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Modelling the First Exothermic Peak during Hydration of Cement incorporating Blast Furnace Slag

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Abstract

3D concrete printing requires well understanding of the hydration of concrete at an early-age. In order to predict the first exothermic peak during the hydration, a model for the blast-furnace slag (BFS)-blended cement is proposed. The kinetic hydration in the pre-induction stage is characterized by means of using the classical Avrami-type nucleation model. The effect of the dosage of BFS on the first exothermic peak was investigated. The dosage ranges from 0 to 40%. Both the arrival time and calorific value obtained from the model agree well with those obtained from the hydration test. This underlines the usefulness of the proposed model.

Keywords: 3D printed concrete, blast furnace slag, hydration heat, first exothermic peak, Avrami model, cement paste

1 Introduction

Numerous studies have been striving to explore the cementitious material alternative to the ordinary Portland cement (OPC), owing to the excessive consumption of natural resources and vast CO₂ emissions during the production of OPC. As one of the favourable candidates, the blast-furnace slag (BFS)-blended cement has been extensively used in 3D concrete printing [1] and anti-sulfate structures. Its hydration evolution is more complex than that of OPC, due to the cementitious and pozzolanic

features of slag [2]. Therefore, it is of significance to study the early-age hydration for further comprehension of long-term behaviour.

Studies on early-age hydration of BFS-blended cement usually adopt electrical and calorimetric methods from macroscopic aspect and scanning electron from microscopic perspective. Among them, the measurement of hydration heat is crucial for identification of the hydration degree. The influence of BFS on hydration heat and mechanical properties has been quantitatively investigated. Negative correlation between BFS content and hydration heat was reported at an early age from the isothermal calorimetry [3,4]. Besides, the hydration heat was found to increase with high fineness at the first four hours [5]. It is generally accepted that the heat production curve exhibits an extra peak due to hydration of BFS [6,7] whereas the retarding or acceleration effects on hydration process are inconsistent [8,9]. A hydration model applicable to BFS-blended cement was proposed in [7,10,11]. In this model, the overall heat production was divided into Portland and slag reactions with individual temperature factors. Gruyaert *et al.* [12] presented that the time at which slag hydration is activated depends only on the environmental temperature, using Arrhenius law to predict the temperature-dependent reaction rate regardless of the first hydration peak.

It is noted that there are few studies on the establishment of hydration model of slag blended cement rather than above empirical models from experimental results. Thermodynamic modelling was carried out in Fernández *et al.* [13] using Gibbs free energy minimization program (GEMS), while a large database is required to supply the code. Kinetic hydration modelling has been performed in some work [14,15], incorporating stoichiometric coefficients without explicit meanings.

In this paper, a new hydration model for BFS-blended cement is proposed, based on the Avrami-Cahn model [16]. It is different from the conventional modelling methods considering the reactions of components. In the presented model, the cement hydration is simulated in a unified way by constructing a BFS dependent heat flow model. Emphasis is laid on the influence of dosages of BFS on the early-age hydration process. Results are verified through comparison with experimental data in Yoon *et al.* [17].

2 Methods

The hydration of BFS-blended cement can generally be divided into two stages [18]: (i) the alkali metal hydroxides, e.g. sulfates, and Portlandite are first produced immediately as the cement is mixed with water; and (ii) the slag is activated to react. The first stage is dominant for the occurrence of first exothermic peak, and the slag content plays a vital role during the hydration. However, the detection of first exothermic peak, dependent heavily on the calorimeter design, is missed if components are mixed outside the calorimeter. Inspired by the above, effects of the dosage of BFS on the first exothermic peak of blended cement paste will be explored by the model presented in the following.

The hydration degree is calculated as follows

$$\alpha_d = \frac{Q(t)}{Q_{\max}}, \quad (1)$$

where α_d is reaction degree, $Q(t)$ is the heat released at the certain moment t and Q_{\max} denotes the maximum heat release. Considering the blended cement paste with given components, the heat flow model of the first exothermic peak is constructed as

$$Q_{\max} \frac{d\alpha_d}{dt} = F(n_b, t), \quad (2)$$

where the left term denotes the heat flow, n_b represents the dosages of BFS. Since the dissolution of cement occurs immediately upon mixing with water, the consistent calorific value of cement grains and dissolution of cement portion is assumed, i.e.

$$\frac{dX}{dt} = \frac{d\alpha_d}{dt}, \quad (3)$$

in which X is the volume fraction of cement consumed. The hydration kinetics of cement are described by the Avrami-Cahn model [16] involving nucleation and growth, which is expressed as

$$\frac{d\alpha_d}{dt} = K_1 \exp(\eta t^n), \quad (4)$$

where K_1 , η , and n are parameters to be determined. These parameters are expressed for Avrami-type model as

$$\begin{cases} K_1 = nk_{avr}t^{n-1} \\ \eta = -k_{avr} \end{cases}, \quad (5)$$

where k_{avr} is the effective rate of overall reaction, n is the Avrami exponent and can be set to one to consider the first-order reaction only.

The effects of BFS component on exothermic process are incorporated mainly on cement pre-induction period [19], hence K_1 is herein assumed to be a function of both n_b and t

$$K_1 = \sum_{i=0}^{+\infty} h_i(n_b) f_i(t). \quad (6)$$

Taking the first order approximation simplifies Eq. (6) into

$$K_1 \approx h_0(n_b) f_0(t), \quad (7)$$

where $h_0(n_b)$ is approximated using following polynomials

$$h_0(n_b) = \sum_{j=0}^{+\infty} U_j \xi(n_b)^j. \quad (8)$$

In Eq. (8), $U_j (j=1, 2, 3, \dots)$ denotes the coefficient of j th term. $\xi(n_b)$ is expressed as an exponential function of n_b raised to the undetermined power ς :

$$\xi(n_b) = n_b^\varsigma. \quad (9)$$

In Eq. (7), the time-dependent term $f_0(t>0)$ is expressed as

$$f_0(t) = \frac{1}{Q_{\max}} H(t^\lambda) t^{0.5}, t > 0, \quad (10)$$

in which H is the constructive function of the form

$$H(t^\lambda) \approx \sum_{k=0}^{n_1} V_k (t^\lambda)^k, \quad (11)$$

where $V_k (k=1, 2, 3, \dots, n_1)$ and λ are parameters to be determined.

Taking the first order approximations of Eqs. (8) and (11) leads to

$$K_1 \approx h_0(n_b) f_0(t) \approx \frac{1}{Q_{\max}} (U_0 + U_1 n_b^\zeta) (V_0 + V_1 t^\lambda) t^{0.5} \quad (12)$$

Substituting Eq. (12) into Eq. (4) results in the hydration model of first exothermic peak for BFS-blended cement

$$Q_{\max} \frac{d\alpha_d}{dt} \approx (U_0 + U_1 n_b^\zeta) (V_0 + V_1 t^\lambda) t^{0.5} \exp(\eta t) \\ = (1 + W_0 n_b^\zeta) (W_1 t^{0.5} + W_2 t^b) \exp(\eta t) \quad (13)$$

$$\left\{ \begin{array}{l} W_0 = U_1/U_0 \\ W_1 = V_0 U_0 \\ W_2 = V_1 U_0 \\ b = \lambda + 0.5 \end{array} \right. , \quad (14)$$

where W_0 , W_1 and W_2 are coefficients to be determined in rearranged form of Eq. (14).

3 Results and discussion

The present first exothermic peak model for the blended cement describes effects of BFS content and hydration time. Results are verified by comparison to microhydration data performed in paper [17]. In the test, the BFS content is varied in the range of 0-40% with a fixed water-binder ratio amounting to 0.5 and environment temperature amounting to 23°C. The measured reaction degrees of $n_b=0$ and 40% are used for parameter identification. The parameters are listed in Table 1. The microhydration heat to reach the first peak versus hydration time up to two hours is shown in Fig. 1.

In all cases, the exothermic peak occurs at first five minutes during the hydration process, mainly due to the immediate dissolution of cement grain. The peaks arrive at 3 min for OPC, 4 min for BFS of 20% and 30%, and 5 min for BFS of 40%. Moreover, the peak calorific value decreases with increasing the replacement ratio of BFS, consistent with previous studies [3,4]. The prediction of arrival time matches well with the experimental data, albeit minor derivations can be observed in calorific prediction. The derivation could be attributed to bias induced by simplified linear approximation of constructive functions.

W_0	ζ	W_1	W_2	b	η
2.488	2.249	21.569	66.81	5.615	4.001

Table 1: Model parameters.

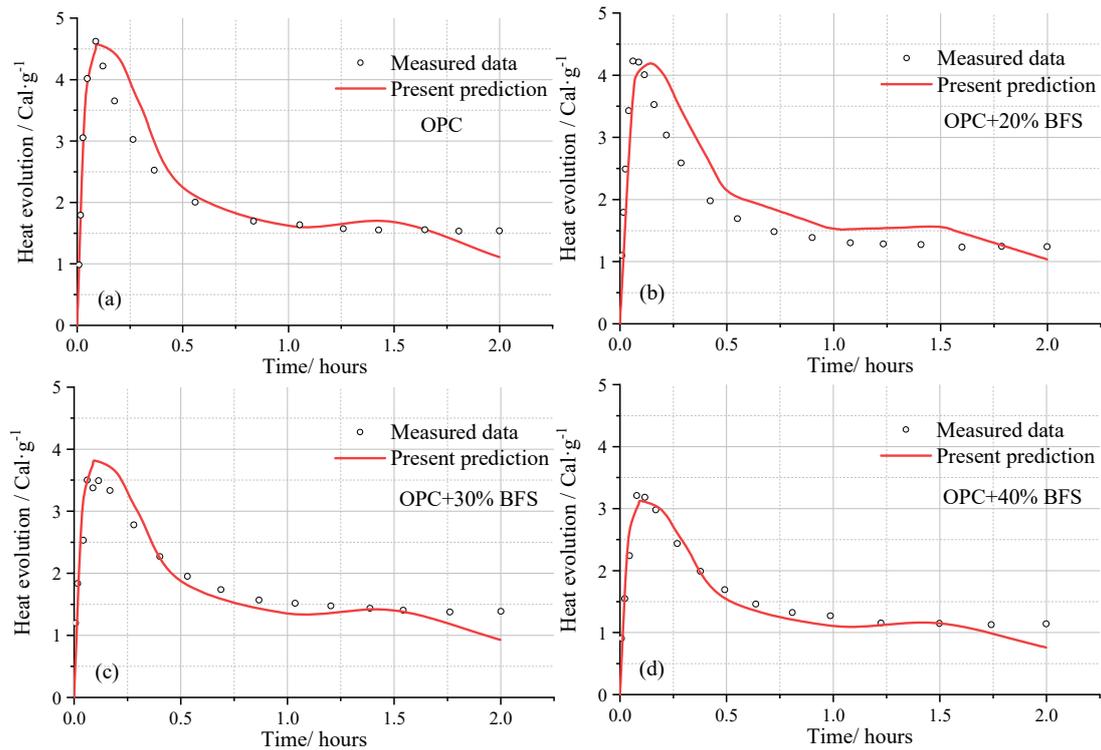


Figure 1: The first exothermic peak of hydration model (solid line) and microhydration data (dot line). (a). ordinary Portland cement (OPC), (b). OPC+20%BFS, (c). OPC+30%BFS, (d). OPC+40%BFS.

4 Conclusions

In this paper, a hydration model for prediction of the first exothermic peak during the hydration of blast-furnace slag (BFS)-blended cement is presented. By assuming that the rate of heat flow is consistent with that of the volume fraction of the consumed cement, the hydration kinematics was characterized with the help of the Avrami-Cahn model with simplifications.

The hydration process of BFS-blended cement with varying content (0-40%) was simulated for water-binder ratio amounting to 0.5 and environment temperature amounting to 23°C. The arrival time of the first exothermic peak was found to be advanced and the calorific value decreased with increasing BFS content. This is consistent with the previous experimental studies. In addition, calculated results were founded to agree well with microhydration data, illustrating the accuracy of the model.

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