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Effect of fly ash on properties evolution of cement based materials

Xiao-Yong Wang *

Department of Architectural Engineering, College of Engineering, Kangwon National University, Chuncheon 200-701, Republic of Korea

HIGHLIGHTS

- Deduced the stoichiometric ratio of fly ash to calcium hydroxide.
- Proposed a blended hydration model for cement–fly ash blends.
- Proposed model is valid for concrete incorporating high volume fly ash.
- Proposed model is valid for concrete with lower water to binder ratios.

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ABSTRACT

Fly ash has been widely used as a mineral admixture to produce high performance concrete. The addition of fly ash mainly represents dilution effect and chemical effect on cement hydration. The dilution effect is a consequence of the replacement of cement by fly ash and results in an increase in the water/cement ratio. The chemical effect is pozzolanic reaction between mineral admixture and calcium hydroxide. This paper presents an analytical model to evaluate the properties evolution of cement–fly ash blends considering both dilution effect and chemical effect. It is found that the stoichiometric ratio of fly ash to calcium hydroxide relates with fly ash replacement ratio. For cement–fly ash blends with a lower to binder ratio and high volume fly ash, the dilution effect is much more significant, the hydration degree of cement is significantly improved, and the compressive strength of cement–fly ash blends is comparable to that of control specimens.

1. Introduction

Fly ash is a by-product of coal-fired electric generating plants and has been widely used as mineral admixtures in normal and high strength concrete. Fly ash improves the performance and quality of fresh concrete and hardened concrete. For fresh concrete, fly ash affects the plastic properties of concrete by improving workability, reducing water demand, reducing segregation and bleeding, and lowering heat of hydration. For hardened concrete, fly ash increases strength, reduces permeability, reduces corrosion of reinforcing steel, increases sulphate resistance, and reduces alkali-aggregate reaction [1].

Abundant researches have been done on physical and chemical properties of fly ash blended concrete. Using an apparent activation energy function, Han et al. [2] evaluated the development of compressive strength of hardening fly ash blended concrete. The influences of fly ash replacement content and water–binder ratio on the apparent activation energy were investigated. Hwang et al. [3] derived an estimation equation for compressive strength development of fly ash blended concrete. The equation used a coefficient to indicate the activity of fly ash as a binder, in the form of a function of age, fly-ash content, and Blaine specific surface area of fly ash. Pane and Hansen [4] investigated blended cement hydration by isothermal calorimetry and thermal analysis. They found that the weight loss due to $Ca(OH)_2$ decomposition of hydration products could be used to quantify the pozzolan reaction, and the reactions of blended cements were slower than Portland cement. From Refs. [2–4], we can see that the reactivity of fly ash relates with water to binder ratio and fly ash replacement ratio. The evolution of properties of cement–fly ash blends relates with reaction degrees of cement and fly ash.

Compared with phenomenological modeling of compressive strength development [2,3] and calcium hydroxide evolution [4] of cement–fly ash blends, some hydration models have proposed to predict properties of fly ash blended concrete. Saeki and

* Tel./fax: +82 33 250 6229.
E-mail address: wxbrave@kangwon.ac.kr

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Monteiro [5] proposed a diffusion equation to describe the pozzlanic reaction between calcium hydroxide and mineral admixtures. The parameters of the prediction model are dependent on the physical and chemical characteristics of mineral admixtures. Schindler and Folliard [6] presented the formulation of a general hydration model for cementitious materials. The proposed hydration model incorporates the effects of following variables: cement chemical composition, cement fineness, supplementary cementing materials, mixture proportions, and concrete properties. De Belie et al. [7] analyzed the isothermal heat evolution of fly ash–cement pastes using the Avrami and Jander equations. Furthermore, from the calculated amount of retained water, chemical shrinkage and volume portion of each reaction product and unreacted particles, the microstructure of cement–fly ash blends is quantified. By separating the reaction of mineral admixture from hydration of Portland cement, Wang and Lee [8] put forward a hydration model for blended cement, and predicted the evolutions of adiabatic temperature rising and chemically bound water using a blended hydration model.

From references [5–8], we can found that the properties (such as calcium hydroxide evolution, chemically bound water evolution, heat evolution, and microstructure evolution) of fly ash blended concrete can be predicted using cement hydration degree and fly ash reaction degree. On the other hand, for fly ash blended concrete, some points are still not clear and deserve further investigations. First, the amount of calcium hydroxide consumed by 1 g reacted fly ash is not fully clarified. Maekawa et al. [9] and Papadakis [10] reported that the stoichiometric ratio of fly ash to calcium hydroxide is constant and does not relate with fly ash replacement ratio. However, Wang et al. [11] found that with the increasing of fly ash replacement ratio, the amount of calcium hydroxide consumed by 1 g reacted fly ash will decrease. So it is necessary to investigate the stoichiometric ratio of fly ash to calcium hydroxide. Second, former researches [5–8] mainly focused on analyzing properties of concrete incorporating low volume fly ash (fly ash replacement ratio is less than 30%). More research is necessary to do about properties evolution of high volume fly ash blended concrete, and a unified hydration model for both low volume fly ash and high volume fly ash blended concrete should be built. Third, former researches [5–11] mainly focused on analyzing properties of concrete with general water to binder ratios ranging between 0.3 and 0.6. More research is necessary to do about properties evolution of fly ash blended concrete with lower water to binder ratio about 0.15–0.2 which is generally used to produce ultra high performance concrete [8].

To clarify these points, this paper presents a general procedure to evaluate the properties evolutions of fly ash blended concrete with different water to binder ratios (ranging between 0.19 and 0.5) and different fly ash replacement ratios (ranging between 0.25 and 0.55). The evolution of calcium hydroxide, chemically bound water and compressive strength of cement–fly ash blended are predicted using cement hydration degree and fly ash reaction degree.

The specific originalities of this study are summarized as follows: First, the stoichiometric ratio of fly ash to calcium hydroxide is proposed. Stoichiometric ratio is an essential parameter for modeling the reactivity of fly ash in cement–fly ash blends. Second, the proposed model is valid for fly ash blended concrete with lower water to binder ratios and higher fly ash replacement ratios. The dilution effect and pozzolanic reaction of fly ash, phase volume fractions of hydrating cement–fly ash blends, and compressive strength development are systematically modeled. Third, the durability of hardened concrete, such as water permeability, chloride penetration and carbonation, are also closely related to hydration degree of cement and reaction degree of fly ash. It is hoped that this detailed study dealing with fly ash reaction will be very helpful in the field of concrete technology.

2. Hydration model of cement–fly ash blends

2.1. Hydration model of Portland cement

The shrinking-core model, which was originally developed by Tomosawa [12] and modified by Park et al. [13] and Maruyama [14], is used in this study to simulate the development of cement hydration. The model considers the rates of formation and destruction in an initial impermeable layer, the activated chemical reaction process, and the following diffusion-controlled process. 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:

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

$$k_d = \frac{B}{\alpha^{1.5}} + C\alpha^3 \tag{1-2}$$

$$D_e = D_{e0} \ln\left(\frac{1}{\alpha}\right) \tag{1-3}$$

where α is the degree of cement hydration; v is the stoichiometric ratio by mass of water to cement (=0.25); w_g is the physically bound water in C–S–H gel (=0.15); ρ_w is the density of water; $C_{w\text{-}free}$ is the amount of water at the exterior of the C–S–H gel; r_0 is the radius of unhydrated cement particles ($r_0 = 3/(S\rho_c)$, the terms S and ρ_c stand for the Blaine surface area and density of the cement, respectively); 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; B controls the rate of the initial shell formation and C controls the rate of the initial shell decay; D_{e0} is the initial value of effective diffusion coefficient.

The amount of water in the capillary pores $C_{w\text{-}free}$ is expressed as a function of the degree of hydration in the previous step as shown in Eq. (1-4).

$$C_{w\text{-}free} = \left(\frac{W_0 - 0.4 * \alpha * C_0}{W_0}\right)^r \tag{1-4}$$

where C_0 and W_0 are the mass fractions of cement and water in the mix proportion, and r is a empirical parameter considering the accessibility of water into an inner anhydrous part through an outer hard shell of the cement particles [15].

The effect of temperature on reaction coefficients is assumed to follow Arrhenius's law [12–14]. By using the proposed Portland cement hydration model, Tomosawa [12] evaluated the heat evolution rate, chemically bound water, and compressive strength of hardening concrete. Park et al. [13] predicted the temperature distribution in high strength concrete using this hydration model. A good correlation was found between the analysis results and experimental results.

2.2. Simulation of the pozzolanic reaction in cement–fly ash blends

The hydration rate of pozzolanic materials depends on the amount of calcium hydroxide in hydrating cement–fly ash blends and the reaction degree of mineral admixtures [5,7]. Compared with the silica fume, the hydration rate of the fly ash is much lower levels due to the larger particle size. In the simulation, it is assumed that the reaction of fly ash is divided into three processes: an initial dormant period, and phase-boundary reaction and diffusion processes. By considering these points, based on the method