} = \frac{\text{Nu}\, D}{2\rho_{1,2} l_{1,2}}(c_\tau - c_{1,2}). \tag{9}$$

After integration for the case $\text{Nu}\, D\rho_{1,2}^{-1} = \text{const}$, subtracting one equation from another and substituting into $dl_{1,2}/d\tau$ their values from equation (1), we obtain

$$\frac{1}{K_1'}(m_1^{2/3} - m_{1,0}^{2/3}) - \frac{1}{K_2'}(m_2^{2/3} - m_{2,0}^{2/3}) = -D(c_1 - c_2)\tau, \tag{10}$$

where

$$K'_{1,2} = \mathrm{Nu}\,\rho_{1,2}^{-1/3}\gamma_{1,2}^{2/3}N_{1,2}^{1/3}. \tag{11}$$

Equations (7) and (10) relate data obtained by analysis of the solid phase in a concentrated suspension of binders with their diffusion (D) and thermodynamic characteristics (c_1 and c_2),

which can be determined from independent experiments by analyzing the liquid phase in dilute systems.

The direct use of equations (7) and (10) is difficult owing to the absence of data on the value of $N_{2,0}$, $l_{2,0}$, and for certain other reasons. An approximate solution can be found for the early stage of hardening of binders, during which, according to studies by a number of authors ([5–8]), the sizes of the growing crystals of the new phase are within the limits $1—5\cdot10^2$ Å, as against $1—5\cdot10^5$ Å for the grains of the initial material. When

$$l_1 \gg l_3 \qquad N_1^{1/3} \ll N_2^{1/3}, \tag{12}$$

which makes it possible to neglect the second term on the left-hand side of equation (7). A similar conclusion is also suggested by the experimentally established fact ([1]) that, for $\tau > 60$ min in concentrated suspensions of clinker minerals with water, the value c_τ approaches the value c_2, so that $c_1 - c_\tau \gg c_\tau - c_2$.

The validity of equation (7) can be checked in several ways.

First, for one and the same monomineral binder, the product $K_1D^{2/3}(c_1 - c_2)$ should remain constant during the experiment; then

$$m_1^{1/3} - m_{1,0}^{1/3} \simeq -K_1D^{2/3}(c_1 - c_2)\tau \simeq -\,\mathrm{const}\cdot\tau, \tag{13}$$

i.e., a linear dependence should be observed between the change in the left-hand side of equation (13) and the duration of hydration τ.

The same dependence should also be expected upon introducing additions of strong electrolytes that do not chemically interact with the binders and affect the rate of their hydration through a change in the solubility of the initial and final products c_1 and c_2, since in this case as well, for each concentration of the addition, the value $K_1D^{2/3}(c_1-c_2)_{\mathrm{add}}$ in equation (13) remains constant during the experiment.

Second, the change in the left-hand side of equation (13) as a function of the concentration of such additions, containing no ions of the same name as the binder substance, should be proportional to the change in the right-hand side of this equation; an analogous dependence should be observed when the hydration process of binders is accelerated by raising the temperature.

Finally, it follows from equation (13) that, at a constant value of τ, the change with temperature of the ratio $(m_1^{1/3} - m_{1,0}^{1/3})_a/(m_1^{1/3} - m_{1,0}^{1/3})_b = B_{\text{rel}}$ for two different binders a and b should be proportional to the change in the quantity $[K_1 D^{2/3}(c_1 - c_2)]_a/[K_1 D^{2/3}(c_1 - c_2)]_b$ for these same substances.

We checked the validity of the derived equations on the silicate constituents of portland-cement clinker: $3\text{CaO} \cdot \text{SiO}_2$ and β-$2\text{CaO} \cdot \text{SiO}_2$. As additions we used K_2SO_4, KCl, and NaNO_4 over a wide range of variation of their concentration.

The selected objects of study are characteristic (the silicate phases are the main ones in portland cement) and convenient, since for them $c_1 \gg c_2$, i.e., the solubility of the newly formed products may be neglected. Then equation (13) is further simplified:

$$\frac{m_1^{1/3} - m_{1,0}^{1/3}}{D^{2/3} c_1 \tau} = -K_1 \tag{14}$$

or

$$\frac{m_1^{1/3} - m_{1,0}^{1/3}}{\tau} \simeq -K_1 D^{2/3} c_1 \simeq k' v \simeq k'' I, \tag{14a}$$

since under conditions of controlled and regulated convection^(4) the dissolution rate of the disks v and the magnitude of the diffusion flux from their surface I

$$v \sim I \sim K_1 D^{2/3} c_1. \tag{15}$$

Equations (13)–(15) were used for the calculations. We determined the data on the quantities D_1, c_1, v, and I by carrying out experiments with pressed disks of $3\text{CaO} \cdot \text{SiO}_2$ and β-$2\text{CaO} \cdot \text{SiO}_2$^(9), the value $m_1^{1/3} - m_{1,0}^{1/3}$ by studying the hydration kinetics of concentrated suspensions of these materials by the gravimetric method; and also from the study^(10):

Table 1

Temp., °C	m_1, %	$-K_1 \cdot 10^4$
20	90	1.0
35	80	1.1
50	72	1.1
65	65	1.1

Table 2

Temp., °C	B_{rel}, after 24 hours	B_{rel}, after 72 hours	$v_{rel} \sim I_{rel}$
20	4.1	4.7	2.4
35	3.7	2.8	2.0
50	2.5	2.4	1.9
65	2.4	2.4	1.8

Table 1 gives the processing of literature data on the hydration kinetics of β-dicalcium silicate^(10) and of our data on its dissolution rate at various temperatures^(9) in accordance with equation (14) (duration of the experiments: 72 hours).

Table 2 gives the ratios of the hydration rates^(10) B_{rel} and dissolution rates^(9) $v_{rel} \sim I_{rel}$ of tricalcium and β-dicalcium silicates at various temperatures.

The experiments showed*, that all three propositions set out above, following from equations (13) and (14), are fulfilled.

Thus, the available data prove the correctness of the theory of hardening of binders developed in the article. It is very important in this connection that the hardening curves of $3CaO \cdot SiO_2$ vary depending on the concentration of the additives in a manner similar to the curves for the change in the degree of hydration of these same specimens.

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* The experimental verification was performed by S. M. Pimenova, V. B. Ratinov, and I. A. Smirnova.

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