V. B. RATINOV, G. D. KUCHERYAEVA, and G. G. MELENT' EVA

1961

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. B. RATINOV, G. D. KUCHERYAEVA, and G. G. MELENT'EVA

THERMODYNAMIC AND DIFFUSION CHARACTERISTICS OF THE SILICATE CONSTITUENTS OF CEMENT UPON THEIR DISSOLUTION IN WATER

(Presented by Academician P. A. Rehbinder, 22 IX 1960)

Below are presented the results of measuring the thermodynamic (metastable solubility) and diffusion characteristics of tricalcium silicate (C_3S) and β-dicalcium silicate (C_2S), knowledge of which is important for constructing a theory of the hardening of cement stone. The solubility of the aluminate constituents of cements was first determined by E. E. Segalova, E. S. Solov' eva, and P. A. Rehbinder (^{1,2}). By the solubility of a binding substance C_p we understand its maximum possible concentration, which corresponds to saturation of the solution with respect to this binder; therefore the value of C_p is related to the change in free energy upon dissolution ΔF by the known relation:

$$C_p = \exp\left\{\frac{\Delta F - \varphi}{RT}\right\}, \tag{1}$$

where $\varphi = RT \ln f$; f is the activity coefficient.

The difficulties in realizing the value C_p for clinker minerals and a number of other salts capable of forming solutions supersaturated with respect to their new formations are due to the fact that, during their interaction with water, intensive crystallization of the new phase* may begin even before the solution reaches the concentration corresponding to the solubility of the initial compound; as a result, from a unit volume of solution per unit time more material will be removed for crystallization of the new formations (usually hydrates) than enters as a consequence of dissolution of the initial substance, and the directly measured concentration of the latter will not reach the value C_p.

Therefore, the solubility of alite and belite was determined by us by several independent methods, including one whose application made it possible to exclude the stage of crystallization of new formations. With the aid of this method it was also possible to measure the diffusion characteristics of binding substances.

The theory of the method was developed by V. G. Levich (^{3}). For the case of rotation in water of a disk made of the material under investigation under

Fig. 1. Kinetics of dissolution in water of disks made from C_3S (a), C_2S (b), C_3SH_2 (v), and $C_2SH(A)$ (g). 1–12°; 2, 3, and 5–20°; 4–30°; 6–40°; 7–50°; 8 and 10–60°; 9–70°

Figure 1: Fig. 1. Kinetics of dissolution in water of disks made from C_3S (a), C_2S (b), C_3SH_2 (v), and $C_2SH(A)$ (g). 1–12°; 2, 3, and 5–20°; 4–30°; 6–40°; 7–50°; 8 and 10–60°; 9–70°

conditions of controlled and regulated convection, the theory gives:

$$C_p = \frac{I\nu^{1/6}}{0.62\omega^{1/2}D^{2/3}}, \tag{2}$$

where I is the magnitude of the diffusion flux

$$I = \frac{m}{s\tau}; \tag{3}$$

m is the amount of dissolved substance; s is the surface of the disk; τ is the time of its dissolution.

* The chemical composition of the new phase may differ from the composition of the initial substance.

Knowing the kinematic viscosity of the solution, v, and setting a constant angular velocity of rotation of the disks, ω, one can find the values of C_p for alite and belite, if their diffusion coefficients D are known. We determined the value of D by carrying out experiments with disks made from calcium hydrosilicates of the same basicity as the corresponding anhydrides C_3SH_2 and $C_2SH(A)$.

Both hydrates were synthesized in a bomb, the first from C_3S, the second from sand and lime*; their solubility was determined by the generally accepted method—by analysis of the solution after equilibrium had been reached between the solid and liquid phases. The concentration of silicate ions was measured colorimetrically, by the colored complex with ammonium molybdate in sulfuric acid medium (4), and the concentration of calcium ions by trilonometrical titration (5). To avoid carbonation, the experiments were carried out under nitrogen. Disks of C_3S, C_2S, and hydrates were prepared by pressing dry powders under pressure up to 20,000 kg/cm^2 in special press molds (6). The adopted procedure ensured good reproducibility of the results of parallel experiments.

Fig. 1. Kinetics of dissolution in water of disks made from C_3S (a), C_2S (b), C_3SH_2 (v), and $C_2SH(A)$ (g). 1–12°; 2, 3, and 5–20°; 4–30°; 6–40°; 7–50°; 8 and 10–60°; 9–70°.

From the data obtained for C_3SH_2 and $C_2SH(A)$ (see Fig. 1), using formula (2), the diffusion coefficients of these hydrates were calculated; we took them to be equal to the values of D for the corresponding anhydrides. The remaining data needed to calculate the value of C_p were found from the experimental curves shown in the figure.

In addition, the disks were also used for another variant of the method for determining the solubility of C_3S and C_2S, which makes it possible to exclude the diffusion coefficient from the calculation and not to resort to calcium hydrosilicates. This method requires carrying out at least two experiments: the first at an initial concentration of the substance under study in solution equal to C_1, and the second C_2. Then equation (2) can be written in the form:

$$I_1 = K(C - C_1), \tag{4a}$$

$$I_2 = K(C_p - C_2). \tag{4 }$$

The constancy of the coefficient K is ensured in dilute solutions by small differences in the values of C_1 and C_2; in this case the values of D and v practically do not change.

Solving equations (4a) and (4) with respect to C_p, we obtain

$$C = \frac{C_2 I_1 - C_1 I_2}{I_1 - I_2}. \tag{5}$$

For $C_1 = 0$, formula (5) is simplified.

* C_3SH_2 was synthesized by L. N. Rashkovich, and $C_2SH(A)$ by O. I. Gracheva, to whom the authors express their gratitude. The purity and phase composition of C_3S, C_2S, and the hydrates were established by chemical and X-ray analyses; the latter was performed by L. N. Rashkovich and O. I. Gracheva on a URS-50I diffractometer.

A formula of analogous type

$$C_p = \frac{C_m v_n - C_n v_m}{v_n - v_m} \tag{5a}$$

was also used by us for processing the ascending branch of the experimental kinetic curve of dissolution of suspensions of C_3S and C_2S.

Here v_n and v_m are the average dissolution rates over arbitrarily chosen time intervals $\Delta\tau_n$ and $\Delta\tau_m$ (or the true rates at the time instants τ_n and τ_m), and C_n and C_m are the corresponding concentrations of the substance in solution.

The solubility of C_3S and C_2S was also determined by us by direct measurement —working with their dilute suspension containing surface-active additives, which inhibit the crystallization process of new formations more strongly than the dissolution of the initial compounds. The absence of substantial crystallization of hydrates in these and in all other experiments was monitored by the constancy of the molar ratio of calcium ions to silicate ions ($C_{\mathrm{Ca}} : C_{\mathrm{SiO_2}}$).

Since the new formations arising from dilute suspensions of C_3S and C_2S have lower basicity than the initial compounds, an increase in the value of $C_{\mathrm{Ca}} : C_{\mathrm{SiO_2}}$ in solution indicated the development of the crystallization process; in the absence of the latter this ratio was constant and equal to 3 and 2, respectively.

The values of C_p for C_3S and C_2S at 20°, obtained by the indicated methods, differed from one another by no more than 10%; this indicated the closeness of the effective diffusion coefficients of molecules and ions during dissolution in water of C_3S, C_2S, C_3SH_2, and $C_2SH(H)$, and the possibility of applying the first method for determining the quantities C_p and D also at elevated temperature. The results of such measurements are presented in Table 1.

Table 1

Thermodynamic and diffusion characteristics of C_2S

Experimental temperature, °C	Solubility C_p, g/l	Diffusion coefficient $D \cdot 10^6$, $\mathrm{cm^2/sec}$	Diffusion flux $I \cdot 10^7$, $\mathrm{g/cm^2 \cdot sec}$	Experimental temperature, °C	Solubility C_p, g/l	Diffusion coefficient $D \cdot 10^6$, $\mathrm{cm^2/sec}$	Diffusion flux $I \cdot 10^7$, $\mathrm{g/cm^2 \cdot sec}$
2	0.155	–	–	40	0.212	6.3	8.3
12	0.172	2.4	3.2	50	0.236	7.4	10.5
20	0.190	3.7	4.3	60	0.258	8.1	12.4
30	0.203	5.2	6.6	70	–	–	14.3

At 2° the solubility of C_3S was 0.256 g/l, at 10° 0.338 g/l, at 20° 0.387 g/l; the diffusion coefficient was respectively $2.6 \cdot 10^{-6}$, $3.0 \cdot 10^{-6}$, and $3.4 \cdot 10^{-6}$ $\mathrm{cm^2/sec}$, and the magnitude of the diffusion flux was respectively $0.5 \cdot 10^{-6}$, $0.67 \cdot 10^{-6}$, and $1.0 \cdot 10^{-6}$ $\mathrm{g/cm^2 \cdot sec}$. (In all cases the rotation rate of the disks was 10 rev/sec.)

From the data obtained, using the equation

$$\frac{d \ln C_p}{dT} = -\frac{Q}{RT^2} \tag{6}$$

the heat of dissolution Q was calculated; for C_2S it was equal to 1.5 kcal/mole, and, by a formula of analogous type, the value of its activation energy of diffusion during dissolution in water, equal to 6.3 kcal/mole.

Knowing the solubility and heat of dissolution of C_2S, one can calculate its other thermodynamic characteristics by known formulas.

The values we determined,

$$I' = \frac{I}{\omega^{-1/2}} \cdot 10^7 \text{ g/cm}^2 \cdot \text{s},$$

for the dissolution in water of gypsum, lime, tricalcium aluminate, C_3S, and C_2S at 20° were, respectively, 8.1; 3.2; 1.9; 1.2; 0.5, and are arranged in the same sequence as the rates of their hardening in concentrated suspensions; this serves as yet another proof of the correctness of the mechanism of hardening of binders developed in works (5-7).

Scientific Research Institute
of Reinforced-Concrete Products, Construction and Nonmetallic Materials

Received
14 IX 1960

REFERENCES CITED

1. E. E. Segalova, E. S. Solov' eva, P. A. Rebinder, DAN, **117**, No. 5 (1957).
2. E. S. Solov' eva, E. E. Segalova, *Koll. zhurn.*, **20**, No. 5 (1958).
3. V. G. Levich, *Physicochemical Hydrodynamics*, Publishing House of the Academy of Sciences of the USSR, 1959.
4. V. M. Bereznyak, V. A. Begma, V. I. Zhuravskaya, *Zav. lab.*, **21**, No. 3, 298 (1955).
5. V. B. Ratinov, Ya. I. Zabezhinskii, T. I. Rozenberg, DAN, **109**, No. 5 (1956); Collection of Papers of VNIIzhelezobeton, issue 1 (1957).
6. V. B. Ratinov, V. A. Grigoryan, *Building Materials*, No. 3 (1960).
7. V. B. Ratinov, T. I. Rozenberg, Collection of Papers of NIIzhelezobeton, issue 2 (1959).

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