Construction and Building Materials 151 (2017) 512–519

Contents lists available at ScienceDirect

Construction and Building Materials

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

Strength development properties of geopolymer paste and mortar with respect to amorphous Si/Al ratio of fly ash

Bokyeong Lee [a], Gyuyong Kim [a,*], Raehwan Kim [b], Bongsuk Cho [c], Sujeong Lee [d], Chul-Min Chon [e]

[a] Department of Architectural Engineering, Chungnam National University, Daejeon 34134, Republic of Korea
[b] Architectural Engineering & Research Team, DAELIM Industrial Co., Ltd., Seoul 03152, Republic of Korea
[c] Environment & Resources Research Group, Research Institute of Industrial Science & Technology, Pohang 37673, Republic of Korea
[d] Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources, Daejeon 34132, Republic of Korea
[e] Geologic Environment Division, Korea Institute of Geoscience and Mineral Resources, Daejeon 34132, Republic of Korea

HIGHLIGHTS

- The compressive strength of geopolymer paste was affected by the Si/Al ratio calculated by the combination of the amorphous Si and Al contents in the fly ash and the alkaline activator.
- The direct correlation between the polymerization reactivity of the geopolymer paste and the compressive strength could not be confirmed from the shift position in the broad hump peak in the X-ray diffraction pattern.
- The compressive strength of geopolymer mortar with 20–40 wt% sand confirms the availability as a construction material.

ARTICLE INFO

Article history:
Received 9 January 2017
Received in revised form 21 April 2017
Accepted 15 June 2017

Keywords:
Fly ash
Amorphous Si/Al ratio
Alkaline activator
Geopolymer paste and mortar
Compressive strength
Polymerization reactivity

ABSTRACT

The strength development properties of geopolymer paste and mortar with 20–40 wt% of sand is analyzed with respect to changes in the Si/Al ratio calculated from a combination of the amorphous Si and Al contents in fly ash and an alkaline activator. Experimental results confirm that the compressive strength of the geopolymer paste is greatly affected by the Si/Al ratio. The geopolymer paste also shows high polymerization reactivity at an early age. Although a direct correlation between the polymerization reactivity of the geopolymer paste and the strength development could not be confirmed from the X-ray diffraction results, the difference in the polymerization reactivity resulting from the strength development is confirmed through scanning electron microscopy. The compressive strengths of the geopolymer mortar with 20–40 wt% of sand after aging for 28 days are 23.7–26.4 MPa, which confirms the possibility of using geopolymer mortar as a construction material.

1. Introduction

Geopolymers are materials that harden at low temperatures owing to the chemical reaction between the aluminosilicate material and an alkaline activator. Since fly ash contains a large amount of reactive silicone (Si) and aluminum (Al), when it is used as a raw material for geopolymers, it hardens owing to polymerization with the alkaline activator. Studies of fly ash-based geopolymers rely on mixing, in which the molarity of the alkaline activator is changed without considering the chemical composition or appearance of the fly ash [1–8]. However, recent studies have attempted to calculate the mixing ratio by considering the amorphous Si and Al contents in the fly ash that can react with the alkaline activator [9–15]. Görhan and Kürklü [6] reviewed the effect of the alkaline activator on the compressive strength of geopolymer mortar after curing it for 24 h at temperatures of 65–85 °C using NaOH (concentrations of 3, 6, and 9 M) as the alkaline activator. They reported that the specimen cured for 24 h at a temperature of 85 °C using a NaOH concentration of 6 M exhibited the highest compressive strength. Palomo et al. [7] reported that a geopolymer cured for 24 h at 85 °C using a NaOH concentration of 8–12 M showed a compressive strength of 35–40 MPa, and a geopolymer with a compressive strength of 90 MPa could be produced by adding waterglass.

Abbreviations: (XRD), X-ray diffraction; (XRF), X-ray fluorescence; (QXRD), quantitative X-ray diffraction; (SEM), scanning electron microscopy.

* Corresponding author.
E-mail address: gyuyongkim@cnu.ac.kr (G. Kim).

http://dx.doi.org/10.1016/j.conbuildmat.2017.06.078
0950-0618/

Somna et al. [8] reported that the compressive strength of a geopolymer increases as the concentration of NaOH increases from 4.5 to 14 M, whereas the compressive strength of a geopolymer decreases at a NaOH concentration of 16.5 M.

In contrast, Ward et al. [9] reported that X-ray diffraction (XRD) analysis based on the Rietveld method quantitatively provides the ratio of the crystalline and amorphous contents of fly ash. They also reported that the amorphous content contained in the sample can be obtained from a combination of the chemical composition and the crystalline content of the sample. Fernández-Jiménez et al. [10] reported that the mechanical strength can be increased by considering the amounts of SiO_2 and Al_2O_3 in the fly ash that can react. Rowles et al. [11,12] produced geopolymers by considering the ratios of Si/Al and Na/Al in metakaolin, and they determined the ideal Na/Al ratio for the charge balance in the bonding network of geopolymers. Chen-Tan et al. [13] used X-ray fluorescence (XRF) and quantitative X-ray diffraction (QXRD) analyses to reveal the amorphous content in fly ash, and they also reviewed the polymerization reactivity of geopolymers resulting from the input of an alkaline activator for maximizing the reaction of the geopolymer. Williams et al. [14,15] calculated the mixing ratio by considering the Si/Al ratio, Na/Al ratio, and the H/Si ratio of the geopolymer from the XRF and QXRD results of the fly ash to be produced. They also reported that a more accurate XRD result can be derived by the using the area ratio method (ARM) and the partial or no known crystal structure (PONKCS) method and that geopolymers can be produced through optimum mixing by taking into account the amount of particles that do not react.

When fly ash is used as the raw material for geopolymers, its polymerization reactivity to the alkaline activator varies depending on the burning condition of the fly ash, the types and contents of the minerals contained within it, the size and shape of the particles, and the storage conditions. Further, if fly ash is made such that it reacts excessively with the alkaline activator in order to obtain high strength, efflorescence occurs on the surface of the geopolymer causing deterioration of the geopolymer quality [16,17]. The method of constantly increasing the molarity of the alkaline activator when producing geopolymers has a high risk of increasing the probability of efflorescence occurring. Therefore, a geopolymer production method that involves considering the amorphous contents of Si and Al in the fly ash that can react is more effective and economical than the method that involves a constant increase in the molarity of the alkaline activator. However, in studies in which where geopolymers were produced by obtaining the amorphous Si/Al ratio in the fly ash [9–15], the polymerization reactivity of the geopolymers, which depends on the mixing with the alkaline activator, the curing temperature, and the curing period, was not analyzed in many cases. Accordingly, the objective of this study is to analyze the polymerization reactivity of geopolymers resulting from the combination of the amorphous Si and Al contents in the fly ash, as calculated by the method proposed by Williams and Riessen [14] and shown in Fig. 1, with the alkaline activator. Furthermore, the objective was to produce a geopolymer mortar with 20, 30, and 40wt% of sand and review the possibility of using geopolymer mortar as a construction material by comparing its strength development properties with those of the geopolymer paste.

2. Experimental procedures

2.1. Materials

Table 1 presents the physical properties of the used materials. The density and Blaine's surface area of the fly ash used in this study were 2.20 g/cm^3 and 3000 cm^2/g, respectively. The densities of the sodium aluminate ($NaAlO_2$), sodium silicate solution ($Na_2SiO_3{\cdot}H_2O$), and the sodium hydroxide (NaOH) used as the alkaline activator for the geopolymer were 1.52, 1.55–1.57, and 2.13 g/cm^3, respectively. The sand used to produce the geopolymer mortar was ISO standard sand, and its density and absorption ratio were 2.50 g/cm^3 and 1.00%, respectively.

2.2. Determination of amorphous composition of fly ash

Table 2 lists the total chemical and amorphous composition of the fly ash used to produce the geopolymer in this study. The total chemical composition of the fly ash was analyzed using an XRF spectrometer (Shimadzu Sequential XRF-1800, Shimadzu, Japan). The sample was produced in the form of beads by using the fused bead method and the loss on ignition (LOI) was measured at temperatures of 1000 °C or higher. The sum of the contents of SiO_2 and Al_2O_3 exceeded 70%, the content of CaO was less than 20%, and the fly ash used in this study can be classified into Class F of ASTM C618. An XRD analysis was carried out to analyze the crystalline and amorphous content of the fly ash. To perform a QXRD analysis of the fly ash, the DIFFRAC^{PLUS} TOPAS 4.2 (Bruker-AXS, Germany) software, which is based on the Rietveld method, was used. The internal standard material added was 10 wt % fluorite (CaF_2, calcium fluoride, 99.985%, Alfa). Further, 8 ml of ethanol was added to the mixture of fly ash and fluorite, and the mixture was then ground for 5 min using a micronizer (McCrone, USA) to create uniformly mixed particles having a size $\leq$5 μm. Then, the mixture was lightly pulverized again after it was dried for 6 h or longer in a 105 °C oven so that it could pass through a 400-μm sieve. XRD analysis was carried out using a D8 Advance diffractometer (Bruker-AXS, Germany). The diffraction patterns were obtained under the following conditions: 2θ range of 5–95°, 0.01° step, 1 s per step; a divergence slit of 0.3° and Soller slit of 2.5°. The XRF and the QXRD analyses revealed that the amorphous SiO_2 content was 38.47%, the amorphous Al_2O_3 content was 11.32%, and the amorphous Si/Al ratio was 2.88.

2.3. Geopolymer synthesis and experimental plan

Table 3 presents the experimental plan. By combining the amorphous Si and Al contents of the fly ash and the alkaline activator, the target Si/Al ratio is set to 1.5, 3.5, and 4.0. The reaction between the fly ash and the alkaline activator is very slow

Table 1
Physical properties of used materials.

Materials	Physical properties
Fly ash	Density: 2.20 g/cm^3, Blaine: 3000 cm^2/g
$NaAlO_2$	Sodium aluminate, Density: 1.52 g/cm^3
$Na_2SiO_3{\cdot}H_2O$	Sodium silicate solution, Density: 1.55–1.57 g/cm^3
NaOH	Sodium hydroxide, Density: 2.13 g/cm^3
Sand	ISO standard sand, Density: 2.50 g/cm^3, Absorption ratio: 1.00%

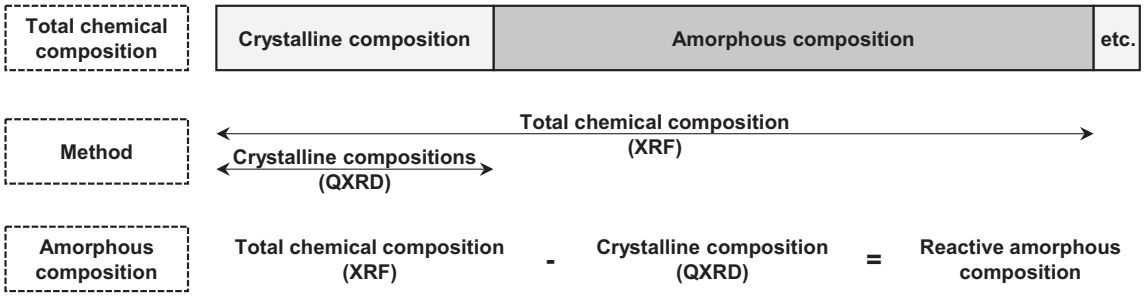

Fig. 1. Calculation method of the amorphous composition of fly ash [14].