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# The mechanical properties of fly ash-based geopolymer concrete with alkaline activators

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## HIGHLIGHTS

- We have developed fly ash-based geopolymer concrete. (FA-Geopol Con.).
- FA-Geopol composition is identified at intermediate $SiO_2/Na_2O$ and $Al_2O_3/Na_2O$ ratio.
- We have analyzed the hardening mechanism through SEM, EDS, XRD, FT-IR, and by porosity assessments.
- We have proposed the relationship between the compressive strength and the tensile strength of FA-Geopol Con.

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## ABSTRACT

As part of the research effort to develop cementless alkali-activated concrete using 100% fly ash as a binder, this paper aims to examine the effects of chemical changes of alkaline activators on the compressive strength of mortar and to analyze the microstructure of the mortar through SEM, EDS, XRD, FT-IR and by porosity assessments. The results showed that chemical changes of the alkaline activators had a significant effect on the early strength with higher molarity. In addition, the analysis of the structure through SEM and EDS indicated that the components having a considerable influence on the structure of the mortar were the Al and Si components. The XRD results revealed that there were no practical differences in the intensity according to the differences in the chemical components of the alkaline activators. On the other hand, the FT-IR analysis made it possible to identify changes in the chemical combination of Si—O—Si and Si—O—Al compared to fly ash and hardened mortar. The analysis of the porosity enabled us to verify indirectly the remarkable mechanical performance which was obtained by the activation of polymerization according to the chemical components of the alkaline activators. A relationship between the compressive strength and the splitting tensile strength of fly ash-based geopolymer concrete is proposed.



## 1. Introduction

Recently, great concern for many researchers has been the development of cementless concrete to reduce drastically the exhaustion of $CO_2$. The theoretical basis of geopolymerization as a major reaction mechanism of cementless concrete was established for the first time by the French researcher Davidovits in 1978, who used kaolinite ($Al_2Si_2O_5(OH)$) and alkaline activators. Thereafter, this topic was studied by numerous researchers [1–4], but active research was impeded due to problems related to production and economic efficiency. However, the recent rise of environmental degradation as a social issue has reactivated research on alkali-activated concrete using industrial by-products such as fly ash and blast furnace slag in Australia, Japan, USA, and Europe, of which several practical applications can be found today. For example, Rangan et al. at Curtin University in Australia proposed a mix design enabling one to secure the optimal compressive strength of alkali-activated concrete using fly ash [5–10]. Also, a fair amount of research has been conducted on alkali-activated concrete using fly ash and blast furnace slag, but this work remains in its early stages [11,12].

On the other hand, the quantities of coal ash, including fly ash produced annually by the thermoelectric power plants in Korea, reached approximately 8.4 billion tons in 2009, which amounted to almost 1.5 times the production of 2005. In addition, this quantity is expected to increase continuously, reaching approximately 9.4 billion tons in 2015 [13]. Even if 42% of the current production of coal ash is actually recycled as a raw material to replace clay in the production of cement or as a mineral admixture for the construction of concrete, the remaining ash is disposed of in marine and in-land landfills, incurring not only an economic burden to

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secure landfill areas but also environmental degradation due to the leakage of water in landfills and the contamination caused by the leakage of the micro-particles constituting coal ash.

Palomo et al. [2] found that different fly ash samples activated with NaOH 8–12 M cured at 85 °C for 24 h produced a material with a compressive strength between 35 and 40 MPa, though this reached nearly 90 MPa if waterglass was added to the NaOH ($SiO_2/Na_2O$ = 1.23). Moreover, in such cases not only is the $SiO_2/Na_2O$ ratio a very important parameter but the water-to-binder ratio must be taken into account [14–16]. Songpiriyakij et al. [17] indicated that the optimum $SiO_2/Al_2O_3$ ratio to obtain the highest compressive strength was 15.9 in fly ash-based geopolymer. Swanepoel and Strydom [18] conducted a study on geopolymers produced by mixing fly ash, kaolinite, sodium silica solution, NaOH and water. Both the curing time and the curing temperature affected the compressive strength, and the optimum strength occurred when specimens were cured at 60 °C for a period of 48 h.

Concrete is a complex and non-uniform materials of which the stress-related mechanical characteristics are influenced not only by the behavior of each constituent material but also by the interactions among these materials. Moreover, most current studies on fly ash-based cementless concrete focused essentially on an investigation of its reaction mechanism using paste or mortar without aggregate materials. The development of compressive strength in alkali-activated mortar was compared with the design equations specified in ACI 209 and EC 2, which are based on the extensive test results of OPC concrete by Yang et al. [11].

Therefore, as part of the research on the development of cementless concrete using fly ash as a binder, this study seeks to investigate changes in strength according to the concentration of an alkaline activator (series 1) and according to the mix ratio of sodium hydroxide (NaOH) and sodium silicate (series 2). Microstructural analyses through SEM, EDS, XRD, FT-IR, and by porosity assessments were conducted to clarify the strength development mechanism of hardened specimens and to identify the relationships among the molarity levels of the alkaline activators, mix ratios, and different ages of concrete so as to verify the applicability of this innovative construction material using fly ash. This study also examines the mechanical properties of fly ash-based geopolymer concrete using coarse aggregate materials by performing compressive strength tests and splitting tensile strength tests and analyzing their uncovered relationships. It is shown here that fly ash-based geopolymer concrete can be used where normal concrete using Portland cement is commonly used.

## 2. Reaction mechanism

Generally, concrete develops strength through the formation of hydrates such as CSH (calcium silicate hydrate; $3CaO\cdot 2SiO_2\cdot 3H_2O$), which is produced by the hydration reaction of water and the ordinary Portland cement typically used as a binder. Moreover, the hardening of fly ash-based geopolymer achieved by dissolving the Al and Si components of fly ash by alkaline activators is known as geopolymerization [19]. This geopolymerization process, indicating a chemical reaction between Al-Si oxides which form the three-dimensional polymer chain Si—O—Al—O, was proposed by Davidovits in 1978. These structures occur in three types: poly(sialate) (—Si—O—Al—O—), poly(sialate-siloxo) (Si—O—Al—O—Si—O), and poly(sialate-disiloxo) (Si—O—Al—O—Si—O—Si—O). The hardening of the geopolymer is believed to be due to the polycondensation of hydrolyzed aluminate and silicate species. The typical geopolymer composition is generally expressed as $nM_2O\cdot Al_2O_3\cdot xSiO_2\cdot yH_2O$, where M is an alkali metal. The most widely adopted alkaline activators are MOH-type caustic alkalis and $R_2O\cdot(n)SiO_2$-type silicates, which are used individually or in combination. Here, M denotes the alkaline activator, which is generally sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium carbonate ($NaCO_3$) or sodium sulfate ($Na_2SO_4$) containing alkaline metal ions such as Na, K and Ca, serving as an accelerator of the reaction speed by activating Al and Si through a reaction with the binder. The second chemical reaction shows the dissolution of water. The acceleration of the dissolution of water by curing during geopolymerization is known to provide discontinuous gel nanopores to the paste, resulting in a further improvement of the performance of the paste. Fig. 1 depicts the hardening mechanism by geopolymerization [20].

Alkali-activated fly ash-based concrete is sensitive to the $SiO_2/Al_2O_3$ ratio and to the $Al_2O_3/Na_2O$ ratio. However, the geopolymerization of the main hardening mechanism of alkali-activated fly ash-based concrete remains unclear.

## 3. Test setup

### *3.1. Test plan*

Fly ash was activated using three NaOH solution samples for series 1 and with a mixture of NaOH 9M and sodium silicate solution for series 2. Table 1 shows the details of the experimental plan for the alkaline activator and the curing conditions. Series 1 used doses of 6, 9 and 12 M of NaOH to examine the reactivity. The reactivity was examined by mixing sodium hydroxide (NaOH) at 9 M with sodium silicate using five doses at different mass ratios (NaOH 9 M:sodium silicate = 0:100, 25:75, 50:50, 75:25, and 100:0), as shown for series 2 in Table 1. Test specimens were prepared to determine the compressive strengths at curing ages of 1, 3, 7, 14, 28, 56, and 91 days in an oven and in air, as explained in Section 3.3.

### *3.2. Materials*

In this study, the fly ash (fineness = 3.550 $cm^2/g$, density = 2.18 $g/cm^3$) originated from the Boryeong power plant in Korea. It exhibits chemical properties corresponding to a class-F material as specified in ASTM C 618, with a mean particle size of 15 μm (90% smaller than 57 μm) and with large quantities of reactive oxide with 81.1% of silicon dioxide ($SiO_2$) and aluminum oxide ($Al_2O_3$), less than 6% of calcium oxide (CaO), and maximum loss on ignition (LOI) of less than 5%, as shown in Table 2. The Si and Al components contribute to the development of the strength of concrete through Al—Si geopolymerization which occurs due to the use of alkaline activators and high-temperature curing.

In this study, sodium hydroxide (NaOH) with purity higher than 98% is used as the reagent alkaline activator, enabling the activation of the fly ash. Previous studies reported that the use of a mix of an alkaline activator with sodium silicate, 9–10% of $Na_2O$ and 30% of $SiO_2$ with a solid content of about 40% and a density of 1.39 $g/cm^3$ can activate the geopolymerization process more than the use of a single alkaline activator [18,21–23].

### *3.3. Test method*

The adopted test variables and mix ratios are shown in Tables 3 and 4, showing the chemical composition with respect to the mix proportion.

Series 1 show the specimens used for the analysis of the effects on the compressive strength when varying $SiO_2/Na_2O$ and $Al_2O_3/Na_2O$ under identical $SiO_2/Al_2O_3$ ratios with 6 M, 9 M and 12 M of sodium hydroxide. Series 2 represents the specimens used for the analysis of the effects of the alkaline activator on the compressive strength when varying the mix ratio of NaOH and sodium silicate.

The specimens were constructed using a Hobart mixer by the dry mixing of fly ash and fine aggregates for two minutes followed by three minutes of admixing of the alkaline activator and water. The mixed mortar was then placed in molds with dimensions of 50 × 50 × 50 mm. The specimens were then sealed with vinyl to prevent the evaporation of water during the high-temperature curing process. They were subsequently cured in an oven for 24 h at 60 °C, followed by air-dry curing for 24 h at an ambient temperature (23 ± 2 °C, RH 50%) prior to stripping.

The fresh properties of geopolymer mortar were investigated via a mini-cone slump test. The mini-cone slump test used conformed to the EFNARC specification [24].

The compressive strength was measured in compliance with ASTM C 109 [25] using a UTM with a capacity of 300 kN on the 50 × 50 × 50 mm prismatic specimens. The compression tests were conducted on five prismatic specimens per age. The compressive strength at each age is defined as the mean value of the compressive strengths measured at the corresponding age of which the two values with the greatest degree of deviation are discarded.

XRD was analyzed using a RINT D/max2500 device. The measurement conditions were set as follows: Cuka (nickel filter): 30 kC, 20 mA, scanning speed: 2°/min., 2$\theta$:5 to 70°. SEM/EDS used FE-SEM (S-4800-EDS) under an acceleration