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A multi-phase kinetic model to simulate hydration of slag–cement blends

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ABSTRACT

Ground granulated blast furnace slag, which shows cementitious behavior (latent hydraulic activity) and pozzolanic characteristics (reaction with lime), has been widely used as a mineral admixture in normal and high strength concretes. Hydration of slag–blended cement is much more complex than that of ordinary Portland cement because of the mutual interactions between the cement hydration and the slag reaction. This paper presents a kinetic hydration model for cement–slag blends. The proposed model analyzes the slag reaction separate from cement hydration by considering the production of calcium hydroxide in cement hydration and its consumption in slag reactions. The amount of free water and the amount of calcium hydroxide left in the system were adopted as the control indicators for determining the slag reaction. Using the proposed model, the reaction ratio of slag can be evaluated as a function of curing age, considering the influences of the water to binder ratio, the slag replacement ratio and the curing temperature. Furthermore, the amount of chemically-bound water (self-cementing properties), calcium hydroxide (pozzolanic capabilities), and the heat released from hydration are evaluated by determining the contributions from both the cement hydration and the slag reaction. The evaluated results show good accordance with the experimental results.

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1. Introduction

Ground granulated blast furnace slag (GGBFS) is a glassy, granular material consisting of silicates, aluminosilicate of calcium and other oxides. Ground granulated blast furnace slag shows both cementitious behavior (latent hydraulic activity) and some pozzolanic characteristics (reaction with lime) as well. It has long been used as a mineral admixture to produce and improve the durability of high strength, high performance concrete. In addition, economic and ecologic benefits in the form of energy-saving and resource-conserving properties can be achieved by using slag–blended cement [1,2].

Experimental and practical studies on the influence of slag on concrete's durability and mechanical properties are abundant. Shi and Day [3] and Song et al. [4] reported that the initial pH value of the activator solution plays an important role in dissolving the slag and in promoting the early formation of some hydration products. Wang and Scrivener [5] reported that regardless of the activator used, the main hydration products of alkali–activated slag are calcium silicate hydrates with low C/S ratios, and Chen and Brouwers [6] proposed a reaction model for alkali–activated slag. Stoichiometric reaction models have been developed in order to correlate the mineral composition of slag with the hydration products. Using the proposed models, it is possible to determine the quantities of the hydration products and the composition of the calcium silicate hydrate (C–S–H).

Compared with alkali–activated slag, the slag–blended cement hydration process is more complex, due to the coexistence of cement hydration and slag reaction. Based on the experimental results of reaction stoichiometries among supplementary cementing materials (SCM), chemical bound water and calcium hydroxide, Papadakis [7], Papadakis and Tsimas [8], and Papadakis et al. [9,10] proposed a chemical-based steady-state model which was able to estimate the final material values, such as porosity, chemically-bound water and calcium hydroxide content, while hydrating the supplementary cementing materials (SCM) of blended cement. The influence of mineral admixture on the durability properties, such as chloride attack and carbonation, and on the strength characteristics were also described quantitatively. However, on the construction site, workers and designers are interested in not only the final properties of slag–blended concrete, but also the evolution of the properties over time. Contrasting to Papadakis' chemical-based steady-state model [7–10], some kinetic models [11–20] were proposed to evaluate the development of properties of blended concrete. Schindler and Folliard [11] proposed a general kinetic hydration model that could predict the heat evolution of cementitious materials. This proposed model incorporated the

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effects of cement mineral composition, cement fineness, supplementary cementing materials, mixture proportions, and concrete properties. De Schutter and Taerwe [12,13] and De Schutter [14–16] proposed a kinetic hydration model valid both for Portland cement and blast furnace slag cement in which the heat evolution of blast furnace slag cement was obtained through the superposition of the heat productions for the Portland reaction (P reaction) and a slag reaction (S reaction). Furthermore, Schutter evaluated the evolution of the mechanical properties of young concrete with respect to the degrees of hydration and the risk of thermal cracking in the hardening concrete. However, it should be noticed that Schutter's model does not explicitly consider the interactions between the cement hydration and the reaction of mineral admixtures, such as the producing of calcium hydroxide by cement hydration and the consumption by slag reaction. Hyun [17] and Tomosawa et al. [18] proposed a kinetic model of slag–blended cement hydration in order to evaluate the early-age temperature rise and the evolution of thermal stress inside a mass of concrete. In this model, the residual concentration of water and calcium hydroxide was used as parameters for indicating the rate decline toward the reaction end point. The influence of temperature on cement hydration is analyzed using Arrhenius's law [18]. Maekawa et al. [19] proposed a general hydration model (DuCOM) incorporating fly ash and slag, whose reactions were treated separately from those of ordinary Portland cement, with some of the interactions being taken into account in terms of the free water content and the calcium hydroxide concentration. Most recently, Di Luzio and Cusatis [20,21] proposed a hydrothermal chemical model for high performance concrete. The Pozzolanic reaction of silica fumes was modeled using a kinetic equation similar to that used for cement hydration.

Based on the review of current literature [7–21], it is obvious that the reaction ratio of mineral admixtures plays a critical role in evaluating both the early-age properties [11–20], such as temperature increase and thermal cracks, and the durability of blended concrete [19,20], as measured by porosity and the amount of calcium hydroxide, both of which are related to the carbonation of concrete. The reaction ratio of slag is related to its physical and chemical characteristics, its mixing proportions, and its curing conditions. In this study, based on a similar idea proposed by Maekawa et al. [19], a kinetic hydration model was used to evaluate the reaction ratio of slag, considering the mutual interactions between cement hydration and slag reaction. The amount of free water and calcium hydroxide left in the system were adopted as the control indicators for the slag reaction. By applying the proposed model, the reaction ratio of slag was evaluated as a function of the curing age, taking into account the influence of the water to binder ratio, the slag replacement ratio and the curing temperature. Furthermore, the amount of chemically-bound water (self-cementing properties), calcium hydroxide (pozzolanic capabilities), and the released heat of hydration were determined by evaluating the contributions from both the cement hydration and the slag reaction.

2. Hydration model of ordinary Portland cement

2.1. Hydration model assumptions

In our hydration model we considered the hydration reaction of Portland cement in terms of the influence of the water to cement ratio, the cement particle size distribution, the cement mineral components and the curing temperature. The assumptions of this model are summarized as follows:

1. Cement particles are randomly cast in a representative unit cell space, as shown in Fig. 1. As proposed by Navi and Pignat [22], the length of the edge of the representative unit cell is 100 μm. Our simulation assumed the amount of chemically-bound water for each cement component, C_3S, C_2S, C_3A, and C_4AF, was the same as those proposed by Park et al. [23].

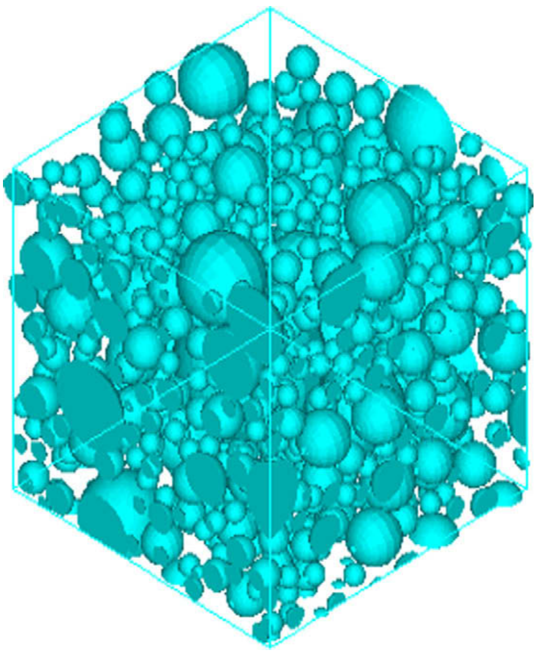

Fig. 1. Cement particles randomly distributed in the cell space.

2. The degree of hydration of the cement components is the ratio of the volume of reacted cement components to the volume of initial cement components. The degree of hydration of cement paste can be regarded as a weighted sum of the cement particles and the mineral components, as shown in Fig. 2.
3. The liquid phase, which was assumed to be water, diffuses through a hydrate layer, reaches the surface of the cement particle and chemically reacts with the cement. The hydrate formed by hydration adheres spherically to the cement particles.
4. The particle size distribution of the cement was approximated using the Rosin–Rammler function [23].

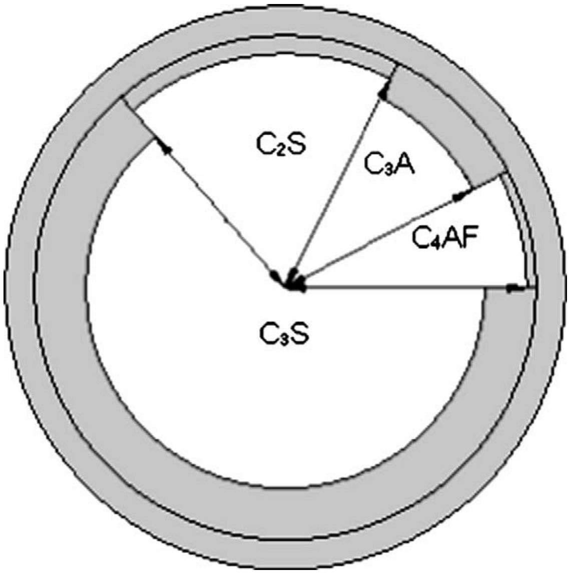

Fig. 2. Schematic of the multi-component hydration model.

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