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Effect of fly ash on the kinetics of Portland cement hydration at different curing temperatures

Mongkhon Narmluk [*], Toyoharu Nawa

Division of Sustainable Resources Engineering, Graduate School of Engineering, Hokkaido University, North13-West8, Kita-ku, Sapporo, 060-8628, Japan

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ABSTRACT

This paper describes the effect of fly ash on the hydration kinetics of cement in low water to binder (w/b) fly ash-cement at different curing temperatures. The modified shrinking-core model was used to quantify the kinetic coefficients of the various hydration processes. The results show that the effect of fly ash on the hydration kinetics of cement depends on fly ash replacement ratios and curing temperatures. It was found that, at 20 °C and 35 °C, the fly ash retards the hydration of cement in the early period and accelerates the hydration of cement in the later period. Higher the fly ash replacement ratios lead to stronger effects. However, at 50 °C, the fly ash retards the hydration of the cement at later ages when it is used at high replacement ratios. This is because the pozzolanic reaction of the large volumes of fly ash is strongly accelerated from early in the aging, impeding the hydration of the cement.

1. Introduction

Fly ash is widely used as a supplementary cementitious material in high performance concrete because of its benefits in enhancing both fresh and long-term concrete properties and as it promotes eco-friendly construction. Investigations have been carried out mainly to elucidate the pozzolanic reaction of fly ash and its effect on the microstructure of the fly ash-cement paste. Escalante et al. [1] reported that, in paste with water to binder (w/b) ratios of 0.50 and cured in water, fly ash enhanced cement hydration at low temperatures slightly but showed a retarding effect at elevated curing temperatures. Although the effect of fly ash on hydration has been established experimentally, the quantitative influence of fly ash on the kinetics of cement hydration is not well understood. In particular, for modern high-performance concretes with low w/b ratios, the effect of the fly ash on the cement hydration may be different [2]. To predict the performance of fly ash concrete accurately throughout its service life, a more quantitative understanding of the effect of fly ash on cement hydration in low w/b ratio cementitious mixtures is needed.

Kinetic modeling based on the shrinking-core theory can be used to quantify the hydration kinetics of cement. For ordinary Portland cement paste, Park [3,4] and Maruyama [5] have demonstrated the use of this model to simulate the hydration of cement in general and of the different cement components. Results showed good agreement between the model simulations and the experimental data. However, only little experimental data were provided for the verification. Recently, Wang et al. [6–9] has described the application of this model in predicting hydration of fly ash blended cement. Cement hydration and the pozzolanic reaction of fly ash were simulated simultaneously by considering the interaction between the production of calcium hydroxide by cement hydration and its consumption by the pozzolanic reaction of fly ash. This work was able to predict hydration related properties such as chemically bound water, paste porosity, and internal temperature rises, however the development of the degree of hydration of the fly ash containing cement has not been fully elucidated. Only measured hydration data for Portland cement paste obtained from [10] was presented as verification of the model. Termkhajornkit [11] and Saengsoy [12] have pointed out that the degree of hydration of the cement in fly ash-cement paste was higher than that in pure Portland cement paste. This suggests that to simulate the hydration kinetics of the cement in fly ash-cement blends using this model, hydration data for the cement in pure Portland cement paste is not suitable for model calibration. Hydration data for this kind of hydration must be obtained specifically from the blended fly ash-cement paste.

The XRD-Rietveld analysis can be used to monitor cement hydration, but in the case of cement containing fly ash, a part of the cement is replaced by fly ash, and thus the relative amounts of individual cement components are lower. This could increase the relative errors of the XRD-Rietveld analysis of the low-content components such as C_3A, and C_4AF [13]. Although there are some studies reported the interactions among the hydration of individual cement components [14,15], these interactions have not been quantitatively established and the mechanisms of these interactions are not well understood. The research to be reported here will first

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[*] Corresponding author. Tel.: +81 11 706 6326; fax: +11 706 7274.
E-mail address: mnarmluk@yahoo.com (M. Narmluk).

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focus on the effect of fly ash on the hydration kinetics of the overall cement phase.

The degree of cement hydration and fly ash reactions can be measured separately by using the XRD-Rietveld analysis and the selective dissolution method as described by Termkhajornkit et al. [16]. The shrinking-core model is then used to determine the kinetic parameters of individual hydration processes. These model parameters represent the apparent hydration kinetics of multiple cement components. The results of experiments conducted at three different curing temperatures will be reported.

2. Theoretical background

2.1. Kinetic model for cement hydration

The shrinking-core model, which was originally developed by Tomosawa [17] and modified in [3–5], is used in this study to simulate the development of cement hydration. This model is expressed as a single equation consisting of three coefficients: k_d the reaction coefficient in the induction period; D_e the effective diffusion coefficient of water through the C–S–H gel; and k_r a coefficient of the reaction rate of cement as shown in Eq. (1) below. These coefficients determine the rate of mass transport through the initial shell layer (a layer of semipermeable, metastable C–S–H product that forms initially when water comes in contact with the cement), the rate of chemical reaction processes, and the rate of diffusion controlled processes. The modeled cement particles are assumed to be spheres surrounded by an initial shell layer. External water diffuses through this layer and reacts with the unhydrated cement at the surface of the core, and then some dissolved ions diffuse outward to the exterior to form new hydration products (C–S–H gel) on the surface of hydrating particles while some take part in forming products locally. Based on this theory, the rate of cement hydration is derived as shown in Eq. (1).

$$\frac{d\alpha}{dt} = \frac{3(S_w / S_0)C_{w-free}}{\left(\nu + w_g\right)\rho_c r_0}\left[\frac{1}{\left(\frac{1}{k_d} - \frac{r_0}{D_e}\right) + \frac{r_0}{D_e}(1-\alpha)^{-1/3} + \frac{1}{k_r}(1-\alpha)^{-2/3}}\right] \tag{1}$$

where α is the degree of cement hydration; ν is the stoichiometric ratio by mass of water to cement (= 0.23); w_g is the physically bound water in C–S–H gel (= 0.15) [6]; ρ_c is the density of the unhydrated cement; C_{w-free} is the amount of water at the exterior of the C–S–H gel; and r_0 is the radius of unhydrated cement particles.

In Eq. (1), the cement particles are assumed to be spherical and of uniform size with an average radius of $r_0 = 3 / \left(S\rho_c\right)$ [3,4]. The terms S and ρ_c stand for the Blaine surface area and density of the cement, respectively. As the hydration progresses, the hydration rate decreases with a reduction in the contact area between cement particles and the surrounding water because of the increase in interconnections among cement particles. This effect is accounted for by the term S_w/S_0 in Eq. (1) where S_w is the effective surface area of the cement particles in contact with water and S_0 is the total surface area if the surface area develops unconstrained [3,4].

The reaction coefficient k_d is assumed to be a function of the degree of hydration as shown in Eq. (2) where B and C are the coefficients determining this factor [3,4]; B controls the rate of the initial shell formation and C controls the rate of the initial shell decay.

$$k_d = \frac{B}{\alpha^{1.5}} + C\alpha^3. \tag{2}$$

In [6–9], the effective diffusion coefficient D_e is assumed to be affected by the tortuosity and pore size of the C–S–H gel and it is expressed in a term for the degree of hydration as shown in Eq. (3). If the C–S–H gel is very porous and has low tortuosity of the pore network, the value of D_e will be high and ions easily diffuse through the gel. The D_{e0} is the initial effective diffusion coefficient of water when C–S–H gel is still only loosely formed at the early period after mixing. With the progress of hydration, the thickness of the C–S–H layer increases, and the diffusivity of water through this layer becomes lower. In [6–9] this effect was expressed by the term $\ln(1/\alpha)$ in Eq. (3) and this term is also included in the model presented here.

$$D_e = D_{e0}\ \ln(1/\alpha). \tag{3}$$

In addition, free water in the capillary pores is depleted as hydration of cement minerals progresses. Some water is bound in the gel pores, and this water is not available for further hydration, an effect that must be taken into consideration in every step of the progress of the hydration [5]. Therefore, the amount of water in the capillary pores C_{w-free} is expressed as a function of the degree of hydration in the previous step as shown in Eq. (4).

$$C_{w-free} = \frac{(W_0 - 0.38 * \alpha * C_0)}{W_0} \tag{4}$$

where C_0 and W_0 are the mass fractions of cement and water in the mix proportion.

The effect of temperature on these reaction coefficients is assumed to follow Arrhenius's law as shown in Eqs. (5a)–(5d) [3].

$$B = B_{20}\ \exp\left(-\beta_1(1/T - 1/293)\right) \tag{5a}$$

$$C = C_{20}\ \exp\left(-\beta_2(1/T - 1/293)\right) \tag{5b}$$

$$D_e = D_{e20}\ \exp(-\beta_3(1/T - 1/293)) \tag{5c}$$

$$k_r = k_{r20}\ \exp\left(-(E/R)(1/T - 1/293)\right) \tag{5d}$$

where β_1, β_2, β_3, and E/R are temperature sensitivity coefficients and B_{20}, C_{20}, D_{e20}, and k_{r20} are the values of B, C , D_e, and k_r at 20 °C.

2.2. Working hypothesis of the deposition mechanism

A reduction in D_e is assumed to take place in concert with the increases in the degree of hydration as suggested by Eq. (3). The physical meaning of this phenomenon can be related to the changes in C–S–H gel tortuosity and gel pore diameters [6–9] but no full explanatory mechanism for this has been established.

It was recently reported that at the early stages of aging the inner product is fragile and has low packing density. It later becomes denser and develops into the commonly encountered C–S–H inner product [18]. Further, the work by Bishnoi and Scrivener [19] has proposed that C–S–H is loosely packed in the beginning and that its packing density increase with hydration.

This allows the proposition that the diffusive properties of the C–S–H layer would decrease due to increases in the packing density of the gel as the hydration progresses. The cause of the increase in packing density as considered in the model here is assumed to be due to the deposition of small C–S–H particles/nuclei on the interior pores of the C–S–H layer.

Jennings [20] proposed that C–S–H gel consists of globules which are the smallest basic particles (C–S–H gel particle) with sizes of about 4.2 nm. A C–S–H gel includes two different kinds of gel pores: large and small gel pores. The diameter of the large gel pores range from 3 to 12 nm, and it is possible that some C–S–H particles deposit on the walls of large gel pores, potentially narrowing the diffusion path diameter or completely blocking it, as suggested in Fig. 1.

In this study, it was assumed that the resistance of the C–S–H layers to ion diffusion is due to both the thickness of the C–S–H layers