

Effect of elevated hot temperatures on hybrid geopolymer synthesized with a mixture of coal fly and bottom ashes

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ABSTRACT

We have employed a mixture of coal fly and bottom ashes as a source materials of geopolymer. To investigate the thermal behavior of the hybrid geopolymer subjected to high temperature, we manufactured the geopolymer under NaOH solution by replacing the content of bottom ash from 0, 20, 40, 60, and 80 % in weight of the total ash mixture. The hybrid geopolymer specimen obtained in these way were exposed to 300, 600, and 900 °C. The variations in compressive strength, thermal conductivity and micro-structure over temperature conditions were investigated. Especially, after exposure to 900 °C, we obtained the highest values of compressive strength and thermal conductivity than the other thermal conditions. It has been confirmed that the strength enhancement come from the phases change of amorphous microstructure matrix into crystalline phases such as cristobalite, anorthoclase, and nepheline in the SEM and XRD results.

Keywords: coal fly and bottom ash geopolymer, thermal behavior, cristobalite, anorthoclase, nepheline

1 INTRODUCTION

In the cement industry, Ordinary Portland Cement (OPC) has been most widely used as a construction materials. But it has many environmental drawbacks of requiring much energy and emitting a large amount of CO₂ world widely [1]. As well as environmental concerns, OPC has been blamed for low durability against many hazards that can be occurred by severe environmental conditions. Especially, when considering that a fire frequently breaks out in a building, thermal durability of construction materials is important for building's safety. In many researches, however, OPC has been proven to be vulnerable to elevated temperature [2]. These shortcomings of OPC have encouraged the search for new alternative materials and geopolymer have been proposed as a novel engineering materials in construction industry.

Geopolymer is a type of alkali-activated materials that can be synthesized by reaction of aluminosilicate raw materials with alkali activator [1]. Recent works have shown that geopolymer has high thermal durability due to its inorganic frameworks [3]. Although many studies have investigated the thermal behavior of the geopolymer employing a homogeneous aluminosilicate source materials, only a few research has been conducted the study of thermal

influence on the geopolymer synthesized with heterogeneous feedstock.

The study presented in this paper was aimed at examining the thermal behavior of the so-called hybrid geopolymer synthesized with heterogeneous source materials, especially the mixture of coal fly and bottom ash, when exposed to elevated hot temperatures of 300, 600, and 900 °C. The compressive strength and thermal conductivity tests were conducted to examine the thermal behavior of the hybrid geopolymer. XRD and SEM analyses were also carried out to investigate the behavior in a microscopic point of view.

2 EXPERIMENTAL

2.1 Materials

The source materials used in this study for synthesizing the geopolymer are the mixture of coal fly ash (FA) and bottom ash (BA). They were provided from Yeongheung Power Plant, South Korea. The original bottom ash initially generated from the power plant was so large with having above a few centimeters that it is not suitable to be used as a binder. Thus it was pulverized and milled using a hammer mill and sieved with No. 200 standard sieve (75 μm). BA, the residue on the sieve after screening, was utilized as one of the source materials for the hybrid geopolymer in this study. The chemical compositions of FA and BA determined by X-ray fluorescence (ZSK primus II, Rigaku, Japan) analysis in oxides are presented in Table 1. According to ASTM C618, FA used in this study can be classified as a Class F fly ash as the calcium content of them is low to be 6.72 and the sum of SiO₂, Al₂O₃ and Fe₂O₃ is greater than 70 %.

Composition (%)	FA	BA
SiO ₂	48.8	53.0
Al ₂ O ₃	23.2	21.3
Fe ₂ O ₃	8.26	11.8
CaO	6.72	5.99
MgO	1.53	1.43
TiO ₂	1.37	1.28
K ₂ O	1.36	1.77
Na ₂ O	0.99	1.09
C	5.22	1.19
Others	2.55	1.15

Table 1: Chemical compositions of FA and BA determined by XRF analysis (wt.%).

As shown in the SEM micrographs and particle size distributions in Figure 1 and 2, respectively, BA has large and irregular particles with a mean diameter of 206.37 μm . On the other hand, FA has relatively small and spherical particles with a mean diameter of 31.80 μm . In this study, a sodium hydroxide solution was used as an alkali activator. NaOH pellets (more than 93 % purity, Duksan pure chemicals, South Korea) were dissolved in tap water for 14 M sodium hydroxide solution.

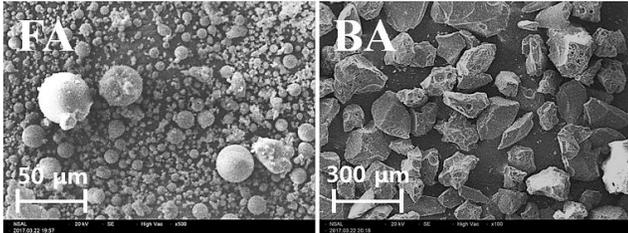


Figure 1: SEM micrographs of FA (left) and BA (right).

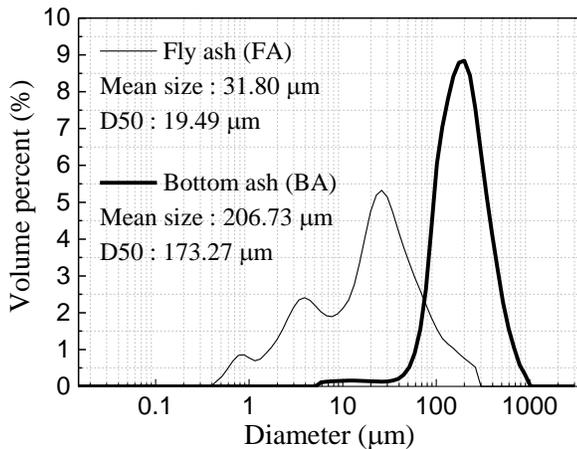


Figure 2: Particle size distributions of FA (thin line) and BA (bold line).

2.2 Experimental Procedures

Mixture designs and curing conditions of the hybrid geopolymer specimens are tabulated in Table 2. BA partially replaced FA at the rate of 0, 20, 40, 60 and 80 percent by weight of total coal ash mixture. The coal ash mixture was blended with a sodium hydroxide solution for 5 minutes using Hobart mixer to ensure the homogeneity of the geopolymer paste. The different ratios of alkali activator to binder for each hybrid geopolymer were determined by monitoring and tuning its consistency where the paste can maintain its initial shape after demolding and at the same time does not become a gel-state. The hybrid geopolymer paste prepared in this way were poured into the 50 × 50 × 50 mm³ cubic mold and then compressed with a hand press having maximum capacity of 5 kN. After compression, the cube-shaped geopolymer paste was detached from a mold, and cured in a 75 °C oven for 24 hours with being sealed by

plastic bag. The hardened geopolymer paste after oven curing were allowed to cool down to room temperature and microwaved under the power of 700 W with household microwave oven (RE-C21VB, SAMSUNG, Korea) for 3 minutes.

Specimen name	FA : BA (wt.:wt.)	Activator/binder (wt./wt.)	Curing condition
34FA100	100:0	0.34	75 °C oven
28FA80	80:20	0.28	for 24 hr.
26FA60	60:40	0.26	→ 700 W
22FA40	40:60	0.22	microwave
28FA20	80:20	0.28	for 3 min.

Table 2: Mixture designs and curing conditions of the hybrid geopolymer specimens.

In this study, all types of hybrid geopolymer specimen, tabulated in Table 2, were subjected to several elevated temperatures to investigate their thermal behaviors. The geopolymer specimen after curing was exposed to 300, 600, and 900 °C at a constant heating rate of 8 °C per minute. The specimen was kept in the given temperature for 2 hours and then naturally cooled to room temperature before conducting property measurements and analyses.

2.3 Property Measurements and Analyses

The thermal conductivity was measured by Thermal Constant Analyzer (TPS-500s, Hot Disk®, Sweden) with fitting the analyzer's sensor between the plane surfaces of two specimens. The compressive strength was tested by compressive strength test machine (PL-9700H, Woojin precision Co., Korea), with an axial load applied on the specimen face. The bulk density was determined by dividing the final weight of the specimen by its final volume. The powder density was measured by gas pycnometer (Accupyc II 1340, Micromeritics, U.S.A.) which requires finely ground geopolymer for sound value. The porosity, which can be calculated with the given values of bulk and powder density, was obtained by following equation.

$$porosity (\%) = \left(1 - \frac{Bulk\ density}{Powder\ density}\right) \times 100 \quad (1)$$

Microstructure analysis was carried out by SEM (Scanning Electron Microscope, Nova Nano SEM 200, FEI, USA) and XRD (X'pert APD, Philips, Netherlands) on the hybrid geopolymer specimen of 26F60 before and after exposure to elevated temperature.

3 RESULT AND DISCUSSION

3.1 Thermal Conductivity and Porosity

The thermal conductivity and porosity results are presented in Figure 3 and 4, respectively. Except for the case of 28FA20, the thermal conductivity of the geopolymer was observed to decrease steadily until the temperature of 600 °C and increase at 900 °C. In all cases of hybrid geopolymers, as the exposure temperature increased, the porosity value also increased.

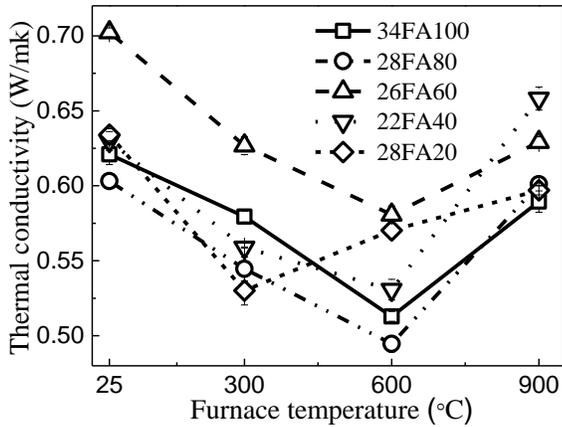


Figure 3: Thermal conductivity results of the hybrid geopolymer specimens before and after exposure to elevated temperature of 300, 600, and 900 °C.

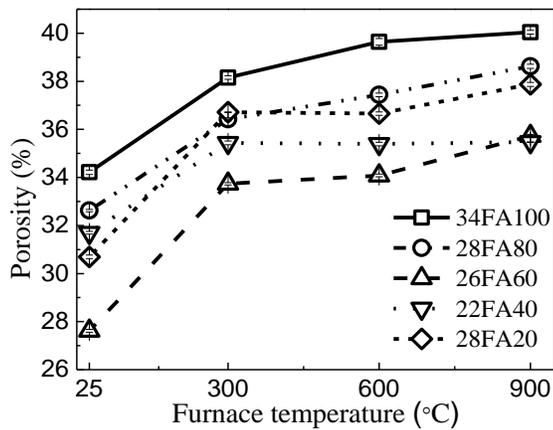


Figure 4: Porosity results of the hybrid geopolymer specimens before and after exposure to elevated temperature of 300, 600, and 900 °C.

Generally, the thermal conductivity is inversely proportional to the porosity [7]. The formation of void due to the evaporation of free water can lower the thermal conductivity because heat transfer within the specimen is more hindered by void rather than the matrix or moisture it contains. In this study, the relations of the thermal conductivity with the porosity were well fitted up to 600 °C, i.e., as the porosity increased, the thermal conductivity

decreased. However, the thermal conductivity after exposed to 900 °C showed an anomaly that the value increased although the porosity at the corresponding temperature was measured to be higher than the value at 600 °C.

The abnormal behavior is associated with the microstructure change in the geopolymer matrix. As a result of that, the void in the geopolymer was filled with sintered matrix resulting in the increase of thermal conductivity and simultaneously allowing the porosity value to slightly increase.

3.2 Compressive Strength

The compressive strength results are presented in Figure 5. There was a different trends in compressive strength over the elevated temperature depending on whether BA was included or not.

The geopolymer specimen of 34FA100 employing only FA as a binder showed a significant increase in compressive strength after exposed to 900 °C despite the fluctuation within a narrow range from 51 MPa to 57 MPa in the temperature range below 600 °C.

On the other hand, in the hybrid geopolymer containing BA, the compressive strength decreased after exposure to 300 and 600 °C. These deteriorations might be attributed to two factors: (1) microcrack, shown in Figure 7 (b) and (c), induced by thermal load [4] and (2) excessive evaporation of water in the specimen during the heating process [5]. After exposure to 900 °C, however, the compressive strength reached the value above or near which the hybrid geopolymer exhibited at ambient. Other research have suggested that the recovery in the compressive strength after exposed to 900 °C can be attributed to the sintering which make geopolymer matrix more compacted [6]. In this study, the microstructure analyses of SEM and XRD in following section also support the fact that the geopolymer had thermally induced matrix with emerging of new crystalline phases after being heated to 900 °C.

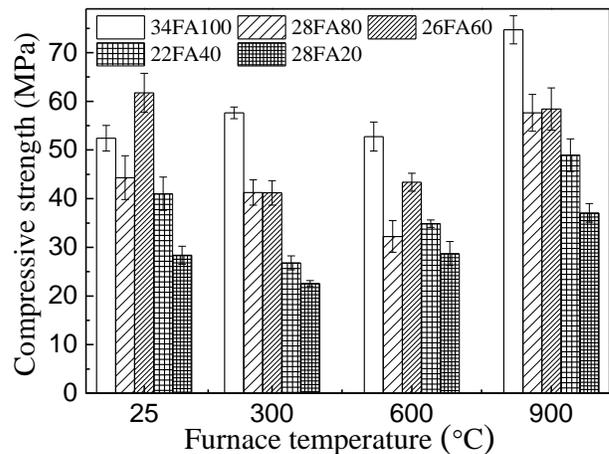


Figure 5: Compressive strength results of the hybrid geopolymer specimens before and after exposure to elevated temperatures of 300, 600, and 900 °C.

3.3 XRD and SEM analyses

X-ray diffraction (XRD) patterns are shown in Figure 6. In the geopolymer without thermal treatment, the crystalline phases of quartz, hematite, mullite, and albite were detected. The XRD patterns after exposed to 300 and 600 °C were identical with the ones at ambient; no additional crystalline phases were observed. On the other hand, the new crystalline phases such as nepheline, anorthoclase, and cristobalite were emerged after exposure to 900 °C.

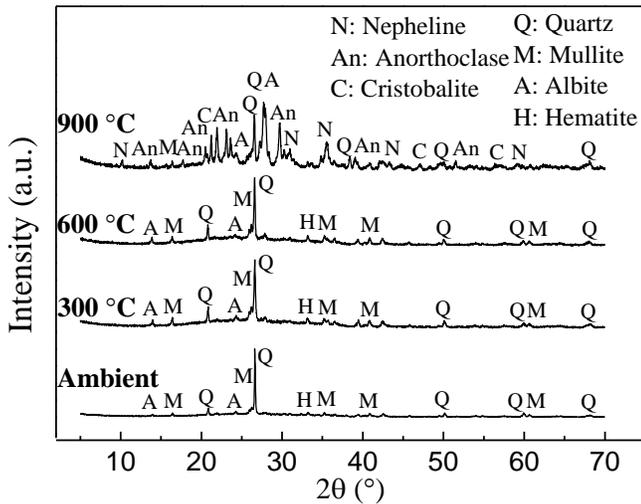


Figure 6: X-ray diffraction patterns of 26FA60 hybrid geopolymer before and after exposure to elevated temperatures of 300, 600, and 900 °C.

SEM micrographs are presented in Figure 7. The hybrid geopolymer matrix containing partially dissolved FA and BA particles was shown in Figure 7(a). In Figure 7(b) and (c), as well as the matrix of the geopolymer, microcracks induced by the thermal load of 300 °C and 600 °C can be found in its matrix. It can be noticed in Figure 7(d) that the hybrid geopolymer exposed to 900 °C has smooth surface through sintering that lead the geopolymer matrix to become more dense and better connected [8].

4 CONCLUSIONS

The compressive strength and thermal conductivity of the hybrid geopolymer reduced when exposed to 300 °C and 600 °C. The loss of strength might be attributed to the microcracks in the geopolymer matrix and excessive evaporation, which also contributed to reduction in thermal conductivity. The geopolymer exposed to 900 °C, however, showed thermally induced microstructure changes, such as onset of new crystalline phases and sintering, with the thermal behaviors of recovery in the compressive strength and the increase in thermal conductivity.

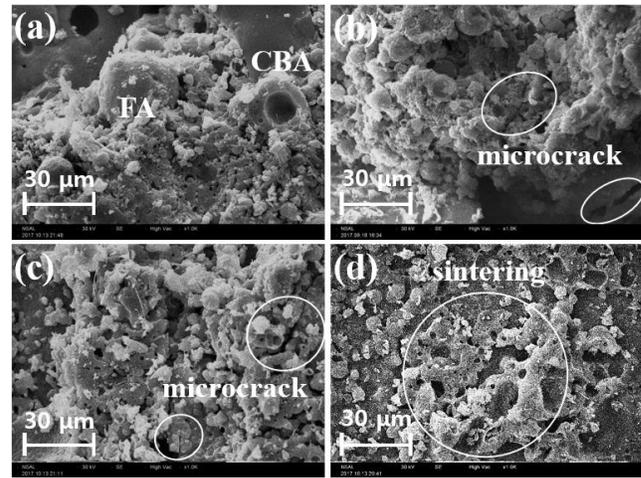


Figure 7: SEM micrographs of 26FA60 hybrid geopolymer before (a) and after exposure to elevated temperatures of 300 (b), 600 (c), and 900 °C (d).

REFERENCES

- [1] J. Davidovits, "Properties of geopolymer cements," Proceedings of 1st International Conference on Alkaline Cements and Concretes, Sci. Res. Inst. On Binders and Mater. Kiev State Tech. Univ., Kiev, Ukraine, 131-149, 1994.
- [2] J. Piasta, "Heat deformation of cement paste phases and the microstructure of cement paste," Materials and Structures, 17, 415-420, 1984.
- [3] P. Duxson, J.L. Provis, G.C. Luckey, and J.S. van Deventer, "The role of inorganic polymer technology in the development of 'green concrete'," Cement and Concrete Research, 37, 1590-1597, 2007.
- [4] M.M. Al Bakri Abdullah, K. Hussin, M. Bnhussain, K.N. Ismail, Z. Yahya, and R.A. Razak, "Fly ash-based geopolymer lightweight concrete using foaming agent," International Journal of Molecular Sciences, 13, 7186-7198, 2012.
- [5] K. Shrotri, "Dynamic Mechanical Properties of Geopolymer-Polymer Composites," Ph. D. Thesis, Rochester Institute of Technology, NY, 2006.
- [6] L. Vickers, Z. Pan, Z. Tao, A.V. Riessen, "In Situ Elevated Temperature Testing of Fly Ash Based Geopolymer Composites," Materials, 9, 445, 2016.
- [7] A. sugawara, Y. yoshizawa, "An investigation on the Thermal Conductivity of Porous Materials and its Application to Porous Rock," Australian Journal of Physics, 14, 469, 1961.
- [8] Z. Pan, J.G. Sanjayan, B.V. Rangan, "An investigation of the mechanisms for strength gain or loss of geopolymer mortar after exposure to elevated temperature," Journal of Materials Science, 44, 1873-1880, 2009.