Influence of fly ash on the pore structure and shrinkage characteristics of metakaolin-based geopolymer pastes and mortars

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HIGHLIGHTS

- The porosity of the geopolymer decreases with the level of fly ash replacement.
- The fly ash substitution leads to higher autogenous shrinkage and lower drying shrinkage.
- The geopolymer mortars provide lower total shrinkage than the pastes.

ARTICLE INFO

ABSTRACT

This study investigates the pore structure and shrinkage behavior of metakaolin-based geopolymer pastes and mortars containing 0–30% fly ash. Fly ash substitution decreases average reactivity of the solid precursors, resulting in a lower reaction rate and accompanying longer reaction time. Composition of the sodium aluminosilicate (N-A-S-H) gel formed in the geopolymers has been changed, and the continued reaction after hardening of the pastes generates a more compact binding gel phase with lower Al/Si ratio. Refinement of the pore structure entails a higher capillary tension developed in the binders to increase the autogenous shrinkage, but also restricts the water evaporation from the pore networks, resulting in a decreased drying shrinkage. The geopolymer mortars provide higher compressive strength and lower total shrinkage when compared with the pastes.

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1. Introduction

Geopolymers, as a family of alkali activated aluminosilicate materials, has gained worldwide interests in the last two decades, due to the main driver of promising a sustainable alternative to Portland cement [1–3]. Precursors used in geopolymers manufacture include calcined clays and various Si- and Al-containing industrial byproducts [4–9], among which metakaolin has higher reactivity and chemical consistency than the others, and has potential to synthesis good thermal resistance [10] and low permeability geopolymers [11,12]. However, there are also drawbacks in the metakaolin-based geopolymers. High specific surface area of the platy metakaolin particles leads to excessive mixing water demand and high yield stress [13]. Moreover, the high water/binder ratio will have apparent deleterious effects on the pore structure, durability and efflorescence of the geopolymer products [11,13].

Fly ash is a solid waste, and has become one of the major materials in the production of geopolymers [14]. Its spherical particles could work as "ball bearing" to reduce viscosity of the paste, and as "micro-aggregate" to improve particle packing to refine pore structure of the binder [13,15]. Many research studies have been aimed at the reaction kinetics, binder chemistry and microstructures of both metakaolin and fly ash geopolymer systems [16–21]. The replacement of fly ash for metakaolin in designing geopolymer mixes usually provides economic potential and good engineering properties [16,22–24]. However, only limited data has been reported at shrinkage characteristics of the metakaolin-based geopolymers with fly ash as a secondary source precursor.

Shrinkage of the alkali-activated materials has been regarded as a serious problem for practical application [25–27]. Collins and Sanjayan [25] reported that pore structure was an essential parameter in determining drying shrinkage of alkali-activated slag concrete. Refinement of the microstructure in the concrete with heat-cuing could restrict water loss during drying, resulting in a reduction in the drying shrinkage [27]. Thus, modifying the pore size distribution should be desirable for mitigating the shrinkage

behavior and crack propagation of the geopolymers [26]. In this study, metakaolin-based geopolymer pastes and mortars containing 0–30% fly ash were prepared to investigate the pore structure and shrinkage behavior of the products. Reaction process, elemental compositions and microstructures were characterized through isothermal conduction calorimetry (ICC), X-ray diffractometry (XRD), mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS). Understanding of the shrinkage behavior of metakaolin-fly ash geopolymer pastes and mortars will provide useful information for future commercial-scale development.

2. Experimentals

2.1. Materials

Metakaolin powder was supplied by Taojinfeng New Materials Co. Ltd. (China) and produced by heating kaolin clay powder at 700 °C for 1 h. Fly ash was supplied by Xuzhou Guohua Power Station (China). Their compositions as detected by X-ray fluorescence (XRF) are given in Table 1. The particle size distribution parameters D_{10}, D_{50} and D_{90} of metakaolin as determined by laser diffraction are 1.4, 5.9 and 17.0 μm, while those for fly ash are 3.3, 14.5 and 82.7 μm. Alkaline activator was prepared by blending sodium silicate solution (Na_2O = 12.8 wt%, SiO_2 = 30.3 wt%, silicate modulus SiO_2/Na_2O = 2.45) with sodium hydroxide pellets (≥96 wt% purity) and distilled water to reach a combined modulus of 1.4 and concentration of 30 wt% (the mass content of SiO_2 and Na_2O in solution). This activator was allowed to equilibrate to room temperature prior to use.

2.2. Geopolymer preparation

Table 2 shows mixing proportions of the precursors and activator. The precursors were mixed with the activator solution for 5 min. The constant liquid to binder ratio (L/B) of 0.62 gave a good workability during mixing. The pastes containing 0, 10, 20 and 30 wt% fly ash were denoted as P0, P10, P20 and P30. The labels 'M' and 'S' represented the geopolymer mortars prepared with sand to binder ratios (S/B) of 0.5 and 1.0, respectively. The specimens were cast into 30 × 30 × 30 mm for measuring compressive strength, and 20 × 20 × 80 mm for measuring shrinkage behavior and residual water. The specimens were cured at the ambient conditions, sealed, and demolded after 24 h.

2.3. Testing and measurement

Shrinkage was reported by measuring six specimens to obtain an average value. The specimens were demolded at 24 h, and then cured at a constant temperature of 24 ± 2 °C and 45 ± 5% relative humidity (RH) during the measuring periods. Polyethylene film was used to wrap the specimens for the autogenous shrinkage tests with the purpose of preventing moisture egress during curing. The shrinkage strain was evaluated in accordance with the specifications of ASTM C 490, using a length comparator along the longitudinal axis at ages of 36 h to 50 days. Linear shrinkage was determined from Eq. (1), where L_{in} (mm) is the demoulded length,

Table 2
Mix proportions of the geopolymer pastes and mortars, and their compressive strengths after 50 days of the autogenous shrinkage experiment curing. Compressive strength is reported as mean and standard deviation among 6 replicate specimens.

Mixtures	FA contents	S/B	Compressive strength (MPa)
P0	0%	0	15.2 ± 1.8
P10	10%	0	15.2 ± 1.4
P20	20%	0	17.6 ± 1.5
P30	30%	0	18.7 ± 1.2
M0	0%	0.5	13.6 ± 1.6
M10	10%	0.5	13.5 ± 1.5
M20	20%	0.5	16.5 ± 1.1
M30	30%	0.5	18.7 ± 1.1
S0	0%	1.0	15.5 ± 1.4
S10	10%	1.0	16.3 ± 1.3
S20	20%	1.0	15.8 ± 1.0
S30	30%	1.0	18.4 ± 1.0

L_{fi} (mm) is the measured length and 75 (mm) is the effective length of the specimens without two head nails.

$$\text{Linear shrinkage} = \frac{L_{in} - L_{fi}}{75} \times 100\% \qquad (1)$$

Mass change was also measured with the same curing conditions as the drying shrinkage test. The weight percentages (wt%) of residual water in the specimens were calculated via Eq. (2), where W_h (g) is the initial weight of water in the specimens, ΔW (g) is the total weight change and W_s (g) is the total weight of the specimens.

$$\text{Residual water} = \frac{W_h - \Delta W}{W_s} \qquad (2)$$

The geopolymerization process was analyzed using a 3114/3236 TAM 83 Air isothermal conduction calorimeter (Thermometric AB, Sweden) at 20 °C by an internal mixing procedure [28]. The solid precursors and geopolymer samples were tested by X-ray diffraction (XRD) using a Thermo ARL9900 machine with Co Kα radiation, with a scanning rate of 2.4°/min from 8 to 80° 2θ, which needed 30 min to obtain a complete diffractogram. The morphologies of polished samples were analyzed using A ZEISS EVO MA18 scanning electron microscope (SEM) with back-scattered electron (BSE). An equipped energy dispersive spectroscopy (EDS) was used to conduct elemental composition analysis. Samples were coated with gold. Mercury intrusion porosimetry (MIP) analysis was conducted using a Poremaster GT-60. The specimens were crushed into granular samples of 1 mm and then dried at 60 ± 2 °C for 6 h, which is expected to have little effect on pore structure of the samples [29]. A WHY-200 Auto Test Compression Machine was used to test the compressive strengths of specimens under autogenous-curing conditions at age of 50-day.

3. Results and discussion

3.1. ICC analysis

Fig. 1 shows the isothermal conduction calorimeter data of the geopolymerization. From Fig. 1a, the fly ash substitution decreases the maximum heat evolution rate in the first peak, which

Table 1
Compositions of metakaolin and fly ash by X-ray fluorescence analysis. LOI is loss on ignition at 1000 °C, wt%.

	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	TiO_2	Na_2O	LOI
Metakaolin	55.87	42.25	0.04	0.04	0.38	0.31	0.20	0.26	0.61
Fly ash	53.00	30.58	4.57	1.25	3.81	1.43	1.08	0.52	2.29