Properties of Lightweight Composites Using Industry Wastes with NaOH Alkaline Activator

Sungyu Park¹, Thomas Neizert², Yunmi Kim³ and Sangsoo Lee*⁴

¹Associate Professor, Division of Architecture, School of Engineering, Mokwon University, Korea
²Professor, Centre for Advanced Manufacturing Technology (CAMTEC), School of Engineering, Auckland University of Technology, Auckland, New Zealand
³The Doctor's Course, Graduate School of Engineering, Hokkaido University, Japan
⁴Professor, Department of Architectural Engineering, School of Engineering, Hanbat National University, Korea

Abstract
Lightweight concrete has been adopted to prefabricated elements such as facades, staircases and wall systems in housing projects. Many research have been carried out on production of lightweight panels without using ordinary portland cement. The objective of this experimental study was to develop construction materials applicable to lightweight wall system by using ground granulated blast furnace slag and paper ash, which are industrial by-products. Specifically, we carried out an experimental research on the properties of a lightweight matrix that could have application to lightweight wall systems without involving any use of Portland cement that emits massive amount of carbon dioxide (CO₂) from chemical process and burning fuel; the major culprit behind global warming. In this study, we used NaOH alkaline activator to achieve the strength of a ground granulated blast furnace slag-based matrix without using general Portland cement. As a result, the mechanism was uncovered as to how NaOH alkaline activator led to the generation of hydrogen gas through reaction with the unreacted Si of paper ash. In addition, we found that construction materials applicable to lightweight wall systems could be manufactured by using ground granulated blast furnace slag and paper ash, industrial by-products.

Keywords: blast furnace slag powder; paper ash; lightweight composites; alkaline activator

1. Introduction
Lightweight wall systems have been a long-standing subject of study exploring methods to reduce the loads on buildings. Many studies have been conducted on the production of lightweight panels without using cement amid rising demand for the eco-friendly performance of lightweight wall products. In other words, studies have been carried out vigorously to produce inorganic binders by using blast furnace slag and fly ash as well as other materials instead of cement.¹⁻⁸

Blast furnace slag is generated under rapid cooling conditions as an industrial by-product discharged during the steel production process, and therefore a glassy coating in an amorphous state is formed on the surface. Blast furnace slag does not react directly with water due to the impermeable glassy coating. This impermeable glassy coating is destroyed under a

*Contact Author: Sangsoo Lee, Professor, Hanbat National University, 125 Dongseodaero, Yoseong-gu, Daejeon, 305-719, Korea
Tel: +82-42-821-1635 Fax: +82-42-821-1590
E-mail: sslee111@hanbat.ac.kr
(Received April 4, 2016; accepted July 12, 2017)
DOI http://doi.org/10.3130/jaabe.16.619

highly alkaline environment particularly by an alkaline activator, gypsum, etc., such as MOH and M₂OₙSiO₂. Thus, the addition of an alkaline activated agent is essential when only blast furnace slag is used without cement. Once the reaction with the blast furnace slag begins, hydration reaction occurs continuously because the necessary materials are supplied from the blast furnace itself.⁹⁻¹²

Meanwhile, it has been common to use a foaming agent when producing lightweight walls. However, a preceding study¹³ shows that lightweight concrete can be manufactured without a foaming agent when blast furnace slag is used with an industrial by-product that reacts with an alkaline activator. Particularly, if paper ash generated as a by-product in the paper industry is used by being mixed with an alkaline activator, it is possible to manufacture lightweight matrix that has same properties as those of existing lightweight concrete even without any foaming agent.

The first study, which investigated an alkaline-activated inorganic binder using ground granulated blast furnace slag, dates back to 1940 in Belgium.¹⁴ Thereafter, more studies have been conducted to investigate the mechanical properties of concrete using ground granulated blast furnace slag and an
alkaline binder to analyze the hydration mechanism and microstructure\(^{15-18}\). Since 2010, studies have been carried out to investigate paper ash as a material for alkaline-activated inorganic binders\(^{3,19,20}\). Such studies began after the discovery that paper ash generated hydrogen gas by reacting with an alkaline activator\(^{13}\). As a result, it was found that paper ash exhibited some inflatability when mixed only with water and drastically increased inflatability of a binder when the paper ash was used with an alkaline activator that had an OH-group\(^{21}\). In particular, NaOH and KOH showed the greatest reaction among caustic alkalis and are known to be very excellent even for reaction with blast furnace slag, suggesting that a low density, high strength, and lightweight matrix could be manufactured.

In this study, we carried out an experimental research to develop the core material of a lightweight wall system without using general Portland cement based on results of preceding studies. In other words, we conducted an experiment to produce a lightweight matrix by using ground granulated blast furnace slag and paper ash, industrial by-products, and alkaline activator that had an OH- group. We verified the mechanism of hydrogen gas generation caused by unreacted Si of paper ash and thereafter set the experimental formulation and carried out the experiment in relation to density and strength properties of the lightweight matrix. In addition, we examined the reaction characteristics of ground granulated blast furnace slag, paper ash, and NaOH, the alkaline activator.

2. Experimental Program
2.1 Experimental Plan

Table 1. shows the experimental plan. Water/Binder was set to 40% to secure strength of the lightweight matrix throughout preliminary experiment. Additionally, ground granulated blast furnace slag and paper ash, industrial by-products, were used as a binder. The replacement ratio of paper ash for ground granulated blast furnace slag was set to 5%. Moreover, NaOH was used as the alkaline activator. Table 2. shows the mixture proportion of the matrix.

2.2 Experimental Method

For mixing, the mixer shown in Fig.1. was used. First, ground granulated blast furnace slag and paper ash were put into the mixer, followed by a dry mixture for 60 seconds at low speed of 65 revolutions per minute. Then, we added the solution, a mixture of alkaline activator and water, which subsequently underwent stabilization to reduce temperature for 24 hours. After mixing for 60 seconds at the same speed, mixing was carried out for 30 seconds at higher speed of 285 revolutions per minute.

Table 1. Experimental Plan

| Experimental factor     | Experimental level                  |
|-------------------------|-------------------------------------|
| Binder type             | Blast Furnace Slag + Paper Ash      |
| Replacement ratio of paper ash | 5%                |
| Alkaline activator      | NaOH                                |
| Addition ratio of NaOH  | 7.8, 9.8, 10.8, 11.8, 12.8(%)       |
| W/B                     | 40%                                 |
| Curing conditions       | Relative humidity 80 ± 5%, Temperature 20 ± 2°C |
| Test items              | Bulk specific gravity, Compressive strength, SEM-EDS |

![Fig.1. Mixer Used for Experiment](image)

For the production of test pieces, we used a cylindrical mold with a diameter of 100 mm and a height of 200 mm in accordance with KS F 2459. The test pieces were filled with paste and then air-dried cured until bubbles ceased to form, which took about 24 hours. The test pieces were cured under constant temperature and humidity conditions within temperature of 20 ± 2°C and humidity of 80 ± 5%, respectively.

Table 2. Mixture Proportion of the Matrix

| Division | W/B (%) | Binder (g) | Water (g) | Alkaline activator (g) |
|----------|---------|------------|-----------|------------------------|
|          |         | Blast furnace slag | Paper Ash | NaOH                   |
| 7.8%     |         | 40          | 95        | 5                      | 40          | 7.8        |
| 9.8%     |         | 40          | 95        | 5                      | 40          | 9.8        |
| 10.8%    |         | 40          | 95        | 5                      | 40          | 10.8       |
| 11.8%    |         | 40          | 95        | 5                      | 40          | 11.8       |
| 12.8%    |         | 40          | 95        | 5                      | 40          | 12.8       |
The compressive strength was measured at the age of 3 days, 7 days, and 28 days. Bulk specific gravity was measured based on the measurements of weight and volume of the matrix which had been dried after being cured for 28 days. Moreover, we measured SEM-EDS after stopping hydration of the test pieces by age in order to verify the reaction product generated by the alkaline activator and to analyze microstructures.

2.3 Materials

The ground granulated blast furnace slag used in this study had a density of 2.91 g/cm$^3$ and fineness of 4,464 cm$^2$/g. In terms of the chemical composition, it was found that CaO comprised the largest proportion with 52.6%, followed by SiO$_2$ with 28.7% as shown in Table 3.

Fig. 2. shows the SEM (Scanning Electronic microscopy) of blast furnace slag. An SEM image of ground granulated blast furnace slag at 1,000 times magnification demonstrates that the blast furnace slag particle size ranges between 40μm and slightly less than 1μm.

We used the paper ash that had been incinerated to dispose of the paper sludge generated in paper mills and measured a density of 2.70 g/cm$^3$ and fineness of 3,600 cm$^2$/g. Table 4. shows the components of paper ash with CaO comprising 58.7% and SiO$_2$ comprising 12.4%, together they make up more than 70%.

Fig. 3. shows an SEM photo of paper ash. The paper ash consisted of quite a number of fine particles smaller than 1μm and also particles larger than 40μm. The form of particles is an aggregate form without any fixed shape.

In addition, Fig. 4. shows results of XRF (X-ray fluorescence) analysis of paper ash. Based on results of the XRF analysis in which paper ash components in an atomic state were detected, Ca comprised the largest proportion with 46.6%, followed by Si which comprised of 25.6%.

3. Results of Experiment and Analysis

3.1 Density and Unit Volume Weight

Fig. 5. shows the bulk specific gravity and computational unit weight of the lightweight matrix. The unit weight was derived based on density and consumption of the materials used. The unit weight showed an insignificant increase as consumption of NaOH increased. Bulk specific gravity exhibited a light weight below 1.0 g/cm$^3$ for all matrices. This is considered attributable to pores formed in the matrix by hydrogen gas generated as a result of the reaction between paper ash and the alkaline activator.

Regarding the properties of the lightweight matrix based on NaOH addition, the bulk specific gravity tended to decrease as NaOH addition increased when NaOH consumption remained below 10.8%. Above 10.8%, density tended to increase as NaOH addition increased. This is considered attributable to the fact that NaOH consumption was somewhat less than the amount for generation of hydrogen gas by paper ash when NaOH addition remained below 10.8%. By contrast, when NaOH addition exceeded 10.8%, NaOH concentration increased which results in a faster reaction and hydrogen gas was generated from the mixing process in which some NaOH may be lost.

3.2 Compressive Strength of Lightweight Matrix

Fig. 6. shows compressive strength test results of the lightweight matrix by age. All matrices showed a compressive strength of 1.5 MPa or higher at the age of 3 days. A compressive strength of 3.8 MPa, the highest, was manifested in the matrix added with 9.8% NaOH at the age of 28 days, and this surpasses the level of compressive strength required by KS F 4039 at the age of 28 days for a lightweight core. Matrices with 9.8% NaOH developed a strength which was somewhat higher
than matrices with 7.8% NaOH and 10.8% NaOH, respectively. This is considered attributable to inadequate activation of blast furnace slag as a result of a decrease in the pH of the binder when the NaOH addition ratio is 7.8%. Thus, the NaOH addition ratio should exceed 7.8% for a lightweight matrix using the paper ash.

### 3.3 Reaction Product

For the production of a lightweight matrix using industrial by-products, $\text{H}_2$ gas generation is considered attributable to paper ash and an alkaline activator. In other words, $\text{H}_2$ gas generation in specimens is considered to be caused by the reaction between water and caustic alkalis that has an OH-group as shown in the reaction formula (1). Such a reaction may be attributable to unreacted Si included in paper ash and can be expressed by the following formula:

$$\text{Si} + 2\text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SiO}_3 + 2\text{H}_2 + 423.8 \text{ (kJ/mol)}$$

(1)

The aforementioned reaction can be verified through experiments as shown in Fig.7. We investigated whether a combustion reaction occurred when the gas generated by paper ash and an alkaline activator was captured and came close to a fire as shown in Fig.7. As a result, it was found that explosion type combustion reaction was caused by $\text{H}_2$.

Fig.8. shows the SEM images of the lightweight matrix. The image (a) in Fig.8. shows a needle-like crystal and agglomerated crystals. This needle-like crystal is found to have a high peak of Na, suggesting that Na not involved in the hydration reaction rose to the surface of the matrix, and was therefore detected. For the agglomerated crystals observed, it is considered that calcium silicate hydrate gel was created, resulting in strength development of the matrix. The image in (c) of Fig.8. shows a crystal shape similar to monosulfate shown in Fig.9. The SEM image (d) shows spherical crystals and a crack with a width of 5 $\mu$m or slightly larger which is considered likely to affect the bending strength of the matrix.

Fig.9. and 10. show the EDS (Energy Dispersive x-ray Spectroscopy) analysis result of the lightweight matrix. The image (a) in Fig.8. shows a needle-like crystal and agglomerated crystals. This needle-like crystal is found to have a high peak of Na, suggesting that Na not involved in the hydration reaction rose to the surface of the matrix, and was therefore detected. For the agglomerated crystals observed, it is considered that calcium silicate hydrate gel was created, resulting in strength development of the matrix. The image in (c) of Fig.8. shows a crystal shape similar to monosulfate shown in Fig.9. The SEM image (d) shows spherical crystals and a crack with a width of 5 $\mu$m or slightly larger which is considered likely to affect the bending strength of the matrix.

Fig.9. and 10. show the EDS (Energy Dispersive x-ray Spectroscopy) analysis result of the lightweight matrix. The image (a) in Fig.8. shows a needle-like crystal and agglomerated crystals. This needle-like crystal is found to have a high peak of Na, suggesting that Na not involved in the hydration reaction rose to the surface of the matrix, and was therefore detected. For the agglomerated crystals observed, it is considered that calcium silicate hydrate gel was created, resulting in strength development of the matrix. The image in (c) of Fig.8. shows a crystal shape similar to monosulfate shown in Fig.9. The SEM image (d) shows spherical crystals and a crack with a width of 5 $\mu$m or slightly larger which is considered likely to affect the bending strength of the matrix.

Fig.9. and 10. show the EDS (Energy Dispersive x-ray Spectroscopy) analysis result of the lightweight matrix. The image (a) in Fig.8. shows a needle-like crystal and agglomerated crystals. This needle-like crystal is found to have a high peak of Na, suggesting that Na not involved in the hydration reaction rose to the surface of the matrix, and was therefore detected. For the agglomerated crystals observed, it is considered that calcium silicate hydrate gel was created, resulting in strength development of the matrix. The image in (c) of Fig.8. shows a crystal shape similar to monosulfate shown in Fig.9. The SEM image (d) shows spherical crystals and a crack with a width of 5 $\mu$m or slightly larger which is considered likely to affect the bending strength of the matrix.

Fig.9. and 10. show the EDS (Energy Dispersive x-ray Spectroscopy) analysis result of the lightweight matrix. The image (a) in Fig.8. shows a needle-like crystal and agglomerated crystals. This needle-like crystal is found to have a high peak of Na, suggesting that Na not involved in the hydration reaction rose to the surface of the matrix, and was therefore detected. For the agglomerated crystals observed, it is considered that calcium silicate hydrate gel was created, resulting in strength development of the matrix. The image in (c) of Fig.8. shows a crystal shape similar to monosulfate shown in Fig.9. The SEM image (d) shows spherical crystals and a crack with a width of 5 $\mu$m or slightly larger which is considered likely to affect the bending strength of the matrix.
Fig. 7. Experiment for Verification of Hydrogen Gas

Fig. 8. SEM Image of Lightweight Matrix

Fig. 9. EDS of Lightweight Matrix

Fig. 10. EDS of Lightweight Matrix
similar to monosulfate. Based on the EDS analysis, monosulfate components, such as Ca, Si, Al and O were detected.

4. Conclusions
This study was conducted on the production of a low density and high strength lightweight matrix by using ground granulated blast furnace slag and paper ash, as well as an alkaline activator and reached the following conclusions within the specified scope:

- The results of this study show that a lightweight matrix can be produced by mixing appropriate amounts of NaOH with ground granulated blast furnace slag and paper ash, which are industrial by-products.
- The optimal addition ratio of NaOH was found to be 10.8% when considering both density and strength of a matrix using ground granulated blast furnace slag and paper ash.
- Based on results of SEM-EDS analysis, we could verify the reaction characteristics of ground granulated blast furnace slag and paper ash. Major products were found to be Ca (OH)\textsubscript{2}, monosulfate, and calcium silicate hydrate gel.

Subsequent studies need to consider the difference in hydrogen gas generation as a function of temperature, depending on the overall work environment.

Acknowledgement
This research were supported by a grant (12 CTAP D01) from the Construction & Transportation Technology Advancement Research Program funded by the Ministry of Land, Infrastructure and Transport of the Korean government, and by a research grant of 2015 Korea Scientific Research Foundation (NRF-2015R1A2A1A 15055706).

References
1) Aguilar, R. A., Diaz, O. B., and Garcia, J. E. (2010) Lightweight concretes of activated metakaolin-fly ash binders, with blast furnace slag aggregates. Construction and building materials, 24(7), pp.1166-1175.
2) Fernández-Jiménez, A., and Palomo, A. (2005) Composition and microstructure of alkali activated fly ash binder: effect of the activator. Cement and concrete research, 35(10), pp.1984-1992.
3) Joseph, D. (2013) A review on Geopolymer cement, Geopolymer Science and Techinics.
4) Zhang, Z., Provis, J. L., Reid, A., and Wang, H. (2014) Geopolymer foam concrete: an emerging material for sustainable construction. Construction and Building Materials, 56, pp.113-127.
5) Zhang, Z., Provis, J. L., Reid, A., and Wang, H. (2015) Mechanical, thermal insulation, thermal resistance and acoustic absorption properties of geopolymer foam concrete. Cement and Concrete Composites, 62, pp.97-105.
6) Abdulllah, M. M. A. B., Hussin, K., Bhnussuin, M., Ismail, K. N., Yahya, Z., and Abdul Razak, R. (2012) Fly ash-based geopolymer lightweight concrete using foaming agent. International journal of molecular sciences, 13(6), pp.7186-7198.
7) Esmaily, H., and Nuranian, H. (2012) Non-autoclaved high strength cellular concrete from alkali activated slag. Construction and Building Materials, 26(1), pp.200-206.
8) Hung, T. C., Huang, J. S., Wang, Y. W., and Fan, Y. C. (2013) Microstructure and properties of metakaolin-based inorganic polymer foams. Journal of Materials Science, 48(21), pp.7446-7455.
9) Song, S., and Jennings, H. M. (1999) Pore solution chemistry of alkali-activated ground granulated blast-furnace slag. Cement and Concrete Research, 29(2), pp.159-170.
10) Shi, C., and Day, R. L. (1996) Some factors affecting early hydration of alkali-slag cements. Cement and Concrete Research, 26(3), pp.439-447.
11) Shi, C., and Day, R. L. (1995) A calorimetric study of early hydration of alkali-slag cements. Cement and Concrete Research, 25(6), pp.1333-1346.
12) Wang, S. D., and Scrivener, K. L. (1995) Hydration products of alkali activated slag cement. Cement and Concrete Research, 25(3), pp.561-571.
13) Lee, K. P., Lee, S. S., and Song, H. Y. (2011) Cementless type eco-friendly lightweight composite panel using industrial by product. Journal of the Architectural Institute of Korea, 27(11), pp.111-118.
14) Purdon, A. O. (1940) The action of alkalis on blast-furnace slag. Journal of the Society of Chemical Industry, 59(9), pp.191-202.
15) Escalante-Garcia, J. I., Fuentes, A. F., Gorokhovsky, A., Faire-luna, P. E., and Mendoza-Suarez, G. (2003) Hydration Products and Reactivity of Blast-Furnace Slag Activated by Various Alkalis. Journal of the American Ceramic Society, 86(12), pp.2148-2153.
16) Song, S., Sohn, D., Jennings, H. M., and Mason, T. O. (2000) Hydration of alkali-activated ground granulated blast furnace slag. Journal of Materials Science, 35(1), pp.249-257.
17) Haba, M. B., Lotthenbach, B., Le Saout, G., and Winnefeld, F. (2012) Influence of slag chemistry on the hydration of alkali-activated blast-furnace slag—Part II: Effect of Al 2 O 3. Cement and Concrete Research, 42(1), pp.74-83.
18) Tänzer, R., Buchwald, A., and Stephan, D. (2015). Effect of slag chemistry on the hydration of alkali-activated blast-furnace slag. Materials and Structures, 48(3), pp.629-641.
19) Park, S. G., Kwon, S. J., Kim, Y. M., and Lee, S. S. (2013) Reaction properties of non-cement mortar using ground granulated blast furnace slag. The Journal of the Korea Contents Association, 13(9), pp.392-399.
20) Lee, S. S., Kim, Y. M., and Park, S. G. (2014) Strength Properties of Alkali-Activated Lightweight Composite with Alkali Activators of Different Types and Amounts, Journal of Korea Institute Building and Construction, 14(4), pp.301-307.
21) Park, S., Kim, Y., and Lee, S. (2015) Foaming Properties of Lightweight Matrix Based with Non-Reacted Si Blast Furnace Slag. Asian Journal of Chemistry, 27(11), 4216.