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PHENOMENOLOGY OF HYDRATION OF INORGANIC BINDERS BASED ON MICROCALORIMETRIC KINETIC DATA

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A self-consistent mathematical model is proposed to describe the heat evolution during the hydration of inorganic binders. Such an approach reflects the sufficient role of the feedbacks in the systems under discussion. The principal physico-chemical reasons for the self-consistent description of the hydration kinetics are argued. To complete the phenomenology of the hydration of binders two more problems are solved: (i) quantitative determination of the characteristic periods of the hydration process, and (ii) the long-range forecast of integral heat evolution.

One of the fruitful and promising fields for the application of isothermal differential microcalorimetry is the kinetic study of the reaction of inorganic binders with water [1]. The use of this technique means the choice of the heat evolution rate $\dot{Q}(\tau)$ as a measure of hydration intensity. The corresponding completeness measure is $Q(\tau) = \int_0^\tau \dot{Q}(t)\,dt$. The chosen values are phenomenological by their nature. The existing phenomenological models include as a principal assumption the possibility to separate the contributions of different stages by suitable boundary conditions. They cannot reflect the unique structural arrangement of binder systems with feedback.

To describe the observable temporal dependence of the heat evolution rate using the ideas of modern heterogeneous kinetics, it is necessary to determine the interrelation between $Q(\tau)$ and $\alpha(\tau)$ (where $\alpha(\tau)$ is the degree of hydration). In general, the proportionality $Q(\tau) = Q_\infty\alpha(\tau)$ is not sufficiently convincing proof. Taking into account the amorphism of the solid phase in direct contact with the mother liquid phase and its further rearrangement, we regard the precipitation of hydrates as two sequential nucleation processes:

$$Q(\tau) = Q_1(\tau)+Q_2(\tau) = Q_{1\infty}\alpha_1(\tau)+Q_{2\infty}\alpha_2(\tau) \tag{1}$$

The quantitative description of these processes is based on the generalization [3]

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of Kolmogorov's probability scheme [2], which leads to the self-consistent models. The two main physico-chemical reasons for the self-consistent description of the hydration kinetics are: (i) the considerable influence of endogenic effects generated in the liquid phase (the formation of unsteady concentration fields, etc.) on the kinetic behaviour of the system, and (ii) the spatial and temporal interrelations between the hydration and diffusion stages. The significance of the endogenic factors is determined by the fact that they perform the feedbacks in the "growing phase—mother medium" system.

Taking (1) into account, the two-dimensional problem of hydration and the three-dimensional problem of the structural rearrangement of the hydrated phase are solved simultaneously, formalism from [3] being used. The equation for $Q_1(\tau)$ was obtained by treating the nucleation and growth of the hydration phase as a result of strong adsorption interactions:

$$Q_1(\tau) = k_1 \int_0^{r_{max}} \mathrm{d}r \left\langle 1 - \exp\left[- \int_0^{\tau} \frac{(g^2(t))'}{4\pi h(t)} \mathrm{d}t \right] \cdot \right. \\ \left. \cdot \exp\left[rg(\tau) - \pi r^2 h(\tau) \right] \right\rangle \tag{2}$$

The auxiliary function $g(\tau)$ is a solution of the self-consistent equation $g(\tau)\dot{g}(\tau) = 2\pi k_2 h(\tau)\ (\exp(-r_1 g(\tau) - \pi r_1^2 h(\tau) - \exp(-r_2 g(\tau) - \pi r_2^2 h(\tau)))$; $h(\tau)$ describes the intensity of nucleus appearance; r = distance; and k_1 and k_2 are model parameters.

The new hydrate phases formed on the interface far from equilibrium are unstable and are characterized by a high specific surface, an imperfect structure and a large number of defects. For this reason, they are irreversibly transformed into a more stable state. To describe this process using Kolmogorov's probability scheme, it is necessary to take into account the coordinate dependence of α [4]. This leads to the equation

$$Q_2(\tau) = \frac{k_3}{z} \int_0^z \left(1 - \exp\left[- \int_{t_1}^{t_2} \mathrm{d}t \cdot I(t) \cdot \right. \right. \\ \left. \left. \cdot \int_{z_1}^{z_2} \left(R^2(\tau, t) - V^2(t) \right] \right) \mathrm{d}V \tag{3}$$

Here, $V(t)$ is directly connected with $Q_1(\tau)$; $I(t)$ is the intensity of nucleus appearance; $R(\tau, t)$ is the law of their growth; z is the normal coordinate; and k_3 is the modul parameter. Values z_1 and z_2 are calculated with the help of simple geometrical considerations. Magnitudes t_1 and t_2 are the solutions of self-consistent

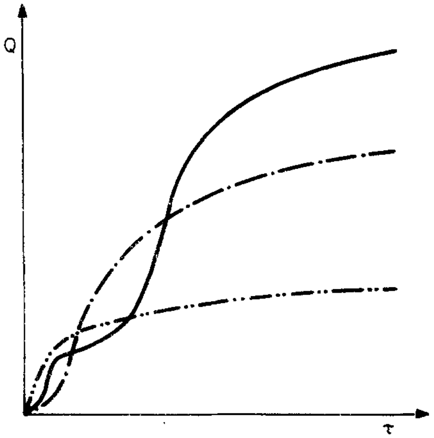

Fig. 1 Typical curves $Q_1(\tau)$ (—··—), $Q_2(\tau)$ (—·—) and $Q(\tau)$ (——)

equations $t_1 = (V(t_1)+k_4\tau-z)/k_4$ and $t_2 = (z+k_4\tau-V(t_2))/k_4$, respectively; k_4 is the model parameter.

Equations (1), (2) and (3) solve the problem of the self-consistent description of the hydration kinetics on the basis of isothermal microcalorimetric data. Corresponding typical curves are shown in Fig. 1.

In addition to this self-consistent model, two more problems were solved to complete the phenomenology of the process under discussion.

The first of them is to distinguish thecharacteristic periods of the hydration process. Apart from the singular points τ_m, τ_{m1} and τ_{m2} defined by the simple condition $\ddot{Q}(\tau) = 0$, we discern three more points, τ_1, τ_2 and τ_3 in which the instantaneous rate is equal to the mean one $1/\tau\left(\int_0^\tau \dot{Q}(t)\,dt - Q_0\right)$, where $Q_0 = Q_{\min} - \tau_{\min}(Q_{\max}-Q_{\min})/(\tau_{\max}-\tau_{\min})$, and $\tau_{\max}$ is the smallest of the values τ_{m1} and τ_{m2} (Fig. 2). At these points the process switches from rapid to slow, or vice versa. Hereby, the induction period may be quantitatively determined (for our sample of Ca_3SiO_5 it lasts for from 0.04 to 1.5 h). Such a distinction of the characteristic periods allows one to analyse the transformations of $\dot{Q}(\tau)$ curves under the influence of different factors (temperature, admixtures, etc.).

The second problem is connected with the long-range forecast of integral heat evolution. This problem is solved by means of the restraint approximation of relationship $Q(\tau)$ by two functions $f_1(t)$ and $f_2(t)$ possessing horizontal asymptotes (Fig. 3). The inevitable assumption that the system undergoes no abrupt changes in the forecast interval was formulated as follows: in curve $Q(\tau)$ there is a point $Q(\tau_0)$ after which the curvature has no local extremes. The approximation functions

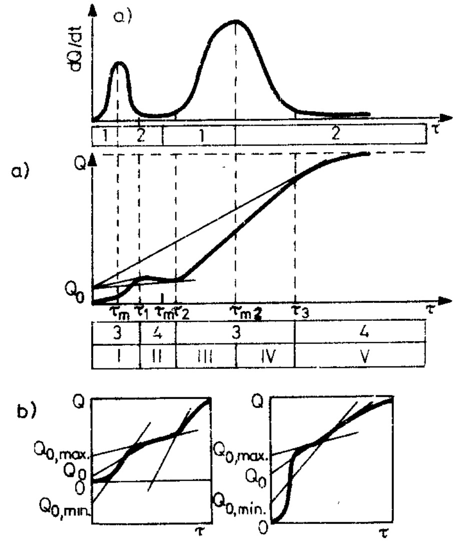

Fig. 2 Determination of the characteristic periods of the hydration process

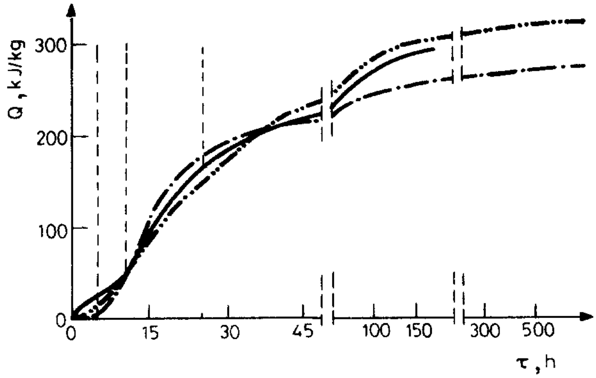

Fig. 3 Long-range forecast of integral heat evolution; $Q(\tau)$ (——), $f_1(\tau)$ (—·—) and $f_2(\tau)$ (—··—). (ordinate: Q, kJ kg^{-1})

ought to cross the experimental one at $\tau^* > \tau_0$. If, after these crossing points, they likewise have no local extremes of curvature, the forecast may be obtained as $Q(\tau) = [f_1(\tau) \pm f_2(\tau)]/2 \pm [f_1(\tau) - f_2(\tau)]/2$. Comparison of the calculated value (274.4 J g^{-1}) with the experimental one (290 J g^{-1}) in the case of ordinary Portland cement confirms the satisfactory quality of the forecast.

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Zusammenfassung — Ein selbstkonsistentes mathematisches Modell zur Beschreibung der Wärmeentwicklung bei der Hydration anorgenischer Bindemittel wird vorgeschlagen. Der Ansatz gibt ausreichend die Rückkopplungen in den betrachteten Systemen wieder. Die physikalisch-chemischen Gründe für die selbstkonsistente Beschreibung der Hydratationskinetik werden diskutiert. Um die phänomenologische Beschreibung der Bindemittel-Hydratation zu vervollständigen, werden zwei weitere Probleme gelöst: (1) die quantitative Beschreibung der charakteristischen Phasen des Hydratationsprozesses, (2) die Langzeit-Vorhersage der integralen Wärmeentwicklung.

Резюме — Основная особенность математической модели, предложенной для описания кинетики тепловыделения при гидратации неорганических вяжущих веществ — ее самосогласованность. Такой подход отражает существенную роль обратных связей в рассматриваемых системах. Обсуждаются основные физико-химические предпосылки самосогласованного описания кинетики гидратации. Наряду с основной моделью, феноменологическое описание процесса гидратации вяжущих веществ включает также: (1) количественное выделение характерных периодов процесса гидратация и (2) долгосрочный прогноз интегрального тепловыделения.