Construction and Building Materials 131 (2017) 381–387

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Blast furnace slag obtained from dry granulation method as a component in slag cement

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HIGHLIGHTS

- Dry granulation slag can be used as an excellent material substitution for cement.
- The crystalline and amorphous C—S—H formed in dry granulation slag cement paste.
- The later strength of dry granulation slag cement mortar was higher than that of cement mortar.

ARTICLE INFO

Article history:
Received 14 June 2016
Received in revised form 7 November 2016
Accepted 11 November 2016

Keywords:
Dry granulation
Compressive strength
Slag cement

ABSTRACT

Blast furnace slag obtained from water quenching is generally used for cement production. However, harmful waste, such as SO_2, H_2S and heavy metals, is discharged into the surrounding environment after water quenching. Dry granulation is an environmentally-friendly treatment, and the performance of dry granulation slag cement is investigated in the study. The results demonstrated that the particle size distribution and XRD pattern of dry granulation slag were similar to those of slag obtained from water quenching. The early strength of cement mortar made from dry granulation slag was very low, less than 50% of the cement clinker strength. Due to the weak reaction with the slag, the content of the CH phase was high. Next the CH phase was consumed in a reaction with dry granulation slag after 28 days. Crystalline and amorphous C—S—H were formed in the hydration of the slag cement paste system from dry granulation, and were measured by XRD and FTIR. The compressive strength data, including SEM study, indicate that dry granulation slag can accelerate the hydration of slag cement in the next stage.

1. Introduction

Blast furnace slag (BFS), a solid waste material, is a coproduct in iron making and is composed primarily of CaO, SiO_2, Al_2O_3 and MgO. Molten slag, which is discharged from the blast furnace, is cooled highly rapidly by water quenching. BFS solidifies into a glassy and granular form to produce a sand-like product [1]. The glassy slag, which shows latent hydraulic activity, is an excellent substituted material for Portland cement [2,3], and can result in a 47.5% reduction in CO_2 emissions when the percentage of cementitious slag in blended cement is from 2.83% to 10.3% [4]. Unfortunately, the large heat content of molten slag is not recovered, and harmful waste, such as SO_2, H_2S and heavy metals, is discharged into the surroundings along with steam or water. Owing to strict energy consumption codes and environmental considerations, increasing attentions is being focused on new methods, such as dry granulation and waste heat recovery system, for the treatment of molten slag [5–7]. In this method, only a little sulfides are discharged. Therefore, this method is, in a real sense, an environmentally-friendly treatment for molten blast furnace slag.

In dry granulation, the molten slag (1450~1650 °C) breaks up into small slag drops via a rotary cup or other atomizers. The slag drops are cooled in cooling bed. Mayumi et al. proposed a rotary disk and rotary drum for granulation of molten slag. Slag particles with a diameter of 1~7 mm were obtained and were cooled in a pair of fluidized beds [8]. Pickering et al. developed a system, which mainly consisted of a rotary cup and a two-stage fluidized bed. In the system, the atomization of molten slag can be accomplished using a rotating cup, following which the high-temperature slag particles of 2 mm diameter were cooled in a fluidized bed [9]. In the plant test, 60% of the heat in molten slag was recovered. The slag particles had a high glass content reaching 95%. In theory, slag particles can be used as raw materials for cement production. In work of Xie et al., molten slag was tapped onto a

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http://dx.doi.org/10.1016/j.conbuildmat.2016.11.040

water-cooled rotating copper disc, and the solid particles were discharged into an enclosed moving bed [10]. Cold nitrogen extracted the waste heat from the slag particles and then entered the waste heat boiler. Akiyama et al. developed a rotary-cylinder atomizing method to produce small slag particles with minimum diameters ranging from 10 to 50% of the nozzle diameter, which were later cooled in a fluidized bed or reaction beds [11]. Liu et al. poured the molten slag into a rotating cup, following which the high-temperature slag particles were collected by a vibration bed, and poured into a waste heat boiler, which was inserted with tubes in a staggered arrangement. The thermal energy, contained in slag particles, was recycled by water in the boiler tubes [12–14]. However, there have been few reports about the reactivity of BFS from the above dry granulation systems.

In the present study, the development of strength in slag cement was investigated with slags from water quenching and dry granulation. Their compressive strengths were compared with that of the neat cement clinker. The structural evolution of the slag cement paste system was measured by X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR), and the microstructure development by Scanning Electronic Microscopy (SEM). Taken together, this results provide a comprehensive and visual foundation for the analysis of the performance of slag cement from dry granulation.

2. Experimental

2.1. Materials

In the experiments, two types of blast furnace slag samples, namely, water quenching slag and dry granulation slag, from the same steel plants were used. Fig. 1(a) shows the granulated blast furnace slag which was produced by water quenching, i.e., water quenching slag, which has been widely used in blended cement. Fig. 1(b) shows dry granulation slag. In this method, molten slag flowed to the center of a rotating cup and formed a liquid slag film on the surface of the rotating cup. Due to the effect of centrifugal force and friction between liquid slag and the rotating cup surface, liquid slag left the center of the rotating cup, and moved towards the edge of the rotating cup. Next, the liquid slag film broke up into ligaments when it left the rotating cup. Finally, the ligaments were granulated into small spherical particles [12]. Fig. 2 shows the schematic diagram of experimental apparatus and granulation for molten slag. The minimum diameter of spherical particles was 0.5 mm and the maximum diameter was 4.3 mm. In the experiment, the initial temperature of molten slag was set to 1450 °C, and the volume flow rate was controlled at 23.4 $cm^3\ s^{-1}$. The diameter of the rotary cup was 130 mm with a rotating speed of 1000 rpm. The major chemical constituents of the blast furnace slag and cement clinker are shown in Table 1.

Water quenching slag and dry granulation slag were ground by ball milling for 35 min each, and were then mixed with the clinker. In the present work, three cement paste systems were investigated: neat cement clinker, and two blended cements, namely, 50% cement clinker: 50% water quenching slag and 50% cement clinker: 50% dry granulation slag.

2.2. Methods

The particle size distributions of the water quenching slag and dry granulation slag were determined by using a laser diffraction particle size analyzer. The cement clinker and two blended slag cements were cast in 20 mm cube molds with a water/cement ratio of 2:1. These samples were first cured in a fog room at 20 °C and at 95% relative humidity for 24 h and later demolded. The cement cube was kept in a water bath with a temperature that was also maintained 20 °C until testing age. The hydration of cement phases was studied using the XRD technique, which was performed on a X-ray diffractometer system using Cu Kα radiation, and running at 40 kV and 40 mA and a scan rate of 7° 2θ/min between 10° and 80° 2θ. Microstructural characterizations of the two slag cement pastes and the cement clinker paste were accomplished using SEM. Fourier Transform Infrared Spectroscopy was used for structural characterization of the three-cement paste. The sample pellets were prepared by compressing 2 mg of the sample powder with 200 mg of KBr under a force of 40 MPa force for 1 min. The spectra were recorded in the range of 500–4000 cm^{-1} with 2 cm^{-1} resolution and 32 scans in each measurement [15].

To determine the compressive strength, the cement mortar was prepared in a 40 × 40 × 160 mm container, with a water/cement ratio of 2:1 and cement/aggregate ratio of 1:3. As before, the cement mortar samples were cured in the fog room at 20 °C and at 95% relative humidity. After 24 h, the cement mortar samples of all types were demoulded and later kept in water at 20 °C for 3, 7 and 28 days.

3. Results and discussion

3.1. Features of two types of slag

Fig. 3(a) shows the particle size distributions for water quenching slag and dry granulation slag. The median sizes (X_{50}) of water

(a) Water quenching slag (b) Dry granulation slag

Fig. 1. Granulated blast furnace slag.