EXPERIMENTAL STUDY ON ACCELERATION OF POZZOLANIC REACTION OF FLY ASH

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ABSTRACT: The aim of this study is to know the effects of alkali solution and additional admixture of calcium hydroxide on the acceleration of the pozzolanic activity of fly ash. Alkali solution such as potassium hydroxide solution in different concentration was used as an activator to accelerate the pozzolanic reaction of fly ash. Fine calcium hydroxide powder was added to mixtures to supply calcium ion for pozzolanic reaction. As a result, the addition of high concentration of alkali ion activator could accelerate the pozzolanic reaction more than low concentration but did not improve flexural strength of mortar.
KEYWORDS: Pozzolan, High volume fly ash, Activator, Alkali solution

1. INTRODUCTION

The application of many types of by-product to concrete has been investigated in terms of environmental conservation and the effective use of resources. Blast furnace slag, fly ash, silica fumes and rice husk ash are conventionally used as mineral admixtures for concrete. Among them, fly ash is focused on Japan especially. Because of economical reasons and stable supplies of energy resources, it is supposed that more coal-fired power plants will be constructed in the future. As a result, a large amount of coal ash will be produced. But there is no space to dump the ash in Japan. The addition of high volume fly ash to concrete must be one of solutions for the effective uses of resource of fly ash. It has been found that concrete containing fly ash gains watertight ability, long term period strength and a reduction in the heat of hydration. When cement is replaced with a large amount of fly ash, however, low early strength and fast neutralization have been pointed out. Large fluctuations in the quality of fly ash are also a problem. Since the pozzolanic reactivity of fly ash depends upon the quality of the fly ash, the rate of pozzolanic reaction and the properties of pozzolanic reaction products cannot be easily understood. According to the previous study, alkali ions such as sodium and potassium ions in pore solution of hydrated cement pastes were significantly reduced when high volume fly ash was used[1]. This result showed alkali ions could be associated with the pozzolanic reaction of fly ash. Although calcium carbonate (limestone powder) was used to supply calcium ions for the pozzolanic reaction of fly ash in the previous study[2], the calcium carbonate did not contribute to the additional supply of calcium ions for pozzolanic reaction.

The aim of this study is to know the effects of concentration of alkali ion activator and additional admixture (calcium hydroxide) on pozzolanic reaction of fly ash and to obtain fundamental data regarding the use of high volume fly ash for concrete. The pozzolanic reactivity of high volume fly ash is investigated mainly in its chemical aspects.

2. EXPERIMENTAL PROCEDURES

2.1 MATERIALS AND MIXTURE PROPORTIONS

In order to know the chemical aspects of pozzolanic reaction, ordinary portland cement containing no slag (NC) was used as cement. Classified fly ash was used as a mineral admixture. The chemical the pozzolanic reaction of fly ash, fine calcium hydroxide powder was added. In order to accelerate the

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compositions and physical characters of these binders are shown in **Table 1**. To supply calcium ions for pozzolanic reactivity of fly ash, potassium hydroxide solution was added. To investigate the effects of the concentration of the activator on the pozzolanic reactivity, 0.1, 0.3 and 0.5 mol/l of potassium hydroxide solutions were used. The mixture proportions are given in **Table 2**. The abbreviation definition of mixtures is shown in **Fig.1**. The replacement ratios of cement with fly ash were 0, 15, 30, 60 and 75% by mass. The water-to-cementitious materials ratio was kept to 0.45.

Table 1. Chemical compositions and physical characters of cement

Type of binder	Chemical compositions (%)									Density	Blaine specific
	ig.loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	(g/cm^3)	surface area (cm^2/g)
NC	0.7	21.1	5.3	2.3	64.6	2.1	1.9	0.26	0.57	3.15	3070
Fly ash	0.9	57	27.7	7.9	0.6	1.1	0.2	0.3	0.4	2.27	3830

2.2 PORE SOLUTION ANALYSIS

Pore solution was extracted by a compression test machine from hardened cement pastes at the ages of 1, 7, 14, 28 and 63 days. The cement paste specimens were sealed up to the extraction. The hydroxide ion concentration in pore solution was determined by neutralization titration with hydrochloric acid immediately after the extraction. The concentration of sodium, potassium and calcium ions (Na^+, K^+, Ca^{2+}) in pore solution was measured with a frame emission spectrophotometer. The solutions were properly diluted when each determination was carried out.

Table2. Mixture proportion

Type	Mass ratio				Activator concentrations (mol/litre)
	W	NC	FA	$Ca(OH)_2$	
PL	0.45	1	-	-	-
BF15B-Ca		0.85	0.15	0.075	0.3
BF30B-Ca		0.7	0.3	0.15	0.3
BF60A		0.4	0.6	-	0.1
BF60A-Ca				0.3	
BF60B				-	0.3
BF60B-Ca				0.3	
BF60C				-	0.5
BF60C-Ca				0.3	
BF75B-Ca		0.25	0.75	0.375	0.3

2.3 PORE SIZE DISTRIBUTION ANALYSIS

Mortar specimens were demoulded 2 days after mixing and cured in water at 20℃ up to the age of testing. At the ages of 7, 28 and 63 days, the pore sizes in mortar were analyzed with a mercury intrusion method.

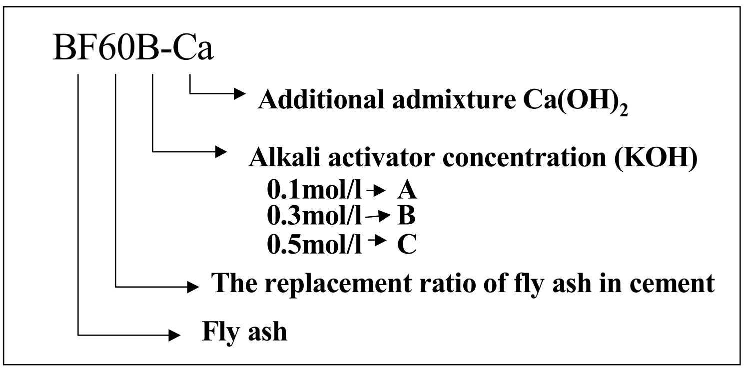


Figure 1. The abbreviation definition of mixtures

2.4 FLEXTURAL STRENGTH AND COMPRESSIVE STRENGTH TEST

Mortar specimens were demoulded 2 days after mixing and cured in water at 20℃ up to the age of testing. At the ages of 7, 14, 28 and 63 days, the flexural strength and compressive strength of mortar specimens were tested.

3. RESULTS AND DISCUSSIONS

3.1 PORE SOLUTION COMPOSITIONS

Figs. 2,3 and **4** show the changes in hydroxide, potassium and calcium ion concentration in pore solution of pastes containing different amounts of fly ash respectively.

As for the paste containing no fly ash, the hydroxide ion concentration was gradually increased, while it was decreased at the longer ages in the cases of pastes containing fly ash. Fly ash consumed alkali ions due to its pozzolanic reaction. Larger decrease in hydroxide ion concentration can be seen for 30% and 60% replacement of fly ash than for 15% and 75% in **Fig. 2**. The activators could contribute to the acceleration of pozzolanic reaction of fly ash.

Similar tendency was shown in **Fig.3**. Potassium ions in addition to hydroxide ions were consumed by the pozzolanic reaction of fly ash. But for 15% replacement of fly ash, the concentration of potassium ion was dramatically decreased at the age of 63 days although the hydroxide ion concentration decreased a little. This reason cannot be clarified in this study.

Regarding the paste containing 60% fly ash, the higher the concentration of activators, the larger the reduction of the hydroxide and potassium ion concentration at the early age as shown in **Figs. 2** and **3**. It was also showed that the activators could accelerate the pozzolanic reaction of fly ash. On the other hand, the addition of calcium hydroxide did not show the significant difference in the concentration of both hydroxide and potassium ions.

The concentration of calcium ion in pore solution of cement pastes containing different amounts of fly ash is shown in **Fig.4**. The calcium ion concentration increased with the increase of the fly ash replacement ratio at the early ages. Since the hydroxide ion concentration decreased with the increase of fly ash, the calcium concentration was increased to keep the solubility product constant. As shown in

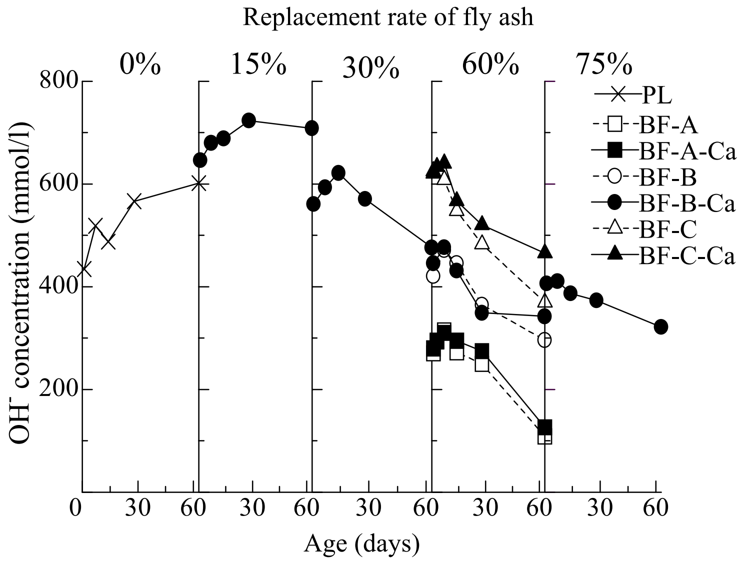


Figure 2. Hydroxide ion concentration in pore solution

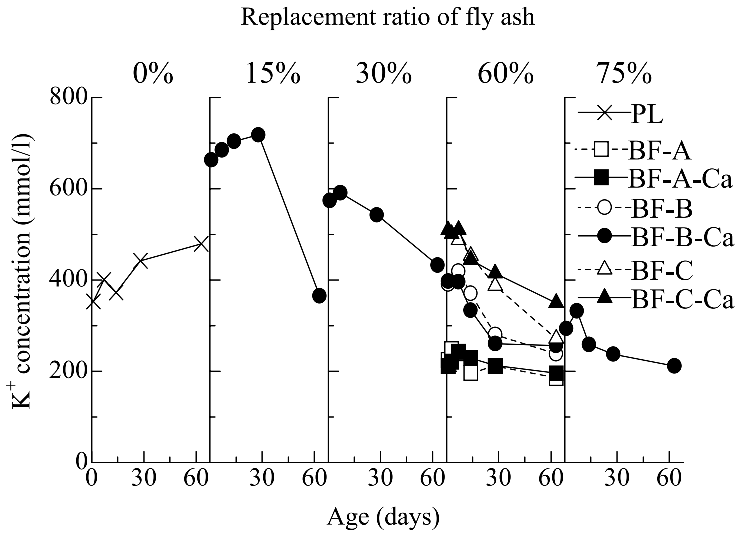


Figure 3. Potassium ion concentration in pore solution

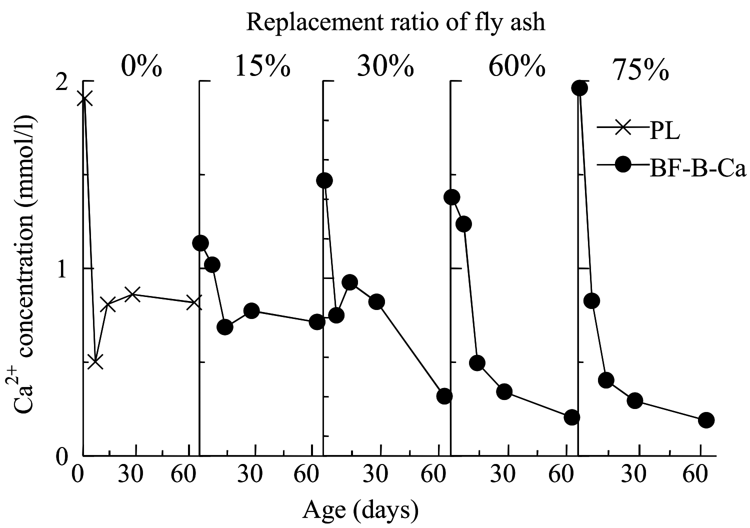


Figure 4. Calcium concentration in pore solution

Fig. 2, the hydroxide ion concentration increased by adding potassium solution to the mixtures. The calcium concentration was decreased to keep the constant solubility product.

The concentration of sodium and calcium ion in pore solution of cement pastes containing 60% replacement of fly ash with different concentration of activator are shown in **Figs. 5** and **6** respectively.

Although the same amount of sodium oxide is contained in each specimen, the concentration of sodium ion was changed in specimens as shown in **Fig.5**. When high concentration of activator was added, lower concentration of sodium ion was measured. It is thought that very high concentration of potassium ion in pore solution controlled the dissolution of sodium ion since potassium ions existed already in mixing water when specimen were mixed. When an additional admixture of calcium hydroxide was added, the concentration of sodium ion was gradually decreased. Sodium ion may also contribute to the acceleration of pozzolanic reaction in some extent.

Compared with specimens containing no additional admixture ($Ca(OH)_2$) in **Fig.6**, the concentration of calcium ion in specimens containing calcium hydroxide was higher. Surplus calcium hydroxide supplies calcium ions as soon as pozzolanic reaction consumes calcium ions.

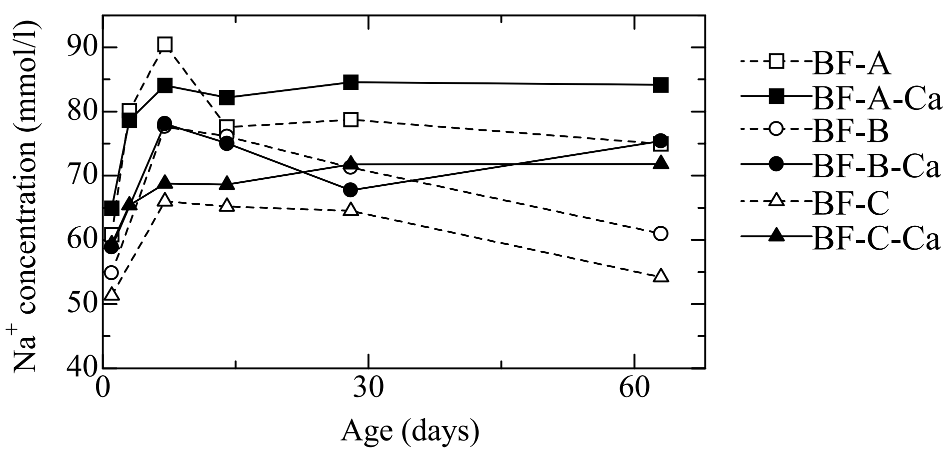


Figure 5. Sodium ion concentration in pore solution of 60% replacement of fly ash

3.2 PORE SIZE DISTRIBUTION ANALYSIS

The pore size distribution of 60% of fly ash mortars containing various concentrations of activator are shown in **Fig.7**. For mortar containing no fly ash (PL), dense microstructure was already formed at the age of 7 days. Few pores over 50 nm in diameter can be seen regardless of the ages. On the other hand, as for mortars containing fly ash and activator, the volume of pores over 50 nm in diameter was large. But the pores over 50 nm in diameter were reduced as the age passed. The microstructure of mortar became dense as the pozzolanic reaction proceeded.

When high concentration of alkali ions was added to the mixtures, small pores existed more compared with mortars containing low concentration of activators. It was shown that pozzolanic reaction was more accelerated by high concentration of alkali ions. Dense microstructures were also formed when calcium hydroxide was added to the mixtures. The pozzolanic reaction was accelerated by calcium hydroxide or the pores in mortar were filled with fine calcium hydroxide powders resulting in the micro-filler effect.

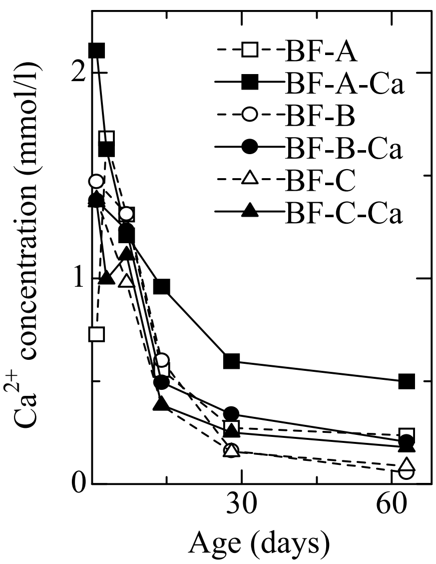
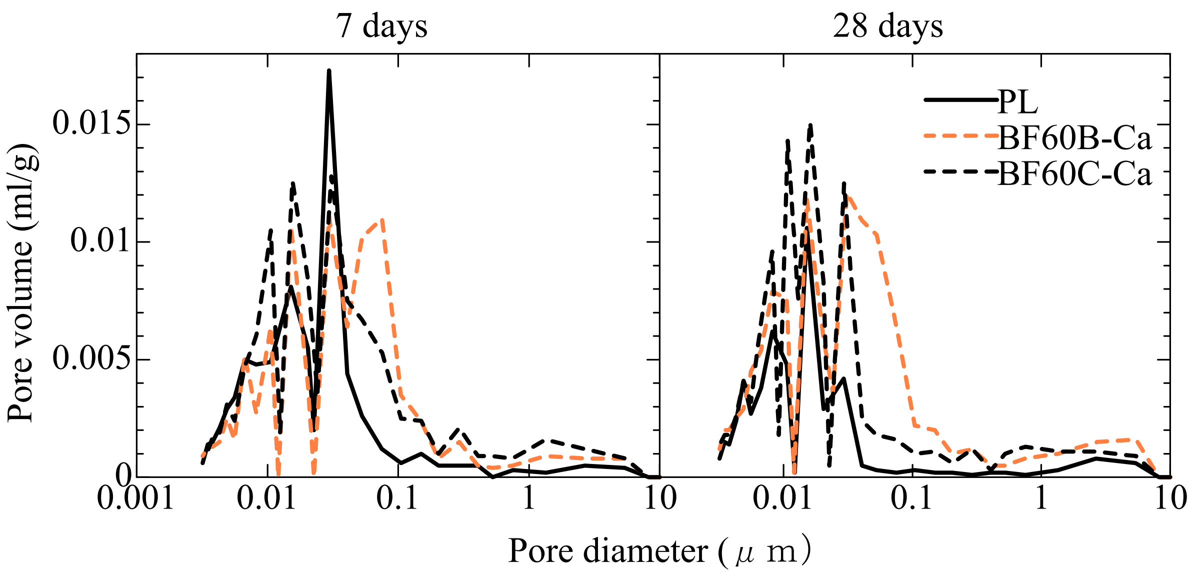
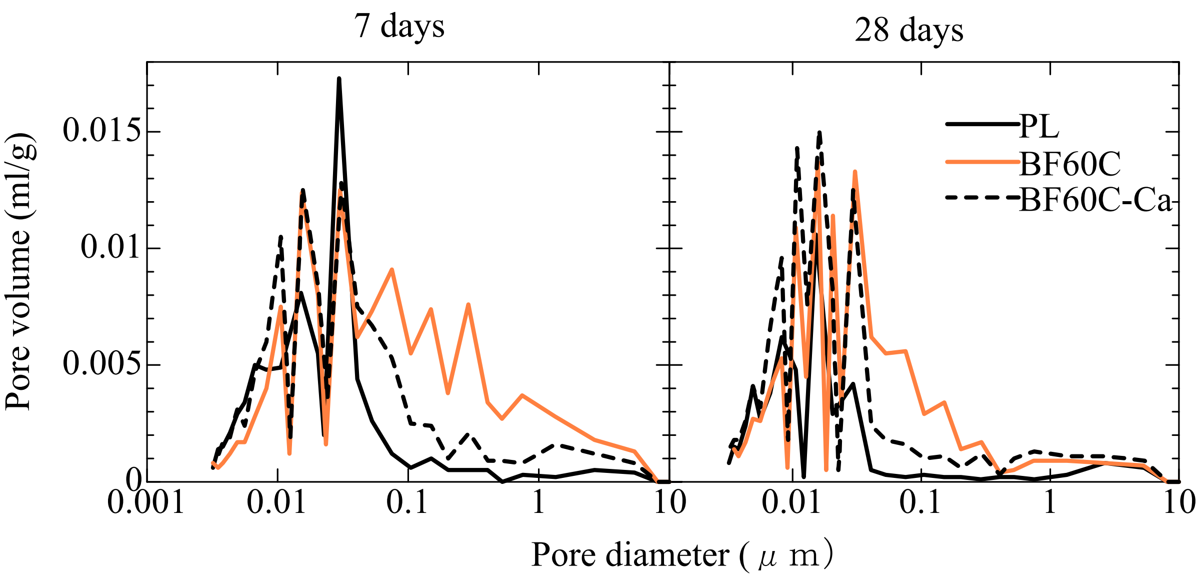


Figure 6. Calcium ion concentration in pore solution of 60% replacement of fly ash



(a) The comparison of the different concentrations of activators



(b) The comparison of mortar with and without calcium hydroxide

Figure 7. Pore size distribution

3.3 FLEXURAL STRENGTH AND COMPRESSIVE STRENGTH TEST

The relationship between flexural strength and age of specimens are shown in **Fig.8**. The additional admixture of calcium hydroxide did not give the significant improvement of the flexural strength of specimens. When 0.5 mol/l of potassium solution was added to the mixture, the flexural strength of specimens with calcium hydroxide was lower than that without calcium hydroxide. The reason must be further investigated.

On the other hand, the additional of 0.5 mol/l of potassium solution improved the compressive strength of mortar as shown in **Fig.9**. Furthermore when calcium hydroxide was added to the mixture, the compressive strength of mortar increased. The gain of the compressive strength of mortar corresponds to the reduction of alkali ions in pore solution and the formation of the dense microstructures.

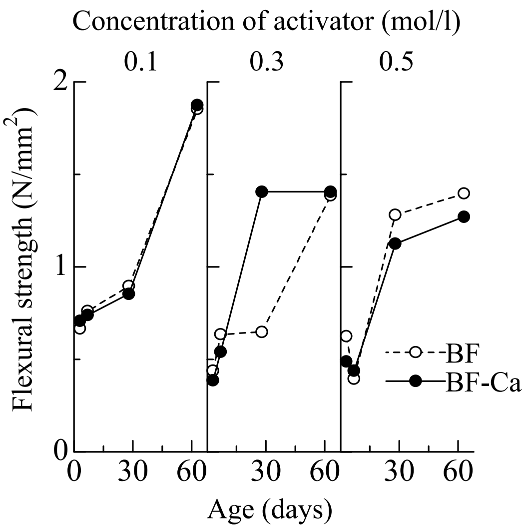


Figure 8. Flexural strength of 60% replacement of fly ash in different concentration of activator

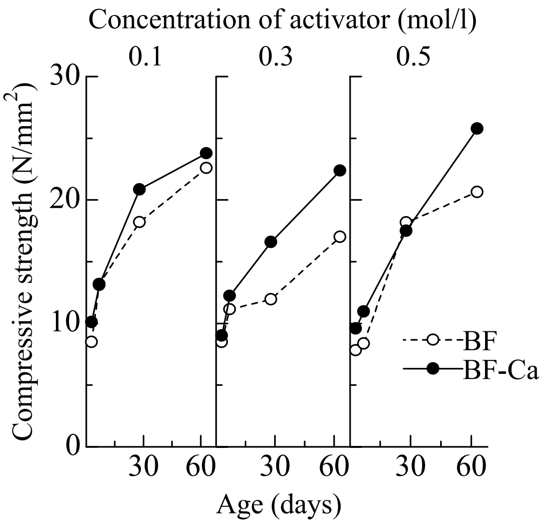


Figure 9. Compressive strength of 60% replacement of fly ash in different concentration of activator

The pozzolanic reaction was accelerated by high concentration of alkali ion solution. And the calcium hydroxide could contribute to the quick supply of the calcium ions for pozzolanic reaction.

4. CONCLUSIONS

(1) When the different concentration of potassium solution was used as an activator to accelerate the pozzolanic reaction, the high concentration of alkali ion activator could accelerate the pozzolanic reaction more than low concentration.
(2) When calcium hydroxide was added to the mixture, dense microstructures were formed and the compressive strength of mortar were improved. Calcium hydroxide could accelerate the pozzolanic reaction.
(3) The activators contributed to the formation of dense microstructure of mortar but did not improve flexural strength of mortar.

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