

Property enhancement of geopolymers after heat treatment

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Geopolymers have attracted interest as an alternative to cement because they release 80% lesser carbon dioxide than cement. Integrated gasification combined cycle (IGCC) slag was used as a raw material for the formation of the geopolymer. Many researchers have investigated the enhancement in the mechanical properties of geopolymers upon high-temperature heat treatment. However, there are few studies on the direct heat treatment of geopolymers. This study compared the effects of two different methods of heat treatment over a wide range of temperature. The highest compressive strength of 55.03 MPa was obtained at 200 °C after direct heat treatment. The X-ray diffraction patterns show that a new crystalline phase of calcium aluminum silicate was formed after heat-treatment at 1100 °C, which was confirmed by thermogravimetry-differential thermal analysis. In conclusion, the compressive strength of geopolymers can be enhanced and the density of geopolymers is also decreased by direct heat treatment at 200 °C. Thus, this approach can be used to make geopolymers for commercial products in the future.

Key words: Geopolymer, IGCC slag, Direct heat treatment, Increasing-temperature heat treatment.

Introduction

Although ordinary Portland cement (OPC) is the most popular construction material in the world, a large amount of CO₂ is released during its production [1]. Currently, CO₂ emissions have been curbed globally in various industries because of the greenhouse effect, and low carbon products and alternative materials to OPC are being studied. “Geopolymer” was first introduced as a substitute for OPC by Davidovits in 1978 [2]. Geopolymer is an inorganic material that releases 80% less carbon dioxide than OPC and provides sufficient mechanical properties for the construction industries [3]. The material is attractive because of various advantages such as higher strength and higher resistance to fire and acid attacks [4]. Geopolymers are usually fabricated by mixing aluminosilicate materials (e.g., metakaolin, fly ash, and integrated gasification combined cycle (IGCC) slag) with an alkali or alkali silicate solution [5]. IGCC slag was used as the raw material for the geopolymer used in this study. The slag, which contains a lot of SiO₂ and Al₂O₃, was obtained from the IGCC process. Geopolymerization involves the dissolution of Al and Si. Hence, IGCC slag is a good source for fabricating geopolymers [6]. IGCC is a type of power technology that is particularly favorable for plant retrofitting so that carbon dioxide can be removed at a convenient stage in the process [7].

Numerous studies have investigated the mechanical properties of geopolymers at elevated temperatures [8,

9]. There are only a few studies on the direct heat treatment of geopolymers at high temperatures after the geopolymerization process, and experimental data on other heat treatments at high temperatures is lacking. Therefore, this research focused on geopolymers fabricated using IGCC slag that underwent two different heat treatments, i.e., direct heat treatment at a high temperature and the increasing-temperature heat treatment, and compared the mechanical properties achieved after these treatments. Their characteristics were also compared at various heat treatment temperatures (100, 200, 300, 400, 500, 700, 900, and 1100 °C). The compressive strength, microstructure, and phase were analyzed after heat treatment at various temperatures. This knowledge helps us understand strength development and the behavior of geopolymers with temperature, allowing their better utilization in future. Improving the mechanical properties will promote the use of this material.

Experimental Procedure

IGCC slag, which is used as the raw material, was generated during the IGCC process, and the chemical composition of the raw material was measured using X-ray fluorescence (XRF) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES, OPTIMA 4300DV, Perkin Elmer, USA). The compositions are shown in Table 1. The chemical composition of the raw material is an important factor for obtaining homogeneous and high strength geopolymers. The IGCC slag was prepared by milling with a fine pulverizer (rotary friction milling) to form particles of size 60–70 μm.

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Table 1. Chemical composition of IGCC slag by XRF and ICP-AES.

XRF		ICP-AES	
Materials	IGCC slag (wt%)	Elements	IGCC slag (ppm)
SiO ₂	49.25	Al	96105.44
Al ₂ O ₃	20.16	Ca	153288.73
Fe ₂ O ₃	5.61	Mg	8714.20
CaO	21.67	Fe	41926.08
MgO	1.28	Cr	52.13
Na ₂ O	0.49	Mn	698.92
K ₂ O	0.48	Zn	Null
TiO ₂	1.07	As	Null
C	0.06	Pb	Null
Loi	0	Cu	Null

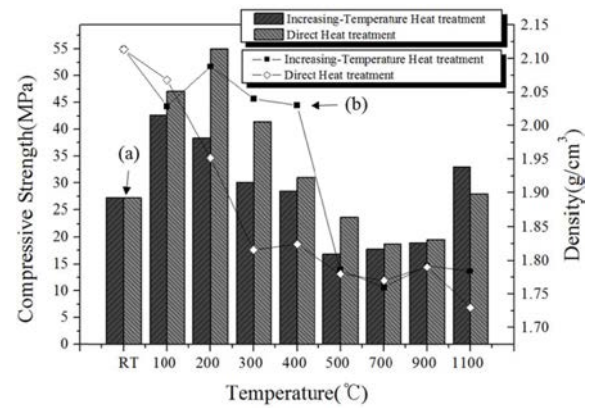
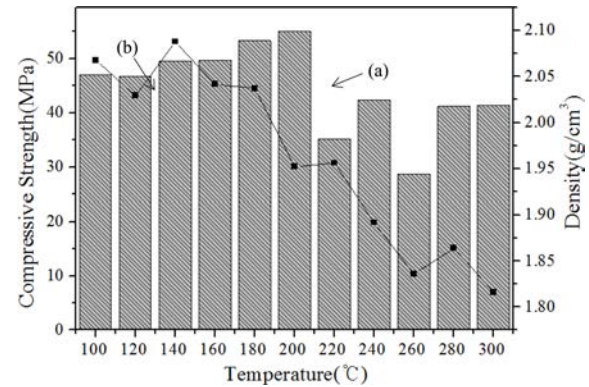
The prepared raw material was mixed with a 15-M alkali activator solution for making geopolymer pastes. A solution of sodium hydroxide pellets was used as the alkali activator (> 97.0% pure, Daejung, Korea) and was prepared in advance (3 hrs before mixing). The samples were mixed with a mortar mixer (Mortar Mixer, HJ, Product code KS-1150-A, Korea) for 5 min. The geopolymer paste was poured into a cubic mold (50 × 50 × 50 mm³), and then the mold was covered with a thin polyethylene film to prevent evaporation of water. The sample was cured for 24 hrs at 70 °C and 100% humidity. After aging for three days, the specimens were exposed to temperatures of 100, 200, 300, 400, 500, 700, 900, and 1100 °C for an hour.

The compressive strength of the geopolymer samples was determined using a compression testing machine (UTM-900NH Series Daejung, Korea). X-ray diffraction (XRD, Rigaku MiniFlex2, 40 kV, 40 mA, and CuK α radiation) was used to determine the phase composition of the reaction products. The data were collected using a nominal 2 θ step size of 0.01°, count time of 0.5 s over a 2 θ range of 5-90°. The microstructure of the geopolymer was observed by scanning electron microscopy (SEM, S-4800, Hitachi, Japan) using secondary electrons. Specimens were coated with platinum prior to imaging at an accelerating voltage of 5 kV. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using a simultaneous thermal analyzer-mass spectrometer (STA-MS, STA 409PC, Netzsch, Germany) in an atmosphere of dry air.

Results and Discussion

Compressive strength and density

Mechanical properties after heat treatment at various temperatures are shown in Fig. 1. The compressive strength increased after direct heat treatment (heat treatment) up to 200 °C, and then gradually decreased up to 900 °C. Here, direct heat treatment means that specimens were placed in the furnace at the target

**Fig. 1.** Mechanical properties of geopolymer after various heat treatment times; (a) compressive strength and (b) density.**Fig. 2.** Compressive strength and density of geopolymers after direct heat treatment from 100 to 300 °C. (a) Compressive strength and (b) density.

temperature. In contrast, the increasing-temperature heat treatment means specimens were sintered from room temperature to the target temperature. In the increasing-temperature heat treatment, the compressive strength showed a maximum at 100 °C, and then gradually decreased with an increase in the temperature up to 900 °C. The compressive strength of geopolymers increased again upon heat treatment at 1100 °C in both the direct and the increasing-temperature heat treatment methods. Geopolymers heat-treated above 1100 °C melted so heat treatment was not conducted above that temperature. Sun et al. suggested that at 1100 °C, the internal structure of the geopolymer matrix densified rapidly, resulting in an increase in the compressive strength [10]. Comparing the different heat treatment methods, it can be seen that the compressive strength was higher after direct heat treatment than the increasing-temperature heat treatment. This is because the bending strength is sensitive to the improvement in the internal microstructural defects at elevated temperatures. Geopolymers at gradually elevated temperatures are exposed more too high temperatures, so adverse effects such as an excessive loss of moisture and thermal stress in the structure may occur [7]. Therefore, direct heat

treatment was a more effective method than the increasing-temperature heat treatment for increasing the compressive strength.

The density of the heat-treated geopolymers gradually decreased with an increase in the temperature, irrespective of the heat treatment methods used because of the evaporation of the internal structural water. In most cases, the density of geopolymers heat-treated by direct sintering was lower than those of geopolymers heat-treated by the increasing-temperature sintering, which is a common result reported in studies for making lightweight materials. Artificial lightweight aggregates became light because of an increase in the number of internal pores during heat treatment by high temperature direct sintering [11].

There was a sharp decrease in density from 200 to 500 °C upon direct heat treatment. Therefore, the direct heat treatment method, especially between 100 and 300 °C, is an effective method of increasing the compressive strength as well as decreasing the density of geopolymers.

To obtain more details on the compressive strength and density of geopolymers heat-treated between 100 and 300 °C and to determine the optimum temperature for heat treatment in the direct method, both properties of the geopolymers were measured after direct heat treatment at 20 °C intervals between 100 and 300 °C, as shown in Fig. 2. The compressive strength increased with an increase in the temperature up to 200 °C. However, thereafter it tends to decrease with an increase in the temperature. The highest compressive strength (55.03 MPa) was obtained at 200 °C with the direct heat treatment. It was hypothesized that geopolymerization proceeded further with the remaining alkali activator within the specimen because the reaction might be caused by the higher activation energy, and the extra heat also helps the hardening of the geopolymer, similar to a thermosetting material, up to 200 °C. The negative effects caused by thermal shock and swelling upon heat treatment above 200 °C may overwhelm the positive effects of heat treatment by direct sintering, as described above. Hence, the compressive strength tends to decrease with an increase in the temperature above 200 °C. The density of the geopolymers heat-treated from 100 to 300 °C decreased with an increase in the temperature in general. This is also a characteristic of direct sintering, which can be seen in many lightweight materials.

XRD and TG-DTA analyses

XRD patterns of the geopolymers were observed after both heat treatment methods to investigate the phase changes upon different heat treatment methods in detail. Fig. 3 shows the XRD patterns of the geopolymers after direct heat treatment. A sodium aluminum silicate hydrate phase was found over the temperature range from room temperature (RT) to 400 °C. The

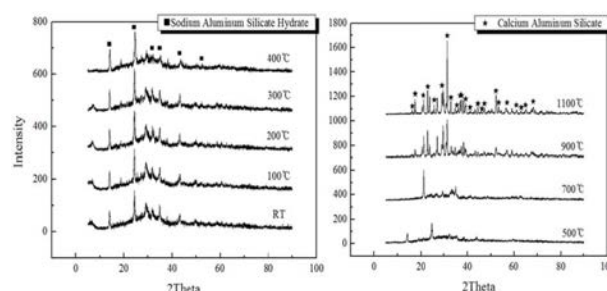


Fig. 3. XRD patterns of geopolymers after direct heat treatment at various temperatures.

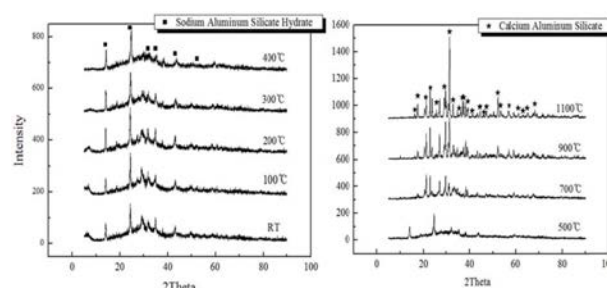


Fig. 4. XRD patterns of geopolymers after the increasing-temperature heat treatment at various temperatures.

peaks of sodium aluminum silicate hydrate decreased with an increase in temperatures up to 500 °C. Thereafter, the peaks completely disappeared at 700 °C. A new crystalline phase of calcium aluminum silicate phase appeared from 900 °C and was fully developed at 1100 °C. These phase transitions may explain the compressive strength variation between 900 and 1100 °C, as shown in Fig. 1. A new phase may contribute to an enhancement in the compressive strength upon heat treatment at 1100 °C in both methods. OPC is primarily composed of calcium aluminum silicate as the main phase. However, in this study, even though calcium aluminum silicate appeared as the main peak at 1100 °C, the compressive strength decreased with an increase in the internal microstructural defects and weak microstructure because of the heat treatment at high temperature.

Fig. 4 shows the XRD patterns of the geopolymers after the increasing-temperature heat treatment. These results were the same as those obtained after direct heat treatment. The sodium aluminum silicate hydrate phase was the main peak over the temperature range from RT to 400 °C. However, a new crystalline phase of calcium aluminum silicate phase appeared at 700 °C. The new crystalline phase of calcium aluminum silicate formed after heat treatment at 1100 °C. TG-DTA analysis was performed to confirm the presence of a new phase at 1100 °C.

Fig. 5 shows the TG-DTA result of a geopolymer. The DTA results showed an endothermic peak at around 143.2 °C and an exothermic peak at around 1155.8 °C. It was concluded that at 143.2 °C as the free

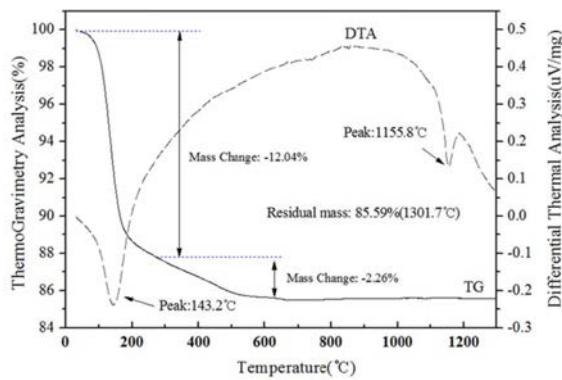


Fig. 5. TG-DTA result of heat treatment at various temperatures.

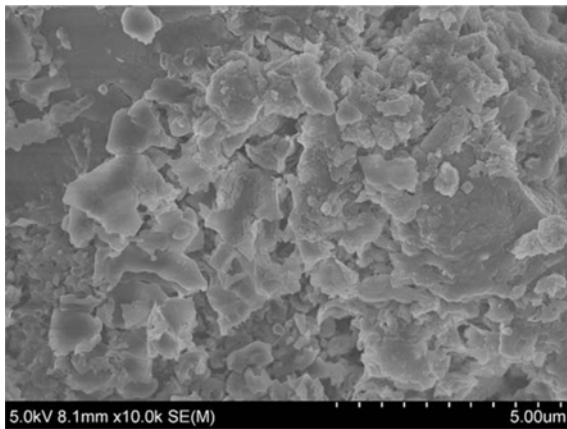


Fig. 6. SEM micrograph of geopolymer before heat treatment.

water in the specimens evaporated, endothermic reactions started occurring, and at 1155.8 °C, with the generation of the calcium aluminum silicate phase, exothermic reactions occurred. In addition, the TG results showed a sudden decrease in the mass at 100 - 300 °C. The free water in the specimens evaporated due to de-hydroxylation [3]. Therefore, a new calcium aluminum silicate phase was confirmed by the XRD and TG-DTA results, and it can be concluded that this new phase might contribute to an extra enhancement of the compressive strength at 1100 °C. However, this enhancement would be meaningless because the absolute value of the compressive strength is far less than that at 200 °C. Therefore, it was concluded that the best and economical way to enhance the compressive strength of the geopolymers is to heat them at 200 °C using the direct method for an hour.

Microstructure

An SEM image of the geopolymer before heat treatment is presented in Fig. 6. Although the morphology of the geopolymer before heat treatment was heterogeneous, the microstructures after the heat treatment were gradually homogenized with an increase in the temperature, as shown in Fig. 7. In particular, liquid phase sintering can be identified in the speci-

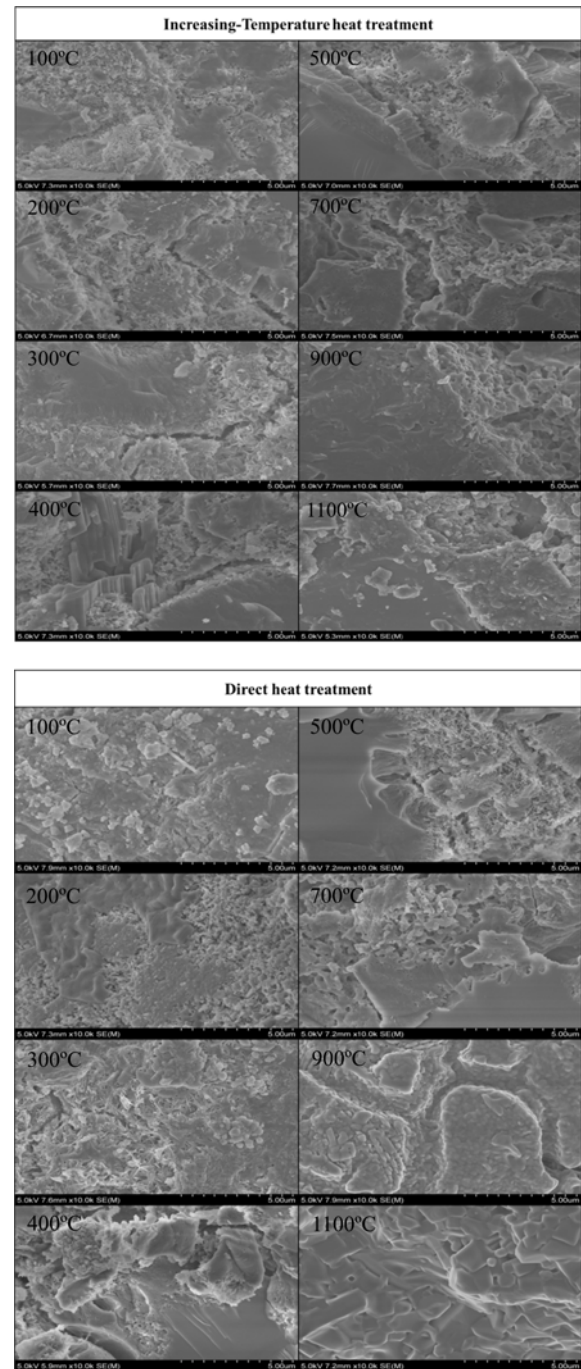


Fig. 7. Microstructures of geopolymers upon heat treatment at various temperatures.

mens sintered by both methods at 900 - 1100 °C. The increase in the compressive strength at 1100 °C by both sintering methods was explained from the phase transition point of view, as mentioned in the previous section. However, this can also be explained from the microstructural point of view, as shown in Fig. 7, because smooth and dense surfaces were observed by liquid phase sintering. There are no particular characteristics of the geopolymers after heat treatment at 200 °C, which means that there is no significant micro-

structural change at this temperature. However, further geopolymerization might be promoted in the matrix of the geopolymers upon increasing the temperature up to 200 °C, analogous to the increase in the compressive strength, as shown in Fig. 1.

As shown in Fig. 7, there was little microstructural difference between the two heat treatment methods. However, a little more liquid phase sintering process can be observed on the specimens heat treated by direct sintering at high temperature. The lower density of geopolymers after direct sintering can also be explained by the greater number of micro-pores in the matrix of the geopolymers heat treated by direct sintering over the temperature range 100 - 500 °C. Therefore, it can be concluded that the density difference in Fig. 1 over the temperature range 100 - 500 °C agrees with the microstructural observations shown in Fig. 7.

Conclusions

The effects of heat treatment on the properties of the geopolymer were investigated and compared between two different heat treatment methods, direct sintering and the increasing-temperature sintering. The highest compressive strength was obtained by direct sintering at 200 °C. It is believed that further geopolymerization was promoted by an increase in the temperature with the remaining alkali activator in the geopolymer.

Peaks of the sodium aluminum silicate hydrate phase appeared in the XRD patterns regardless of the heat treatment method. A new crystalline phase of calcium aluminum silicate appeared at different heat treatment temperatures for the two sintering methods. The DTA results showed an exothermic peak at around 1155.8 °C because of the generation of the calcium aluminum silicate phase, which confirms the phase transition identified by the XRD of the geopolymers heat-treated above 1100 °C.

More liquid phases (smooth surfaces) can be observed on the specimens heat treated by direct sintering at high

temperature. The lower density of geopolymers after direct sintering can also be explained by the greater number of micro-pores in the matrix of the geopolymers heat treated by direct sintering between 100 and 500 °C.

In conclusion, the direct sintering method appears to be the most economical and fast method of heat treatment of geopolymers for enhancing the compressive strength as well as for making them light. The optimum heat treatment temperature was 200 °C for obtaining the best compressive strength.

Acknowledgments

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