



Early-age hydration and mechanical properties of high volume slag and fly ash concrete at different curing temperatures



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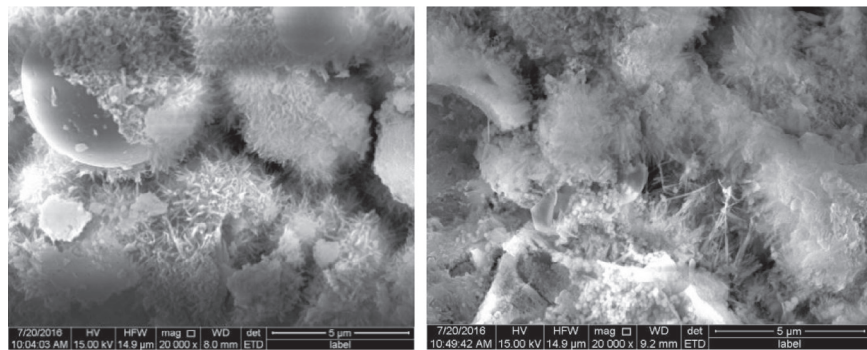
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HIGHLIGHTS

- The dilution, filler and retardation effects of high volume GGBS and FA are observed to affect early age hydration of cement.
- The hydration process of binders with FA is found to be more sensitive to temperature than that with GGBS.
- The equivalent age equation exactly predicts the early age strength development at ambient temperature.

GRAPHICAL ABSTRACT



(a) Mixed with 55%FA

(b) Mixed with 55%GGBS

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ABSTRACT

Multiple Supplementary Cementitious Materials (SCM) in large quantities have been used in quasi-mass concrete to minimize the crack risk. Yet the hydration process of concrete with high volume addition of SCM, especially effect of temperature on the early stage hydration, has been rarely investigated. In this paper, early age hydration progress and mechanical properties of concrete with high volume GGBS and FA were studied under different curing temperatures. The results show that high volume GGBS and FA accelerate the cement hydration in early age due to the dilution and filler effects. However, the hydration was slowed down when the addition of FA is up to 55% and 70%. Compared to binders with GGBS, the hydration process of binders with FA are more sensitive to temperature. The results also imply the necessity of the introduction of a range factor of hydration degree for effective estimation of E_a for binders with high volume of SCM. The equivalent age equation effectively predicts the early age strength development of high volume SCM concrete curing under changing temperature in an actual structure and what needed to do is to modify the activation energy by considering the hydration progress of binder with high volume SCM.

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1. Introduction

With the construction of the super high-rise buildings, hydroelectric power plant and domestic underground railway construction, the quasi-mass concrete are becoming more and more widely used in these structures? The main problem exists in the use of the

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quasi-mass concrete is rapid release of hydration heat at early age and the heat is hard to conduct, which results in an considerable temperature differences between internal and external part. The temperature gradient causes tensile stress which poses the structure to the risk of crack [1]. One of the effective methods to minimize the crack risk is to add SCM (Supplementary Cementitious Materials) with high volume fraction to decrease the hydration heat at early age.

GGBS (Ground Granulated Blast-furnace Slag) and FA (Fly Ash) are industrial by-products which are rich in silica and alumina phases. They are likely to cause heavy metal pollution to the environment if they cannot be effectively used. Related research [2,3] indicated that, the addition of SCM can help reduce the rate and amount of heat releasing at early age, also it can help further increase the mechanical properties of concrete structures by pozzolanic reaction at later aging times. Utilization of GGBS and FA can not only promote the reduction of CO₂ emission by using less cement, take full use of industrial by-products, but can also reduce the risk for cracking by controlling the heat release during hydration.

However, the relatively slower hydration rate of SCM and the consequently lower early age strength has been the reason limiting range of its applications. Karen [4] proposed that the early age strength of the cementitious materials with SCM mainly came from the hydration of the clinker of the cement. Therefore, it is important to understand the reaction, modified by the presence of high volume SCM.

As we know, activation energy, which characterizes the sensitivity of cementitious materials hydration to temperature, is required for estimating early age strength by “equivalent age method”. Literatures [5,6] conclude that adding fly ash can decrease the activation energy while adding blast-furnace slag increases the activation energy of the binder. Furthermore, literatures [7,8] show that cementitious materials mixed with fly ash appear to be more sensitive to the temperature compared to the mixture with GGBS.

According to the background above mentioned, this paper aims at: studying the effects of SCMs addition on the hydration process of the binder, as well as its effects on the mechanical properties of the concrete at early age. Also the effects of temperature on the hydration degree of the binder with high volume addition of SCMs and the relationship between the activation energy and hydration degree are investigated as well. Furthermore, the strength development of the concrete at early age is calculated based on the equivalent concrete age model.

2. Materials and methods

2.1. Materials

The REFERENCE cement type P.I 42.5 (hereafter abbreviated as PC) complying with Chinese standard GB8076-2008 was used in this study, FA and GGBS were employed as Supplementary Cementitious Materials (SCM). The polycarboxylate-based superplasticizer with solid content of 40% was provided by SOBUTE NEW MATERIALS CO.Ltd.

Chemical and physical properties of the raw materials are given in Tables 1 and 2 respectively.

2.2. Sample preparation

In order to illustrate the effect of SCM with different dosages on the hydration of cement paste and other related properties of concrete, concrete with different mixture proportions were prepared, given in Table 3.

2.3. Curing conditions

The hydration process of cementitious materials is closely related to the curing conditions including temperature and humidity. Therefore, the property development of concrete is strongly dependent on the curing conditions. In order to

Table 1
Chemical compositions of the raw materials (wt%).

	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	K ₂ O	SO ₃
PC	20.49	4.80	61.03	2.23	2.75	0.83	2.17
GGBS	30.6	16.3	38.2	6.60	0.80	0.46	2.66
FA	46.8	30.3	9.2	0.59	2.95	0.83	2.96

simulate the temperature variations within actual field conditions, two types of curing conditions including standard curing condition (SC) and temperature matched curing condition (TMC) were adopted in the investigation.

- i. SC is the curing condition with temperature at 20 ± 1 °C and relative humidity > 95%.
- ii. TMC is the curing condition simulated the evolution of temperature collected from an actual structure in a curing box, and Fig. 1 presented the typical temperature evolution of an actual structure.

2.4. Experiments and methods

2.4.1. Measurement of hydration heat

Isothermal calorimetry was used to measure the hydration heat of cement paste at 20 °C, 35 °C, and 50 °C. The pure water was used as reference to conduct this test. Before testing, the specimens were mixed using a blender for approximately 120 s in the water bath at a given temperature, and then the paste with the weight of 13 g was cast into a plastic bottle. The temperature of the specimen and the equipment is assured to reach the prescribed value.

2.4.2. Measurement of mechanical properties

Specimens of a size 100 × 100 × 100 (mm³) were prepared for the compressive strength and splitting tensile strength tests. The compressive strength and splitting tensile strength were tested after 1, 3, 7, 28 days of curing under standard condition (SC), and after 1, 3, 5 days of curing under temperature matched condition (TMC), according to the Chinese National Standard GB/T 50081-2002.

3. Results and discussion

3.1. Effect of high volume GGBS and FA on early age hydration kinetic of PC at 20 °C

According to the literatures [9,10], the effect of GGBS and FA on the hydration of the cement include dilution effect, filler effect and chemical effect.

The dilution effect, which is equivalent to increase the effective water to cement ratio (w/c), is proportional to the replacement level. Therefore, the incorporation of GGBS or FA may be seen to enhance the long-term hydration of cement with what has been termed a “dilution” effect [2,11,12].

The filler effect, which is related to GGBS or FA grains interposed between cement grains separating the reactive grains, can provide relatively more space available for the hydrates of the clinker phases to form in, and relatively larger surfaces as the sites for the heterogeneous precipitation and growth of hydrates. Some research regarded this as stimulation effect, accelerating the dissolution process and stimulating the hydration of Portland cement [2]. However, in early process, slowing down of clinker hydration in the presence of fly ash has been reported by numerous papers [13–15].

The chemical effects can be understood from two perspectives. Firstly, the initial GGBS or FA can be chemically activated by alkalis and calcium hydroxide released from clinkers. Secondly, the GGBS is likely to react with the calcium and aluminum ions released by its own dissolution, which is called auto-pozzolanic reaction [2,11,13].

Under isothermal conditions, the heat released in mortars was used as an indicator of the advancement of the hydration reactions. The heat flow and the cumulative released heat for all compositions, normalized by clinker content, are shown in Fig. 2 (image a, b, c) and Fig. 3 (image a, c, e) respectively. The relative cumulative heat, defined as the released heat ratio between a given mix and the reference mix (C100), is also plotted. See Fig. 3 image (b), (d) and (f). In the following sessions, these effects would be

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