



Mechanical Performance of Fly-Ash-Based Green Geopolymer Composites Subjected to Elevated Temperatures†

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This paper discusses the effect of Na₂O content, SiO₂/Na₂O mole ratio and elevated temperature on the mechanical performance of fly-ash-based inorganic green geopolymer composites. Fly-ash-based geopolymers, which were manufactured with varying alkali contents (4-8 % of fly ash weight) and SiO₂/Na₂O mole ratios (0.6-1.4), were subjected to elevated temperatures up to 900 °C. The geopolymer composites and their performance were evaluated on the basis of weight loss and strength loss after temperature exposure. In addition, mineralogical changes due to the elevated temperature exposure were studied using X-ray diffraction. Investigation of microstructures as well as microprobe analysis was performed using scanning electron microscopy, Fourier-transform infrared spectroscopy and mercury intrusion porosimetry. The results showed that the fly-ash-based geopolymer responded significantly to high temperature conditions.

Keywords: Elevated temperature, Fly-ash-based geopolymer, Mechanical performances.

INTRODUCTION

Geopolymers are an alternative to portland cement that can be used to produce concrete without the considerable carbon dioxide emissions. Among the aluminosilicate materials, metakaolin and fly ash are the most favorable raw materials for geopolymer production. However, metakaolin-based geopolymer has limited availability and high cost. Therefore, most of the recent research on geopolymer uses fly ash as the binder¹⁻⁴.

Dissolution of the solid aluminosilicate source by alkaline hydrolysis produces aluminate and silicate species. The dissolution process is rapid at a high pH and this quickly creates a supersaturated aluminosilicate solution. In concentrated solutions, this process results in the formation of a gel, as the oligomers in the aqueous phase form large networks by condensation. After gelation, the system continues to rearrange and reorganize, as the connectivity of the gel network increases, resulting in the three-dimensional aluminosilicate network commonly attributed to geopolymers. These processes of structural reorganization determine the microstructure and pore distribution of the material, which are critical in determining many physical properties⁵⁻⁸.

The dissolution process starts with an attack to the fly-ash particles by the alkaline solution⁹⁻¹⁵. As a result, the reaction

product is generated both inside and outside the individual cells until the ash particle is completely or almost completely consumed. At the same time, reaction products are created as the alkaline solution penetrates the larger sphere and fills up the interior space with reaction products, forming a dense matrix. Due to the massive precipitation of reaction products, some smaller particles are covered with the products, forming a crust that prevents contact with an alkaline solution, resulting in an unreacted fly ash particle.

The existing studies investigated the superior heat resistance of geopolymers, which are reactant products of sodium silicate and potassium silicate with metakaolin that demonstrate thermal stability up to 1200-1400 °C. These materials contain "ceramic-like properties"^{10,11}. The thermal behaviour of fly-ash-based geopolymers, however, has not been sufficiently investigated, although the favorable characteristics-such as the increase in strength and fire resistance-are expected when geopolymers are exposed to elevated temperature. The present research focuses on determining the influence of high temperatures (ranging from 80-900 °C) on the properties of geopolymer materials based on low-calcium fly ash from Korea. This study also investigates the effect of elevated temperature exposure on the geopolymer pastes and aggregate composites (geopolymer concrete).

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EXPERIMENTAL

Fly ash is the alumino-silicate material used in the synthesis of geopolymeric binder in this research. The chemical composition of the sodium silicate solution is shown in Table-1. The low-calcium fly ash used in this experiment was sourced from the Namdong power plant in Korea. Its mineral and chemical compositions are shown in Table-2. The specific gravity was 2.42 g cm^{-3} and Blaine specific surface was $4,013 \text{ cm}^2 \text{ g}^{-1}$. The fly ash's particle size distribution is illustrated in Fig. 1.

TABLE-1
CHEMICAL AND PHYSICAL PROPERTIES
OF LIQUID SODIUM SILICATE

Na ₂ O (%)	SiO ₂ (%)	SiO ₂ /Na ₂ O (wt. ratio)	Density (20 °C, g cm ⁻³)
9.18	29.11	3.17	1.40

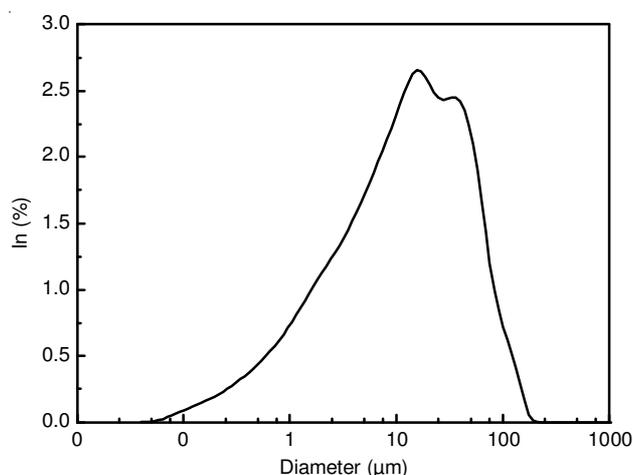


Fig. 1. Particle size distribution of fly ash

Geopolymer paste: In this study, two series of geopolymer paste samples were made, differing in their composition. In series 1, samples were prepared using a sodium hydroxide/sodium silicate solution, providing 6 % sodium (weight % by fly ash) in mixtures and SiO₂/Na₂O mole ratio of 0.6-1.4 (mix No. 1-6). In series 2, the prepared samples provided a 1.0 SiO₂/Na₂O mole ratio and 4-8 % Na₂O (mix No. 6-7) in mixtures. The liquid/solid ratio of all samples is 0.55. The mix proportions of the geopolymer paste are shown in Table-3. The mould size used was 50 mm × 50 mm × 50 mm. All samples were cured undisturbed for 24 h at room temperature before being subjected to high temperature curing (80 °C, relative humidity of 95 %) for another 24 h in a chamber. At the end of the

curing regime, the samples were removed from their moulds and allowed to cool before mechanical tests were performed.

Post-thermal test: An electrically heated furnace designed for a maximum temperature of 1200 °C was used. Samples were subjected to temperatures of up to 900 °C at an incremental rate of about 5 °C/min from room temperature inside the furnace. All the samples were mechanically characterized to evaluate the residual strength after abrupt but not prolonged exposure to high temperatures, in an attempt to simulate the conditions prevailing in the event of accidental fire. Test samples were subjected to strong thermal shock by placing them directly inside a furnace at different temperature (300, 600 and 900 °C). They were subsequently kept in this high temperature for 2 h and then exposed to ambient temperature.

In addition, the raw materials as well as the samples tested under post-thermal conditions were analyzed using thermogravimetric/differential thermal analysis, X-ray diffraction, Fourier-transform infrared spectroscopy and mercury intrusion porosimetry.

RESULTS AND DISCUSSION

Compressive strength of geopolymer pastes: The compressive strength of each sample after exposure to different temperatures was compared to an unheated sample's strength. The strength changes are shown in Tables 4 and 5. The results indicate that the samples prepared at SiO₂/Na₂O mole ratio of 0.6, 0.8, 1.0, 1.2 and 1.4 had a tendency to increase in strength. As the temperature exposure increased from 300 to 900 °C, the samples' strength values increased as well. In considering the effects of Na₂O on the samples, the researchers noted that the higher the Na₂O content, the greater the compressive strength increases. Also, the effect of high temperature exposure (300-900 °C) showed a trend similar to that of the effect of SiO₂/Na₂O mole ratio.

Visual change of geopolymer pastes: The samples displayed significant colour change during exposure to the higher temperatures. After exposure to 300 °C, the samples had no distinctive colour changes, remaining the dark grey of the original sample colouration. After exposure to 600 °C, the colour changed to lighter grey. The colour then impressively changed at 900 °C to red, accompanied by a ceramic-like surface texture.

Microstructures of geopolymer pastes: The XRD and FTIR techniques were used to acquire a better understanding of the possible transformations in the untreated samples as well as in the samples subjected to post-thermal tests as a result of exposure to high temperatures. The present analysis focussed on the description and interpretation of the changes observed

TABLE-2
CHEMICAL COMPOSITION OF THE FLY ASH USED

Chemical component	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	SO ₃	LOI ^a	Total
Weight (%)	4.42	56.00	24.00	5.39	1.44	1.38	1.00	0.19	4.80	98.62

^aLoss of ignition.

TABLE-3
MIXING PROPORTIONS OF GEOPOLYMER PASTES

Mix number	1	2	3	4	5	6	7	8
Na ₂ O content (%)	6	6	6	6	6	4	6	8
SiO ₂ /Na ₂ O mole ratio	0.6	0.8	1.0	1.2	1.4	1.0	1.0	1.0

TABLE-4
EFFECTS OF $\text{SiO}_2/\text{Na}_2\text{O}$ MOLE RATIO AND POST-THERMAL TEMPERATURE ON COMPRESSIVE STRENGTH

Post-thermal condition	Compressive strength (MPa)				
	$\text{SiO}_2/\text{Na}_2\text{O}$ mole ratio				
	0.6	0.8	1.0	1.2	1.4
–	–	5.5	13.2	17.0	19.7
300 °C	6.5	9.8	20.3	28.3	35.1
600 °C	8.0	14.7	38.0	40.7	48.2
900 °C	18.9	33.1	49.1	52.8	66.6

Na_2O content of alkali activator = 6 %; liquid-solid ratio = 0.55.

TABLE-5
EFFECTS OF Na_2O CONTENT AND POST-THERMAL TEMPERATURE ON COMPRESSIVE STRENGTH

Post-thermal condition	Compressive strength (MPa)		
	Na_2O content (% by wt. of fly ash)		
	4 %	6 %	8 %
–	–	13.1	32.2
300 °C	3.9	24.3	47.8
600 °C	8.0	30.1	54.7
900 °C	17.2	49.2	75.2

$\text{SiO}_2/\text{Na}_2\text{O}$ mole ratio = 1.0; liquid-solid ratio = 0.55.

in the mineralogy and microstructure of materials made with alkali-activated fly ash.

Fig. 2 shows the diffractograms for the original fly ash and the geopolymer paste matrix after the high temperature tests. The majority of crystalline phases present in the initial ash (quartz and mullite) were barely affected by the activation process or exposure to high temperature. The halo characteristic of the vitreous phase in the initial ash (located in the 20-30° 2 θ range) shifted to 2 θ values of 25-30° as a result of alkaline activation. This shift is indicative of the formation of an alkaline aluminosilicate gel as the main reaction product, which may be a determining factor in temperature-induced strength change. Slight changes in intensity are observed in this halo with rising temperatures but are difficult to quantify. Zeolites formed as secondary reaction products. Hydroxysodalite ($\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{OH}$) formed in the initial geopolymer paste matrix as a minority crystalline phase during activation. In a sufficiently alkaline medium, hydroxysodalite is so thermodynamically stable that it crystallizes fairly quickly and easily.

In this study, the FTIR spectra of samples (Fig. 3) were acquired using an Avatar 36 FTIR Spectrometer in absorbance mode within the frequency range of 4000-400 cm^{-1} . The main band due to Si-O and Al-O vibrations (Si-O-Si and Al-O-Si), which is at 1062 cm^{-1} in the original fly ash, moves towards lower frequencies (1000 cm^{-1}) in the geopolymers. The shift is interpreted as the result of Al penetration into the original structure of the Si-O-Si skeleton, similar to those bands which were detected in the zeolites. Following the hydrolyzation of the raw materials, a structural reorganization occurs in which aluminum ions are incorporated into the SiO_4 tetrahedra, forming the Si-O-Al network. The aluminum ions act as a perturbation of silicate stretching vibrations, much as metal cations in other silicates such as sodium.

This region (about 1,062 cm^{-1}) corresponds to the strongest peak in the unreacted raw material spectra and is therefore thought to be the result of unreacted raw material present in geopolymers. In samples exposed to the high post-thermal

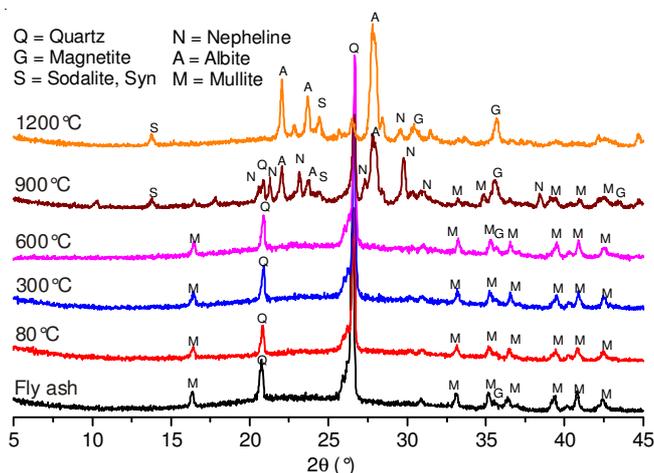


Fig. 2 Diffractogram for the post-thermal treatment samples

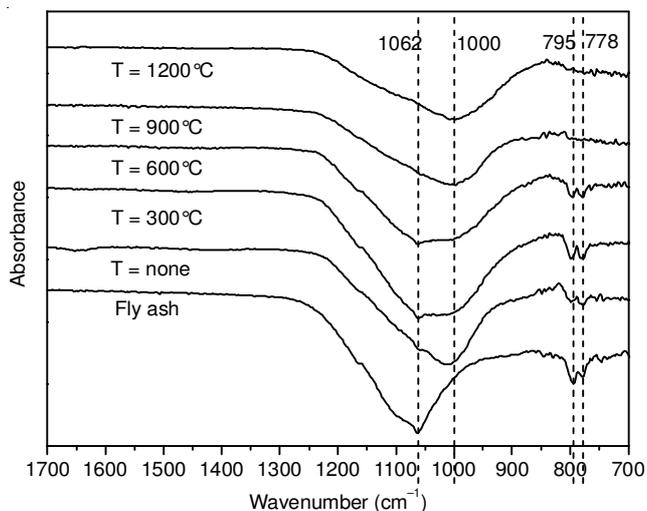


Fig. 3. FTIR spectra for the post-thermal treatment samples

temperatures (900 and 1200 °C), the band disappears. When geopolymer pastes were exposed to high post-thermal temperatures (900 and 1200 °C) and later cooled, the band at 800 cm^{-1} , due to AlO_4 vibrations, disappears.

The Netzsch STA 409 PC Luxx differential scanning calorimeter was used for combined TG/DTA. The samples were heated from 10-1000 °C at a rate of 10 °C/min in air. The analysis results obtained for the working samples are given in Fig. 4. The DTA curve for ordinary cement paste had two peaks, at around 130 and 450 °C. The first was associated with the loss of adsorbed water and calcium-silicate-hydrates gel decomposition, whereas the second was attributed to the decomposition of $\text{Ca}(\text{OH})_2$. As for the TG curve, these

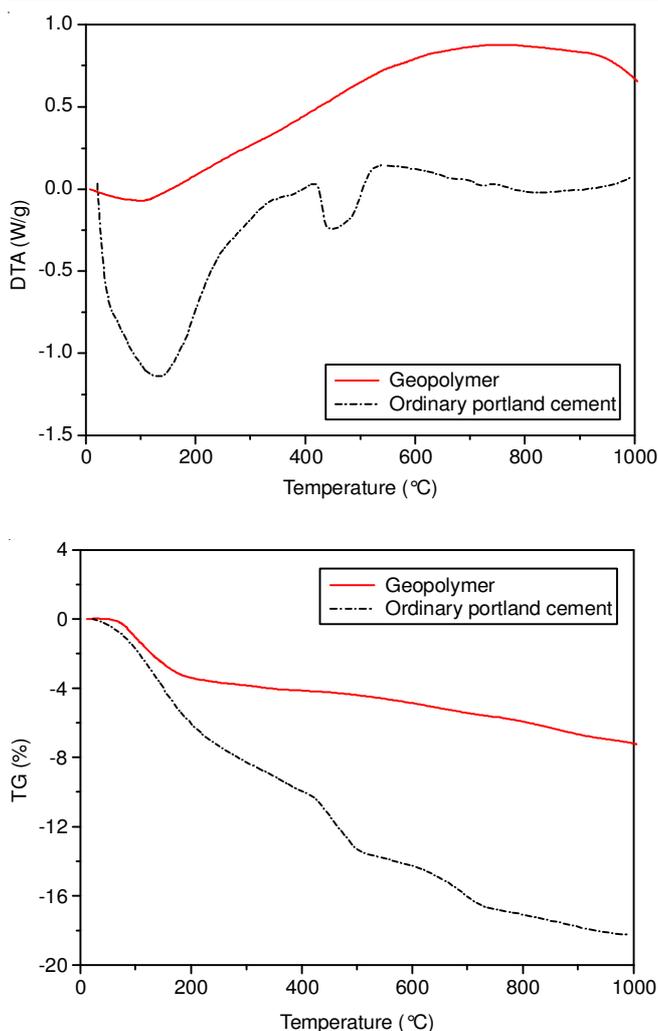


Fig. 4. DTA and TG curves for the samples

transformations involved weight loss. While the DTA curve for the alkali-activated fly ash pastes also had one wide peak at around 100 °C, it was less intense than the portland cement signal. As with the portland cement, this peak was associated with the loss of adsorbed and combined water in gel.

The comparison of the TG curves for the two samples showed that the weight losses were visibly lower in the activated fly ash than in the portland cement paste (Fig. 4). The implication is that the fly ash sample does not readily decompose when exposed to high temperatures, so it would appear to be more structurally stable than portland cement at those temperatures.

The pore size distributions and cumulative volumes of intrusion resulting from the MIP testing of the geopolymer paste mixtures Nos. 6, 7 and 8 from Table-3. It was possible to verify that specimens with more Na₂O contain smaller average pore diameters and porosities. (For example, when Na₂O is 4, 6 and 8 % at 80 °C, porosities are 0.33, 0.30 and 0.26 mL mg⁻¹, respectively). Also, the higher firing temperature is, the larger the average pore diameters, but the smaller the porosities. This means that as the firing temperature increases, the compressive strengths of the geopolymer paste also increase and thus geopolymer pastes can be considered to have effec-

tively changed to denser microstructures. Under firing temperature up to 900 °C, pore diameters less than 1000 nm almost disappeared and new pores of which diameters ranged between 2000 and 4000 nm were obtained.

Firing the geopolymer above 300 °C results in changes in its microstructure (Fig. 8). Unlike ordinary portland/pozzolanic cements, geopolymers do not form calcium-silicate-hydrates for matrix formation and strength, but utilize the polycondensation of silica and alumina precursors and a high alkali content to attain structural strength. The composition of the geopolymer is similar to natural zeolitic materials, but the microstructure is amorphous or semi-crystalline instead of crystalline. Scanning electron microscopy (SEM) was used to investigate the surface of fly ash before and after reacting with NaOH solution, there are the significant changes of microstructure after firing at 300-900 °C with pores up. However in case of firing at 1200 °C, the development of these pores is possibly connected to decomposition of the material on heating.

Conclusion

The purpose of this study was to explore the effect of post-thermal treatment on the strength and microstructure of geopolymer composites. A series of geopolymer pastes were fabricated and tested. The residual compressive strength was measured under various temperature conditions. The microstructures of geopolymer composites were also analyzed to investigate the structural change. Based on the results of the present investigation, the following conclusions were drawn. The fly-ash-based geopolymer pastes tended to increase in strength with higher values of SiO₂/Na₂O mole ratio and temperature exposure up to 300-900 °C. When exposed to 300 °C, the samples showed no colour changes and remained dark grey. After exposure to 600 °C, however, the colour changed to lighter grey. At 900 °C, the samples' colour then impressively changed to red, accompanied by a ceramic-like surface texture. After exposure to high temperatures, hydroxysodalite formed in the initial geopolymer paste matrix during activation. In a sufficiently alkaline medium, hydroxysodalite is so thermodynamically stable that it crystallized quickly. In FTIR, following hydrolyzation, a structural reorganization occurs in the aluminum ions. The strongest peak in the unreacted raw material spectra is therefore thought to result from unreacted raw material present in the geopolymers. With exposing temperature up to 900 °C, the peak was located 1062-1000 cm⁻¹. The micropore of which diameters less than 1000 nm almost disappear and new pores of which diameters ranging between 2000 and 4000 nm form at a high temperature. At high temperatures, the pores showed significant changes of microstructure. However when fired at 1200 °C, the pores showed decomposition on heating.

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