Analysis of the hydration reaction of the Portland cement composition based on the hydration equation

Yuya YODA1, Yutaka AIKAWA* and Etsuo SAKAI*

Center for Construction Engineering, Shimizu Institute of Technology, Shimizu Corporation, 3–4–17 Etsunuma, Koto-ku, Tokyo 135–8530, Japan
*Department of Metallurgy and Ceramics Science Graduate, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2–12–1 Ookayama, Meguro-ku, Tokyo 152–8532, Japan

Using the expanded Tomosawa theory, we simulated the experimental values of the hydration reaction of ordinary Portland cement (OPC) compositions and chose the hydration parameters for each component. Furthermore, we compared the superposition of the simulated data of the components and the measured values of the hydration reaction of the OPC. There was a good agreement between the superposition of the simulation data and experimental data of the OPC.

©2017 The Ceramic Society of Japan. All rights reserved.

Key-words : Tomosawa theory, Hydration reaction, Portland cement, Elementary component, Simulation, Rate of reaction, Reaction ratio, Coefficient of mass transfer, Effective diffusion coefficient, Particle size distribution

1. Introduction

The hydration reaction of ordinary Portland cement (OPC) involves four types of hydration components: a-lite (C3S), belite (C2S), aluminate (C3A), and ferrite (C4AF). It has been considered that the hydration process of OPC involves several correlated reactions among the four components. For these four components, there is data on several measurements of the hydration reaction, but the correlation reactions among the components have not been quantitatively reported. In order to analyze the characteristics of the hydration reaction and to study the mechanism of the hydration reaction, it is necessary to superpose the simulation of the measured hydration reaction of the four components.

Tomosawa2) suggested a hydration equation for OPC; however, the reaction time is a very complex function of the reaction ratio. In addition, representing the reaction ratio as a function of reaction time is analytically impossible. Therefore, reaction rates that vary according to the components cannot be superposed onto the OPC under a common axis of reaction time. Incidentally, we have already generalized the fundamental equation. Multiple reaction rates that vary according to the components can be superposed under a common axis of reaction time using an infinite series of Bessel polynomials as a function of the reaction time.3) The characteristics of the hydration reaction are defined through the physical meaning of the fitting parameters $k_r$, $B_\theta$, $C_\theta$, and $D_\theta$ in the Tomosawa equation.4)

By using the fundamental equation, it is possible to superpose the simulated results of the hydration reaction of the four elementary components of OPC and discuss the difference between the superposed and measured hydration reactions of OPC.

2. Theoretical analysis

Tomosawa’s equation for the analysis of the hydration reaction of cement is as follows:\(^2\)

$$-\frac{d\alpha}{dt} = \frac{3}{\rho_c \rho_0} \frac{1}{r_0(1/\alpha)^{\frac{1}{3}}} \left( \frac{1}{k_d} + \frac{1}{k_e} \right) + \frac{1}{D_e} \left( \alpha^{1/3} - (2 - \alpha)^{1/3} \right)$$

where $-d\alpha/dt$ is the rate of reaction, $\alpha$ is the degree of non-reaction ($1 - \alpha$ is the reaction ratio), $r_0$ is the particle radius, $C_{w_0}$ is the water concentration around the particle, $\nu$ is the ratio of chemical stoichiometry in the water-cement reaction, $\rho_c$ is the density of cement, $k_r$ is the coefficient of reaction velocity, and $k_d$ is the coefficient of mass transfer at the stage when a rapid reaction occurs immediately upon contact with water. Thus, it can be written as a function of $\alpha$ as:

$$k_d = \frac{B_d}{(1 - \alpha)^{\frac{1}{3}}} + C_d (1 - \alpha)^{\frac{1}{3}}$$

$$D_e = D_h \left[ \ln \frac{1}{1 - \alpha} \right]^2$$

This is introduced in order to modify the reaction ratio $1 - \alpha$, which decreases more rapidly than in the ordinary diffusion process at the stage where the reaction rate decreases after the most active reaction is completed and the degree of hydration reached at $1/\nu$, $D_h$ becomes $D_e$. It takes the common values $\nu = 0.25$, $\rho_c = 3.15 [g/cm^3]$, and $C_{w_0} = 1$.

Because Eq. (1) deals with one particle radius only, it has to be expanded Eq. (1) in a general size distribution system as:\(^2\)

$$-\frac{d\alpha}{dt} = - \sum f(r_i) \frac{d\alpha(r_i, t)}{dt}$$

where $f(r_i)$ is the normalized particle size distribution of OPC and $r_i$ is the radius of the $i$-th particle.

It is assumed that the hydration reaction of OPC is a linear combination of the hydration reactions of each component (C3S, C2S, C3A, and C4AF).
The degree of hydration of each component can be analyzed from the difference between the simulation result from Eq. (4) as the OPC and the hydration reaction of each component, as shown in Fig. 1.

The specimens were mixed and cured indoors at the three curing temperatures 20 ± 2°C in curing tanks for accurate control of the temperature. After the predetermined aging times (1, 3, 6, 9, 12, 18, 24 h and 2, 3, 7, 14, 28 days), the hydration was stopped using amorphous phase. The hardened materials were then taken as the quantity of combined water for each hydration product; the hydration conversion into anhydrous minerals and hydrated products were also determined via XRD method is virtually the same as that determined by the XRD analysis, as shown in Fig. 1.

Comparison of the values obtained using the two methods of quantification.

The degree of hydration of each mineral (C3S, C2S, C4AF, C3A) was added (10 mass %), as an internal standard method is essentially the same as that determined by the XRD analysis (PDXL ver. 2.1.3.4, Rigaku). In addition, aluminum oxide added (10 mass %), as an internal standard method is essentially the same as that determined by the XRD analysis (PDXL ver. 2.1.3.4, Rigaku). In addition, aluminum oxide added (10 mass %), as an internal standard method is essentially the same as that determined by the XRD analysis (PDXL ver. 2.1.3.4, Rigaku).
Fig. 3. Reaction ratios of (a) C₃S, (b) C₂S, (c) C₃A and (d) C₄AF in OPC.

Fig. 4. Rates of reaction of (a) C₃S, (b) C₂S, (c) C₃A and (d) C₄AF in OPC.


\[
\begin{align*}
    \text{C}_3\text{S} & \quad \text{C}_3\text{A} & \quad \text{C}_4\text{AF} & \quad \text{C}_4\text{S} \\
\end{align*}
\]

Fig. 5. Fitting parameters for the (a) reaction rate \(k\), (b) formation of the protective layer with no diffusion \(B_d\), (c) destruction of the protective layer \(C_d\), and (d) effective diffusion \(D_{eq}\) in Eq. (1).

Fig. 6. Comparison between the superposition of the experimental data of the four elements in OPC (rhomb) and the superposition of the simulated values of the four elements in OPC (dotted curve). The solid curve represents the experimental data of OPC with respect to the reaction ratio (a) and the rate of reaction (b).

dislocation state. The dislocation state possesses a transition structure between the crystalline state and melting state, which arises when a chemical reaction with a large atomic rearrangement occurs. We considered that the differences between the superposition of the experimental values of the four elements in the OPC and the experimental data of the OPC at the initial stage of hydration \(<10\) h were due to this reason.

5. Conclusion

We simulated the hydration reaction of the individual components of OPC for the first time and compared it with the actual hydration reaction. The superposition of the simulated values of the four elements of the hydration reaction in the OPC agreed well with the experimental data of the OPC. Therefore, it was clear that during the hydration reaction, the interactions among the individual components in the OPC were almost negligible.

References

1) I. Maruyama, T. Matsuishi, T. Noguchi, Y. Hosokawa, and K. Yamada, Nippon kenchikugakai kouzou-kei ronbunsyu (Japan Architectural Institute structure system papers) 75, 681–688 (2010) [in Japanese].
2) F. Tomosawa, Cement gijyutu nenpo (Cement technology annual report) 28, 53–57 (1975) [in Japanese].
3) Y. Aikawa, D. Atarashi and E. Sakai, J. Ceram. Soc. Japan, 122, 93–95 (2014).
4) Y. Aikawa, D. Atarashi, T. Nakazawa and E. Sakai, J. Ceram. Soc. Japan, 122, 810–816 (2014).
5) Y. Aikawa, D. Atarashi, S. Miyahara, N. Siribudhawan and E. Sakai, J. Ceram. Soc. Japan, 123, 1073–1079 (2015).
6) P. Stutzman and S. Leigh, *NIST Technical Note*, 1441, 34–43 (2002).

7) Y. Yoda, Y. Aikawa, D. Atarashi and E. Sakai, *Cement Science and Concrete Technology*, 68, 118–125 (2014) [in Japanese].

8) K. Paku, F. Tomozawa, T. Noguchi, and Y. Murata, *Concrete kogaku nenji hokokusyu (Collection of concrete engineering annual article reports)* 19, 187–192 (1997) [in Japanese].

9) M. Daimon, *Cement Science (JME Material Science)*, 56, 1 (1989).