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Research paper

Using fly ash to partially substitute metakaolin in geopolymer synthesis

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ABSTRACT

Metakaolin-based geopolymers containing between 0 and 40% fly ash were prepared, to study the influence of fly ash substitution on the reaction process and products. At constant liquid/solid ratio, the partial replacement of metakaolin by fly ash reduces the rate of reaction, but the reaction continues for an extended duration and so is still able to achieve a relatively high extent of reaction and provide a comparable 28-day compressive strength when the replacement is less than 30%. The replacement of 10% of the metakaolin by fly ash gives an increased reaction extent (as measured by isothermal conduction calorimetry), and also a higher 28-day compressive strength, by 15%. The porosity of the geopolymer increases with the level of fly ash replacement, and pore refinement and ongoing reaction of fly ash particles during the first month of curing are also apparent.

1. Introduction

Geopolymers are a new family of cementitious materials with three-dimensional aluminosilicate gel structures, formed by chemical activation of solid aluminosilicate-containing precursor materials at low temperature (Van Deventer et al., 2012). Precursors used in geopolymer synthesis can include various aluminosilicate materials (Xu and Van Deventer, 2001; Andini et al., 2008), among which metakaolin (calcined kaolin) has high reactivity and generally high purity compared to the others, and has been shown to lead to the synthesis of geopolymers with high strength (Duxson et al., 2005) and low permeability (Zhang et al., 2010a). However, there are also drawbacks related to high water demand in metakaolin-based geopolymer mix design (Provis et al., 2010).

In the current study, fly ash is used to partially replace metakaolin to make geopolymer materials with a view towards application as a construction material. Kaolin is a non-renewable (although abundant) clay resource, while fly ash is a solid waste obtained by electrostatic or mechanical precipitation from the flue gases of furnaces fired with coal. More than 500 million tons of fly ashes are generated each year by power stations as well as the petrochemical industry, but the average utilization level is only about 20–30%, mainly in the cement and concrete industry as a supplementary cementitious material or filler (Ahmaruzzaman, 2010). Therefore, fly ash deserves special attention for its environmental and economic potential in geopolymer synthesis. However, as not all fly ashes are highly reactive (Duxson and Provis, 2008), it is often desirable to blend fly ashes with other geopolymer precursors in designing mixes with acceptable strength and microstructural development rates.

Many research studies have demonstrated the microstructure of fly ash-based geopolymers under various synthesis conditions (Andini et al., 2008; Bakharev, 2005; Slavík et al., 2008; Rattanasak and Chindaprasirt, 2009; Winnefeld et al., 2010). From the scanning electron microscopy (SEM) images available in the literature, one common feature of fly ash-based geopolymers is the visibly porous microstructure, which has recently been highlighted by the use of Wood's metal intrusion porosimetry (Lloyd et al., 2009a) and X-ray microtomography and nanotomography (Provis et al., 2011, 2012) to directly visualize the pore network structures in these materials. This porous structure influences the leachability, permeability and durability of the materials (Lloyd et al., 2010), which can thus determine the potential areas of application. For example, low permeability is required for protection of embedded steel reinforcing (Lloyd et al., 2010), for application as a coating for marine concrete (Zhang et al., 2010b), or when the geopolymer is used as a matrix for immobilization of radioactive or toxic wastes (Provis and Van Deventer, 2007). Hence, a deep understanding of the role of fly ash as a secondary source material in metakaolin-based geopolymers is necessary. However, only limited data have been reported related to the incorporation of fly ash in metakaolin-based geopolymers. This study reveals some of the influences of incorporation of fly ash on the geopolymerization process and the microstructure of products, particularly on a microstructural level and in terms of the progress of the reaction process as measured by calorimetry.

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2. Experimentals

2.1. Materials

Metakaolin was obtained from Taojinfeng New Materials Co. Ltd. (Fujian, China) and the fly ash was supplied by Yangzi Power Station (Nanjing, China). Table 1 gives their composition as detected by X-ray fluorescence (XRF), and Fig. 1 shows the results of X-ray diffraction analysis using an ARL 9900 series workstation (Thermal Scientific) with Co–Kα radiation (generated at 40 kV, 40 mA), scanning at a rate of 2.4°/min. From Fig. 1 it is clear that metakaolin is largely amorphous, with a small quantity of quartz as an impurity phase, and a small amount of residual kaolinite. The fly ash used contains large amounts of mullite and quartz phases in addition to the main amorphous phase, and no notable iron-rich crystalline phases. The particle size distribution parameters D_{10}, D_{50} and D_{90} of metakaolin as determined by laser diffraction are 1.4 μm, 5.9 μm, and 17.0 μm, while those for the fly ash are 4.6 μm, 22.3 μm and 62.3 μm. The particle surface areas of metakaolin and fly ash are 1.84 m^2/g and 0.86 m^2/g respectively, as given by laser particle analysis.

The alkaline activator used was a mixture of chemical grade sodium hydroxide solution and commercial sodium water glass (Heyi Chemical Eng. Co. Ltd., Nanjing, with original modulus of 3.33, Na_2O 9.28 wt.%, SiO_2 29.91 wt.%), combined to give a molar ratio SiO_2:Na_2O of 1.2. Distilled water was then added to adjust the total dissolved solid concentration to 35 wt.%.

2.2. Geopolymer preparation

Metakaolin and the designated percentage of fly ash were first dry-mixed, and then mixed with the alkaline activator solution at a constant liquid/solid ratio of 0.6 mL/g in a mortar mixer for 3–5 min. The homogeneous paste was cast into cylindrical plastic molds (Ø25 × 37.5 mm) for 24 h to enable setting and hardening, at 25 ± 2 °C and relative humidity 95 ± 5%. The demolded specimens are denoted GFA0, GFA10, GFA20, GFA30 and GFA40 according to their fly ash content: 0%, 10%, 20%, 30% and 40% by mass of metakaolin plus fly ash respectively. Specimens were crushed into small fragments at ages of 1, 7 and 28 days, and stored in absolute alcohol until testing.

2.3. Testing methods

2.3.1. Setting time and strength

The setting time of the fresh geopolymer paste was tested according to ASTM C191 with a manually operated standard Vicat apparatus. Compressive strength of hardened geopolymer specimens was tested using a WHY-200 Auto Compressive Resistant tester (Shanghai Hualong, China) at 7 and 28 days, at a loading speed of 0.5 mm/min.

2.3.2. Isothermal calorimetry

Previous works (Zhang et al., 2009, 2012; Yao et al., 2009) have shown that isothermal calorimetry is a useful method to observe the geopolymerization process. The measurement was conducted using a 3114/3236 TAM 83 Air (Thermometric AB, Sweden) isothermal calorimeter by an internal mixing procedure: 2.000 g of dry-mixed solid raw materials and 1.6 mL of activating solution (in the injector) were first stored in the reaction ampoule for 6 h to minimize outside heat turbulence. Once the activator solution was injected, the mini-blender started mixing (2 min mixing time), and the data logger began to record the heat flow.

Table 1
Chemical composition of metakaolin and fly ash by XRF test (mass %; LOI: loss on ignition).

	SiO_2	Al_2O_3	K_2O	MgO	Fe_2O_3	CaO	TiO_2	P_2O_5	Na_2O	LOI
Metakaolin	55.87	42.25	0.31	0.04	0.38	0.04	0.20	0.14	0.26	0.61
Fly ash	55.86	31.74	1.15	0.39	3.28	1.67	1.24	0.18	0.42	3.42

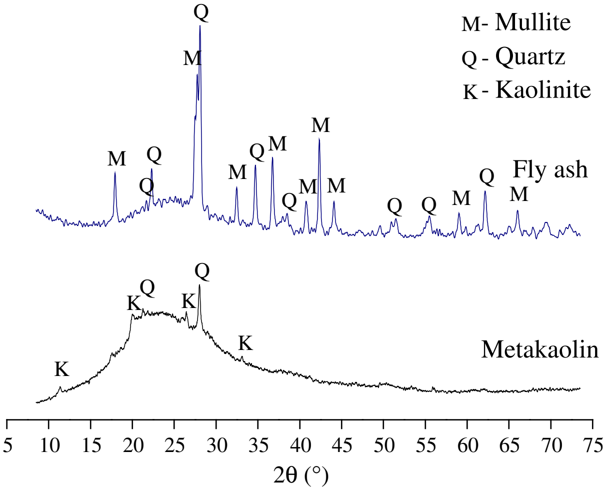

Fig. 1. XRD patterns of metakaolin and fly ash.

2.3.3. Mercury intrusion porosimetry (MIP)

To analyze the pore structure of geopolymers, MIP was performed using a PoreMaster GT-60 instrument (Quantachrome, USA). The surface tension of mercury was taken to be 0.48 N/m, and the contact angle used in the Washburn equation calculations was 140° (Zhang et al., 2010b). The test was carried out in two steps: a low pressure step from 5.7 kPa to 144.2 kPa for filling with mercury and removing air; and a high pressure step from 144.2 kPa to 219.8 MPa for measuring pores. Before testing, geopolymer specimens at the age of 28 days were crushed into granular samples of around 3 mm and stored in absolute alcohol for at least 24 h, then dried at 105 °C for 4 h.

2.3.4. Scanning electron microscopy (SEM)

A scanning electron microscope (JEOL Ltd., Japan) was used to analyze the morphology of the fracture surface of specimens GFA0 at 28 d, and GFA40 at 1 d, 7 d and 28 d. All samples were sprayed with a thin Au coating to enhance conductivity, and tested at an accelerating voltage of 15 kV.

3. Results and discussion

3.1. Effects of fly ash on geopolymerization

The effects of fly ash on geopolymerization as characterized by isothermal calorimetry are shown in Figs. 2 and 3. Heat evolution rate data are plotted separately from the beginning of mixing to 2 h (Fig. 2a) and up to 72 h (Fig. 2b), so that the influence of fly ash in the initial stage of reaction is more distinguishable. In Fig. 2a, as the content of fly ash increases from 0% to 40%, the maximum rate of heat evolution consistently decreases from 28.4 mW/g to 17.7 mW/g. The data for the metakaolin system are consistent with the isothermal calorimetry results of Granizo and Blanco (1998); Granizo et al. (2000) and also the differential scanning calorimetry results of Rahier et al. (1996b), who found maximum heat evolution rates of ~15–25 mW/g during the geopolymerization of various metakaolins. Higher fly ash content causes the maximum exothermic rate to be achieved later, and broadens both the first (Fig. 2a) and second (Fig. 2b) exothermic peaks.

From Fig. 2, it is clear that the partial replacement of metakaolin by fly ash decreases the initial rate of heat evolution due to the first stages of dissolution of the solid precursors; the first exothermic peak is not only less intense, but also delayed, by the addition of fly ash. This result is slightly surprising, as a simple dilution of the metakaolin by a