

Bloating Mechanism for Artificial Light Weight Aggregate of Surface Modification with Coal ash

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ABSTRACT

We manufacture artificial lightweight aggregates (ALWAs) using bottom-ash as the primary raw material. We coat the ALWA surfaces with low-melting point materials in order to enable them to bloat, which is essential to reduce the bulk density of the aggregate. Then, we sinter the prepared aggregates at 1000, 1100, and 1200°C using either the direct or two-step firing schedules. Finally, we evaluate the properties of the fired samples through analyzing their bulk density, water absorption, and microstructure. The surface-modified samples result in a reduction of their bulk density by 0.3 ~ 0.4 g/cm³ regardless of the firing method used. Based on these results, we conclude that this approach could provide a viable method for the mass-production of ALWAs from industrial waste such as bottom-ash.

Key words : *Lightweight aggregate, Bottom-ash, Bloating, Direct firing, Two-step firing*

1. Introduction

Among the total domestic consumption of electric power, approximately 37% is generated by thermal power plants. However, the process produces over 9 million tons of coal ash as a by-product as of year 2010. Only about 5.25 million tons of them are recycled. The rest, normally consisting of relatively coarse ash with high contents of carbon, are mostly discarded for land-reclamation. This causes problems to the thermal power plants since a rather high expense is needed for an additional construction and management of ash-treating pond.

More serious problem is the fact that the amount of discarded coal ash is increasing since there are more thermal power plants constructed every year. Thus, the coal ash recycling is a critical issue to be resolved. Consequently, research for the viable methods to reuse the waste becomes an urgent task to be investigated.¹⁻⁵⁾

Domestically, various reports on the coal ash recycling and its feasibility study are available that include; for uses as a concrete admixture mainly utilizing the fly ash, as a filler material for road pavement, and as an aggregate for cement mortar replacing the smaller portion of aggregates. We have also involved in researches on the coal ash recycling, and recently, have extended our focus to the industrial wastes recycling especially for manufacturing of artificial lightweight aggregates (ALWA).

Various researches on the waste treatments include; the

property improvement of ALWA with the additions of fluxes³⁾, the feasibility study for ALWA for concrete by utilizing industrial wastes⁴⁾, the manufacturing method of ALWA using the reclaimed ash from thermal power plants⁶⁾, the sintered properties of ALWA prepared from coal ash and limestone⁷⁾, etc. These studies contributed for the reuses of waste materials and established its technical methods. Despite all these efforts, the present status is still far from satisfactory.

Studies on the ALWA mainly focused on the reduction of aggregate's bulk density by bloating. The bloating mechanism involves in the oxidation of carbon followed by reduction of iron that generate gases for bloating. Lee¹⁾ produced the ALWA by adding iron into the batch of mainly coal ash and pointed out that the bloating process was limited due to the cracks on the aggregate surface at the presence of FeO-based melt phase.

Kang *et al.*²⁾ investigated the effects of various carbon sources and its contents on the generation of bloating gases for the ALWA by utilizing coal ash. They presented two difficult cases of achieving lightweight where the lesser contents of carbon resulted in insufficient generation of bloating gases and the excessive contents of carbon in unsatisfactory densification. Tsai *et al.*³⁾ studied the bloating characteristics of ALWA from the recycled sludge in terms of SiO₂-Al₂O₃-flux ratio and found that the properties of ALWA was difficult to predict due to the diversity of raw material in composition-wise.

This study involves in the manufacturing of ALWA from the coal ash for land-reclamation by employing the surface coating technique with low-melting materials such as slag, dredged-soil, and acidic clay. We sintered the coated aggregates via both direct and two-step firing schedules. We expected that

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the formation of surface melt layer at firing temperatures successfully trap bloating gases.

We investigated the properties of the foamed aggregates and analyzed the characteristics of bloating mechanism. We finally, based on the results, examined the feasibility of this approach to the mass production of ALWA.

2. Experimental Procedure

2.1. Raw materials

Coal ash, the main raw material, is the discharged bottom-ash from the combustion of bituminous coal in Y thermal power plant. Coating materials used for experiments are dredged-soil that occurred during the plant construction, slag from plasma-melting furnace, and acidic clay (Donghae Chemicals Ind. Co. Ltd., Korea). All raw materials were ground < 100 μm using a pin mill. The chemical compositions of the ground raw materials were analyzed by XRF (ZSR- 100e, Rigaku, Japan) as shown in Table 1.

2.2. Preparation and analysis of ALWA

The preliminary samples were made of 100% of each raw materials alone (bottom-ash, dredged-soil, slag, or acidic clay) that was ground to < 100 μm to evaluate their behaviors under firing. Based on the results from the preliminary samples, the mixed samples of bottom-ash and dredged-soil with the wt. ratio of 70 : 30 were prepared. The specific wt. ratio is based on the fact that bottom-ash itself has no plasticity and has not enough bloating capability at low temperatures due to its high refractoriness. Dredged-soil, however, can provides the necessary plasticity to bottom-ash and could contribute in lowering the refractoriness of the mixture.

All samples formed into the sphere-like shapes with diameters of about 10 mm. In addition, to observe how each raw materials behave on the surface of aggregates, we coated the

surfaces of the formed aggregates with about 5 wt% of flux materials such as slag, dredged-soil, or acidic clay. We, then, dried the coated samples in a dryer of 105°C for 24 h. We selected two firing methods, a direct firing and a two-step firing, to modulate and optimize the escaping rate of bloating gases and the densification and vitrification rates of surface.

In the case of direct firing, we sintered at maximum temperatures of 1000°C, 1100°C, and 1200°C for 10 min to minimize the loss of bloating gases. In the case of two-step firing, on the contrary, we first sintered at lower temperature of 900°C and increased the temperature up to 1150°C for the secondary sintering and surface vitrification. This procedure could provide the maximum generation of useful bloating gases and, at the same time, their escape out of aggregates could be minimized.

Three different schedules were adopted for the two-step firing; (I) 7 min at 900°C+3 min at 1150°C, (II) 10.5 min at 900°C+ 4.5 min at 1150°C, and (III) 14 min at 900°C+ 6 min at 1150°C as shown in Fig. 1. After firing, we measured bulk density and water absorption of each sample according to KS L 3114 standard. We also analyzed the microstructure of cross-sectional surfaces under the optical microscope (Camscope, DSC-105, Sometch, Korea) to observe the effects of coating materials, temperature, and firing methods.

3. Results and Discussion

3.1. Melting behaviors of raw materials on surface

ALWA achieves its low densities by bloating, and the bloating mechanism involves in generation of gases and their trapping inside of the aggregates. The organic matters and carbon included in raw materials can generate bloating gases by oxidation during firing. After a densified layer forms on the surface shell, no further oxidation will take place. Instead, a reducing atmosphere is created inside of aggregates and several reduction processes will take place:

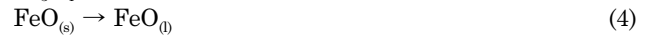
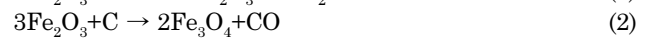
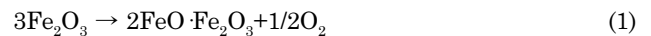


Table 1. Chemical Compositions of Raw Materials (wt%)

	Bottom-ash	Dredged-soil	Slag	Acidic clay
SiO ₂	60.82	70.05	48.61	56.74
Al ₂ O ₃	25.42	14.25	12.40	13.10
Fe ₂ O ₃	4.14	3.78	5.47	7.42
CaO	1.00	0.78	21.00	3.58
MgO	0.94	0.18	2.55	2.60
Na ₂ O	0.08	2.4	0.620	1.98
K ₂ O	3.23	2.67	1.01	2.41
TiO ₂	0.84	0.79	0.72	1.10
P ₂ O ₅	0.12	0.03	1.03	0.52
MnO	0.03	0.00	0.37	0.14
C	1.74	0.00	0.00	0.00
SO ₃	0.43	0.00	0.00	0.00
Cr ₂ O ₃	0.00	0.00	0.69	0.00
Ig loss	1.04	4.04	0.00	10.40
Total	100	100	100	100

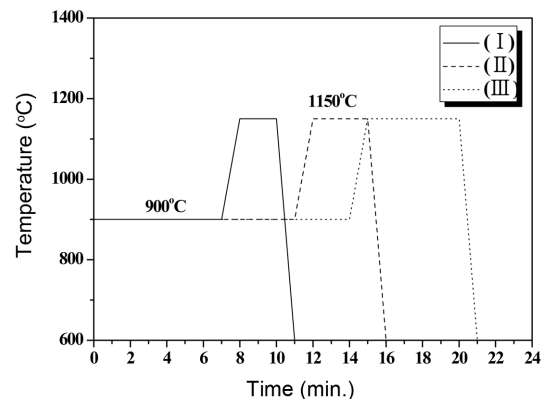


Fig. 1. Schedules of two-step firing.

It is believed that Reaction (1) ~ (3), which involve in the generation of oxygen and CO are responsible for the bloating action and, thus, the reduction of aggregate bulk density.¹⁾ Trapping the generated gases, however, depends on the densification of aggregate surface. At firing temperatures, the surface of aggregates should densify close to a gas-tight state and should be able to expand by the pressure build-up of the bloating gases. Vitreous surface of low-melting compounds is highly desirable since it can form almost pore-free layer and provide viscous flow as the sintering mechanism so that the surface can flow under the pressure applied by gases.⁴⁾

Figure 2 shows bulk densities and water absorptions of different raw materials at various temperatures. The sample of 100% slag started its sintering at 700°C and formed

vitreous surface above 900°C eliminating all of its pores and reducing the water absorption down to almost zero. In the case of acidic clay, its bulk density decreased drastically in temperature range of 1000 ~ 1100°C. Its water absorption, however, started to decrease at 700°C and gradually reduced down to about 4%. It indicates that acidic clay can form vitreous phase at relatively low temperatures. The increase of water absorption at 1100°C seems to be caused by the cracks on the surface as shown in optical images in Fig. 3.

Dredged-soil showed a decreasing tendency of bulk density starting at about 1000°C and decreasing water absorption in the temperature range of 1100 ~ 1200°C which is indicative of the formation of vitreous phase. In the case of samples of 100% bottom-ash, they showed some tendency of

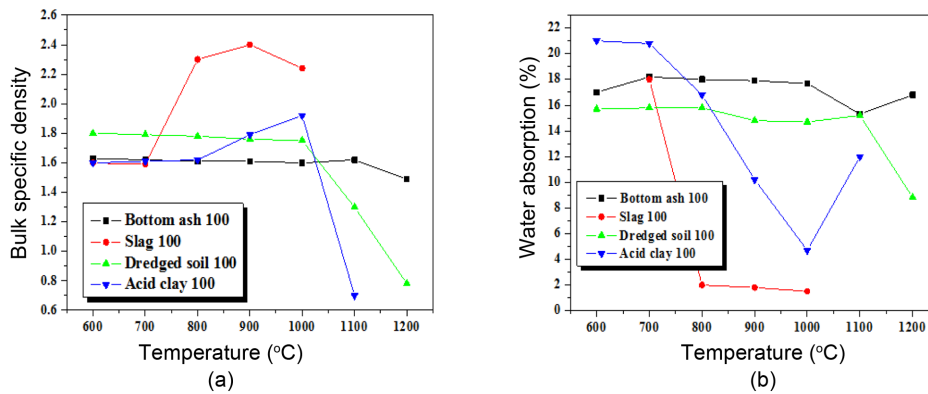


Fig. 2. Physical properties of aggregates of various raw materials with temperature: (a) bulk density and (b) water absorption.

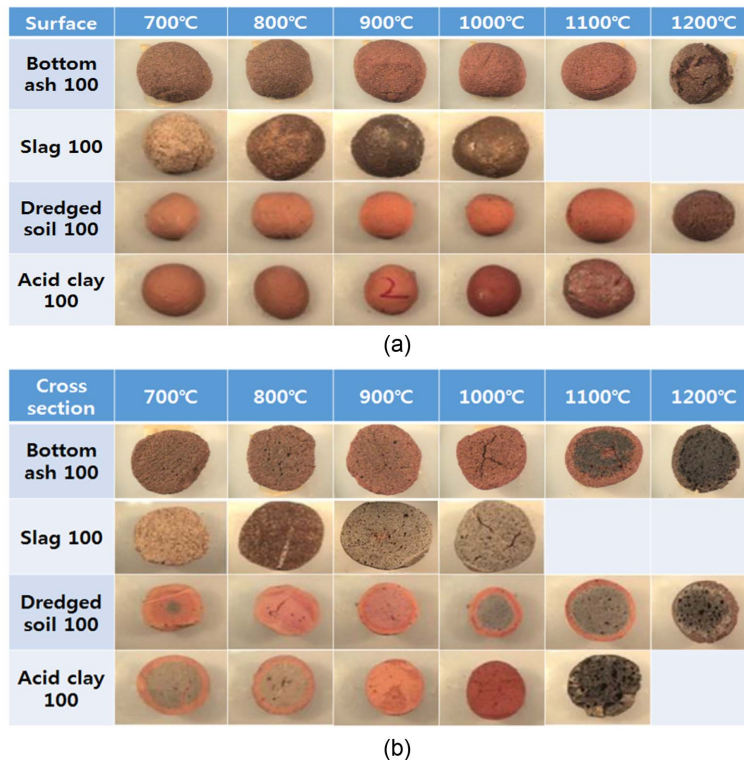


Fig. 3. Microstructure of various lightweight aggregates with temperature: (a) surface and (b) cross section.

decreasing bulk density above 1100°C. But they showed no noticeable bloating probably due to its high refractoriness. They also showed, just like the case of acidic clay, increase in water absorption starting at 1200°C with the cracks on the surface.

Surface images in Fig. 3 show that slag forms vitreous phase starting at 900°C and tightly encloses the sample with the surface layer. Both surface and cross-sectional surface images of samples with acidic clay show that vitreous phase start to form at 700°C and gradually encloses the sample with the surface layer. In the case of dredged-soil, black core starts to form at 1000°C and vitreous phase in the temperature range of 1100 ~ 1200°C.

3.2. Properties of surface-modified ALWA

3.2.1. Direct firing

As shown in Fig. 2, aggregates of 100% bottom-ash showed surface vitrification and bloating starting at 1200°C. On the contrary, all three aggregates of 100% of slag, dredged-soil, or acidic clay showed surface vitrification starting at much lower temperatures.

Figure 4 shows bulk density and water absorption of

aggregates made of bottom-ash with or without coating. Without coating, the sample's behavior is similar to the 100% bottom-ash as shown in Fig. 2. It shows no densification on surface or bloating up to 1100°C maintaining its bulk density of 1.6 g/cm³. Its bulk density reduced down to 1.2 g/cm³ at 1200°C with surface vitrification and bloating.

All coated aggregates, on the contrary, started the bloating at 1000°C, and achieved low bulk densities of 1.3 ~ 1.4 g/cm³ satisfying the KS F 2534 standard for an ALWA. This can be confirmed in cross-sectional images in Fig. 5 that the uncoated aggregates form black core and large pores at 1200°C, while coated aggregates form pores starting at 1000°C.

Figure 4(b) shows the contradicting tendency in bulk density and water absorption between uncoated and coated aggregates. This attributes to the fact that the coating layer is applied less densely (Fig. 6). The reason that this tendency is different from the water absorption in Fig. 2(b) is that the surface of uncoated aggregates were under the maximum-temperature exposure for 10 min by direct firing and, thus, their sintering proceeded more than the case for the coated aggregates.

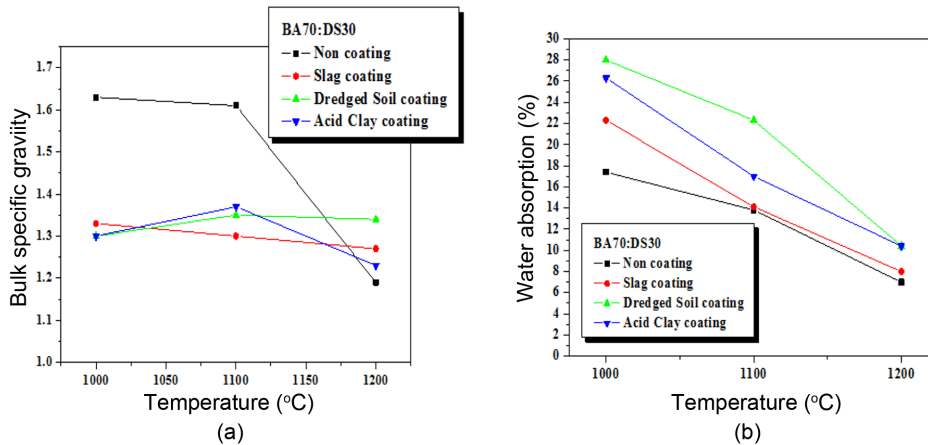


Fig. 4. Physical properties of direct-fired aggregates with temperature (BA70:DS30).

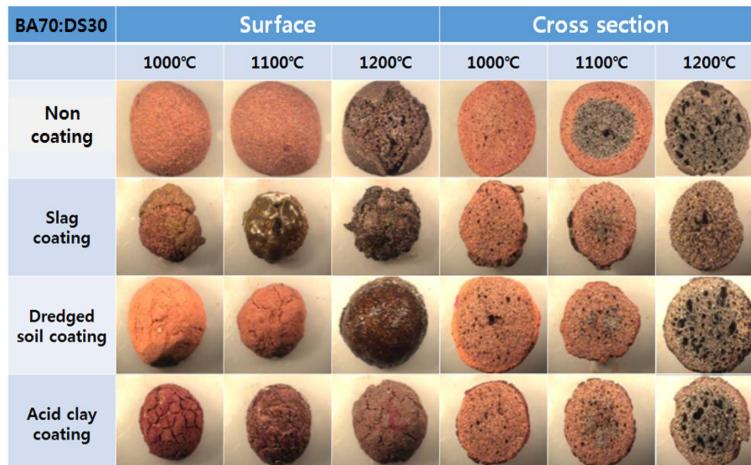


Fig. 5. Microstructure images of direct-fired ALWA with different coatings.

3.2.2. Two-step firing

ALWA are produced by sintering in a rotary kiln in mass production line and the aggregates travel from low-temperature zone to high-temperature zone. Direct firing can describe the bloating behavior but can not properly describe the process of gas trapping. The two-step firing in this study is designed to evaluate both the bloating and gas trapping mechanisms.

As shown in Fig. 4, the coated samples showed surface densification starting at 1000°C under direct firing. We, thus, determined the temperature for first step firing at 900°C. The uncoated aggregates showed bloating at 1100 ~ 1200°C under the two-step firing. We, thus, set the maximum temperature at 1150°C for three different holding times; 10 min (I), 15 min (II), 20 min (III) (Fig. 1).

Figure 6 shows bulk density and water absorption of aggregates made of bottom-ash with coating and fired in two steps in terms of firing temperature and raw materials for coating. Compared to the uncoated samples, the coated samples by two-step firing at 900°C for 7 min plus at 1150°C for 3 min decreased its bulk density by 0.3 ~ 0.4 g/cm³. All coated aggregates showed lower bulk densities in all temperature range of firing.

This indicates that the uncoated aggregates generate more gases at 900°C when the holding time is prolonged. The gases, however, escape out of aggregates since the aggregate surface can not keep them due to the lack of densification that leads to no bloating. On the contrary, the coated aggregates are able to achieves densification and vitrification on surface at 1150°C. The aggregates are eventually able to be bloated and reduce their bulk densities. By comparing between the direct firing and the two-step firing, we confirmed that trapping of bloating gases has more critical effects than its amount generated on the formation of foamed aggregates which leads to the importance of surface densification and vitrification on bloating.

In the case of slag coated aggregates, the generation of foam gases and vitrification proceeded at the same time at 900°C. Therefore, bloating took place in the case (I), while sintering took place in the cases of (II) and (III) resulting increase in bulk density, which can be considered almost same as the behavior of bulk density in Fig. 2(a).

Figure 7 is optical images of two-step fired specimen of aggregates coated with each raw materials. They revealed many pores generated in the interior of aggregates compared to the uncoated aggregates owing to the low-melting

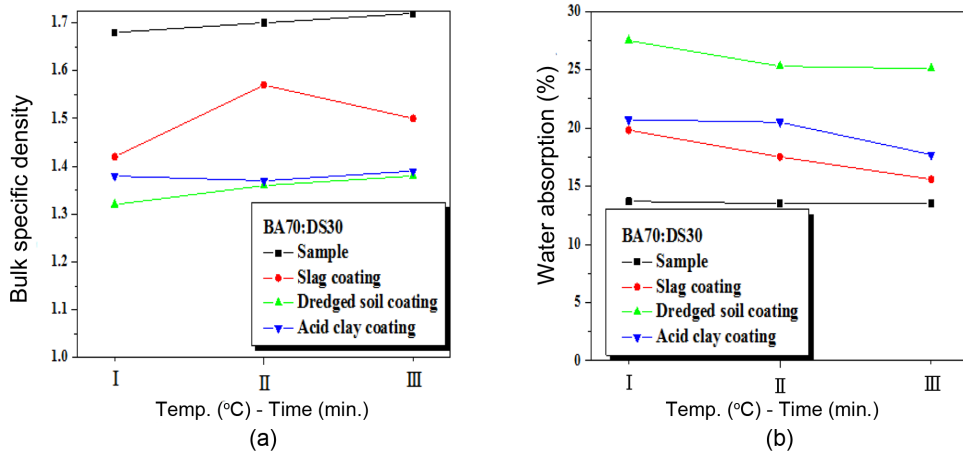


Fig. 6. Physical properties of two-step fired aggregates with temperature (BA70:DS30): (a) bulk density and (b) water absorption.

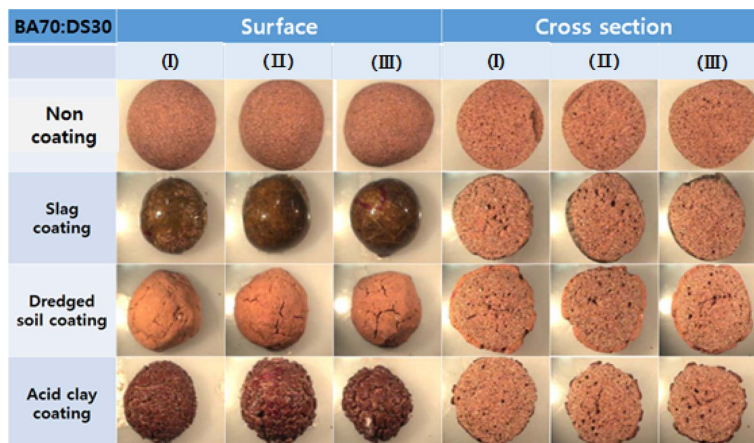


Fig. 7. Microstructure images of two-step fired ALWA with different coatings.

coat layer. It is confirmed that the decreasing tendency of bulk density is similar to the case of direct firing. By two-step firing, trapping behavior of bloating gases was evaluated. We expect that the results of this study on bloating behavior could be adopted to the rotary kiln in an actual mass production line.

4. Conclusion

Based on the firing characteristics of waste materials such as bottom-ash, dredged-soil, slag, and acidic clay, we prepared a mixed sample of bottom-ash and dredged-soil with the wt. ratio of 70:30 and formed into the sphere-like shapes with diameters of about 10mm as ALWA. Dredged-soil effectively moderated bottom-ash's lack of plasticity and too-high of refractoriness making the mixture appropriate for an ALWA.

With the coating on surface of aggregate with low-melting oxides, bloating is achieved during the direct firing or the two-step firing. Findings on the mechanism of bloating are:

1) Compared to the uncoated samples, the coated samples with low-melting materials such as slag, dredged-soil, or acidic clay reduces the bulk density of aggregates by $0.3 \sim 0.4 \text{ g/cm}^3$ when they were fired under either schedule at relatively low temperature of 1100°C .

2) We fired the aggregates directly or in two steps to modulate the rate of the gas generation and its escape out of aggregates along with the densification and vitrification rates on surface. We concluded that the trapping of bloating gases has more critical effects than its amount generated on the formation of bloated aggregates.

3) Both direct firing or a two-step firing show same tendency of reducing the bulk density of aggregates and, thus, give a promising aspect when these procedures are implemented under the conditions of mass production.

Acknowledgments

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REFERENCES

1. K. G. Lee, "Bloating Mechanism for Coal Ash with Iron Oxide," *J. Korean Assoc. Cryst. Growth. Technol.*, **24** 77-83 (2014).
2. S. H. Kang, K. G. Lee, Y. T. Kim, and S. G. Kang, "Effects of Chemicophysical Properties of Carbon on Bloating Characteristics of Artificial Lightweight Aggregates Using Coal Ash," *Adv. in Sinter. Sci. Technol. II*, **232** 35-42 (2011).
3. C.-C. Tsai, K.-S. Wang, and I.-J. Chiou, "Effect of SiO_2 - Al_2O_3 -Flux Ratio Change on the Bloating Characteristics of Lightweight Aggregate Material Produced from Recycled Sewage Sludge," *J. Hazard. Mater.*, **134** [1-3] 87-93 (2006).
4. S. H. Kang and K. G. Lee, "Bloating Mechanism of Artificial Lightweight Aggregate for Recycling the Waste Glass(in Korean)," *J. Korean Ceram. Soc.*, **47** [5] 445-49 (2010).
5. S. J. Lee and T. Y. Lee, "Field Tests for the Application of Bottom-ash and Shred Tire as Fill Materials," *J. Korean Geo-Environ. Soc.*, **14** [10] 29-37 (2013).
6. K. D. Kim, J. H. Kim, Y. T. Kim, S. G. Kang, and K. G. Lee "Production of Lightweight Aggregates Using Power Plant Reclaimed Ash(in Korean)," *J. Korean Ceram. Soc.*, **47** [6] 583-89 (2010).
7. D. S. Kim, C. K. Lee, and J. H. Park, "Sintering Properties of Artificial Lightweight Aggregate Prepared from Coal Ash and Limestone(in Korean)," *J. Korean Ceram. Soc.*, **39** [3] 259-64 (2002).
8. C. M. Riley, "Relation of Chemical Properties to the Bloating of Clay," *J. Am. Ceram. Soc.*, **34** [4] 121-28 (1951).
9. P. S. Nicholson, "Kinetics of Oxidation of Natural Organic Materials in Clays," *J. Am. Ceram. Soc.*, **53** [3] 154-58 (1970).
10. V. A. Abdakhimov and E. C. Abdrakhimova, "Formation of the Black Core in High-speed Firing of Floor Tiles," *Glass Ceram.*, **56** [7-8] 263-65 (1996).
11. W. E. Brownell, "Black Coring in Structural Clay Products," *J. Am. Ceram. Soc.*, **40** [6] 179-87 (1957).
12. M. A. Kang, S. G. Kang, K. G. Lee, and Y. T. Kim, "Fabrication of Artificial Light-weight Aggregates of Uniform Bloating Properties Using a Temperature-raising Sintering Method(in Korean)," *J. Korean Ceram. Soc.*, **49** [2] 161-66 (2012).