

# Effect of the CaO Content on Microstructure and Mechanical Strength of Fly Ash-Based Geopolymer

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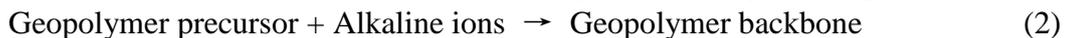
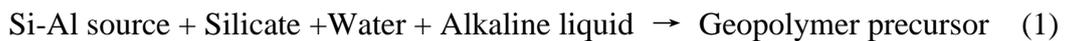
## Abstract

A fly-ash-based geopolymer exhibits many excellent properties, such as high compressive strength, good acid resistance and low shrinkage. Therefore, this material has emerged as a promising new cement alternative in the field of building and construction materials. In this study, two types of fly ash, one containing CaO at more than 10 wt% (denoted as C-F/A) and one containing CaO at less than 10 wt% (denoted as F-F/A), were used to produce a geopolymer with an activating alkaline NaOH solution. In addition, the strength development mechanism of each type of fly ash was analyzed by examining the compressive strength which developed, the crystal phases which formed, and the microstructures. The concentration of the NaOH solution and the curing temperature for fabricating the geopolymers were 0~16 M and 70/24h, respectively. The strength development of the F-F/A-based geopolymer was due to the generation of a zeolite phase, evidence of the geopolymerization of coal ash. The compressive strength of the C-F/A-based geopolymer had higher values than those of the F-F/A-based geopolymer at all concentrations of NaOH. In the C-F/A-based geopolymer, the strength is considered to have developed owing to a pozzolanic reaction by which a silica-rich precursor in the presence of water was converted to a calcium silicate hydrate (denoted as C-S-H) with good cementing properties, in addition to a geopolymer reaction.

**Keywords:** Geopolymer, Fly ash, Zeolite, Pozzolan

## 1 Introduction

The development of ecofriendly materials which are fabricated by recycling processes using waste materials is currently very important because the amount of industrial waste is increasing rapidly. The considerable amount of waste and CO<sub>2</sub> released by the building industry has a significant impact on the environment [1]. Cement is one of the most common materials in this industry. The production of cement typically accounts for at least 5-7% of all CO<sub>2</sub> emissions [2-5]. Recently, there have been a very important development of a new type of high-performance inorganic cementitious material, i.e., geopolymer, around the world. Geopolymeric cement, a type of three-dimensional aluminosilicate gel binder, was introduced in the inorganic cementitious world by Davidovits in the late 1970s [6]. Most waste materials, such as fly ash, blast furnace slag and mine tailings, contain sufficient amounts of reactive alumina and silica that can be used as source materials for in situ geopolymerization reactions. In previous work, many source materials containing Al and Si elements, such as building residue, fly ash, furnace slag, and certain pure Al-Si minerals and clays (kaolinite and metakaolinite) were studied for application to geopolymers [7-8]. During the polycondensation reaction, the tetrahedral units are linked in an alternating manner to yield the geopolymer material. The geo-polymerization reaction that creates a polymeric backbone of aluminum and silicon atoms is described in Eqs. 1 and 2 [9].



The source material for the geopolymer is commonly classified as C-class (contents of CaO > 10wt%) or F-class (contents of CaO < 10wt%) fly ash (denoted as C-F/A and F-F/A, respectively).

In this study, C-class fly ash containing CaO at more than 30 wt% was selected as the raw material with which to formulate a geopolymer, and its physical properties were investigated. Specifically, the optimal processing condition of the concentration of an alkali activator to fabricate a strong geopolymer using C-F/A was assessed. For this purpose, a phase analysis and microstructural observations of the compressive strength of the geopolymers were conducted.

## 2 Experimental Procedures

The source materials for the geopolymer were C-F/A and F-F/A, which had been discharged and reclaimed at the 'Y' thermal power plant in South Korea. The chemical composition of the C-F/A and F-F/A materials as determined by X-ray fluorescence (XRF, Spectro 2000) is shown in Table 1.

Table 1. Chemical Compositions of the Raw Materials (wt %)

Raw Materials	Oxides											
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	S	C	I.g
C-F/A	24.7	10.3	4.0	38.4	5.0	4.5	0.8	0.5	0.1	10.2	0.3	1.1
F-F/A	53.2	16.0	2.0	7.3	13.1	2.7	1.4	0.6	0.3	-	-	3.6

The main components of C-F/A are CaO, silica, and alumina, while those of F-F/A are silica, alumina, and iron oxide.

The processing parameters used to create the geopolymer are shown in Table 2. The alkali activator used was sodium hydroxide (Duksan Pure Chemicals, 99.3%, Korea). The preparation of the alkali activator solution was done by stirring NaOH and distilled water with a magnetic bar at RT. A cylindrical green compact of the geopolymer 20 mm in diameter and 20 mm high was formed by compressing a mold at a constant pressure of 80 MPa for 10 seconds. Pressing samples reduces the porosity, which affects the mechanical properties. The specimen then was covered with a polyethylene zippered bag to prevent the evaporation of the moisture and to maintain the internal humidity at 99%. It was then cured for 24h at 70°C.

Table 2. Experimental Parameters for the Geopolymeric Processing Method

Raw materials	NaOH activator concentration	L/S ratio	Curing condition
C-F/A or F-F/A	0~16 M	0.2	70°C/24h

\* L/S ratio refers to the liquid-to-solid ratio.

The phase analysis of the fabricated geopolymers was carried out using an X-ray diffractometer (XRD, Rigaku MiniFlex2) with CuK $\alpha$  radiation generated at 40 kV and 40 mA. The microstructure of the geopolymers was observed by means of scanning electron microscopy (SEM, S-4800 HITACHI, Japan) using secondary electrons. The specimens were coated with platinum prior to the SEM imaging process, which used an accelerating voltage of 5 kV. The compressive strength of a cylindrical geopolymer using an UTM (UTM-900NH Series Daekyung, Korea) was measured with a head speed of 5cm/min. Averaged data were obtained from three to five samples.

### 3 Results and Discussion

#### 3.1 F-F/A-Based Geopolymer

The XRD results for the as-received fly ash samples, F-F/A and C-F/A, are shown in Fig. 1. Only quartz is shown in the as-received F-F/A. The compressive strength and density of the F-F/A-based geopolymer activated with various concentrations of the NaOH solution are shown in Fig. 2. The compressive strength and density of the F-F/A-based geopolymer increase with the concentration of the NaOH solution.

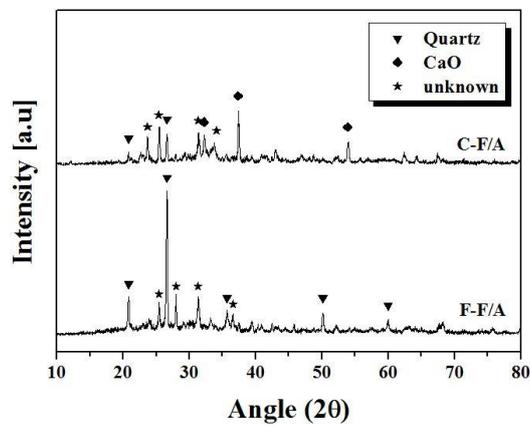


Fig. 1. XRD results for the as-received C-F/A and F-F/A

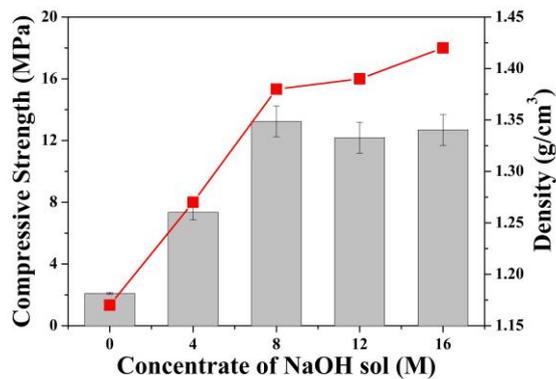


Fig. 2. The compressive strength (bar) and density (■) of the F-F/A-based geopolymer activated with various concentrations of the NaOH solution. Here, 0M indicates the specimen activated with distilled water.

The compressive strength of geopolymer reached approximately 12 MPa when the concentration of the alkaline activator of NaOH solution exceeded 8M. This indicates that a sufficient geopolymeric reaction requires a certain concentration of the NaOH solution.

The XRD pattern of the F-F/A-based geopolymer activated with various concentrations of the NaOH solution are shown in Fig. 3. For the geopolymer activated with 0~4 M of the NaOH solution, the main phase is only quartz, indicating that there was no noticeable geopolymerization reaction. Zeolite as a minor phase, however, was found to have developed in the specimen activated by more than 8M of the NaOH solution, in addition to the main phase, i.e., quartz.

These findings are in good agreement with the compressive strength of the geopolymer shown in Fig. 2. The generation of zeolite, evidence of the geopolymerization of coal ash, is considered to be a cause of the enhancement of the compressive strength of geopolymer. Excessive alkalinity, however, appears to obstruct the polycondensation reaction of geopolymers because the compressive strength of the geopolymer decreased when the concentration of NaOH solution exceeded 8M.

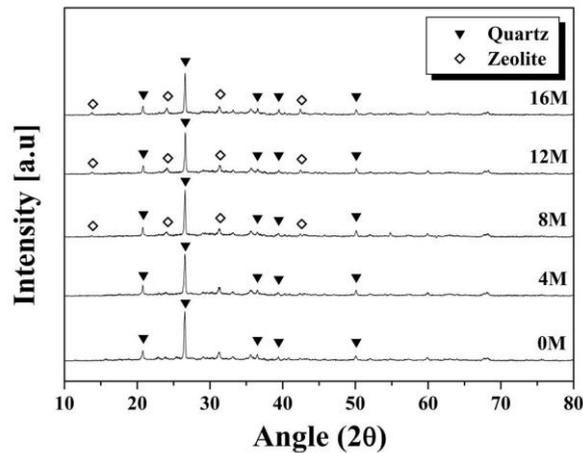


Fig. 3. XRD pattern of F-F/A-based geopolymer activated with various concentrations of the NaOH solution [ $\diamond$  = Zeolite,  $(\text{Na}_6(\text{Si}_6\text{Al}_6\text{O}_{24})(\text{H}_2\text{O})_{7.92}((\text{CH}_2\text{OH})_2)_{1.2})$ ]. Here, 0M indicates the specimen activated by distilled water.

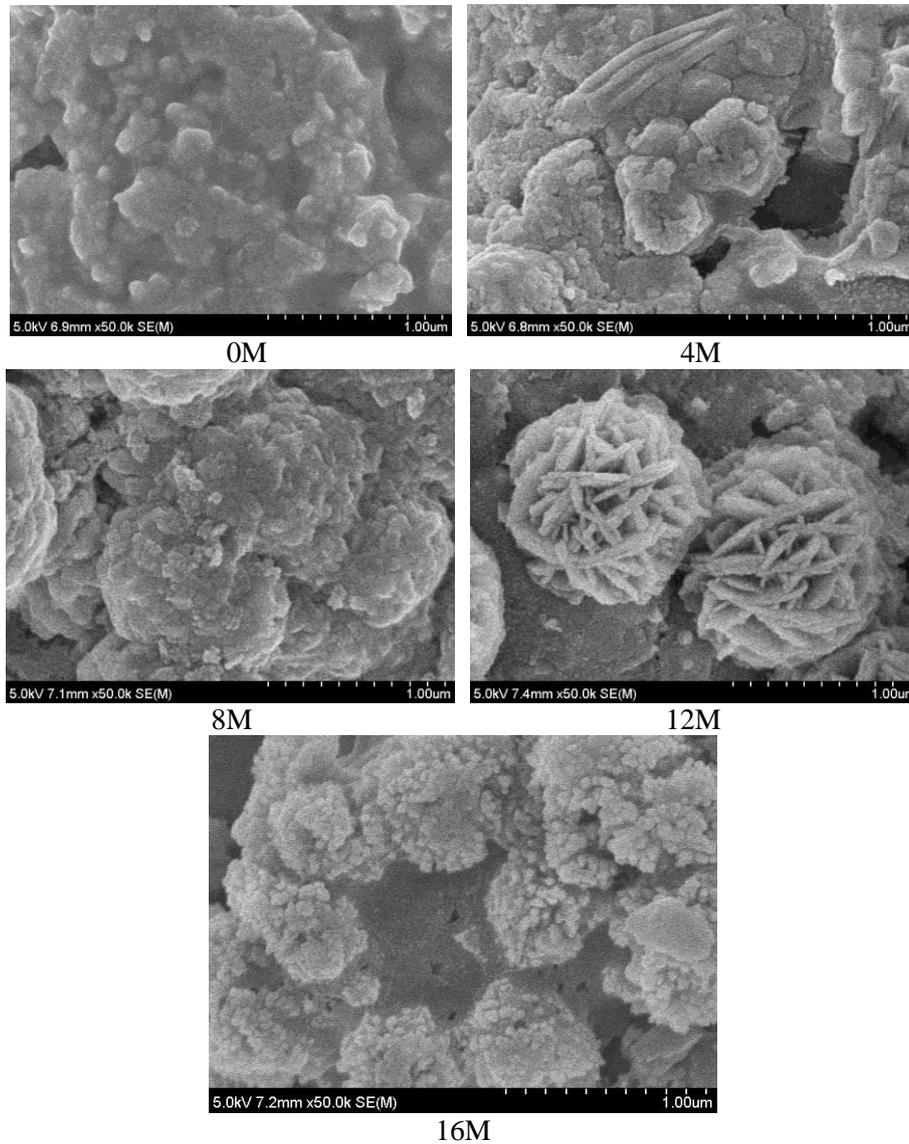


Fig. 4. Microstructure of the F-F/A-based geopolymer activated with various concentrations of the NaOH solution (x 50,000). In the figure, 0M indicates the specimen activated by distilled water.

The microstructures of the F-F/A-based geopolymer activated with various concentrations of NaOH solution are shown in Fig. 4. There was no crystal phase in the specimen activated with distilled water (denoted as 0 M), and tiny grains less than  $0.1 \mu\text{m}$  size were partially formed in the specimen made with the 4M NaOH solution. Small grains formed all around the specimen activated with the 8M NaOH solution. Flower-shaped crystals  $1 \mu\text{m}$  in size were generated in the

specimen activated of the 12M NaOH solution. The flower-shaped crystals consisted of sheet-shaped crystals 500~800 nm thick; the sheet-shaped crystals resemble the petals of a flower. The sheet-shaped crystals, however, disappeared and small grains about 200 nm in size formed on the surfaces of bud-shape grains in the geopolymer activated with the 16 M NaOH solution.

According to the XRD results shown in Fig. 3, zeolite formed in the C-F/A-based geopolymer activated with NaOH solution exceeding 8M. Thus, the several crystals and grains shown in the microstructure in Fig. 4 are considered as zeolite. The shapes of the zeolite crystals varied depending on the concentration of the NaOH solution.

### **3.2 C-F/A-Based Geopolymer**

The compressive strength and density levels of the C-F/A-based geopolymer activated with various concentrations of NaOH solution are shown in Fig. 5. The compressive strength of the C-F/A-based geopolymer had higher values than those of the F-F/A-based geopolymer at all concentrations of NaOH.

$\text{Ca(OH)}_2$  and calcium silicate hydrate (denoted as C-S-H) were formed in the geopolymer made with C-F/A, as shown in Fig. 6. The alkaline  $\text{Ca(OH)}_2$  generated by the hydration of the components containing calcium induced a pozzolanic reaction of fine silica in the fly ash, thereby developing the mechanical strength of the specimen [10]. The pozzolanic reaction converts a silica-rich precursor in the presence of water to a C-S-H, with good cementing properties. In the C-S-H phase, the ratio Ca/Si, or C/S, and the number of water molecules can vary and the stoichiometry may differ.

At a higher molarity level of the NaOH solution exceeding 8M, the decreased strength is thought to be due to the formation of a reactive gel. When a high concentration of alkaline solution exists in the voids of the geopolymer mortar, the silica reacts with the alkaline solution to produce a reactive gel which easily absorbs moisture to expand and thus induce cracks in the geopolymer [11, 12]. Therefore, the development of strength in the geopolymer made with C-F/A is mainly due to the pozzolanic reaction caused by  $\text{Ca(OH)}_2$  and the formation of the C-S-H phase by the hydration reaction of CaO and silica, in addition to the development of strength owing to the geopolymerization reaction.

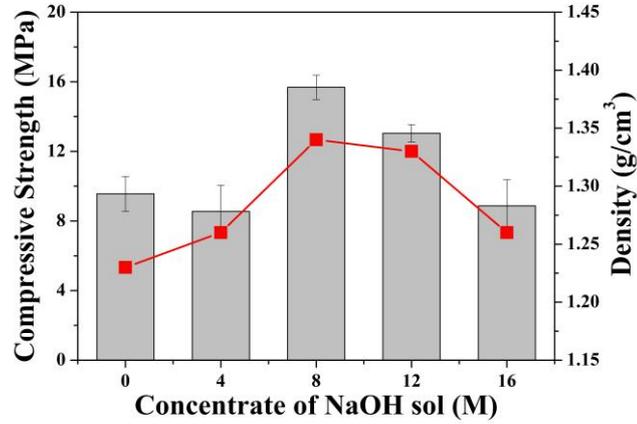


Fig. 5. The compressive strength (bar) and density (■) of the C-F/A-based geopolymer activated with various concentrations of the NaOH solution. Here, 0M indicates the specimen activated by distilled water.

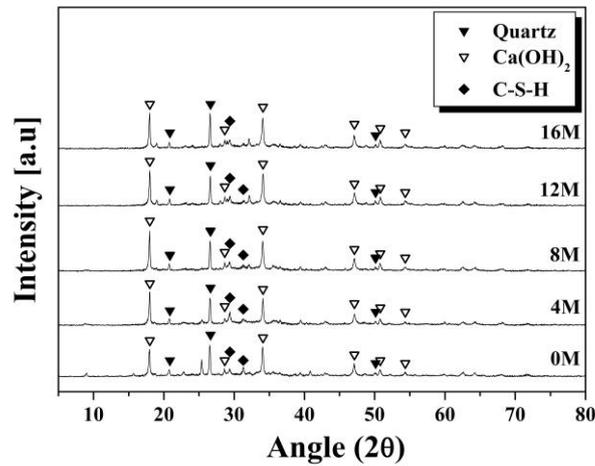


Fig. 6. XRD patterns of C-F/A-based geopolymers activated with various concentrations of the NaOH solution (♦ = C-S-H,  $(\text{Ca}_5(\text{SiO}_4)_2(\text{OH})_2)$ ). 0M indicates the specimen activated by distilled water.

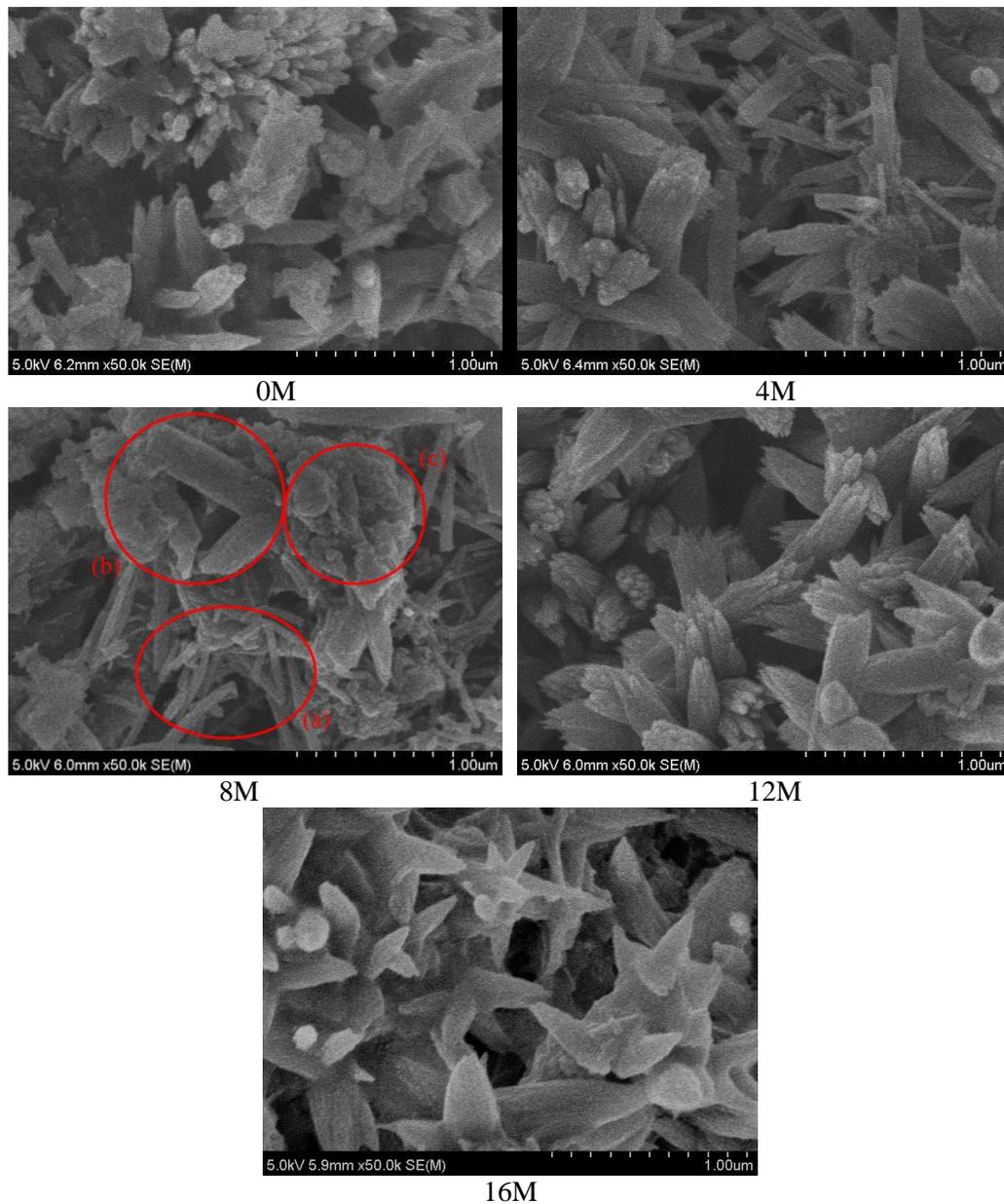


Fig. 7. Microstructure of the C-F/A-based geopolymer activated with various concentrations of the NaOH solution. Here, 0M represents the specimen activated with distilled water.

The microstructures of the C-F/A-based geopolymer activated with various concentrations of the NaOH solution are shown in Fig. 7. The microstructures of the C-F/A-based geopolymer differed considerably from those of the F-F/A-based geopolymer. In the specimen activated with the 8M NaOH solution, there were many crystals of various shapes, including a needle-like shape, a pillar shape, and clusters (agglomerates) consisting of small particles. When combining the microstructure observed with the XRD results, many of the crystals of various shapes

formed are considered to be  $\text{Ca}(\text{OH})_2$  and/or the C-S-H phase. A more precise conclusion, however, can be reached only if more experiments are performed.

## 4 Conclusion

For the F-F/A-based geopolymer activated with 0~4 M of NaOH solution, the main phase is only quartz, indicating that there was no noticeable geopolymerization reaction. Zeolite as a minor phase developed in the specimen activated with NaOH solution at more than 8M. The generation of the zeolite phase, evidence of the geopolymerization of coal ash, causes an enhancement in the compressive strength of the geopolymer. Excessive alkalinity, however, obstructed the polycondensation reaction of the geopolymers, as the compressive strength of the geopolymer decreased when the concentration of NaOH solution exceeded 8M.

The compressive strength of the C-F/A-based geopolymer had higher values than those of the F-F/A-based geopolymer at all concentrations of NaOH.  $\text{Ca}(\text{OH})_2$  and calcium silicate hydrate (denoted as C-S-H) formed in the specimen made with C-F/A. The alkaline  $\text{Ca}(\text{OH})_2$  generated by the hydration of oxide components containing calcium induced a pozzolanic reaction of the silica-rich precursor in the fly ash and converted the precursor in the presence of water to a C-S-H, with good cementing properties. At higher molarity of a NaOH solution above 8M, the decreased strength is thought to be due to the reactive gel which formed, which easily absorbs the moisture to expand and thus induce cracks in the geopolymer. The development of the strength of the geopolymer made with C-F/A, therefore, is mainly due to the pozzolanic reaction caused by  $\text{Ca}(\text{OH})_2$  and the formation of the C-S-H phase via the hydration reaction of CaO and silica, in addition to geopolymerization.

There were many crystals of various shapes, such as a needle-like shape, a pillar shape, and clusters (agglomerates) consisting of small particles in the C-F/A-based geopolymer activated with the 8M NaOH solution, while flower-shaped crystals 1  $\mu\text{m}$  in size were generated in the F-F/A-based geopolymer activated with the 12M NaOH solution. The flower-shaped crystals consisted of sheet-shaped crystals which were 500~800 nm thick.

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## References

- [1] D. Hardjito, S. E. Wallah, D. M. J. Sumajouw, B. V. Rangan, On the development of fly ash-based geopolymer concrete, *ACI. Materials Journal*, **101** (2004), 467-472. <http://dx.doi.org/10.14359/13485>

- [2] IEA, *CO<sub>2</sub> Emissions from Fuel COMbustion*, Interinational Energy Agency, Paris, France, 2008. [http://dx.doi.org/10.1787/co2\\_fuel-2008-en-fr](http://dx.doi.org/10.1787/co2_fuel-2008-en-fr)
- [3] P. Friedlingstein, R. A. Houghton, G. Marland, J. Hackler, T. A. Boden, T. J. Conway, J. G. Canadell, M. R. Raupach, P. Ciais, C. Le Quere, Update on CO<sub>2</sub> emissions, *Nat Gesci.*, **3** (2010), 811-812. <http://dx.doi.org/10.1038/ngeo1022>
- [4] UNSTATS, Greenhouse Gas Emissions by Sector (Absolute Value), United Nations Statistical Division, New York, (2010).
- [5] J. M. Allwood, J. M. Cullen, R. L. Milford, Options for achieving a 50% cut in industrial carbon emissions by 2050, *Environmental Science and Technol.*, **44** (2010), 1888-1894. <http://dx.doi.org/10.1021/es902909k>
- [6] J. Davidovits, Geopolymers and geopolymeric materials, *J. Thermal. Anal.*, **35** (1989), 429-441. <http://dx.doi.org/10.1007/bf01904446>
- [7] J. G. S. van Jaarsveld, J.S.J. van Deventer, L. Lorenzen, The potential use of geopolymeric materials to immobilize toxic metals: Part 1. Theory and applications, *Miner. Eng.*, **10** (1997), 659-669. [http://dx.doi.org/10.1016/s0892-6875\(97\)00046-0](http://dx.doi.org/10.1016/s0892-6875(97)00046-0)
- [8] J.G.S. van Jaarsveld, J.S.J van Deventer, L. Lorenzen, Factors affecting the immobilization of metals in geopolymerized flyash, *Metall. Mater. Trans. B*, **29** (1998), 283-291. <http://dx.doi.org/10.1007/s11663-998-0032-z>
- [9] J.G.S. van Jaarsveld, J.S.J. van Deventer, A. Schwartzmann, The potential use of geopolymeric materials to immobilise toxic metals: Part2. Material and leaching characteristics, *Miner. Eng.*, **12** (1999), 75-91. [http://dx.doi.org/10.1016/s0892-6875\(98\)00121-6](http://dx.doi.org/10.1016/s0892-6875(98)00121-6)
- [10] K.O. Kwon, K.R. Kong, M.G. Lee, H.C. Kang, The effect of meta-kaolin on the pozzolan reaction of lightweight porous concrete, *Resources Processing*, **55** (2008), 115-119. <http://dx.doi.org/10.4144/rpsj.55.115>
- [11] J.T. Song, J.Y. Kim, D.W. Ryu, S.Y. Go, K.S. Han, Hydration of the fly ash-CaO system in presence of various chemical activators, *Journal of the Korean Ceramic Society*, **35** (1998), 185-195.
- [12] S.H. Hong, S.H. Han, K.K. Yun, A case study for deterioration due to alkali-silica reaction in the cement concrete pavement, *Journal of the Korea Concrete Institute*, **18** (2006), 355-360.

<http://dx.doi.org/10.4334/jkci.2006.18.3.355>

- [13] Y. Lee and S. Kang, Characterization of fly-ash-based geopolymer containing CaO of over 30 weight percent, *Advanced Science and Technology Letters*, **130** (2016), 77-81.  
<http://dx.doi.org/10.14257/astl.2016.130.17>

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