- *Technical Paper* -

POZZOLANIC REACTION OF FLY ASH CEMENT PASTE IN THE PRESENCE OF ALKALI ACTIVATOR

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ABSTRACT

In this study, the effects of types and activation time of alkali activators on pozzolanic reaction of the paste with 0% and 40% replacement of fly ash were investigated by examining the $Ca(OH)_2$ content and the pore volume. The results showed the presence of alkali activator decreased the $Ca(OH)_2$ content, total and 20-330 nm ranged diameter pore volume, whereas it increased the 3-20 nm ranged diameter pore volume of fly ash cement paste. The alkali-injected starting time 1 month after casting was more effective in reducing 20-330 nm ranged diameter pore volume than 3 months after casting.

Keywords: pozzolanic reaction, alkali activator, $Ca(OH)_2$ content, pore volume

1. INTRODUCTION

Fly ash has been used widely in replacing a partial of cement which is one of the main materials used for concrete construction. One of the main reasons for replacing of cement with fly ash in concrete is that it has pozzolanic properties. Pozzolanic properties of fly ash are well-known that its reactive silica and alumina chemically react with calcium hydroxide ($Ca(OH)_2$ - CH) formed from cement hydration in the presence of the water at normal temperature to form the compounds which have the cementitious properties such as calcium silicate hydrate (C-S-H) and calcium aluminate hydrate (C-A-H) [1].

Therefore, CH content is used commonly to evaluate the progress of pozzolanic reaction in fly ash cement paste [2, 3, 4, 5] because CH content in fly ash cement system is calculated by CH content formed from cement hydration and CH content consumed by pozzolanic reaction of fly ash. Thus, the reduction of CH content in the matrix is observed as pozzolanic reaction of fly ash occurs [2, 3, 6]. Besides the decrease in CH content, the increase in C-S-H and C-A-H filling the pores of the matrix is also observed. It was found that the cumulated partial pore volume ratios of 20-330 nm and 3-20 nm ranged diameter in fly ash cement system are one of the factors used for estimating the progress of pozzolanic reaction of fly ash [7].

However, it was also reported that pozzolanic reaction of fly ash is slower than cement hydration in the early age and even after a long period [2, 6] because of using a partial of fly ash replacement for cement, resulting in the low pH of pore solution in the matrix [5, 8]. When the pH of pore solution or the concentration of alkalis in the matrix is not high enough, the Si-O-Si links (or Al-O-Al links) of fly ash have not to be disrupted. It was demonstrated that this disruption of the Si-O-Si links (or Al-O-Al links) occurs at a pH of 12.5 at room temperature [9] and more than 13 at 20^{o}C in NaOH solution [8]. Thus, the common way of getting a high pH system is the addition of alkali ions in the fly ash cement system [10, 11, 12].

In the present study, CH contents in the pastes with 0% and 40 % replacement of fly ash in the presence of alkali activator injected 1 month or 3 months after casting were investigated in order to evaluate the effects of alkali activator as well as the alkali activation time on pozzolanic reaction of fly ash cement paste. The alkali activation time is defined as the starting time of alkali injection into the paste. Furthermore, the pore structure of alkali-activated samples was also studied by mercury intrusion porosimetry (MIP). The results of activated samples were also compared with those of control samples and water-injected samples.

2. EXPERIMENTS

2.1 Materials

The cementitious materials used in this study were high-early-strength Portland cement, and fly ash which met the standard values of Type II per JIS A 6201 (fly ash for concrete). The chemical composition and physical properties of the materials are shown in Table 1.

2.2 Preparation of fly ash cement paste

The water to binder ratio was constant 0.3 throughout the investigation for considering pre-tensioned pre-stressed concrete production. Fly ash was used to replace high-early-strength Portland cement at

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Table 1 Chemical composition and physical properties of cementitious materials

Properties	Cement	Fly ash
SiO_2 (%)	20.30	57.7
Fe_2O_3 (%)	2.71	5.43
Al_2O_3 (%)	4.96	27.54
CaO (%)	65.49	1.26
MgO (%)	1.21	1.06
SO_3 (%)	2.98	0.36
Na_2O (%)	0.22	0.44
K_2O (%)	0.35	0.76
Loss on ignition (%)	1.19	2.8
Density (g/cm^3)	3.14	2.21
Blaine specific surface area (cm^2/g)	4590	3290

the ratios of 0% and 40% by mass. The pastes were mixed in a mechanical mixer and were cast in the 40 mm cube mould, and were sealed by aluminum and adhesive tape to prevent water loss as well as carbonation. Then, the syringe with a capacity of 1 ml, of which the plunger was disconnected, was inserted in the center of the sample as shown in Fig. 1. All samples were demoulded 24 hours after casting and cured in sealed condition at 20^{o}C.

2.3 Injection of water or alkali activator

Water and each alkali activator were injected through the syringes 1 month or 3 months after casting by pouring the solution in the syringes naturally, i.e. no use of any pressures into the samples (see Fig. 1). Alkali activators were 0.1 mol/l of NaOH solution (pH = 13) and about 0.02 mol/l of saturated $Ca(OH)_2$ solution (pH = 12.6).

2.4 Measurement of CH content and porosity

At the ages of 1, 2, 4, 8, and 10 months, CH content in plain cement paste (FA0) and fly ash cement paste (FA40) was measured by thermal gravimetric analysis (TGA) at the point of the needle of the syringe obtained from Fig. 1. CH content was calculated based on the ignited mass of the sample and the mass loss due to dehydration of CH. This mass loss was determined from DTG curve between the initial and final temperature of the corresponding DTG peak [3].

The porosity was measured by mercury intrusion porosimeter (MIP). The samples for the pore volume test ranging 2.5-5 mm in size were obtained by crushing and selecting the section, which was around the position of the needle, of the hardened fly ash cement paste cubes. After that, these samples were soaked in acetone to stop further hydration and dried in a vacuum desiccator for 24 hours before MIP measurement. MIP is based on a non-wetting liquid like mercury introduced into the cylindrical pore under stringently controlled pressure. The determination of the diameter of the cylindrical pores into which mercury has intruded is calculated using the following Washburn equation [13]:

$$D = -4\gamma\cos\theta / P \qquad (1)$$

Where,

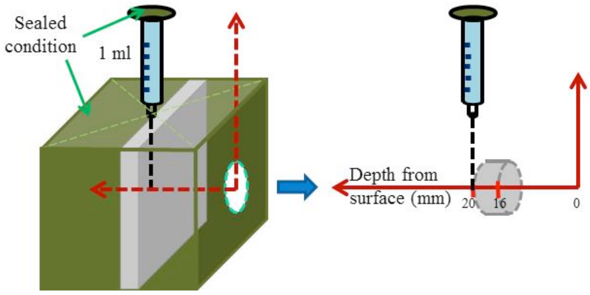


Fig.1 Preparation of samples for analyzing CH content

D: The diameter of pores (μm)

γ: The surface tension of mercury (assuming a value of 480mN/m)

θ: The contact angle of mercury on the paste (taken as 140^o)

P: The pressure at which mercury is intruded into the pore (mN/m^2)

The MIP equipment used in this study has the maximum pressure of 414x10^6 N/m^2. The pore structures of the paste at the age of 4 months were measured at a diameter range of 3 nm to 300 μm.

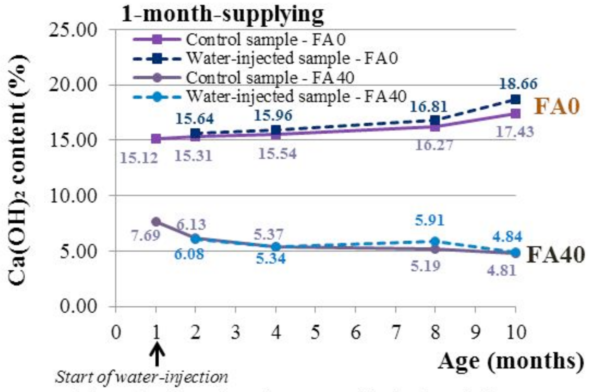
3. RESULTS AND DISCUSSIONS

3.1 CH content

(1) Effect of water or alkali injection in the case of 1-month-supplying

CH content in control samples, which were samples without supplying any water or alkali activator, and water-injected samples with the time, is shown in Fig. 2. The table in this figure (or the next figures) shows the water- or alkali-injected volumes into the paste observed at the corresponding CH content measurement ages. Generally, CH content in FA0 increased while CH content in FA40 decreased as the curing age progressed. It indicates that the cement paste was still continuing to hydrate with the time whereas pozzolanic reaction of fly ash occurred with reduction of CH content. In addition, the results showed that the water injection increased CH content in FA0 both of the early and later ages, while the water injection decreased slightly CH content in FA40 at the ages of 2 and 4 months and it only increased CH content at the age of 8 months and too slightly increased CH content at the age of 10 months. It is obvious that the water injection was effective on promoting cement hydration of FA0 at the early and even later ages regardless of the water volume. Besides the effect of water injection on cement hydration, water injection also affected pozzolanic reaction of fly ash cement paste (FA40) in reducing CH content a little at the early age (i.e. 2 and 4 months) and at the later age (i.e. 10 months) as shown in Fig. 2.

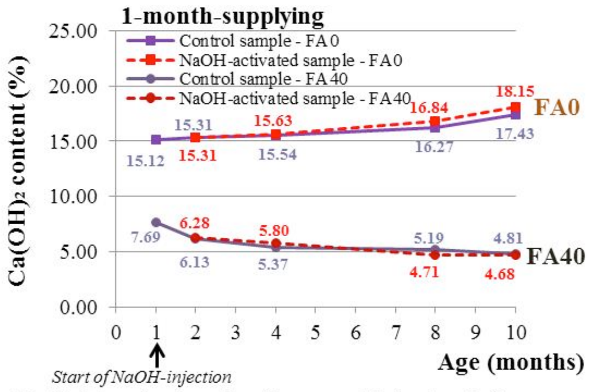
CH content in control and NaOH-activated samples is shown in Fig. 3 and $Ca(OH)_2$-activated samples is shown in Fig. 4. In the case of FA0, CH content in alkali-activated sample was equal to or smaller than that in control sample at the early ages (i.e. 2 and 4 months), while that in alkali-activated sample was larger than that in control sample at the later ages



Water-injected volume into the paste with the time (ml)

Ages (months)	2	4	8	10
FA0	0.10	0.26	0.69	1.00
FA40	0.05	0.05	0.10	0.14

Fig.2 CH content in control and water-injected samples with the time in case of 1-month-supplying



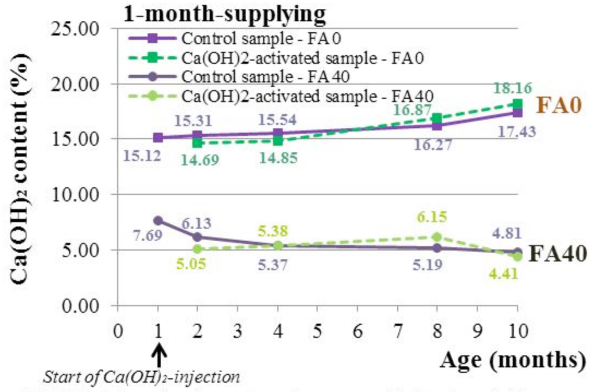
NaOH-injected volume into the paste with the time (ml)

Ages (months)	2	4	8	10
FA0	0.10	0.26	0.69	1.00
FA40	0.05	0.05	0.10	0.20

Fig.3 CH content in control and NaOH-activated samples with the time in case of 1-month-supplying

(i.e. 8 and 10 months). It indicates that the alkali activation for the sample without fly ash played a negative role toward production of $Ca(OH)_2$ at the early age. This can be explained that at that time, it was difficult for cement paste to release Ca^{2+} ion to the outside due to high alkali concentration of alkali activator. At the later age, the larger CH content in alkali-activated sample was due to water from alkali solution which chemically reacted with the compounds of cement.

In the case of FA40, CH content in NaOH-activated sample was nearly equal to that of control sample at the age of 2 months and a little smaller than that of control sample at the ages of 8 and 10 months as shown in Fig. 3. CH content in $Ca(OH)_2$-activated sample was smaller than that of control sample at the ages of 2 and 10 months and nearly equal to that of control sample at the age of 4 months as shown in Fig. 4. The reduction of CH content shows that pozzolanic reaction of fly ash was accelerated by alkali activator.



$Ca(OH)_2$-injected volume into the paste with the time (ml)

Ages (months)	2	4	8	10
FA0	0.10	0.26	0.70	1.00
FA40	0.05	0.05	0.08	0.20

Fig.4 CH content in control and $Ca(OH)_2$-activated samples with the time in case of 1-month-supplying

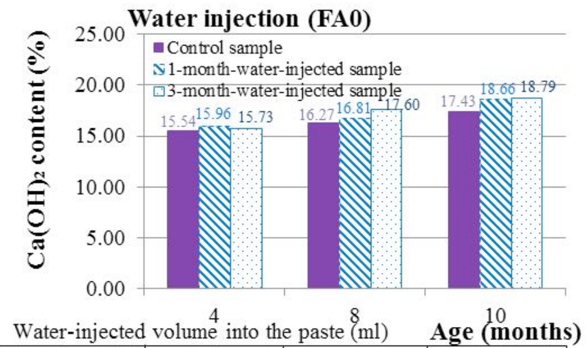
The larger CH content in alkali-activated samples (in the case of NaOH-activated sample at the age of 4 months and in the case of $Ca(OH)_2$-activated sample at the age of 8 months) would be discussed in the next section.

Furthermore, it appears CH content in $Ca(OH)_2$-activated samples was smaller than that in water-injected and NaOH-activated samples at the ages of 2 and 10 months (see Figs. 3 and 4). This implies that $Ca(OH)_2$ solution was more effective in decreasing CH content in fly ash cement paste than water and NaOH solution injection.

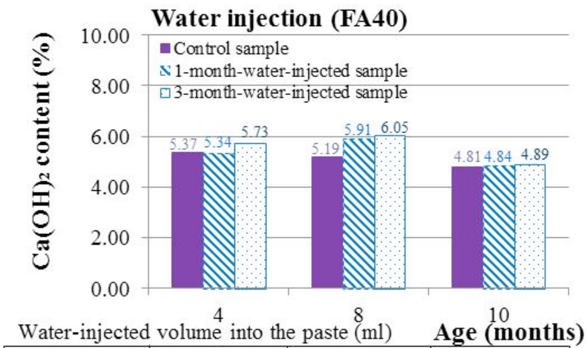
(2) Effect of the activation time

The comparison of CH content in FA0 between control samples, 1-month-water-injected samples and 3-month-water-injected samples is shown in Fig. 5 left. The water injection increased CH content in FA0 independently of water injection time. Moreover, CH content in 3-month water injection was larger than that in control or 1-month water injection despite of the smaller water-injected volume into the paste. It indicates 3-month water injection was more effective on accelerating cement hydration than 1-month water injection. This can be explained that the cement paste had enough water to hydrate at the early age, resulting in 1-month water injection only contributing to cement hydration slightly. At the later age, however, the paste had insufficient water to hydrate because the partial of the water reacted with the chemical compounds of cement at the early age. Therefore, 3-month water injection promoted cement hydration significantly.

The comparison of CH content in FA40 between control samples, 1-month-water-injected samples and 3-month-water-injected samples is shown in Fig. 5 right. 3-month water injection was more effective in increasing CH content in FA40 than 1-month water injection at the age of 4 months with the smaller water-injected volume into the paste. At the age of 8 months, water injection also increased CH content in FA40 regardless of the water injection time. At the age

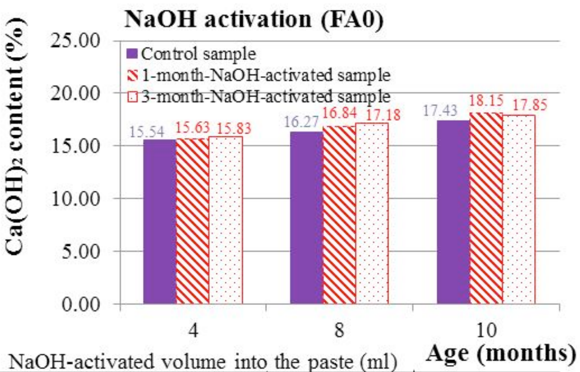


Ages(months)	4	8	10
1-month	0.26	0.69	1.00
3-month	0.06	0.10	0.22

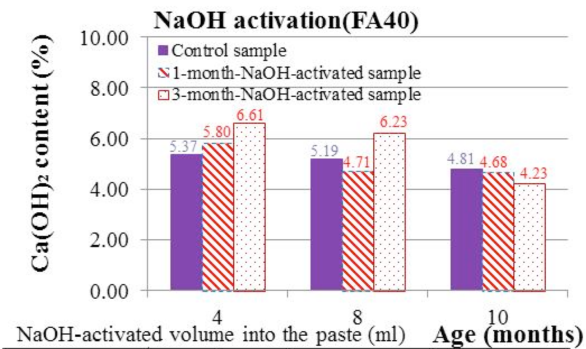


Ages (months)	4	8	10
1-month	0.05	0.10	0.14
3-month	0.04	0.09	0.24

Fig.5 Effect of water injection time on CH content in FA0 (left) and FA40 (right)

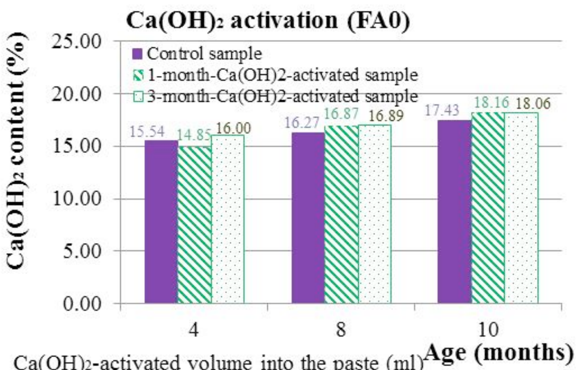


1-month	0.26	0.69	1.00
3-month	0.06	0.09	0.34

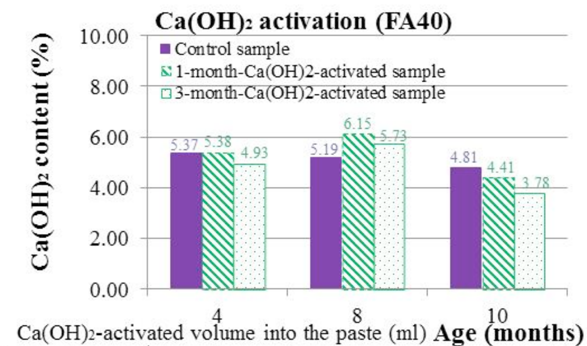


Ages (months)	4	8	10
1-month	0.05	0.10	0.20
3-month	0.04	0.10	0.27

Fig.6 Effect of NaOH activation time on CH content in FA0 (left) and FA40 (right)



1-month	0.26	0.70	1.00
3-month	0.06	0.10	0.34



Ages (months)	4	8	10
1-month	0.05	0.08	0.20
3-month	0.04	0.10	0.27

Fig.7 Effect of $Ca(OH)_2$ activation time on CH content in FA0 (left) and FA40 (right)

of 10 months, however, three cases were about the same CH content regardless of the water injection. It indicates that 3-month water injection was more effective in accelerating cement hydration in the early stages, and promoting pozzolanic reaction of FA40 in the later stages than 1-month water injection.

The comparisons of CH content in FA0 and FA40 between control samples, 1-month-NaOH-activated samples and 3-month-NaOH-activated samples are shown in Fig. 6. The comparisons of CH content in FA0 and FA40 between control samples, 1-month-$Ca(OH)_2$-activated samples and 3-month-$Ca(OH)_2$-activated samples are shown in Fig. 7.

According to Fig. 6 and Fig. 7 left, alkali activator increased CH content in FA0 regardless of the activation time. As shown in Fig. 6 right, it can be found that CH content in 1-month-NaOH activated samples (FA40) was smaller than that in control samples at the ages of 4 months and 8 months while that in 3-month-NaOH-activated sample was only smaller than that in control sample at the age of 10 months. It demonstrates that 1-month NaOH activation could be more effective in reducing CH content than 3-month NaOH activation.

According to Fig. 7 right, 1-month-$Ca(OH)_2$ activation and 3-month-$Ca(OH)_2$ activation were the

Table 2 Total porosity of the paste at the age of 4 months

	Activation time	Type of solution injection	Total porosity (mm^3/g)
FA0	No activation	Control	114.4
	1-month activation	0.26 ml $Ca(OH)_2$	95.4
		0.26 ml NaOH	98.8
		0.26 ml Water	89.5
	3-month activation	0.06 ml $Ca(OH)_2$	77.8
		0.06 ml NaOH	87.2
		0.06 ml Water	78.4
FA40	No activation	Control	125.0
	1-month activation	0.05 ml $Ca(OH)_2$	123.1
		0.05 ml NaOH	108.7
		0.05 ml Water	114.0
	3-month activation	0.04 ml $Ca(OH)_2$	115.0
		0.04 ml NaOH	118.8
		0.04 ml Water	105.1

same in reducing CH content in FA40 at the ages of 4 months and 10 months. In addition, CH content in 3-month-alkali-activated sample was smaller than that in 1-month-alkali-activated sample at the ages of 4, 8, and 10 months. It indicates 3-month $Ca(OH)_2$ activation was more effective in reducing CH content more than 1-month $Ca(OH)_2$ activation.

As the above mentioned, though CH contents in alkali-activated samples were larger than those in control samples at the ages of 4 and 8 months in the case of NaOH activation and at the age of 8 months in the case of $Ca(OH)_2$ activation, that could not imply that the alkali-supplying was not effective in accelerating pozzolanic reaction. This might be due to the fact that CH content in alkali-activated samples included CH content formed from cement hydration and CH content from supplying alkali activator and the consumption of CH content by pozzolanic reaction.

In brief, the water injection promoted cement hydration and pozzolanic reaction. In addition, 3-month water injection was more effective in promoting cement hydration at the early ages as well as pozzolanic reaction of FA40 at the later ages. Meanwhile, the alkali activation decreased slightly CH content in FA40 independenty of alkali activation time. Moreover, this effectiveness can depend on the type of alkali solution.

3.2 Porosity

(1) Effect of water or alkali injection in the case of 1-month- supplying

The total porosity of the paste without and with 1-month or 3-month water or alkali injection measured at the age of 4 months by MIP is shown in Table 2. The value and the ratio of pore volume of 20-330 nm and 3-20 nm ranged diameter of the paste without and with 1-month alkali activation measured at the age of 4 months are shown in Fig. 8.

From Table 2, the total porosity of FA0 at the age of 4 months was smaller than that of FA40 regardless of the presence of alkali activator. The total porosity of solution-injected plain cement paste (FA0)

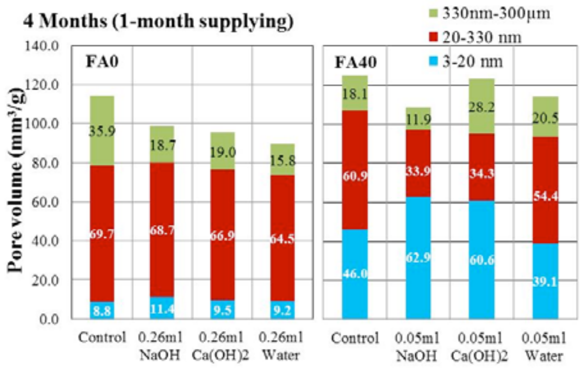


Fig.8 Effect of alkali activator on the pore volume of FA0 (left) and FA40 (right) at the age of 4 months

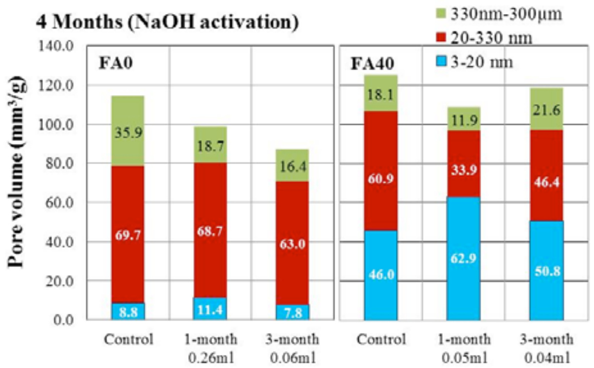
was smaller than that of control plain cement paste because cement hydration was promoted by the water from solution injection. This tendency was also observed in the case of solution-injected fly ash cement paste (FA40). It demonstrates not only cement hydration but also pozzolanic reaction was accelerated by water or alkali injection.

According to Fig. 8, the pore volume ratio of 20-330 nm and 3-20 nm ranged diameter of alkali-activated fly ash cement paste kept significantly decreasing and increasing tendencies respectively when compared with control sample, as well as compared with water-injected sample which had the smaller total pore volume, while those of water or alkali-injected plain cement paste was not observed. This tendency was also found by Yamamoto and Kanazu's research [7], indicating pozzolanic reaction of fly ash particles was accelerated in the presence of alkali activator. Based on this tendency, it could be explained that its pore volume of 3-20 nm ranged diameter was increased and pore volume of 20-330 nm ranged diameter was decreased significantly despite of the slightly smaller total porosity of 1-month-$Ca(OH)_2$- activated fly ash cement paste than that of control sample as shown in Table 2. It indicates pozzolanic reaction of fly ash particles was accelerated in the presence of saturated $Ca(OH)_2$ solution. It should be noted here that the nearly same CH content in 1-month-$Ca(OH)_2$-activated fly ash cement paste as that of control sample was observed at the age of 4 months (see Fig. 4).

In the case of 1-month-NaOH-activated samples, although CH content in NaOH-activated sample was larger than that in control sample at the age of 4 months (see Fig. 3), the decrease of the pore volume of 20-330 nm ranged diameter and the increase of the pore volume of 3-20 nm ranged diameter were also observed in the case of NaOH-activated sample (FA40) at the age of 4 months (see Fig. 8).

(2) Effect of the activation time

The pore volume of 20-330 nm and 3-20 nm ranged diameter of the paste without and with 1-month alkali activation and with 3-month alkali activation at the age of 4 months are shown in Fig. 9. Compared with control sample, the decrease of the pore volume of



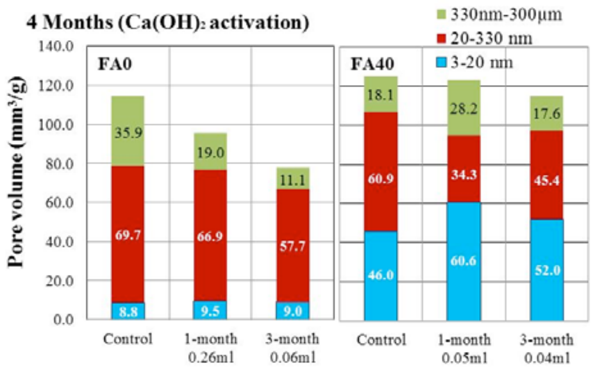


Fig.9 Effect of NaOH activation time (top) and $Ca(OH)_2$ activation time (bottom) on the pore volume of FA0 (left) and FA40 (right) at the age of 4 months

20-330 nm ranged diameter and the increase of the pore volume of 3-20 nm ranged diameter of FA40 were also observed significantly in both of 1-month and 3-month alkali activation whereas those of FA0 were not observed. Combined to Table 2, the total pore volume of both of them was smaller than that of control sample. It indicates 1-month and 3-month alkali activation was effective in accelerating pozzolanic reaction of fly ash cement paste although they had the larger amount of CH than control sample at the age of 4 months (see Figs. 3 and 4). On the other hands, 1-month alkali activation was more effective in reducing the pore volume of 3-20 nm ranged diameter of FA40 than 3-month alkali activation.

4. CONCLUSIONS

(1) Water injection promoted cement hydration of plain cement paste as well as pozzolanic reaction of fly ash cement paste. 3-month water injection was more effective in promoting cement hydration in the early stages while accelerating pozzolanic reaction of fly ash in the later stages than 1-month water injection.

(2) Alkali activator was effective a little in reducing the $Ca(OH)_2$ content in fly ash cement paste, indicating pozzolanic reaction of fly ash particles was accelerated. In addition, $Ca(OH)_2$ activation was more effective in reducing the $Ca(OH)_2$ content in fly ash cement paste than NaOH activation.

(3) Alkali activators were effective in fly ash cement paste to reduce total and 20-330 nm ranged diameter pore volume with accordance of pozzolanic reaction.

(4) 1-month alkali activation was effective in fly ash cement paste to reduce 20-330 nm ranged diameter pore volume more than 3-month alkali activation.

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REFERENCES

[1] Mehta, P. K., “Natural pozzolans: Supplementary cementing materials in concrete,” CANMET Special Publication 86, 1987, pp. 1-33.

[2] Bery, E. E., Hemmings, R. T. and Cornelius, B. J., “Mechanism of hydration reactions in high volume fly ash pastes and mortars”, Cem. Concr. Compos., Vol. 12, 1990, pp. 253-261.

[3] Sakai, E. et al., “Hydration of fly ash cement”, Cem. Concr. Res., Vol. 35, 2005, pp. 1135-1140.

[4] Lam, L., Wong, Y. L. and Poon, C. S., “Degree of hydration and gel/paste ratio of high volume fly ash/cement systems”, Cem. Concr. Res., Vol. 30, 2000, pp. 747-756.

[5] Zhang, Y. M, Sun, W. and Yan, H. D., “Hydration of high volume fly ash cement pastes”, Cem. Concr. Compos., Vol. 22, 2000, pp. 445-452.

[6] Feldman, R. F., Carette, G. G. and Malhotra, V. M., “Studies on of development of physical and mechanical properties of high-volume fly ash-cement paste”, Cem. Concr. Compos., Vol. 12, 1990, pp. 245-251.

[7] Yamamoto, T. and Kanazu, T., “Experimental explanation of compacting effect on hydration phases and strength development mechanism derived from pozzolanic reaction of fly ash, J. of JSCE, E, Vol. 63, No.1, 2007, pp. 52-65.

[8] Bijen, J., “Benefits of slag and fly ash”, Construct. and Build. Mater., Vol. 10, 1996, pp. 309-314.

[9] Tang, M. and Han, S., “Effect of $Ca(OH)_2$ on alkali-silica reaction”, J. of Chi. Sil. Soc., Vol. 9, 1981, 160-166.

[10] Li, D. et al., “The influence of alkalinity on activation and microstructure of fly ash”, Cem. Concr. Res., Vol. 30, 2000, pp. 881-886.

[11] Fu, X. et al., “Studies on high strength slag and fly ash compound cement”, Cem. Concr. Res., 30, 2000, pp. 1239-1243.

[12] Fan, Y. et al., “Activation of fly ash and its effects on cement properties”, Cem. Concr. Res., Vol. 29, 1999, pp. 467-472.

[13] Wasburn, E. W., “Note on method of determining distribution of pore sizes in porous material”, Pro. of the National Academic of Science, USA, Vol. 7, 1921, pp. 115-120.