

Journal of Zhejiang University-SCIENCE A (Applied Physics & Engineering) ISSN 1673-565X (Print); ISSN 1862-1775 (Online) www.jzus.zju.edu.cn; link.springer.com E-mail: jzus\_a@zju.edu.cn



# Relation between drying shrinkage behavior and the microstructure of metakaolin-based geopolymer<sup>\*</sup>

Shi-kun CHEN<sup>1</sup>, Cheng-lin WU<sup>†‡2</sup>, Dong-ming YAN<sup>†‡1</sup>, Yu AO<sup>1</sup>, Sheng-qian RUAN<sup>1</sup>, Wen-bin ZHENG<sup>3</sup>, Xing-liang SUN<sup>4</sup>, Hao LIN<sup>3</sup>

<sup>1</sup>Institute of Engineering Materials, College of Civil Engineering and Architecture, Zhejiang University, Hangzhou 310058, China <sup>2</sup>Department of Civil, Architectural, and Environmental Engineering, Missouri University of Science and Technology, Rolla, MO 65409-0030, USA

<sup>3</sup>Zhejiang Communications Investment Expressway Construction Management Co., Ltd., Hangzhou 310024, China <sup>4</sup>Zhejiang Communications Investment Expressway Operation Management Co., Ltd., Hangzhou 310024, China <sup>†</sup>E-mail: wuch@mst.edu; dmyan@zju.edu.cn

Received Nov. 3, 2020; Revision accepted Feb. 14, 2021; Crosschecked Sept. 23, 2021

**Abstract:** The drying shrinkage of geopolymers poses significant limitations on their potential as constructive materials. In this study, the drying shrinkage of metakaolin-based geopolymer (MKG) with different initial water/solid ratios and pore structures was investigated experimentally. According to mini-bar shrinkage experiments, the drying shrinkage-water loss relation of MKG showed two-stage behavior. The initial water/solid ratio influences the critical water loss and span of the pausing period of the shrinkage curves but not the general trend. Combined with the microstructure characterization and physical estimation, the underlying dependency of the shrinkage on the pore structure of the binder was elucidated. Capillary pressure, surface energy change, and gel densification dominate the drying shrinkage of MKG at different water loss stages. The findings indicate that besides porosity control, finer tuning of the pore size distribution is needed to control the drying shrinkage of MKG.

Key words: Geopolymer; Drying shrinkage; Microstructure; Modeling https://doi.org/10.1631/jzus.A2000513 CLC number: TU526

# 1 Introduction

The environmental burden added by the ordinary Portland cement (OPC) industry leads to the need for more sustainable construction materials. Geopolymer, as a newly developed binder system, has drawn attention from scientists and engineers for its ecobenefits, such as low CO<sub>2</sub> emission and energy consumption (Turner and Collins, 2013; Habert and

© Zhejiang University Press 2021

Ouellet-Plamondon, 2016). Geopolymers are made from alkali-activation of many pozzolanic aluminosilicate sources, such as metakaolin, fly ash, slag, and bottom ash (Antunes Boca Santa et al., 2017; Panda and Tan, 2018; Li et al., 2019; Yousefi Oderji et al., 2019). They possess many superior characteristics compared with OPC, such as high early strength (Davidovits, 1994), fire resistance (Duxson et al., 2007), and corrosion durability (Thokchom et al., 2009). These good characteristics are mainly due to the unique gel structure of the binder, which is composed of 3D aluminosilicate networks with covalent bonds, balanced alkali ions (Na, K, etc.), and nanopores (Davidovits, 1991; White et al., 2011). However, this gel structure also has some drawbacks, such as severe shrinkage on drying and potential risk of cracking. These drawbacks significantly constrain

<sup>&</sup>lt;sup>‡</sup> Corresponding author

<sup>\*</sup> Project supported by the National Key R&D Program of China (No. 2018YFB0605700) and the National Natural Science Foundation of China (Nos. 51879230 and 51778570)

ORCID: Shi-kun CHEN, https://orcid.org/0000-0002-3160-4101; Cheng-lin WU, https://orcid.org/0000-0001-7733-1084; Dong-ming YAN, https://orcid.org/0000-0003-2522-3342

the practical application of geopolymers. Therefore, extensive research has been conducted on this problem.

In early studies, Hardjito et al. (2004) concluded that fly ash-based geopolymer concrete has an extremely small drying shrinkage. However, other studies have shown that the drying shrinkage is dependent on the curing conditions. Wallah and Rangan (2006) found that an ambiently cured fly ash geopolymer had significantly larger drying shrinkage than that of OPC. However, when heat treatment was applied, the drying shrinkage was significantly reduced (Khan et al., 2019). Beside the curing conditions, Wang et al. (2010) and Castel et al. (2016) further found that the shrinkage of the geopolymer is closely related to its composition parameters (such as NaOH concentration, liquid/solid ratio, sodium silicate-to-NaOH ratio, silicate content of the solution, and calcium content). The inclusion of fibers and filler could also remedy the crack risk from drying shrinkage (Punurai et al., 2018; Xiang et al., 2019; Si et al., 2020). Moreover, Kuenzel et al. (2012) discovered a critical residual water content for the metakaolin-based geopolymer (MKG). The shrinkage of MKG significantly increased when the residual water content fell below this critical value during drying. They also stated that this critical water content (referred to as 'structural water content' in previous studies) varies with composition. Recent studies have revealed that the pore structure plays an important role in the drying shrinkage of geopolymers (Ma and Ye, 2015; Mobili et al., 2016; Yang et al., 2017). It is suspected that the high tensile stresses within the fine pores of the geopolymers may be the cause of these high drying shrinkages (Mosale Vijayakumar, 2014; Mastali et al., 2018). Different initial water contents could greatly alter the porosity of geopolymer and result in different drying shrinkage behaviours (Boca Santa et al., 2018; Novais et al., 2018). Moreover, additional materials (such as calcium bentonite or shrinkage reducing admixture) could also change the pore features and shrinkage behavior of geopolymers (Ling et al., 2019; Huang, 2020). Although these studies have revealed some important features of drying shrinkage of geopolymers, the quantitative relation between drying shrinkage and microstructure is still undetermined. An understanding of the relation between drying shrinkage and microstructure is important for the long-term durability design of geopolymers (Amran et al., 2021). In this study, we conducted both experimental and modeling investigations to reveal the underlying mechanism of drying shrinkage for MKG. Based on a mini-bar shrinkage test, microstructural characterization, and physical modeling, the drying shrinkage-water loss relations of MKGs with different initial water/solid ratios (WSRs) were quantitatively analyzed. The relations between the drying shrinkage of MKG and its unique microstructure were discussed.

# 2 Experiments

## 2.1 Materials and synthesis

The WSR was varied to produce MKGs with different porosities and pore structures. The geopolymer binder was made from commercial metakaolin (Metamax, BASF Co., Germany) and a laboratory-prepared activator. The chemical composition of the metakaolin powder was determined by X-ray fluorescence analysis (XRF-1800, Shimadzu, Japan), as shown in Table 1. The particle morphology was characterized by scanning electronic microscopy (Quanta FEG650, FEI, USA), as shown in Fig. 1. The particle size distribution was characterized using a laser particle size analyzer (LS-230, Beckman Coulter, USA), as shown in Fig. 2.

The activating solution was prepared with a commercial waterglass (WG) solution (Hengli Chemical Co., Ltd., China) and a pellet of sodium hydroxide (Sinopharm Chemical Reagent Co., Ltd., China). The WG contained 26.0% (in weight) SiO<sub>2</sub> and 8.2% (in weight) Na<sub>2</sub>O, and the pelleted sodium hydroxide included analytical reagent (AR) level chemical reagents with a purity of 98%.

To prepare the activating solution, the pellet of sodium hydroxide was dissolved in the WG solution with the ratio of 0.12:1 to achieve a molar SiO<sub>2</sub>/Na<sub>2</sub>O ratio of 1.55. The solution was then mixed with metakaolin powder and additional water to make the binder paste. The WSR of these pastes varied according to the compositions listed in Table 2. When the paste was mixed well, it was cast into steel molds and sealed in plastic bags. Then, these cast specimens were cured in a chamber at a temperature of  $(20\pm1)^{\circ}$ C with the humidity above 95% until testing.

## 2.2 Mini-bar shrinkage test

After 7 d of curing, the specimens were demolded and cleaned with absorbent paper to achieve a surface dry state prior to the test. As shown

Table 1 Chemical composition of the metakaolin powder

Component	Content (%)	Component	Content (%)
Al <sub>2</sub> O <sub>3</sub>	39.68	Fe <sub>2</sub> O <sub>3</sub>	0.42
$SiO_2$	57.26	Na <sub>2</sub> O	0.28
TiO <sub>2</sub>	1.78	K <sub>2</sub> O	0.22
CaO	0.03	LOI*	0.33

LOI: loss on ignition



Fig. 1 Micromorphology of metakaolin powder as received



Fig. 2 Particle size distribution of metakaolin powder as received

in Fig. 3, the linear shrinkage during the drying process was measured on a mini-bar specimen with a size of 25 mm×25 mm×280 mm, which is referred to the test standard JC/T 603 (NDRC, 2004) and ASTM C490 (ASTM, 2017). This configuration is selected to decrease nonuniformity of drying (by small cross section size) and relative errors (by long measurement length).



Fig. 3 Mini-bar specimens

First, its initial weight and length were measured with an electrical balance and a Vernier caliper, respectively. Then the specimens were sealed with silica gel desiccant in plastic bags and stored in (20±1)°C drying oven. This simulates a low humidity drying condition as the silica gel desiccant creates an environment with 21%–24% relative humidity (RH) at initial sealing and 45%-55% RH at the opening of the bags. The silica gel desiccant method had been used to test the shrinkage of concrete in a low RH environment (Nastic et al., 2019). The samples were carefully taken out and measured in terms of their weight and length changes. After the measurements, the desiccant was renewed, and the specimens were placed back in the plastic bags, sealed, and allowed to continue to cure in the same oven (Fig. 4).

When the weight and length changes slowed down, the drying temperature was increased to 60 °C and 80 °C on the 4th and 11th days, respectively. The raised temperatures further accelerated the drying process and simulated harsher drying conditions at high temperatures (Brue et al., 2017; Nastic et al.,

 Table 2 Compositions of the synthesized geopolymer binders

		-				
Mixture	Metakaolin powder (g)	WG solution (g)	Additional water (g)	Si/Al (mol/mol)	Na/Al (mol/mol)	WSR
WSR65	100	155.26	8.66	2	1	0.65
WSR70	100	155.26	17.11	2	1	0.70
WSR75	100	155.26	25.05	2	1	0.75
WSR80	100	155.26	33.24	2	1	0.80

2019). All tests ended on the 17th day owing to unstable damage to the MKG.

The linear shrinkage ( $\varepsilon_L$ ) was calculated from the length change of the specimen according to Eq. (1). The water loss (*w*) was calculated from the weight change according to Eq. (2). Three parallel specimens were used for each group.

$$\varepsilon_{\rm L} = \frac{L - L_0}{L_0},\tag{1}$$

$$w = \frac{M - M_0}{V_0},$$
 (2)

where *L* and *M* are the measured length and weight of the specimen during the drying process, respectively,  $L_0$  and  $M_0$  are the initial length and weight of the specimen, respectively, and  $V_0$  is the bulk volume of the sample.



Fig. 4 Illustration of measurement and drying process

# 2.3 Scanning electron microscopy (SEM) characterization

The morphologies of the dried MKGs at different length scales were characterized using a field emission environmental scanning electron microscope (ESEM) (Quanta FEG650, FEI, USA) at an accelerating voltage of 20 kV. The samples were cut from the tested mini-bars after the shrinkage test and manually split with a sharp knife. The naturally formed fracture surface was characterized by SEM to avoid a loss of details during polishing.

# 2.4 Mercury intrusion porosimetry (MIP) characterization

To explore the pore structure of the binder, the mercury intrusion porosimetry (MIP) method was used. An AutoPore IV 9510 instrument (Micrometrics, USA) with a pressure range of  $3.45 \times 10^3$  to  $4.14 \times 10^8$  Pa was used. This equipment can include the porosity from pores that are larger than 3 nm. As a convenient and effective technique, MIP provides relatively reliable information about the pore structures in cementitious materials (Gallé, 2001; Ma, 2014), although there is still some debate on its application (Diamond, 2000).

## 3 Results and discussion

# 3.1 Water loss and drying shrinkage

Because no solute in pore solution of hardened MKGs is evaporable and the carbonation is limited by the sealing of the plastic bags, the major change of specimen weight is from the evaporation of the water contained in the pore solution. Thus, water loss was regarded as equal to the weight change of specimens.

Fig. 5 shows the water loss and drying shrinkage changes as a function of the drying time.

The drying shrinkage and water loss showed different trends during the three successive drying steps.

Step 1: drying at 20 °C. The water loss of different groups gradually increased from 0 to 0.17-0.25 g/mL (depend on WSR) during this step. The average loss rate was approximately 0.043-0.063 g/(mL·d). Additionally, the drying shrinkages increased to 0.18%-0.21% during the first 1 d or 2 d and then exhibited a pausing period with little fluctuation during the following days.

Step 2: drying at 60 °C. As the drying temperature was raised, the water loss rates increased significantly. The average loss rate increased to approximately 0.105–0.135 g/(mL·d) after the elevation and then gradually decreased to 0.0032–0.0063 g/(mL·d) during the next 7 d of drying. The total water loss during this stage was 0.25–0.31 g/mL. However, the drying shrinkages still showed a pausing period during the first day of this step. Then, the shrinkages started to increase again with rates of 0.127% –0.141% each day. The shrinkage increased to 1.12% –1.20% at the end of this step. Step 3: drying at 80 °C. Although the temperature was elevated to 80 °C, there was no significant amount of water lost (less than 0.05 g/mL) during this drying step. However, the drying shrinkages showed a significant increase (with average rates of 0.13% -0.19% each day) during this step. The drying shrinkages reached approximately 1.97%–2.26% at the end of this test.

The test data was re-organized to show the variation in the drying shrinkage versus the water loss in Fig. 6.

A critical water loss value (of approximately 0.29–0.41 g/mL depending on the WSR) was observed. This divides the shrinkage response into two stages:



Fig. 5 Water loss (solid lines) and drying shrinkage (dashed lines) variation vs. drying time



Fig. 6 Drying shrinkage vs. water loss relation

Stage I: water loss below the critical water loss value. During this stage, the drying shrinkage in-

creased and then entered a pausing period (approximately 0.05–0.40 g/mL). The critical value and span of the pausing period were approximately proportional to the initial WSR.

Stage II: water loss above the critical water loss value. After a transforming period (approximately 0.29–0.50 g/mL), the drying shrinkages sharply increased when the water loss was beyond the critical value. The trends of the shrinkage curves for different mixtures are very similar after the water loss exceeds the critical value. The drying shrinkages of all mixtures showed a linear relationship with water loss after the critical value.

The observed trend in drying shrinkage of MKG is consistent with the findings of Kuenzel et al. (2012). They also found that MKG showed two different drying shrinkage stages before and after a critical state. The main difference is that the shrinkage values measured before the critical state in our experiment (0.17%-0.27%) are significantly higher than those (approximately 0.04%-0.11%) in previous study (Kuenzel et al., 2012). This difference is due to the different reference times during the drying shrinkage test (the 7th day in our experiment and the 56th day in previous experiments). The earlier reference time allows measurements of early-stage shrinkage, which produced the higher recorded values. Interestingly, the critical water loss and span of the pausing period is almost proportional to the initial WSR. This indicates that the MKG with higher WSR may be more stable in terms of drying shrinkage when the humidity environment fluctuates. The underlying mechanisms of these behaviors will be explained in the following sections.

#### 3.2 Pore systems in MKG

As revealed by previous studies (Kriven et al., 2006; Kong et al., 2007; Maitland et al., 2011), the majority of the pores in geopolymers are on the microscale ( $<5 \mu$ m), which is consistent with our SEM and MIP results. The SEM results also show that all samples have similar pore system which consists of pores at different scales. As an example, a set of results from the WSR70 sample is shown in Fig. 7.

From Fig. 7, a three-leveled hierarchical pore system was identified in the binder:

1. Level I–meso pores (void size of  $>5 \mu m$ ): the binder at the sub-millimeter scale was found to be



Fig. 7 Multi-scale pore systems in MKG: (a) level I, meso pores; (b) level II, micro pores; (c) level III, nanopores

homogeneous (Fig. 7a). However, some air bubbles and meso cracks occurred on this scale. They are usually introduced by mixing or fractures. Their presence is quite random. From the SEM and MIP measurements, the volume fraction of these voids was found to be low (<1.6%), which was considered to have little influence on the binder shrinkage. 2. Level II–micro pores (void size within 5 nm to 5  $\mu$ m): the matrix on the micrometer to submicrometer scale showed a very porous nature (Fig. 7b). The binder consists of a clustered aluminosilicate gel. Among these granular clusters, a large volume fraction of interstitial micro pores and micro cracks formed. These micro voids were highly interconnected and resulted into a large porosity (33.29% -43.34% in these experiments), as shown by the MIP results in Fig. 8a. Similar findings were reported by Duxson et al. (2005) and Maitland et al. (2011).



Fig. 8 Total porosity (a) and density (b) measured by MIP

3. Level III–nanopores (void size of <5 nm): the high-resolution SEM images (Fig. 7c) indicate that the gel clusters consist of nano-sized gel globules, which produce interconnected nanopores. Similar findings were reported from previous TEM studies (Kriven et al., 2006) and molecular dynamics simulations (Sadat et al., 2016). Chemically bound water in the form of silanol or aluminol groups may be contained in these networked cavities in gel clusters (Duxson et al., 2005; Zheng et al., 2010). However, the size of these pores is usually out of the range of detection for MIP and thus not commonly acknowledged in other studies. Hence, their contributions to the porosity may have been underestimated.

A closer look at the level II micro pores in MKGs with different WSRs (Fig. 9) brought our attention to the slight shift in the characteristic pore size and porosity as the WSR increased. This shift was also confirmed by the MIP results.

As shown in Fig. 10, the characteristic pore size increased from 11.05 nm to 21.09 nm when the WSR increased from 0.65 to 0.80. Simultaneously, the total porosity measured by MIP also increased from 34.26% to 44.08% (Fig. 8a). This increase in porosity was mainly due to the level II micro pores (5 nm to 5 µm) and led to a significant decrease in the bulk densities (Fig. 8b). However, the skeletal densities that were calculated by subtracting the micro and meso porosities measured by MIP were relatively stationary (approximately 2.01 g/mL to 2.05 g/mL) as the WSR changed. This indicated that the nano-sized pore structure was independent of the initial WSR. These pores are, however, closely related to the polycondensation of aluminosilicate networks on the molecular scale (Sadat et al., 2016). This finding agrees with the results reported by Kuenzel et al. (2012), who pointed out that "structural water" (water contained in the nanopores) is an intrinsic property, and was mainly determined by the chemical compositions of the aluminosilicate networks.

## 3.3 Modeling drying shrinkage

The three main driving forces behind the shrinkage behavior were identified and are explained below. Their relationship with the volumetric shrinkage strain is also expressed quantitatively.

1. Capillary pressure-induced shrinkage

The first driving force is the capillary pressure, which is caused by the emptying of the micro pore water. As the water in the geopolymer is gradually evaporated from the saturated binder, air invades the pore space within the sample. The interface between the air and pore water forms a curved liquid-gas meniscus. This develops an internal pressure between the air and water owing to the surface tension along the interface (de Gennes et al., 2004). This internal



Fig. 9 Micro-morphology of WSR65 (a), WSR70 (b), WSR75 (c), and WSR80 (d) specimens

pressure, which is usually referred to as the Laplace pressure or capillary pressure, results in the shrinkage of the MKG.

The random level II micro pore systems (Fig. 11a) in geopolymers are approximated as an interconnected network of cylindrical pores, as shown in Fig. 11b. The level I meso pore system (>5  $\mu$ m) is currently ignored due to its extremely low volume fraction (<1.6%) and its negligible influence on the capillary pressure (<0.1 MPa). As the water is gradually replaced by air flowing from the larger to smaller pores, the pore space is divided into water-and air-filled components.

Inside the water-filled pores, the capillary

pressure due to the formation of menisci can be calculated by the Young-Laplace equation (Young, 1832; Wittmann, 1973):

$$P_{\rm c} = P_{\rm a} - P_{\rm l} = -\gamma \left(\frac{1}{R_{\rm l}} + \frac{1}{R_{\rm 2}}\right) = -\frac{2\gamma \cos\psi}{R_{\rm c}}, \quad (3)$$

where  $P_c$  is the Laplace pressure or capillary pressure,  $P_a$  is the gas pressure,  $P_1$  is the liquid pressure,  $\gamma$  is the surface tension of the liquid,  $R_1$  and  $R_2$  are the curves radii of two perpendicular directions,  $R_c$  is the Kelvin radius, and  $\psi$  is the contact angle.

Typically, the Kelvin radius can be calculated from the Kelvin equation (Pinson et al., 2015):



Fig. 10 Cumulative (a) and differential (b) pore size distribution measured by MIP



Fig. 11 Simplified model for the shrinkage mechanism during loss of micro pore water: (a) random pores system; (b) equivalent cylindrical pore system

$$R_{\rm c} = -\frac{2\gamma_{\rm w}a^3}{kT\ln(h)},\tag{4}$$

where  $\gamma_w$  is the surface tension of water,  $a^3$  is the characteristic volume of a water molecule in the liquid state, *k* is the Boltzmann constant, *T* is the absolute temperature, and *h* is the RH.

In this study, we calculated the Kelvin radius by using the information from the pore structure in the MKG binder. First, we considered the cumulative pore volume distribution (CPVD), which was expressed as the relation between the cumulative porosity and the pore diameters (as demonstrated in Fig. 12),

$$v(D) = \frac{V_D}{V_0},\tag{5}$$

where D is a given pore diameter,  $V_D$  is the cumulative volume of pores with a diameter larger than D.



Fig. 12 Illustration of cumulative pore volume distribution (CPVD) function

The evaporation of pore water always begins from the larger pores and then progresses into smaller ones. Thus, the water loss can be related to the air-filled pore volume according to Eq. (6) (here, "air-filled" is the state without the bulk water but with a thin layer of adsorbed water on the pore wall surface),

$$w = \rho_{\rm w} v(D_{\rm c}), \tag{6}$$

where  $\rho_w$  is the density of water, and  $D_c$  is the corresponding minimum micro pore size that is currently filled with air.

Inversely, we could also calculate the currently air-filled pore size,  $D_c$ , from Eq. (6):

$$D_{\rm c} = v^{-1} \left( \frac{w}{\rho_{\rm w}} \right), \tag{7}$$

where  $v^{-1}()$  is the inverse function of the CPVD v(), which can be linearly interpolated from the CPVD curves.

Assuming the contact angle of the capillary menisci to the pore wall is zero because of the presence of the absorbed water layer, the Kelvin radius is given by half the minimum air-filled pore diameter:

$$R_{\rm c} = -\frac{D_{\rm c}}{2}.$$
 (8)

Then, the capillary pressure can be directly calculated from the water loss as

$$p_{\rm c} = -\frac{4\gamma_{\rm w}}{D_{\rm c}} = -\frac{4\gamma_{\rm w}}{v^{-1} \left(\frac{w}{\rho_{\rm w}}\right)}.$$
(9)

As previous theoretical studies (MacKenzie, 1950; Thokchom et al., 2009) have shown, the capillary pressure acts as the effective stress of a partially saturated porous solid. The deformation due to this effective stress can be calculated as

$$\varepsilon_{\rm V,c} = S_{\rm c} p_{\rm c} \left( \frac{1}{K_{\rm b}} - \frac{1}{K_{\rm s}} \right), \tag{10}$$

where  $\varepsilon_{V,c}$  is the volumetric strain due to the capillary pressure,  $K_b$  is the bulk modulus of a porous solid, and  $K_s$  is the bulk modulus of the solid part.

 $S_{\rm c}$  is the saturation (the water-filled pore volume fraction), which can be calculated as

$$S_{\rm c} = \frac{\phi_{\rm c} - \frac{W_{\rm c}}{\rho_{\rm w}}}{\phi_{\rm c}},\tag{11}$$

where  $w_c$  is the water loss of capillary pore, and  $\phi_c$  is the capillary porosity, which is the sum of the level I and level II porosities.

Because  $K_s$  is usually much greater than  $K_b$  for a medium with a large porosity, Eq. (10) can be simplified as:

$$\varepsilon_{\rm V,c} = \frac{S_{\rm c} p_{\rm c}}{K_{\rm b}}.$$
 (12)

2. Surface energy change-induced shrinkage

In addition to deformation owing to the capillary pressure, the empty micro pore water causes a change in the surface energy of the gel clusters. This change is equivalent to an increase in surface tension applied on the micro pore walls, and produces drying shrinkage (Ye and Radlińska, 2016).

This change in surface energy ( $\Delta \Pi$ ) can be calculated from the change in surface area of the air-filled pores and the surface tension of the adsorbed water layers (Bangham and Razouk, 1937a; Hansen, 1987; Pinson et al., 2015):

$$\Delta \Pi = \kappa_{\rm s} \gamma_{\rm s} - \kappa_{\rm s,0} \gamma_{\rm s,0}, \qquad (13)$$

where  $\kappa_s$  is the specific pore surface area (sum of the pore surface area divided by the sample volume) that is currently filled by air,  $\kappa_{s,0}$  are the corresponding values of the saturated state and thus are considered to be zero (Pinson et al., 2015),  $\gamma_s$  is the surface tension of the water layer at the partially covered state, and  $\gamma_{s,0}$  is the surface tension at the fully covered state.

The specific pore surface area,  $\kappa_s$ , can be directly derived from the cumulative pore surface area distribution (CPSD), s(D):

$$\kappa_{\rm s} = \frac{s(D)}{V_0},\tag{14}$$

where s(D) is calculated from the CPVD v(D) by considering the differential relation between the volume and side surface area of a cylinder pore.

$$\frac{\mathrm{d}s(D)}{\mathrm{d}D} = \frac{4}{D} \frac{\mathrm{d}v(D)}{\mathrm{d}D}.$$
 (15)

The surface tension of the adsorbed water layer,  $\gamma_s$ , can be calculated by the Gibbs equation (Feldman and Sereda, 1964; Pinson et al., 2015):

$$\gamma_{\rm s} = \gamma_{\rm s,0} - \frac{kT}{a^2} \int_{h_0}^h \theta \frac{\mathrm{d}h}{h},\tag{16}$$

where  $\theta$  is the surface coverage, *a* is the characteristic length of a water molecule, and *h*<sub>0</sub> is the relative humidity of the fully covered state (100% RH).

The current relative humidity can be inversely calculated from the Kelvin equation and current emptied pore diameter:

$$\ln(h) = -\frac{4\gamma_{\rm w}a^3}{kTD_{\rm c}}.$$
 (17)

As demonstrated by Pinson et al. (2015), the surface tension for the fully covered state is considered to be the same as the surface tension between the air and bulk water, which is  $\gamma_{s,0}=\gamma_w$ . Moreover, the surface coverage at a given RH can be calculated using the Langmuir equation (Langmuir, 1918):

$$\theta = \frac{\alpha h}{1 + \alpha h},\tag{18}$$

where  $\alpha$  is a constant related to the energy of adsorption, which is assumed to be 65 according to the generally accepted value used in the Brunauer-Emmett-Teller (BET) approach. This value corresponds to the presence of a single monolayer of pore surface-adsorbed water at a RH of 11% (Hagymassy Jr et al., 1969).

The Bangham equation (Bangham and Razouk, 1937b; Pinson et al., 2015) describes the shrinkage deformation due to the change in the surface energy of a solid:

$$\varepsilon_{\rm V,s} = -\frac{\Delta \Pi}{K_{\rm b}(1-2\mu)},\tag{19}$$

where  $\varepsilon_{V,s}$  is the volumetric strain due to the change in surface energy, and  $\mu$  is Poisson's ratio of the medium.

3. Gel densification-induced shrinkage

As the micro pore water is drained out, the water deeply constrained in the level III nanopores eventually transports to the surface and evaporates. This part of the nanopore water has been generally referred to as "structural water" in previous studies (van Jaarsveld et al., 2002; Rahier et al., 2007; Kuenzel et al., 2012). The lost nanopore water  $(w_s)$  can be calculated as

$$w_{\rm s} = w - \phi_{\rm c} \rho_{\rm w}. \tag{20}$$

The deformation mechanism of a gel network is simply modeled as the densification of a package of inter-attracted molecular spheres (Fig. 13).

The liquid spheres (light gray spheres in Fig. 13b) represent hydroxyls and confined water in the nanopores, which were removed from the networks in our study. The solid spheres (dark gray spheres in Fig. 13b) represent the aluminosilicate back bones that collapse during densification. Because of the difference in neighborhood connections, not all voids left by removed liquid spheres closed (Fig. 13b). The reduced volume of the gel network was assumed to be a fraction of the removed liquid volume. Thus, the volumetric strain caused by nanopore water loss would be

$$\varepsilon_{\rm V,g} = \frac{\Delta V_{\rm g}}{V_0} = \frac{f(w_{\rm s})\Delta V_{\rm w}}{V_0} = f(w_{\rm s})\frac{w_{\rm s}}{\rho_{\rm w}},\qquad(21)$$

where  $\Delta V_g$  is the volume change of the gel owing to the loss of nanopore water, f() is the fraction function, and  $\Delta V_w$  is the volume of the lost nanopore water.

Due to the lack of nanoscale information, the form and value of  $f(w_s)$  could not be determined theoretically. An empirical form was thus obtained by fitting the experimental data:

$$f(w_{\rm s}) = 1 - \frac{w^*}{w_{\rm s}} \arctan\left(\frac{w_{\rm s}}{w^*}\right), \qquad (22)$$

where parameter  $w^*$  is related to the span of the transforming period and its influence on function shape is demonstrated in Fig. 14.

Upon substituting Eq. (22) into Eq. (21), the shrinkage due to the nanopore water loss is:

$$\mathcal{E}_{\mathrm{V,g}} = \frac{w_{\mathrm{s}}}{\rho_{\mathrm{w}}} - \frac{w^{*}}{\rho_{\mathrm{w}}} \arctan\left(\frac{w_{\mathrm{s}}}{w^{*}}\right). \tag{23}$$

# 3.4 Comparisons and discussion

By combining the shrinkages from all three driving forces, (1) the capillary pressure, (2) the surface energy change, and (3) the gel densification, we obtained the total volumetric shrinkage as



Fig. 14 One parameter fraction function with varied parameters



Fig. 13 Simplified model for the shrinkage mechanism during loss of nanopore water: (a) molecular network system; (b) equivalent sphere system

$$\varepsilon_{\rm V} = \varepsilon_{\rm V,c} + \varepsilon_{\rm V,s} + \varepsilon_{\rm V,g}. \tag{24}$$

Additionally, the linear shrinkage was calculated as (Hobbs, 1971)

$$\varepsilon_{\rm L} = \frac{\varepsilon_{\rm V}}{3}.$$
 (25)

Table 3 lists the parameters used in our model. The density,  $\rho_w$ , surface tension,  $\gamma_w$ , characteristic size of the water, a, and Boltzmann constant, k, were taken from Kumar et al. (2014). Adsorption parameter,  $\alpha$ , was taken from Pinson et al. (2015). The initial RH,  $h_0$ , was assumed to be 100%; the samples were sealed and cured in a high-humidity environment after casting. The temperature T used in the estimation is selected to be 20 °C (293.15 K), in order to simplify the calculation process. In fact, the high temperature accelerates the drying process and increases water loss in experiments. However, if we are only considering the time-invariant relation between the drying shrinkage and water loss at a given water loss level, the influence of temperature is very small. The calculated surface tension and RH at a given water loss level varies little when the temperature is raised from 20 °C to 80 °C. These variations only lead to a relative change of shrinkage of less than 0.04%. Thus, the simplification of temperature is selected. Poisson's ratio and bulk modulus used in the estimation were taken from previous experiments (Chen, 2015). The gel densification parameter was determined by least square fitting, and the coefficients of determination of the fitting curves were all above 0.95.

Fig. 15 shows a comparison of the modeling and experimental results.

The general trend of the predicated drying shrinkage versus the water loss was consistent with the experimental results. We recognized some important facts:

1. The capillary stress dominated the shrinkage during the early part of stage I. Its maximum effect occurred at a water loss of approximately 0.03–0.06 g/mL. As the water in level II micro pores the capillary stress effect started to decay due to a grad-ually evaporated and the pores filled with air, decrease in saturation. This is similar to the previous prediction on drying shrinkage of C-S-H gel (Pinson et al., 2015). However, this decay has not yet been confirmed experimentally in geopolymer materials, and is something which should be considered in future studies.

2. The surface energy change-induced shrinkage began to dominate the shrinkage process during the latter part of stage I. The pore size distribution of the tested samples and the test conditions (h=45%-55%, T=20-60 °C) led to similar shrinkage values in both the surface energy change-dominated regime and the capillary stress-dominated regime. Thus, the increase in the former complemented the decrease in the latter during the change to the dominant mechanism. Thus, a pausing period in the shrinkage-water loss curves was evident. Moreover, the span of the pausing period was proportional to the micro porosity and thus positively related to the initial WSR.

3. The porosity and pore size distribution together controlled the drying shrinkage during stage I. For example, because the characteristic pore size in

Doromotor	Value					
Farameter	WSR65	WSR70	WSR75	WSR80		
Bulk modulus, $K_b$ (GPa)	3.5	2.8	2.2	2.0		
Gel densification parameter, $w^*$ (g/mL)	0.110	0.055	0.050	0.045		
Coefficient of determination, $R^2$	0.965	0.977	0.967	0.986		
Water density, $\rho_w$ (g/mL)	1.0					
Water surface tension, $\gamma_w$ (mN/m)	72.8					
Characteristic size of molecular water, a (nm)	0.278					
Boltzmann constant, $k$ (J/K)	$1.38 \times 10^{-23}$					
Adsorption parameter, $\alpha$	65					
Initial RH, $h_0$ (%)	100					
Absolute temperature, $T(K)$	293.15					
Poisson's ratio, $\mu$	0.3					

Table 3 Parameters used to estimate the shrinkage

830



Fig. 15 Model estimation vs. experiment results: (a) WSR65; (b) WSR70; (c) WSR75; (d) WSR80

WSR65 (11.05 nm) was small compared to that in the other mixtures (13.74–21.09 nm), the capillary pressure was more intensive for this mixture. However, the lower porosity and larger bulk modulus of this sample remedied the high capillary pressure and thus resulted into a shrinkage similar to that in the other three mixtures. This indicates that control of drying shrinkage in MKG required simultaneous optimization of both the porosity and the pore size distribution.

4. The densification of the gel dominated the drying shrinkage during stage II. When the water loss began in stage II, the gel densification-induced shrinkage increased rapidly. After a short transforming period (within a water loss that was approximately equal to  $w^*$ ), the gel densification-induced volumetric shrinkage was equivalent to the loss of the nanopore water volume. The resulting gel densification shrinkages reached 7–10 times those of the capillary

shrinkage and the surface shrinkage at a water loss of 0.5 g/mL. Thus, the prevention of the loss of nanopore water is essential for controlling drying shrinkage damage to MKG. To avoid this, the water loss should not be above a critical value (approximately 0.29–0.41 g/mL for mixtures with different WSRs in this study).

# 4 Conclusions

The following conclusions were drawn from the combined experimental and modeling study:

1. The three-leveled pore system of the MKG binder resulted in two-stage drying shrinkage behavior. The initial WSR indirectly influenced the shrinkage behavior of MKG owing to its effect on the pore structures.

2. During the early drying stage (stage I), the loss of micro pore water controlled the shrinkage. The dominant driving force of the drying shrinkage transformed from capillary stress to surface energy change during this stage. The porosity and pore size distributions both controlled the drying shrinkage during this transformation.

3. During the latter drying stage (stage II), the loss of nanopore water and gel densification became the dominant factors. At this point, the volume of MKG drastically reduced (by as much as 7–10 times the shrinkage during stage I). Thus, this must be avoided in applications by keeping the water loss lower than the critical value, which is also dependent on the micro porosity and initial WSR.

Beyond these conclusions, the drying shrinkage problem of geopolymers is complex and multi-scale in nature. Many shrinkage mechanisms, especially those on the nanoscale, need to be further elucidated. More studies are needed to completely uncover these basic mechanisms.

#### Contributors

Shi-kun CHEN: conceptualization, data curation, formal analysis, methodology, visualization, writing—original draft; Cheng-lin WU: methodology, validation, writing—review & editing; Dong-ming YAN: conceptualization, project administration, supervision, resources, funding acquisition, writing —review & editing; Yu AO: investigation, data curation; Sheng-qian RUAN: investigation, writing—review & editing; Wen-bin ZHENG: resources; Xing-liang SUN: resources; Hao LIN: resources.

#### **Conflict of interest**

Shi-kun CHEN, Cheng-lin WU, Dong-ming YAN, Yu AO, Sheng-qian RUAN, Wen-bin ZHENG, Xing-liang SUN, and Hao LIN declare that they have no conflict of interest.

#### References

Amran M, Debbarma S, Ozbakkaloglu T, 2021. Fly ash-based eco-friendly geopolymer concrete: a critical review of the long-term durability properties. *Construction and Building Materials*, 270:121857.

https://doi.org/10.1016/j.conbuildmat.2020.121857

- Antunes Boca Santa RA, Soares C, Riella HG, 2017. Geopolymers obtained from bottom ash as source of alumino silicate cured at room temperature. *Construction and Building Materials*, 157:459-466. https://doi.org/10.1016/j.conbuildmat.2017.09.111
- ASTM (American Society of Testing Materials), 2017. Standard Practice for Use of Apparatus for the Determination of Length Change of Hardened Cement Paste,

Mortar, and Concrete, ASTM C490/C490M-17. ASTM International.

https://doi.org/10.1520/C0490\_C0490M-17

Bangham DH, Razouk RI, 1937a. Adsorption and the wettability of solid surfaces. *Transactions of the Faraday Society*, 33:1459-1463.

https://doi.org/10.1039/TF9373301459

Bangham DH, Razouk RI, 1937b. The wetting of charcoal and the nature of the adsorbed phase formed from saturated vapours. *Transactions of the Faraday Society*, 33:1463-1472.

https://doi.org/10.1039/tf9373301463

Boca Santa RAA, Kessler JC, Soares C, et al., 2018. Micro structural evaluation of initial dissolution of aluminosilicate particles and formation of geopolymer material. *Particuology*, 41:101-111.

https://doi.org/10.1016/j.partic.2017.12.007

Brue FNG, Davy CA, Burlion N, et al., 2017. Five year drying of high performance concretes: effect of temperature and cement-type on shrinkage. *Cement and Concrete Research*, 99:70-85.

https://doi.org/10.1016/j.cemconres.2017.04.017

Castel A, Foster SJ, Ng T, et al., 2016. Creep and drying shrinkage of a blended slag and low calcium fly ash geopolymer concrete. *Materials and Structures*, 49(5): 1619-1628.

https://doi.org/10.1617/s11527-015-0599-1

- Chen SK, 2015. Study of Basic Mechanical Properties and Influential Factors of Metakaolin-based Geopolymer. MS Thesis, Zhejiang University, Hangzhou, China (in Chinese).
- Davidovits J, 1991. Geopolymers: inorganic polymeric new materials. *Journal of Thermal Analysis*, 37(8):1633-1656. https://doi.org/10.1007/BF01912193
- Davidovits J, 1994. Properties of geopolymer cements. Proceedings of the 1st International Conference on Alkaline Cements and Concretes, p.131-149.
- de Gennes PG, Brochard-Wyart F, Quéré D, 2004. Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves. Springer, New York, USA, p.1-31. https://doi.org/10.1007/978-0-387-21656-0
- Diamond S, 2000. Mercury porosimetry: an inappropriate method for the measurement of pore size distributions in cement-based materials. *Cement and Concrete Research*, 30(10):1517-1525.

https://doi.org/10.1016/S0008-8846(00)00370-7

Duxson P, Provis JL, Lukey GC, et al., 2005. Understanding the relationship between geopolymer composition, microstructure and mechanical properties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 269(1-3):47-58.

https://doi.org/10.1016/j.colsurfa.2005.06.060

Duxson P, Lukey GC, van Deventer JSJ, 2007. Physical evolution of Na-geopolymer derived from metakaolin up to 1000 °C. *Journal of Materials Science*, 42(9):3044-3054. https://doi.org/10.1007/s10853-006-0535-4 Feldman RF, Sereda PJ, 1964. Sorption of water on compacts of bottle-hydrated cement. I. The sorption and lengthchange isotherms. *Journal of Applied Chemistry*, 14(2): 87-93.

https://doi.org/10.1002/jctb.5010140206

- Gallé C, 2001. Effect of drying on cement-based materials pore structure as identified by mercury intrusion porosimetry. *Cement and Concrete Research*, 31(10):1467-1477. https://doi.org/10.1016/S0008-8846(01)00594-4
- Habert G, Ouellet-Plamondon C, 2016. Recent update on the environmental impact of geopolymers. *RILEM Technical Letters*, 1:17-23.

https://doi.org/10.21809/rilemtechlett.v1.6

Hagymassy Jr J, Brunauer S, Mikhail RS, 1969. Pore structure analysis by water vapor adsorption: I. *t*-curves for water vapor. *Journal of Colloid and Interface Science*, 29(3): 485-491.

https://doi.org/10.1016/0021-9797(69)90132-5

- Hansen W, 1987. Drying shrinkage mechanisms in Portland cement paste. *Journal of the American Ceramic Society*, 70(5):323-328.
- https://doi.org/10.1111/j.1151-2916.1987.tb05002.x Hardjito D, Wallah SE, Sumajouw DMJ, et al., 2004. On the development of fly ash-based geopolymer concrete. *Materials Journal*, 101(6):467-472. https://doi.org/10.14359/13485
- Hobbs DW, 1971. The dependence of the bulk modulus, Young's modulus, creep, shrinkage and thermal expansion of concrete upon aggregate volume concentration. *Matériaux et Construction*, 4(2):107-114. https://doi.org/10.1007/BF02473965
- Huang Y, 2020. Influence of calcium bentonite addition on the compressive strength, efflorescence extent and drying shrinkage of fly-ash based geopolymer mortar. *Transactions of the Indian Ceramic Society*, 79(2):77-82. https://doi.org/10.1080/0371750X.2020.1719206
- Khan I, Xu TF, Castel A, et al., 2019. Risk of early age cracking in geopolymer concrete due to restrained shrinkage. *Construction and Building Materials*, 229: 116840.

https://doi.org/10.1016/j.conbuildmat.2019.116840

- Kong DLY, Sanjayan JG, Sagoe-Crentsil K, 2007. Comparative performance of geopolymers made with metakaolin and fly ash after exposure to elevated temperatures. *Cement and Concrete Research*, 37(12):1583-1589. https://doi.org/10.1016/j.cemconres.2007.08.021
- Kriven WM, Bell JL, Gordon M, 2006. Microstructure and microchemistry of fully-reacted geopolymers and geopolymer matrix composites. *In*: Bansal NP, Singh JP, Kriven WM, et al. (Eds.), Advances in Ceramic Matrix Composites IX, Volume 153. John Wiley & Sons, Hoboken, USA, p.227-250.

https://doi.org/10.1002/9781118406892.ch15

Kuenzel C, Vandeperre LJ, Donatello S, et al., 2012. Ambient temperature drying shrinkage and cracking in metakaolinbased geopolymers. *Journal of the American Ceramic*  Society, 95(10):3270-3277.

https://doi.org/10.1111/j.1551-2916.2012.05380.x

- Kumar A, Ketel S, Vance K, et al., 2014. Water vapor sorption in cementitious materials-measurement, modeling and interpretation. *Transport in Porous Media*, 103(1):69-98. https://doi.org/10.1007/s11242-014-0288-5
- Langmuir I, 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, 40(9):1361-1403. https://doi.org/10.1021/ja02242a004
- Li ZM, Zhang SZ, Zuo YB, et al., 2019. Chemical deformation of metakaolin based geopolymer. *Cement and Concrete Research*, 120:108-118. https://doi.org/10.1016/j.cemconres.2019.03.017
- Ling YF, Wang KJ, Fu CQ, 2019. Shrinkage behavior of fly ash based geopolymer pastes with and without shrinkage reducing admixture. *Cement and Concrete Composites*, 98:74-82.

https://doi.org/10.1016/j.cemconcomp.2019.02.007

Ma HY, 2014. Mercury intrusion porosimetry in concrete technology: tips in measurement, pore structure parameter acquisition and application. *Journal of Porous Materials*, 21(2):207-215.

https://doi.org/10.1007/s10934-013-9765-4

- Ma Y, Ye G, 2015. The shrinkage of alkali activated fly ash. Cement and Concrete Research, 68:75-82. https://doi.org/10.1016/j.cemconres.2014.10.024
- MacKenzie JK, 1950. The elastic constants of a solid containing spherical holes. *Proceedings of the Physical Society. Section B*, 63(1):2-11. https://doi.org/10.1088/0370-1301/63/1/302
- Maitland CF, Buckley CE, O'Connor BH, et al., 2011. Characterization of the pore structure of metakaolin-derived geopolymers by neutron scattering and electron microscopy. *Journal of Applied Crystallography*, 44(4):697-707.

https://doi.org/10.1107/S0021889811021078

- Mastali M, Kinnunen P, Dalvand A, et al., 2018. Drying shrinkage in alkali-activated binders–a critical review. *Construction and Building Materials*, 190:533-550. https://doi.org/10.1016/j.conbuildmat.2018.09.125
- Mobili A, Belli A, Giosuè C, et al., 2016. Metakaolin and fly ash alkali-activated mortars compared with cementitious mortars at the same strength class. *Cement and Concrete Research*, 88:198-210.

https://doi.org/10.1016/j.cemconres.2016.07.004

- Mosale Vijayakumar R, 2014. Evaluating Shrinkage of Fly Ash-slag Geopolymers. MS Thesis, University of Illinois at Urbana-Champaign, Champagne, USA.
- Nastic M, Bentz EC, Kwon OS, et al., 2019. Shrinkage and creep strains of concrete exposed to low relative humidity and high temperature environments. *Nuclear Engineering and Design*, 352:110154.

https://doi.org/10.1016/j.nucengdes.2019.110154

NDRC (National Development and Reform Commission), 2004. Standard Test Method for Drying Shrinkage of

Mortar, JC/T 603-2004. National Standards of the People's Republic of China (in Chinese).

Novais RM, Ascensão G, Ferreira N, et al., 2018. Influence of water and aluminium powder content on the properties of waste-containing geopolymer foams. *Ceramics International*, 44(6):6242-6249.

https://doi.org/10.1016/j.ceramint.2018.01.009

Panda B, Tan MJ, 2018. Experimental study on mix proportion and fresh properties of fly ash based geopolymer for 3D concrete printing. *Ceramics International*, 44(9):10258-10265.

https://doi.org/10.1016/j.ceramint.2018.03.031

Pinson MB, Masoero E, Bonnaud PA, et al., 2015. Hysteresis from multiscale porosity: modeling water sorption and shrinkage in cement paste. *Physical Review Applied*, 3(6):064009.

https://doi.org/10.1103/PhysRevApplied.3.064009

- Punurai W, Kroehong W, Saptamongkol A, et al., 2018. Mechanical properties, microstructure and drying shrinkage of hybrid fly ash-basalt fiber geopolymer paste. *Construction and Building Materials*, 186:62-70. https://doi.org/10.1016/j.conbuildmat.2018.07.115
- Rahier H, Wastiels J, Biesemans M, et al., 2007. Reaction mechanism, kinetics and high temperature transformations of geopolymers. *Journal of Materials Science*, 42(9):2982-2996.

https://doi.org/10.1007/s10853-006-0568-8

Sadat MR, Bringuier S, Asaduzzaman A, et al., 2016. A molecular dynamics study of the role of molecular water on the structure and mechanics of amorphous geopolymer binders. *The Journal of Chemical Physics*, 145(13): 134706.

https://doi.org/10.1063/1.4964301

Si RZ, Dai QL, Guo SC, et al., 2020. Mechanical property, nanopore structure and drying shrinkage of metakaolinbased geopolymer with waste glass powder. *Journal of Cleaner Production*, 242:118502.

https://doi.org/10.1016/j.jclepro.2019.118502

- Thokchom S, Ghosh P, Ghosh S, 2009. Effect of water absorption, porosity and sorptivity on durability of geopolymer mortars. *Journal of Engineering and Applied Sciences*, 4(7):28-32.
- Turner LK, Collins FG, 2013. Carbon dioxide equivalent (CO<sub>2</sub>-e) emissions: a comparison between geopolymer and OPC cement concrete. *Construction and Building Materials*, 43:125-130.

https://doi.org/10.1016/j.conbuildmat.2013.01.023

van Jaarsveld JGS, van Deventer JSJ, Lukey GC, 2002. The

effect of composition and temperature on the properties of fly ash-and kaolinite-based geopolymers. *Chemical Engineering Journal*, 89(1-3):63-73.

https://doi.org/10.1016/S1385-8947(02)00025-6

- Wallah SE, Rangan BV, 2006. Low-calcium Fly Ash-based Geopolymer Concrete: Long-term Properties. Curtin University of Technology, Perth, Australia.
- Wang Q, Zhang CY, Ding ZY, et al., 2010. Research on shrinkage of slag-based geopolymer concrete. *Materials Review*, 24(10):65-67 (in Chinese).
- White CE, Provis JL, Llobet A, et al., 2011. Evolution of local structure in geopolymer gels: an in situ neutron pair distribution function analysis. *Journal of the American Ceramic Society*, 94(10):3532-3539.

https://doi.org/10.1111/j.1551-2916.2011.04515.x

Wittmann FH, 1973. Interaction of hardened cement paste and water. *Journal of the American Ceramic Society*, 56(8): 409-415.

https://doi.org/10.1111/j.1151-2916.1973.tb12711.x

Xiang JC, Liu LP, Cui XM, et al., 2019. Effect of fuller-fine sand on rheological, drying shrinkage, and microstructural properties of metakaolin-based geopolymer grouting materials. *Cement and Concrete Composites*, 104: 103381.

https://doi.org/10.1016/j.cemconcomp.2019.103381

- Yang T, Zhu HJ, Zhang ZH, 2017. Influence of fly ash on the pore structure and shrinkage characteristics of metakaolin-based geopolymer pastes and mortars. *Construction and Building Materials*, 153:284-293. https://doi.org/10.1016/j.conbuildmat.2017.05.067
- Ye HL, Radlińska A, 2016. A review and comparative study of existing shrinkage prediction models for Portland and non-Portland cementitious materials. *Advances in Materials Science and Engineering*, 2016:2418219. https://doi.org/10.1155/2016/2418219
- Young T, 1832. An essay on the cohesion of fluids. Proceedings of the Royal Society of London, 1:171-172. https://doi.org/10.1098/rspl.1800.0095
- Yousefi Oderji S, Chen B, Ahmad MR, et al., 2019. Fresh and hardened properties of one-part fly ash-based geopolymer binders cured at room temperature: effect of slag and alkali activators. *Journal of Cleaner Production*, 225:1-10. https://doi.org/10.1016/j.jclepro.2019.03.290
- Zheng L, Wang W, Shi YC, 2010. The effects of alkaline dosage and Si/Al ratio on the immobilization of heavy metals in municipal solid waste incineration fly ash-based geopolymer. *Chemosphere*, 79(6):665-671. https://doi.org/10.1016/j.chemosphere.2010.02.018

834