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Effects of relative humidity on the properties of fly ash-based geopolymers

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HIGHLIGHTS

- The effects of relative humidity (RH) on mechanical and microstructural properties of a FA-based GP have been studied.
- The highest mechanical strength was observed at RH of 70%.
- The microstructural analyses were performed using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) tests.

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ABSTRACT

The investigation into geopolymers (GPs) is developing rapidly due to the properties they offer. In spite of this, few researchers have reported on the relative humidity (RH) during the curing process and its impacts on alkali-activated fly ash-based geopolymers. This study investigates the mechanical and microstructural properties of alkali-activated fly ash (FA) based geopolymers cured at various RH ratios at 75 °C. Compressive and flexural strength tests were conducted to determine the mechanical properties, and X-ray diffraction (XRD), as well as scanning electron microscopy (SEM) tests were carried out to study the microstructural properties of the mixtures. The study revealed that both compressive and flexural strengths improved when RH was set at 70%. The microstructural analysis indicated a mixture of unreacted fly ash particles, some crystals, and a reacted gel phases as the geopolymerization products.

1. Introduction

Ordinary Portland Cement (OPC) is usually used as the binder to produce concrete, the most widely utilized construction material around the world. The cement industry is one of the largest sources of carbon dioxide (CO_2) emission, the release of CO_2 into the atmosphere by cement plants are approximately 5–7% of total global carbon dioxide [1,2]. Therefore, the global cement industry is facing an urgent need for alternative technologies which can reduce the carbon footprint of cement production. This has encouraged research into environmentally friendly alternatives such as geopolymers.

Geopolymers (GPs) due to the properties, such as high-temperature applications, fire and heat resistant coatings [3–5] are growing as an important alternative for Portland cement; to reduce the carbon dioxide (CO_2) emissions associated with the clinker process. The CO_2 footprint of geopolymer concrete is about 9% lower as compared to equivalent concrete with 100% OPC binder [6].

GPs are usually synthesized of an aluminum silicate as source materials with an alkaline chemical activator, such as potassium hydroxide (KOH), sodium hydroxide (NaOH), potassium silicate or sodium silicate [7–9]; of these activators, soluble alkali silicates are considered as the most effective activators for majority of the GPs [10]. The concentration level and type of the activator play an important role in the mechanical and microstructural properties of resultant geopolymers [3]. Increasing the activator concentration beyond an ideal concentration, may not only prevent strength development of GPs, but also lead to detrimental effects such as efflorescence and brittleness [11]. The desired Si/Al ratio is reported around 2 [12–14], and the SiO_2/Na_2O content is between 1 and 1.5 [15–17]. The optimum modulus for NaOH has been reported around 7–10 M especially when low calcium alumino-silicates such as class F fly ash are used [3,18,19]. Interestingly, KOH due to its higher alkalinity in comparison with NaOH seems to possess a higher extent of dissolution; however, in reality, NaOH is more capable of making silicate and aluminate monomers [20–23].

The geopolymerization process comprises of the following steps: (i) dissolution of the aluminosilicate solids in the highly alkaline aqueous solution, (ii) formation of oligomeric precursors

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consisting of Si–O–Si/Si–O–Al, (iii) polycondensation of the oligomers to build up a three-dimensional aluminosilicate network and finally (iv) hardening by cross-linking of the whole system into a polymeric structure thorough bonding of the undissolved solid particles into an established network [23–28].

The empirical formula of the poly-(sialates) is as follows:

$$Mn\{-(SiO_2)z - AlO_2\}n \cdot wH_2O \quad (1)$$

where M is a cation such as K^+, Na^+ or Ca^{2+}; n and z, are numbers of repeating units. Other cations such as Li^+, Ba^{2+}, NH^{4+} and H_30^+ may also be present in the built network [21,29–32].

Some literature has reported relative humidity as one of the most important factors influencing compressive strength [4,33]. However, few researchers have reported on the relative humidity during the curing process and its effects on alkali-activated fly ash- based GP properties. This research aimed to study the effects of relative humidity (RH) in a wide range for an alkali-activated fly ash based geopolymer. The effect of RH in different values on mechanical and microstructural properties of a FA-based GP has been studied. The microstructure of the geopolymeric phase was investigated using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

2. Experimental work

2.1. Materials

In this study, Class F fly ash (FA) conforming to ASTM C 618 [33] was utilized. The alkaline activators were sodium silicate (Na_2SiO_3) (composed of 28.18% SiO_2, 8.62%, Na_2O, and H_2O 63.20% by mass) and SiO_2/Na_2O molarity of 3.27, as well as sodium hydroxide (NaOH) pellets (≥96%). It has been reported that when the water glass molar ratio is higher than 2 the dissolution of sodium silicate becomes very complicated and its rate decreases [4,10,17]. Therefore, in this study, NaOH was added to a sodium silicate solution to produce a sodium silicate solution with a lower modulus. To this end, the proper amount of sodium hydroxide pellet was mixed 24 h before casting with distilled water to obtain the desired NaOH molar ratio of 10 M.

2.2. Sample preparation

The dry FA was mixed with the slurry containing Na-silicate and NaOH (10 M) for 5 min. The fresh samples were casted in 40 × 40 × 160 mm plastics moulds, and then vibrated for 3 min using a vibrator machine. All samples were cured at 75 °C with various relative humidities of 30%, 50%, 70%, and 90% for 24 h. Afterward, the hardened samples were demoulded, and sealed in plastic bags for another 24 h at room temperature. The mix proportion is listed in Table 1.

3. Testing methods

3.1. Microstructural analysis

Most of the microstructural testing methods require a sample pre-conditioning drying, which may drastically change the morphological and mechanical test results of geopolymers [34]. This has caused the application of acetone drying approach in this study. For this purpose, samples were exposed to liquid acetone under applied vacuum to remove the free water and consequently to stop the reaction at particular ages.

3.1.1. X-Ray diffraction (XRD) analysis

The samples were X-rayed with a Diffractometer System XRD D8. Da Vinci operated at 40 kV and 40 mA using Cu Kα radiation in the range of 5° to 70°2θ. The data for quantitative analysis was collected using a step size of 0.02°, and scan speed of 3°/min. Rietveld refinement was performed using Topas 5. The difference between the sum of the analyzed weight fractions for all crystalline phases and 100% was calculated to obtain the amorphous level.

3.1.2. Scanning Electron Microscopy (SEM)

The raw materials and the microstructural development of geopolymer mixtures were microscopically performed by using a COXEMEM-30PLUS Scanning Electron Microscope (SEM) under high vacuum pressure at 20 kV accelerating voltage. Energy dispersive X-ray spectroscopy (EDX) was also utilized to determine the phase analysis of the FA. All GP investigations have been done on fractured surfaces.

3.2. Mechanical strength

The compressive and flexural strength of GPs samples were measured according to ASTM C109-93 [35] and ASTM C348-14 [36], respectively. A MTS servo hydraulic testing machine at the loading rate of 500 N/s was used to perform the compressive strength tests. In order to measure the flexural strength, the specimens were casted in the molds of 40 × 40 × 160 mm. Following the flexural tests, the broken pieces were subjected to the compressive strength tests. Three samples tested for flexural strengths and each sample was broken into two pieces. The obtained six samples were then tested to measure compressive strength.

4. Results and discussion

4.1. Characterization results

The chemical composition and physical properties of FA are shown in Table 2, derived via XRD and EDX measurements. According to the Table 2, FA contains low CaO and loss of ignition (L.O.I) content, as well as appropriate Si/Al ratio and amorphous phase. Fig. 1 shows the morphology of the FA. As shown, FA is primarily composed of spherical shaped particles. The XRD patterns of FA, seen in Fig. 2, shows a broad "amorphous hump" between 20° and 30°, which is a characteristic for fly ash. Mullite, Quartz, Hematite and Calcite were also determined as the crystalline structures of FA, derived using XRD analysis.

4.2. Mechanical strength

The compressive strength of the geopolymer mixtures at different RH ratios are reported in Fig. 3. As the results show, raising the RH to 70% led to a relatively increase in the compressive strength. In fact, the compressive strength increased from 29 MPa in FA samples cured at RH of 30% to 33 MPa in samples with RH of 70%. This

Table 1
Mix proportion of the geopolymers.

Sample ID	FA (wt.%)	Na-silicate (wt.%)	10 M NaOH (wt.%)	Si/Al ratio	SiO_2/Na_2O ratio	Water/solid ratio
100FA	69	21.28	9.72	2.10	1.30	0.26

Water and solid are calculated considering the total content of water and solid including 10 M NaOH + Na-silicate solution.