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Effect of Injection of NaOH Solution on Pozzolanic and Hydration Reactions in Low-Calcium Fly Ash Cement Paste

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ABSTRACT

Alkali activation at normal temperature by an injection of NaOH solution into fly ash cement paste was investigated. It was reported that the injection of NaOH solution from the age of 1 month accelerated the pozzolanic reaction in cement paste with 40% replacement with fly ash. However, this injection was not effective in accelerating the pozzolanic reaction in cement paste with 20% replacement with fly ash at the age of 2 months. Moreover, it affected the production of $Ca(OH)_2$ adversely in the cement paste in the short term after injection.

The present study aims at investigating the effect of injection of NaOH solution from the age of 6 months on reactions in cement paste with 0% (FA0), 20% (FA20) and 40% (FA40) replacement with fly ash so that the cement hydration and pozzolanic reaction should be accelerated more effectively from directly after the injection. In addition to NaOH solution at a concentration of 0.1mol/L, water or no solution was also injected into the paste through an installed syringe for comparison.

As a result, the injection of solution increased the $Ca(OH)_2$ content in FA0, whereas it reduced the $Ca(OH)_2$ content in FA20 and FA40 at the ages of 8 and 10 months. The injection of NaOH solution or water from the age of 6 months increased the consumption of $Ca(OH)_2$ by the pozzolanic reaction in FA20 and FA40 more than that of no solution. According to the porosity, the volume ratios of pores ranging 20-330 nm in diameter to the total pore of FA20 and FA40 activated by water or NaOH solution were also reduced.

In conclusion, the injection of NaOH solution from the age of 6 months was effective in promoting the cement hydration in FA0 and accelerating the pozzolanic reaction in FA20 and FA40.

INTRODUCTION

The utilization of fly ash as a partial replacement of cement has been required in durable concrete technology because it can improve the durability of concrete significantly [Hooton 2015]. It also reduces a huge amount of carbon dioxide (CO_2) emission from the cement manufacturing [Shi 1998; Owens et al. 2010] and the construction cost [Siddique et al. 2009]. However, the replacement of cement with fly ash causes the lower early strength of fly ash concrete than cement concrete [Marthong and Agrawal 2012]. This is due to slow pozzolanic reaction of low-calcium fly ash particles [Poon et al. 2000; Totanji et al. 2004]. Therefore, to expand the use of fly ash in sustainable concrete technology, such as an application to pre-stressed concrete requiring high early strength, acceleration of the pozzolanic reaction of fly ash particles is desired.

Activation on the pozzolanic reaction of fly ash has been investigated in order to increase the use of fly ash more. Alkali activation has been concluded to be the most effective method for accelerating the pozzolanic reaction of fly ash particles [Shi and Day 2001; Saraswathy 2003]. This activation is known as chemical activation by the addition of alkali solution at mixing. This addition of alkali solution is the common way to get a high pH system which corrodes the surface of fly ash, breaks the silica or alumina chains in fly ash particles and accelerates the pozzolanic reaction of fly ash [Fan et al. 1999; Ryu et al. 2013]. Sodium hydroxide (NaOH) solution is suggested to be one of strong alkali activator to accelerate the pozzolanic reaction of fly ash [Owens et al. 2010]. Nevertheless, this activation also depends on the mixing process and curing temperature. It was confirmed that the degree of hydration of fly ash activated at normal temperature is lower than that of fly ash activated at high temperature [Li et al. 2000], which could limit to apply in the practice.

Alkali activation at normal temperature was suggested by the injection of alkali solution into fly ash cement paste in order to accelerate the pozzolanic reaction of fly ash particles continuously [Bui et al. 2015]. It was reported that the injection of NaOH solution from the age of 1 month accelerated the pozzolanic reaction in the cement paste with 40% replacement with fly ash. However, this injection was not effective in accelerating the pozzolanic reaction in the cement paste with 20% replacement with fly ash at the age of 2 months. Moreover, it affected the production of calcium hydroxide ($Ca(OH)_2$) adversely in the cement paste without fly ash in the short term after the injection. This was explained by the fact that it is difficult for cement to release Ca^{2+} ion due to high concentration of alkali solution injected from the age of 1 month [Bui et al. 2015]. Martinez-Ramiez and Palomo also reported that degree of hydration of portland cement is reduced by the presence of high alkali solution [Martinez-Ramiez and Palomo 2001].

Therefore, the present study aims at investigating the effect of injection of NaOH solution from the later age than 1 month, i.e. from the age of 6 months, on reactions in the cement paste with 0%, 20%, and 40% replacement with fly ash so that the cement hydration and pozzolanic reaction should be accelerated more effectively from directly after the injection.

EXPERIMENTAL INVESTIGATION

Materials. Cement used in this study was high-early-strength portland cement for ensuring the early strength of paste. This type of cement met the standard values of JIS R 5210 (portland cement) and ASTM standard C150-04 (standard specification for portland cement). Low-calcium fly ash used for replacing cement met the requirements of type II per JIS A 6201 (fly ash for concrete) and class F per ASTM standard C618 (standard specifications for coal fly ash and raw or calcined natural pozzolan). Table 1 shows the chemical compositions and physical properties of the high-early-strength portland cement and low-calcium fly ash.

Table 1. Chemical Compositions and Physical Properties of Cementitious Materials

		High-early-strength portland cement	Low-calcium fly ash
Chemical compositions	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
Physical properties	Density (g/cm^3)	3.14	2.21
	Blaine specific surface area (cm^2/g)	4590	3290

Preparation of specimens. Paste specimens were prepared with a low water to binder ratio of 0.30, with which an injection of solution should be an effective method for promoting the pozzolanic and hydration reactions in the fly ash cement pastes. Low-calcium fly ash was used to replace the high-early-strength portland cement at mass ratios of 0%, 20%, and 40% (hereafter, abbreviated as FA0, FA20, and FA40, respectively). The pastes were mixed in a mechanical mixer and cast in 40-mm cube molds, and then the placing surfaces of specimens were sealed with aluminum tapes to prevent water loss and carbonation. After that, a 1-mL syringe from which the plunger had been removed was inserted into the center of the specimen. Mixing and preparations of specimens were conducted at 20°C. All paste specimens were demolded 24h after casting, and then cured in sealed condition at 20°C as shown in Figure 1.

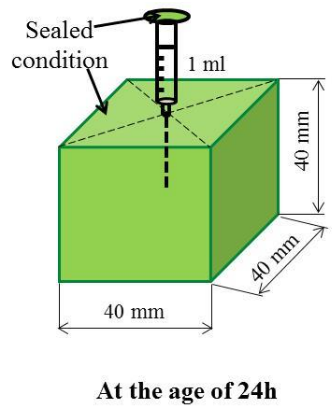

Figure 1. Preparation of Specimen at the Age of 24h

Method for injection of solution. Similar to the previous study [Bui et al. 2015], the solution was supplied through the 1-mL installed syringe as shown in Figure 2. The starting time of injection of solution in this study was considered to be the age of 6 months, but not the age of 1 month as investigated in the previous study [Bui et al. 2015]. Solutions used in this study were 0.1mol/L NaOH solution and water for comparison. They were allowed to be imbibed naturally into the pastes over time, i.e. there could be a gradient of injected liquid from the tip of the needle outwards. The volume and gradient of injected liquid should be dependent on individual hydration and microstructure of paste specimens. No solution was also injected into the paste specimens for the control.

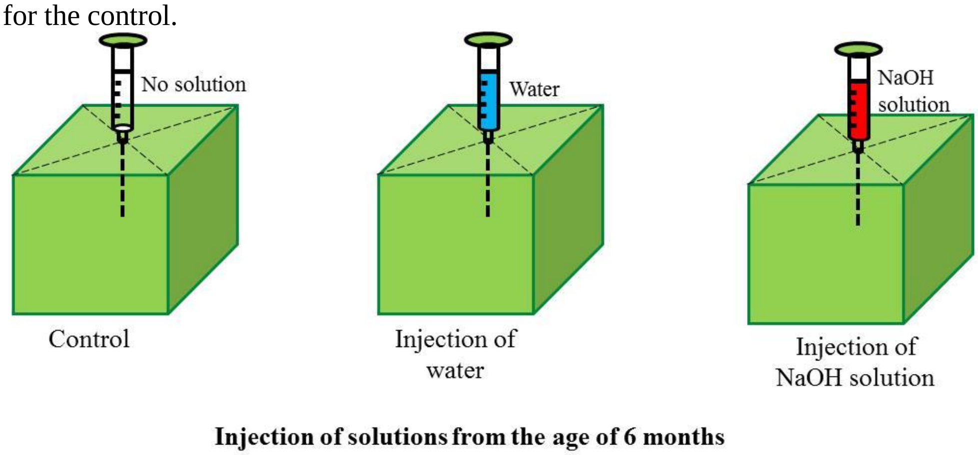

Figure 2. Method for Injection of Solution

Differential thermal analysis and thermal gravimetry (DTA-TG). The $Ca(OH)_2$ content in the paste specimens was measured by simultaneous differential thermal analysis and thermal gravimetry (DTA-TG) apparatus at the designated months (i.e. at the ages of 8 and 10 months). As shown in Figure 3, a sample was drilled out and collected as powder at the point of the needle of the syringe (i.e. the depth of 16-20 mm from the surface of specimen). The powder sample was soaked in ethanol for 24h to stop further hydration and dried in a vacuum desiccator for 24h before TG analysis. The $Ca(OH)_2$ content in the paste specimens was calculated from the ignited mass and the mass loss due to the dehydration of $Ca(OH)_2$ [Sakai et al. 2005].

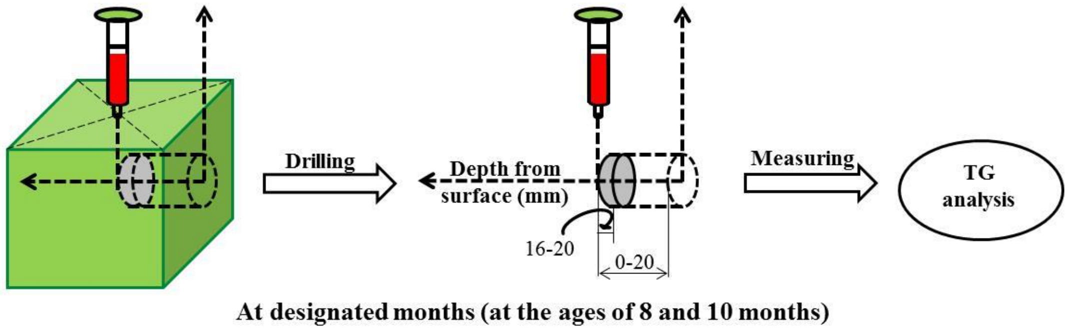

Figure 3. Preparation of Sample for TG Analysis

Mercury intrusion porosimetry (MIP). The measurements of $Ca(OH)_2$ content and porosity were conducted on the same specimen. The porosity of the paste sample obtained by crushing the hardened paste specimen and selecting in the size ranged 2.5-5.0 mm from around the position of the needle was measured by mercury intrusion porosimetry (MIP) as shown in Figure 4. Similar to TG analysis, the samples were soaked in ethanol for 24h to stop further hydration and dried in a vacuum desiccator for 24h before MIP measurement. The MIP equipment operates at a maximum pressure of 414×10^6 N/m^2. The porosity of the pastes was measured over a diameter range of 3 nm-300 µm at the ages of 10 months.

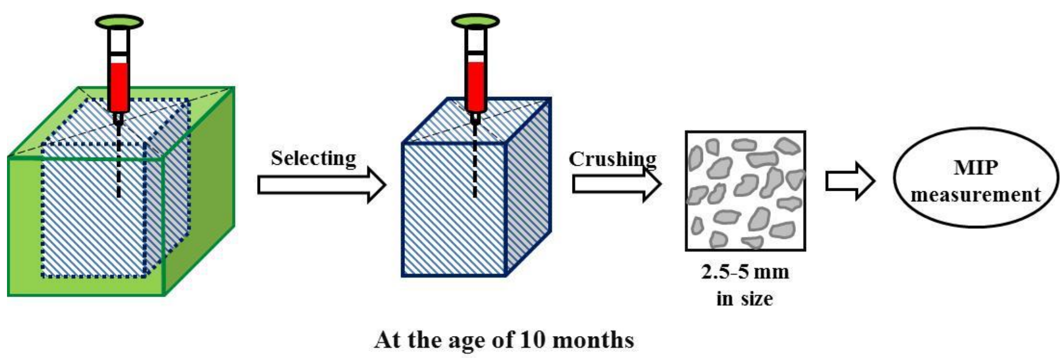

Figure 4. Preparation of Sample for MIP Measurement

RESULTS AND DISCUSSIONS

$Ca(OH)_2$ content. The $Ca(OH)_2$ content at the point of the needle in each FA0, FA20, and FA40 specimen into which water or NaOH solution was injected from the age of 6 months is compared with control specimens into which no solution was injected as shown in the left and right of Figure 5, respectively. The

$Ca(OH)_2$ content in FA0 specimens for the injection of water or NaOH solution was larger than that for no injection at the ages of 8 and 10 months. It indicates that the injection of NaOH solution from the age of 6 months did not affect the production of $Ca(OH)_2$ adversely in FA0 specimens as shown in the previous study with the injection of NaOH solution from the age of 1 month [Bui et al. 2015]. Briefly, the injection of water or NaOH solution from the age of 6 months promoted the cement hydration in FA0 specimens, resulting in the increase in the $Ca(OH)_2$ content in the cement paste.

Meanwhile, the $Ca(OH)_2$ contents in FA20 and FA40 for the injection of water or NaOH solution were smaller than that for no injection at the ages of 8 and 10 months. It shows that the injection of water or NaOH solution from the age of 6 months was effective in accelerating the pozzolanic reaction in both FA20 and FA40 specimens, resulting in the decrease in the $Ca(OH)_2$ content in the low-calcium fly ash cement paste.

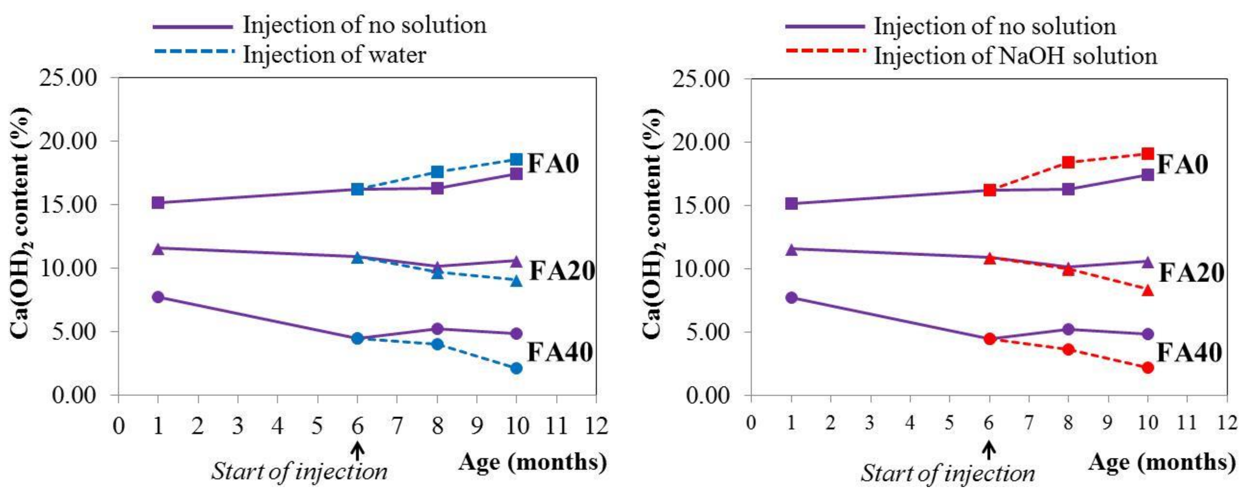

Figure 5. Effects of Injection of Water (Left) and Injection of NaOH Solution (Right) on the $Ca(OH)_2$ Content in FA0, FA20, and FA40 Specimens

Consumption of $Ca(OH)_2$. Figure 6 presents the consumption of $Ca(OH)_2$ by the pozzolanic reaction in each case (the injection of no solution, the injection of water, and the injection of NaOH solution) calculated by equation (1) [Zhang et al. 2000]:

$$CH_{cons.} = CH_{PC}(c/(c+f)) - CH_{FC} \qquad (1)$$

where $CH_{cons.}$ is the consumption of $Ca(OH)_2$ by the pozzolanic reaction in each case (%), CH_{PC} is the $Ca(OH)_2$ content in the cement paste (FA0) in each case (%), CH_{FC} is the $Ca(OH)_2$ content in the low-calcium fly ash cement paste (FA20 or FA40) in each case (%), (c/(c+f)) is the mass ratio of cement in the binder (cement + fly ash), (FA20: (c/(c+f)) = 0.8 and FA40: (c/(c+f)) = 0.6).

The consumptions of $Ca(OH)_2$ by the pozzolanic reaction in FA20 and FA40 specimens for no injection increased with time. However, the rates of consumptions kept constant from the age of 6 months to the age of 10 months in FA40 specimens as shown in the right of Figure 6. Therefore, the injection of NaOH solution at a concentration of 0.1mol/L from the age of 6 months should supply OH^- ion and could accelerate the pozzolanic reaction in the fly ash cement systems.

According to Figure 6, the consumptions of $Ca(OH)_2$ by the pozzolanic reaction in FA20 and FA40 specimens for the injection of NaOH solution or water were higher than those for no injection at the ages of 8 and 10 months. It can be also seen that the injection of NaOH solution increased the consumption of $Ca(OH)_2$ by the pozzolanic reaction in FA20 specimens more than that of water at the ages of 8 and 10 months. As a result, the injection of NaOH solution accelerated the pozzolanic reaction in FA20 more than that of water. The injection of NaOH solution also increased the consumption of $Ca(OH)_2$ by the pozzolanic reaction in FA40 specimen more than that of water at the age of 8 months. However, the consumptions of $Ca(OH)_2$ by the pozzolanic reaction in FA40 specimens in both cases of the injection of NaOH solution and water were nearly the same at the age of 10 months.

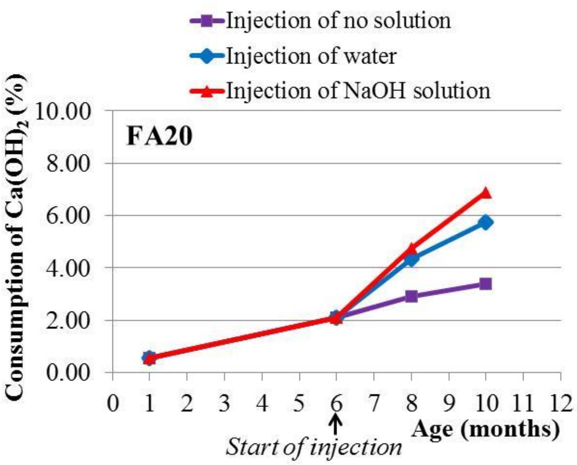

Figure 6. Effects of Injection of Water and NaOH Solution on the Consumption of $Ca(OH)_2$ by the Pozzolanic Reaction in FA20 (Left) and FA40 (Right) Specimens

Porosity. The cumulative pore volumes of FA0 (top), FA20 (middle) and FA40 (bottom) in each case (the injection of no solution, the injection of water, and the injection of NaOH solution) are shown in figure 7. It can be found that the injection of solution (water or NaOH solution) from the age of 6 months reduced the total pore volume of FA0 specimens significantly at the age of 10 months. The improved pore structure of FA0 at the age of 2 months was also observed in the case of the injection of solution from the age of 1 month as shown in the previous study [Bui et al. 2015]. It is considered that the injection of water or NaOH solution from the age of 6 months also promoted the cement hydration in FA0, resulting in improving the pore structure of the cement paste.

Meanwhile the injection of water or NaOH solution from the age of 6 months reduced the total pore volume of FA20 and FA40 specimens slightly at the age of 10 months as shown in middle and bottom of Figure 7. Additionally, the volumes of 20-330 nm and 3-20 nm diameter pores of FA20 and FA40 specimens in each case (the injection of no solution, the injection of water, and the injection of NaOH solution) at the age of 10 months are shown in Figure 8 in order to estimate the effect of injection of solution on the degree of the pozzolanic reaction in the fly ash cement paste. Compared with no injection, the volume ratios of 20-330 nm pores to total volume decreased and those of 3-20 nm pores increased in FA20 and FA40 specimens, but not in FA0 specimens for the injection of water or NaOH solution. According to Yamamoto and Kanazu [Yamamoto and Kanazu 2007], these show that the pozzolanic reaction in FA20 and FA40 was accelerated by the injection of water or NaOH solution from the age of 6 months.

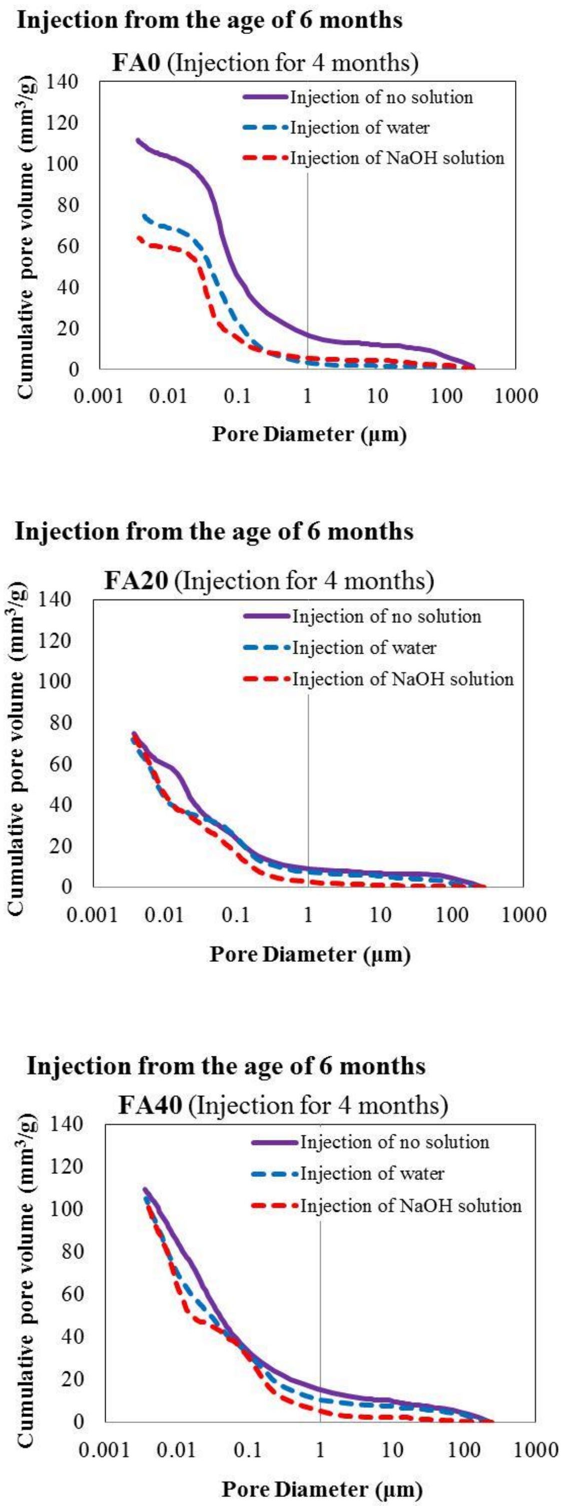

Figure 7. Effects of Injection of Water and NaOH Solution on the Cumulative Pore Volume of FA0 (Top), FA20 (Middle), and FA40 (Bottom) Specimens at the Age of 10 Months

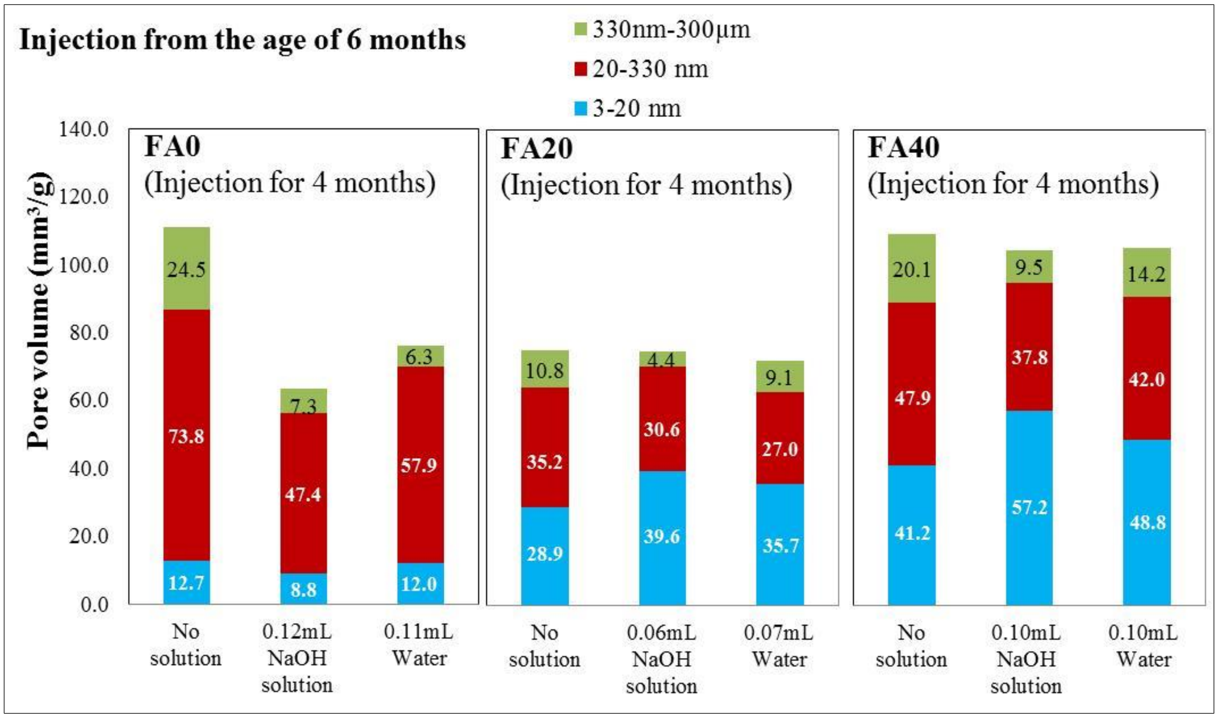

Figure 8. Effects of Injection of Water and NaOH Solution on the Pore Size Distribution of FA0 (Left), FA20 (Middle), and FA40 (Right) Specimens at the Age of 10 Months

CONCLUSION

The following conclusions can be drawn from this study:

- An injection of water or NaOH solution from the age of 6 months promoted the cement hydration in the cement paste, resulting in the increase in $Ca(OH)_2$ content at the ages of 8 and 10 months and the improvement of the pore structure at the age of 10 months.
- In addition to reducing the $Ca(OH)_2$ content, an injection of NaOH solution from the age of 6 months increased the consumption of $Ca(OH)_2$ by the pozzolanic reaction in the cement paste with 20% replacement with fly ash at the ages of 8 and 10 months more than that of water. This effectiveness was also observed in the cement paste with 40% replacement with fly ash at the age of 8 months. However, the increase in consumption of $Ca(OH)_2$ by the pozzolanic reaction in the cement paste with 40% replacement with fly ash for both cases of injection of water and NaOH solution was nearly the same at the age of 10 months.
- Although an injection of water or NaOH solution from the age of 6 months reduced slightly the total pore volume, it affected the pore size distribution of the cement paste with 20% and 40% replacement with fly ash, with the decrease in the volume ratios of 20-330 nm pores to total volume and the increase in that of 3-20 nm pores at the age of 10 months.

As a consequence, an injection of NaOH solution from the age of 6 months promoted the cement hydration and accelerated the pozzolanic reaction in the fly ash cement pastes effectively from directly after the injection. Owing to the effective injection of NaOH solution from the age of 6 months simulated as an original model of internal curing, the application of a type of internal curing agent which could supply NaOH solution for fly ash concrete from the age of 6 months should be investigated in the future.

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