Effective method for analysis of the rate of hydration of Portland cement based on size distribution

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The fundamental equation of the rate of hydration derived by Tomozawa, which was originally applied to a single particle, was applied to the hydration process of Portland cement using a size distribution function. We generalized the fundamental equation to apply it to particle size distribution system. Actually, multiple reaction rates that vary according to the particle size can be superposed under a common axis of reaction time using an infinite series of Bessel polynomials as a function of the reaction time. By simulating the heat liberation with the hydration rate equation in terms of the size distribution, the parameters in the equation could be accurately determined.

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1. Introduction

The hydration process of Portland cement contains several extremely complex multi-reactions. Tomozawa \(^1\) suggested a well-known hydration rate equation for Portland cement from an industrial point of view. The hydration rate equation and experimental data for the heat liberation rate are compared to conventionally determine, several parameters for the hydration rate equation using one particle approximation.\(^2\)\(^3\)

The Tomozawa equation of hydration only considers the hydration reaction of one particle. Cement powder actually has a particle size distribution, and the hydration behavior differs for differently sized cement particles. Therefore, a hydration rate equation that explains the hydration behavior of one particle cannot represent the actual hydration behavior of a complete system with a size distribution.

Until now, hydration reactions of cement based on the hydration rate equation have been analyzed using a one-particle model, but actual cement particles have different sizes. When solving the hydration rate equation, the reaction time is represented by a very complex function for the reaction rate, and representing the reaction rate as a function of the reaction time analytically is impossible; therefore, multiple reaction rates that vary according to the particle size cannot be superposed under a common axis of reaction time. In order to superpose multiple reaction rates under a common reaction time axis, we used a general power series expansion method. Thus, the numerical solution to the reaction rate can be expanded in an infinite series of Bessel polynomials as a function of the reaction time, which makes superposition under a common axis of reaction time possible.

2. Superposition of the hydration rate equation

Tomozawa’s equation is given as follows:\(^1\)\(^3\)

\[
- \frac{d\alpha}{dt} = \frac{3C_{w\infty}}{\nu\rho_0 r_0^2} \frac{1}{r_0^2} \left( \frac{1}{k_d + k_f} \right) + \frac{\alpha^{1/3} - [2 - \alpha]^{-1/3}}{D_c} , \tag{1}
\]

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

\[
k_d = \frac{B_d}{1 - \alpha} + C_d(1 - \alpha)^{1/3} \tag{2}
\]

where \(B_d\) is the coefficient for the formation of a protective layer with no diffusion, and \(C_d\) is the coefficient for the destruction of the protective layer. The effective diffusion coefficient \(D_e\) is written as a function of \(\alpha\):

\[
D_e = D_c \left[ \ln \frac{1}{1 - \alpha} \right]^2 \tag{3}
\]

This is introduced in order to modify the reaction rate, which decreases more rapidly than the ordinal diffusion process in the stage when the reaction rate decreases after the most active reaction is completed. It takes the typical values, \(\nu = 0.25\), \(\rho_c = 3.15[\text{g/cm}^3]\), and \(C_{w\infty} = 1\). Figure 1 shows the rate of heat liberation for several values of \(r_0\) calculated from Eq. (1) by using the parameters listed on the right-side column in Table 1. Equation (1) deals only with one particle of radius \(r_0\), but cement particles actually have a size distribution caused both naturally and artificially. For example, the size distribution of Portland cement particles, \(f(r_i)\), as shown in Fig. 2 is normalized as

\[
\sum_i f(r_i) = 1 \tag{4}
\]

where \(r_i\) is the radius of the \(i\)-th particle.
In order to apply Eq. (1), which only considers particles with one radius, to a system of cement particles, the equation must be generalized to a formulation for a general size distribution system:

$$\sum_i f(r_i) \frac{d\alpha(r_i,t)}{dt}$$

The numerical solution of Eq. (1) is represented as $t = \text{func.}(\frac{d\alpha}{dt})$. There is no way to derive the form of the reaction rate $\frac{d\alpha}{dt}$ as a function of $t$ analytically, and the reaction rate $\frac{d\alpha(r_i, t)}{dt}$ cannot be superposed for all particle sizes $r_i$ because the reaction rate of different particle radii $r_i$ has no common horizontal axis $t$. The numerical solution of Eq. (1) at particle radius $r_i$ is written as

$$\sum_i f(r_i) \frac{d\alpha(r_i,t)}{dt} \equiv \Phi(r_i,t)$$

where $\Phi$ is a function of $t$.

In order to possible to superpose the reaction rate $\Phi(r_i, t)$ about all particle sizes $r_i$, we formulated the reaction rate to a power series expansion as a function of $t$ by using appropriate normalized orthogonal eigen functions. In general, an arbitrary function is expressed by the Fourier series as

$$\phi(r_i, t) = \frac{1}{2\pi} \sum_{s=0}^{\infty} \varepsilon_s \int_0^{t_m} \Phi(r_i, \lambda) \cos \frac{\pi(t - \lambda)}{t_m} d\lambda$$

where $\varepsilon_s$ is the solution to

$$\nu J_1(v) - h t_m J_0(v) = 0,$$

$h$ is a fitting parameter, and $J_s(x)$ is the following Bessel function:

$$J_s(x) = \sum_{n=0}^{\infty} \frac{(-1)^n x^{n+s}}{2^{n+s} s! \Gamma(n + s + 1)}.$$
For example, \( r_i \) in Eq. (8) is taken as equal to the averaged radius \( \langle r \rangle \), as shown in Fig. 4. For Bessel series \( \phi(r_i, t) \) of Eq. (8) \((s = 1\text{--}100)\), the trace of the initial stage has more detail than the case of Fourier series \( \phi(r_i, t) \) of Eq. (7) \((s = 1\text{--}100)\), because the latter method cannot follow the rapid change in the initial stage caused by the Gibbs phenomenon.

Now that each \( \phi(r_i, t) \) can be represented as a function of \( t \), \( \phi(r_i, t) \) can be superposed on different \( r_i \), and the reaction rate of a cement particle system with a size distribution is given by

\[
-\frac{d\sigma}{dr} = \sum_{i=1}^{N} f(r_i) \phi(r_i, t)
\]  

(9)

3. Simulation for heat liberation of Portland cement with size distribution

The heat liberation of Portland cement was measured using a conduction calorie meter; the size distribution is shown in Fig. 2. Both the experimental data (solid curve) and simulation data (dotted curve) from Eq. (9) are plotted in Fig. 5. The fitting parameters in Eq. (1) are listed in Table 1. Fitting parameters are also listed for a simple system with a single averaged particle size \( \langle r \rangle \) called the averaged radius system. The differences between fitting parameters for the size distribution system and averaged radius system can clearly be seen. Therefore, the averaged radius system should not be used as an approximation when examining the reaction rate of cement with a size distribution. Thus, the fitting parameters for the size distribution system listed in Table 1 most accurately describe the intrinsic properties of Portland cement.

Table 1. Fitting parameters in Eq. (1) that are calculated using the size distribution in the left-side column, and the averaged radius system in the right-side column

| Size distribution sys. | Averaged radius sys. |
|------------------------|----------------------|
| \( k_r \) [cm/h]       | \( 1.3 \times 10^{-6} \) | \( 9.3 \times 10^{-7} \) |
| \( B_d \) [cm/h]       | \( 1.0 \times 10^{-6} \) | \( 1.2 \times 10^{-9} \) |
| \( C_d \) [cm/h]       | \( 9.0 \times 10^{-5} \) | \( 1.1 \times 10^{-4} \) |
| \( D_e \) [cm²/h]      | \( 7.0 \times 10^{-12} \) | \( 4.0 \times 10^{-12} \) |

4. Conclusion

We expanded the hydration reaction equation that supports a single particle into one that can be applied to a general particle size distribution. We were able to identify various parameters for Portland cement concerning the hydration reaction.

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