Microstructure and mechanical properties of FA/GGBS-based geopolymer

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Abstract. This study presents the microstructure and mechanical properties of geopolymer paste made from low-calcium fly ash (FA) and ground granulated blast-furnace slag (GGBS) through alkalination. The use of GGBS and FA is not only for sustainable construction but also for reducing the emission of CO₂ due to the use of Portland cement. Different replacement ratios of GGBS to FA were used to determine the effect of GGBS presented to the compressive strength of geopolymer specimens. The alkaline activator solution used is a combination of sodium hydroxide (NaOH) 14 M and sodium silicate (Na₂SiO₃). A compressive strength test on cylindrical specimens (50 mm x 100 mm) at the ages of 7, 14, and 28 days was carried out. The results showed that the compressive strength increased with the increase of GGBS in the mixes (up to 100 MPa). Moreover, SEM-EDS, XRD, and TG-DTA characterization methods were conducted to investigate the microstructure, phase composition, and thermal stability of the geopolymer specimens respectively.

1 Introduction

The demand of environmentally friendly construction materials throughout the world is increasing, as the world is facing a serious problem due to environmental degradation. Traditional cement manufacturing consumes a large quantity of energy and emits high amounts of carbon dioxide due to calcination of limestone and combustion of fossil fuel [1-3]. Carbon dioxide (CO₂) is known as the main heat-trapping gas largely responsible for most of the average global warming over the past several decades. Given its high emissions and critical impact on environment, the cement industry is an obvious field refer to in order to reduce CO₂ emissions. In this context, materials prepared by geopolymerization processes can be used as binders, instead of the cement binder in mortar and concrete [2].

Geopolymer cements are manufactured differently from Portland cement. They can be obtained through inexpensive and eco-friendly synthetic procedures. Geopolymers have a three-dimensional amorphous structure [4] and can be synthesized from by-products such as fly ash, blast furnace slag or geological materials such as kaolinite [1,5-6]. Fly ash (FA) and ground granulated blast-furnace slag (GGBS), by-products from coal power plants and blast furnaces from the manufacturing iron industry respectively, have been commonly

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used as additive or cement replacement materials to improve the mechanical and durability properties of cement concrete [7-9]. However, fly ash-based geopolymer has a very long setting time, which is one of the obstacles to using it in the construction industry presently. Therefore, to improve the setting time of fly ash-based geopolymer, GGBS was introduced in the mixes [10]. Apart from this, the mechanical strength of ordinary Portland cement (OPC) is strongly affected by the formation of calcium silicate hydrate (C-S-H) gel, whereas the strength of geopolymer is affected by the poly-condensation of the silica and alumina source [10].

There are many parameters affecting geopolymerization. In this experimental study, the effect of the replacement of fly ash by GGBS on the properties of geopolymer was investigated.

2 Experimental

2.1 Materials

In this study, fly ash (fineness = 3.550 cm²/g, density = 2.24 g/cm³) and GGBS (fineness = 4.170 cm²/g, density = 2.91 g/cm³) were prepared as precursors. The chemical compositions and XRD patterns of both precursors are shown in Table 1 and Figure 1 respectively.

Table 1. Chemical compositions of raw materials by EDS analysis.

Composition	Fly ash (mass%)	GGBS (mass%)
SiO ₂	68.44	34.45
Al ₂ O ₃	20.65	14.06
Fe ₂ O ₃	4.18	0.27
CaO	2.25	43.78
K ₂ O	1.53	0.23
TiO ₂	1.19	0.56
MgO	0.58	5.84
Na ₂ O	-	0.24
LOI	2.9	0.05

Fig. 1. XRD pattern of precursors, (a). GGBS, and (b). Fly ash.

2.2 Synthesis of geopolymer

In this experimental study, the alkaline activator solution used was a combination of sodium hydroxide and sodium silicate. The sodium hydroxide solution was prepared in 14

M by dissolving 560 grams sodium hydroxide pellets in water to form a one litre solution. The alkaline solution was prepared one day prior to mixing. The alkaline solution to binder and sodium silicate to sodium hydroxide ($\text{Na}_2\text{SiO}_3/\text{NaOH}$) ratios were 0.45 and 2.0 (Na_2SiO_3 in $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio was calculated as Na_2SiO_3 solution + water added for appropriate consistency), respectively.

Five series of geopolymer pastes were prepared. The reference paste contained no GGBS. The other four series were prepared by partially replacing fly ash with GGBS by mass, with replacement levels ranging from 15% to 60% with an interval of 15%.

FA and GGBS were mixed for 2 minutes using an automatic mixer before contact with the activator solution. The sodium hydroxide solution and sodium silicate were added and mixed with the raw materials rapidly and continuously to form geopolymer paste. The fresh geopolymer paste was casted in plastic cylinders with a dimension of 50 mm in diameter and 100 mm in height. The specimens were cured at 70°C and 70% RH for 24 hours and then kept at room temperature for the rest of 24 hours before demoulding. After being demoulded, all specimens were stored and cured at 20°C and 60% RH.

2.3 Characterizations and measurements

A compressive strength test was conducted using a universal testing machine with a compression capacity of 250 kN. The loading rate was 0.2 mm/min.

Samples for analysis of microstructures with different dosages of GGBS were taken from the failure surfaces of the specimens after the loading test. The morphology of geopolymer specimens were observed by scanning electron microscopy (SEM) of JEOL JSM-6010PLUS, in which energy dispersive spectroscopy (EDS) mapping was conducted to investigate the distribution of elements in the specimens. It was carried out at 15 kV of accelerated voltage.

The X-Ray diffraction (XRD) test was conducted to investigate the phase composition of the specimens. The test was carried out using a Bruker AXS D2 Phaser X-ray diffractometer in 2-theta range of 10-65 deg using a Cu $\text{K}\alpha$ X-ray source. The sample was prepared into powder form.

The thermo gravimetric analysis (TGA) was performed using simultaneous DTA-TG apparatus DTG-60H to study the thermal stability of the geopolymer. The tests were carried out with a heating rate of 10°C/min from room temperature to 1000°C.

3 Results and discussions

3.1 Compressive strength

Fig. 2 shows the relationship between the compressive strength and the GGBS dosage in the mixes at the curing ages of 7, 14, and 28 days. The compressive strength of the geopolymer paste was found to increase with the increase in the amount of GGBS in the mixes. However, the compressive strength of all specimens with different dosages of GGBS remained almost constant between 7 days and 28 days. In this experimental study, the compressive strength is strongly affected by the amount of GGBS in the mixes. Since GGBS contains a high amount of calcium, C-S-H gel was formed and thus contributed to the strength development of geopolymer specimens [10]. Another factor that contributes to the strength development is the concentration of the alkali solution. Budh and Warhade reported that as the molarity increases, compressive strength increases [11]. The solubilisation of Si and Al from the silica-alumina source by alkali hydroxide enhances the development of geopolymeric bonds. When no alkali hydroxide solution is used, the paste

becomes too viscous, cannot solidify, and the specimens acquire practically no strength [12].

3.2 Characterization of microstructure

Fig. 3 shows the micrograph of the geopolymer specimens. Some unreacted fly ash spheres were found in all specimens; however for specimens with 45% and 60% replacement of fly ash, the geopolymeric gels were clearly found to co-exist with C-S-H gels. Calcium and silicon resulting from the dissolution of GGBS react to form a C-S-H gel. The formation of C-S-H gel along with the silico-aluminates structures significantly contribute to high strength. It can be observed that the specimens with a higher dosage of GGBS have denser structures, and as a result, higher strength was observed.

Fig. 2. Effect of GGBS on the compressive strength of geopolymer paste specimens.

Fig. 3. SEM micrographs of geopolimer specimens with (a) 0%, (b) 15%, (c) 30%, (d) 45%, (e) 60% of replacement by GGBS.

Fig. 4. XRD patterns of geopolymer specimens (Q=Quartz; M=Mullite).

Fig. 4 shows the XRD results of the geopolymer paste with different dosages of GGBS. As can be observed in the XRD pattern, the mullite's and quartz's peaks from the original fly ash remained, even after the activation with the alkali solution and the addition of GGBS. The diffraction pattern of the sample with 0% of GGBS shows the amorphous hump at 15-40° 2-theta which confirmed the formation of amorphous geopolymeric gels. When the GGBS was presented in the mixes, the amorphous characteristic of the geopolymer did not change; however the new diffraction peak was found to be generated around 30° 2-theta which was noticed as a formation of calcium silicate hydrate. The increase of GGBS in the mixes resulting in the increase of the peak intensity of C-S-H indicated that there is an increase in the formation of calcium silicate hydrate.

3.3 Thermo-gravimetric analysis

Fig. 5 represents the thermo-gravimetric analysis curves for the geopolymer specimens under different dosages of GGBS. A sharp decrease in mass before 200°C was noticed due to the evaporation of free water [13]. Above 200°C, a slow-rate continuous mass loss was observed. In this stage, the mass loss is attributed to the dehydroxylation of the chemically bound water [13]. The specimen containing 60% GGBS featured the lowest thermal stability. This was considered due to the high formation of C-S-H gel; some of the chemically bound water from C-S-H would be lost followed by the complete decomposition of C-S-H at elevated temperatures [14]. In this study, the formation of C-S-H has a significant impact on the strength development of geopolymer; however, the C-S-H decomposition at high temperatures may partially cause damage to the structure of the specimen.

Fig. 5. Thermal stability of geopolymer paste under different dosage of GGBS.

4 Conclusion

Raw materials play an important role in the properties of geopolymers. In this experimental study, the effect of the addition of GGBS on the compressive strength and microstructure of geopolymer paste was investigated. It was found that the presence of GGBS in the mixes significantly increased the compressive strength of geopolymer paste specimens. The higher compressive strength of the specimens as the amount of GGBS was increased was considered due to the formation of calcium silicate hydrate gel that helps to form denser structures. The highest compressive strength was found at 60% of fly ash replacement by GGBS. The SEM micrograph and XRD result show that the formation of C-S-H gel becomes prominent as GGBS increases. However, too much formation of C-S-H may harm the structure of the specimen at high temperatures due to decomposition. Despite having the highest compressive strength, the thermo-gravimetric analysis revealed that the replacement of fly ash by 60% GGBS has the lowest thermal stability, and therefore in this study 45% GGBS is considered as the optimum replacement of fly ash.

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