

Flowability and Strength Development Characteristics of Bottom Ash based Geopolymer

Si-Hwan Kim, Gum-Sung Ryu, Kyung-Taek Koh, and Jang-Hwa Lee

Abstract—Despite of the preponderant role played by cement among the construction materials, it is today considered as a material destructing the environment due to the large quantities of carbon dioxide exhausted during its manufacture. Besides, global warming is now recognized worldwide as the new threat to the humankind against which advanced countries are investigating measures to reduce the current amount of exhausted gases to the half by 2050. Accordingly, efforts to reduce green gases are exerted in all industrial fields. Especially, the cement industry strives to reduce the consumption of cement through the development of alkali-activated geopolymer mortars using industrial byproducts like bottom ash. This study intends to gather basic data on the flowability and strength development characteristics of alkali-activated geopolymer mortar by examining its FT-IT features with respect to the effects and strength of the alkali-activator in order to develop bottom ash-based alkali-activated geopolymer mortar. The results show that the 35:65 mass ratio of sodium hydroxide to sodium silicate is appropriate and that a molarity of 9M for sodium hydroxide is advantageous. The ratio of the alkali-activators to bottom ash is seen to have poor effect on the strength. Moreover, the FT-IR analysis reveals that larger improvement of the strength shifts the peak from 1060 cm^{-1} (T-O, T=Si or Al) toward shorter wavenumber.

Keywords—Bottom Ash, Geopolymer mortar, Flowability, Strength Properties.

I. INTRODUCTION

COAL ash stands for the residual substance after the instantaneous combustion of coal at $1500 \pm 200\text{ }^\circ\text{C}$ in suspended state and is generally divided into fly ash and bottom ash[3]. The thermoelectric power plants in Korea produced about 4.5 million tons of coal ash in 2000 and increased up to 8.3 million tons in 2010 [3], [7].

Besides, following the advances realized in the construction technology accompanying the boom of the industrial sector in the 20th century, the consumption of cement experienced tremendous growth together with significant development of its utilization technology achieved by numerous researchers. However, despite of the preponderant role played by cement

among the construction materials, it is today considered as a material destructing the environment due to the large quantities of carbon dioxide exhausted during its manufacture[11]. Global warming is now recognized worldwide as the new threat to the humankind against which advanced countries are investigating measures to reduce the current amount of exhausted gases to the half by 2050 [5], [9].

Accordingly, efforts to reduce green gases are exerted in all industrial fields. Especially, the cement industry strives to reduce the consumption of cement [16] through the development of alkali-activated geopolymer mortars using industrial byproducts like bottom ash [13]. Coal ash is widely used as binder for the fabrication of alkali-activated geopolymer mortar. In the case of fly ash, 70 to 80% of the production is recycled in all types of industrial sectors based on the results of dedicated researches. On the other hand, the lack of development in the recycling technology for bottom ash results in merely 30% of recycling while the remaining production is buried in landfills [4].

The fly ash used in the research on alkali-activated geopolymer mortar promotes the development of strength through the geopolymerization with the Si and Al components [5], [9], [10]. Therefore, the development of strength through geopolymerization can be sufficiently achieved by bottom ash composed mainly by Si and Al. However, bottom ash exhibits significantly higher fineness, uneven granulometry and grain shape, and weaker reactivity than fly ash. Several researchers pulverized bottom ash and applied the so-obtained powder in alkali-activated geopolymer mortar to solve these drawbacks [2], [14], [15].

Accordingly, this study investigates the effects of the alkali-activator in order to develop alkali-activated geopolymer concrete using a binder constituted by bottom ash improved to a level corresponding to class F fly ash. In addition, the FT-IR features are examined with respect to the content in blast furnace slag and the curing duration to gather basic data on the flowability and strength development characteristics of alkali-activated geopolymer mortar.

II. TEST SETUP

A. Materials

Table I compares the physical and chemical properties of fly ash and bottom ash milled by vibration. Fig. 1 plots the particle size distribution of fly ash and bottom ash. The milled bottom ash secures a fineness equivalent to fly ash and its chemical composition includes large contents in the reactive oxides SiO_2 (58.3%) and Al_2O_3 (22.2%). In addition, the bottom ash that

Si-Hwan Kim is with the Structural Engineering Research Division, Korea Institute of construction Technology(KICT), Goyang, Korea (phone: +82-31-910-0714; fax: +82-31-910-0715; e-mail: shkim@kict.re.kr).

Gum-Sung Ryu is with the Structural Engineering Research Division, Korea Institute of construction Technology(KICT), Goyang, Korea (e-mail: ryu0505@kict.re.kr).

Kyung-Taek Koh is with the Structural Engineering Research Division, Korea Institute of construction Technology(KICT), Goyang, Korea(e-mail: ktgo@kict.re.kr).

Jang-Hwa Lee is with the Structural Engineering Research Division, Korea Institute of construction Technology(KICT), Goyang, Korea (e-mail: jhlee@kict.re.kr).

was treated by a drying system satisfies the unburned carbon criterion (less than 3.0) for type 1 fly ash specified by KS L 5405. The milling process executed to increase the fineness of bottom ash did not affect its chemical composition and changed only its physical properties.

Sodium hydroxide (SH, NaOH) and sodium silicate (SS, Na₂SiO₃) reagents are used as alkali-activators. Sodium silicate is used in a solution with water content of 60.4% so as to achieve a ratio of SiO₂/Na₂O of 3.0. Grade 6 sand (SiO₂ = 95%, density = 2.62 g/cm³) is used as fine aggregate.

B. Test Method

Table II arranges the test setup established for the evaluation of the influence of the alkali-activator. The influence of the activator is analyzed in terms of 3 factors to examine the flowability and compressive strength: the ratio of the alkali-activator to bottom ash (activator/BA ratio); the molarity of sodium hydroxide; and, the mix ratio of the alkali-activators (SH:SS, in mass ratio).

Table III arranges the test setup for the FT-IR analysis with respect to the strength. Since the sand includes large content in

SiO₂, it may induce errors in the analysis of the micro-structure. Therefore, sand is discarded from the test setup and the analysis is performed using bottom ash paste. Molarities of 3M and 12M of NaOH are considered to examine the difference according to low and high molarities. Fineness of 5500 cm²/g is applied for the analysis of the influence of high fineness. Blast furnace slag with large content in CaO is introduced to complement the problem brought by the high temperature curing required the alkali-activated geopolymer mortar. This will enable to analyze the correlation between the compressive strength under ambient temperature curing and FT-IR analysis results.

The alkali-activated geopolymer mortar adopted in this study was fabricated by introducing first the binder and fine aggregate in a 10 liter-mixer, dry mixing during 2 minutes at 30-40 rpm, followed by mixing during 3 minutes at 70-80 rpm

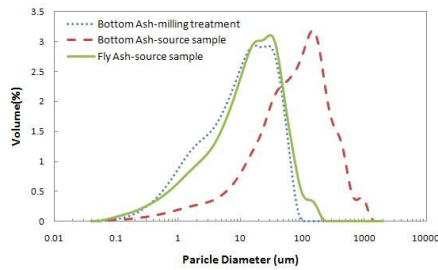


Fig. 1 Particle size distribution of fly ash and bottom ash

TABLE III
TEST PLAN OF FT-IR ANALYSIS

Factors		Variables
NaOH Molarity	Type	NaOH, Na ₂ SiO ₃
	Concentration of NaOH (M)	3, 6, 9, 12
	manufacturing time	manufacturing in advance
room temperature	Mixture ratio (SH:SS)	35:65
	Type	blast furnace slag
	Addition ratio(%)	0, 15, 30
Specific surface area	Curing condition	Temp. : 23±2 °C humidity : 65±10%
	Type	4,000, 5,500 cm ² /g

TABLE I
PROPERTIES OF COAL ASH

Types	Items	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	SO ₃ (%)	L.O.I	Specific surface area (cm ² /g)	Density (g/cm ³)
Bottom ash (raw)		57.70	23.60	9.36	4.57	0.16	0.71	0.01	1640	2.39
Bottom ash		58.30	22.20	7.62	4.40	1.52	0.18	0.03	3900	2.51
Fly ash (FA)		57.50	24.60	5.26	4.72	1.34	0.73	2.5	3669	2.08

TABLE II
TEST VARIABLES AND MIX DESIGN OF ACTIVATOR INFLUENCE

Series	Mix No.	W/B ratio	Mix proportion (g)				NaOH molarity (mol/ℓ)	SH:SS	Remark
			Sand	BA	SH	SS			
1	1	0.55			308	572	9	50:50	Effect of alkali activator/bottom ash ratio
	2	0.60			336	624			
	3	0.65	2400	1600	364	676			
	4	0.70			392	728			
2	5					6	50:50	Effect of molarity	
	6	0.60	2400	1600	480	480			
	7					9			
	8					15			
3	9			704	176	9	80:20	Effect of SH/SS ratio	
	10			572	308		65:35		
	11	0.55	2400	1600	440		440		50:50
	12			308	572		35:65		
	13			176	704		20:80		

after introduction of the alkali-activators. Thereafter, 50×50×50 mm mortar specimens were fabricated and sealed curing was performed during 48 hours at 60°C. The compressive strength was measured at 3, 7, 14 and 28 days while the specimens were subjected to ambient temperature curing at 23±2°C (humidity 65±10%). The compressive strength corresponds to the average strength obtained from 3 specimens.

III. TEST RESULTS AND DISCUSSION

A. Ratio of Alkali-Activator to Bottom Ash

The strength development of alkali-activated geopolymer mortar is achieved by the geopolymerization. The geopolymerization initiates the hardening by the melting of the main components SiO₂ and Al₂O₃ of the coal ash (bottom ash and fly ash) by the highly concentrated alkali-activator [1]. The reaction mechanism of the geopolymerization remains unclear but the Si and Al components of coal ash and the Si, Na, OH⁻, H₂O of the alkali-activators are known to apply as the chemical reactants of the mechanism [11]. Accordingly, the existence of an appropriate ratio of coal ash and alkali- activator is certain and needs to be investigated.

This study examines the effects of the ratio of bottom ash (BA) to alkali-activator on the flowability and compressive strength by varying this ratio. Figs. 2 and 3 arrange the corresponding results. When varying the mass ratio of bottom ash to alkali-activator from 0.55 to 0.70, the compressive strength reaches 52 MPa at 28 days for the ratio of 0.55. The minimum compressive strength per age shows a difference of approximately 10% compared to the maximum value.

The flowability decreases significantly from 205 mm to 145 mm according to the reduction of the mass ratio. Such results can be explained by the reduction of the water contained in the alkali-activator. This indicates that the mass ratio of 0.55 provides sufficient chemical composition for the geopolymerization to occur. Therefore, it appears that the use of a mass ratio of 0.55 to 0.60 is advisable in terms of flowability.

B. Molarity of NaOH

Sodium hydroxide (NaOH) is used as alkaline reagent in the alkali-activator. Fig. 4 shows the influence of the molarity of NaOH on the compressive strength. The water content is seen to increase for 6M resulting in poor strength development even under high temperature curing. Besides, remarkable strength is developed for 12M and 15M. The early strength development for 9M appears to reach merely 30% of that for 12M but the difference in the strength reduces with older ages. These results indicate that higher molarity is advantageous for the early strength development since the glassy membrane is broken in highly alkaline environment. Moreover, the difference in the strength at older age reduces because the 9M molarity includes sufficient Na⁺ ions necessary for the geopolymerization.

Fig. 5 presents the flowability with respect to the molarity of NaOH. It appears that low molarity with large water content is advisable in terms of the flowability. Molarities of 12M and 15M having poor water content result in the loss of workability.

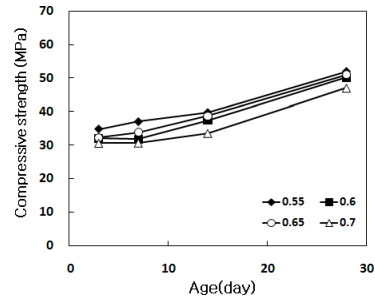


Fig. 2 Influence of activator/BA ratio on the compressive strength

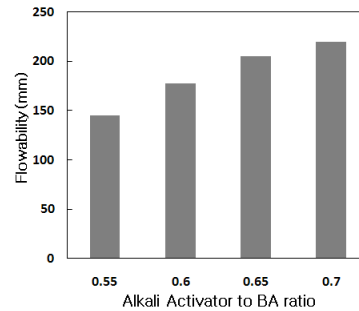


Fig. 3 Influence of activator/BA ratio on the flowability

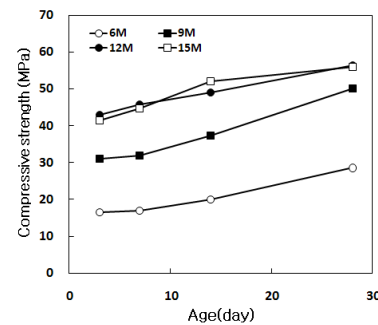


Fig. 4 Influence of activator/BA ratio on the compressive strength

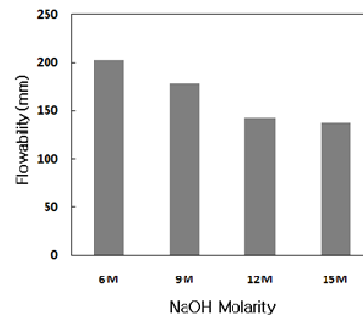


Fig. 5 Influence of NaOH molarity on the flowability

Accordingly, in view of the test results, the adoption of 9M among the molarities of 6M and 9M enabling to secure the flowability seems to be advantageous for the development of strength.

C. Mix Ratio of Alkali-Activators

Fig. 6 plots the flowability measured before curing on alkali-activated mortars with mix ratios of sodium hydroxide to sodium silicate of 80:20 (Na₂O/SiO₂=0.30), 65:35

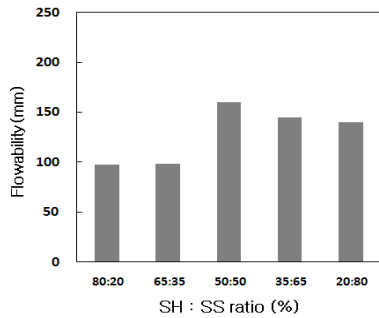


Fig. 6 Influence of sodium silicate (SS) to NaOH(SH) liquid ratio by mass on the flowability

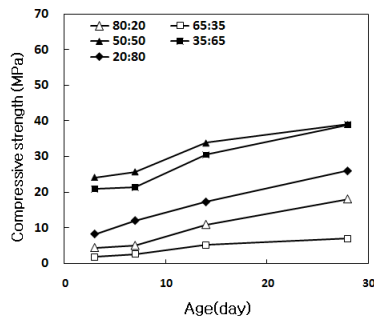


Fig. 7 Influence of sodium silicate (SS) to NaOH(SH) liquid ratio by mass on the compressive strength

($\text{Na}_2\text{O}/\text{SiO}_2=0.58$), 50:50 ($\text{Na}_2\text{O}/\text{SiO}_2=0.93$), 35:65 ($\text{Na}_2\text{O}/\text{SiO}_2=1.36$) and 20:80 ($\text{Na}_2\text{O}/\text{SiO}_2=1.92$) fabricated in advance to examine the effect of the mix ratio of the alkali-activator on the flowability. The mix ratios with the most advantageous flowability are 50:50 and 35:65. The larger loss of the flowability experienced with larger mix ratios is caused by the strong viscosity exhibited by sodium silicate. For the sodium hydroxide, the increase of the proportion of $\text{Na}_2\text{O}/\text{SiO}_2$ with larger mix ratios results in the separation of the silica in the solution, which leads to changes in the physical properties of the alkali-activator and, in turn, influences the flowability. Moreover, each mortar was put in a vinyl pack and sealed, and the hardening state was observed after 1 hour of exposure to ambient temperature. The results showed that the mortars using mix ratios of 35:65 and 20:80 did not harden and secured flowability. The mortars using other mix ratios initiated hardening between 20 minutes and 1 hour and could not secure flowability and workability.

Bottom ash-based mortar achieves its strength development by the activation of the geopolymerization under highly alkaline environment. This geopolymerization is a chemical reaction forming Si-O-Al-O bond by initiating the chemical reaction of Si-Al minerals under highly alkaline condition [17]. The geopolymerization is accelerated by generating higher alkaline environment through the production of NaOH by the reaction of sodium silicate with water.

Fig. 7 shows the compressive strength per age according to the mix ratio of the alkali-activator. The most remarkable strength development is observed for the alkali-activator mix ratios of 50:50 and 35:65 with compressive strength of 40 MPa. This can be explained by the increase of Si and Na components

apart from the Si and Al components of bottom ash, which induce the geopolymerization and improve the strength. Besides, the degradation of the strength can be attributed to the reduction in Si content with large quantity of sodium hydroxide and the relatively lesser content in Na^+ with larger quantity of sodium silicate, which impede the activation of the geopolymerization.

In addition, the stabilization process of the sodium hydroxide and sodium silicate mix changes NaOH into Na_2O and H_2O which, in turn, change the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of the sodium silicate. In view of the test results, setting occurred during the storage of the solution when the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio was lower than 1.36. This changed the physical properties and resulted in the loss of the strength. The observation of the influence of the fabrication time of the alkali-activator showed that, if the alkali-activator is not prepared in advance and is not stabilized, bottom ash will react precipitously [6] and harden before molding. Accordingly, the mix ratio of 35:65 (SH:SS) for the alkali-activator is recommended considering the storability of the alkali-activator and the flowability and compressive strength of mortar.

D. FT-IR Analysis

A FT-IR (Fourier Transform Infrared Spectrophotometer; IFS 66/S) with an effective range of $550\text{--}4000\text{ cm}^{-1}$ is used for the analysis. For the FT-IR analysis, alkali-activated geopolymer pastes were fabricated for each test variable. Any improvement of the strength of the paste indicates chemical change since this improvement is caused by the geopolymerization of bottom ash and the alkali-activator. Accordingly, the raw bottom ash and the powders of the specimens per strengths were analyzed by FT-IR and the large variations of the peaks were identified and examined.

Fig. 8 shows the compressive strength and flowability per test variable. The compressive strength with respect to the NaOH molarity of the alkali-activator increases with higher molarities. The past using blast furnace slag to induce the strength development at ambient temperature exhibits better strength than the paste using 100% of bottom ash. In concern with the influence of the fineness, higher fineness is seen to improve the strength.

The FT-IR spectra related to the 3 selected test variables are plotted in Figs. 9 to 11 including the spectrum for the raw bottom ash. The largest variation of the spectrum peak of the raw bottom ash occurs at wavenumber of $1000\text{--}1100\text{ cm}^{-1}$ for the T-O (T=Si or Al) bond [13]. The peak center of the T-O bond of the raw bottom ash appears at about 1060 cm^{-1} . The peak is known to shift to lower frequencies due to the influence of the reaction products newly produced by the alkali-activator [8]. The location of the shifted peak differs according to the Al/Si ratio of the reaction products. Since the Al-O bond length is longer than that of the Si-O bond but is weaker, the angle of the T-O-T bond reduces with further replacement of the Si^{+4} ions by Al^{+3} ions and leads to the shift of the peak to lower frequencies [13]. Therefore, higher strength of the alkali-activated geopolymer paste indicates more active geopolymerization and larger exchange of Si and Al ions.

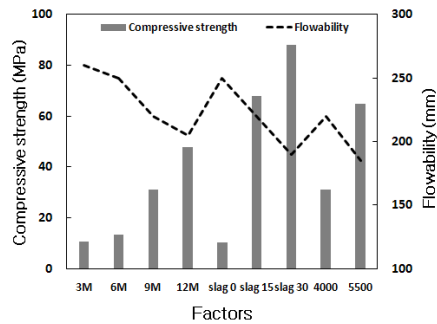


Fig. 8 Compressive strength and flowability with respect to test variables

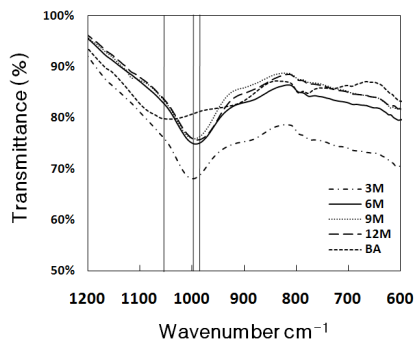


Fig. 9 FT-IR spectra according to NaOH molarity

The spectra of Fig. 9 show that the T-O bond of the raw bottom ash occurs at 1060 cm^{-1} but shifts to low frequencies ($980\text{--}999\text{ cm}^{-1}$) with further increase of the molarity and further improvement of the strength. This can be explained by the fact that higher molarity favors the corrosion of the glassy membrane of bottom ash from which the internal Si and Al components activate the geopolymerization.

The spectra of Fig. 10 correspond to the paste admixed with blast furnace slag to induce the strength development at ambient temperature [12]. It can be seen that the T-O bond peak of the raw bottom ash shifts toward low frequencies of $962\text{--}991\text{ cm}^{-1}$, which indicates that geopolymerization occurs easily also at ambient temperature owing to the hydration heat provoked by the CaO content. Moreover, the spectra relative to the fineness (Fig. 11, $985\text{--}997\text{ cm}^{-1}$) reveal that the strength improves as much as the reaction of the alkali-activator with the internal Si and Al components of bottom ash is activated by further physical breakage of the glassy membrane.

IV. CONCLUSION

This study investigated the influence of the alkali-activator and the FT-IR characteristics of alkali-activated geopolymer mortar using bottom ash as binder. The following conclusions could be derived.

1) The largest compressive strength was developed for a value of 0.55 for the mass ratio of the alkali-activator to bottom ash. The flowability appeared to increase with larger mass ratio. This means that the mass ratio of 0.55 provided sufficient chemical components needed for the geopolymerization. Therefore, the adoption of a mass ratio running around 0.55 to 0.60 is advisable in terms of the flowability.

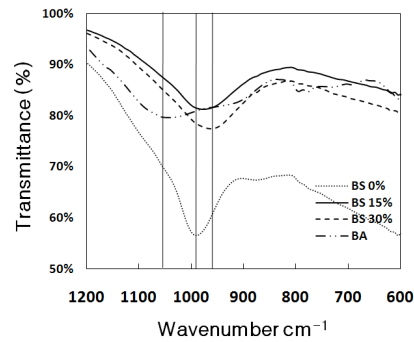


Fig. 10 FT-IR spectra according to blast furnace slag

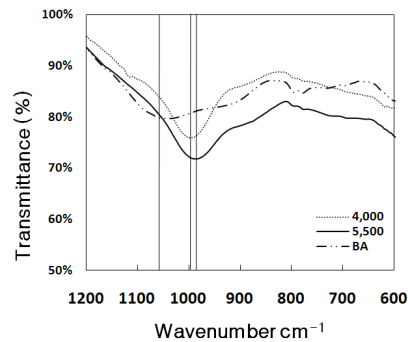


Fig. 11 FT-IR spectra according to specific surface area

- Higher concentration of sodium hydroxide was seen to favor the corrosion of the glassy membrane of bottom ash and, by the way, lead to higher compressive strength. Besides, lower concentration with larger water content was seen to be advantageous for the flowability. The molarity of 9M increased the flowability compared to 12-15M and also resulted in a strength reaching 90% of the ultimate compressive strength at 28 days.
- The mix proportions of the alkali-activator advantageous in terms of flowability and strength appeared to be 50:50 and 35:65. It was seen that preparing the alkali-activator in advance so as to stabilize it should be recommended. When the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio dropped below 1, silica separated from the solution and changed the physical properties of the alkali-activator. Accordingly, attention should be paid to the preparation of the alkali-activator.
- The T-O (T=Si or Al) bond peak of the raw bottom ash occurred at 1060 cm^{-1} , and the peak shifted due to the change of the bond structure caused by the geopolymerization. The T-O bond peak shifted to lower frequencies owing to further activation of the geopolymerization at higher strength.

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