



# Hydration heat evolution and kinetics of blended cement containing steel slag at different temperatures



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## ABSTRACT

Hydration heat characteristics of blended cement containing up to 50% steel slag were studied at 25 °C, 45 °C and 60 °C by isothermal calorimeter. Kinetics equations were used to explore kinetics of blended cement. Kinetics parameters,  $n$ ,  $K$ , and  $E_a$ , were calculated and analyzed. Results indicated that the activity of steel slag was very low. Steel slag accelerated the hydration of aluminates but decelerated the hydration of silicates in cement clinker. Small amount of steel slag affected little the hydration process of cement. Elevated temperature obviously promoted the hydration of blended cement. The hydration of blended cement containing no more than 35% steel slag was controlled by nucleation of hydrates in acceleration period and by diffusion of ions in decay period. The hydration of blended cement containing 50% steel slag was mostly dominated by phase boundary reaction, then directly by diffusion.  $E_a$  increased with increasing steel slag content.

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## 1. Introduction

Mineral admixtures are widely used in modern concrete either in blended cements or added separately in the concrete mixer [1]. The use of mineral admixtures such as ground granulated blast furnace slag, fly ash and silica fume which have both pozzolanic and latent hydraulic properties can improve the properties of concrete and limit environmental impact as well as bring economic benefits. With the resource shortage and rising price of slag, fly ash and other quality mineral admixtures, developing more kinds of mineral admixtures that leads to sustainable concrete design and greener environment is a valuable work. Currently, steel slag shows a good potential as mineral admixture in concrete.

Steel slag is the industrial waste discharged from the steel-refining process in a conversion furnace. It accounts for approximately 15–20% by mass of the steel output [2,3]. More than 80 million tons of steel slag is discharged in China every year [4]. However, the current utilization rate of steel slag in China is only 22%, far behind the developed countries [5]. Thus, intensive research work is needed for high utilization rate of steel slag. A more attractive approach is the replacement of cement by steel slag. The chemical compositions of steel slag consist of CaO 45–60%, SiO<sub>2</sub> 10–15%, Al<sub>2</sub>O<sub>3</sub> 1–5%, Fe<sub>2</sub>O<sub>3</sub> 3–9%, FeO 7–20%, MgO

3–13%, and P<sub>2</sub>O<sub>5</sub> 1–4% [6]. And its main minerals consist of C<sub>3</sub>S, C<sub>2</sub>S, C<sub>4</sub>AF, C<sub>2</sub>F, C<sub>12</sub>A<sub>7</sub>, RO phase (CaO–FeO–MnO–MgO solid solution) and free–CaO [6–8]. Due to the minerals of C<sub>3</sub>S, C<sub>2</sub>S, C<sub>4</sub>AF, C<sub>2</sub>F, and C<sub>12</sub>A<sub>7</sub>, steel slag has hydraulic properties. But the activity of the cementitious minerals in steel slag is much lower than that in Portland cement [9]. It is related to the crystalline state, the cementitious phases of steel slag crystallize much better than that of Portland cement clinker owe to the low cooling rate of steel slag. Meanwhile, steel slag has large amount of non-active components, such as RO phase and Fe<sub>3</sub>O<sub>4</sub>.

The effect of steel slag on the early hydration of Portland cement has been studied by several researchers. Kourounis et al. [6] investigated the properties and hydration of blended cements with steel slag and found that blended cement developed lower early-age strength compared to Portland cement and its strength decrease was high when the content of steel slag was high. The addition of steel slag slowed down the hydration of blended cements, and the blended cements showed longer setting time than Portland cement. Tsakiridis et al. [8] studied the utilization of steel slag for Portland cement clinker production and pointed out that the addition of steel slag by 10.5% in the raw meal did not affect the hydration process during Portland cement production. Wang et al. [10] found that the dormant period of blended cement containing steel slag is longer than that of Portland cement. Monshi and Asgarani [11] found that blending 10% extra iron slag to a cement composed of 49% iron slag, 43% calcined lime and 8% steel slag kept the compressive strength of concrete for type I

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**Table 1**  
Chemical compositions of cement and steel slag (w/%).

Composition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> O <sub>eq</sub>	f-CaO	LOI
Cement	20.55	4.59	3.27	62.50	2.61	2.93	–	–	0.53	0.83	2.08
Steel slag	12.77	2.12	23.49	49.17	3.54	0.23	1.02	0.91	0.45	–	1.86

Na<sub>2</sub>O<sub>eq</sub> = Na<sub>2</sub>O + 0.658 K<sub>2</sub>O; w: mass fraction.

Portland cement. Kriskova et al. [12] found that mechanical activation significantly increased the reactivity of steel slag due to the increase in surface area and amorphous phase, and the amount of heat released per surface area increased with milling time. Wang et al. [13] also found that super-fine steel slag exhibited a much higher activity at early ages, but its activity was still obviously lower than that of Portland cement. Liu and Li [14] pointed that the early hydrations of cement and steel slag tended to hinder each other, especially in the case of large replacement ratio of steel slag and high fineness of steel slag. Li et al. [15] proposed a new method for modifying the chemical and mineralogical compositions of steel slag by adding industrial wastes to molten basic oxygen furnace steel slag, the modification reduced the free-CaO content and remarkably improved the cementitious property of steel slag. Wang et al. [16] found that the initial alkalinity of hydration condition could promote the early hydration of active components in steel slag, but the hydration degree of non-active components is very low even under strong alkaline condition with pH value of 13.8.

Based on a review of current literatures, it is obvious that blended cement has a low early-age strength and long initial setting time by replacing part of cement with steel slag. In order to improve the activity of steel slag, methods of mechanical activation, mineral modification and alkalinity activation are used. However, the hydration heat evolution of blended cement containing steel slag which belongs to the main characteristics of the early-stage hydration process was investigated very rarely in the past. Meanwhile, there is little information regarding the hydration kinetics of blended cement containing steel slag, which is important to understand the hydration process and mechanism of blended cement. Moreover, most investigations are carried out with small amount or single content of steel slag or at room temperature. Therefore, study of detailed heat evolution behavior and kinetics of blended cement containing steel slag are needed. In this paper, the hydration heat evolution rate and cumulative hydration heat of blended cement containing 0, 10%, 20%, 35% and 50% steel slag were measured within 168 h at 25 °C, 45 °C and 60 °C by an isothermal calorimeter. By applying the kinetics equations [17–19], the reaction of blended cement was evaluated as a function of hydration time, taking into account the steel slag content and curing temperature. Then the hydration reaction mechanism of blended cement containing steel slag was determined.

## 2. Experimental

### 2.1. Materials

PI 42.5 Portland cement conforming to Chinese National Standard GB175-2007 and basic oxygen furnace steel slag were used. The chemical compositions of cement and steel slag are shown in Table 1. The mineralogical phases of steel slag, which were determined by XRD analysis, using a TTR III-X-ray diffractometer (Cu Ka, 45 kV, 200 mA), are given in Fig. 1. According to the calculation method of alkalinity proposed by Mason [20], the alkalinity of steel slag is 3.59, which is indicated that steel slag used in this paper has high alkalinity. As shown in Table 1, CaO, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, Al<sub>2</sub>O<sub>3</sub> are the main oxides of steel slag, its chemical compositions are similar to that of Portland cement. But there are significant differences in mineralogical phases between Portland cement and steel slag. The main difference in steel slag is the high contents of iron oxide and RO phase, which have no cementitious properties and do not combine to form hydraulic phases.

The specific surface areas of Portland cement and steel slag are 350 m<sup>2</sup>/Kg and 458 m<sup>2</sup>/Kg, respectively. The particle size distribution which was measured by a laser particle size analyzer (MASTER SIZER 2000) is presented in Fig. 2. It is evident that steel slag was finer than cement in the range of fine particles, up to 6 μm, and steel slag was coarser than cement when the particle size was greater than 60 μm, while the particle size of steel slag between 6 ~ 60 μm are much less than cement.

### 2.2. Test method

The hydration heat evolution rate and cumulative hydration heat of blended cement containing steel slag were measured with an isothermal calorimeter (TAM Air from TA instruments). The tests were performed at three constant temperatures (25 °C, 45 °C and 60 °C) within 168 h. TAM Air has eight parallel twin-chamber measuring channels: one chamber containing the sample, another containing the reference. In order to avoid considerable temperature differences between the paste and the isothermal environment, the binder and water were kept at a temperature close to the measurement temperature before mixing. After manually mixing homogeneously, the pastes were immediately placed into the chamber maintained at a constant temperature. The hydration heat evolution rate and cumulative hydration heat of

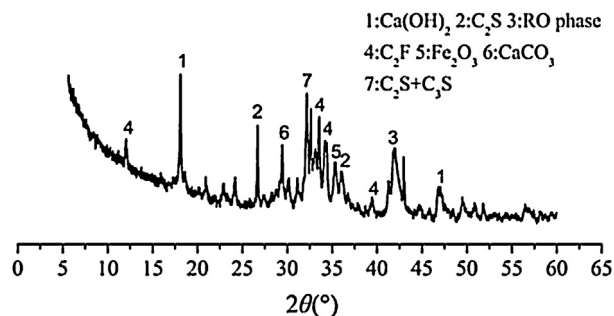


Fig. 1. XRD pattern of steel slag.

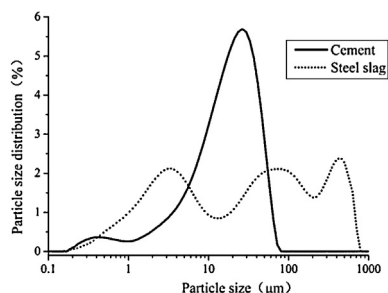


Fig. 2. Particle size distribution of cement and steel slag.

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