Characterization of metakaolin-based lightweight geopolymers with various foaming agents

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In this study, lightweight foamed geopolymers based on metakaolin were synthesized and characterized. By considering the compressive strength, density, and crystal phase of the specimens according to the type and amount of forming agent, the possibility of replacing Al powder, a foaming agent, with Si sludge in lightweight foamed geopolymers was analyzed. The specimens foamed with Al powder had lower density than those with Si sludge. However, the compressive strength of the former was higher than that of the specimens foamed with Si sludge, owing to a more uniform pore distribution and microstructure. Through this study, lightweight foamed geopolymers having density of 0.36~1.05 g/cm³ and compressive strength of 0.7~4.7 MPa can be prepared by controlling the process conditions such as the amount of Si sludge added, alkali activator concentration, L/S ratio, etc. The possibility of Si sludge replacing Al powder as a foaming agent thus has been demonstrated. The lightweight foamed geopolymer fabricated in this study can be applied to various fields as it can meet the required physical properties according to the application.

Key words: Geopolymer, Light Weight, Si Sludge, Metakaolin.

Introduction

Environmental problems caused by greenhouse gases have occurred in almost all countries around the world since the 2000s. Carbon dioxide, in particular, is a major greenhouse gas. Research to reduce carbon dioxide emissions is being actively conducted around the world [1]. Currently, Portland cement is widely used as a binding material in the construction and civil engineering field. The cement manufacturing industry meanwhile consumes a great deal of energy and emits enormous amounts of carbon dioxide gas during the heat treatment of limestone ($CaCO_3$) and the combustion of fuel [2, 3]. Specifically, 0.4 to 1.0 tons of carbon dioxide is discharged to produce one ton of cement, which accounts for 5-7% of the total carbon dioxide generated by mankind [4, 5]. From this point of view, geopolymers are attracting attention in the production of binders compared to Portland cement concrete as greenhouse gas is rarely generated depending on the weight value of reactive materials of feedstock (SiO_2, NaOH, etc.) [6, 7].

The term "geopolymer" refers to an inorganic polymer synthesized by the chemical reaction of an alumino-silicate precursor with an alkali solution [8]. It is generally prepared by reacting raw materials of rich in Si and Al such as metakaolin with alkali activators such as sodium hydroxide, potassium hydroxide or water glass [9-11]. Geopolymers consist of three-dimensional polymer chains. When an alkali solution is brought into contact with an alumino-silicate oxide as a raw material, Si and Al ions are dissolved. The dissolved ions are polymerized into AlO_4 and SiO_4 tetrahedral precursors [12, 13]. The basic form of the polymer chain produced by the polymerization of precursors is -Si-O-Si-O-Si-. Na^+ ions added to the chain as activators and Al^{3+} ions are substituted at Si^{4+} sites to form a network structure in the form of -Si-O-Al (Na)-O-Si-. This network structure finally generates a polymer structure in the form of $Mn[-(Si-O_2)_z-Al-O]_n-wH_2O$ by a complex reaction, where M is an alkali ion such as Na^+, K^+, Li^+, Ca^{2+}, or Ba^{2+}, Z is 1 to 3, and n is the degree of polymerization. Because of this polymer structure, industrial waste such as blast furnace slag and fly ash, which are mostly composed of Si and Al, are highly applicable as geopolymer materials [14].

Geopolymers have the advantages of excellent mechanical strength, heat resistance, and chemical resistance [15]. Microstructure and mechanical properties of geopolymer highly depends on its composition and curing routes, including type of alkaline cation and its content, Si/Al ratio, M_2O/H_2O ratio, M_2O/SiO_2 ratio, temperature, and humidity, among others [16]. Recently, porous geopolymers with intentional pores have attracted considerable attention for application to high value-added fields such as thermal insulation, soundproofing, and fire resistance [16]. On the other hand, the weight reduction of the construction material has an economic

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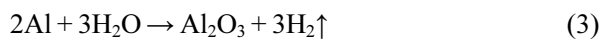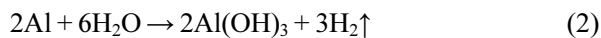 E-mail: sgkang@kgu.ac.kr

advantage because it reduces the weight-bearing burden on each member composing a building. In addition, lightweight materials have low thermal conductivity, which can be expected to provide thermal insulation [17, 18]. For this reason, research to reduce the weight of geopolymers by containing a foaming agent in the manufacturing process have been actively conducted.

In general, there are two common ways to create pores in geopolymers. The first is to use chemical agents to create bubbles by chemical reactions during geopolymer curing and to trap the bubbles in the specimen, and the second is the use of foaming agents, which release the bubbles during mechanical mixing of the geopolymer slurry [19, 20]. The porosity of the lightweight geopolymer is highly dependent on the kind and amount of foaming agent added. It is important to precisely control the manufacturing conditions in order to prevent bubbles from collapsing when the generated bubbles are brought into contact with each other [21].

Al, H_2O_2, Zn, etc. have been used as foaming agents. Recently, V. Medri et al. reported that foamed geopolymers can be prepared through hydrogen gas generation by adding various types of Si [22-24]. Like Al, a reactive metal powder, Si also reacts with water and hydroxides in an alkaline environment to produce hydrogen gas [20]. Reiva et al. reported the pore formation reaction of Si and Al [25]. First, the reaction between Si and alkali activator is shown in Eq. (1).

$$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2\uparrow \qquad (1)$$
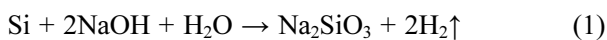
The reactions Al and water or alkali reaction are shown in Eq. (2), (3), and (4).

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2\uparrow \qquad (2)$$

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2\uparrow \qquad (3)$$

$$2Al + 2OH^- + 6H_2O \rightarrow 2Al(OH)_4^- + 3H_2\uparrow \qquad (4)$$

Si also has a similar reaction scheme in which gas is generated by reacting with water or an alkali like Al, a conventional foaming agent. Therefore, Si could be used as a foaming agent. In this study, lightweight foamed geopolymers based on metakaolin were synthesized and characterized. The goal of this study is to replace the existing foaming agent Al with the waste resource Si sludge in synthesizing lightweight foamed geopolymers. In particular, by considering the compressive strength, density, and crystal phase of the specimens according to the type and amount of forming agent, the possibility of replacing Al powder with Si sludge was analyzed.

Experimental

Metakaolin was used as a raw material of the geopolymer. The alkali activator used to activate the geopolymer reaction was sodium hydroxide (Sodium Hydroxide, Duksan, Extra Pure Grade, 93-100%). Alkali activators are prepared by mixing distilled water and sodium hydroxide in a specific molarity. Si sludge used as a foaming agent originates from the silicon wafer cutting process for semiconductors. The particle size of Si sludge used was only 106? or less obtained through the grinding and sieving process. Al powder used as another foaming agent in this study was 99.9% pure and had a particle size of less than 106? like as Si sludge.

Metakaolin and alkali activator were mixed in a bowl for 15 min to activate the geopolymer reaction. The mixed slurry was placed in a $5 \times 5 \times 5 cm^3$ brass mold and compressed with a hand compact. In the curing process, in order to prevent cracking caused by rapid evaporation of water, the green body molded in the mold was put in a zipper bag made of polyethylene together with the mold and then cured at 70 °C for 24 h. After curing, the specimens were aged at room temperature for 3 days.

The chemical composition and crystal phase of metakaolin and the fabricated geopolymer were analyzed using XRF (X-ray Fluorescence; SPECTRO 2000) and XRD(X-ray Diffractometer; MiniFlex II, Rigaku, Japan), respectively. The compressive strength of the produced geopolymer was measured using a universal testing machine (UTM).

Results and Discussion

Table 1 shows the chemical composition of metakaolin indicating that the contents of SiO_2 and Al_2O_3 were 52.1 and 38.5 wt%, respectively. The Si:Al atomic ratio of metakaolin was calculated as 1.14. Al and Si ions could be eluted when an alkaline activator solution is contacted with the alumino-silicate materials, and they can be cured to a dense solid by polycondensation. This process is called a geopolymeric reaction. The geopolymeric reaction might generate various polymers such as poly-sialate–siloxo, poly-sialate–disiloxo, etc. relying upon the ratio of SiO_2/Al_2O_3 in the batch [26].

The ratios of Si/Al of poly-sialates, poly-sialate–siloxo, and poly-sialate–disiloxo are 1, 2, and 3, respectively. It is crucial for the geopolymeric reaction to generate an ortho-sialate oligomer with a Si/Al ratio = 1 because the rate of room temperature polymerization of oligo-sialates was 100 to 1,000 times faster than that

Table 1. XRF of Metakaolin (wt%).

Na₂O	MgO	Al₂O₃	SiO₂	SO₃	K₂O	CaO	TiO₂	Fe₂O₃	Total
0.1	0.3	38.5	52.1	0.2	0.8	2.1	0.5	5.3	100.0

of ortho-silicate or oligo-siloxo units [27]. Among the geopolymers based on various industrial wastes, Si/Al = 17.5 was also reported [28]. Therefore, the present raw material, metakolin with a Si/Al ratio = 1.14, can be considered to be usable as a raw material of geopolymers.

The crystal phase of metakaolin analyzed by XRD is shown in Fig. 1. There were several phases. First, the large humps, indicating that there was a significant amount of amorphous phase in the material. It can be seen also that quartz (SiO_2) and kyanite (Al_2SiO_5) crystal phases also exist. The cations such as Si and Al could be dissolved out from metakaolin when the metakaolin is brought into contact with the alkali solution, owing to the presence of an amorphous phase. It is, therefore, judged to be suitable as a raw material for fabricating geopolymer.

Si sludge is a waste resource emitted during the process of manufacturing silicon wafers for solar cells and semiconductor modules. During the process, about 40% of the silicon is produced as sludge-type waste containing 2% Al_2O_3, a polishing powder used for polishing Si wafers. Although the sludge contained 2% Al_2O_3 phase, the XRD analysis shows only Si crystal peaks, as in Fig. 2.

The compressive strength and density of specimens with a liquid/solid ratio (L/S ratio) ranging from 0.5 to 0.7 were measured and the results are shown in Fig. 3. No foaming agent was added, and the concentration of alkali activator solution used was 9 M. The density decreases with the amount of water because the space occupied by the excess water turned into pores during the drying process. For example, the density of the specimen made with L/S values of 0.5 and 0.7 were 1.5 and 1.37 g/cm^3, respectively. As the L/S ratio increased from 0.5 to 0.7, the compressive strength value decreased from 4.2 to 3.4 MPa, respectively, owing to a decrease in density with an increasing L/S ratio. The specimens shown in Fig. 3 were dense geopolymers without use of a foaming agent, but the compressive strength values
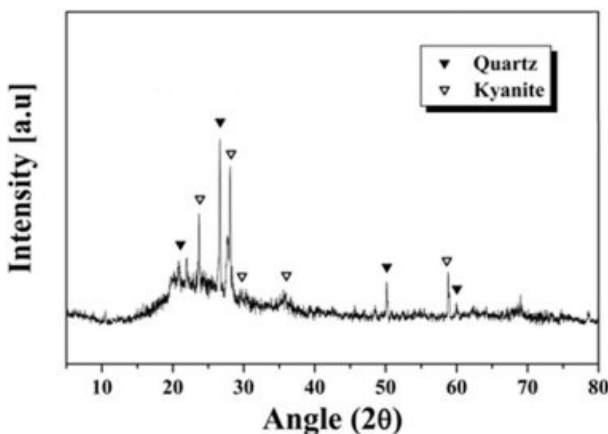
were very low. This is because the molar concentration of the alkali activator used in the specimen preparation was too low. As will be mentioned later in Fig. 5, for the best compressive strength specimens, the concentration of the alkali activator should be 15 M.

XRD analysis results of the specimens according to the L/S ratio are shown in Fig. 4. Regardless of the manufacturing conditions, quartz, kyanite, and zeolite-A crystal phases appeared in all specimens. Quartz and kyanite originate from the starting material, metakaolin. The zeolite phase, which is composed of alumino-silicate crystals, has a chemical formula similar to $Mn[-(Si-O_2)_z-Al-O]_n-wH_2O$, which is the structure of geopolymers. The existence of zeolite phases in the specimen is known to be evidence that the geopolymeric reaction occurred. The zeolite crystals usually can accommodate a wide variety of cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, and others, being rather loosely held. The peak intensities of most of the crystal phases did not change significantly with the L/S ratio, and meanwhile
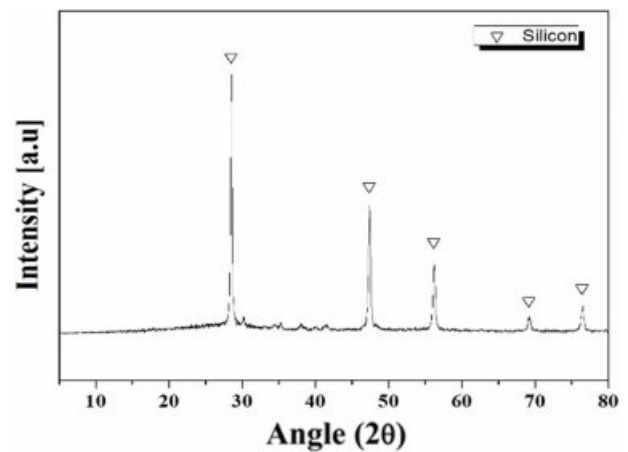

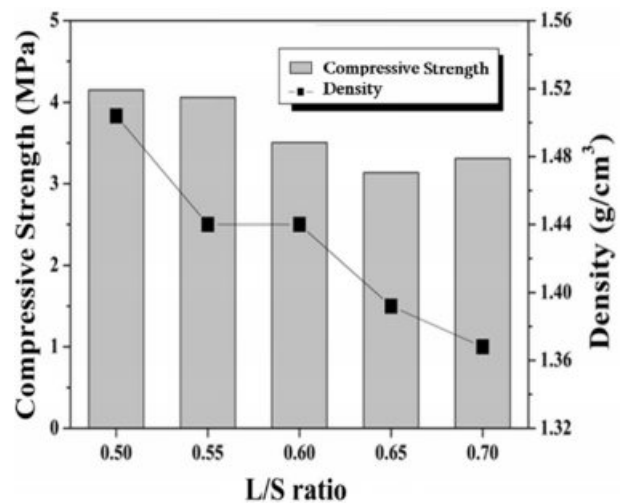Fig. 2. XRD pattern of Si sludge used as forming agent.

Fig. 3. Compressive strength and density of geopolymers made with various L/S ratios. Alkali activator concentration used was 9 M and no foaming agent was added.
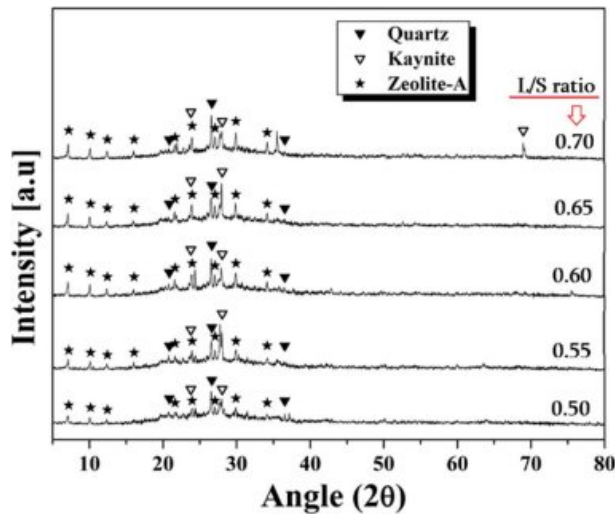

Fig. 1. XRD pattern of metakaolin used as starting material for fabricating geopolymers.

Fig. 4. XRD pattern of geopolymers made with various L/S ratios. Alkali activator concentration used was 9 M and no foaming agent was added.
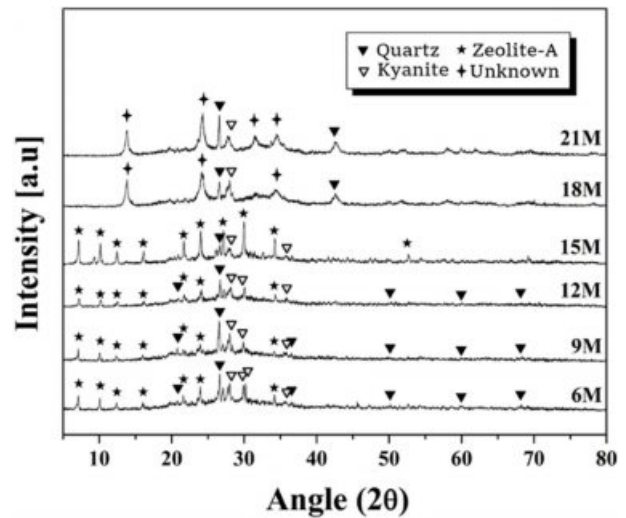

Fig. 6. XRD pattern of geopolymers made with various alkali solution concentrations. L/S ratio used was 0.6.
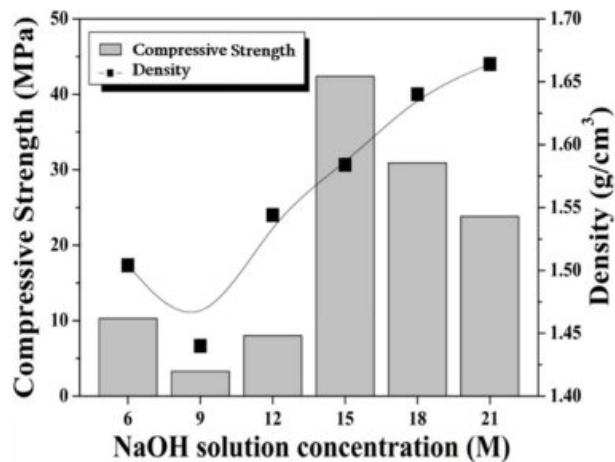

Fig. 5. Compressive strength and density of geopolymers made with various alkali solution concentrations. L/S ratio used was 0.6.

the zeolite-A crystals showed a slight increase in peak intensity with the L/S ratio. As the ions move faster in the liquid phase, the higher the L/S ratio is, the easier the Al and Si ions will be eluted. As a result, the geopolymer reaction took place vigorously through the rich liquid phase, resulting in better generation of the zeolite phase.

The effect of the alkali activator concentration upon the compressive strength and density of the specimen prepared with a L/S ratio of 0.6 is shown in Fig. 5. The density of the specimen has a tendency to increase with increasing activator concentration, except for the specimen of 9 M NaOH. However, the compressive strength was highest at 42 MPa when the concentration of the activator used was 15 M. It is believed that excess alkali interfered with the geopolymer reaction with an alkali activator of 15 M or more. The increase in the density with the concentration of the alkaline solution is likely due to the composition of the liquid phase.

The liquid phase used in this study is a mixture of water and NaOH. The resulting alkaline solution with high molarity is heavier than pure water. Therefore, the higher the molar concentration of the alkaline solution is, the higher the unit weight of the solution will be, and thus the density of the specimen increases.

The XRD analysis results of the specimens prepared with various molar concentrations of alkaline solution are shown in Fig. 6. The L/S ratio used was 0.6. As mentioned earlier, quartz and kaynite originate from the starting material, metakaolin, and the new phase generated by the geopolymeric reaction is zeolite-A crystal. The peak intensity of the zeolite-A crystals tended to increase with the molarity of the alkaline solution within the range of 6-15 M, but the zeolite-A phase disappeared and unknown crystal peaks appeared at a molarity of 18 M or more. As mentioned above, the presence of the zeolite phase is evidence that a geopolymer reaction has taken place. Therefore, the use of an alkaline solution with an excessive molar concentration of 18 moles or more was found to interfere with the geopolymer reaction.

Analyzing the XRD results in Fig. 5 with the compressive strength data in Fig. 6, it can be seen that the compressive strength values increased with the zeolite crystal peak intensity. Thus, it can be seen that the excess alkali activator not only inhibits the geopolymer reaction but also produces an unknown crystalline phase (possibly a Na-based crystalline phase). The resulting unknown crystalline phase lowered the compressive strength value of the specimen. Therefore, for preparing the geopolymer in the present study, the optimum value of the alkaline solution concentration was determined to be 15 M. However, it is thought that the discussion of the exact relationship between the mechanical strength value and the type of crystal phases formed identified by XRD results may be possible when the

additional experiments is performed.

The compressive strength and density of foamed geopolymers containing 1 wt% Si sludge and 15 M NaOH as a function of the L/S ratio are shown in Fig. 7. The density decreased with the L/S ratio. Overall, a lightweight specimen with a density of 0.35 to 1.1 g/cm³ was produced. As shown in Eq. (1), the Si sludge generates hydrogen gas upon contact with water. The generated hydrogen gas is trapped inside the geopolymer and expands to make the geopolymer into a porous structure. As the amount of water in the geopolymer increases, the Si sludge generates more bubbles, which ultimately reduces the density of the specimen. The compressive strength of the specimens was 1.2-8.7 MPa in a L/S ratio ranging from 0.6 to 0.8, with a maximum compressive strength at a L/S ratio of 0.65. When the L/S ratio is 0.6, the dissolution rate of the Si and Al ions is not high enough, and consequently the geopolymer reaction is suppressed and the strength is considered to be low. The compressive strength of the specimen decreased with the L/S ratio in a L/S ratio range of 0.7-0.8. The reason for this is that more porous structures were produced as the amount of water increased. In particular, the strength of specimen made with an L/S ratio of 0.8 was too low to be measured by UTM.

The density and compressive strength of lightweight foamed geopolymer specimens prepared using two kinds of foaming agents, Al powder and Si sludge, are shown in Figs. 8 and 9, respectively. The concentration of alkali activator used when preparing the specimen was 15 M and the L/S ratio was set at 0.65. The specimens foamed with Si sludge had decreased density from 1.33 to 1.06 as the amount of Si sludge added was increased within a range of 0.3-1.0 wt%. The
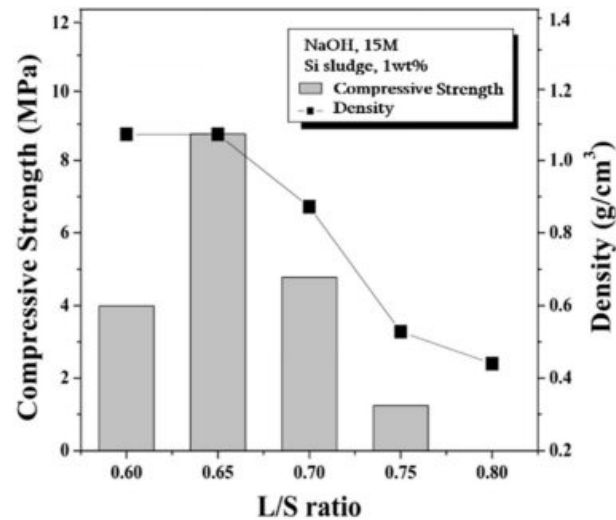
specimens foamed with Al powder had a lower density overall than the Si foamed specimens, and the density change with the amount of Al powder added was not significant. Regardless of the type of foaming agent, the compressive strength decreased as the amount of foaming agent added increased. Overall, the compressive strength of the Al powder-added specimens was higher than that of the Si sludge-added specimens. In particular, in the case of 0.7 wt% foaming agent added, the Al powder-added specimen showed 20.5% higher compressive strength than the Si sludge-added specimen. This is thought to be due to the more uniform pore distribution and microstructure of the specimens made with Al powder than those made with Si sludge, as shown in Fig. 10.

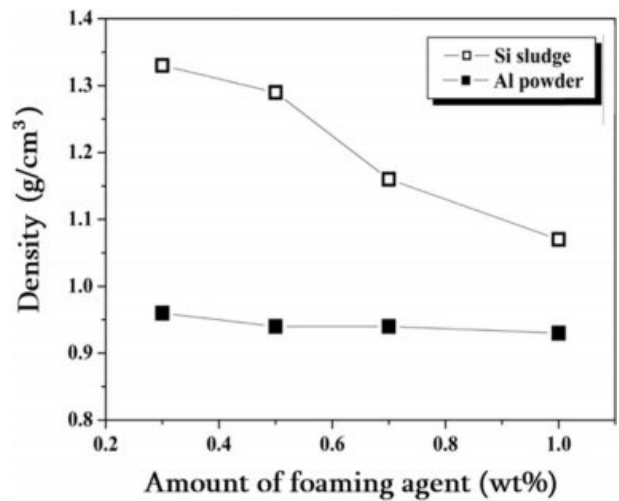Fig. 10 shows photographs of specimens foamed with Al powder (a) and Si sludge (b). The samples

Fig. 8. Graph of density changes of light-weight geopolymers made of Si sludge and Al Powder. Alkali activator concentration used was 15 M, and the L/S ratio used was 0.65.

Fig. 7. Compressive strength and density of light weight geopolymers made with various L/S ratios. Alkali activator concentration used was 15 M, and amount of Si sludge added was 1.0 wt%.
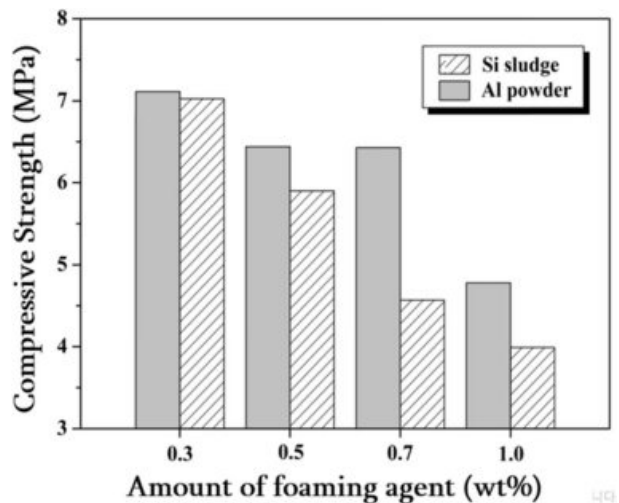
Fig. 9. Compressive strength of light-weight geopolymers made of Si sludge and Al Powder. Alkali activator concentration used was 15 M, and the L/S ratio used was 0.65.

made of Al powder had larger pores than those of the samples made of Si sludge. For this reason, the density of specimens made of Al powder was lower than that of Si sludge. However, it can be seen that the pore size distribution and microstructure of the specimens prepared by Al powder are more uniform than that of the specimens prepared by Si sludge. A non-uniform pore size distribution and microstructure causes the specimen to degrade in terms of compressive strength.

In order to investigate the effect of the large amount of Si sludge addition on the weight reduction of the geopolymer, the density and compressive strength of the specimens prepared with 5 to 20 wt% Si sludge were measured and the results are shown in Fig. 11. The density of geopolymers decreased with the amount of Si sludge added. For example, the densities of the specimen made with 5 and 20 wt% of Si sludge addition were 0.51 and 0.36, respectively. On the other hand, the compressive strength made with 5 wt% Si sludge added was 1.1 MPa, but decreased to 0.8 MPa for the specimen with 10 wt% Si sludge. However, when the added amount was more than 15%, the compressive strength increased conversely with the Si
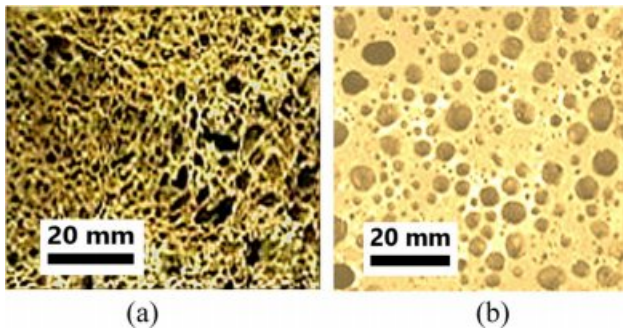
sludge. For example, the compressive strength of the specimen made with 20 wt% Si sludge was 2.5 MPa. The reason why the compressive strength of the specimen made with the foaming agent 15% or more is increased is that bubbles generated on the surface escape easily from the specimen before the specimen is hardened. As a result, the surface was denser than the interior. Of course, there are still many pores inside the specimen, and thus the density decreases with the amount of blowing agent. Due to densification of the surface, it is thought that the compressive strength increased again in the specimen with more than 15wt% of Si sludge. This phenomenon can be seen in Fig. 12. The pores near the surface of the specimen are small, while the pores in the inner part are large.

As a result, it was possible to manufacture metakaolin-based lightweight foamed geopolymers having compressive strength of 0.7-2.4 MPa and density of 0.51-0.36 by using 5-20 wt% of Si sludge instead of Al powder as a
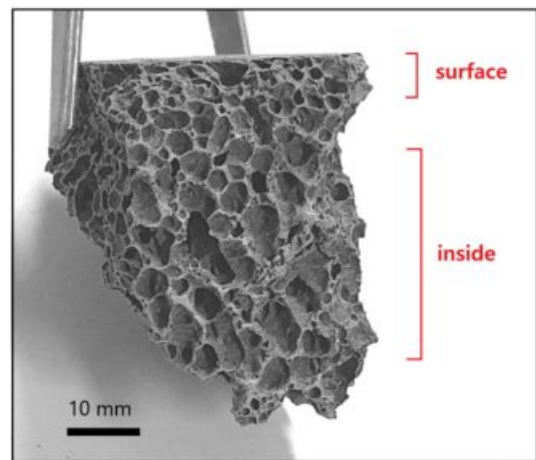

Fig. 10. Optical photograph of light-weight geopolymers made of 0.5 wt% (a) Si sludge and (b) Al Powder. Alkali activator concentration was used 15 M, and the L/S ratio used was 0.65.

Fig. 12. Picture of fractured surface for foamed geopolymer made with 15 wt% Si sludge.
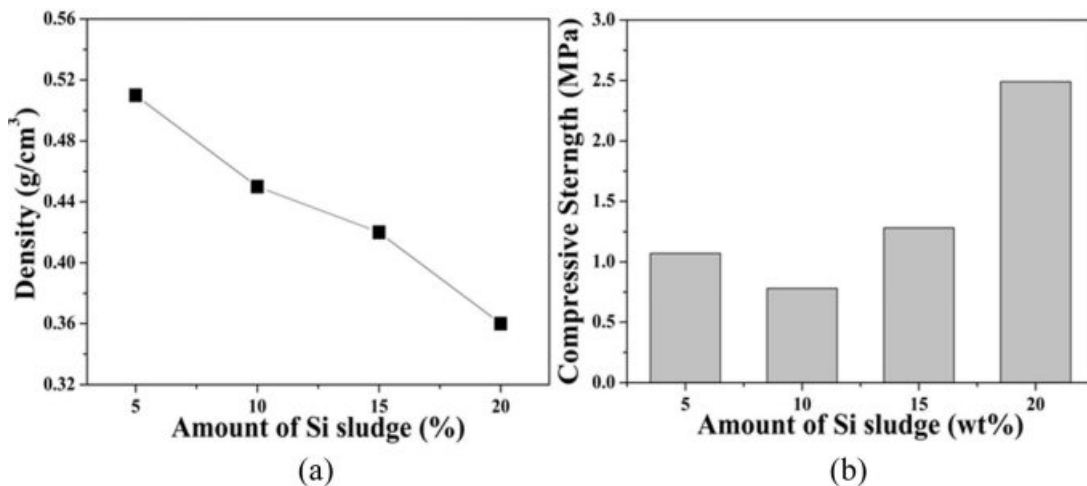

Fig. 11. Physical properties of light-weight geopolymers made with various amounts of Si sludge; (a) density, and (b) compressive strength. Alkali activator concentration used was 15 M, and the L/S ratio used was 0.65.

foaming agent in this study.

Conclusion

In this study, experiments were carried out for the purpose of replacing Al powder, which is used mainly in manufacturing lightweight foamed geopolymer, with Si sludge produced as industrial waste, and we have drawn the following conclusions.

1) The presence of zeolite crystalline phases generated in metakaolin geopolymer specimens indicates that a geopolymeric reaction occurred in the specimen.

2) As a higher L/S ratio is employed, the zeolite phase is well formed due to the active geopolymer reaction caused by easy dissolution of Al and Si ions. Considering formability and reactivity, an L/S ratio of 0.6 ~ 0.65 is suitable for the production of metakaolin-based geopolymers.

3) Increasing the molarity of the alkali activator increased the zeolite crystal peak in XRD analysis, but above 15 M, the excess alkali inhibited the geopolymer reaction and the zeolite crystal phase generation.

4) Partial densification was observed near the surface of the specimen made with more than 15 wt% of Si sludge, resulting in an increase in compressive strength.

5) By adding Si sludge in the place of Al powder, which is a conventional foaming agent, it was possible to manufacture lightweight foamed geopolymer based on metakaolin. By controlling the process conditions such as the concentration of alkali activator, L/S ratio, and the amount of Si sludge added, specimens with a density of 0.36 to 1.05 g/cm^3 and compressive strength of 0.7 to 4.7 MPa could be prepared.

Acknowledgments

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