

Effect of Heat Treatment on Geopolymer Using Spent Materials

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Abstract

Geopolymer has many application fields like thermal insulation and fire resistant materials because it possesses excellent properties such as low bulk density, high permeability, low thermal conductivity, and high surface area. In this study, geopolymer was fabricated by using spent materials and alkali activator. Spent catalyst slag which was obtained after metals recovery of spent catalyst was used as raw material for making geopolymer. After a heat treatment of the geopolymer, the maximum strength (90MPa) was expressed at 500 °C, after then, from 700°C up to 1100°C the strength tended to decrease. Through the XRD analysis, it was confirmed that the C-S-H phase existed at a low temperature, but more than 700°C it was completely changed in the C-A-S phase. In the microstructure observation, more than 500°C it could be seen that the micropores occurred. Despite the confirmation of the micropores in the specimen at 500°C, the compressive strength appeared a maximum. It is believed that the reason it looked up to the maximum compressive strength at 500°C was due to the activation of

unreacted material in the specimen and it promoted to offset the effect of the micropores generated inside the specimen. It was considered that at the heat treatment more than 500°C, it was conducted dehydroxylation reaction and inside micropores occurred at the same time, and the strength was sharply reduced. In conclusion, the heat treatment method at 500°C for geopolymer had a positive effect on improving the compressive strength.

Keywords: Geopolymer, Heat Treatment, Spent Catalyst Slag, Compressive Strength

1 Introduction

Geopolymers are worth as cement substitutes and fascinating material from ecofriendly construction industries. Because, they release 80% less CO₂ than OPC (Ordinary Portland Cement) and have sufficient mechanical strength like OPC [1]. Geopolymerization involves a chemical reaction between the dissolution of Al and Si at highly alkaline activator and mild temperatures yielding amorphous to polymeric structures, which consist of Si–O–Al and Si–O–Si bonds [2]. Also, geopolymers are inorganic aluminosilicate polymers fabricated from aluminosilicate materials or by-product materials such as metakaolin, blast furnace slag, fly ash and spent catalyst slag with alkali activator solution. In this study, spent catalyst slag was used as raw material of geopolymer. Recently, quantity of platinum-based spent catalyst is increased due to rapid development of industrial. Spent catalyst was fused with fusing agent in order to obtain metals of the platinum group [3]. However, the method produced a lot of wasted spent catalyst slag and the slag affected adverse environmental. Therefore, it is necessary to recycle spent catalyst slag for protecting environment.

Geopolymers have many applications because which have fire resistance and excellent thermal stability, with very little gel structural degradation observed up to 700–800 °C [4]. A lot of scholars have reported geopolymer of heat treatment such as effect of elevated temperatures. The effect of heat treatment on strength is generally influenced by the extent to they can be deformed without fracture, the ductility of a specimen [5]. In addition, which formulations exhibit good thermal resistance due to deleterious effects caused by certain types of secondary phases and aggregates or fillers [6].

However, no dedicated study has been reported about to improve mechanical properties of geopolymer with heat treatment as direct sintering. Therefore, the current study has examined the effect of heat treatment of geopolymer which fabricated by spent catalyst slag as raw material to improve mechanical properties. The mechanism of compressive strength enhancement of the geopolymer was also speculated through the analysis of results.

2 Methodology

2.1 Materials

Raw material of the geopolymer was spent catalyst slag. The slag was obtained after fusing spent catalyst for obtaining metals of the platinum group. Figure 1 shows the XRD pattern of spent catalyst slag as raw material. XRD pattern of spent catalyst was totally amorphous peak without any diffraction line.

Table 1 shows the chemical composition of spent catalyst slag. Spent catalyst slag were prepared from milling for 12hour with planetary ball mill (SFM-1 desk-top planetary ball mill, MTI, USA) and the particles passed a 106 μ m sieve (testing sieve, CHUNG GYE INDUSTRIAL MFG, Co, Korea). Alkali activator solution was used sodium hydroxide pellets (above 97.0% of purity DAEJUNG, Korea).

2.2 Synthesis

The conditions for fabricating geopolymer are organized in Table 2. To synthesis geopolymer spent catalyst used as raw material. Spent catalyst slag were dry mixed for 1min to obtain a uniform mixture. Alkali activator which was prepared combined distilled water with sodium hydroxide one day before mixing was then added to the mixture. The paste was mixed for 5min until became homogeneous and then poured into 5x5x5cm³ cubic mold. The mold was sealed to prevent water loss, which was cured for 24 hours at 70°C, 100% humidity. After processing through three days of the aging stage, geopolymer was exposed heat treatment 1hour. After heat treatment, compressive strength and unit volume weight were measured.

Table 1. Chemical composition of spent catalyst slag and silicon sludge by XRF

Materials	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	Fe ₂ O ₃	K ₂ O	TiO ₂	P ₂ O ₅	ZO ₂
Spent catalyst slag	29.71	35.81	22.66	7.75	0.18	0.64	0.39	0.4	0.5	1.96

Table 2. Conditions for fabricating geopolymer

Heat treatment	Mol concentration	Water/Solid ratio
Room temperature	12M	0.2
500°C		
700°C	15M	
900°C		
1100°C		

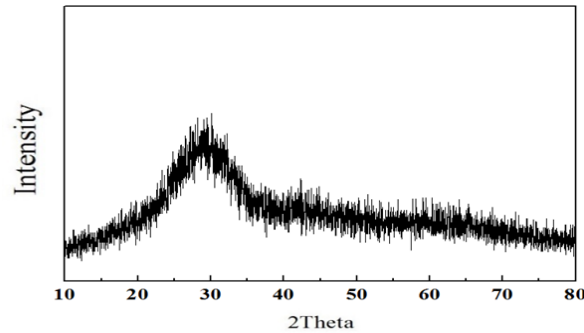


Fig. 1. XRD pattern of spent catalyst slag as raw material

2.3 Heat treatment and analysis

The Specimens after 3 day curing were annealed between 500~1000°C by inserting them direct to the furnace at the desiring temperature. Specimens were then annealed for an hour in the furnace at each temperature.

XRD analysis was performed on the sample with its compressive strength already measured, in order to perform crystalline analysis. X-ray diffraction (XRD, Rigaku MiniFlex2), operated at 40kV, 40mA and, CuK α radiation. The data was collected by using a nominal 2θ step size of 0.01°, count time of 0.5s and 2θ range of 5-90°. The compressive strength were measured by a compression tester (UTM-900NH Series DAEKYUNG, Korea). The microstructure of geopolymer was observed by SEM (scanning electron microscope, S-4800, HITACHI, Japan). Specimens were coated with platinum prior to imaging in the SEM of accelerating voltage of 5kV.

3 Results and Discussion

3.1 Compressive strength

Figure 2 showed the compressive strength and the weight of unit volume of the specimens in accordance with the molar concentration and sintering temperature, after firing the spent catalyst geopolymer slag between 500 ~ 1000°C. When the physical property differences between the molar concentrations were analyzed, it can be confirmed that the expression was the highest strength in 12M, and the more concentration increased, the more strength decreased. This can be seen by dividing the physical and chemical reasons. Physical reasons have been reported to be due to the most appropriate surface area at 12M in the case of the spent catalyst having a particle size of 106 μ m or less [7]. Therefore, it was considered at the large amount of the molar concentration of 15M or more, the remaining excess hydroxide ion which did not react was generated and the alumino-silicate gel was chemically formed very quickly as a factor that degrades the compressive strength [8]. When the temperature increased, the expression had

the highest strength at 500°C and the maximum strength of 90.7MPa was expressed in 12M. The reason that the compressive strength increased with the temperature was thought that as the unreacted alkali activator remaining inside began to react, as the temperature was increased.

Thus, geopolymerization additionally happen in the specimen, as well as the liquid phase sintering (liquid sintering) reaction took place in a high temperature and the microstructure appeared to be in increases of the strength due to being compact (dense) [9]. After the heat treatment at more than 500°C, it seemed a tendency that strength was decreased, which as with the heat treatment on the third day, the water that was left inside, that is, free water in specimens eliminated at 550°C so that due to the weakness of the internal structure, thereby it was determined the compressive strength of the specimen decreased. It could be found the elimination of free water at 550°C via the TG-DTA (Thermogravimetry-Differential Thermal Analysis) results shown in Section 3.3.

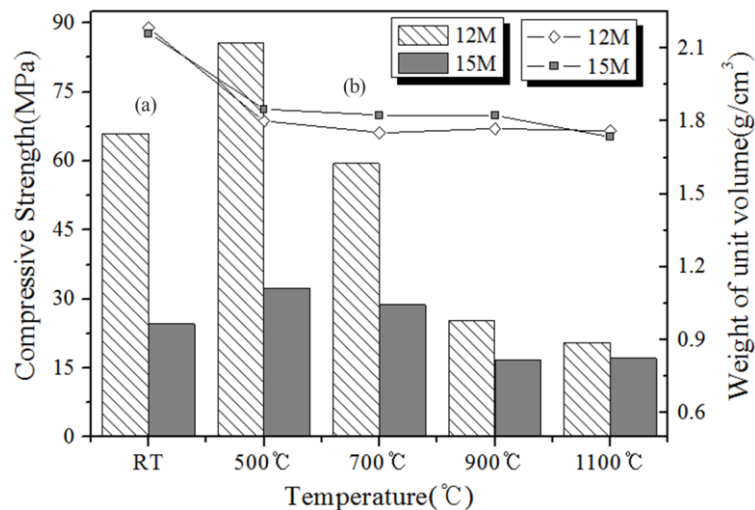


Fig. 2. Compressive strength and weight of unit volume of geopolymer specimens with respect to the mol concentration of alkali activator and annealing temperature. (a) Compressive strength and (b) Weight of unit volume

3.2 XRD

Figure 3 showed the change of XRD pattern in the spent catalyst slag geopolymer for two molar concentration of the alkali activator in accordance with the annealing temperature. At RT (Room Temperature), it was found in both the 12M and 15M, the calcium silicate hydrate (C-S-H) phase appeared as the main peak and the zeolite phase was also present. When the temperature was increased to 500°C, the free water in matrix was evaporated due to dehydroxylation, and the C-S-H phase was reduced and the zeolite phase appeared as the main peak. As zeolite was the sodium aluminum silicate hydrate phase, the peak should be reduced due to the dehydroxylation, but it was believed that the remaining alkali activator still existed because the geopolymerization continued to cause a reaction

with increasing the temperature. Thus, in case of not the direct sintering at high temperature of but sintering from room temperature to high temperature, it was expected to be observed the different XRD pattern. From 700°C up to 1100°C, all the hydrate phases had gone and the calcium aluminum silicate phase appeared as the main peak, and with increasing temperature, the peak was increasing [10]. Calcium aluminum silicate phase primarily constituted of the main phase in the OPC with the expression of a high intensity, but in this study, it has been thought because of the direct sintering at high temperature, free water was rapidly evaporated and as the microstructure was weak as well as decreased the compressive strength.

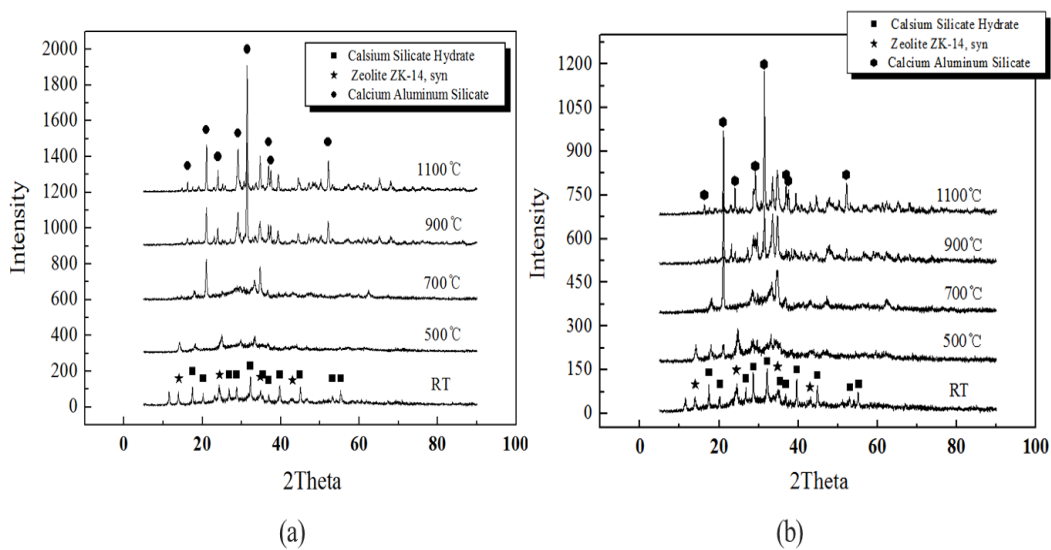


Fig. 3. XRD patterns of geopolymers specimens with two different concentration of alkali activator according to the temperature of heat treatment. (a) 12M and (b) 15M

3.3 TG-DTA

Figure 4 showed the change of XRD pattern in the spent catalyst slag geopolymers for two molar concentration of the alkali activator in accordance with the annealing temperature. At RT (Room Temperature), it was found in both the 12M and 15M, the calcium silicate hydrate (C-S-H) phase appeared as the main peak and the zeolite

Figure 4 showed the TG-DTA results for the specimens produced of two molar concentrations. In the DTA results, it was showing an endothermic peak at about 130°C and an exothermic peak at around 977°C. It was considered that at 130°C as the free water in the specimens was evaporated, the endothermic reactions were taking place, and at 977°C, as generating the calcium aluminum silicate phase, the exothermic reaction took place. In addition, the TG results, it could be seen that the sudden decrease of mass in the two specimen to 550°C. This was considered as a phenomenon as being already explained, the free water in the specimen was evaporated due to dehydroxylation. Thus, as it could be seen

in Figure 2, it was determined that the sharp decrease in the weight of unit volume at 500°C was caused because of this dihydroxylation [11].

Figure 5 showed the microstructure of the spent catalyst slag geopolymer made of the concentration of the alkali activator's 12M. In case of the spent catalyst geopolymer, it was confirmed that it had a very dense microstructure from RT, and from more than 500°C, as increasing the temperature, as shown in Figure 5 small micropores were increasing more and more. It could not be determined only by microstructures pictures presented in this study, the micropores were caused by whether the internal matrix swelling or the destruction of geopolymer network by internal pressure instantaneous increases in the specimen due to steam generated during dehydroxylation reactions or by whether the internal shrinkage due to the sintering phenomena that happened during high temperature sintering process. However, as it could be seen in Figure 5, it seemed sure the micropores formed at high temperature more than 500°C affected the reduction in strength of the samples.

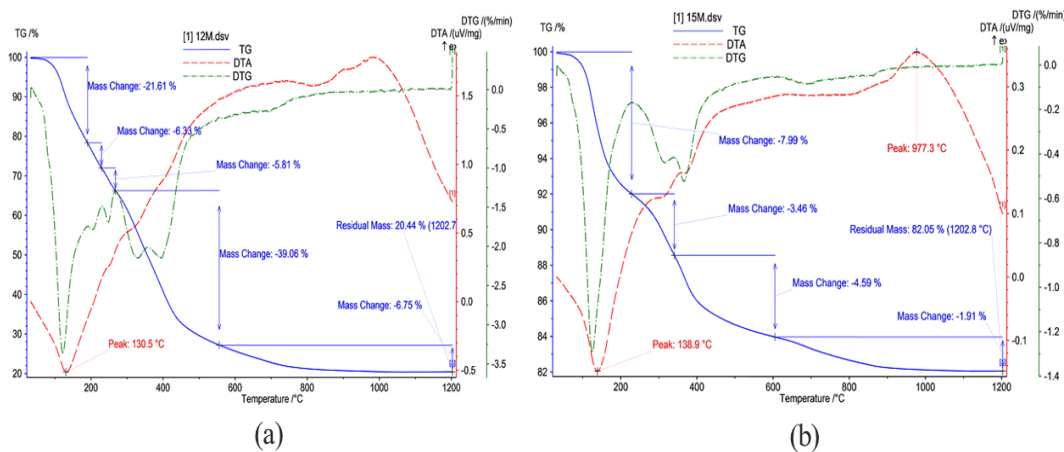


Fig. 4. TG-DTA graphs from geopolymer specimens made with two different concentration of alkali activator. (a) 12M and (b) 15M

Although the identification for the occurrence mechanism of the micropores would be necessary for the next, referring to the case of 500°C specimen, it was determined not to be generated the internal pressure increases in the specimen due to water vapor at the immediately before temperature that dehydroxylation reaction occurred. As shown in Figure 2, by increasing the annealing temperature to 500°C, it could be confirmed the phenomenon that the intensity kept increasing. However, despite the strength development, it was also confirmed the presence of micropores in the specimen annealing at 500°C. This meant that the impact of dehydroxylation reaction on the strength of the specimen was much larger than which of micropores, and it is determined that despite the presence of micropores, the strength was increased up to 500°C by promoting the geopolymerization reaction of unreacted alkali activator and amorphous materials with increasing temperature. In conclusion, as the temperature was increased up to 500°C by the direct sintering at high temperature, due to activation of the unreacted material geopo-

lymerization continued to occur, and it offset the effect of the micropores generated inside the specimen tissue and strength enhancement extent also remain, but it was believed that when the heat treatment at more than 500°C, the strength was reduced rapidly due to the dehydroxylation reaction and the occurrence of internal micropores.

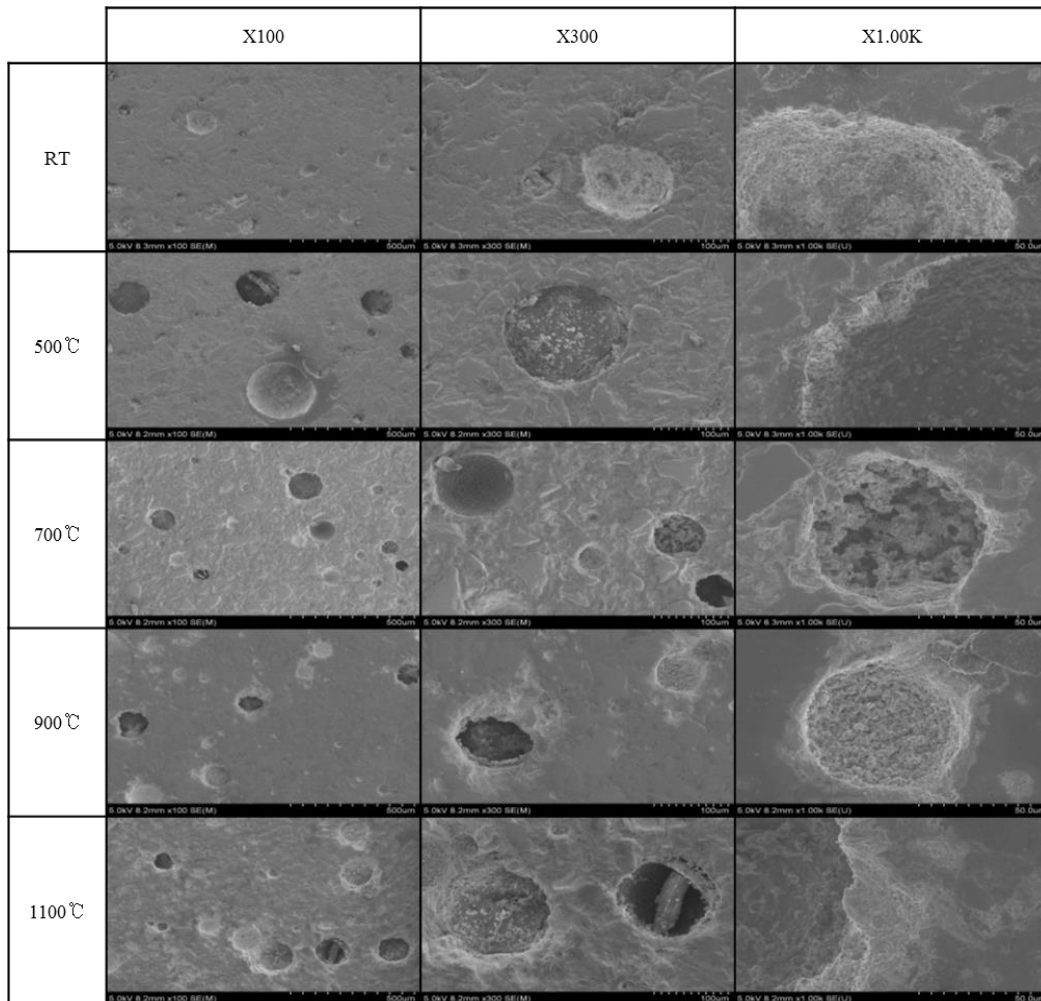


Fig. 5. SEM micrographs of geopolymers with 12M at various annealing temperature

4 Conclusions

In this study, by using the spent catalyst slag with the alkali activators, it was analyzed the effects of heat treatment proceeds by direct heat methods for promoting strength of geopolymer produced at room temperature and having 3 days curing. As a result, the maximum compressive strength (90MPa) was expressed at 500°C, and since then the strength tended to decrease from 700°C up

to 1100°C. It was interpreted by the XRD, TG-DTA and SEM, and it was confirmed that the XRD had at more than 700°C the full phase change in the C-A-S phase. In the TG result, it was confirmed that the free water was eliminated at 550°C. Therefore, it was predicted the reduction in strength of the specimen by increasing internal pressure due to the evaporation of moisture and free water inside material during the direct heat treatment with over 550°C temperature. In the microstructure observation, it was seen that the micropores occurred at over 500°C, but it could not be affirmed the generation of the micropores whether due to dehydroxyle reaction, whether due to a high temperature heat treatment, and also, it could not be interpreted they had a direct effect on the compressive strength of the specimen. Because, even though it was confirmed the micropores in the specimen at 500°C, the compressive strength appeared a maximum. The reason was that as the temperature was increased up to 500°C by the direct heat treatment due to activation of the unreacted material, it was determined that geopolymerization continued to occur and the strength is increase as it offset the effect of the micropores generated inside the specimen matrix, and also remain. When the heat treatment to more than 500°C was in progress, dehydroxylation reaction and inside the micropores were generated at the same time, it was considered that the strength was rapidly lowered.

In the future, it will conduct the systematic study of the strength promotion mechanism and the micropores formation mechanism in high-temperature through the comparison of the direct sintering and the temperature-raising sintering at high temperature that conducted in this study. Also it will also conduct research on lightweight geopolymer added bloating agent.

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