- Technical Paper -

EFFECT OF ALKALINE ACTIVATOR AND CURING METHOD ON THE COMPRESSIVE STRENGTH OF CEMENTLESS FLY ASH BASED ALKALI-ACTIVATED MORTAR

Gyung-Taek KOH*1, Hyun-Jin KANG*2, Gum-Sung RYU*3 and Jang-Hwa LEE*4

ABSTRACT

This study investigates the effects of alkaline activator and curing method on the compressive strength of mortar for the development of cementless alkali-activated concrete using 100% of fly ash as binder. Results reveal that alkali-activated mortar with compressive strength of 70MPa at age 28 days can be fabricated in case of performing atmospheric curing after curing at 60°C during 48 hours when using alkaline activator made of NaOH of 9M and sodium silicate with proportions of 1:1.

Keywords: fly ash, alkali-activated mortar, compressive strength, curing method, alkaline activator

1. INTRODUCTION

Portland cement is responsible of about 7% of the CO_2 gases exhausted in the world since it is produced under extremely high heat (1,450°C) during the fabrication of clinker and about 0.7 to 1.0 ton of CO_2 gases are discharged to produce 1ton of cement. With respect to such situation, the cement industry endeavors efforts to reduce CO_2 through the use of blended cement adopting fly ash and blast furnace slag or through the production of cement under lower temperatures. However, such methods are showing limitations in reducing effectively and significantly the CO_2 exhausted during the production of cement.

Besides, the amount of coal ash including the fly ashes produced annually in thermal power plants in Korea averages 6 million tons, which is expected to continuously increase in the years to come. Even if about 42% of these coal ashes are currently exploited as raw material for the fabrication of cement or reused as admixtures for concrete, the remaining fly ashes are disposed through seashore or land filling. Such disposal is not only economically burdening in view of the securing of reclaimed land but is also leading to environmental problems.

Regard to such backgrounds, recent researches have been actively performed for the development of cementless alkali-activated concrete using blast furnace slag and fly ash as binder instead of cement[1, 5, 8]. Despite problems of constructability and shrinkage have been pointed out for alkali-activated concrete using blast furnace slag, reports stated that such concrete presents remarkable strength development even at normal temperature making it possible to produce high strength concrete with compressive strength ranging between 40MPa and 70MPa[3, 4].

In addition, in the case of cementless concrete using fly ash, it is known that strength is practically not developed at normal temperature and that high temperature curing is required to activate the polymerization[2, 5]. However, the lack of systematic researches on the alkaline activator, curing temperature and curing conditions is still impeding its fabrication[6].

Accordingly, this study intends to contribute to the development of cementless alkali-activated concrete using 100% of fly ash as binder through the examination of the type and concentration of alkaline activator, the mix proportion of alkaline activator, the temperature and duration of high temperature curing and the curing conditions after high temperature curing.

2. TEST PROGRAMS

2.1 Materials and mix proportion

The fly ash adopted in this study is produced from the thermal power plant of Boryeong in Korea. Its chemical composition and physical properties are listed in Table 1. This fly ash is composed of large quantities of constituents required for the polymerization with contents of 81.1% of SiO_2 and Al_2O_3. The fly ash presents a spherical microstructure as shown in Fig. 1 and the surface of the particles is enclosed in glassy chain. The polymerization of fly ash breaks this glassy chain and activates the internal reactive substances. It is known that the glassy chain is broken by improving the strong alkaline environment around the fly ash particles or performing high temperature curing[8, 9].

This study uses KOH and NaOH with degrees of purity larger than 98% as alkali activators of fly ash with respective molarities of 6, 9 and 12M for the fabrication. Moreover, sodium silicate (Na_2O 10%,

*1 Research Fellow, Korea Institute of Construction Technology, Dr.E., JCI Member
*2 Researcher, Structural Material Research Division, Korea Institute of Construction Technology, M.E.
*3 Researcher, Korea Institute of Construction Technology, M.E. JCI Member
*4 Vice president, Korea Institute of Construction Technology, Dr.E.

Table 1 Properties of fly ash

Items / Types	Surface area (cm^2/g)	Density (g/cm^3)	L.O.I	Chemical composition (%)					
				SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Fly ash	3,550	2.18	3.2	55.3	25.8	5.5	2.9	0.8	0.3

Table 2 Summary of experimental programs

Investigated item	Type of alkaline activator	Mole concentration of alkaline activator	Ratio of SH:SS	Curing Temperature-times	Curing conditions	Measuring age(days)
Type of alkaline activator	NaOH KOH	9M	1:1	60°C-48hrs	Atmospheric curing	1,3,7,28
Mole concentration of alkaline activator	NaOH	6, 9, 12M	1:1	60°C -48hrs	Atmospheric curing	1,3,7,28
NaOH(SH) to sodium silicate(SS) ratio by mass	NaOH	9M	1.25:0.75 1:1 0.75:1.25	60°C -48hrs	Atmospheric curing	1,3,7,28
Curing method	NaOH	9M	1:1	30°C -24,48,72hr 60°C -24,48,72hr 90°C -24,48,72hr	Atmospheric Curing/water curing	1,3,7,28

SiO_2 30%, solid content 40%) is mixed with these alkali activators for the activation of the polymerization[9,11]. Sand (density 2.62g/cm^3, average grain diameter 0.3~0.5mm, SiO_2 93%) is used as fine aggregates.

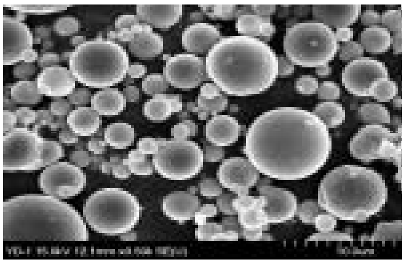


Fig.1 SEM micrograph of fly ash (×5,000)

Table 3 Mixture proportions of mortar(by weight)

Water	Fly ash	NaOH/ KOH	Sodium Silicate	Sand
0.1	1	0.25	0.25	1.5

2.2 Testing method

Table 2 arranges the test items examined in this study. Table 3 lists the reference mix proportions adopted in this study. Based on such mix proportions, investigation is done on the type of alkaline activator, the effect of the molarity as well as on the temperature and duration of curing. Furthermore, the mix proportion of NaOH and sodium silicate is 1:1 (molar ratio of Na_2O/SiO_2 of 1.12). Examination is also performed for proportions of 1.25:075 (molar ratio of Na_2O/SiO_2 of 1.65) and 0.75:1.25 (molar ratio of Na_2O/SiO_2 of 0.80) to observe the effect of the mix ratio.

In order to analyze the effect of the curing temperature and duration on the strength of the fly ash-based alkali activated mortar, curing was performed at 30, 60 and 90°C during 24, 48 and 72 hours under conditions maintaining relative humidity of 65±10% prior to air-dried curing at 23±2°C (R.H of 65±10%) and water curing until the test age.

The mortar was manufactured by mixing at first fly ash and fine aggregates in a 10 liter mixer at speed of 30~40rpm during 2 minutes, followed by 3 minutes of mixing at 70~80rpm after introduction of water and alkaline activator composed of NaOH and sodium silicate fabricated 1 day earlier.

The so-manufactured mortar was subjected to flow test in compliance with JIS R 5201 and its compressive strength was measured at 1, 3, 7 and 28 days on specimens fabricated with dimensions of 50×50×50mm. The flow of mortar appeared to range from 178 to 183mm according to the test conditions.

3. TEST RESULTS AND OBSERVATIONS

3.1 Effects of alkaline activators

(1) Type of alkaline activator

Fig. 2 illustrates the effects of the type of alkaline activator on the compressive strength under identical molarities. It is seen that the use of KOH as alkaline activator is leading to higher compressive strength at all ages compared to NaOH. Such result can be attributed to the difference of alkaline activator used per 1M.

Accordingly, examination was done of the effects of identical contents of alkaline activators on the compressive strength. The corresponding results are shown in Fig. 3, in which it can be seen that identical amounts of alkaline activators are practically not influencing the compressive strength according to the type of activator. However, boiling phenomenon occurred suddenly during the fabrication of aqueous solution of KOH, which brought difficulties in its manufacture. In addition, KOH was also disadvantageous in an economical point of view. Therefore, the use of NaOH as alkaline activator is recommended when fabricating fly ash-based alkali activated concrete. Accordingly, NaOH was used as alkaline activator in the subsequent tests.

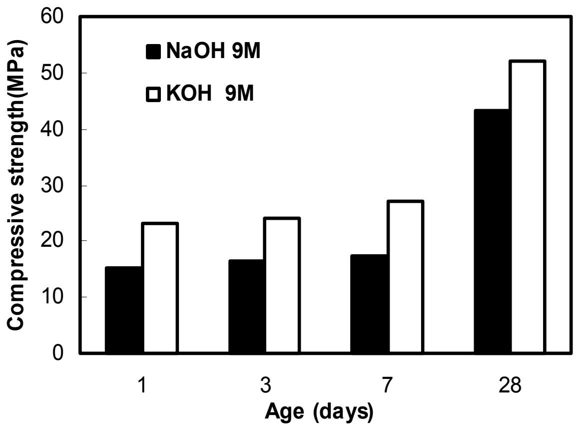


Fig. 2 Effects of the type of alkaline activator on the compressive strength under identical molarities

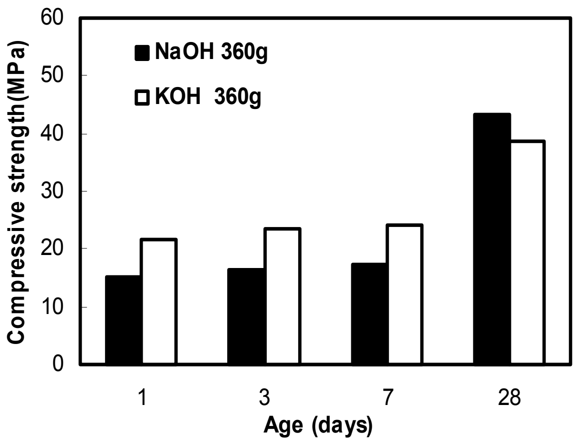


Fig. 3 Effects of the type of alkaline activators on the compressive strength under identical contents

(2) Concentration of alkaline activator

Fig. 4 shows the effects of the concentration of alkaline activator on the compressive strength. Larger molar concentration of NaOH appears to improve the strength. Especially, high strength larger than 40MPa and 50MPa are developed at age 28 days for respective molarities of 9M and 12M. Such results can be interpreted as the activation of the reactions with the internal Si and Al constituents following the breakage of the glassy chain of fly ash due to the larger alkalinity provoked by the increase of the molarity of NaOH[2, 6, 11].

Consequently, even if larger molar concentration of NaOH contributes to the increase of the strength, problems remain due to the fabrication of the NaOH solution as well as the loss of economic efficiency.

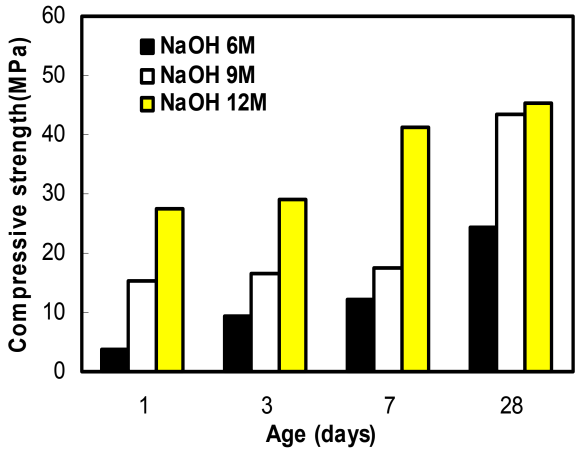


Fig. 4 Effects of the molarity of NaOH on the compressive strength

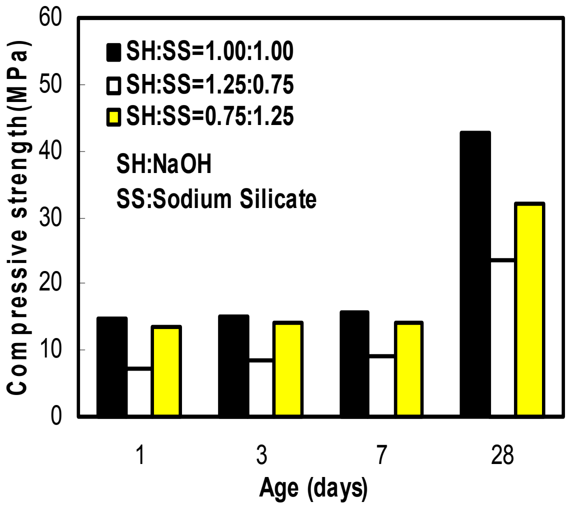


Fig. 5 Effects of the mixing ratio of NaOH and sodium silicate on the compressive strength

(3) Mix ratio of NaOH and sodium silicate

Fig. 5 illustrates the effects of the mix ratio of alkaline activators on the compressive strength. The mix ratio of SH to SS of 1:1 is producing higher strength than the ratios of 0.75:1.25 and 1.25:0.75. Here, it is known that NaOH is activating the polymerization of the internal Si-Al by breaking the glassy chain of fly ash. In addition, sodium silicate by reacting with water is generating NaOH and $Si(OH)_4$, which is promoting polymerization following the increase of Si and Na constituents[5, 8, 10]. According to previous studies, the mixed use of NaOH and sodium silicate in adequate proportions has been reported to be advantageous for the development of strength.

In this study, the mixed use of NaOH and sodium silicate with proportions of 1:1 that is, a molar ratio of Na_2O to SiO_2 of 1.12, resulted in the largest reactivity of fly ash with Si and Al constituents and led to remarkable development of the strength.

3.2 Effects of curing method

(1) Curing temperature

Fig. 6 presents the effects of the curing temperature on the compressive strength. Even if improvement of the compressive strength appeared with higher curing temperature until age 7 days, the strength tended to reverse on the contrary for curing temperatures of 60°C and 90°C at age 28 days. Despite the strength improved significantly from age 7days to 28 days for a curing temperature of 60°C, improvement was practically unobservable for the curing temperature of 90°C. Similarly to the results of previous studies[6, 8, 10], high temperature curing for alkali activated concrete is acting advantageously at early strength but appears to have adverse effect on the long-term strength. The reason for such phenomenon remains still not elucidated but an explanation can be given by the enclosing of the particles of the binder by the reactants generated by the high temperature, which impede further reactions, or by the occurrence of micro-cracks[8]. Even if this study could not elucidate the reason for the loss of strength due to high temperature, further studies are planned to explain the strength development mechanism through the analysis of the structural change of the hardened paste according to the curing temperature and age.

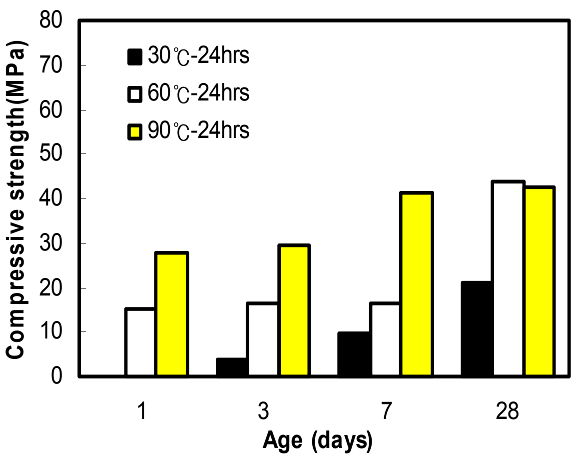


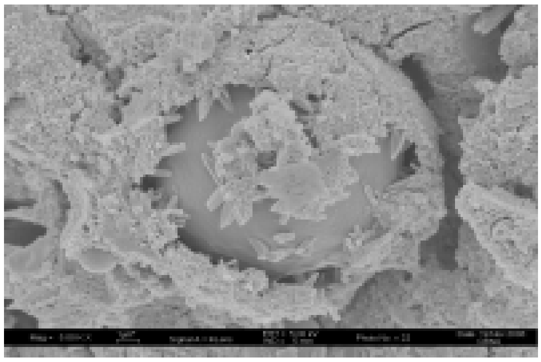
Fig. 6 Effects of curing temperature on the compressive strength

Fig. 7 shows SEM photographs at age 28 days according to the curing temperature. In the case of curing performed at 30°C, it can be seen that substances start to be generated by the polymerization around the round particles of fly ash. On the contrary, for curing temperatures of 60°C and 90°C, the fly ash particles tend to disappear completely letting bar-shaped reactants to be generated through polymerization.

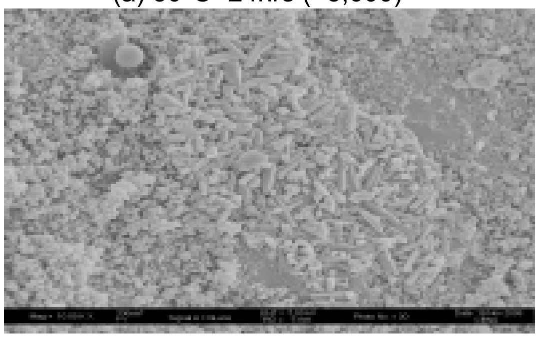
(2) Duration of high temperature curing

Fig. 8 shows the strengths resulting from the performing of curing at temperatures of 30, 60 and 90°C during 24, 48 and 72 hours, respectively. For curing at 30°C, strength started to develop at age 3 days to reach approximately 13MPa at 7 days, and 21~25MPa at 28 days according to the duration of high temperature curing.

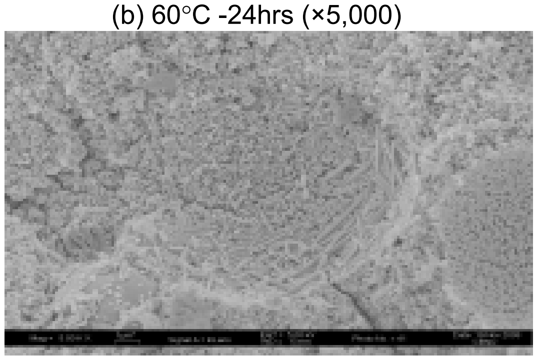
In the case of curing at 60°C, relatively high strength of about 15MPa is developed even after 24 hours of curing. Until age 7 days, it appears that the strength improved with longer curing duration. In addition, between age 7 days and 28 days, curing at high temperature during 48 hours and 72 hours is seen to enhance significantly the strength to reach high strength larger than 70MPa. At age 28 days, high temperature curing duration of 48 hours appears to result in slightly higher strength than duration of 72 hours. Based on these results, it can be presumed that a curing duration of 48 hours is required to evaporate the internal moisture of mortar so as to accelerate the activation of polymerization of fly ash at high temperature curing of 60°C.



(a) 30°C -24hrs (×5,000)



(b) 60°C -24hrs (×5,000)



(c) 90°C -24hrs (×5,000)

Fig. 7 SEM photographs according to the curing temperature

In the case of curing at 90°C, high strength of about 27MPa is developed at 1 day even after 24 hours of curing. For curing duration of 48 and 72 hours, high strength exceeding 40MPa is developed at age 3 days. However, increase of the strength could practically not be observed between age 7 days and 28 days for curing at 90°C regardless of the curing duration.

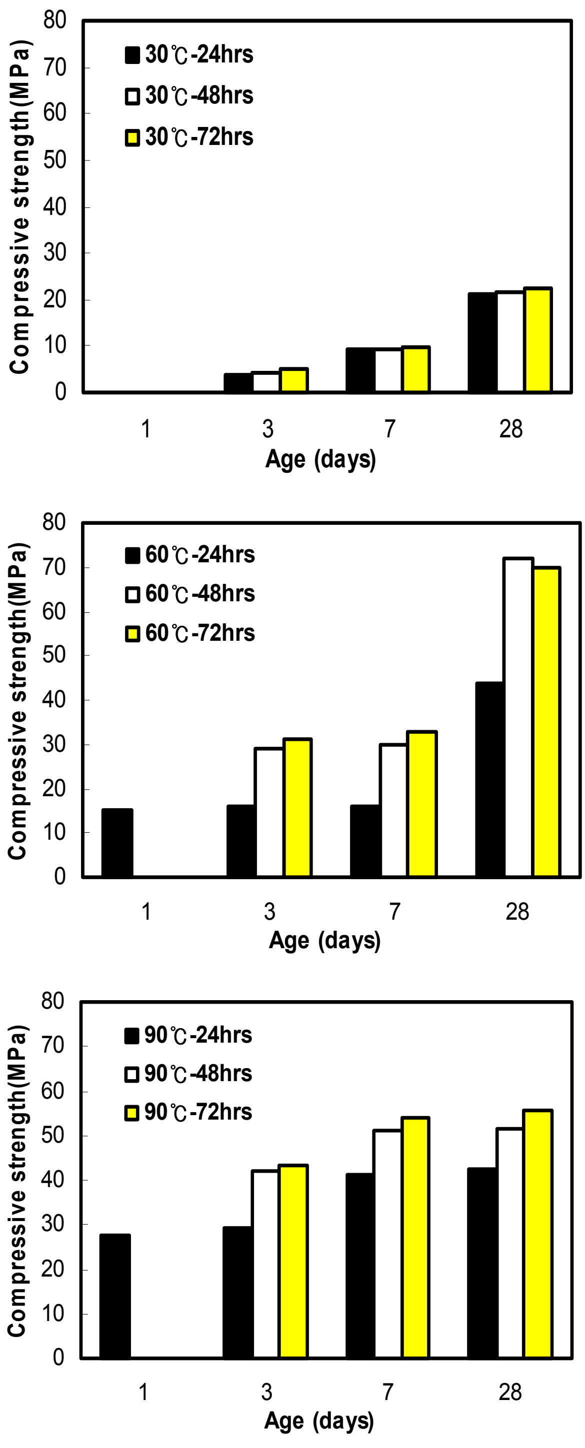


Fig.8 Effect of the duration of high temperature curing on the compressive strength

(3) Curing conditions after high temperature curing

Fig. 9 shows the effects of the curing conditions after 48 hours of high temperature curing at 60°C and 90°C on the compressive strength. In the case of curing at 60°C, practically no effect of the curing conditions could be observed on the strength until age 7 days. However, atmospheric curing at age 28 days appears to lead to significant difference of about 28MPa in the strength compared to water curing. This difference can be explained by the difference in the action of the polymerization provoked by the extent of internal moisture evaporation according to the curing condition after high temperature curing. In addition, curing at 90°C appears to have lesser effect of the curing conditions than at 60°C. Consequently, performing atmospheric curing after high temperature curing seems to be effective on the increase of the strength. Especially, more remarkable effect appears in the case of high temperature curing at 60°C.

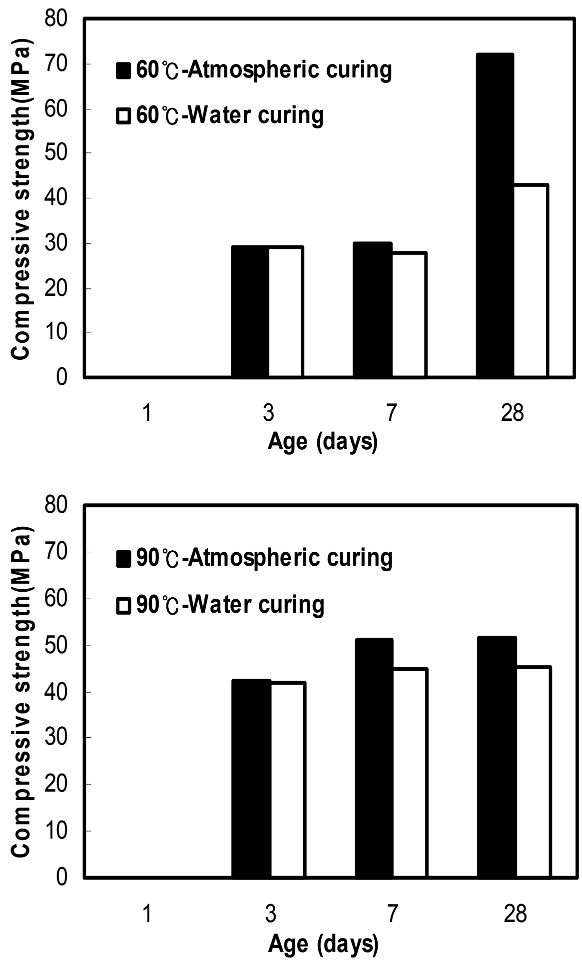
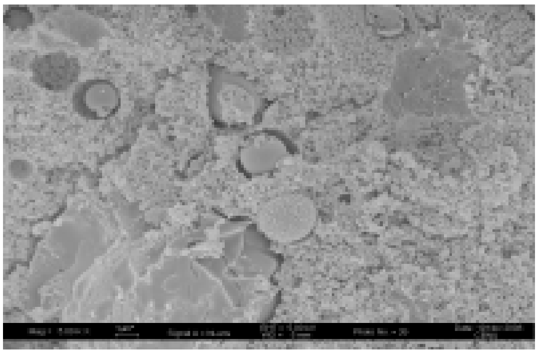


Fig.9 Effects of curing conditions after high temperature curing on the compressive strength

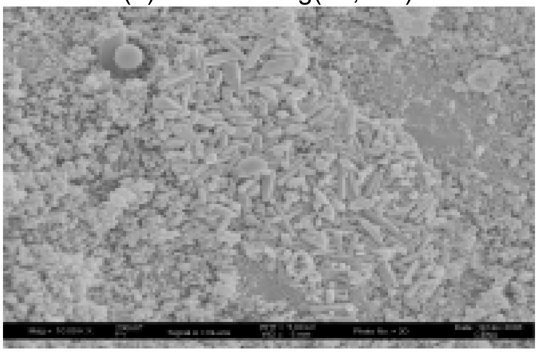
Fig. 10 shows SEM photographs according to the curing conditions after the execution of curing at 60°C. In the case where water curing is performed, polymerization appears to be rather inactive letting the fly ash particles with their round shapes. On the other hand, in the case of air-dried curing, round-shaped fly ash particles can practically not be observed, which means that bar-shaped structure has been generated in large quantities through polymerization.

3. CONCLUSIONS

The effects of alkaline activators and curing method on the compressive strength of mortar have been investigated for the development of cementless concrete using 100% of fly ash as binder. The following conclusions can be drawn from the results.



(a) Water curing(×5,000)



(b) Atmospheric curing(×5,000)

Fig. 10 SEM photographs according to the curing conditions after high temperature curing

(1) When considering the fabrication stability and economic efficiency of the alkaline activators, NaOH appeared to be preferable to KOH. The strength improved according to the increase of the molar concentration of NaOH, which revealed that the strength could be controlled through the molar concentration. In addition, the mixed use of NaOH and sodium silicate with proportions of 1:1 (molar ratio of Na_2O to SiO_2 of 1.12) activated the reaction of fly ash with Si and Al constituents and resulted in the most remarkable development of the strength.

(2) In the case of concrete requiring high strength at early age, higher curing temperatures appeared to be advantageous. Curing at 60°C during approximately 48 hours is recommended for concrete requiring high strength at age 28 days. Moreover, performing atmospheric curing after high temperature curing appeared to be more effective for the development of strength than water curing. Especially, such effect is magnified for curing at 60°C.

(3) Based on these results, it has been analyzed that alkaline activators fabricated with proportions of 1:1 of 9M NaOH and sodium silicate should be used and that atmospheric curing should be performed after curing at 60°C during 48 hours to produce high strength alkali-activated mortar exhibiting compressive strength of 70MPa at age 28 days.

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