

**Effects of Internal Alkali Activation on
Chemical and Mechanical Properties of
Fly Ash Cement Systems**

(フライアッシュ・セメント系の化学的・力学的特性に及ぼす
内部アルカリ活性化の影響)

September 2015

Bui Phuong Trinh

ABSTRACT

Fly ash concrete has been used widely in the construction because of taking the advantages of the improved durability, effective cost, and environmental protection. However, low-calcium fly ash concrete has the lower strength than the cement concrete due to slow pozzolanic reaction of fly ash. This results in its limitation for the production of high strength concrete. In the recent years, several studies have suggested alkali activations to accelerate the pozzolanic reaction of fly ash particles. One of alkali activations is performed by mixing one or some types of alkaline solutions with fly ash directly and curing at high temperature, which could limit to apply in the practical use. The curing condition at normal temperature in alkali activation needs to be considered as the more practical method. In addition to the alkali activation, internal curing has been investigated for improving the properties of high strength concrete with a low water to binder ratio. Nevertheless, the previous studies of internal curing have discussed only the effects of internal water supplied from internal curing agents (such as pre-wetted lightweight aggregate, super absorbent polymers, porous ceramic waste aggregate (PCWA), and so on) on some properties of concrete. The internal acceleration for pozzolanic reaction by using PCWA imbibing an alkali solution, however, has not been investigated in the fly ash concrete yet. Based on this background, the aim of this study is to investigate an internal alkali activation (IAA) on the fly ash cement systems cured at normal temperature so that the fly ash concrete using PCWA imbibing alkali solution could get the maximized strength and enhanced durability.

To achieve the above-mentioned purpose, this thesis is organized as follow:

Chapter 1 describes the background, aims, and methodology of this study.

Chapter 2 provides a brief literature review about the effects of fly ash, the mechanisms and effects of internal curing, and the alkali activation on the chemical reaction and the long-term mechanical properties of the fly ash cement systems.

Chapter 3 presents the experimental program consisting of materials and mixture proportions, the fundamental models as IAA, the mixing and casting progress, the curing condition for the fly ash cement system. The experiments of fundamental models were performed to study the effects of IAA on the chemical and mechanical properties of the fly ash cement systems. They were (1) an original model through an installed syringe, (2) a model of internal activation by using PCWA. In addition, the effects of IAA on the mechanical properties of fly ash concrete using PCWA prepared in saturated-surface dry condition after the immersion in alkali solution for 7 days were investigated. Three types of IAA used in this study were (1) 0.1mol/L NaOH solution (pH = 13.0), (2) saturated Ca(OH)_2 solution (pH = 12.6), and (3) water for a reference. In addition to the effects of types of IAA, the effects of starting time of IAA on the pozzolanic reaction of fly ash cement systems were also studied. Cement systems with 0%, 20% and 40 mass% of fly ash replacement ratios were used, while the concrete using PCWA by 0% and 40 vol.% of coarse aggregate replacement ratios were used in this study. In order to evaluate the effects of IAA, the measurements of Ca(OH)_2 (CH) content and porosity, the calculation of CH consumption by the pozzolanic reaction, and test of the compressive strength of concrete were carried out by thermal gravimetric analysis, mercury intrusion porosimetry, and strength test, respectively. In addition, a confirmation by SEM examination was performed on this study.

Chapter 4 discusses the effects of types and starting time of IAA on the chemical reaction of the fly ash cement systems by examining the CH content and consumption of CH. The experiments demonstrates that IAA not only decreased the CH content but also increased the CH consumption by the pozzolanic reaction in the cement paste with 40% replacement of fly ash (FA40). Moreover, an injection of saturated Ca(OH)_2 solution reduced the CH content and increased the consumption of CH in FA40 more than that of water or NaOH solution. In addition to the effects of types of IAA, it can be found that IAA from 3 months after casting

increased the consumption of CH by pozzolanic reaction in FA40 more than that from 1 month after casting. Briefly, IAA was effective in accelerating the pozzolanic reaction and promoting the cement hydration of the fly ash cement systems. This was also confirmed by SEM examination.

Chapter 5 discusses the effects of IAA on the mechanical properties of the fly ash cement systems by measuring the porosity and hardness, and testing the compressive strength of the fly ash concrete. It shows that IAA decreased the total pore volume in FA40. Furthermore, pore size distribution was altered by IAA, with the decrease in the volume ratio of 20-330 nm pores to the total pore and the increase in that of 3-20 nm pores in FA40. It indicates that IAA was effective in accelerating the pozzolanic reaction of the fly ash cement systems. According to the decrease in the volume ratio of 20-330 nm pores to the total pore and the increase in that of 3-20 nm pores, it can be said that the IAA from 3 months after casting was more effective in accelerating the pozzolanic reaction of the fly ash cement paste at the age of 12 months than that from 1 month after casting. The experiment by using the model of internal activation with PCWA indicates that IAA also improved the microstructure of interfacial transition zone (ITZ) and bulk paste in the fly ash cement systems at the age of 6 months. In addition, the effects of IAA by using PCWA on the mechanical properties of the fly ash concrete can be briefly concluded that although the short- and long-term compressive strengths in the fly ash concrete using 40% replacement of PCWA imbibing the alkali absorption were nearly the same as those without PCWA, the macropore volume (pores ranging 0.05 – 50 μm) was reduced in the presence of IAA at the ages of 28, 182, and 364 days. Moreover, pore size distribution was altered by IAA, with the decrease in the volume ratio of 20-330 nm pores to the total pore and the increase in that of 3-20 nm pores. Briefly, the pozzolanic reaction of the fly ash cement systems was accelerated by IAA, with the decrease in the volume ratio of 20-330 nm pores to the total pore, the increase in the volume

ratio of 3-20 nm pores, and the improved ITZ microstructure although the enhanced compressive strength was not shown.

Chapter 6 proposes the mechanisms of IAA accelerating the pozzolanic reaction as well as promoting the cement hydration of the fly ash cement system. In addition, the differences in the starting time of IAA mechanism affecting the microstructure development in FA40 and the differences of each type of IAA in the activation mechanism of the fly ash particles are also described.

Chapter 7 states the conclusions of this study. Recommendations for future work are also provided.

CONTENTS

ABSTRACT	i
CONTENTS	v
LIST OF FIGURES	x
LIST OF TABLES	xvii
ACKNOWLEDGEMENTS	xviii

CHAPTER 1: INTRODUCTION

1.1 GENERAL	1-1
1.2 INTERNAL ALKALI ACTIVATION (IAA) ON FLY ASH CEMENT SYSTEMS	1-5
1.3 AIMS OF THE RESEARCH	1-5
1.4 METHODOLOGY OF THE RESEARCH	1-6
1.5 THESIS OUTLINE	1-7
References	1-8

CHAPTER 2: LITERATURE REVIEWS

2.1 FLY ASH	2-1
2.1.1 Properties of fly ash	2-2
2.1.2 Effects of fly ash	2-5
2.2 INTERNAL CURING	2-13
2.2.1 Definition	2-14
2.2.2 Mechanism	2-14
2.2.3 Effects of internal curing	2-16
2.3 ALKALI ACTIVATION	2-20

2.3.1 Definition	2-21
2.3.2 Mechanism	2-21
2.3.3 Effects of alkali activation	2-24
2.4 SUMMARY	2-27
References	2-28

CHAPTER 3: EXPERIMENTAL PROGRAM

3.1 MATERIALS	3-1
3.1.1 Cement	3-1
3.1.2 Fly ash	3-2
3.1.3 Alkali solution	3-3
3.1.4 Aggregate (porous ceramic waste aggregate - PCWA)	3-3
3.1.5 Admixture	3-5
3.2 MIXTURE PROPORTION	3-6
3.2.1 Paste	3-6
3.2.2 Concrete	3-6
3.3 METHOD OF IAA	3-7
3.3.1 Original model of IAA	3-8
3.3.2 Model of IAA using PCWA	3-10
3.3.3 IAA on fly ash concrete	3-11
3.4 MIXING, CASTING AND CURING	3-12
3.4.1 Mixing and casting	3-12
3.4.2 Curing condition	3-12
3.5 TEST PROCEDURE	3-12
3.5.1 Differential thermal analysis and thermogravimetry (DTA-TG)	3-12

3.5.2 Hardness measurement	3-13
3.5.3 Compressive strength	3-15
3.5.4 Mercury intrusion porosimetry (MIP)	3-15
3.5.5 Scanning electron microscopy (SEM)	3-16
3.6 SUMMARY	3-16
References	3-17

CHAPTER 4: EFFECTS OF IAA ON CHEMICAL REACTION OF FLY ASH CEMENT SYSTEMS

4.1 EFFECTS OF IAA ON Ca(OH) ₂ CONTENT	4-1
4.1.1 Effects of IAA	4-1
4.1.2 Effects of types of IAA	4-3
4.1.3 Effects of starting time of IAA	4-7
4.2 EFFECTS OF IAA ON CONSUMPTION OF Ca(OH) ₂	4-10
4.2.1 Effects of IAA	4-11
4.2.2 Effects of types of IAA	4-13
4.2.3 Effects of starting time of IAA	4-14
4.3 CONFIRMATION OF EFFECTS BY SEM IMAGES	4-16
4.4 SUMMARY	4-20
References	4-21

CHAPTER 5: EFFECTS OF IAA ON MECHANICAL PROPERTIES OF FLY ASH CEMENT SYSTEMS

5.1 EFFECTS OF IAA ON POROSITY IN FLY ASH CEMENT SYSTEM	5-1
5.1.1 Porosity	5-1

5.1.2 Relationship between consumption of $\text{Ca}(\text{OH})_2$ and porosity	5-10
5.2 EFFECTS OF IAA ON HARDNESS OF ITZ IN FLY ASH CEMENT SYSTEMS	5-11
5.2.1 Effects of internal saturated $\text{Ca}(\text{OH})_2$ solution supplied from one PCWA	5-11
5.2.2 Effects of types of IAA supplied from one PCWA	5-14
5.3 EFFECTS OF IAA ON COMPRESSIVE STRENGTH AND POROSITY OF FLY ASH CONCRETE	5-16
5.3.1 Compressive strength	5-16
5.3.2 Porosity	5-18
5.3.3 Relationship between compressive strength and porosity	5-20
5.4 SUMMARY	5-21
5.4.1 Fly ash cement paste	5-21
5.4.2 Fly ash cement paste with one PCWA	5-22
5.4.3 Fly ash concrete	5-23
References	5-23

CHAPTER 6: DISCUSSIONS OF MECHANISM OF INTERNAL ALKALI ACTIVATION

6.1 MECHANISM OF IAA ON MICROSTRUCTURE DEVELOPMENT IN PLAIN CEMENT PASTE	6-1
6.2 MECHANISM OF IAA ON MICROSTRUCTURE DEVELOPMENT IN FLY ASH CEMENT PASTE	6-3
6.3 DIFFERENCES OF STARTING TIME IN IAA MECHANISM ON MICROSTRUCTURE DEVELOPMENT IN FLY ASH CEMENT PASTE	6-4
6.4 DIFFERENCES OF TYPES OF ALKALI SOLUTION IN ACTIVATION MECHANISM OF POZZOLANIC REACTION IN FLY ASH PARTICLE	6-6

References	6-9
------------	-----

CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS	7-1
-----------------	-----

7.2 RECOMMENDATION	7-3
--------------------	-----

Appendix

LIST OF FIGURES

Figures	Title
1.1	Global CO ₂ production
2.1	Process of fly ash production at a power station
2.2	Physical model of the reaction in fly ash cement system
2.3	CH content relative to the cement content in PC and FC pastes (based on ignited weight) with w/b = 0.3
2.4	SEM images of fly ash cement system at the ages of 3 days (left) and 28 days (right)
2.5	SEM images of hydrated fly ash cement paste at the ages of 3 days (left) and 120 days (right)
2.6	Porosity of cement paste with and without fly ash after 1 week and 1 year at 20°C
2.7	Relationship between the strength and the total pore volume (left), and the volume of pores from 20 to 330 nm in diameter (<i>right</i>)
2.8	Trend of compressive strength of concrete (w/b = 0.38) when OPC is replaced with only fly ash
2.9	Compressive strength development of mortars (w/c = 0.5)
2.10	Pore size distribution of the concrete mixes at w/b = 0.24 at the ages of 28 days (left) and 90 days (right)
2.11	Relationship between micro hardness and fly ash replacement
2.12	Averaged intensity of water as a function of distance from the surface of LWA, n = 20
2.13	Illustration of the difference between external and internal curing
2.14	Compressive strength of all mortar mixtures

- 2.15 Compressive strengths and degree of hydration after 1, 3, and 8 days of sealed curing for control and internal curing – IC high performance mortar
- 2.16 Effect of addition of the porous ceramic coarse aggregate on compressive strength development (left) and gain of compressive strength between 7 and 28 days for mixtures with internal curing compared to the control samples (right)
- 2.17 SEM images of mortar microstructure for fly ash blended cement without (top) and with (bottom) internal curing at magnifications of 1200× (left) and 2400× (right)
- 2.18 Effect of internal curing on ITZ of mortar with w/c = 0.3 under sealed curing condition at 120 days by SEM images when compared with ITZ of mortar without internal curing
- 2.19 Effect of pH on the dissolution of amorphous SiO₂ (left) and Effect of pH and temperature on the concentration of dissolved silicium in NaOH solution for fly ash and silica fume (right)
- 2.20 Development of the OH⁻ concentration in the pore water of cement paste with fly ash and fine quartz sand at temperature of 20°C, with water/(cement + pfa) = 0.45, pfa is class F fly ash
- 2.21 Schematic mechanism of fly ash in alkali activator
- 2.22 Degree of reaction of fly ash
- 2.23 Micrographs of (a) original fly ash and fly ash activated by (b) 1M, (c) 2M, (d) 3M, and (e) 4M of NaOH solution after 7 days of hydration
- 2.24 Effect of concentration of activator on compressive strength (left) and pore size distribution (right)
- 3.1 Preparation of PCWA

- 3.2 Sample preparation. Cement paste samples were cast in 40-mm cube molds. A 1-ml syringe with the plunger removed was installed so that the tip of the needle was positioned at the center of the cube to allow the addition of water or alkali solution
- 3.3 Activation methods for each mixture proportion (FA0 and FA40) under each condition ((1) no injection, (2) Water injection, (3) NaOH injection, (4) saturated Ca(OH)_2 injection) 1 or 3 months after casting
- 3.4 Sample preparation using one PCWA
- 3.5 Sample preparations for DTA-TG
- 3.6 Samples preparation for hardness measurement
- 3.7 Method of harness measurement of PCWA, ITZ and bulk paste
- 3.8 Sample preparations in fly ash cement system for MIP measurement
- 3.9 Flow chart of experimental program
- 4.1 Comparison of CH content at the age of 2 months in FA0, FA20, and FA40 between untreated control samples and samples into which water, NaOH solution or saturated Ca(OH)_2 solution was injected at 1 month
- 4.2 Comparison of CH content in FA0 between untreated control samples and samples into which water, NaOH solution or saturated Ca(OH)_2 solution was injected at 1 month
- 4.3 Comparison of CH content in FA0 between untreated control samples and samples into which water, NaOH solution or saturated Ca(OH)_2 solution was injected at 3 months
- 4.4 Comparison of CH content in FA40 between untreated control samples and samples into which water, NaOH solution or saturated Ca(OH)_2 solution was injected at 1 month

- 4.5 Comparison of CH content in FA40 between untreated control samples and samples into which water, NaOH solution or saturated $\text{Ca}(\text{OH})_2$ solution was injected at 3 months
- 4.6 Effect of starting time of water injection on CH content in FA0 at the ages of 6 (left), 8 (middle), and 12 (right) months
- 4.7 Effect of starting time of NaOH solution injection on CH content in FA0 at the ages of 6 (left), 8 (middle), and 12 (right) months
- 4.8 Effect of starting time of saturated $\text{Ca}(\text{OH})_2$ solution injection on CH content in FA0 at the ages of 6 (left), 8 (middle), and 12 (right) months
- 4.9 Effect of starting time of water injection on CH content in FA40 at the ages of 6 (left), 8 (middle), and 12 (right) months
- 4.10 Effect of starting time of NaOH solution injection on CH content in FA40 at the ages of 6 (left), 8 (middle), and 12 (right) months
- 4.11 Effect of starting time of saturated $\text{Ca}(\text{OH})_2$ solution injection on CH content in FA40 at the ages of 6 (left), 8 (middle), and 12 (right) months
- 4.12 Consumption of CH at the age of 2 months by the pozzolanic reaction (left) and its normalization (right) of the control sample and the samples into which water or alkali solution was injected at 1 month
- 4.13 Comparison of consumption of CH by pozzolanic reaction between untreated control samples and samples into which water, NaOH solution or saturated $\text{Ca}(\text{OH})_2$ solution was injected at 1 month
- 4.14 Comparison of consumption of CH by pozzolanic reaction between untreated control samples and samples into which water, NaOH solution or saturated $\text{Ca}(\text{OH})_2$ solution was injected at 3 months

- 4.15 Effect of starting time of water injection on consumption of CH by pozzolanic reaction at the ages of 6 (left), 8 (middle), and 12 (right) months
- 4.16 Effect of starting time of NaOH solution injection on consumption of CH by pozzolanic reaction at the ages of 6 (left), 8 (middle), and 12 (right) months
- 4.17 Effect of starting time of saturated $\text{Ca}(\text{OH})_2$ solution injection on consumption of CH by pozzolanic reaction at the ages of 6 (left), 8 (middle), and 12 (right) months
- 4.18 SEM images ($1,300\times$) of the matrix at 6 months of the control sample (a) and sample activated by saturated $\text{Ca}(\text{OH})_2$ solution from 3 months (b)
- 4.19 SEM micrographs of fly ash particles at 6 months in the control sample (a) and sample activated by saturated $\text{Ca}(\text{OH})_2$ solution from 3 months (b) imaged at three magnifications [$1,800\times$ (1), $4,500\times$ (2), $9,000\text{--}10,000\times$ (3)]
- 4.20 SEM micrographs of fly ash particles at 12 months in the control sample (a) and sample into which water was injected at 3 months (b) imaged at two magnifications [$5,000\times$ (1), $10,000\times$ (2)]
- 5.1 Comparison of porosity at the age of 2 months in FA0 (left), FA20 (right), and FA40 (bottom) between untreated control samples and samples into which water or saturated $\text{Ca}(\text{OH})_2$ solution was injected at 1 month
- 5.2 Comparison of porosity in FA0 between untreated control samples and samples into which water, NaOH solution or saturated $\text{Ca}(\text{OH})_2$ solution was injected at 1 month
- 5.3 Comparison of porosity in FA0 between untreated control samples and samples, into which water, NaOH solution or saturated $\text{Ca}(\text{OH})_2$ solution was injected at 3 months
- 5.4 Comparison of porosity in FA40 between untreated control samples and

samples into which water, NaOH solution or saturated Ca(OH)_2 solution was injected at 1 month

- 5.5 Comparison of porosity in FA40 between untreated control samples and samples into which water, NaOH solution or saturated Ca(OH)_2 solution was injected at 3 months
- 5.6 Effect of starting time of water injection on porosity in FA0 at the ages of 6 (left), 8 (middle), and 12 (right) months
- 5.7 Effect of starting time of NaOH solution injection on porosity in FA0 at the ages of 6 (left), 8 (middle), and 12 (right) months
- 5.8 Effect of starting time of saturated Ca(OH)_2 solution injection on porosity in FA0 at the ages of 6 (left), 8 (middle), and 12 (right) months
- 5.9 Effect of starting time of water injection on porosity in FA40 at the ages of 6 (left), 8 (middle), and 12 (right) months
- 5.10 Effect of starting time of NaOH solution injection on porosity in FA40 at the ages of 6 (left), 8 (middle), and 12 (right) months
- 5.11 Effect of starting time of saturated Ca(OH)_2 solution injection on porosity in FA40 at the ages of 6 (left), 8 (middle), and 12 (right) months
- 5.12 Relationship between consumption of CH and volumes of pores ranging 20-330-nm (left) and 3-20-nm (right) in diameter in FA40
- 5.13 Effect of internal saturated Ca(OH)_2 solution from one PCWA on the hardness in FA0
- 5.14 Effect of internal saturated Ca(OH)_2 solution from one PCWA on the hardness in FA40
- 5.15 Effect of types of IAA supplied from one PCWA on the hardness in FA0 (top) and FA40 (bottom) at the age of 1 day

- 5.16 Effect of types of IAA supplied from one PCWA on the hardness in FA0 (top) and FA40 (bottom) at the age of 6 months
- 5.17 Compressive strengths of the specimens
- 5.18 Total pore volumes of concretes over time
- 5.19 Total pore volumes of macro pores (ranging 0.05 - 50 μ m in diameter) of concretes over time
- 5.20 Effect of IAA on pore volumes of fly ash concrete at the ages of 28, 182, and 364 days
- 5.21 Relationship between compressive strength and macro pore volume (pores ranging from 0.05 to 50 μ m) of specimens
- 6.1 Illustration of the difference in microstructure development between the plain cement paste without (left) and with IAA (right) over time
- 6.2 Illustration of the difference in microstructure development between the fly ash cement paste without (left) and with IAA (right) over time
- 6.3 Illustration of the differences in microstructure development between the fly ash cement paste without IAA (a), with AA at mixing (b), with IAA 1 month after casting (c), and with IAA 3 months after casting (d) over time
- 6.4 Mechanism of pozzolanic reaction in fly ash particle
- 6.5 Illustration of the differences in activation mechanism among (a) no activation, (b) water activation, (c) NaOH solution or saturated Ca(OH)₂ solution activation

LIST OF TABLES

Tables	Title
1.1	Worldwide cement production in 2013
2.1	Degree of reaction of fly ash in fly ash cement pastes
2.2	Test batch of fly ash hydrating (mass%)
3.1	Chemical composition of high-early-strength Portland cement
3.2	Physical properties of high-early-strength Portland cement
3.3	Chemical composition of fly ash
3.4	Physical properties of fly ash
3.5	Properties of aggregate
3.6	Physical properties of SP8HV _M
3.7	Physical properties of Master Air 202
3.8	Mixture proportion of concrete
3.9	Properties of fresh concrete
3.10	Volumes of water, NaOH, and saturated Ca(OH) ₂ solution imbibed into the pastes over time in the case of the injection from the age of 1 month (mL)
3.11	Volumes of water, NaOH, and saturated Ca(OH) ₂ solution imbibed into the pastes over time in the case of the injection from the age of 3 months (mL)

ACKNOWLEDGEMENTS

First and foremost, I am deeply grateful for the continuous support, insight and patience of my supervisors, Prof. Kenji Kawai, without his constant trust and guidance, this thesis would not have been completed. I am indebted to Prof. Takaaki Ohkubo, Prof. Takashi Tsuchida, Associate Prof. Kenichiro Nakarai as my co-supervisors, and Assistant Prof. Yuko Ogawa for their kind assistance and supervision.

I must also thank the Japanese Government (Monbukagakusho: MEXT) Scholarship Student for the funding support during my PhD course.

I am particularly grateful to Mr. Yuhei Ito, all of my lab members, and my true friends for helping me get through the difficult times, for all the emotional support in the last three years.

Last, but not least, I would like to express my gratitude to my family for providing an endless support and a loving environment for me. I hope I make you proud. Thank you for making my life is more meaningful in every way.


CHAPTER 1

INTRODUCTION

1.1 GENERAL

Cement is an essential and basic ingredient of concrete because it is able to combine with water to form a cement paste. The cement paste acts as the glue to bind the other constituents (fine and coarse aggregate) and to create the type of stone, called “concrete”. Concrete is used as a construction material more than any other materials in the world due to the superior properties of concrete. For example: higher strength as well as development of strength over time, more durability and longer service life than others, higher fire resistance than wood, and so on. Therefore, the world demand for the use of this material in the construction has been increasing, resulting in the more increase in the cement production. Around 3,310 million metric tons of cement were used in 2010, while around 4,000 and 4,180 million metric tons of cement were produced in 2013 and 2014, respectively [1, 2]. Vietnam and Japan were two countries in terms of ranging of 8th and 9th in a list of top countries by cement production in 2013 as shown in Table 1.1.

Table 1.1 Worldwide cement production in 2013 [1]

Rank ^	Country/Region ⇄	mil Tonnes ⇄
	<i>Others</i>	597
	2013 World Production	4000
1	 People's Republic of China	2,480 ^[2]
2	 India	280
3	 United States	77.8
4	 Iran	75
5	 Brazil	70
6	 Turkey	70
7	 Russia	65
8	 Viet Nam	65
9	 Japan	53
10	 Saudi Arabia	50
11	 South Korea	49
12	 Egypt	46
13	 Mexico	36
14	 Indonesia	58
15	 Thailand	35
16	 Germany	34
17	 Pakistan	32
18	 Italy	29
19	 Algeria	21 ^[3]

In recent decades, the production of cement, however, has been designated as a major source of greenhouse gas emission because of the huge emissions of carbon dioxide (CO₂) into the atmosphere. According to statistics data, the cement production releases up to 5% of worldwide human-made emissions of CO₂. Among them, 50% is from the chemical process, 40% from burning kiln fuel and 10% from purchased electricity and transport, as shown in Figure 1.1. It was reported that the cement production in Japan accounted for 4% of total CO₂ emission in 2013. [3]. Based on the data of cement production and consumption in 2011, the Vietnamese Ministry of Trade and Industry estimated that one ton of cement produced approximately one ton of CO₂ emissions while the demand of cement usage has increased every year [4].

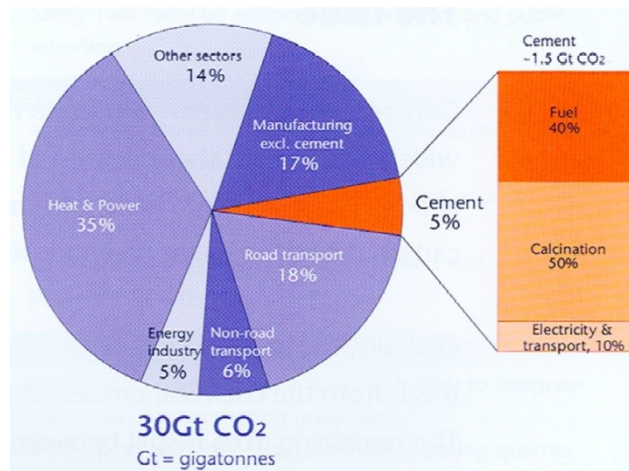


Figure 1.1 Global CO₂ production [5]

Several approaches have been suggested to mitigate the emissions of CO₂ from the cement production. One of the approaches is a partial replacement of cement by supplementary cementing materials, which also have the cementitious properties as cement. Fly ash, commonly known as a supplementary cementing material, is used widely for the partial replacement of cement in concrete industry due to its principal benefits. Besides the mitigation of the CO₂ emission, the cement replacement with fly ash reduces the construction cost, increases the workability, improves the ultimate strength and durability of concrete and so on [6 - 9]. Based on the chemical composition, fly ash is divided into two classes: low- and high-calcium fly ash. When cement is replaced with low-calcium fly ash, the strength of fly ash concrete is sometimes lower than cement concrete [10]. This is due to the pozzolanic reaction in fly ash cement system which occurs by a slow degree at the early age [11 - 13], even though the reaction continues at a constant degree at the later age [14]. Therefore, the proper curing in the long term has been proposed in the production of fly ash concrete to accelerate the pozzolanic reaction of fly ash [6, 13]. This also causes fly ash concrete not to be used so popularly as cement concrete in the production of pre-stressed pre-cast concrete.

In addition to proper curing, an alkaline activation on fly ash particles has been suggested so that its pozzolanic reaction occurs quicker [15]. Many researchers have combined one or more types of alkali activators with mixing water directly and applied the high temperature curing in order to activating fly ash particles [16 - 17] for fly ash geopolymer concrete [18]. Although this alkali activation can accelerate the pozzolanic reaction of fly ash, the effects also depend on the chemical composition of fly ash, the mixing progress and high temperature curing, which could limit to apply in the practical use. The curing condition at normal temperature in alkali activation needs to be considered as the more practical method.

On the other hand, internal curing has been discovered as the new technology that is very hopeful for producing concrete with increasing the early-age strength by reducing the risk of early-age cracking and enhancing durability [19, 20]. When compared with external curing condition, internal curing is able to supply water internally with more uniform distribution [19]. Several researchers have demonstrated the significant effects of internal water curing on promoting the cement hydration in concrete by using pre-wetted lightweight aggregate [19 - 24], super absorbent polymers [25 - 27], porous ceramic waste aggregate [28, 29], and so on.

In recent years, fly ash concrete using porous ceramic waste aggregate (PCWA) which is prepared in saturated-surface dry condition after the immersion in water has been investigated. It was reported that its strength is improved because PCWA supplies the internal water throughout the paste, and then promotes the cement hydration and the pozzolanic reaction [28]. The internal acceleration for pozzolanic reaction by using PCWA immersed in an alkali solution, however, has not been investigated in the fly ash concrete yet.

In this present research, an internal alkali activation was therefore applied to the fly ash cement systems cured at normal temperature so that the fly ash concrete using PCWA imbibing alkali solution could get the maximized strength and enhanced durability.

1.2 INTERNAL ALKALI ACTIVATION (IAA) ON FLY ASH CEMENT SYSTEMS

Internal alkali activation (IAA) is a combination of the alkaline activation on the fly ash reaction and the application of internal curing by using PCWA. PCWA is a waste generated from roof tile in the northern area of the Chugoku district in the western Japan [18, 19]. It is considered to be an internal curing agent due to its absorption of water [24, 25]. In this study, an alkaline solution supplied from PCWA would play a role as IAA on the fly ash cement systems cured at normal temperature.

Firstly, IAA was carried out by using two fundamental models in order to estimate more obviously its effects on the pozzolanic reaction and the porosity of the fly ash cement paste cured at normal temperature as well as the microstructure of interfacial transition zone (ITZ) microstructure between PCWA and bulk paste. One model was an original model through an installed syringe while the other was a model of internal activation by using one PCWA.

Second, IAA was carried out by using PCWA, prepared in saturated-surface dry condition after the immersion in alkaline solution for 7 days, to investigate its effects on the mechanical properties and porosity of the fly ash concrete cured at normal temperature. These models are described more in detail in the sections 3.3, 3.4, and 3.5.

This internal alkaline solution would play a role of water as a need for the cement hydration of cement system and a role of alkalinity as a need for the pozzolanic reaction of the fly ash cement system. IAA could be therefore considered as the new point of view for improving the short- and long-term properties of fly ash concrete using porous ceramic waste aggregate, and cured at normal temperature.

1.3 AIMS OF THE RESEARCH

As mentioned in 1.1, some previous studies on low-calcium fly ash concrete have concluded its lower strength than the cement concrete due to slow pozzolanic reaction of fly ash,

whereas some studies on alkaline activation have reported its effects on pozzolanic reaction by mixing alkaline solution with fly ash directly and curing at very high temperature. Meanwhile, some studies on internal curing have discussed the effects of internal water supplied from PCWA on some properties of concrete. The present study deals with the effects of internal alkali activation on the chemical and mechanical properties of the fly ash cement systems cured at normal temperature.

The aims of this research are:

- To study the effects of the type and starting time of IAA on the chemical reactions and mechanical properties of the fly ash cement system by developing an original model through an installed syringe as IAA.
- To study its effect on hardness of interfacial transition zone (ITZ) and bulk paste in the fly ash cement system through an model of internal activation by one PCWA, which was put in the center of the specimen, as an internal curing agent.
- To study the short term and long term mechanical properties of fly ash concrete using PCWA imbibing alkaline solution.

1.4 METHODOLOGY OF THE RESEARCH

High-early-strength Portland cement and low-calcium fly ash were used as the cementitious materials for making fly ash cement system. PCWA prepared in saturated-surface dry condition after the immersion in alkaline solution for 7 days was used as an agent of IAA for promoting the cement hydration and accelerating the pozzolanic reaction of the fly ash cement system. Alkaline solutions used in this research were 0.1mol/L sodium hydroxide (NaOH) solution (pH = 13.0), and saturated Ca(OH)₂ solution (pH = 12.6), and water was also used for a reference.

The properties of fly ash cement systems studied were chemical and mechanical properties. Its chemical properties included the Ca(OH)_2 (hereafter, CH) content and the consumption of CH by pozzolanic reaction in the fly ash cement pastes. Additionally, its mechanical properties were mainly hardness of ITZ and bulk paste in the fly ash cement systems, compressive strength of concrete and porosity of fly ash cement paste and concrete.

1.5 THESIS OUTLINE

This thesis is organized as follow:

Chapter 1 describes the background, aims and methodology of this study.

Chapter 2 provides a brief literature review about the effects of fly ash, the mechanisms and effects of internal curing, and the alkali activation on the chemical reaction and long-term mechanical properties of fly ash cement systems.

Chapter 3 presents the experimental program consisting of materials and mixture proportions, the fundamental models as IAA, the mixing and casting progress, the curing condition for the fly ash cement system. The test procedures were carried out to study the effects of IAA on the chemical reaction and the long-term mechanical properties of the fly ash cement systems.

Chapter 4 discusses the effects of IAA on the chemical reaction of the fly ash cement systems by examining the CH content and the consumption of CH.

Chapter 5 discusses the effects of IAA on the mechanical properties of the fly ash cement systems by testing hardness and compressive strength and measuring porosity. In addition, the relationship between the CH consumption and porosity of the fly ash cement systems using IAA are given in this chapter.

Chapter 6 proposes a mechanism of IAA. In addition, the differences in starting time of IAA mechanism on the microstructure development in the fly ash cement paste and the

mechanism of each type of alkali solution activating on the fly ash particles are also described.

Chapter 7 states the conclusion of this research. Recommendations for future work are also provided.

References

1. U.S. Geological Survey, Mineral Commodity Summaries, February 2014. Available from: <<http://minerals.usgs.gov/minerals/pubs/commodity/cement/mcs-2014-cemen.pdf>>
2. The Statistics Portal, United States and World Cement Production in 2010 and 2014 (in million metric tons), 2014.
Available from: <<http://www.statista.com/statistics/219343/cement-production-worldwide/>>.
3. PBL Netherlands Environmental Assessment Agency, Global CO₂ emissions per region from fossil-fuel use and cement production, 2013. Available from:
<<http://www.pbl.nl/en/infographic/global-co2-emissions-per-region-from-fossil-fuel-use-and-cement-production>>.
4. Environmental Construction Industry, 2011.
Available from: <<http://moitruong.xaydung.gov.vn/moitruong>>.
5. The Cement Sustainability Initiative Progress, 2005. Available from: <www.wbcsd.org>.
6. Bijen J, 1996. Benefits of slag and fly ash. Constr Build Mater 10:309-314.
7. Thomas M, 2007. Optimizing the Use of Fly ash in Concrete. Portland Cement Association.
Available from: <http://www.cement.org/docs/default-source/fc_concrete_technology/is548-optimizing-the-use-of-fly-ash-concrete.pdf?sfvrsn=4>.
8. Solis AV, Durham SA, Rens KL and Ramaswami A, 2010. Sustainable concrete for the urban environment: a proposal to increase fly ash use in concrete, Proceedings of a Conference

on Green Streets and Highways (Weinstein N (ed)). ASCE, Denver, Colorado.

9. Nath P, and Sarker P, 2011. Effect of fly ash on the durability properties of high strength concrete, The Twelfth East Asia-Pacific Conference on Structural Engineering and Construction, *Procedia Engineering* 14:1149-1156.
10. Marthong C and Agrawal TP, 2012. Effect of fly ash additive on concrete properties. *International J of Engineering Research and Applications* 2:1986-1991.
11. Poon CS, Lam L, Wong YL, 2000. A study on high strength concrete prepared with large volumes of low calcium fly ash. *Cem Concr Res* 30:447-455.
12. Lam L, Wong YL, and Poon CS, 2000. Degree of hydration and gel/space ratio of high-volume fly ash/cement systems. *Cem Concr Res* 30:747-756.
13. Totanji H, Delatte N, Aggoun S, Duval R, and Danson A, 2004. Effect of supplementary cementitious materials on the compressive strength and durability of short-term cured concrete, *Cem Concr Res* 34:311-319.
14. Wang Q, Feng J, Yan P, 2012. The microstructure of 4-year-old hardened cement-fly ash paste. *Constr Build Mater* 29:114-119.
15. Glukhovskiy V.D, 1967. *Soil Silicate Articles and Structures*, Ed. Budivelnyk Publisher, Kiev, Ukrainian.
16. Li D, Chen Y, Shen J, Su J, Wu X, 2000. The influence of alkalinity on activation and microstructure of fly ash. *Cem Concr Res* 30:881-886.
17. Katz A, 1998. Microscopic study of alkali-activated fly ash. *Cem Concr Res* 28:197-208.
18. David WL, Andi AA, Thomas KM, Indubhushan P, Arie W, 2015. Long term durability properties of class F fly ash geopolymer concrete. *J Mater Struct* 48:721-731.
19. Castro J, Ignor DIV, Golias M, Weiss W, 2010. Extending internal curing concepts to mixtures containing high volumes of fly ash. *Inter Bri Conf*.
20. Bent DP and Weiss WJ, 2011. Internal curing: A 2010 State-of-the-Art Review. NISTIR

7765. Available from: <<http://concrete.nist.gov/~bentz/NISTIR7765.pdf>>.

21. Weber S, Reinhardt H, 1995. A Blend of Aggregates to Support Curing of Concrete. Proceed of the Inter Symposium on Structural Lightweight Aggregate Concrete. Eds. Holand I, Hammer TA, Fluge F, Sandefjord, Norway. 662-671.
22. Bentur A, Igarishi S, Kovler K, 2001. Prevention of Autogenous Shrinkage in High Strength Concrete by Internal Curing Using Wet Lightweight Aggregates. *Cem Concr Res* 31:1587-1591.
23. Lo TY, Cui HZ, Li ZG, 2004. Influence of Aggregate Pre-wetting and Fly Ash on Mechanical Properties of Lightweight Concrete. *Waste Management* 24: 333-338.
24. Henkensiefken R, Briatka P, Bentz D, Nantung T, Weiss J, 2010. Plastic shrinkage cracking in internal cured mixtures made with pre-wetted lightweight aggregate. *Concr Inter* 32:49-54.
25. Jensen OM, Hansen PF, 2001. Water-entrained cement-based materials: I. Principle and theoretical background, *Cem Concr Res* 21:647-654.
26. Jensen OM, Hansen PF, 2002. Water-entrained cement-based materials: II. Experimental Observations, *Cem Concr Res* 32:973-978.
27. Iragashi S, Watanabe A, 2006. Experimental study on prevention of autogenous deformation by internal curing using super-absorbent polymer particles. Proceed of Inter RILEM Confer – Volume Changes of Hardening Concrete: Testing and Mitigation, RILEM Publication S.A.R.L 77-86.
28. Nukushina T, Seiki S, Nakagawa S, Sato R, 2009. Experimental investigation on mechanical performace of concrete containing fly ash improved by internal curing with porous ceramic waste aggregate. Proceed. *JCI* 31:241-246.
29. Suzuki M, Meddah MS, Sato R, 2009. Use of porous ceramic waste aggregate for internal curing of high performance concrete. *Cem Concr Res* 39:373-381.

CHAPTER 2

LITERATURE REVIEWS

This chapter presents a brief literature review of mechanisms and effects of fly ash, internal curing, and alkali activation on the chemical reaction and mechanical properties of the fly ash cement systems.

2.1 FLY ASH

Fly ash is a by-product of combustion of pulverized coal in power plants. The process of fly ash collection at a power station is as follows: coal is fed to the mill that grinds it to a very fine powder; then, this powder is fed into the boiler to produce heat required for power station; during the coal combustion process, minerals in the coal (such as clay, feldspar, quartz and shale) fuse in suspension, are cooled rapidly and solidified into glassy alumina silicate spheres – called fly ash; from the exhaust gas, they are collected by either electrostatic precipitator or bag house (as shown in Figure 2.1).

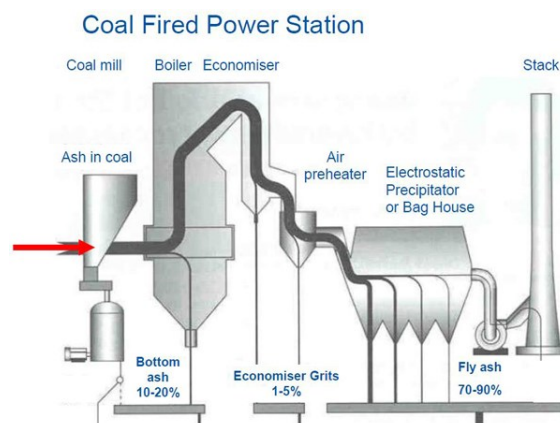


Figure 2.1 Process of fly ash production at a power station [1]

Fly ash was one of the environmental impact factors due to its release into the atmosphere in the past. However, it is now generally stored at coal power plants or placed in landfills. According to American Coal Ash Association, about 43% of fly ash is used as a pozzolanic material for a partial replacement for cement in the concrete production [2] due to owning the following properties:

2.1.1 Properties of fly ash

Physical and chemical properties of fly ash are the most important factors, contributing on the various applications of fly ash.

(1) Physical properties

Fly ash is a finely divided powder, similar to cement, consisting mostly of glassy sphere particles, either solid or hollow. The particle sizes of fly ash range in size from 0.5 μm to 50 μm . The specific surface area of fly ash may vary from 170 to 1000 m^2/kg [3]. The bulk density (mass per unit volume including air between particles) of fly ash can vary from 540 to 1500 kg/m^3 , depending on with or without close compaction, while the specific gravity of fly ash usually ranges from 1.9 to 3.0 kg/m^3 [4]. The color of fly ash can also vary from gray to black, depending on the content of the unburned carbon in the ash [4].

(2) Chemical properties

The chemical properties of fly ash are hugely influenced by the content as well as the properties of the coal burned and the techniques of handling and storage. The principal chemical compositions of fly ash are silica, alumina, iron and calcium. The minor components of fly ash are magnesium, sulfur, sodium, potassium and varying amounts of carbon, as measured by the loss on ignition (LOI). Crystalline compounds are presented in small amounts because some phases in the pulverized coal are not fused completely.

Based on the chemical composition, fly ash is divided into two classes according to ASTM C618:

Class F - Fly ash normally produced from burning anthracite or bituminous coal. It has pozzolanic properties. *In this research, class F fly ash was used for making fly ash cement system.*

Class C - Fly ash normally produced from lignite or subbituminous coal. Besides having pozzolanic properties, it also has some cementitious properties. Some Class C fly ashes may contain lime higher than 10 %.

According to the Japan Industrial Standard (JIS) of “Fly Ash for Use in Concrete, JIS A 6201”, fly ash is divided into four classes:

Class-I is high quality fly ash with the loss on ignition (LOI) less than 3.0% and Blaine fineness more than 5000 cm²/g.

Class-II is fly ash with LOI less than 5.0% and Blaine fineness more than 2500 cm²/g. *Fly ash used in this study met the standard values of class II in JIS A 6201.*

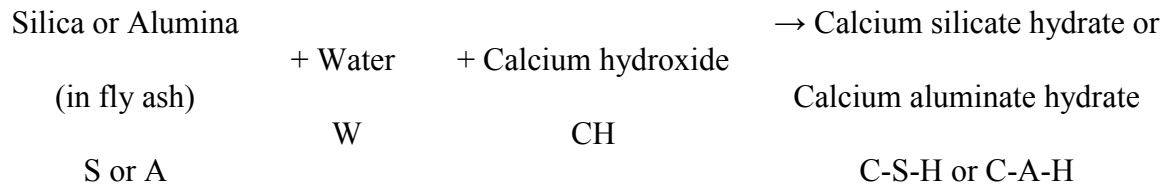
Class III is fly ash owning high LOI ranging from 5.0 to 8.0%.

Class IV is fly ash with low Blaine fineness from 1500 cm²/g.

(a) Pozzolanic properties

A pozzolan is a siliceous or aluminous material and usually exists in finely divided form. Although it possesses little or no cementitious properties, its reactive silica and alumina chemically react with calcium hydroxide in the presence of water at normal temperature to form compounds possessing cementitious properties. Fly ash is also known as one of the pozzolans, used commonly in the world due to possessing the pozzolanic properties.

The reaction of reactive silica and alumina in fly ash with calcium hydroxide is called “pozzolanic activity” or “pozzolanic reaction”. This reaction can also be understood as follows:



(b) Mechanism of pozzolanic reaction between fly ash and cement

The reaction mechanism in fly ash cement system is explained by the physical model as follows:

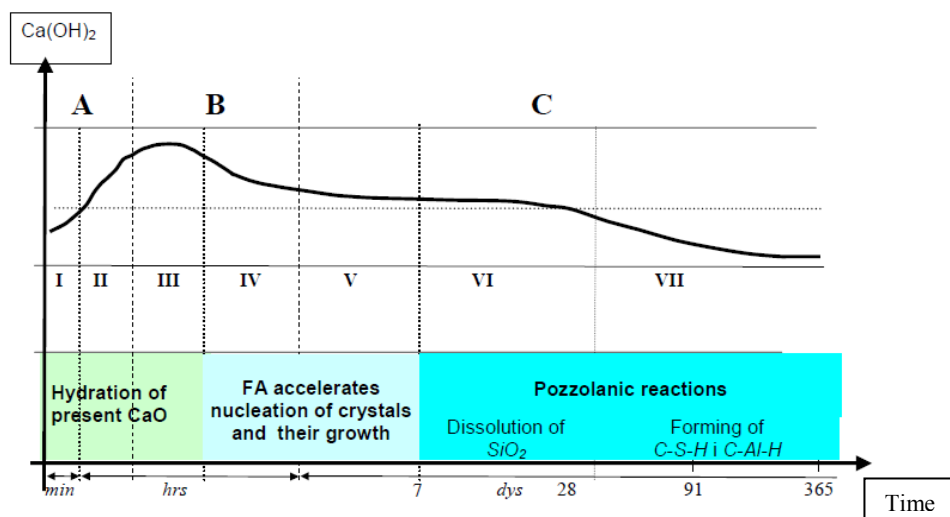


Figure 2.2 Physical model of the reaction in fly ash cement system

A: the early stage; B: the medium stage; C: the late stage [5]

The reaction mechanism of fly ash cement system can be divided into 7 periods (I, II, III, IV, V, VI, and VII) as shown in Figure 2.2. In the early stage, there are two periods: pre-induction (as shown in I) is the period when cement hydration starts and hydration products

(C-S-H, C-A-H and $\text{Ca}(\text{OH})_2$) are created; then follows a period which is called induction and during this period, physical changes in cement paste are proven as its gradual solidification (as shown in II). Fly ash in this early stage acts as the inert material which accelerates the hardening of cement paste by acting as the nucleus for sedimentation of C-S-H, C-A-H and $\text{Ca}(\text{OH})_2$ formed from cement hydration. After that, the medium period, at which the reaction accelerates and the cement hydration continues as well as the new hydration productions are formed (as shown in III and IV), starts. In the late stage, the cement paste becomes solidified due to the crystal growth (as shown in V), and the pH in the pore of cement paste increases, resulting in the increase of the dissolution of molecules of amorphous SiO_2 (as shown in VI). After that, pozzolanic reaction starts to occur and develop; the fly ash particles are covered and surrounded with hydration products (as shown in VII).

2.1.2 Effects of fly ash

(1) Effects on the society and community

The general effects of cement replacement with fly ash include three aspects: environmental, technical and economic aspects.

The first and most important aspect is environmental impact. Cement manufacturing results in a high amount of CO_2 emissions, which strongly contributes to the greenhouse effect and to global warming. On the other hand, fly ash is an industrial by-product; 70 – 80% of fly ash produced goes to landfill if not used in concrete [8]. Therefore, the replacement of cement with fly ash in concrete can reduce the environmental impact from the cement production.

The second benefit is technical aspect. The use of fly ash increases the workability, late strength and impermeability, and enhances the durability of the concrete. This will be discussed more specifically in the section 2.1.2.3.

The third benefit is economic aspect. As the replacement ratio of fly ash increases, the cost to produce concrete decreases.

In brief, the use of fly ash as a partial replacement for cement in concrete will reduce greenhouse gas emission, alleviate a fly ash disposal problem, save natural resources, produce a high quality concrete and save the cost of construction.

(2) Effects on paste

(a) The degree of reaction

The rate of pozzolanic reaction is dependent on the properties of the fly ash, such as the fineness of particles, chemical composition, active phase content, and so on. Some external factors (the mix proportion, water content for the formation of hydration products and the curing temperature) have been found to control the rate of pozzolanic reaction [6, 7]. It was found that the pozzolanic reaction does not occur for the first 7 days, while fly ash starts to react and consume Ca(OH)_2 until 28 days [8]. The degrees of fly ash reaction range about from 10% to 14% and 15% to 20% at the ages of 28 days and 90 days, respectively [9].

It was explained that fly ash acts as a space filler in the early age [5], whereas it actually reacts with Ca(OH)_2 formed from cement hydration to form C-S-H or C-A-H in the long term [10]. Additionally, unreacted fly ash particles are observed more than 80% in the pastes with the 45% to 55% replacement of fly ash at the age of 90 days [11], and still remain 72.7% after 4 years in the hardened fly ash cement paste [12]. It was reported that the higher fly ash replacement, the lower rate of pozzolanic reaction of fly ash cement paste at lower water to binder ratio, as shown in Table 2.1 [7].

Table 2.1 Degree of reaction of fly ash in fly ash cement pastes [7]

w/b Ratio	% Fly ash	Degree of reaction of fly ash (%)		
		7 Days	28 Days	90 Days
0.24	25	5.7	13.9	22.6
0.24	45	5.3	12.8	16.5
0.19	25	5.1	13.7	17.5
0.19	45	4.9	10.8	14.8

(b) Reduction of Ca(OH)₂ content

Although the Ca(OH)₂ (hereafter, CH) content in the fly ash cement paste is the results from the hydration of cement and pozzolanic reaction of fly ash, the reduction of CH content generally indicates the degree of pozzolanic reaction in fly ash cement pastes. In other words, the pozzolanic reaction of fly ash leads to a reduction in CH content [8, 11]. It was also found that the more the replacement of cement with fly ash, the more the reduction of CH content, [11] (as shown in Figure 2.3).

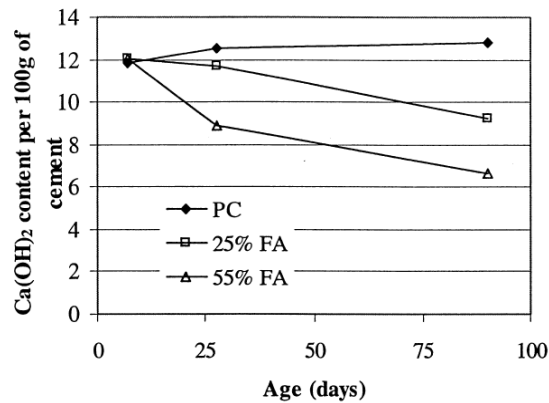


Figure 2.3 CH content relative to the cement content in PC and FC pastes (based on ignited weight) with w/b = 0.3 [11]

(c) SEM images

Instead of determining the rate of the reaction by the amount of calcium hydroxide, some researchers applied SEM images for evaluating the pozzolanic reaction of fly ash cement paste. Figure 2.4 shows that the surface of fly ash was smooth at 3 days, indicating pozzolanic reaction did not occur. Meanwhile, it was covered by C-S-H gel at the age of 28 days, indicating pozzolanic reaction starts to occur at that time [13].

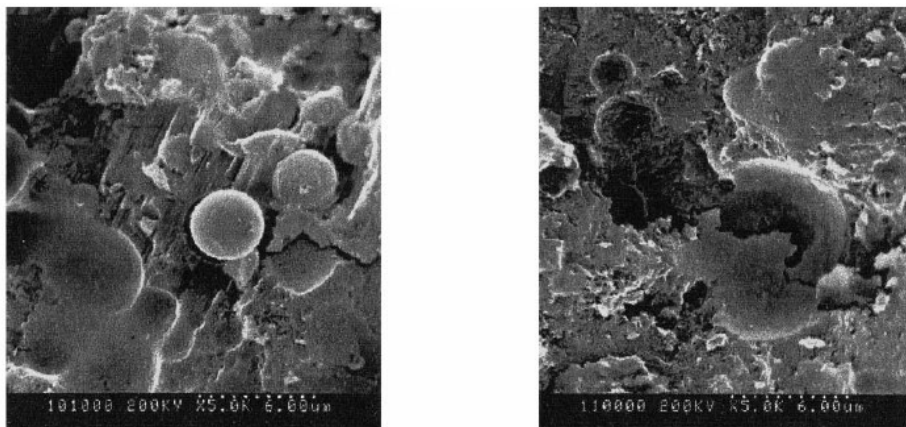


Figure 2.4 SEM images of fly ash cement system at the ages of 3 days (left) and 28 days (right) [13]

Figure 2.5 shows the differently attacked spheres of fly ash particles for different extent of pozzolanic reaction by SEM/EDX examination. According to Figure 2.5 left, the spherical of fly ash particle was slightly attacked by Ca(OH)_2 formed from the cement hydration and an average compositional ratios of $\text{Ca/Si} = 1.67$ and $\text{Si/Al} = 3.76$ from EDX analysis. According to Figure 2.5 right, it was fully covered with hydration products, indicating the pozzolanic reaction occurred largely at the age of 120 days, with $\text{Ca/Si} = 1.30$ and $\text{Si/Al} = 2.45$ [14].

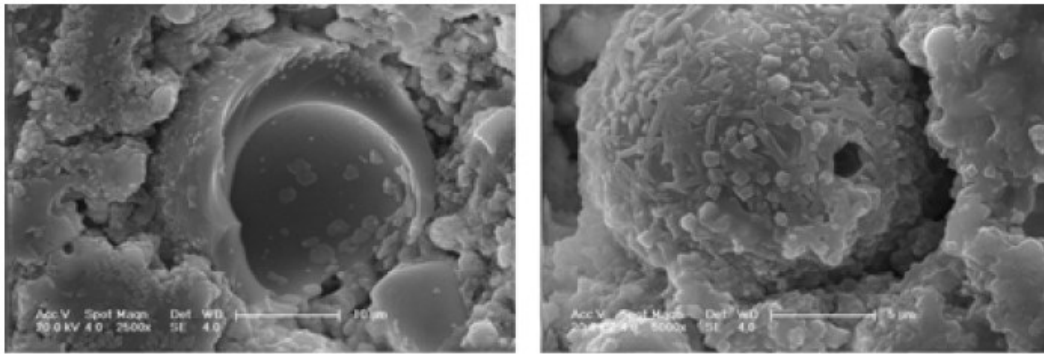


Figure 2.5 SEM images of hydrated fly ash cement paste at the ages of 3 days (left) and 120 days (right) [14]

(d) Pore structure

Generally, the porosity of cement paste with and without fly ash is measured by mercury intrusion porosimetry (MIP). It is noted that the porosity of fly ash cement paste is coarser at the early age, but it becomes finer than of plain cement paste at the later ages (as shown in Figure 2.6) [15].

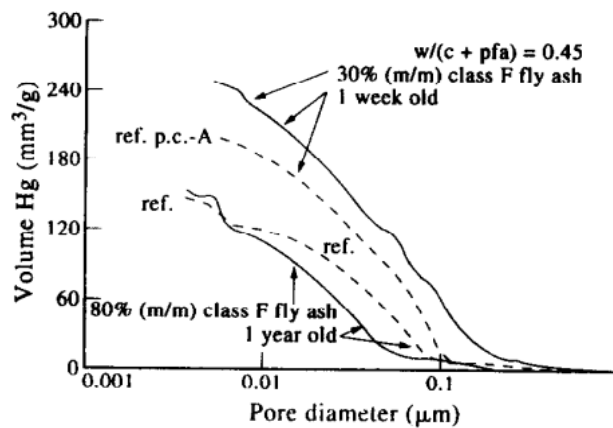


Figure 2.6 Porosity of cement paste with and without fly ash after 1 week and 1 year at 20°C [15]

Yamamoto and Kanazu tried to estimate the degree of the pozzolanic reaction of the fly ash cement paste, and reported that the volume of pores from 20 to 330 nm in diameter decreased

relative to the total pore volume, and that of pores from 3 to 20 nm in diameter increased as the pozzolanic reaction proceeded after 91 days. Moreover, the relationship between the strength and the total pore volume as well as the volume of pores from 20 to 330 nm in diameter were also found (as shown in Figure 2.7) [16].

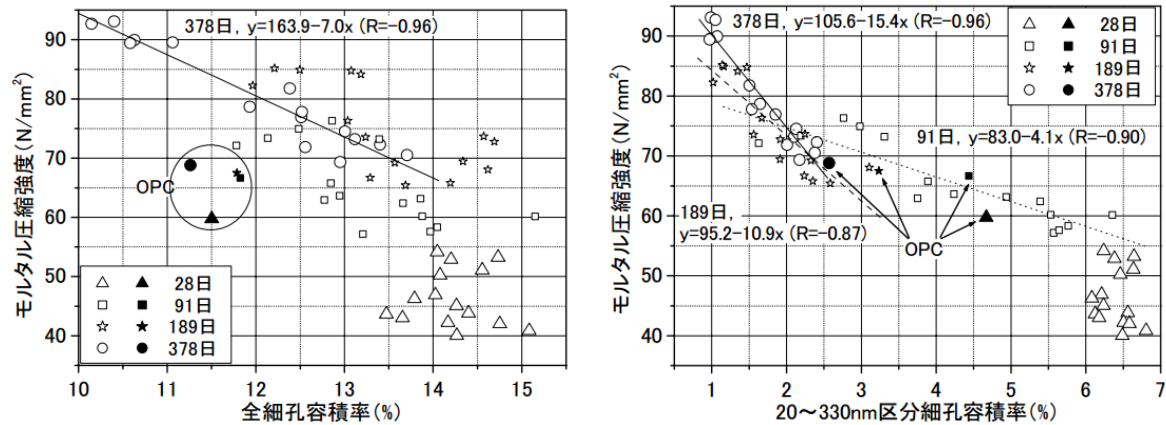


Figure 2.7 Relationship between the strength and the total pore volume (left), and the volume of pores from 20 to 330 nm in diameter (right) [16]

(3) Effects on concrete

(a) Properties of fresh concrete

First of all, fly ash can improve workability of fresh concrete due to the spherical shape [17]. Moreover, the pump-ability of fresh concrete is also improved significantly because the spherical shape of fly ash particles reduces the friction between the concrete and the pump line. In addition, fly ash has been shown to decrease heat of hydration because of the replacement for the high cement content. Fly ash also makes fresh concrete more cohesive and less prone to segregation and bleeding [18].

(b) Properties of hardened concrete

Compressive strength

Effects of fly ash on the compressive strength of concrete are very varied. It depends on many factors such as its fineness, its chemical composition, the water to binder ratio, and so on. The early-age compressive strength of low-calcium fly ash concrete is sometimes low due to very slow pozzolanic reaction [19, 20]. In addition, it can be seen that the more the fly ash replacement, the more the reduction of the strength. This trend was confirmed by Kayali and Ahmed (as shown in Figure 2.8) [21].

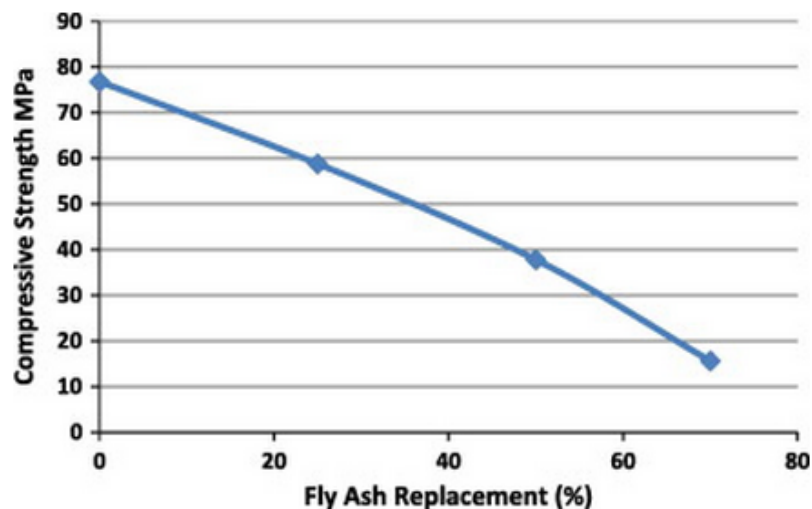


Figure 2.8 Trend of compressive strength of concrete ($w/b = 0.38$) when OPC is replaced with fly ash [21]

Meanwhile the late-age compressive strength is improved and the strength gain generally increases for much longer periods [18, 22]. V.G. Papadakis explained that its early strength was reduced because of lower activity of large fly ash particles. The strength, however, became higher than that of specimen without fly ash after 6 months and 1 years (as shown in Figure 2.9) [22].

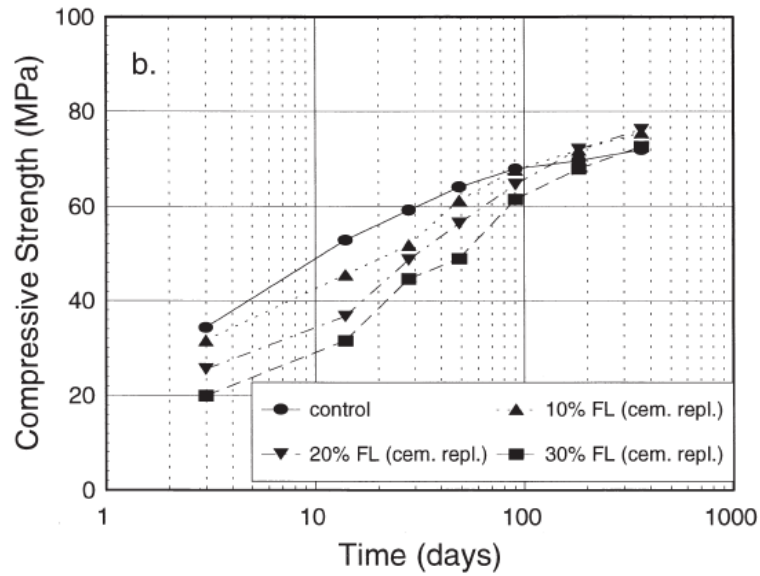


Figure 2.9 Compressive strength development of mortars ($w/c = 0.5$) [22]

Porosity

Figure 2.10 shows that the total pore volume of fly ash concrete was reduced when compared with normal concrete. In addition, the more the replacement of cement with fly ash, the more the reduction of total pore volume [7].

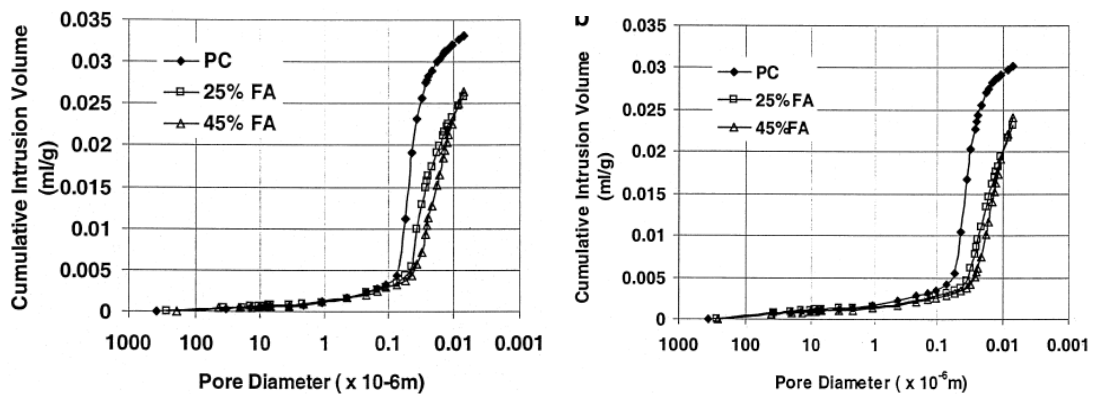


Figure 2.10 Pore size distribution of the concrete mixes at $w/b = 0.24$ at the ages of 28 days (left) and 90 days (right) [7]

Micro hardness

Micro hardness of concrete is usually measured by Vicker indenter, which is described more in detail in 3.5.2. Figure 2.11 shows the relationship between micro hardness and fly ash replacement. It demonstrates that the higher the fly ash replacement, the lower the value of micro hardness [23].

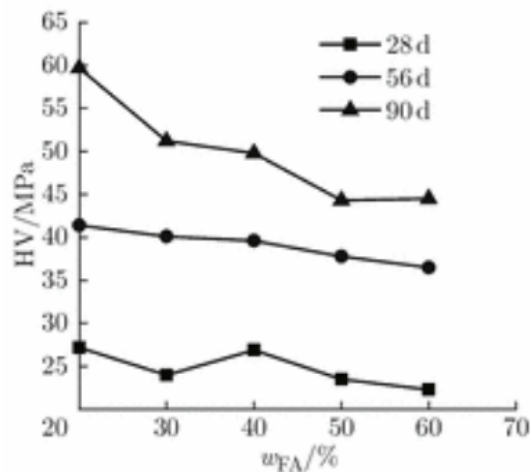


Figure 2.11 Relationship between micro hardness and fly ash replacement [23]

2.2 INTERNAL CURING

As the above mentioned, the early-age strength of low-calcium fly ash concrete is sometimes lower than that of cement concrete when part of cement is replaced with fly ash. This is due to the pozzolanic reaction in fly ash cement system which occurs by a slow degree at the early age [7, 10], even though the reaction continues at constant degree at the later age [11, 13]. Therefore, the proper curing in the long term has been proposed in the production of fly ash concrete to accelerate the pozzolanic reaction of fly ash [15]. In recent years, internal curing has been suggested as a new technology that is very hopeful for producing concrete with increasing the early-age strength by reducing the risk of early-age cracking and enhancing durability [24].

In brief, some aggregates, which can absorb significant amounts of water, are suggested for the use as the internal curing agents. For example: pre-wetted lightweight aggregate [24 - 29]; super absorbent polymers [30 - 32], porous ceramic waste aggregate [33, 34], and so on.

2.2.1 Definition

The American Concrete Institute in 2010 defined internal curing as “supplying water throughout a freshly placed cementitious mixture using reservoirs, via pre-wetted lightweight aggregates, that readily release water as needed for hydration or to replace moisture lost through evaporation or self-desiccation” [35].

2.2.2 Mechanism

It was noticed that lightweight aggregates (LWA) absorb significant amount of mixing water which can be released into the paste during hydration of cement paste [36]. The movement of internal water from lightweight aggregate to paste occurs since the pores in paste are always smaller than the pores of lightweight aggregate, even at early hydration ages. As a result, the capillary stress would develop, leading to “increase the driving force that pulls water out of the lightweight aggregate” [37]. It was observed that the transfer of water into cement paste matrix was in the range of 3 to 8 mm from the surface of saturated lightweight aggregate at 21 hours after casting (as shown in Figure 2.12) by the application of neutron radiography to cement [38]. It indicates that internal curing process is quick [39].

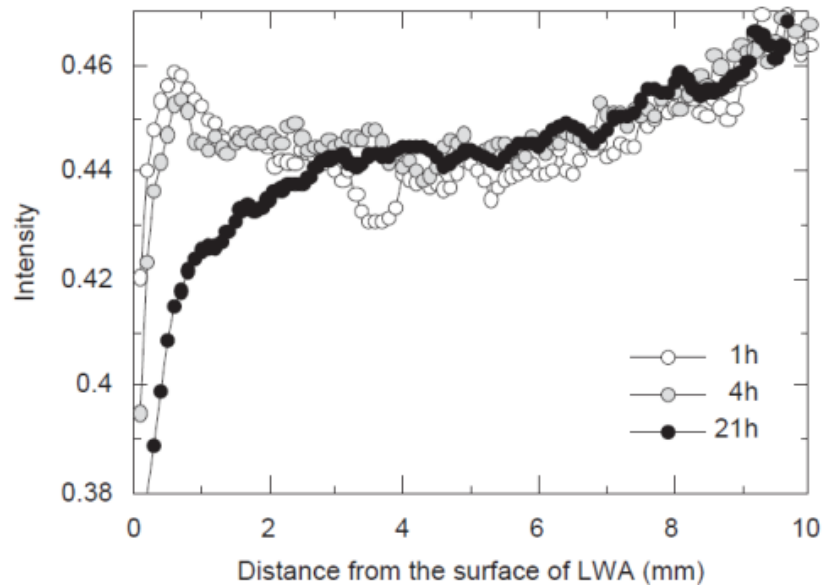


Figure 2.12 Averaged intensity of water as a function of distance from the surface of LWA, n = 20 [38]

Figure 2.13 illustrates the mechanism of internal curing by the comparison between external curing and internal curing. For external curing condition, external water penetration ability is only several millimeter into the top surface of concrete with the low water to cement ratio, whereas for internal curing, the water filled intrusions are distributed more equally across the cross section and make the cured zone for the entire paste system [25].

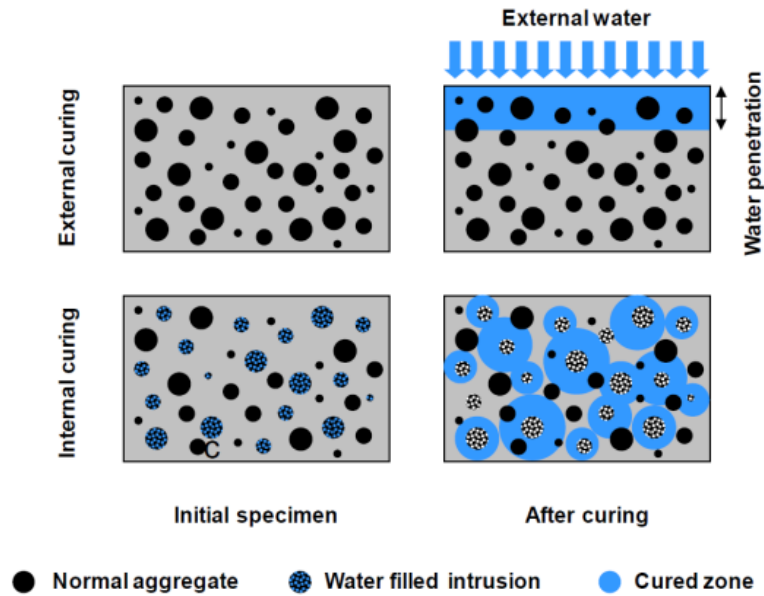


Figure 2.13 Illustration of the difference between external and internal curing [25]

2.2.3 Effects of internal curing

(1) Compressive strength

The influence of internal curing on compressive strength of paste or concrete depends on many factors, such as mix proportion, type of cement, the water to cement ratio, curing condition. Schiltter et al. investigated the influence of pre-wetted fine lightweight aggregate as an internal curing agent on compressive strength of mortar mixtures as shown in Figure 2.14. M-0 is a plain mortar while M-11 and M-24 is mortar using 11% and 23.7% replacement of pre-wetted lightweight aggregate by volume. As a result, M-11 and M-24 show a 2% reduction in strength until 28 day and an 8% reduction in strength at the age of 90 days. The reduction in strength is due to the weakness effected of pre-wetted lightweight aggregate [40].

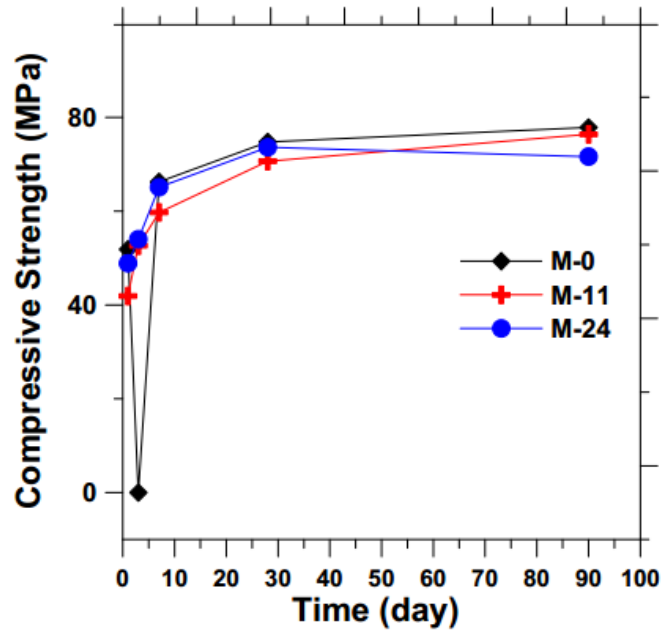


Figure 2.14. Compressive strength of all mortar mixtures [40]

Similar to Schiltter et al.'s research, the decrease of strength is observed at the early age (at 1 day in [41] and less than 7 days in [29]). This is due to the relative weak cement paste at the early age and the lower strength of saturated lightweight aggregate [41] or porous ceramic waste aggregate (PCWA) [29] than normal concrete. However, the strength is enhanced at the later ages (as shown in Figure 2.15 and Figure 2.16 top) because the water contained in the pores of saturated lightweight aggregate or PCWA promotes the hydration of cement at the later ages, resulting in the increase of the gain of the compressive strength (as shown in Figure 2.15) with increasing the lightweight aggregate replacement (as shown in Figure 2.16 bottom). [29].

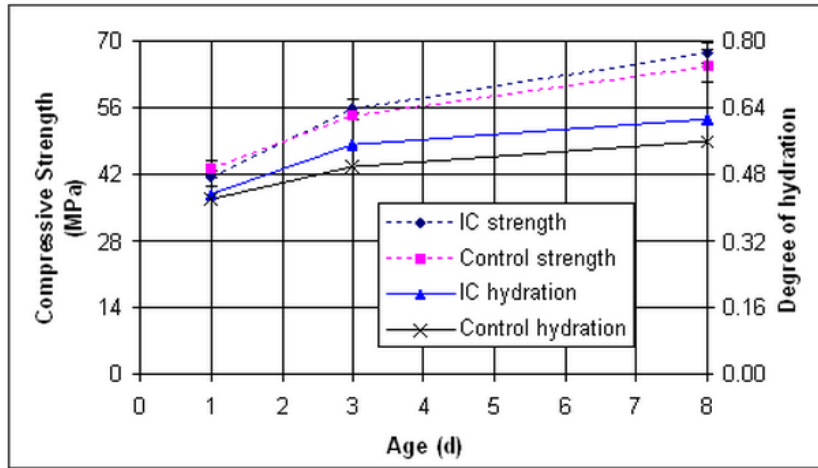


Figure 2.15 Compressive strengths and degree of hydration after 1, 3, and 8 days of sealed curing for control and internal curing – IC high performance mortar [41]

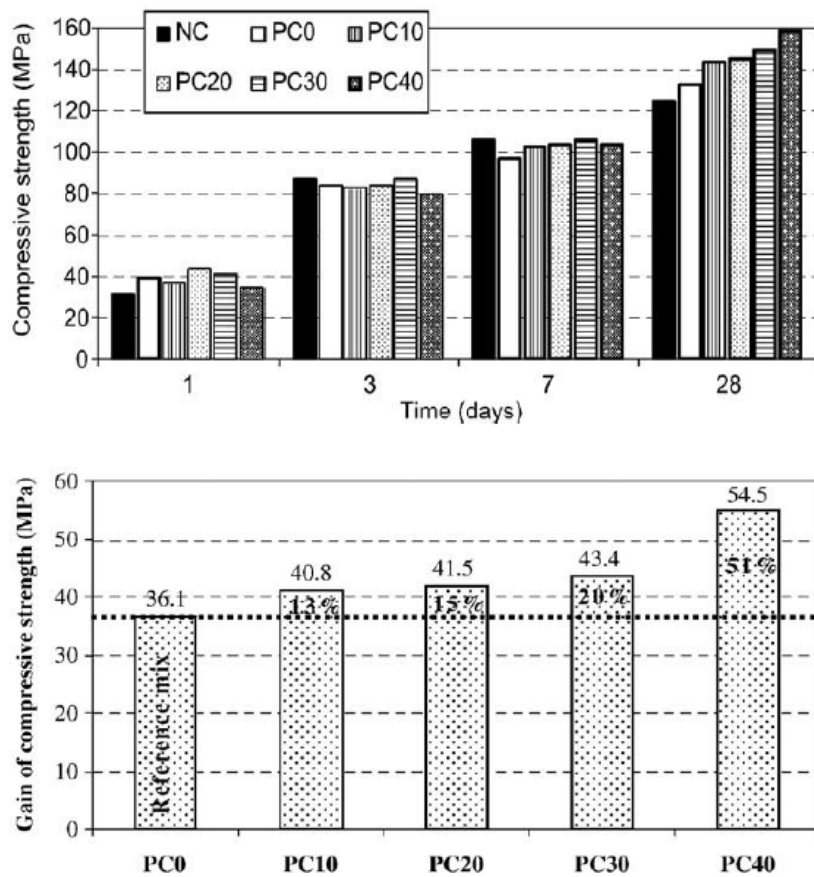


Figure 2.16 Effect of addition of the porous ceramic coarse aggregate on compressive strength development (top) and gain of compressive strength between 7 and 28 days for mixtures with internal curing compared to the control samples (bottom) [29]

(2) Microstructure

The influences of internal curing on the microstructure of hardened cement paste or mortar or concrete have been also observed by using SEM images. When compared with the microstructure of specimens without internal curing, microstructure of specimens with internal curing has fewer and smaller pores and less calcium hydroxide (as shown in Figure 2.17). It was explained that the internal curing water promoted pozzolanic reaction of fly ash at the later age, resulting in more hydration products, which are able to fill the pores [42].

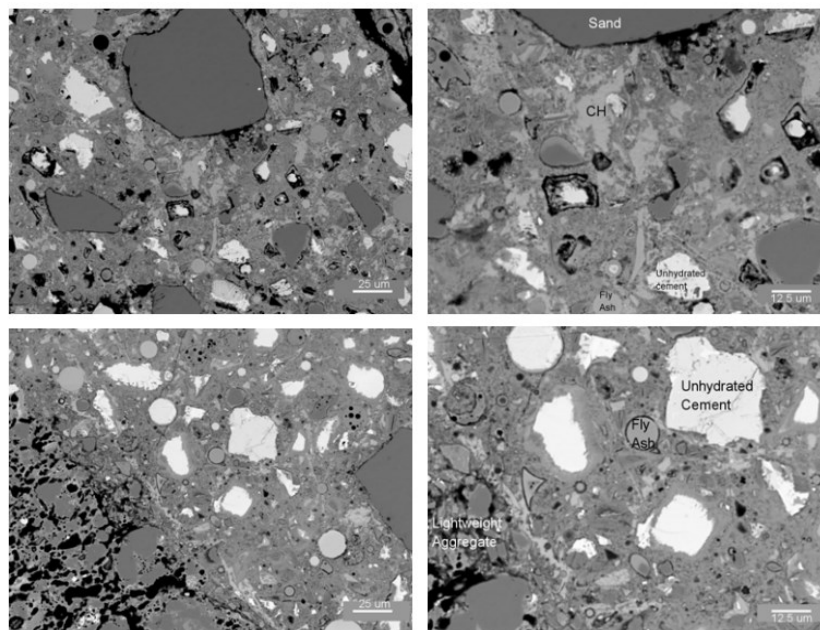


Figure 2.17 SEM images of mortar microstructure for fly ash blended cement without (top) and with (bottom) internal curing at magnifications of 1200 \times (left) and 2400 \times (right) [42]

On the other hand, the interfacial transition zone (ITZ) between the cement paste and normal aggregate plays an important role in determining the mechanical properties of concrete. Generally, the ITZ zone is known as the weakest zone in concrete because this zone possess the differences in microstructure between cement paste and aggregate, resulting in the existence of “wall effect”. This wall effect causes the ineffective packing of cement particles

near the aggregate, leading to the more porous zone having some 15 to 20 μm in width, especially, the calcium hydroxide tends to fill this zone [43].

The ITZ microstructure between cement paste and water-absorbed aggregate has been supposed to access the effect of internal curing. It can be confirmed that the microstructure of ITZ becomes denser and more homogeneous and contains the less calcium hydroxide due to the effect of the internal curing water which promotes the hydration near the aggregate surface [44]. This observation is in agreement with the results of Dale P. Bentz and Paul E. Stutzman's research (as shown in Figure 2.17) [42].

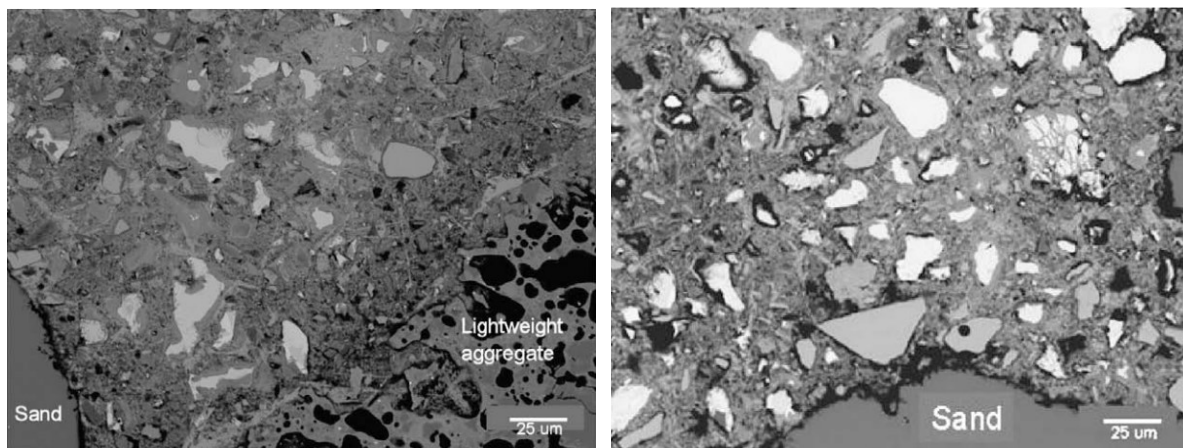


Figure 2.18 Effect of internal curing on ITZ of mortar with $w/c = 0.3$ under sealed curing condition at 120 days by SEM images when compared with ITZ of mortar without internal curing [42]

2.3. ALKALI ACTIVATION

A number of methods for accelerating the pozzolanic reaction in fly ash cement systems have been investigated, including physical, thermal, and chemical activation [45 – 52]. Physical activation consists of mechanically grinding the fly ash to fine powder [45 – 46]. Thermal activation is achieved by the application of high temperatures to fly ash to remove carbon, sulfur and other impurities [47]. Chemical activation involves treatment of fly ash particles

with an alkali solution directly. Chemical activation is more effective in accelerating the pozzolanic reaction of fly ash particles than either physical or thermal activation [48 – 50].

2.3.1 Definition

Alkali activation is known as chemical activation. As mentioned in 1.1, an alkali activation is applied to accelerate the pozzolanic reaction of fly ash cement system because the pozzolanic reaction occurs in the presence of water and high alkali concentration.

2.3.2 Mechanism

Two reasons of slow pozzolanic reaction of fly ash cement paste have been suggested to study the mechanism of alkali activation. One of them is the dense and chemically stable glassy surface layer of fly ash particles. The other is the cross-linked silica-tetrahedral (Si-O-Si) or cross-linked alumina-tetrahedral (Al-O-Al) chains in fly ash particles. This glassy surface layer has to be corroded and these links have to be broken so that the silica or alumina becomes reactive with water at normal temperature [15, 51]. It was found that the disruption of these links occurs at a pH of more than 12.5 of pore solution in the fly ash cement system at room temperature [53] and more than 13 at 20°C in sodium hydroxide solution [15] as shown in Figure 2.19. Therefore, the concentrations of alkali activators in this study were selected as follows: the pH of NaOH solution for the injection in this study was 13.0 while that of Ca(OH)₂ solution was 12.6.

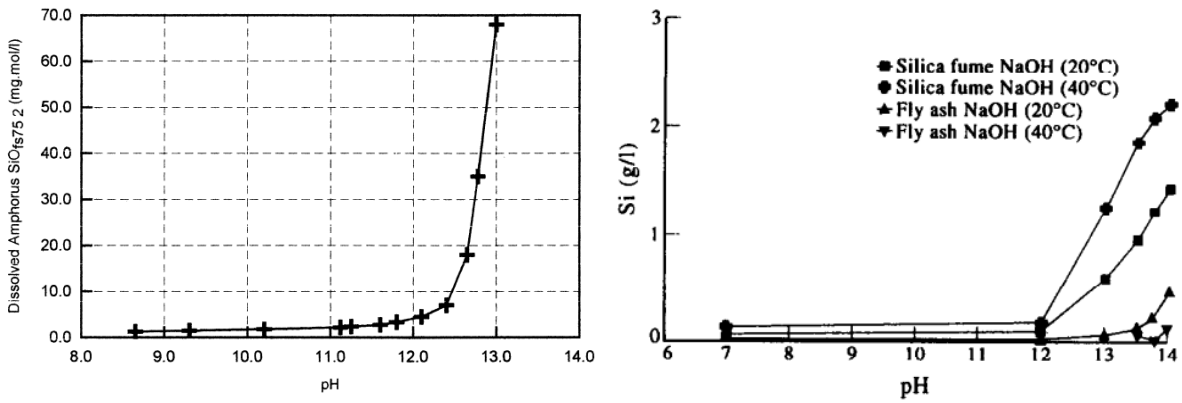


Figure 2.19 Effect of pH on the dissolution of amorphous SiO₂ (left) [53] and Effect of pH and temperature on the concentration of dissolved silicon in NaOH solution for fly ash and silica fume (right) [15]

However, the pore solution in the fly ash cement system is less alkaline than cement system as shown in Figure 2.20. As a result, the pozzolanic reaction occurs very slowly.

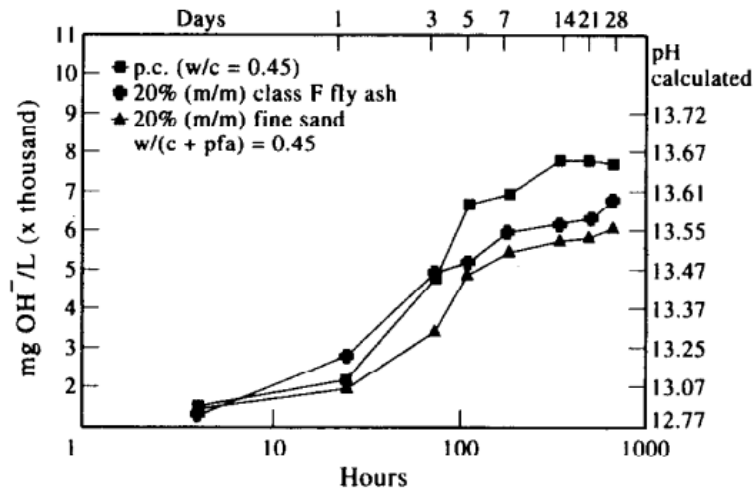


Figure 2.20 Development of the OH⁻ concentration in the pore water of cement paste with fly ash and fine quartz sand at temperature of 20°C, with water/(cement + pfa) = 0.45, pfa is class F fly ash [15]

From these reasons, the common way of getting a high pH system is the addition of alkali ions in that system [13, 51]. Gum Sung Ryu et al. depicted schematically the mechanism of fly ash in the presence of alkali activator from the experimental results (as shown in Figure 2.21). Due to the attack of alkali activator on chemically stable glassy surface layer, the corrosion at the surface of fly ash starts to occur. This corrosion makes the internal reactants easily penetrate and activate. If the OH⁻ ions outside fly ash are continuously increased, the Si-O-Si and Al-O-Al will be disrupted and Si⁴⁺ and Al³⁺ ions will be released. They will combine to Ca²⁺ or Na⁺ ion of alkali activator, and then react to form reaction products, which will grow and harden, resulting in the structure denser [54].

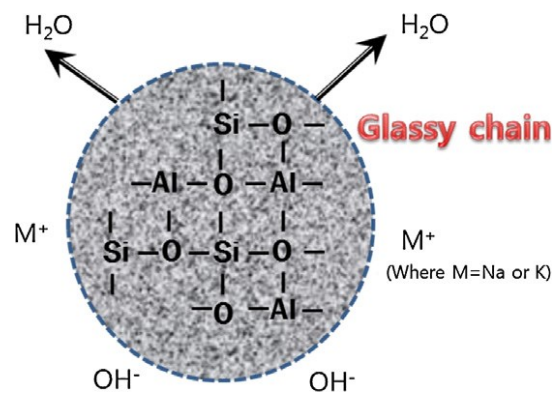
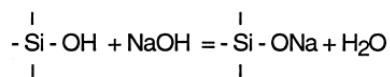


Figure 2.21 Schematic mechanism of fly ash in alkali activator [54]

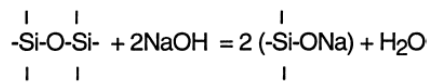
Additionally, Yueming Fan et al. concluded the activation mechanism of sodium hydroxide (NaOH) by the following reactions:

(a) Neutralization of surface silica-alumina groups:

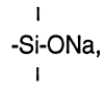


This neutralization is repeated on new surfaces, known as corrosion of fly ash.

(b) Gradually destroying of inside silica-alumina chain, resulting in [(Si,Al)O₄]_n disruption:



Due to the solubility of



Na^+ is replaced by Ca^{2+} , forming sedimentary calcium silicate hydrate [51].

2.3.3 Effects of alkali activation

A number of researches have been conducted on the activation of fly ash particles by using alkali activators, so called “geopolymer”. Strongly alkaline activators containing $\text{Ca}(\text{OH})_2$, NaOH , KOH , Na_2CO_3 , water glass and so on are frequently used [55]. Their effects on the chemical and mechanical properties of fly ash cement systems vary because these effects depend on the type and concentration of alkali activators, chemical composition of fly ash, or mixing and curing progresses [9, 13, 47, 55].

(1) Activation of fly ash particles (no cement) - Geopolymer

(a) Effect of type of alkali activator on degree of reaction of fly ash

It was confirmed that the effect of type of alkali activator on degree of reaction of fly ash particles was obvious at early stage of hydration by evaluating the degree of reaction. The degrees of reaction of F0 (original fly ash cured at room temperature), F2 (fly ash treated with NaOH and $\text{Ca}(\text{OH})_2$ solution, and cured at 60°C) and F3 (fly ash treated with a mixture of $\text{Ca}(\text{OH})_2$, gypsum, and Na_2SO_4 solution and cured at 60°C) are 1.28%, 43.67% and 16.18%, respectively at 7 days. It is observed that the effect of Na_2SO_4 was more efficient, while the effect of a mixture of NaOH and $\text{Ca}(\text{OH})_2$ was not observed significantly at later ages (as shown in Figure 2.22) [13].

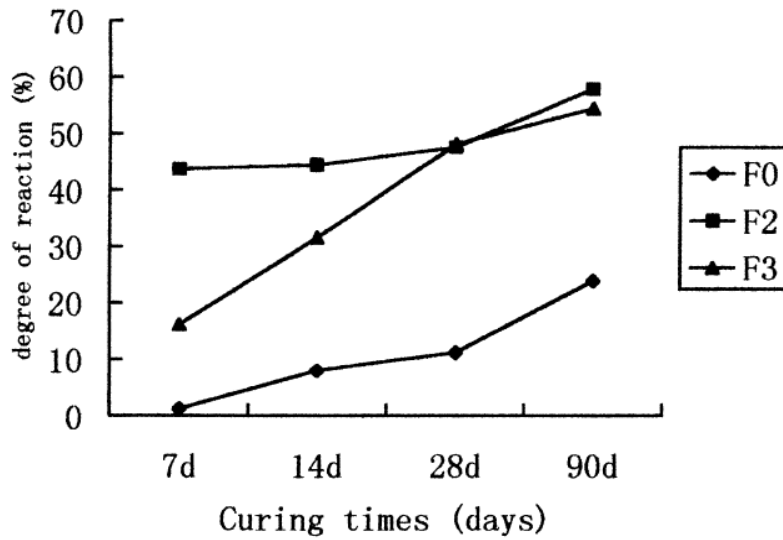


Figure 2.22 Degree of reaction of fly ash [13]

Table 2.2 Test batch of fly ash hydrating (mass%) [13]

	Fly ash	NaOH	Ca(OH) ₂	Gypsum	Na ₂ SO ₄
F0	100				
F2	100	2	25		
F3	100		25	6	4

(b) Effect of concentration of alkali activator on degree of reaction of fly ash

Figure 2.23 shows that the effect of concentration of NaOH solution on the degree of reaction of fly ash by a comparison of SEM images between original fly ash and fly ash activated by different concentration solution [56]. The fly ash particles in Figure 2.23b seemed to be similar to the original fly ash particles in Figure 2.23a. This can be explained by due to low concentration of the solution which was not strong enough to react with fly ash. Meanwhile, fly ash particles in Figure 2.23c were more deeply etched in Figure 2.23d and the glassy phase of fly ash was dissolved extensively in Figure 2.23e, resulting in the more continuous matrix which is more solid and less porous. It implies the higher the concentration of alkali activator, the more significant the effect of activator on activation of pozzolanic reaction in fly ash particles.

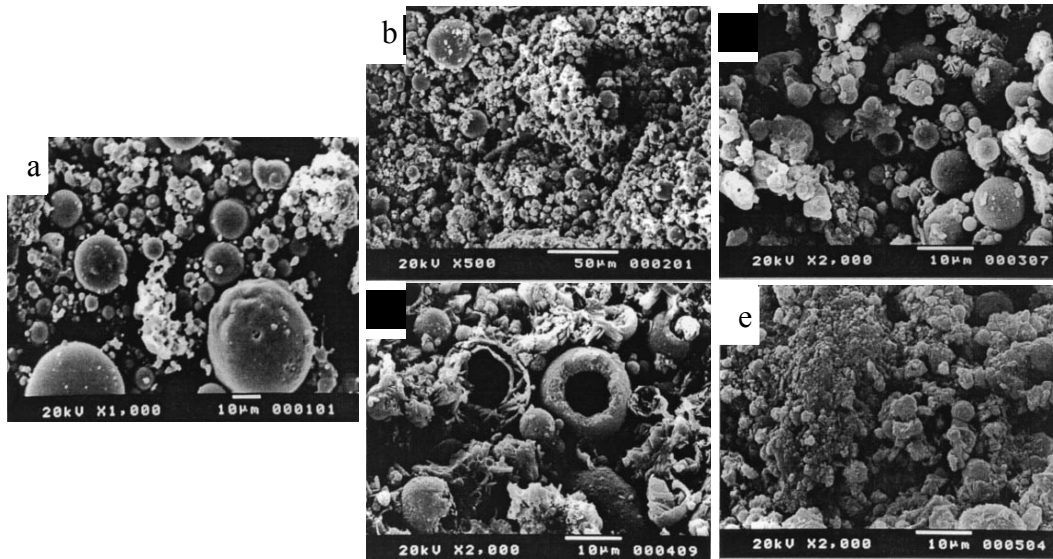


Figure 2.23 Micrographs of (a) original fly ash and fly ash activated by (b) 1M, (c) 2M, (d) 3M, and (e) 4M of NaOH solution after 7 days of hydration [56]

(c) Effect on mechanical properties

Concrete made with the alkali-activated fly ash has the compressive strength more than 40MPa after short thermal curing times [9]. Many researchers have produced concrete using many different types of alkaline activators that have comparable or superior compressive strength to concrete made with ordinary Portland cement (OPC). T. Bakharev created no-cement concrete using fly ash activated with sodium hydroxide (NaOH) with 2-day compressive strength of 10 MPa and 28-day compressive strength of 60 MPa [57]. Another study using Class F fly ashes from different sources activated with NaOH with 28-day compressive strengths of 29-66 MPa [58].

(2) Effect of activation on mechanical properties of fly ash cement paste

In addition to geopolymers, Paweena Jariyathitipong et al. investigated the effects of alkali solution and additional admixture of calcium hydroxide on activation of fly ash cement system. As a result, the addition of high concentration of alkali ion could accelerate the

pozzolanic reaction more than its low concentration (as shown in Figure 2.24 left) and the addition of calcium hydroxide as a Ca^{2+} ion supplier improves microstructure by reducing the volume of pores from 0.1 to 1 μm in diameter (as shown in Figure 2.24 right). However, the microstructure at the early age is more porous and the flexural strength is not improved [52].

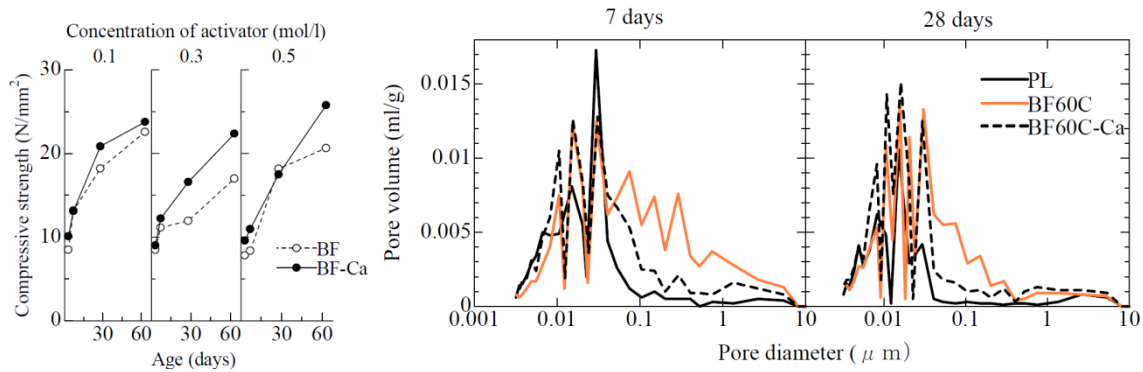


Figure 2.24 Effect of concentration of activator on compressive strength (left) and pore size distribution (right) [52]

This alkali activation in almost of these researches has been mainly carried out by adding an alkali solution or mixture of many alkali solutions in the mixing water of fly ash systems which are cured at the elevated temperature. In addition, this activation also depends on the mixing progress, and applied high temperature for curing. This may limit to apply in the practice.

2.4 SUMMARY

Based on some previous studies presented above, an internal alkali activation (IAA) of the pozzolanic reaction in the low-calcium fly ash cement systems cured at normal temperature is suggested in the present study. A replacement of cement with fly ash would reduce a huge amount of CO_2 emissions. Meanwhile, a combination of internal curing and alkali activation using porous ceramic waste aggregate as an internal-alkali-activating agent would accelerate

the pozzolanic reaction and promote the cement hydration in the fly ash cement systems with a low water to binder ratio. All above issues could bring many benefits in the production and application of high strength fly ash concrete.

References

1. Fly ash Australia, What is fly ash, 2015.

Available from: <<http://www.flyashaustralia.com.au/WhatIsFlyash.aspx>>.

2. American Coal Ash Association. Available from: <www.aaa-usa.org>.

3. U.S Department of Transportation - Federal Highway Administration, Coal fly ash, 2012.

Available from:

<<http://www.fhwa.dot.gov/publications/research/infrastructure/structures/97148/cfa51.cfm>>.

4. Ahmaruzzaman M, 2010. A review on the utilization of fly ash. Progress in Energy and Combustion Science 36:327-363.

5. Čojbašić L, Stefanović G, Sekulić Ž, Heckmann S, 2005. Influence of the fly ash chemical composition on the Portland cement and fly ash mixture hydration mechanism. J Mecha Eng 3:117-125.

6. Hanehara S, Tomosawa F, Kobayakawa M, Hwang K, 2001. Effects of water/powder ratio, mixing ratio of fly ash, and curing temperature on pozzolanic reaction of fly ash in cement paste. Cem Concr Res 31:31-9.

7. Poon CS, Lam L, Wong YL, 2000. A study on high strength concrete prepared with large volumes of low calcium fly ash. Cem Concr Res 30:447-455.

8. Sakai E, Miyahara S, Ohsawa S, Lee SH, Daimon M, 2005. Hydration of fly ash cement. Cem Concr Res 35:1135-1140.

9. Ferna'ndez-Jime'nez A, Palomo A, 2005. Composition and microstructure of alkali activated fly ash binder: Effect of the activator. Cem Concr Res 35:1984-1992.

10. Lam L, Wong YL, and Poon CS, 2000. Degree of hydration and gel/space ratio of high-volume fly ash/cement systems. *Cem Concr Res* 30:747-756.
11. Berry EE, Hemmings RT, Cornelius BJ, 1990. Mechanism of hydration reactions in high volume fly ash pastes and mortars. *Cem Concr Compos* 12:253-261.
12. Wang Q, Feng J, Yan P, 2012. The microstructure of 4-year-old hardened cement-fly ash paste. *Constr Build Mater* 29:114-119.
13. Li D, Chen Y, Shen J, Su J, Wu X, 2000. The influence of alkalinity on activation and microstructure of fly ash. *Cem Concr Res* 30:881-886.
14. Lei W, Zhen H, Xinhua C, 2011. Characterization of pozzolanic reaction and its effect on the C-S-H gel in fly ash-cement paste. *J.of Wuhan University of Technology-Mater. Sci. Ed*:319-324.
15. Bijen J, 1996. Benefits of slag and fly ash. *Constr Build Mater* 10:309-314.
16. Yamamoto T, Kanazu T, 2007. Experimental explanation of compacting effect on hydration phases and strength development mechanism derived from pozzolanic reaction of fly ash. *J JSCE* 63-1:52-65.
17. Marthong C, Agrawal TP, 2012. Effect of fly ash additive on concrete properties. *Inter. J of Engineering Research and Applications* 2:1986-1991.
18. Copeland K, *Fly ash Properties and Uses*, 2011. Available from:
<<http://www.monolithic.org/blogs/construction/fly-ash-properties-and-uses>>.
19. Huang CH, Lin SH, Chang CS, Chen HJ, 2013. Mix proportions and mechanical properties of concrete containing very high-volume of Class F fly ash. *Constr Build Mater* 46:71-78.
20. Nath P, Sarker P, 2011. Effect of fly ash on the durability properties of high strength concrete. *The Twelfth East Asia-Pacific Conference on Structural Engineering and Construction, Proceed. Engineering* 14:1149-1156.

21. Kayali O, Ahmed MS, 2013. Assessment of high volume replacement fly ash concrete – Concept of performance index. *Constr Build Mater* 39:71-76.
22. Papadakis VG, 1999. Effect of fly ash on Portland cement systems. Part I. Low-calcium fly ash. *Cem Concr Res* 29:1727-1736.
23. Wang Z, Wand Q, Wei Y, 2012. Effects of Mineral Admixtures and Superplasticizers on Micro Hardness of Aggregate-Paste Interface in Cement Concrete. *J. Shanghai Jiaotong Univ.* 12:629-634.
24. Bent DP, Weiss J, 2011. Internal curing: A 2010 State-of-the-Art Review. NISTIR 7765. Available from: <<http://concrete.nist.gov/~bentz/NISTIR7765.pdf>>.
25. Castro J, Ignor DV, Golias M, Weiss J, 2010. Extending internal curing concepts to mixtures containing high volumes of fly ash. *Inter Bri Conf.*
26. Henkensiefken R, Briatka P, Bentz D, Nantung T, Weiss J, 2010. Plastic shrinkage cracking in internal cured mixtures made with pre-wetted lightweight aggregate. *Concr Inter* 32:49-54.
27. Weber S, Reinhardt H, 1995. A Blend of Aggregates to Support Curing of Concrete. *Proceed of the Inter Symposium on Structural Lightweight Aggregate Concrete*. Eds. Holand I, Hammer TA, Fluge F, Sandefjord, Norway. 662-671.
28. Bentur A, Igarishi S, Kovler K, 2001. Prevention of Autogenous Shrinkage in High Strength Concrete by Internal Curing Using Wet Lightweight Aggregates. *Cem Concr Res* 31:1587-1591.
29. Lo TY, Cui HZ, Li ZG, 2004. Influence of Aggregate Pre-wetting and Fly Ash on Mechanical Properties of Lightweight Concrete. *Waste Management* 24: 333-338.
30. Jensen OM, Hansen PF, 2001. Water-entrained cement-based materials: I. Principle and theoretical background, *Cem Concr Res* 21:647-654.
31. Jensen OM, Hansen PF, 2002. Water-entrained cement-based materials: II. Experimental

Observations, *Cem Concr Res* 32:973-978.

32. Iragashi S, Watanabe A, 2006. Experimental study on prevention of autogenous deformation by internal curing using super-absorbent polymer particles. *Proceed of Inter RILEM Confer – Volume Changes of Hardening Concrete: Testing and Mitigation*, RILEM Publication S.A.R.L 77-86.

33. Suzuki M, Meddah MS, Sato R, 2009. Use of porous ceramic waste aggregate for internal curing of high performance concrete. *Cem Concr Res* 39:373-381.

34. Nukushina T, Seiki S, Nakagawa S, Sato R, 2009. Experimental investigation on mechanical performance of concrete containing fly ash improved by internal curing with porous ceramic waste aggregate. *Proceed. JCI* 31:241-246.

35. American Concrete Institute, *Internal curing*, 2010.

36. Kliger P, 1957. Early high strength concrete for prestressing. *Proceed World Conference on Prestress Concrete*.

37. Henkensiefken R, 2008. Internal curing in cementitious systems made using saturated lightweight aggregate, Master Thesis, Purdue University, West Lafayette.

38. Maruyama I, Kanematsu M, Noguchi T, Iikura H, Teramoto A, Hayano H, 2009. Evaluation of water transfer from saturated lightweight aggregate to cement paste matrix by neutron radiography. *Nuclear Instruments and Methods in Physics Research A* 605:159-162.

39. Trtik P, Munch B, Weiss J, Kaestner A, Jerien I, Josic L, Lehmann E, Lura P, 2011. Release of internal curing water from lightweight aggregates in cement paste investigated by neutron and X-ray tomography. *Proceeding of the Ninth World Conference on Neutron radiography* 651:244-249.

40. Schlitter J, Henkensiefken R, Castro J, Raoufi K, Weiss J, 2010. Development of internally cured concrete for increased service life. Final Report of Joint transportation research program.

Available from: < <http://docs.lib.purdue.edu/cgi/viewcontent.cgi?article=2610&context=jtrp>>

41. Bentz DP, Halleck PM, Grader AS, Roberts JW, 2006. Water movement during internal curing: Direct observation using X-ray microtomography. *Concrete International* 28:39-45.
42. Bentz DP, Stutzman PE, 2008. Internal curing and Microstructure of high performance mortars, ACI SP-256. *Internal curing of high performance concretes: laboratory and fields experiences*. American Concrete Institute, Farmington Hills, MI:81 – 90.
43. Scrivener KL, Crumbie AK, Laugesen P, 2004. The Interfacial Transition Zone (ITZ) between cement paste and aggregate in concrete. *Interface Science* 12:411-421.
44. Peled A, Castro J, Weiss J. Atomic Force Microscopy Examinations of Mortar Made by Using Water-Filled Lightweight Aggregate. *Transportation Research Record* 2141.
45. Chindaprasirt P, Jaturapitakkul C, Sinsiri T, 2005. Effect of fly ash fineness on compressive strength and pore size of blended cement paste. *Cem Concr Compos* 27:425-428.
46. Celik O, Damci E, Piskin S, 2008. Characterization of fly ash and its effects on compressive strength properties of Portland cement. *Ind J Eng Mater Sci* 15:443-440.
47. John MF, 2005. Changes in fly ash with thermal treatment. *World of Coal Ash (WOCA)*, Lexington, Kentucky, USA.
48. Saraswathy V, Muralidharan S, Thangavel K, Srinivasan S, 2003. Influence of activated fly ash on corrosion-resistance and strength of concrete. *Cem Concr Compos* 25:673-680.
49. Caijun S, Robert LD, 2001. Comparison of different methods for enhancing reactivity of pozzolans. *Cem Concr Res* 31:813-818.
50. Caijun S, Yixin S, 2002. What is the most efficient way to activate the reactivity of fly ash? 2nd Material Specialty Conference of the Canadian Society for Civil Engineering, Montréal, Québec, Canada, June 5-8.
51. Fan Y, Yin S, Wen Z, Zhong J, 1999. Activation of fly ash and its effects on cement

properties. *Cem Concr Res* 29:467-472.

52. Jariyathitipong P, Kawai K, Sato R, Tsuchida S, 2002. Experimental study on acceleration of pozzolanic reaction of fly ash. *Proceed of JCI* 24:105-110.

53. Tang M, Han S, 1981. Effect of $\text{Ca}(\text{OH})_2$ on alkali-silica reaction. *J. of Chinese Silicate Society* 9:160-166.53. Katz A, 1998. Microscopic study of alkali-activated fly ash. *Cem Concr Res* 28:197-208.

54. Ryu GS, Lee YB, Koh KT, Chung YS, 2013. The mechanical properties of fly ash based geopolymer concrete with alkaline activators. *Constr Build Mater* 47:409-418.

55. Shui Z, Yu R, Dong J, 2011. Activation of fly ash with dehydrated cement paste. *ACI Materials Journal*, Title no. 108-M23.

56. Katz A, 1998. Microscopic study of alkali-activated fly ash. *Cem Concr Res* 28:197-208.

57. Bakharev T, 2005. Geopolymeric materials prepared using Class F fly ash and elevated temperature curing. *Cem Concr Res* 35:1224-1232.

58. Alvarez-Ayuso E, Querol X, Plana F, Alastuey A, Moreno N, Izquierdo M, Font O, Moreno T, Diez S, Vázquez E, Barra M, 2008. Environmental, physical and structural characterisation of geopolymer matrixes synthesised from coal (co-)combustion fly ashes. *J. of Hazardous Materials* 154:175-183.

CHAPTER 3

EXPERIMENTAL PROGRAM

This chapter describes the experimental program including (1) materials and mixture proportions, (2) the fundamental models as internal alkali activation (IAA), (3) the mixing, casting and curing condition for the fly ash cement system. In addition, this chapter also shows the test procedures to study the effects of types and starting time of IAA on the chemical and mechanical properties of the fly ash cement systems.

3.1 MATERIALS

3.1.1 Cement

Cement used in this study was high-early-strength Portland cement for ensuring the strength of concrete. This type of cement met the standard values of JIS R 5210 (Portland cement). The chemical compositions and the physical properties of this type of cement are shown in Tables 3.1 and 3.2, respectively.

Table 3.1 Chemical composition of high-early-strength Portland cement

Chemical composition	JIS R 5210	Measured value
SiO ₂ (%)	-	20.3
Fe ₂ O ₃ (%)	-	2.71
Al ₂ O ₃ (%)	-	4.96
CaO (%)	-	65.49
MgO (%)	less than 5.0	1.21
SO ₃ (%)	less than 3.5	2.98
Na ₂ O (%)	-	0.22
K ₂ O (%)	-	0.35
Cl ⁻ (%)	less than 0.02	0.008
Loss on ignition (%)	less than 5.0	1.19

Table 3.2 Physical properties of high-early-strength Portland cement

Physical properties		JIS R 5210	Measured value
Density	g/cm ³	-	3.14
Blaine specific surface area	cm ² /g	more than 3300	4590
Setting time	Initial set h-min	more than 45 min	1-52
	Final set h-min	less than 10 h	2-57
Compressive strength N/mm ²	1-day	more than 10.0	27.2
	3-day	more than 20.0	48.4
	7-day	more than 32.5	57.2
	28-day	more than 47.5	66.2

3.1.2 Fly ash

Fly ash used in this study met the standard values of type II per JIS A 6201 (fly ash for concrete) and class F per ASTM C618 (standard specifications for coal fly ash and raw or calcined natural pozzolan). The chemical composition and physical properties of fly ash are shown in Tables 3.3 and 3.4, respectively.

Table 3.3 Chemical composition of fly ash

Chemical composition	ASTM C618	JIS A 6201	Measured value
SiO ₂ (%)	} more than 70.0	more than 45	57.7
Fe ₂ O ₃ (%)		-	5.43
Al ₂ O ₃ (%)		-	27.54
CaO (%)	-	-	1.26
MgO (%)	-	-	1.06
SO ₃ (%)	less than 5.0	-	0.36
Na ₂ O (%)	-	-	0.44
K ₂ O (%)	-	-	0.76
Loss on ignition (%)	less than 6.0	less than 5.0	2.8

Table 3.4 Physical properties of fly ash

Physical properties		ASTM C618	JIS A 6201	Measured value
Density	g/cm ³	-	more than 1.95	2.21
Blaine specific surface area	cm ² /g	-	more than 2500	3290
Moisture content	%	-	less than 1.0	0.1
Percent flow	%	-	more than 95	108
Activity index %	28-day	more than 75	more than 80	81
	91-day	-	more than 90	96

3.1.3 Alkali solution

Two alkali solutions used in this study to accelerate the pozzolanic reaction of the fly ash cement paste were 0.1 mol/L sodium hydroxide solution (pH = 13.0) and saturated Ca(OH)₂ solution (pH = 12.6). In addition, water was also used for the reference.

The sodium hydroxide (NaOH) was in pellets form with 97% purity. The NaOH solution was prepared by dissolving the pellets in pure water.

The saturated Ca(OH)₂ solution was also prepared by dissolving the Ca(OH)₂ in finely ground form in pure water until bringing about white precipitation of solid Ca(OH)₂. After stirring this solution and waiting for formation of the precipitate, this solution was filtered and the filtrate was used as saturated Ca(OH)₂ solution.

3.1.4 Aggregate

Crushed sand, crushed stone and porous ceramic waste aggregate (PCWA) were used as the aggregate in the concrete. The physical properties of all aggregates are listed in Table 3.5.

Table 3.5 Properties of aggregate

Materials	Type - Notation	Properties
Fine aggregate	Crushed sand - S	Surface-dry specific gravity: 2.62 g/cm ³ Water absorption: 1.16%
Coarse aggregate	Crushed stone (15 – 05mm and 20 – 05 mm) - G	Surface-dry specific gravity: 2.65 g/cm ³ Water absorption: 0.62%
	Porous ceramic waste aggregate - PCWA	Surface-dry specific gravity: 2.26 g/cm ³ Water absorption: 8.70%

PCWA is a waste derived from porous ceramic roof tiles in the northern area of the Chugoku district in western Japan. In addition, PCWA was considered as an internal curing agent because it is able to absorb a large amount of water (as shown in Table 3.5). When compared with the artificial aggregate, PCWA has a lower crushing value than the artificial aggregate despite of a smaller water absorption of PCWA. Therefore, this waste aggregate should be utilized for partial replacement of the crushed stone so that it played a role as an internal curing activating agent in this study. In order to utilize as an internal curing agent most effectively, after being dried PCWA in an oven completely, PCWA was immersed for 7 days in each solution ((1) water, (2) 0.1mol/L NaOH, and (3) saturated Ca(OH)₂ solution), as shown in Figure 3.1.

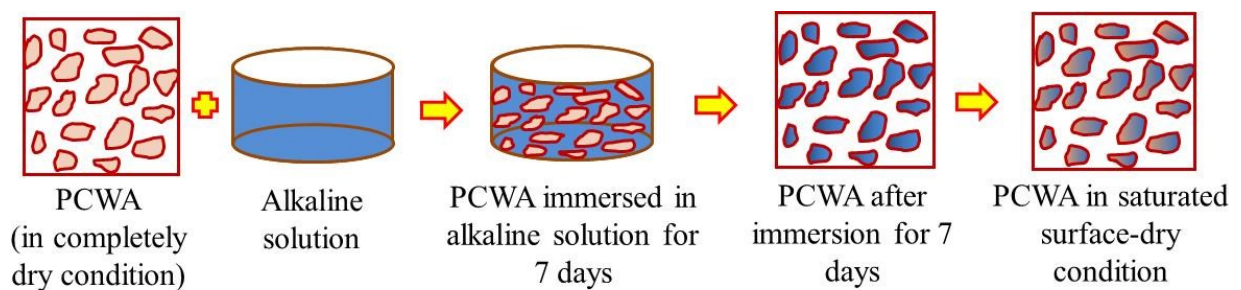


Figure 3.1 Preparation of PCWA

In order to evaluate the alkali absorption of PCWA, the concentration of hydroxide ions retained in PCWA was determined by the neutralization titration with HCl. As a result, the

concentration of hydroxide ions retained in PCWA was nearly the same as or smaller slightly than the concentration of alkaline solution prepared for the immersion of PCWA for 7 days. It indicates PCWA could be used as an internal alkali activating agent.

3.1.5 Admixture

Admixtures used in this study were superplasticizer and air entraining agent.

(1) Superplasticizer

Superplasticizer with a brand name of Master Glenium SP8HV_M is polycarboxylic acid ether-based high performance air entraining and water reducing admixture for high strength concrete. The advantages of using SP8HV_M include enhancing the effect of dispersion for cement grain; reducing the viscosity of the fresh concrete; improving the workability and pump ability; reducing the mixing water, resulting in enhancing the strength of concrete and so on. The physical properties of SP8HV_M are shown in Table 3.6.

Table 3.6 Physical properties of SP8HV_M

Main component	Appearance	Density at 20°C (g/cm ³)	Total alkali content* (%)	Chloride ion content* (%)
Polycarboxylic acid ether	Reddish brown liquid	1.04 – 1.11	1.1	0

* Total amount of alkali and chloride ion contents is analytical value.

(2) Air entraining agent

Air entraining agent with a brand name of Master Air 202 met the standard values of type I per JIS A 6204 (chemical admixture for concrete). It is possible to entrain air with high quality and stably in concrete. When using Master Air 202, the mixing water can be reduced, resulting in improving the workability for fresh concrete and the durability for hardened concrete. The physical properties of Master Air 202 are shown in Table 3.7.

Table 3.7 Physical properties of Master Air 202

Main component	Appearance	Density at 20°C (g/cm ³)	Total alkali content* (%)	Chloride ion content* (%)
Modified rosin acid compound-based anionic surfactant	Brown liquid	1.02 – 1.06	1.7	0.01

* Total amount of alkali and chloride ion contents is analytical value.

3.2. MIXTURE PROPORTION

3.2.1 Paste

Low-calcium fly ash was used to replace the high-early-strength Portland cement at mass ratios of 0% (FA0), 20% (FA20), and 40% (FA40). A water to binder ratio of 0.30 in cement pastes was kept constant and similar to concrete in the section 3.2.2.

3.2.2 Concrete

Eight concrete mixtures prepared in this study had a constant water to cementitious materials ratio of 0.30 and water content of 165 kg/m³. The low water to binder ratio in concrete is one of factors, which increase its strength. When the low water to binder ratio is used, however, the concrete can need the water for the reactions to proceed over time. Therefore, internal curing or internal alkali activation by using PCWA would be effective in the high strength concrete with a low water to binder ratio.

The partial replacements of high-early-strength Portland cement with low-calcium fly ash were 0 % and 40 % by mass. The replacements of PCWA were 0 % and 40 % by volume. Superplasticizer and air-entraining agent were used to meet the designed values. The concrete mixtures were designated with the following codes: FA0G0, FA0G40(Wa), FA0G40(Na), FA0G40(Ca), FA40G0, FA40G40(Wa), FA40G40(Na), and FA40G40(Ca). The digits following FA show the partial replacements of cement with fly ash, which varies from 0 % (FA0) to 40 % (FA40). The digits following G show the PCWA replacements, which are 0 %

(G0), and 40 % (G40). The letters of Wa, Na and Ca show the kinds of solution ((1) water, (2) NaOH solution, and (3) saturated Ca(OH)₂ solution) in PCWA. Details of eight mixture proportions and the measured properties of all the fresh concrete types are listed in Tables 3.8 and 3.9, respectively.

Table 3.8 Mixture proportion of concrete

Designation	W/(C+FA) (%)	Replacement ratio		Unit content (kg/m ³)										
		FA (mass %)	PCWA (vol. %)	W	C	FA	S	G	PCWA					
FA0G0	30	0	0	165	550	0	751	854	0					
FA0G40(Wa)			40					330	220	677	512	295		
FA0G40(Na)											0	854	0	
FA0G40(Ca)												512	295	
FA40G0		40	40		0	330	220				677	854	0	
FA40G40(Wa)					40			330	220	677		512	295	
FA40G40(Na)												0	854	0
FA40G40(Ca)													512	295

Table 3.9 Properties of fresh concrete

Designation	W/(C+FA) (%)	Replacement ratio		Designed values	Measured values										
		FA (mass %)	PCWA (vol. %)	Air content (%)	Air content (%)	Slump (cm)	Temp. (°C)								
FA0G0	30	0	0	4.5±1.5	6.0	21.5	25.3								
FA0G40(Wa)			40		330	220	677	6.0	22.0	25.3					
FA0G40(Na)								0	5.4	20.0	20.3				
FA0G40(Ca)									3.4	12.5	22.2				
FA40G0		40	40					0	330	220	677	4.6	26.0	18.7	
FA40G40(Wa)					40	330	220	677				4.3	21.0	19.5	
FA40G40(Na)												0	4.5	21.0	21.2
FA40G40(Ca)													4.6	20.5	21.3

Remark: Temp. : Temperature

3.3. METHOD OF IAA

As mentioned in 1.2, IAA was performed by applying two fundamental models in order to estimate more obviously its effects on the chemical and mechanical properties and porosity of fly ash cement paste cured at normal temperature. They were (1) an original model through an installed syringe and (2) a model of IAA by using one PCWA.

3.3.1 Original model of IAA

This model was carried out by applying alkaline solution naturally through an installed 1-ml syringe, which was inserted in the center of a cubic cement paste specimen after casting, as shown in Figure 3.2. The alkaline solutions and water were allowed to be imbibed naturally through the permeability of the pastes, i.e., no additional pressure was applied to force the liquid into the pastes. No solution was also injected into the paste specimens for the control as shown in Figure 3.3.

This model is considered to be an IAA by using PCWA in concrete. Therefore, the size of the syringe was decided considering the volume of internal water supplied from PCWA in concrete, which will be discussed in the section 3.3.3.

The starting time of alkaline solution supply was considered as the time when the fly ash cement paste did not have enough water for cement paste to hydrate as well as alkalinity for the pozzolanic reaction to occur. It is known that the pozzolanic reaction proceeds slowly at the age of 1 month and become quite constant from the age 3 months or later [2, 5]. Therefore, the starting time of IAA was selected to be at 1 and 3 months for the study on the effects of starting time of IAA on the chemical and mechanical properties of the fly ash cement systems.

In this model, the effect of types and starting time of IAA on the pozzolanic reaction of fly ash cement systems was studied by examining the Ca(OH)_2 content and porosity.

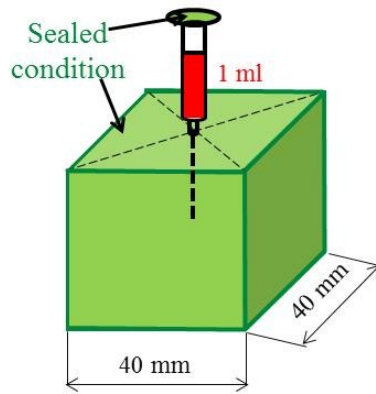


Figure 3.2 Sample preparation. Cement paste samples were cast in 40-mm cube molds. A 1-ml syringe with the plunger removed was installed so that the tip of the needle was positioned at the center of the cube to allow the addition of water or alkali solution

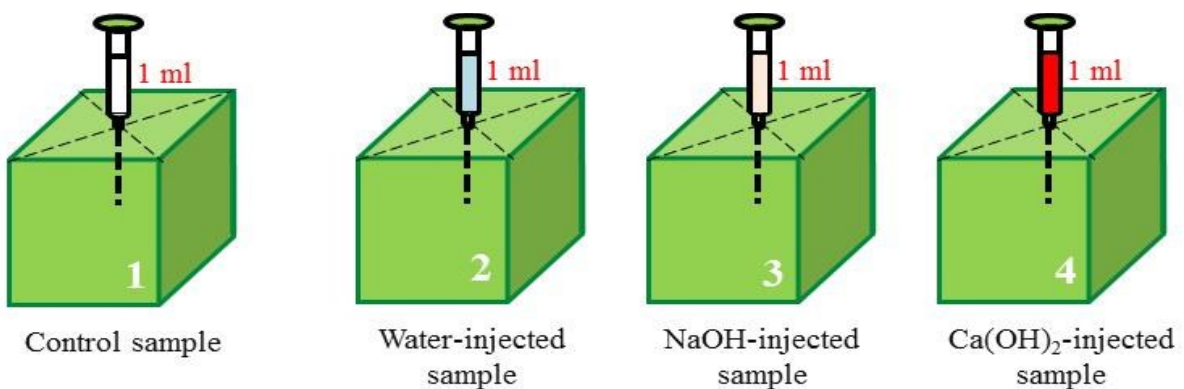


Figure 3.3 Activation methods for each mixture proportion (FA0 and FA40) under each condition ((1) no injection, (2) Water injection, (3) NaOH injection, (4) saturated Ca(OH)_2 injection) 1 or 3 months after casting

In addition, the volume of solution imbibed over time was also observed for a future reference of the volume of water, NaOH, or saturated Ca(OH)_2 solution supplied from PCWA to the paste over time. The volumes of water, NaOH, and saturated Ca(OH)_2 solution imbibed into the pastes as shown in Tables 3.10 and 3.11 for the reference purpose were cumulative values from the injection to the designated measuring time. These volumes of solution imbibed into the pastes depend on the individual differences in the microstructure of the specimens.

Table 3.10 Volumes of water, NaOH, and saturated Ca(OH)₂ solution imbibed into the pastes over time in the case of the injection from the age of 1 month (mL)

Mix proportion	Solution	The volume of solution (water or alkali) imbibed into the pastes over time (1-month injection)					
		2M	4M	6M	8M	10M	12M
FA0	Water	0.10	0.26	0.38	0.69	1.00	0.57
	NaOH			0.40	0.69	1.00	0.57
	Ca(OH) ₂			0.40	0.70	1.00	0.65
FA40	Water	0.05	0.05	0.35	0.10	0.14	0.20
	NaOH			0.36	0.10	0.20	0.33
	Ca(OH) ₂			0.31	0.08	0.20	0.31

Remark: M: months (the age)

Table 3.11 Volumes of water, NaOH, and saturated Ca(OH)₂ solution imbibed into the pastes over time in the case of the injection from the age of 3 months (mL)

Mix proportion	Solution	The volume of solution (water or alkali) imbibed into the paste over time (3-month injection)				
		4M	6M	8M	10M	12M
FA0	Water	0.06	0.17	0.10	0.22	0.20
	NaOH	0.06	0.15	0.09	0.34	0.20
	Ca(OH) ₂	0.06	0.15	0.10	0.34	0.20
FA40	Water	0.04	0.06	0.09	0.24	0.15
	NaOH	0.04	0.06	0.10	0.27	0.15
	Ca(OH) ₂	0.04	0.06	0.10	0.27	0.11

Remark: M: months (the age)

3.3.2 Model of IAA using PCWA

This model was conducted using one porous ceramic waste aggregate which was installed in the center of the specimens as shown in Figure 3.4. The aim of this model was to study the effects of IAA on the microstructure of the interfacial transition zone (ITZ) between PCWA and bulk paste in the fly ash cement systems by measuring the hardness.

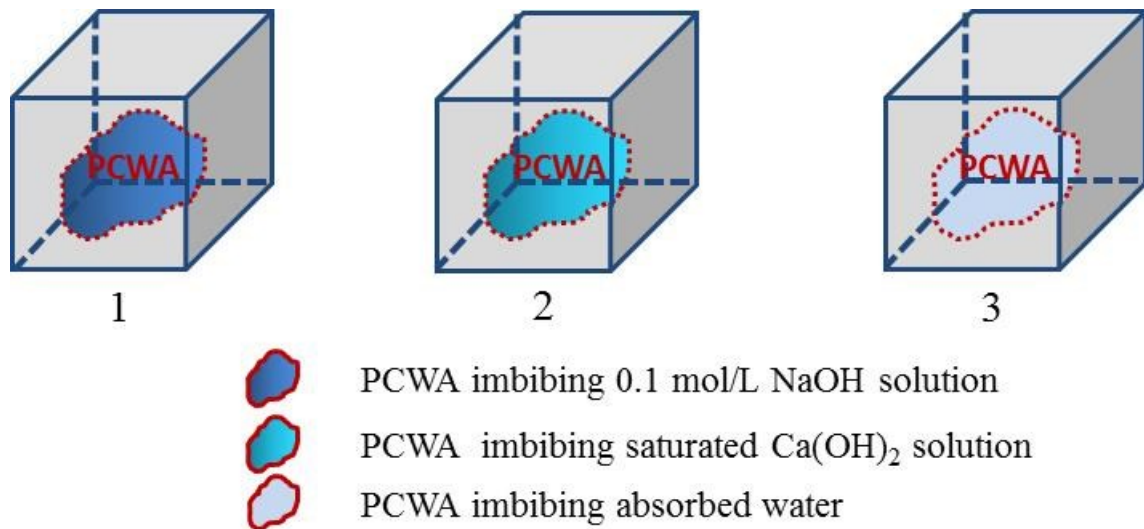


Figure 3.4 Sample preparation using one PCWA

3.3.3 IAA on fly ash concrete

IAA was carried out by using PCWA, prepared in saturated-surface dry condition after the immersion in alkaline solution for 7 days, to investigate its effects on the mechanical properties of fly ash concrete cured at normal temperature. According to Suzuki et al., 40% replacement of PCWA increased the compressive strength more significantly than 10%, 20%, or 30% replacement at the age of 28 days due to maximum internal water supplied from PCWA [1].

Furthermore, this replacement of PCWA was also calculated and compared with the original model of IAA by using an installed 1-ml syringe described in 3.3.1. According to Table 3.5, the value of maximum absorption of PCWA is 8.7% by weight.

(1) In the case of concrete using PCWA

The PCWA content is 295 kg for replacing crushed stone. As a result, the water absorbed in PCWA would be 23.6 kg ($=295 \times 8.7\% / (1+8.7\%)$) or 0.0236 m^3 in 1 m^3 of concrete.

(2) In the case of model from 1-ml syringe

Supposed that the water imbibed from 1-ml syringe into the matrix was 1 ml in a 4-cm cubic specimen, it would be 0.0156 m^3 ($=1/64$) or 15.6 kg in 1m^3 of concrete. This value is smaller slightly than the water in PCWA as the above-mentioned.

Based on the above issues, the replacements of PCWA selected in this study were therefore 0 % and 40 % by volume so that IAA would maximize its effects on promoting the cement hydration and accelerating the pozzolanic reaction of the fly ash cement systems.

3.4 MIXING, CASTING AND CURING

3.4.1 Mixing and casting

Pastes were mixed in a mechanical mixer, cast in 40-mm cube molds, and sealed with aluminum and adhesive tape to prevent water loss and carbonation. During the mixing process, the temperature of the materials, mixer, and molds was maintained at 20 °C.

Concrete were mixed in a mixer and cast in a cylindrical specimen of 100-mm diameter and 200-mm height, and sealed with aluminum and adhesive tape.

3.4.2 Curing condition

All of paste specimens were demolded 24 hours after casting, then sealed and cured at 20 °C.

All of concrete specimens were cured in the sealing condition at 20°C after casting.

3.5 TEST PROCEDURE

3.5.1 Differential thermal analysis and thermogravimetry (DTA-TG)

The CH content of control pastes that were not treated with water or alkali activator was measured by simultaneous differential thermal analysis and thermal gravimetry (DTA-TG) apparatus (DTG-60H, Shimadzu Corporation, Japan) at the designated months. As shown in Figure 3.5, at the point of the needle, a 4mm-section sample was drilled out and collected as powder. The sample was soaked in ethanol for 24 hours to stop further hydration and dried in a vacuum desiccator for 24 hours before thermal gravimetry analysis. The temperature of

DTA-TG apparatus was installed at a rate of 20°C/min up to 100°C and kept at 100°C for 30 minutes to remove free water completely, and then at 20°C/min up to 1000°C. The CH content was calculated from the ignited mass of the sample and the mass loss due to the dehydration of CH. This mass loss was determined from the differential thermal gravimetry (DTG) curve between the initial and final temperatures of the corresponding DTG peaks [2]. For fly ash cement pastes into which water, NaOH or saturated Ca(OH)₂ solution was injected 1 month and 3 months after casting, the CH content was measured by DTA-TG apparatus at the ages of 2, 4, 6, 8, 10, and 12 months.

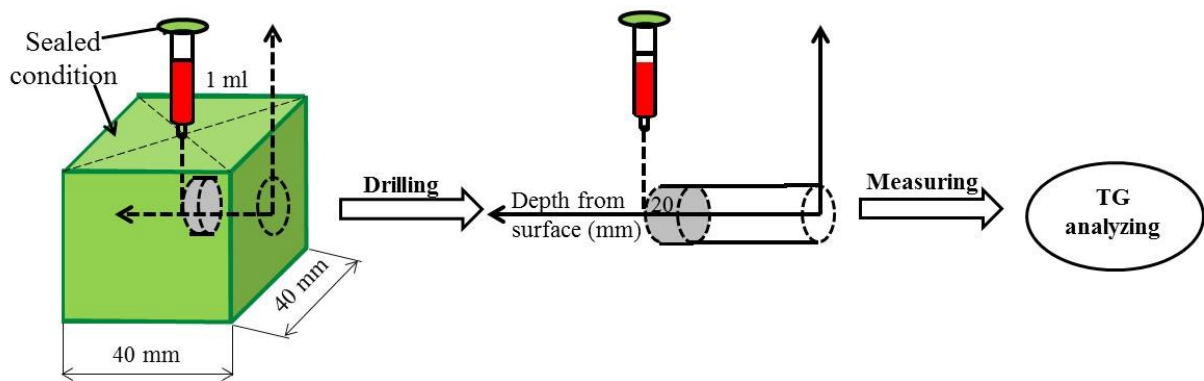


Figure 3.5 Sample preparations for DTA-TG

3.5.2 Hardness measurement

Each specimen at the ages of 1 day, 1 month, and 6 months in the case of IAA by using one PCWA was cut from the center of the specimens with the thickness of 5 mm as shown in Figure 3.6. Then, all the specimens were soaked in the acetone for 24 hours so that the cement hydration and the pozzolanic reaction were stopped completely. Then, they were dried completely for 24 hours in a vacuum desiccator.

The surface of the specimen was polished by abrasive compound with the fineness of 3000 and a flat glass plate in order to identify easily the diamond-shape indentation that is formed on the surface of the specimen by the Vickers indenter. Then, the specimen was also washed

more than 5 minutes by using an ultrasonic cleaner to remove foreign substances on the surface of the sample after polishing. After being washed 3 times, the specimen was dried in a vacuum desiccator for 24 hours before hardness measurement. The Vickers micro hardness in the paste measured at 11 points within a distance of 0 to 5000 μm from the surface of PCWA with 5 different positions is shown in Figure 3.7. In order to evaluate the hardness as well as the width of ITZ, the micro hardness of PCWA and the bulk paste was also measured approximately 10 points.

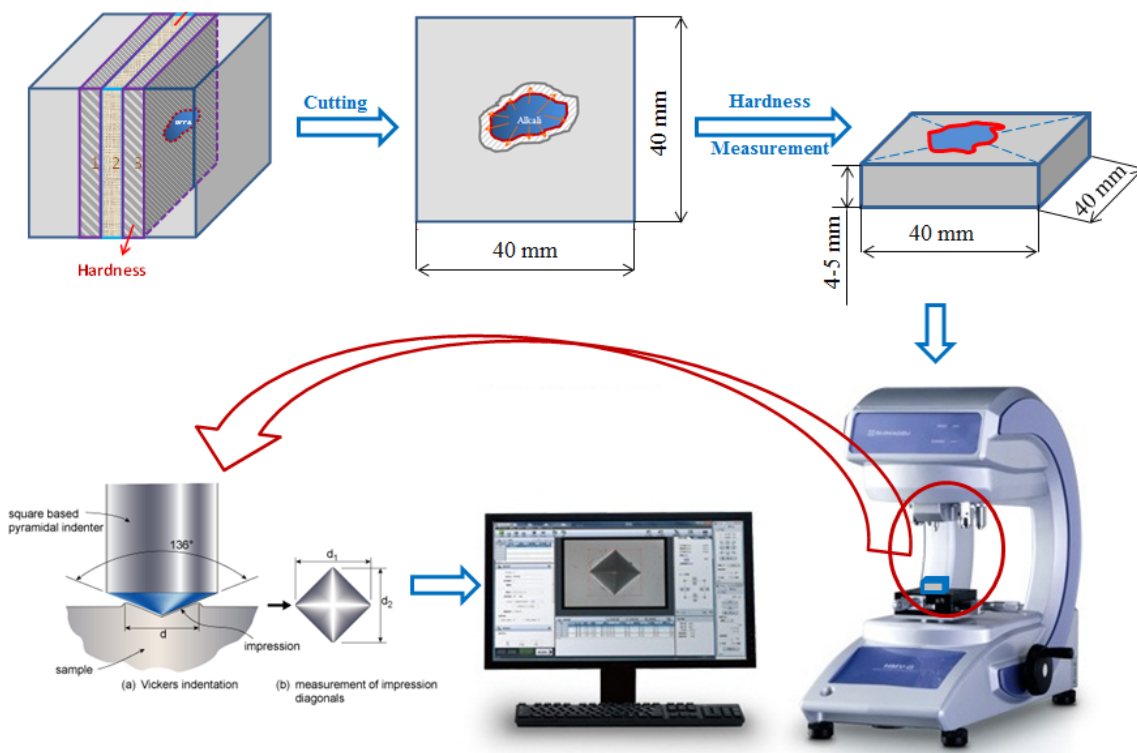


Figure 3.6 Samples preparation for hardness measurement

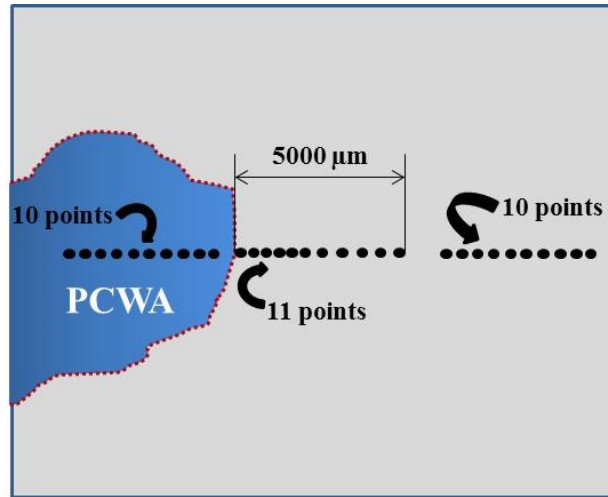


Figure 3.7 Method of harness measurement of PCWA, ITZ and bulk paste

3.5.3 Compressive strength

At the ages of 7, 28, 56, 91, 182, and 364 days, three cylindrical specimens of 100 mm diameter and 200 mm height were tested for the compressive strength of concrete per JIS A 1108 (Method of test for compressive strength of concrete).

3.5.4 Mercury intrusion porosimetry (MIP)

The porosity was measured by mercury intrusion porosimetry (POREMASTER 60, Shimadzu Corporation, Japan). Samples for mercury intrusion porosimetry (MIP) measurement were obtained by crushing the hardened paste cubes and selecting material in the size range 2.5–5.0 mm from around the position of the needle (see Figure 3.8). Meanwhile, the concrete samples for MIP measurement were crushed and selected in the size range 2.5-5.0 mm from the broken concrete samples after testing the compressive strength. Samples were soaked in ethanol for 24 hours to stop further hydration and dried in a vacuum desiccator for 24 hours before MIP measurement. The MIP equipment used in this study operates at a maximum pressure of $414 \times 10^6 \text{ N/m}^2$. The pore size distribution of the pastes was measured over a diameter range of 3 nm -300 μm .

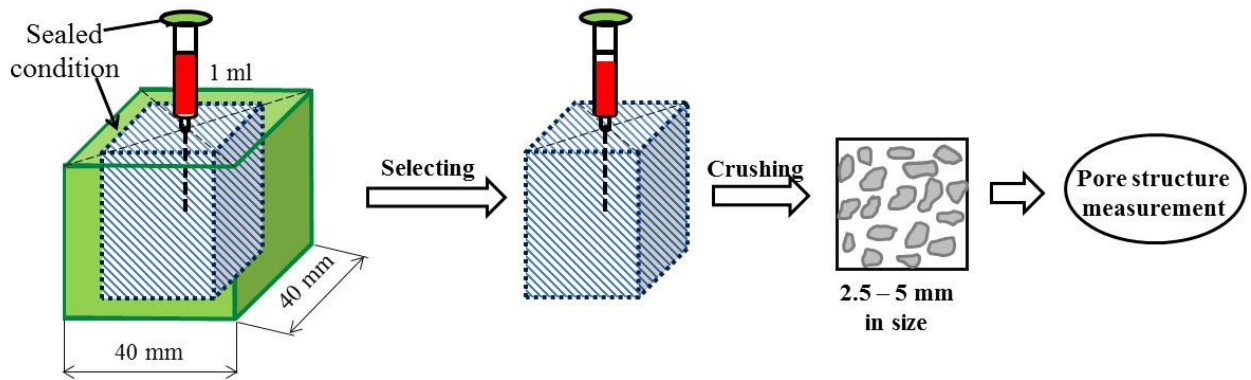


Figure 3.8 Sample preparations in fly ash cement system for MIP measurement

3.5.5 Scanning electron microscopy (SEM)

Specimens for scanning electron microscopy (S-5200, Hitachi, Ltd., Japan) observation were selected from near the position of the needle in broken hardened paste cubes at the ages of 6 and 12 months. The specimens were soaked in ethanol for 24 hours and then dried in a vacuum desiccator for a further day before scanning electron microscopy (SEM) analysis. Samples were coated with Pt before observation. To obtain clear images, specimens less than 1 mm in size were imaged with an accelerating voltage of 3 kV.

3.6 SUMMARY

Generally, the experimental program in this study can be carried out according to the following diagram:

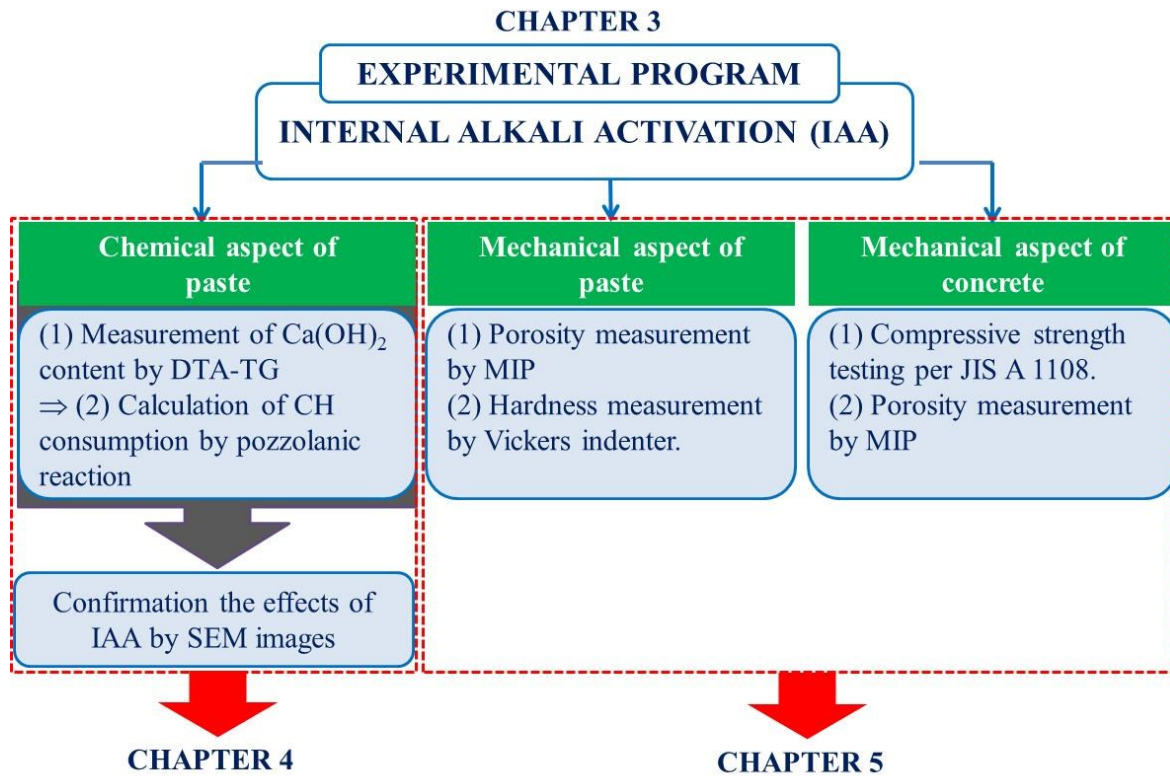


Figure 3.9 Flow chart of experimental program

References

1. Suzuki M, Meddah MS, Sato R, 2009. Use of porous ceramic waste aggregate for internal curing of high performance concrete. *Cem Concr Res* 39:373-381.
2. Sakai E, Miyahara S, Ohsawa S, Lee SH, Daimon M (2005) Hydration of fly ash cement. *Cem Concr Res* 35:1135-1140.
3. Japan Institute Standard. JIS R 5210 (Portland cement), JIS A 6201 (Fly ash for concrete), JIS A 6204 (Chemical admixture for concrete), and JIS A 1108 (Method of test for compressive strength of concrete).
4. ASTM International. ASTM C618 (Standard Specification for coal fly ash and raw of calcined natural pozzolan for use in concrete).
5. Termkhajornkit P, Nawa T, Nakai M, Saito T, 2005. Effect of fly ash on autogenous shrinkage. *Cem Concr Res* 35:473-782.

CHAPTER 4

EFFECTS OF IAA ON CHEMICAL REACTION OF FLY ASH CEMENT SYSTEMS

Effects of IAA on the chemical reaction of the fly ash cement systems are discussed in this chapter by analyzing the $\text{Ca}(\text{OH})_2$ (hereafter, CH) content of the fly ash cement pastes in the section 4.1, calculating the consumption of CH by the pozzolanic reaction in the section 4.2, and examining SEM images for the confirmation of the effects of IAA in the section 4.3.

4.1 EFFECTS OF IAA ON $\text{Ca}(\text{OH})_2$ CONTENT

The CH content at the point of the needle of all samples at the ages of 2, 4, 6, 8, 10, and 12 months was measured by DTA-TG described in 3.5.1 (Chapter 3). Effects of IAA on the CH content at the ages of 2 months for the plain cement paste (FA0) and the fly ash cement paste (FA20 and FA40) in the case of the injection 1 month after casting are discussed in the section 4.1.1. In addition, effects of types and starting time of IAA on the CH content in FA0 and FA40 more than 4 months after casting are discussed in the sections 4.1.2 and 4.1.3.

4.1.1 Effects of IAA

The CH contents in FA0, FA20, and FA40 samples into which water, NaOH solution, or saturated $\text{Ca}(\text{OH})_2$ solution was injected at 1 month are compared with the untreated control samples at the age of 2 months as shown in Figure 4.1. Compared with the control (no injection), the injection of water

increased the CH content independent of fly ash replacement. It is evident that the water injection promoted the cement hydration of the paste with and without the fly ash replacement.

In the case of the injection of alkali solution (NaOH solution and saturated $\text{Ca}(\text{OH})_2$ solution), it can be said that the presence of alkali solution caused the CH content in FA0 to decrease slightly 1 month after the injection. It indicates the alkali solution injection for the sample without fly ash played a negative role toward the production of CH. This may be explained by the fact that it was difficult for the cement paste to release Ca^{2+} ion to the outside due to the high alkali concentration of pore solution supplied from the injected alkali solution, resulting in limiting the production of CH in the case of the plain cement paste. Thus, the CH content of the activated samples was smaller than that of the control samples. According to Figure 4.1, the CH contents of activated samples were larger than that of the control samples in FA20. The CH content of the sample activated by NaOH solution was approximately equal to that of the control sample in FA40, while the CH content of the sample activated by saturated $\text{Ca}(\text{OH})_2$ solution was smaller than that of the control sample in FA40. It indicates that the alkali solutions were actually effective on the acceleration of the pozzolanic reaction after the activation for 1 month in FA40 in the case of the injection at 1 month.

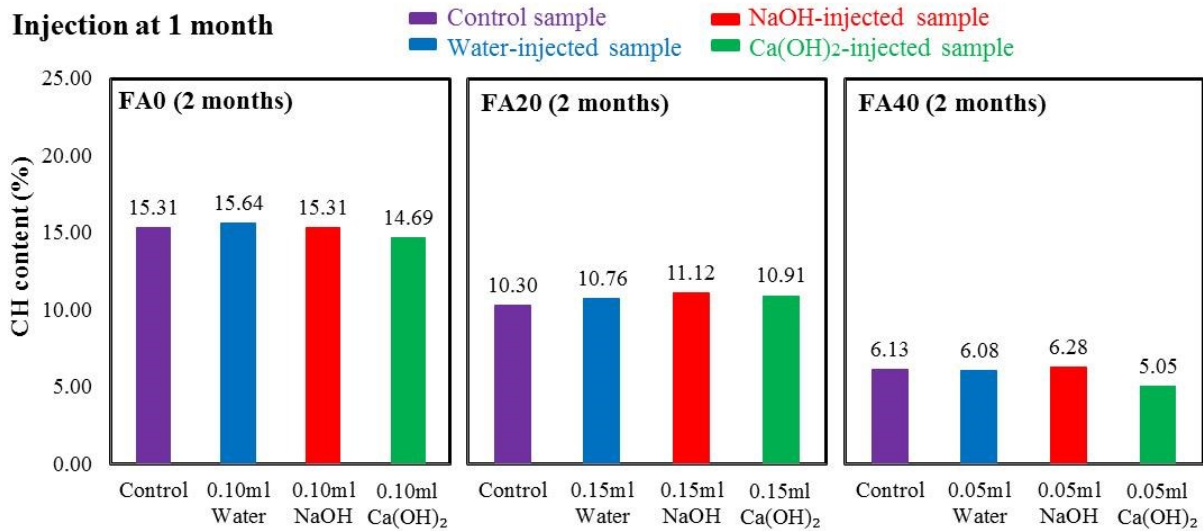


Figure 4.1 Comparison of CH content at the age of 2 months in FA0, FA20, and FA40 between

untreated control samples and samples into which water, NaOH solution or saturated Ca(OH)₂ solution was injected at 1 month

4.1.2 Effects of types of IAA

(1) Plain cement paste (FA0)

The CH contents in FA0 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected at 1 and 3 months are compared with the untreated control samples as shown in Figures 4.2 and 4.3. According to Figure 4.2, the injection of alkali solution (NaOH and saturated Ca(OH)₂) at 1 month slightly decreased the CH content in FA0 while the injection of water at 1 month increased the CH content in FA0 at the age of 4 months. It shows that the injection of alkali solution at 1 month for the sample without fly ash played a negative role toward the production of CH at the early ages (not only at 2 months but also at 4 months). At the later ages (i.e. 10 and 12 months), the higher CH contents in all cases of samples into which solution was injected than those in the untreated control sample was due to the cement hydration promoted by water supplied from alkali solution. It is obvious that the injection of solution at 1 month promoted the cement hydration in FA0 at the ages of 10 and 12 months. The increases in the CH content of FA0 were also observed at the ages of 4, 10, and 12 months in the case of

the injection of solution at 3 months, as shown in Figure 4.3.

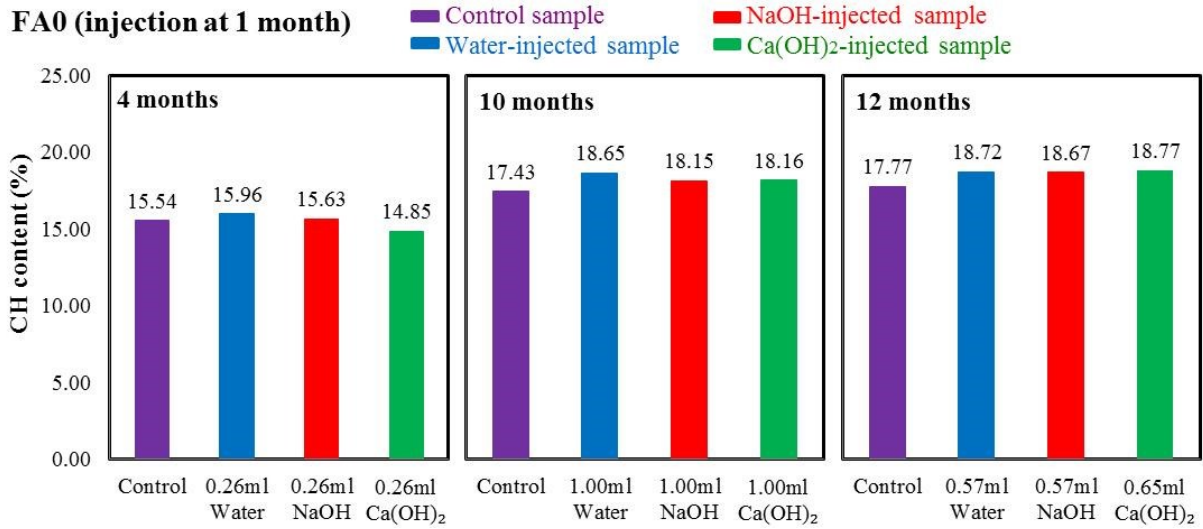


Figure 4.2 Comparison of CH content in FA0 between untreated control samples and samples into

which water, NaOH solution or saturated Ca(OH)₂ solution was injected at 1 month

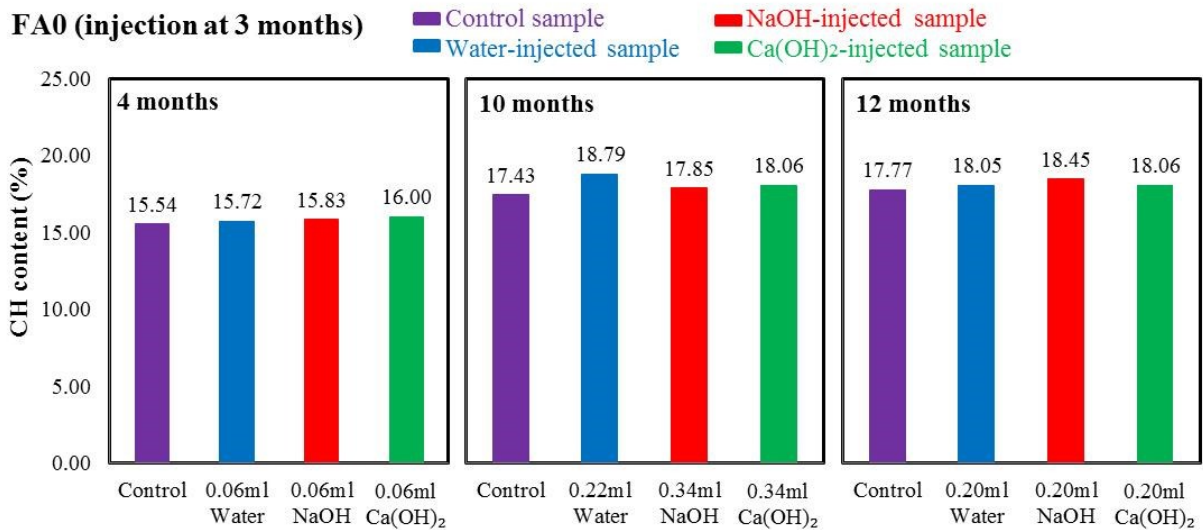


Figure 4.3 Comparison of CH content in FA0 between untreated control samples and samples into

which water, NaOH solution or saturated Ca(OH)₂ solution was injected at 3 months

(2) Fly ash cement paste (FA40)

The CH contents in FA40 samples into which water, NaOH solution, or saturated $\text{Ca}(\text{OH})_2$ solution was injected at 1 and 3 months are compared with the untreated control samples as shown in Figures 4.4 and 4.5. At the age of 4 months, the CH contents in the samples into which saturated $\text{Ca}(\text{OH})_2$ solution was injected at 1 or 3 months were nearly same as or lower than those in the untreated control samples, while those in the sample into which water or NaOH solution was injected were higher than those in the untreated control samples. It shows the injection of saturated $\text{Ca}(\text{OH})_2$ solution was more effective in reducing the CH content in FA40 than the injection of water or NaOH solution at the ages of 4 months independently of starting time of the injection.

Though the CH contents in some samples into which solution was injected were higher than those in the untreated control samples at the ages of 4 months in the case of the of injection of water and NaOH solution, it could not imply that the internal supplying of solution was not effective in accelerating the pozzolanic reaction. This might be attributed to the fact that the cement hydration of the samples into which water or NaOH solution was promoted more.

However, the effects of the injection of solution at 1 and 3 months in reducing the CH content were observed at the ages of 10 and 12 months. The reduction of the CH content implies that the pozzolanic reaction of fly ash was accelerated by the injection of solution [1, 2, 3]. In addition, the reduction of the CH content in the case of the injection of saturated $\text{Ca}(\text{OH})_2$ solution was larger than that in the case of the injection of water or NaOH solution at the ages of 10 and 12 months. It was confirmed again that the injection of saturated $\text{Ca}(\text{OH})_2$ solution was more effective in accelerating the pozzolanic reaction of the fly ash cement paste than the injection of water and NaOH solution.

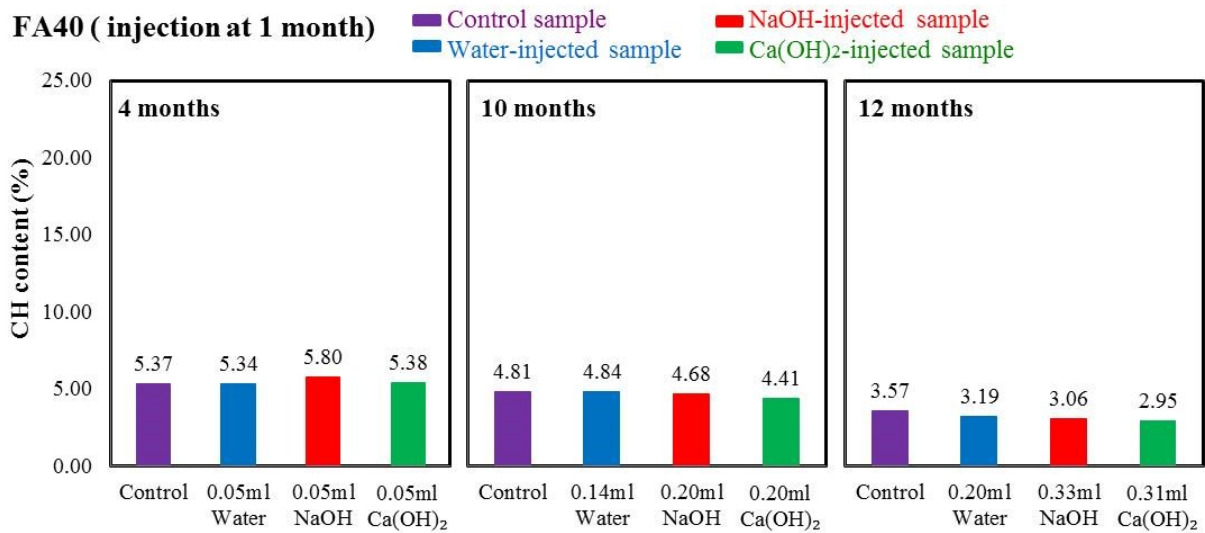


Figure 4.4 Comparison of CH content in FA40 between untreated control samples and samples into which water, NaOH solution or saturated Ca(OH)₂ solution was injected at 1 month

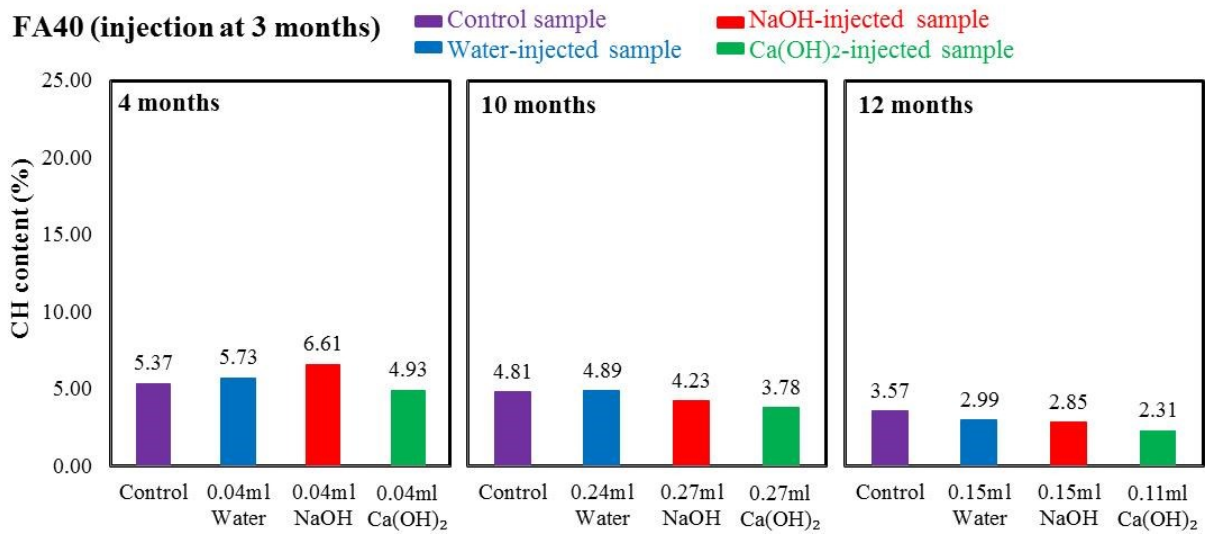


Figure 4.5 Comparison of CH content in FA40 between untreated control samples and samples into which water, NaOH solution or saturated Ca(OH)₂ solution was injected at 3 months

4.1.3 Effects of starting time of IAA

(1) Plain cement paste (FA0)

Figures 4.6, 4.7, and 4.8 show the effects of starting time of water, NaOH solution, and saturated $\text{Ca}(\text{OH})_2$ injection on the CH content in FA0, respectively. In all cases at each age (i.e. 6, 8, and 12 months), the CH content in the injection of solution at 3 months was nearly the same as or higher than that in the injection of the control or the solution at 1 month in FA0 although the injection at 3 months had the shorter period of injection than the injection at 1 month. It indicates the injection of solution at 3 months was more effective in promoting the cement hydration than the injection of solution at 1 month. This can be explained that the cement paste had enough water to hydrate at the early age, resulting in the injection of water at 1 month only slightly contributing to the cement hydration. At the later age, however, the paste had insufficient water to hydrate because the partial water reacted with the chemical compounds of cement at the early age. Therefore, the injection of water at 3 months promoted the cement hydration more than the injection of water at 1 month.

FA0 (injection of water)

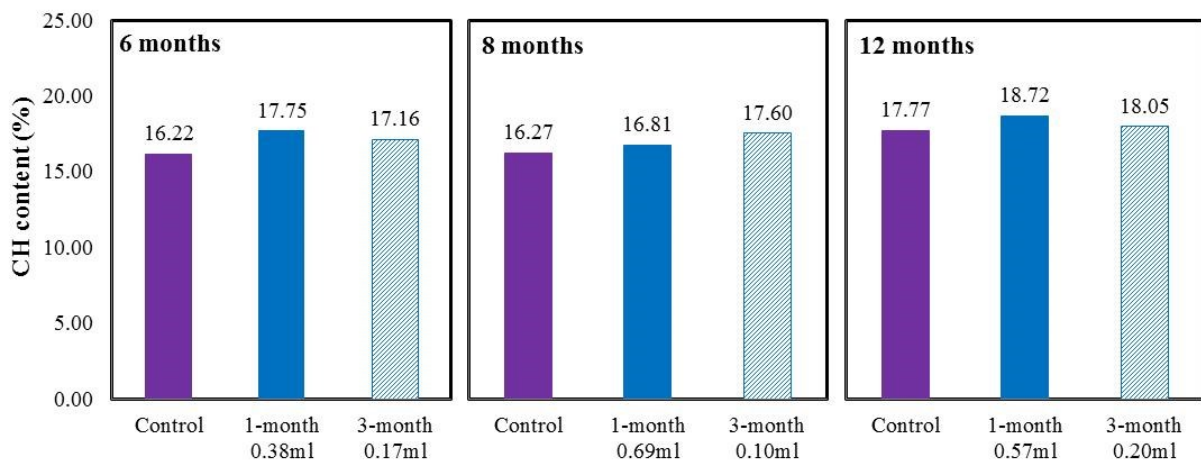


Figure 4.6 Effect of starting time of water injection on CH content in FA0 at the ages of 6 (left), 8 (middle), and 12 (right) months

FA0 (injection of NaOH solution)

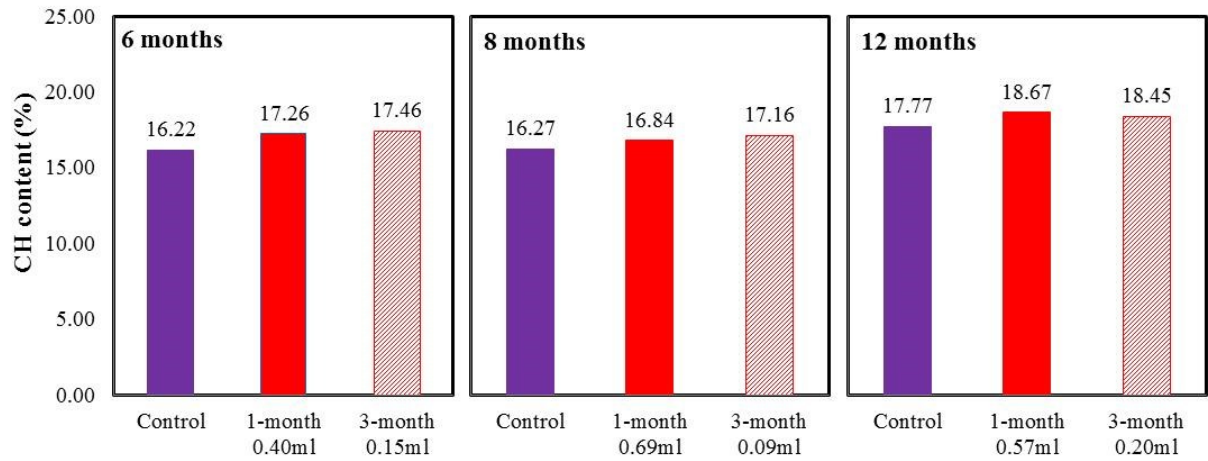


Figure 4.7 Effect of starting time of NaOH solution injection on CH content in FA0 at the ages of 6 (left), 8 (middle), and 12 (right) months

FA0 (injection of saturated Ca(OH)₂ solution)

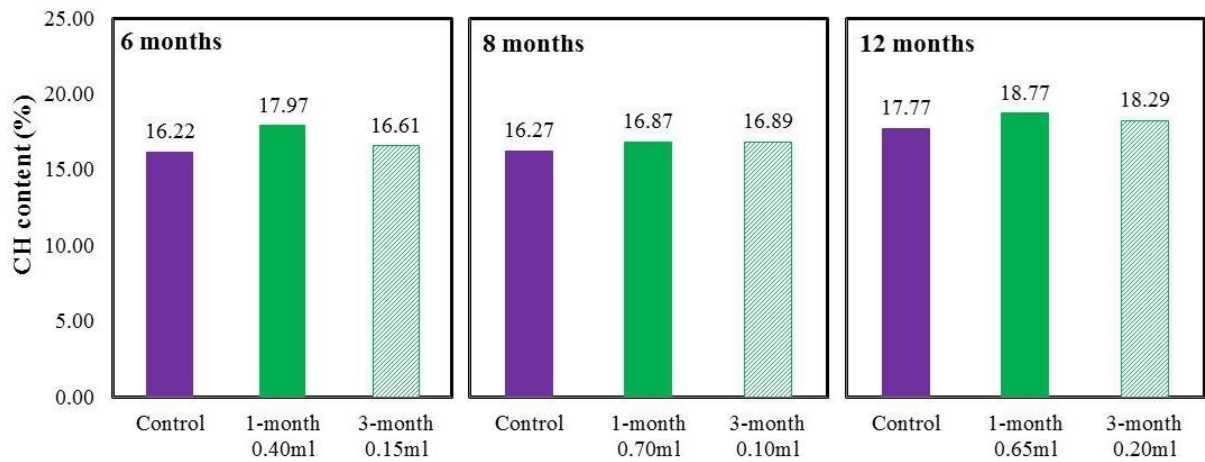


Figure 4.8 Effect of starting time of saturated Ca(OH)₂ solution injection on CH content in FA0 at the ages of 6 (left), 8 (middle), and 12 (right) months

(2) Fly ash cement paste (FA40)

Figures 4.9, 4.10, and 4.11 show the effects of starting time of water, NaOH solution, and saturated Ca(OH)_2 injection on the CH content in FA40, respectively. In all kinds of solutions, the CH content in the samples into which solution was injected at 3 months was higher at the ages of 6 and 8 months than that in the samples into which solution was injected at 1 month. It can be said that the injection of solution at 3 months promoted the cement hydration in FA40 more at the ages of 6 and 8 months than the injection of solution at 1 month. However, the CH content in the samples into which solution was injected at 3 months was lower at the ages of 12 months than that in the samples into which solution was injected at 1 month. It shows the injection of solution at 3 months accelerated the pozzolanic reaction in FA40 more at the ages of 12 months than the injection of solution at 1 month.

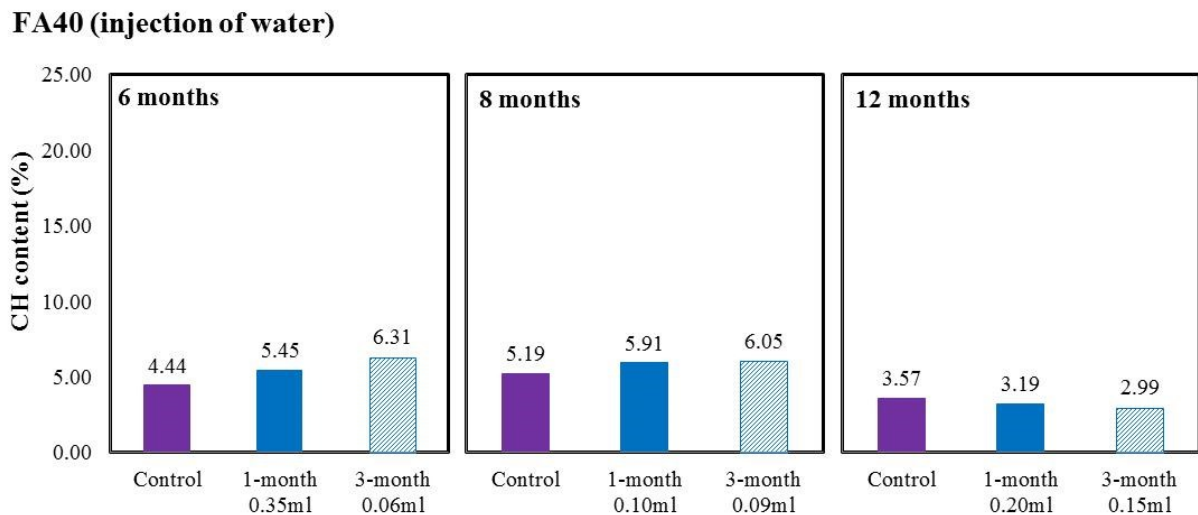


Figure 4.9 Effect of starting time of water injection on CH content in FA40 at the ages of 6 (left), 8 (middle), and 12 (right) months

FA40 (injection of NaOH solution)

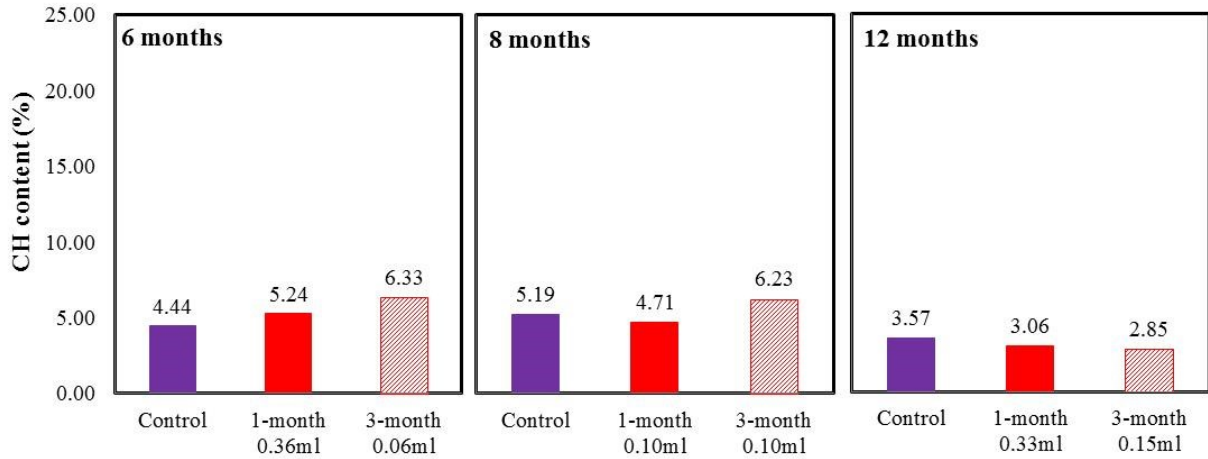


Figure 4.10 Effect of starting time of NaOH solution injection on CH content in FA40 at the ages of 6 (left), 8 (middle), and 12 (right) months

FA40 (injection of saturated $\text{Ca}(\text{OH})_2$ solution)

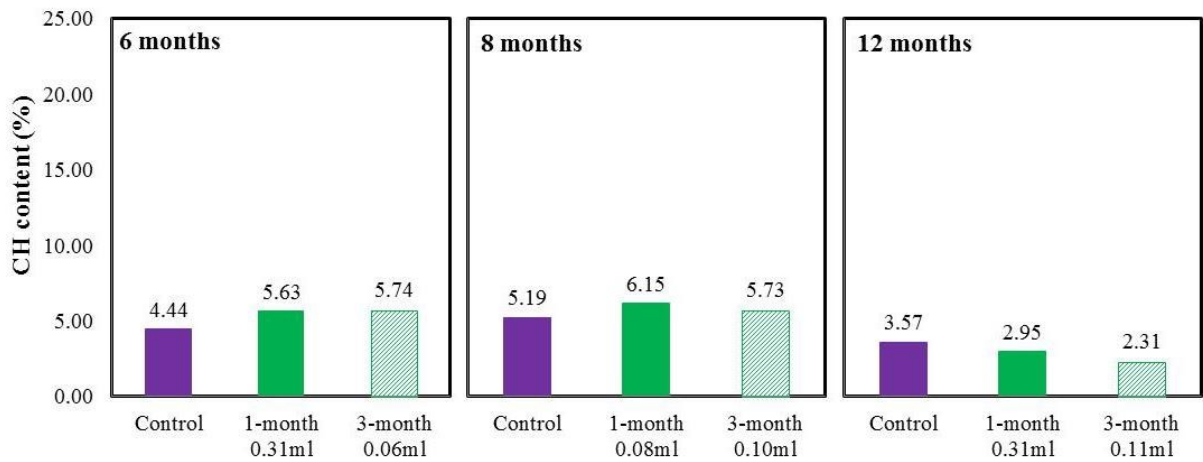


Figure 4.11 Effect of starting time of saturated $\text{Ca}(\text{OH})_2$ solution injection on CH content in FA40 at the ages of 6 (left), 8 (middle), and 12 (right) months

4.2 EFFECTS OF IAA ON CONSUMPTION OF $\text{Ca}(\text{OH})_2$

Supposed that the CH content formed by cement in FA20 or FA40 is almost the same as that in FA0, the consumption of CH by the pozzolanic reaction is described by Equation 1:

$$CH_{\text{cons}} = CH_{\text{FA0}} (c/(c+f)) - CH_{\text{FA20 or FA40}}, \quad (1)$$

where CH_{cons} is the consumption of CH by the pozzolanic reaction (%), CH_{FA0} is the CH content of FA0 (%), $CH_{\text{FA20 or FA40}}$ is the CH content of FA20 or FA40 (%), and $(c/(c+f)) = 0.6$ is the mass ratio of cement in the binder (cement + fly ash).

The effects of IAA on the consumptions of CH at the ages of 2 months by the pozzolanic reaction of the samples into which water or alkali solution was injected at 1 month are also considered for the comparison with those of the control samples and discussed in section 4.2.1. In addition, the effects of types and starting time of IAA on the consumption of CH by the pozzolanic reaction more than 4 months after casting are discussed in sections 4.2.2 and 4.2.3. These consumptions of CH in each case of the injection of water, NaOH, and saturated $\text{Ca}(\text{OH})_2$ solution were also calculated according to the equation (1).

4.2.1 Effects of IAA

The consumptions of CH at the age of 2 months by the pozzolanic reaction of the control samples and the samples into which water or alkali solution was injected at 1 month are shown in Figure 4.12 left. In the case of the samples into which water or alkali solution was injected with 20% replacement of fly ash, the consumption of CH was smaller than that of the control sample. This may be explained by the fact that the water promoted the cement hydration more in FA20. This is also compatible with the higher CH content of the samples into which water or alkali solution was injected with 20% replacement of fly ash than that of the control samples (Figure 4.1). Thus, these additional hydration products covered the surfaces of the fly ash particles more, resulting in the postpone of the pozzolanic reaction of fly ash

particles in FA20 [4]. In the case where the water or alkali solution was injected into FA40, the consumption of CH for water injection and saturated $\text{Ca}(\text{OH})_2$ solution activation was larger than that for the control sample, while that for the NaOH solution activation was slightly smaller than that for the control sample.

Furthermore, compared with the consumption of CH between FA20 and FA40, the normalization is also shown in Figure 4.12 right. It can be found that the consumption of CH for FA40, which had 2 times as high the fly ash content as FA20, was 2.6 and 4.5 times as large as that for FA20 in the case of the NaOH solution activation and saturated $\text{Ca}(\text{OH})_2$ solution activation, respectively, and these consumptions were larger than that of the control sample and the sample into which water was injected with the values of 1.6 and 1.9 times, respectively. It indicates IAA was more effective in accelerating the pozzolanic reaction in FA40.

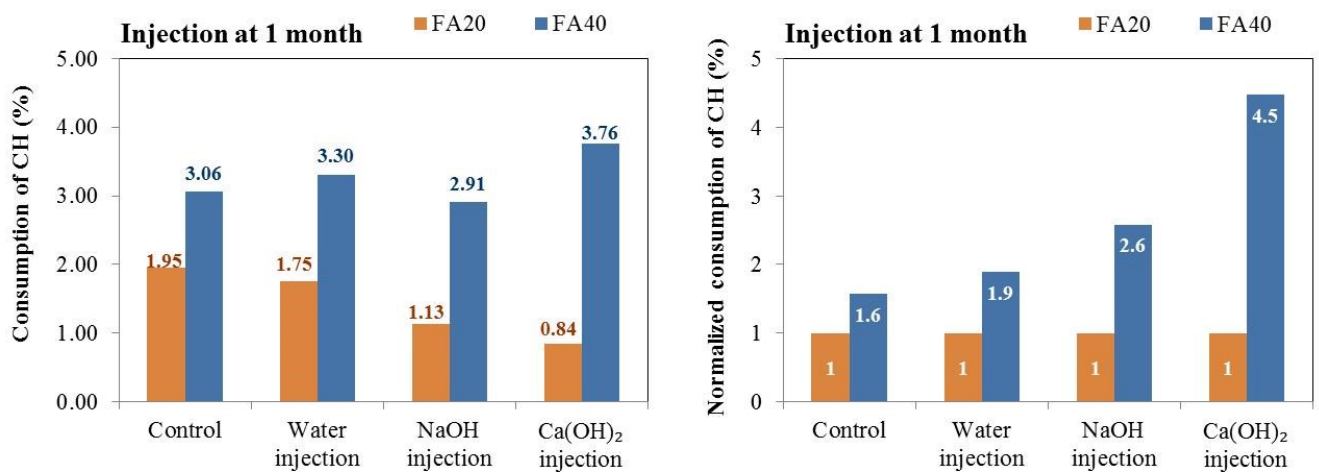


Figure 4.12 Consumption of CH at the age of 2 months by the pozzolanic reaction (left) and its normalization (right) of the control sample and the samples into which water or alkali solution was injected at 1 month

4.2.2 Effects of types of IAA

The consumptions of CH by the pozzolanic reaction in the samples into which water, NaOH solution, or saturated $\text{Ca}(\text{OH})_2$ solution was injected at 1 and 3 months are compared with the untreated control samples as shown in Figures 4.13 and 4.14. The consumptions of CH by the pozzolanic reaction in the samples into which solution was injected at 1 or 3 months were larger than those of the untreated control samples at the ages of 10 and 12 months, except for the age of 4 months. The reductions of CH consumption in the case of solution injection were observed at the age of 4 months when compared with those in the case of no injection. As a result, the CH content formed by cement in FA40 could be higher than in FA0 for each case of the injection [5]. At the ages of 10 and 12 months, the larger consumption of CH in the case of the injection of saturated $\text{Ca}(\text{OH})_2$ solution than that in the case of the injection of water and NaOH solution confirms again that the injection of saturated $\text{Ca}(\text{OH})_2$ solution was more effective in accelerating the pozzolanic reaction of fly ash cement paste than the injection of water and NaOH solution.

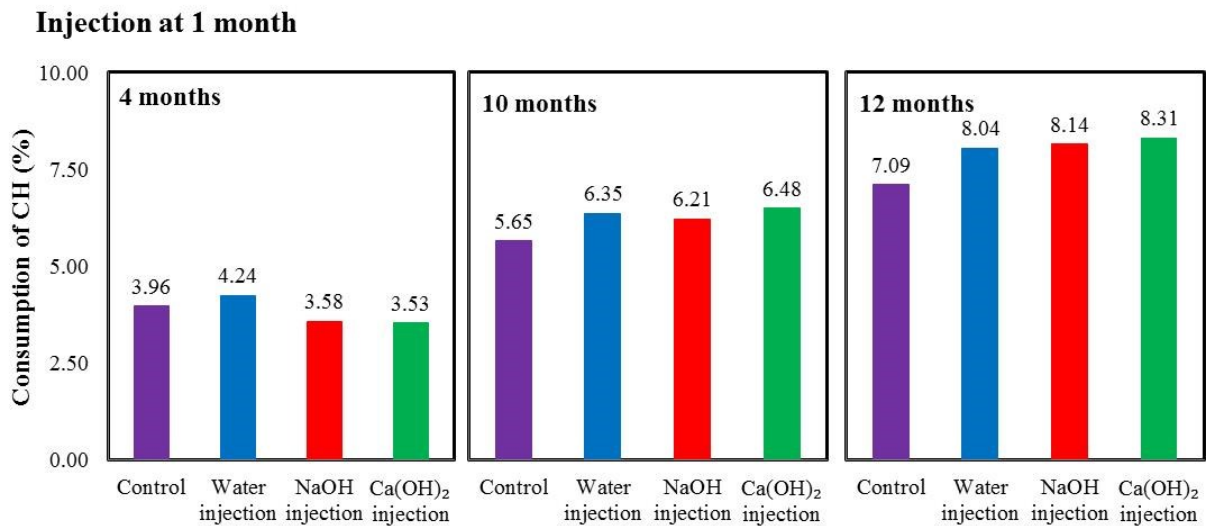


Figure 4.13 Comparison of consumption of CH by pozzolanic reaction between untreated control samples and samples into which water, NaOH solution or saturated $\text{Ca}(\text{OH})_2$ solution was injected at 1 month

Injection at 3 months

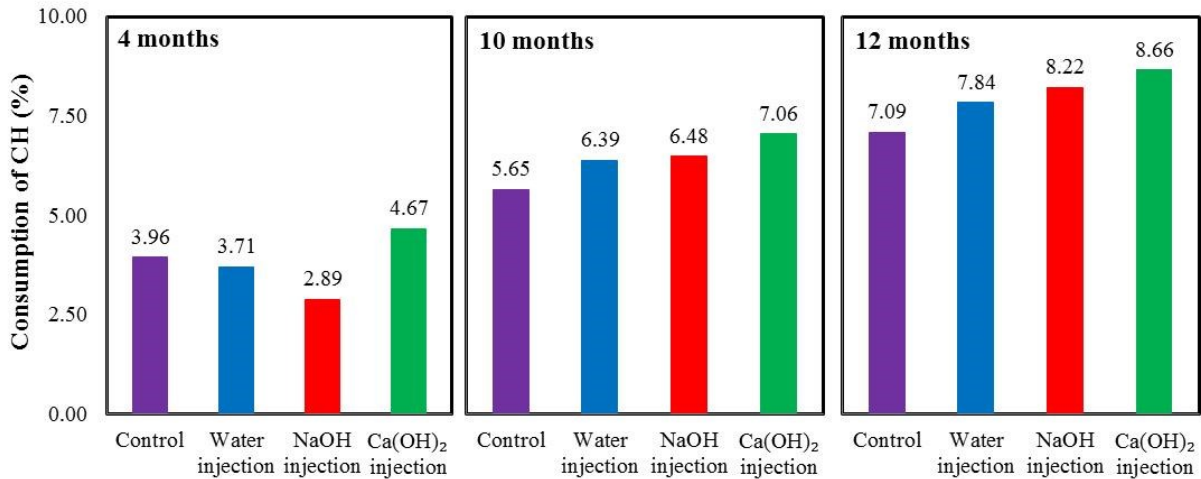


Figure 4.14 Comparison of consumption of CH by pozzolanic reaction between untreated control samples and samples into which water, NaOH solution or saturated Ca(OH)₂ solution was injected at 3 months

4.2.3 Effects of starting time of IAA

Figures 4.15, 4.16, and 4.17 show the effects of starting time of water, NaOH solution, and saturated Ca(OH)₂ solution injection on the consumption of CH by the pozzolanic reaction, respectively. According to Figures 4.16 and 4.17, the consumption of CH at the age of 12 months in the sample into which alkali solution was injected at 3 months was larger than that in the untreated control sample and the sample into which alkali solution was injected at 1 month. Meanwhile, the consumption of CH in the sample into which alkali solution was injected at 3 months was smaller than that in the sample into which alkali solution was injected at 1 month as shown in Figure 4.15 due to the shorter injection. It can be seen that the injection of alkali solution at 3 months accelerated the pozzolanic reaction in FA40 more at the age of 12 months than the injection of alkali solution at 1 month.

Injection of water

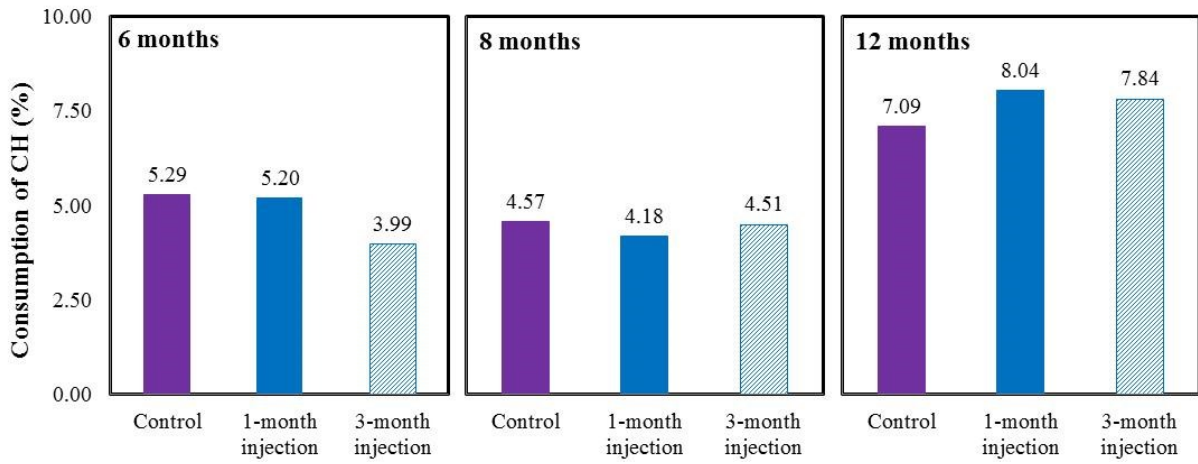


Figure 4.15 Effect of starting time of water injection on consumption of CH by pozzolanic reaction at the ages of 6 (left), 8 (middle), and 12 (right) months

Injection of NaOH solution

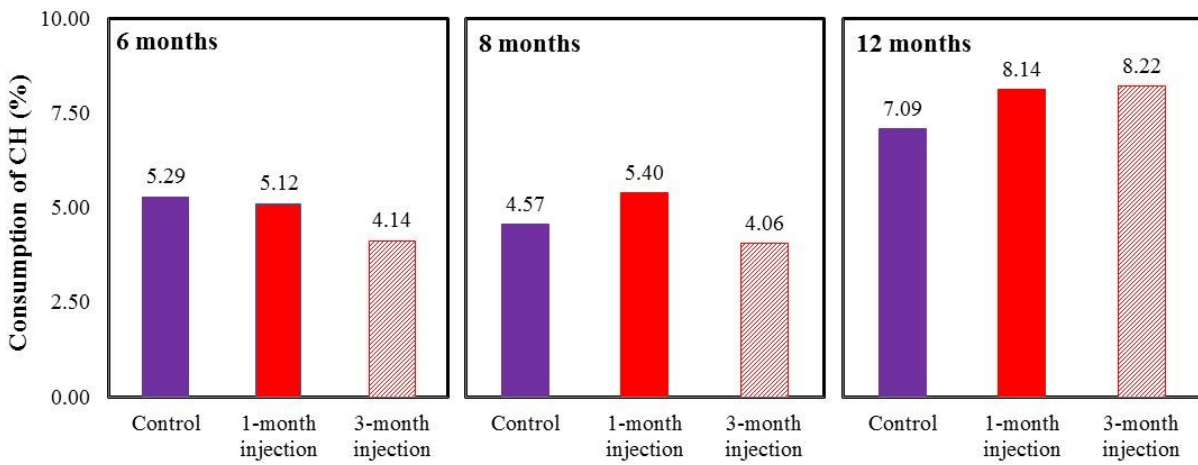


Figure 4.16 Effect of starting time of NaOH solution injection on consumption of CH by pozzolanic reaction at the ages of 6 (left), 8 (middle), and 12 (right) months

Injection of saturated Ca(OH)_2 solution

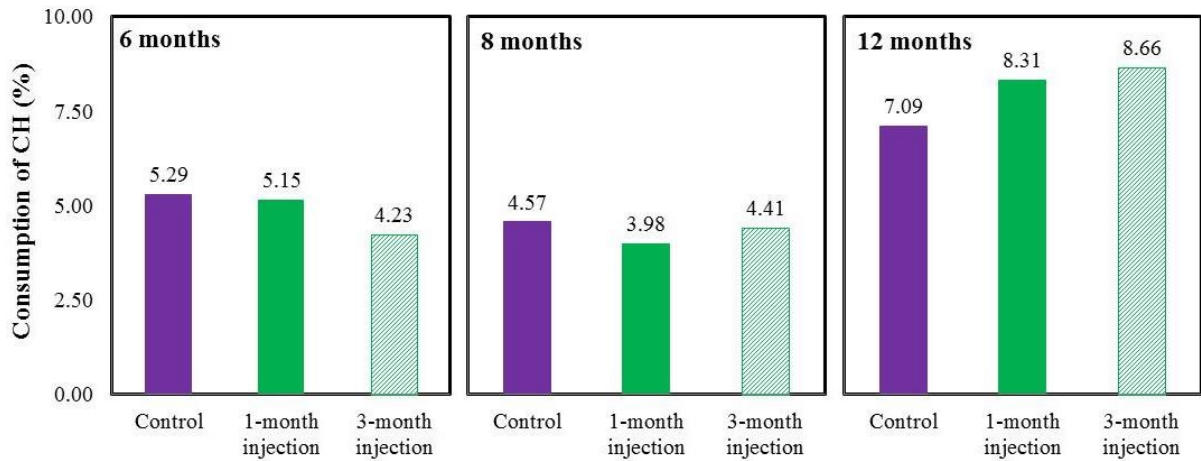


Figure 4.17 Effect of starting time of saturated Ca(OH)_2 solution injection on consumption of CH by pozzolanic reaction at the ages of 6 (left), 8 (middle), and 12 (right) months

4.3 CONFIRMATION OF EFFECTS BY SEM IMAGES

SEM images of the fly ash cement matrix at the age of 6 months of the control sample and sample activated by saturated Ca(OH)_2 solution from 3 months are shown in Figure 4.18. Fly ash particles persisted in both matrixes; however, the size and shape of particles in the matrix of the control sample (a) were easily distinguished at a magnification of $1,300\times$, whereas those of the sample activated by saturated Ca(OH)_2 solution from 3 months (b) were unclear. This may be explained by the reaction of fly ash particles with the additional Ca(OH)_2 from alkali activation, which formed hydration products on the particle surfaces [6]. This demonstrates that the activation by saturated Ca(OH)_2 solution from 3 months was effective in accelerating the pozzolanic reaction of the fly ash cement paste.

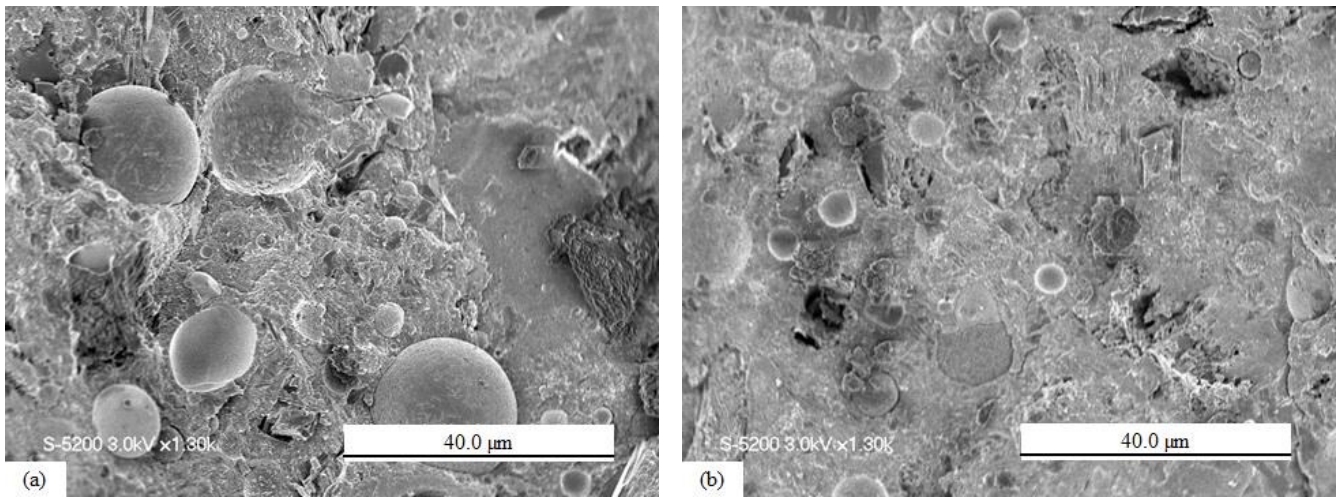


Figure 4.18 SEM images (1,300×) of the matrix at 6 months of the control sample (a) and sample activated by saturated Ca(OH)_2 solution from 3 months (b)

Detailed SEM images of single fly ash particles at the age of 6 months in the control sample and the sample activated by saturated Ca(OH)_2 solution from 3 months are shown in Figure 4.19. Figure 4.19 (a1), (a2), and (a3) show the matrix and fly ash particles in the control sample. The fly ash particle surfaces in the control sample were etched with slight depressions, and the overall spherical shapes were still clear, indicating that unreacted fly ash particles remained in the fly ash cement paste at the age of 6 months. Fly ash particles in the sample activated by saturated Ca(OH)_2 solution from 3 months (Figure 4.19 (b1), (b2), and (b3)) were extensively etched, with deeper depressions caused by erosion by the saturated Ca(OH)_2 solution when compared with those in the control sample (Figure 4.19 (a1), (a2), and (a3)). In addition, the particles were surrounded partially with hydration products formed by the pozzolanic reaction (Figure 4.19 (b1), (b2), and (b3)).

Figures 4.18 and 4.19 confirm that the activation by saturated Ca(OH)_2 solution from 3 months was effective in accelerating the pozzolanic reaction of the fly ash cement paste at 6 months, though its Ca(OH)_2 content was higher than that of the control sample (see Figures 4.9, 4.10, and 4.11).

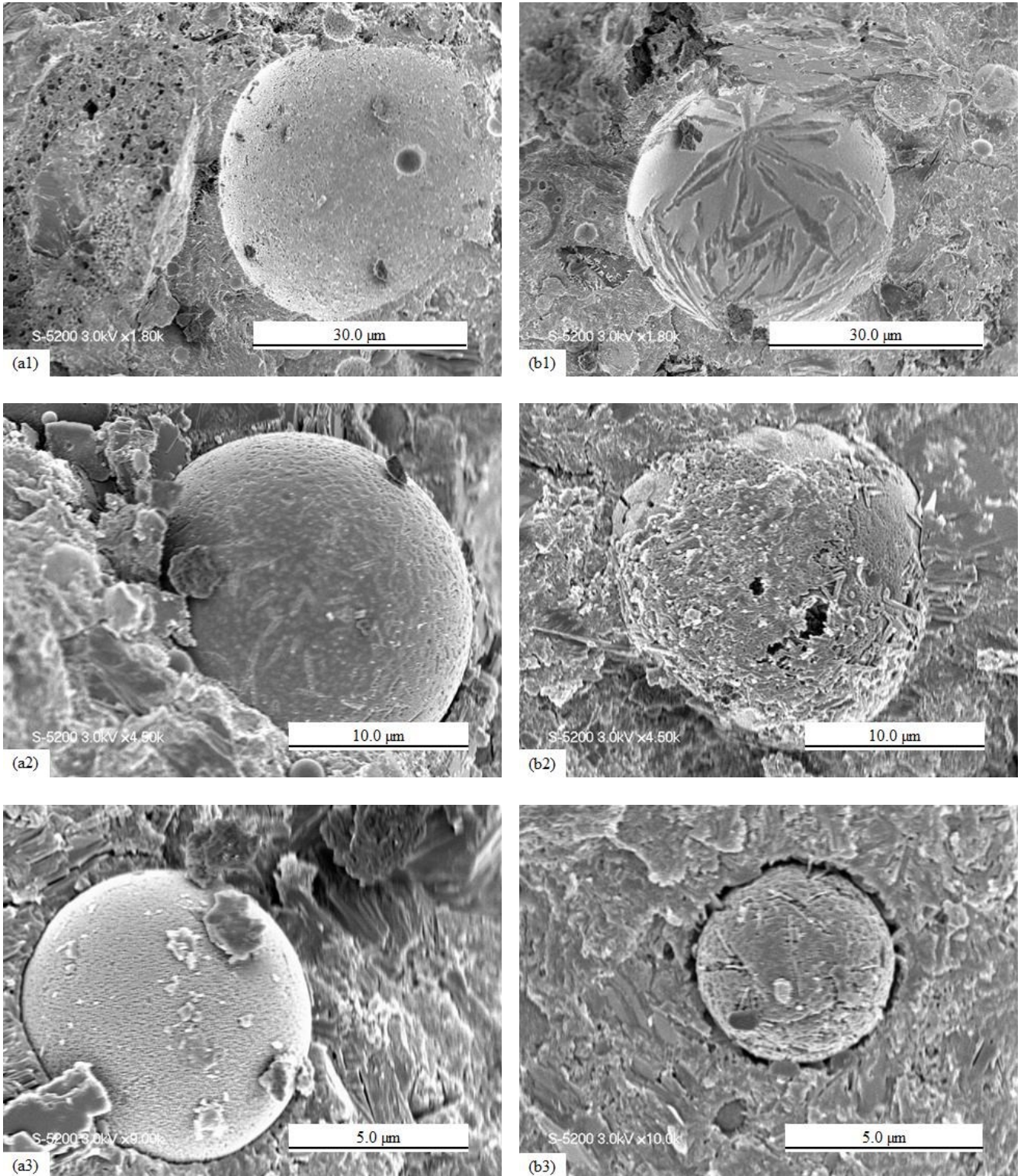


Figure 4.19 SEM micrographs of fly ash particles at 6 months in the control sample (a) and sample activated by saturated Ca(OH)₂ solution from 3 months (b) imaged at three magnifications [1,800× (1), 4,500× (2), 9,000–10,000× (3)]

Figure 4.20 shows detailed SEM images of single fly ash particles at the age of 12 months in the control

sample and sample into which water was injected at 3 months. As shown in Figure 4.20 (a), the shape and size of fly ash particles were still distinguished clearly even at 12 months when compared with those at 6 months as shown in Figure 4.19 (a). It indicates that the degree of the pozzolanic reaction in the control sample was very slow and continuously proceeded at a constant rate from 6 months to 12 months. Meanwhile, the size and shape of particles in the matrix of the 3-month-water-injected sample (Figure 4.20 b) were unclear because they were extensively surrounded extensively with hydration products formed by the pozzolanic reaction. This may be explained by the reaction of fly ash particles with the additional $\text{Ca}(\text{OH})_2$ from cement hydration promoted by the water injection. As a result, the injection of water at 3 months was effective in accelerating the pozzolanic reaction of the fly ash cement paste at later ages (i.e. 12 months).

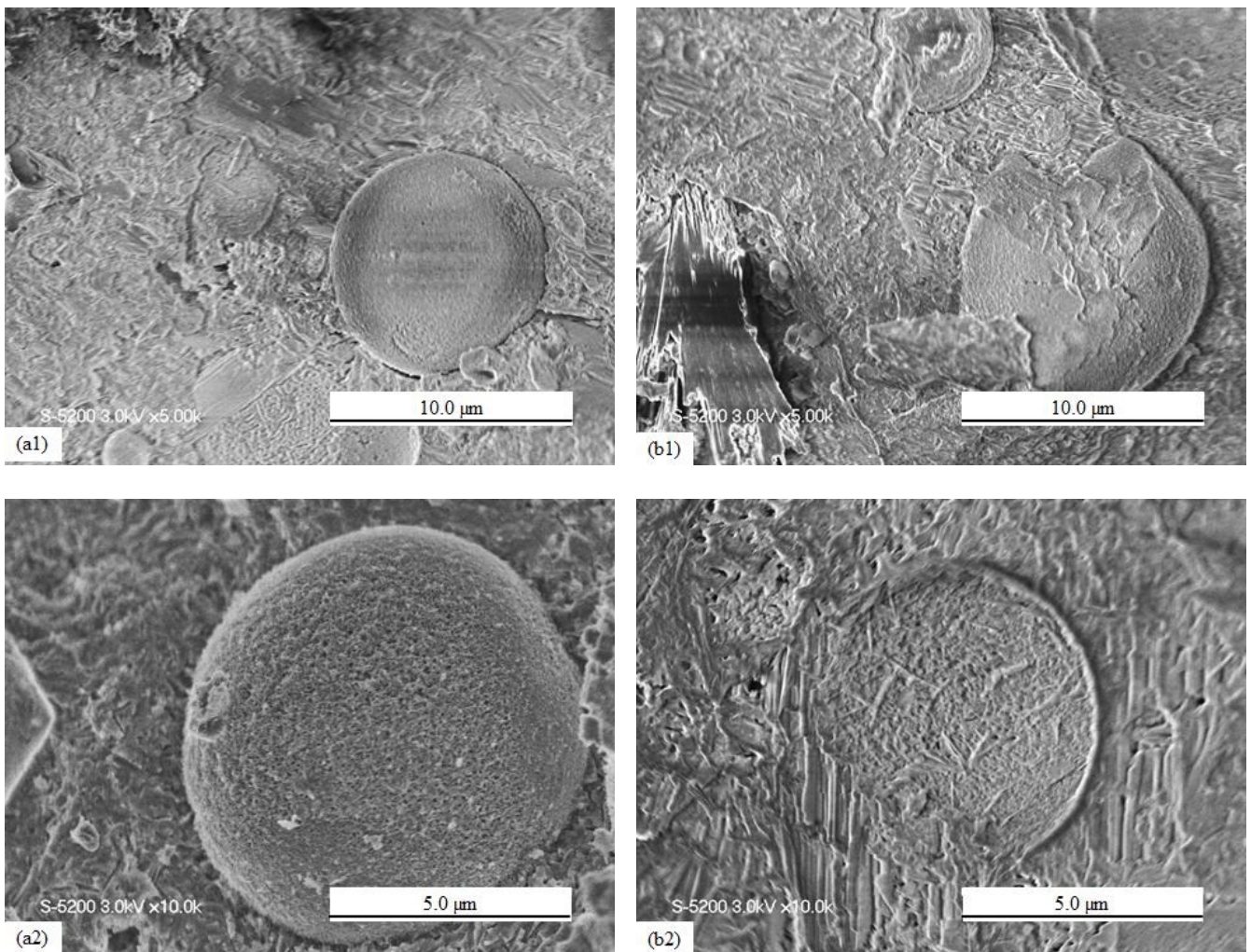


Figure 4.20 SEM micrographs of fly ash particles at 12 months in the control sample (a) and sample into which water was injected at 3 months (b) imaged at two magnifications [5,000× (1), 10,000× (2)]

4.4 SUMMARY

Based on some previous studies and experimental results in this chapter, the following conclusions can be drawn:

(1) Effects of IAA on pozzolanic reaction of fly ash

An injection of alkali solution could prevent the production of CH at the ages of 2 and 4 months in the plain cement paste (FA0) in the case of the injection at 1 month, while an injection of water increased the CH content in FA0 after the injection at 1 month.

In the case of the fly ash cement paste (FA20 and FA40), an injection of alkali solution 1 month after casting was more effective in reducing the CH content and increasing the consumption of CH by the pozzolanic reaction in FA40 than in FA20. It indicates IAA was more effective on the acceleration of the pozzolanic reaction in FA40 than in FA20.

(2) Effect of types of IAA on pozzolanic reaction of fly ash

An injection of saturated $\text{Ca}(\text{OH})_2$ solution caused a reduction in the CH content and an increase in the consumption of CH in FA40 more than that of water or NaOH solution. It indicates that the pozzolanic reaction of the fly ash particles was accelerated by the saturated $\text{Ca}(\text{OH})_2$ solution activation more than by water or NaOH solution activation.

(3) Effects of starting time of IAA on pozzolanic reaction of fly ash

An injection of solution at 3 months increased the CH content in FA0 more than an injection of solution at 1 month.

The injection of water at 1 month increased the consumption of CH by the pozzolanic reaction more than the injection of water at 3 months due to the longer period of injection.

The injection of alkali solution at 3 months increased the consumption of CH by the pozzolanic reaction more than the injection of alkali solution at 1 month.

References

1. Berry EE, Hemmings RT, Cornelius BJ, 1990. Mechanism of hydration reactions in high volume fly ash pastes and mortars. *Cem Concr Compos* 12:253-261.
2. Feldman RF, Carette GG, Malhotra VM (1990) Studies on of development of physical and mechanical properties of high-volume fly ash-cement paste. *Cem Concr Compos* 12:245-251.
3. Sakai E, Miyahara S, Ohsawa S, Lee SH, Daimon M, 2005. Hydration of fly ash cement. *Cem Concr Res* 35:1135-1140.
4. Zeng Q, Li K (2015) Reaction and microstructure of cement-fly ash system. *Mater Struc* 48:1703-1716.
5. Zhang YM, Sun W, Yan HD (2000) Hydration of high-volume fly ash cement pastes. *Cem Concr Compos* 22:445-452.
6. Fernandez J, Palomo A, Lopez H (2006) Engineering properties of alkali activated fly ash concrete. *ACI Mater J* 103:106-112.

CHAPTER 5

EFFECTS OF IAA ON MECHANICAL PROPERTIES OF FLY ASH CEMENT SYSTEMS

Effects of IAA on the mechanical properties of the fly ash cement systems are discussed in this chapter by measuring the porosity of the fly ash cement pastes in section 5.1, measuring the hardness of interfacial transition zone (ITZ) and bulk paste of the fly ash cement paste using one porous ceramic waste aggregate (PCWA) in the section 5.2, and testing the compressive strength as well as measuring the porosity of the fly ash concrete in the section 5.3.

5.1 EFFECTS OF IAA ON POROSITY IN FLY ASH CEMENT SYSTEMS

5.1.1 Porosity

Porosity in the fly ash cement system was measured by MIP as mentioned in section 3.5.4. The pore size distribution of the pastes was measured over a diameter range of 3 nm to 300 μm . However, the entrained air should range from 50 to 200 μm in size [1]. Therefore, results of their total pore volumes should be considered to range from 3 nm to 50 μm in size. The effects of IAA on porosity at the age of 2 months for the plain cement paste (FA0) and the fly ash cement paste (FA20 and FA40) in the case of the injection of solution 1 month after casting are discussed in the section (1). In addition, the effects of types and starting time of IAA on porosity in FA0 and FA40 after more than 4 months are discussed in the sections (2) and (3).

(1) Effect of IAA

The total pore volumes and the volumes of pore ranging 20-330 nm and 3-20 nm in diameter of the samples into which water was injected at 1 month and their comparison with the control samples are shown in Figure 5.1. The total pore volumes of the samples into which water or saturated $\text{Ca}(\text{OH})_2$ solution was injected at 1 month were smaller than that of the control samples in FA0 and FA40, except for FA20. It indicates IAA was effective in improving the porosity of the paste by promoting the cement hydration more.

To estimate the degree of the pozzolanic reaction of the fly ash cement paste, it was reported that the volume of pores from 20 to 330 nm in diameter decreases to the total pore volume, and that of pores from 3 to 20 nm in diameter increases as the pozzolanic reaction proceeds [2]. It was observed that the volume ratios of 20-330 nm pores to the total pore decreased and those of 3-20 nm pores increased in the case of FA40 into which the saturated $\text{Ca}(\text{OH})_2$ solution was injected at 1 month. This is also compatible with the decrease in the CH content in the case of the paste activated by saturated $\text{Ca}(\text{OH})_2$ solution 1 month after casting with 40% replacement of fly ash (as shown in Figure 4.1 in Chapter 4).

In the case of FA20 into which water or alkali solution was injected at 1 month, the less decrease of pores from 20 to 330 nm and less increase of pores from 3 to 20 nm in the volume ratio than that in the control sample was observed. This is also compatible with the smaller consumption of CH of samples into which water or alkali solution was injected at 1 month than that of the control sample (as shown in Figure 4.12 in Chapter 4).

In conclusion, it can be said that the activation by water or saturated $\text{Ca}(\text{OH})_2$ solution 1 month after casting was effective in accelerating the pozzolanic reaction in FA40.

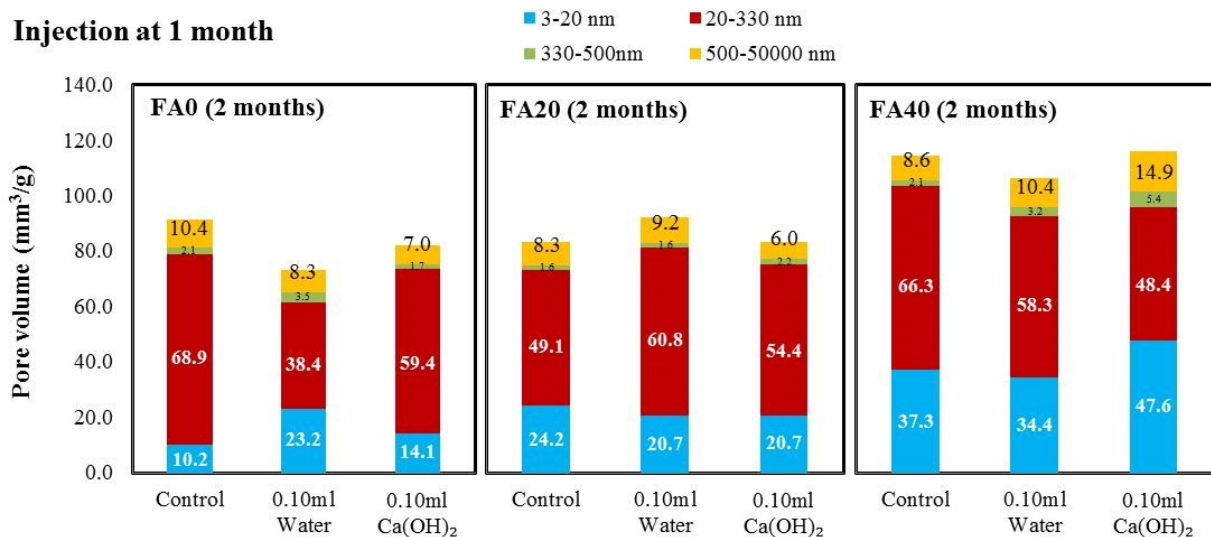


Figure 5.1 Comparison of porosity at the age of 2 months in FA0 (left), FA20 (right), and FA40 (bottom) between untreated control samples and samples into which water or saturated Ca(OH)₂ solution was injected at 1 month

(2) Effects of types of IAA

(a) Plain cement paste (FA0)

The total pore volumes in FA0 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected at 1 and 3 months are compared with the untreated control samples at the ages of 4, 10, and 12 months shown in Figures 5.2 and 5.3. Generally, the total pore volume of samples decreases as the curing time increases. In addition, the total pore volumes of samples into which solution was injected internally were smaller than those of the control samples regardless of types of IAA at the ages of 4, 10, and 12 months. It indicates the internal injection of solution was effective in promoting the cement hydration in FA0, resulting in more hydration products filling the large pores in the paste.

FA0 (injection at 1 month)

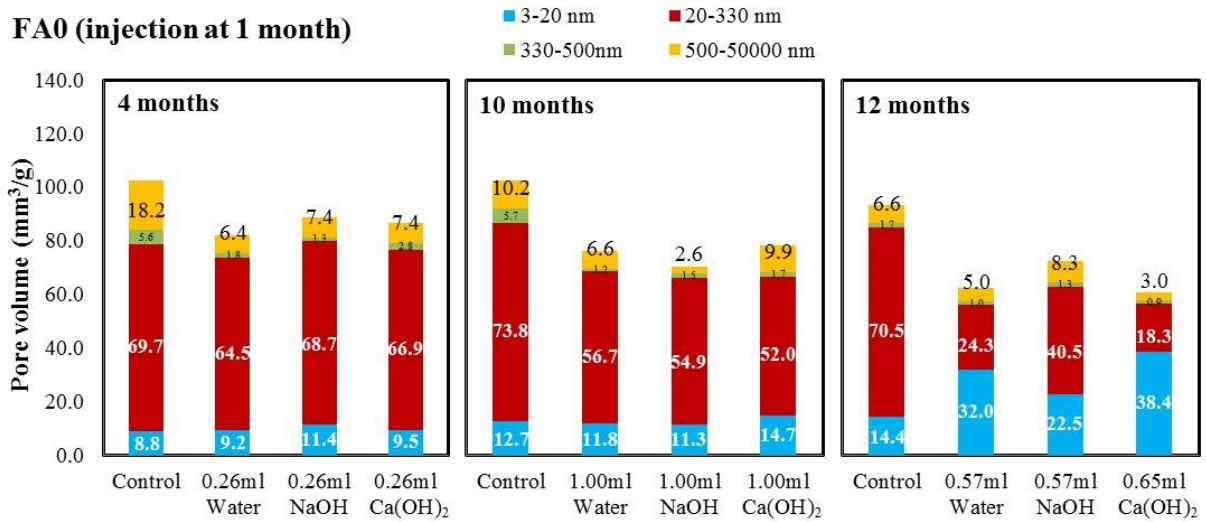


Figure 5.2 Comparison of porosity in FA0 between untreated control samples and samples into which water, NaOH solution or saturated Ca(OH)₂ solution was injected at 1 month

FA0 (injection at 3 months)

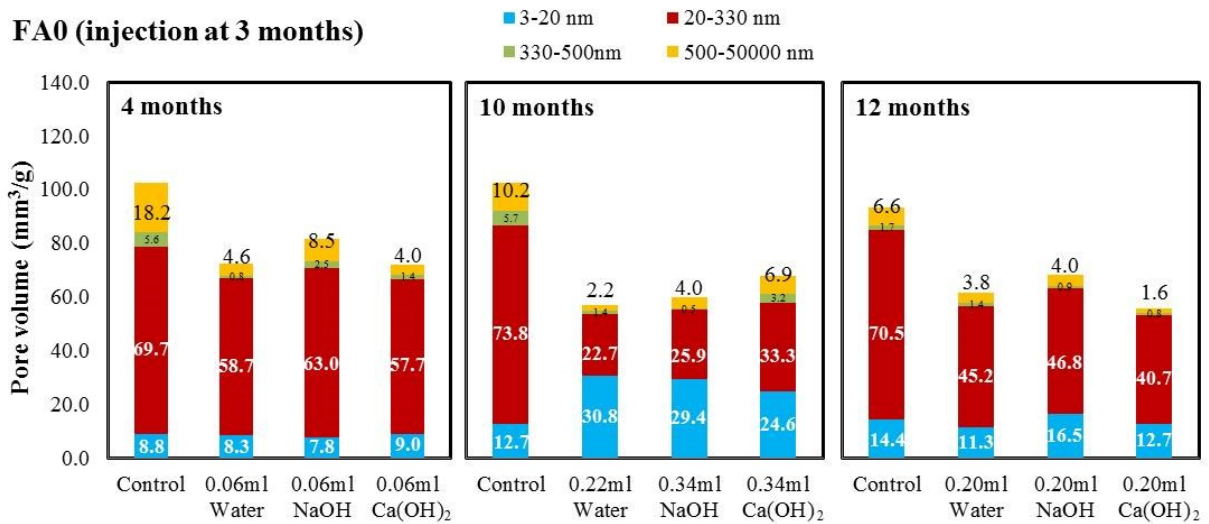


Figure 5.3 Comparison of porosity in FA0 between untreated control samples and samples into which water, NaOH solution or saturated Ca(OH)₂ solution was injected at 3 months

(b) Fly ash cement paste (FA40)

The total pore volumes in FA40 samples into which water, NaOH solution, or saturated Ca(OH)_2 solution was injected at 1 and 3 months are compared with the untreated control samples at the ages of 4, 10, and 12 months as shown in Figures 5.4 and 5.5, respectively. Similar to FA0, the total pore volume of samples decreases as the curing time increases. Additionally, the total pore volumes of the samples into which solution was injected internally were smaller than those of the control samples.

Furthermore, the volume ratio of pores from 20 to 330 nm in diameter to the total pore decreased, and that of pores from 3 to 20 nm in diameter increased in the case of the fly ash cement paste (FA40) into which solution was injected internally at the ages of 4, 10, and 12 months, except for the result at 12 months for the sample into which saturated Ca(OH)_2 solution was injected. This implies that the pozzolanic reaction was accelerated by water injection, NaOH solution activation, and saturated Ca(OH)_2 solution activation. In addition, a decrease in the volume ratio of 20-330 nm pores to the total pore volume in the samples activated by saturated Ca(OH)_2 solution was more significant than that in the control samples, and even more than that in the samples (FA40) into which water or NaOH solution was injected, except for the result at 4 months for the injection 3 months after casting (as shown in Figure 5.5). This demonstrates the internal activation by saturated Ca(OH)_2 solution was more effective in accelerating the pozzolanic reaction of the fly ash cement paste than the internal injection by water and NaOH solution regardless of starting time of IAA.

FA40 (injection at 1 month)

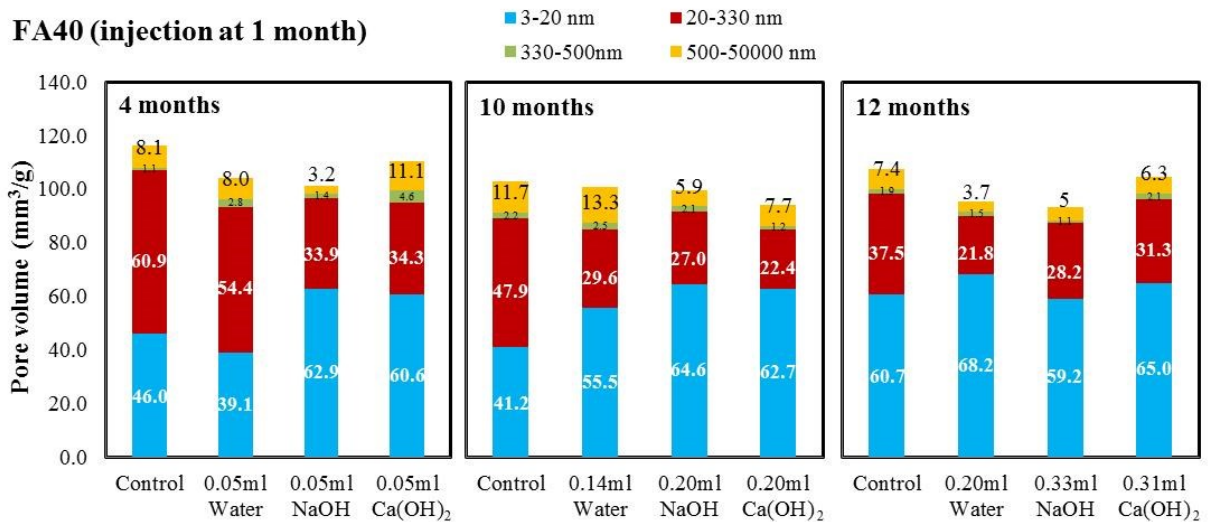


Figure 5.4 Comparison of porosity in FA40 between untreated control samples and samples into which water, NaOH solution or saturated Ca(OH)₂ solution was injected at 1 month

FA40 (injection at 3 months)

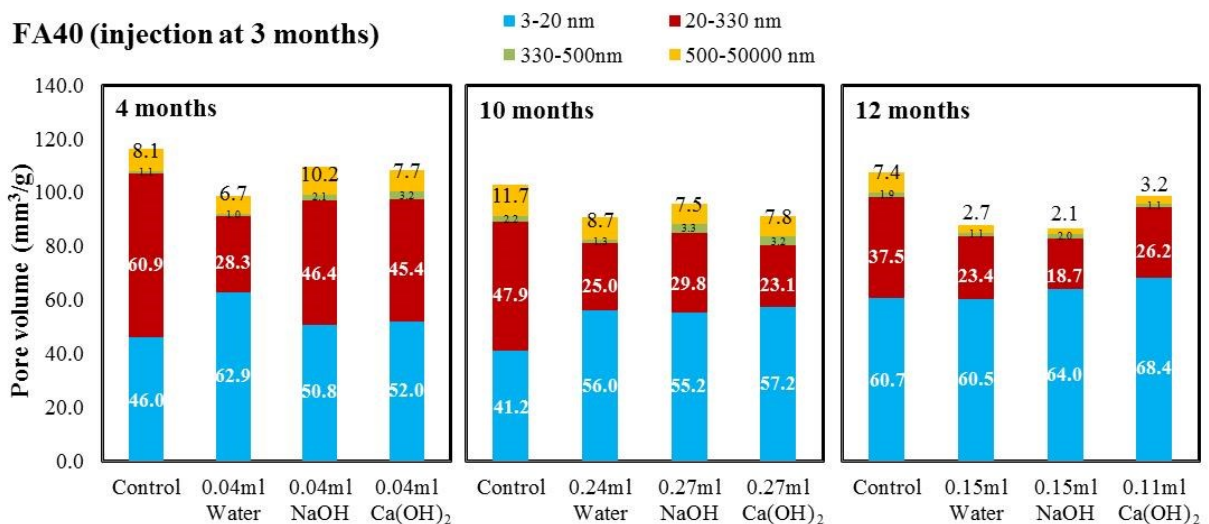


Figure 5.5 Comparison of porosity in FA40 between untreated control samples and samples into which water, NaOH solution or saturated Ca(OH)₂ solution was injected at 3 months

(3) Effects of starting time of IAA

(a) Plain cement paste (FA0)

Figures 5.6, 5.7, and 5.8 show the effects of starting time of the injection of water, NaOH solution, and saturated Ca(OH)₂ solution on porosity in FA0 over time, respectively.

Generally, the total pore volumes of the samples into which solution was injected at 3 months were smaller than those of the control samples and even those of the samples into which solution was injected at 3 months over time. It can be seen that the injection of solution at 3 months promoted the cement hydration more than the injection of solution at 1 month.

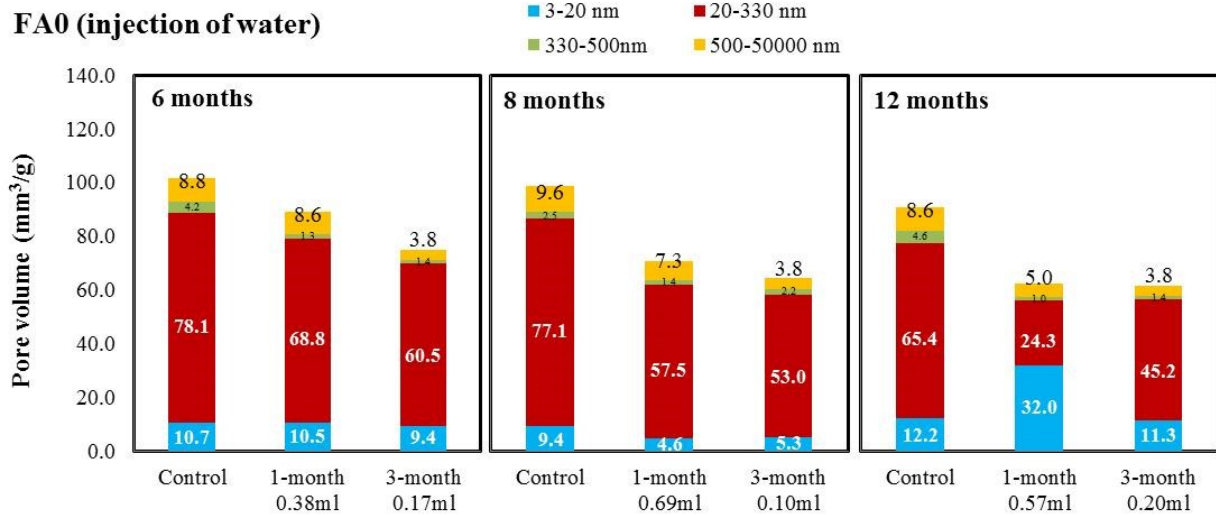


Figure 5.6 Effect of starting time of water injection on porosity in FA0 at the ages of 6 (left), 8 (middle), and 12 (right) months

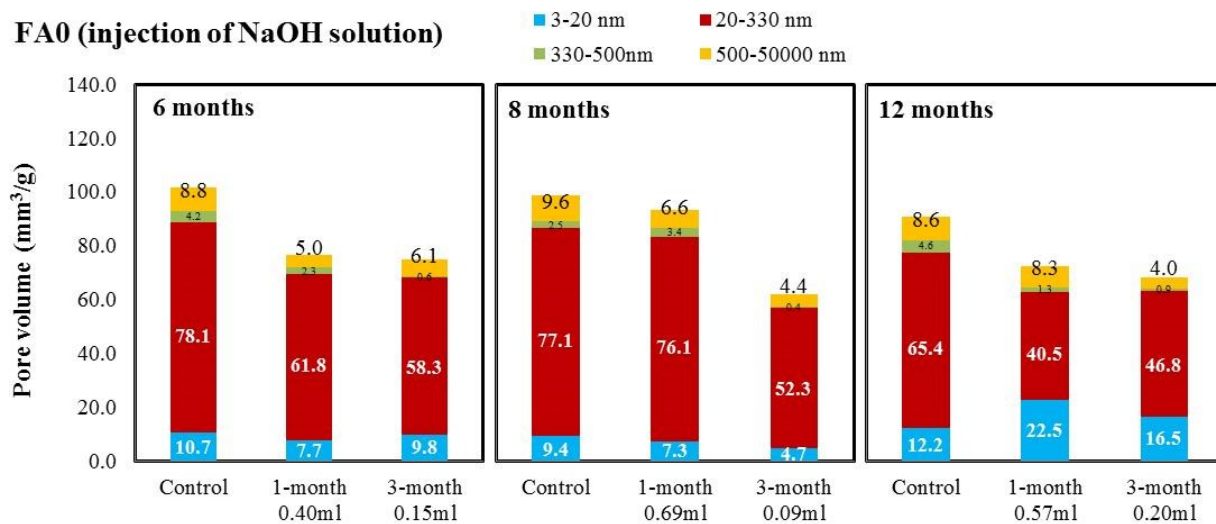


Figure 5.7 Effect of starting time of NaOH solution injection on porosity in FA0 at the ages of 6 (left), 8 (middle), and 12 (right) months

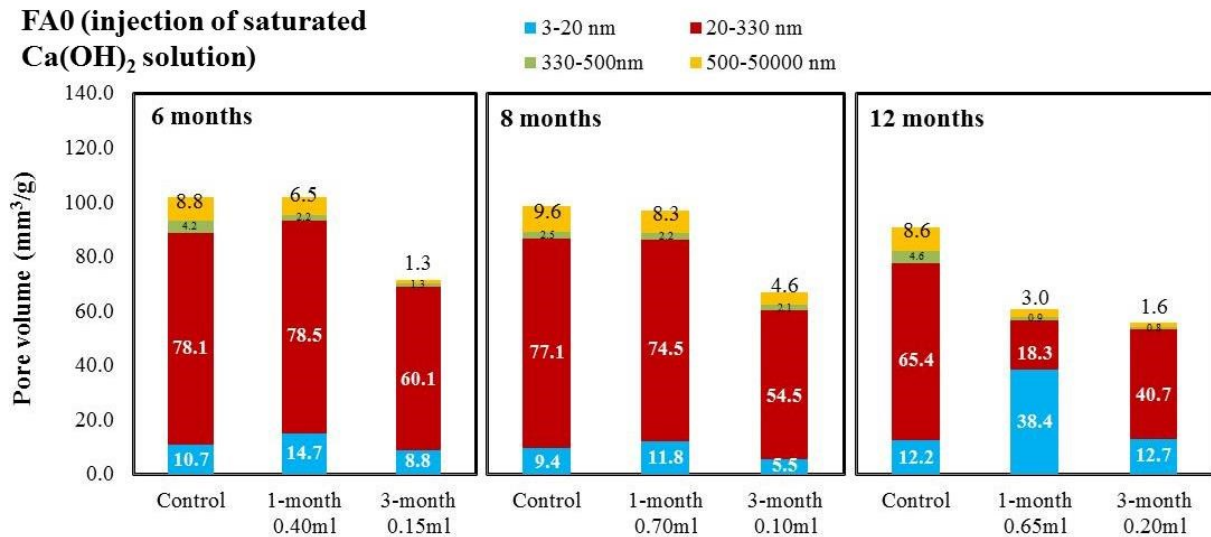


Figure 5.8 Effect of starting time of saturated Ca(OH)₂ solution injection on porosity in FA0 at the ages of 6 (left), 8 (middle), and 12 (right) months

(b) Fly ash cement paste (FA40)

The volume ratios of 20-330 nm pores to the total pore and those of 3-20 nm pores were also investigated for estimating the effects of the starting time of IAA on the pozzolanic reaction of the fly ash cement paste. Figures 5.9, 5.10 and 5.11 show the effects of the starting time of internal water, NaOH solution and saturated Ca(OH)₂ solution injection on pore volumes in FA40 at the ages of 6, 8, and 12 months, respectively. According to Figures 5.9 and 5.10 left and middle, in the case where FA40 samples into which water or NaOH solution was injected, the injection 1 month after casting decreased the volume ratio of 20-330 nm pores to the total pore more and increased the volume ratio of 3-20 nm pores to the total pore, respectively more than that 3 months after casting. This can be due to the longer period of the injection of water or NaOH solution. Meanwhile, as shown in Figure 5.11 left and middle, the decrease in the volume ratio of pores from 20 to 330 nm in diameter to the total pore and the increase in the volume ratio of pores from 3 to 20 nm in diameter in the injection of saturated Ca(OH)₂ solution at 1 month were observed nearly the same as those in the injection of saturated

Ca(OH)₂ solution at 3 months. It confirms that the injection of saturated Ca(OH)₂ solution at 3 months accelerated the pozzolanic reaction of FA40 more than the injection of saturated Ca(OH)₂ solution at 1 month, while the injection of water or NaOH solution at 1 month promoted the pozzolanic reaction of FA40 more at the ages of 6 and 8 months than the injection of water or NaOH solution at 3 months. In addition, it can be found that the injection of solution at 3 months accelerated the pozzolanic reaction of FA40 more at the late age (i.e. 12 months) than the injection of solution at 1 month because the volume ratios of 20-330 nm pores to the total pore volume in the injection at 3 months were smaller than those in the injection at 1 month (as shown Figures 5.9, 5.10, and 5.11 right).

FA40 (injection of water)

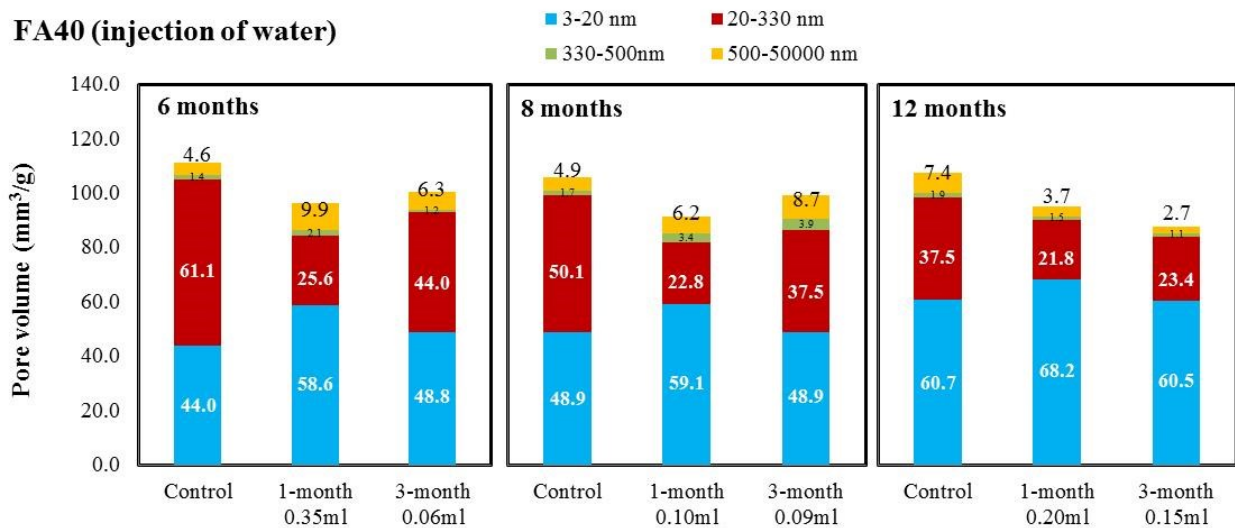


Figure 5.9 Effect of starting time of water injection on porosity in FA40 at the ages of 6 (left), 8 (middle), and 12 (right) months

FA40 (injection of NaOH solution)

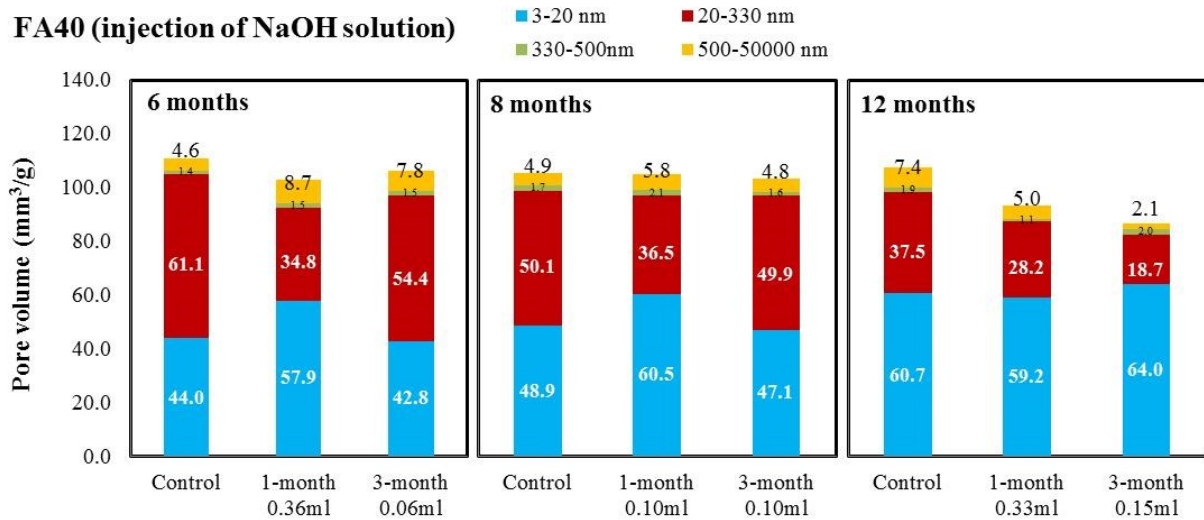


Figure 5.10 Effect of starting time of NaOH solution injection on porosity in FA40 at the ages of 6 (left), 8 (middle), and 12 (right) months

FA40 (injection of saturated Ca(OH)₂ solution)

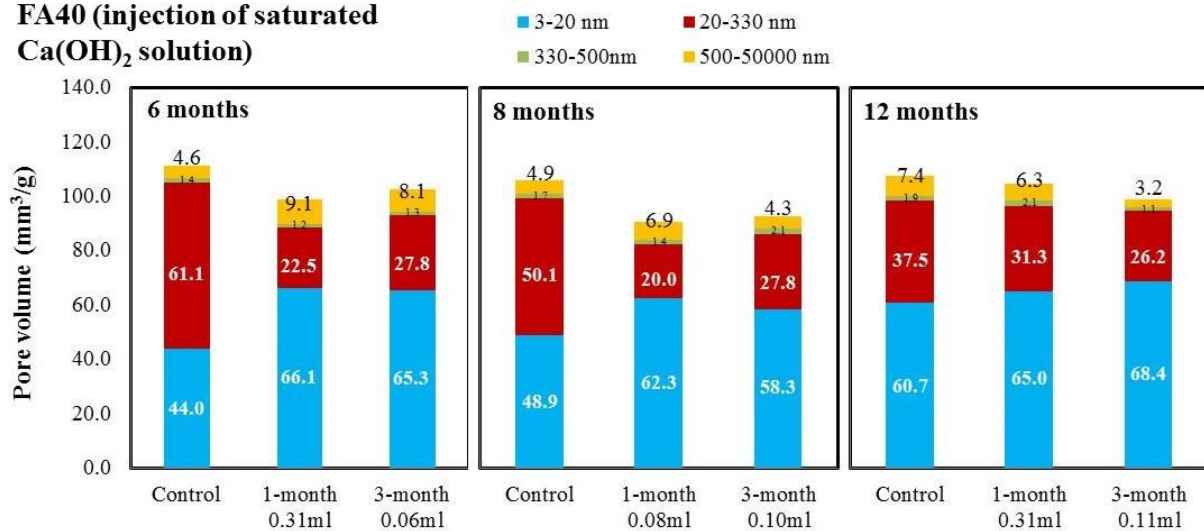


Figure 5.11 Effect of starting time of saturated Ca(OH)₂ solution injection on porosity in FA40 at the ages of 6 (left), 8 (middle), and 12 (right) months

5.1.2 Relationship between consumption of CH and porosity

Figure 5.12 shows the relationship between the consumption of CH and the volumes of pores ranging 20-330 nm (a) and 3-20 nm (b) in diameter in FA40 for all of three cases (control, the injection at 1 month, and the injection at 3 months). The designation of control in Figure 5.12

shows in the case of no injection, while that of IAA shows in the case of water, NaOH solution, and saturated $\text{Ca}(\text{OH})_2$ solution injection. It appears that there is a negative correlation between the consumption of CH and the volume of pores ranging 20-330 nm (left), and a positive correlation between the consumption of CH and the volume of pores ranging 3-20 nm (right).

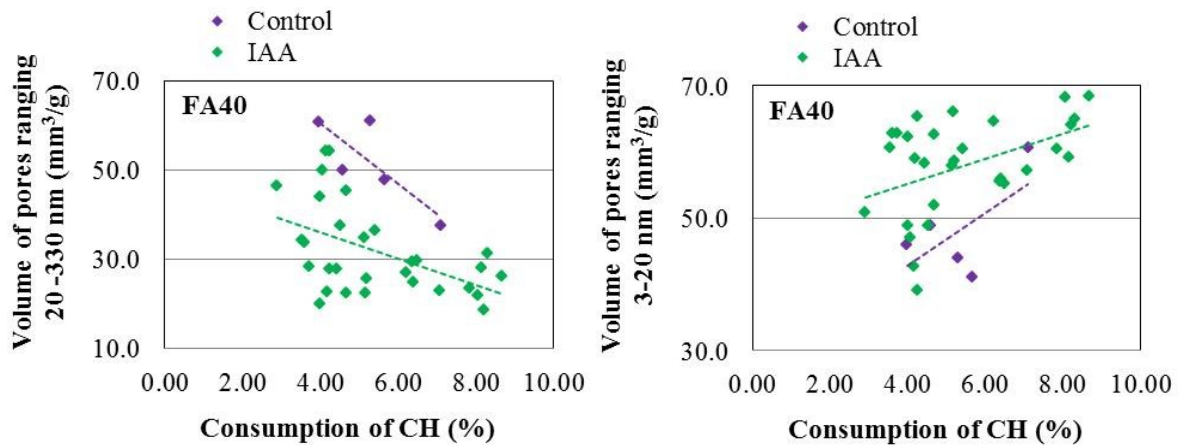


Figure 5.12 Relationship between consumption of CH and volumes of pores ranging 20-330 nm (left) and 3-20 nm (right) in diameter in FA40

5.2 EFFECTS OF IAA ON HARDNESS OF ITZ IN FLY ASH CEMENT SYSTEMS

The hardness of the interfacial transition zone (ITZ) and bulk paste in the fly ash cement system was measured by Vicker indenter as shown in the sections 3.3.2 and 3.5.2 (Chapter 3). The Vickers micro hardness was measured at 11 points within a distance of 0 to 5000 μm from the PCWA surface with 5 different positions. Effects of types of IAA on the hardness of ITZ and bulk paste in the cement paste (FA0) and the fly ash cement paste (FA40) are discussed in this section.

5.2.1 Effects of internal saturated $\text{Ca}(\text{OH})_2$ solution supplied from one PCWA

Figures 5.13 and 5.14 show the effects of internal saturated $\text{Ca}(\text{OH})_2$ solution supplied from

one PCWA on the hardness of ITZ and bulk paste in FA0 and FA40 over time, respectively. Each value is an average of 5 results from 5 different positions ($n = 5$). The hardness of ITZ and bulk paste in both FA0 and FA40 increased as the curing age increased. It shows the cement hydration in FA0 and pozzolanic reaction in FA40 was continuing to progress over time.

On the other hand, the hardness values fall down at the distance of 10 μm and rose at the distance of 200 μm from the PCWA surface as shown in Figures 5.13 and 5.14. It shows the thickness of ITZ between PCWA and bulk paste could be 200 μm . In this study, the larger thickness of ITZ than a previous study [3] could be attributed to the partial water supplied from one PCWA in which saturated $\text{Ca}(\text{OH})_2$ solution was absorbed at the early ages (during casting).

According to Figures 5.13 and 5.14, the hardness of ITZ was nearly the same as that of the bulk paste at the age of 1 day while that was smaller than that of the bulk paste in both FA0 and FA40 at the ages of 1 and 6 months. It appears there is no difference of hardness value in FA0 and FA40 between ITZ and bulk paste at the age of 1 day. However, there was a significant difference in the hardness value between the ITZ of 10-100 μm and bulk paste at the ages of 1 and 6 months. Therefore, a comparison of the hardness between these specimens and the untreated specimens without PCWA needs to be given in the future.

According to Figures 5.13 and 5.14, the hardness of ITZ and bulk paste in FA40 was smaller than that in FA0 at the ages of 1 day and 1 month, while that was nearly the same as that in FA0 at the age of 6 months. It indicates the replacement of cement with fly ash reduced the hardness at the initial stages (i.e. 1 day and 1 month). It can be explained that in the fly ash cement paste with constant water to binder ratio, the fly ash replacement increases the water to cement ratio, resulting in reducing the hardness. This was also observed in Zhen-jun et al.'s research [4]. However, the internal saturated $\text{Ca}(\text{OH})_2$ solution supplied from PCWA

improved the microstructure of ITZ and bulk paste in FA40 at the age of 6 months. This results in the increase in the hardness of ITZ and bulk paste in FA40, which was nearly the same as that in FA0 at the age of 6 months.

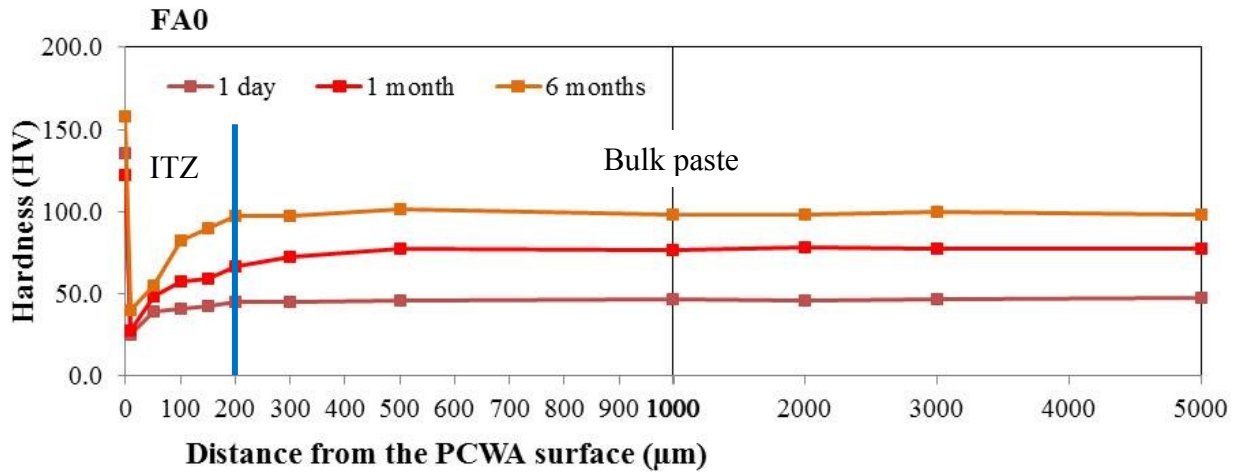


Figure 5.13 Effect of internal saturated $\text{Ca}(\text{OH})_2$ solution from one PCWA on the hardness in FA0

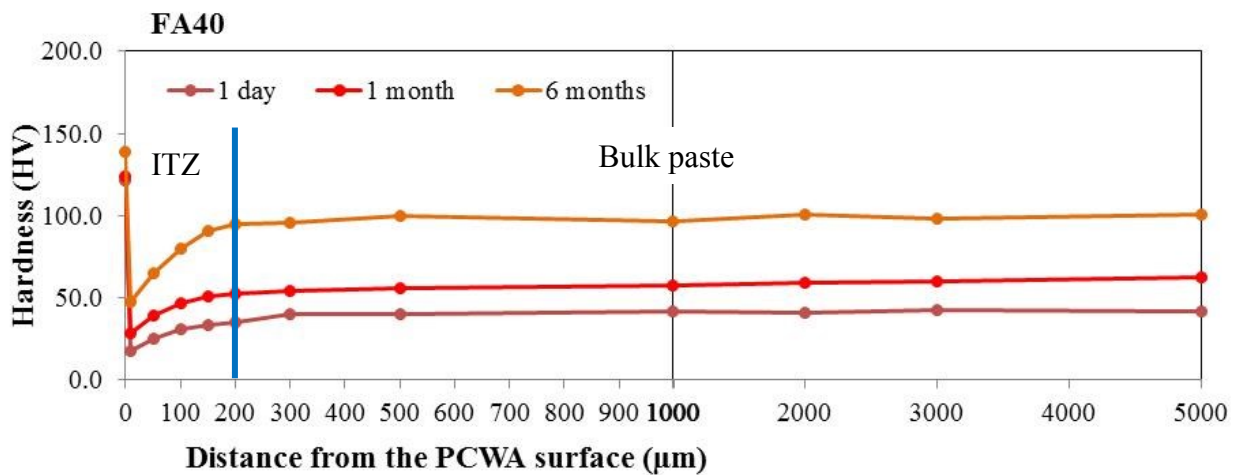


Figure 5.14 Effect of internal saturated $\text{Ca}(\text{OH})_2$ solution from one PCWA on the hardness in FA40

5.2.2 Effects of types of IAA supplied from one PCWA

Figures 5.15 and 5.16 show the effects of types of IAA (water, NaOH solution and saturated Ca(OH)_2 solution) supplied from one PCWA on the hardness of ITZ and the bulk paste in FA0 (top) and FA40 (bottom) at the ages of 1 day and 6 months. Each value is an average of 5 results from 5 different positions ($n = 5$).

According to Figure 5.15, the effects of water, NaOH solution, or saturated Ca(OH)_2 solution supplied from one PCWA on the hardness of ITZ and bulk paste were nearly same at the age of 1 days independently of fly ash replacement.

According to Figure 5.16 top, it is shown that the hardness of ITZ and bulk paste in FA0 in all cases (water, NaOH solution, and saturated Ca(OH)_2 solution) were nearly same at the age of 6 months. However, the NaOH solution or saturated Ca(OH)_2 solution supplied from one PCWA increased the hardness values of ITZ and bulk paste in FA40 more than water supplied from one PCWA at the age of 6 months. It indicates that alkali solution supplied from one PCWA increased the hardness values of ITZ and bulk paste in FA40 more than water supplied from one PCWA at the age of 6 months.

When a comparison between Figures 5.15 and 5.16 was made, the hardness values of ITZ and bulk paste in FA40 were observed smaller than that in FA0 at the age of 1 day and nearly the same at the age of 6 months when IAA was applied from the model of internal activation by using one PCWA. It can be said that IAA also improved the ITZ microstructure between PCWA and bulk paste, and increased the values of ITZ and bulk paste in FA40 at the age of 6 months.

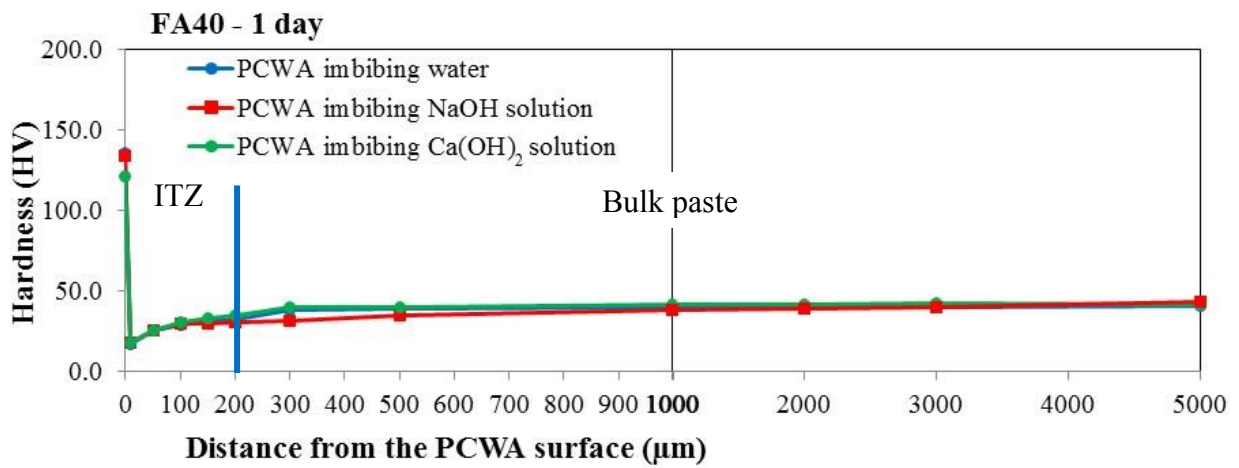
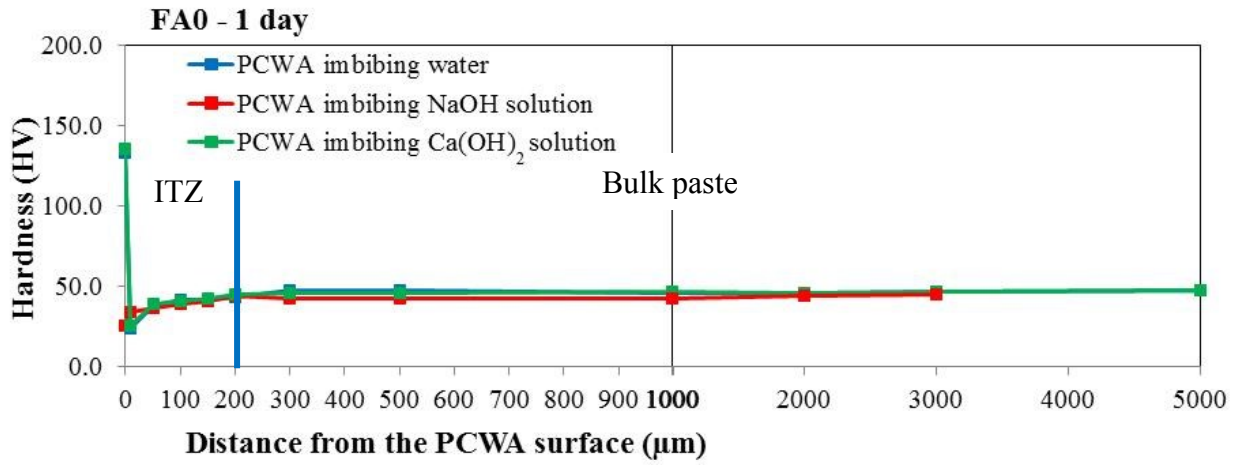


Figure 5.15 Effect of types of IAA supplied from one PCWA on the hardness in FA0 (top) and FA40 (bottom) at the age of 1 day

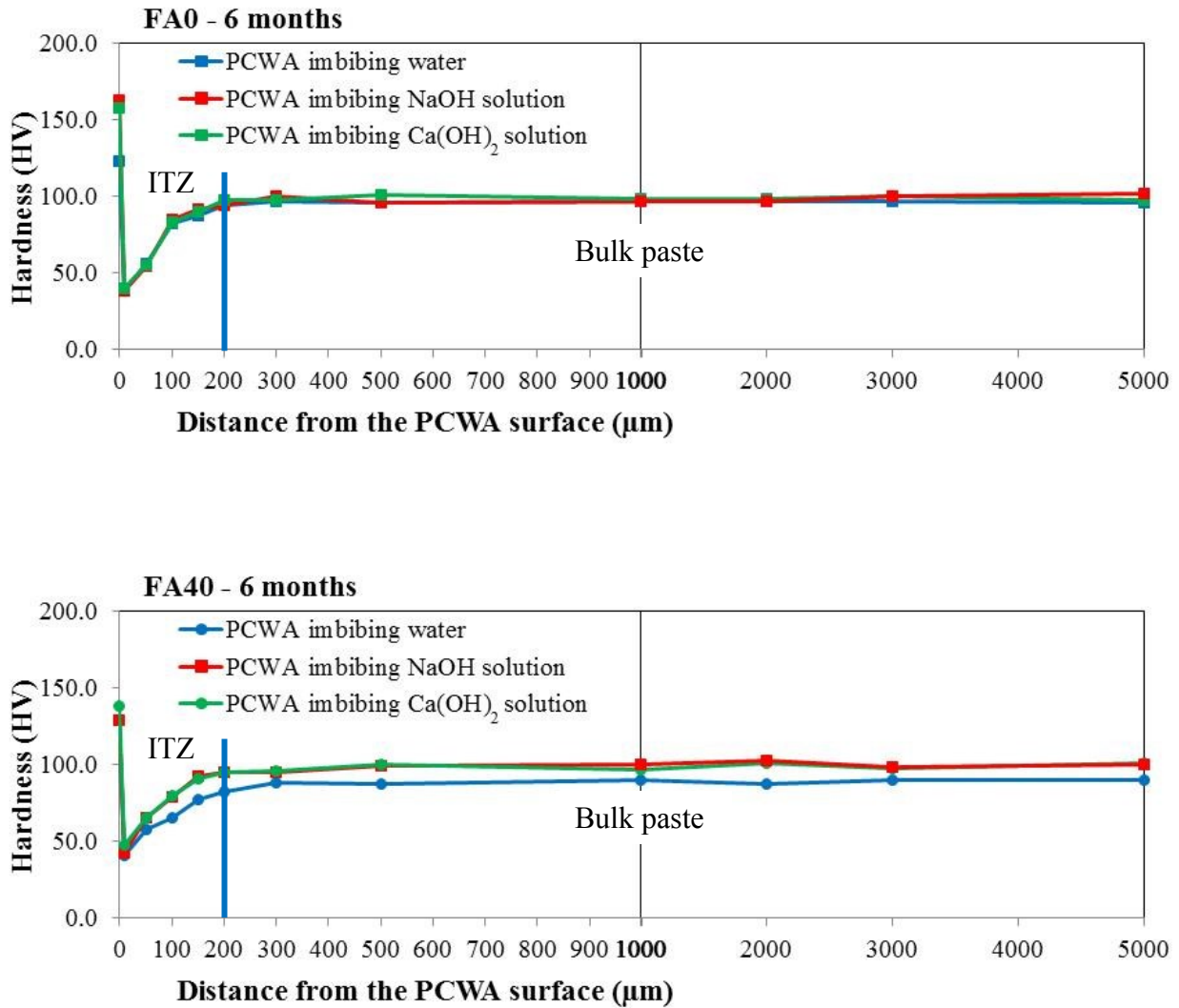


Figure 5.16 Effect of types of IAA supplied from one PCWA on the hardness in FA0 (top) and FA40 (bottom) at the age of 6 months

5.3 EFFECTS ON IAA ON COMPRESSIVE STRENGTH AND POROSITY OF FLY ASH CONCRETE

5.3.1 Compressive strength

The compressive strengths of eight mixture proportions are shown in Figure 5.17. Each value is an average of three test results, whose standard errors range from 0.06 to 1.88 N/mm². All compressive strengths of specimens at the age of 1 day were higher than 35 N/mm², which is

required for pre-tensioned pre-stressed concrete in JSCE [5]. It indicates all the concretes in this study can be applicable to pre-tensioned pre-stressed concrete.

Figure 5.17 shows the compressive strength in FA0 with PCWA imbibing saturated $\text{Ca}(\text{OH})_2$ solution (FA0G40(Ca)) was larger than that without PCWA (FA0G0) or with PCWA imbibing water (FA0F40(Wa)) over time. It can be attributed partially by the lower air content and slump (as shown in Table 3.9 in Chapter 3). Meanwhile, the compressive strength in FA40 with 40% replacement of PCWA imbibing solution (water, NaOH solution and saturated $\text{Ca}(\text{OH})_2$ solution) (FA40G40(Wa), FA40G40(Na) and FA40G40(Ca)) was smaller slightly at the ages of 7, 28, and 91 days and nearly same at the ages of 182 and 364 days when compared with that in FA40 without PCWA. It could not imply that the effects of IAA by using PCWA were not observed on promoting the cement hydration and accelerating the pozzolanic reaction in the fly ash concrete.

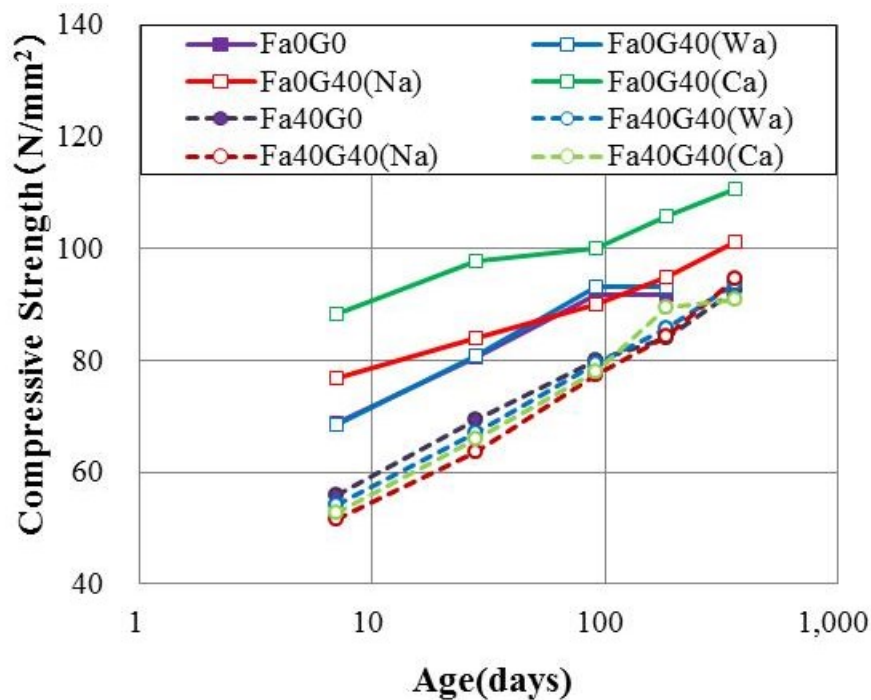


Figure 5.17 Compressive strengths of the specimens

5.3.2 Porosity

Porosity in the fly ash concrete was also measured by MIP as mentioned in section 3.5.4. Results of their total pore volumes should be also considered to range in size from 3 nm to 50 μm to ignore the effect of entrained air. The total pore volumes of all eight mixture proportions at the ages of 28, 182, and 364 days are shown in Figure 5.18. It can be said that the total pore volume of concrete was reduced as the curing age progressed. When compared with reference concrete (FA0), fly ash concrete (FA40) was coarser independently of PCWA replacement.

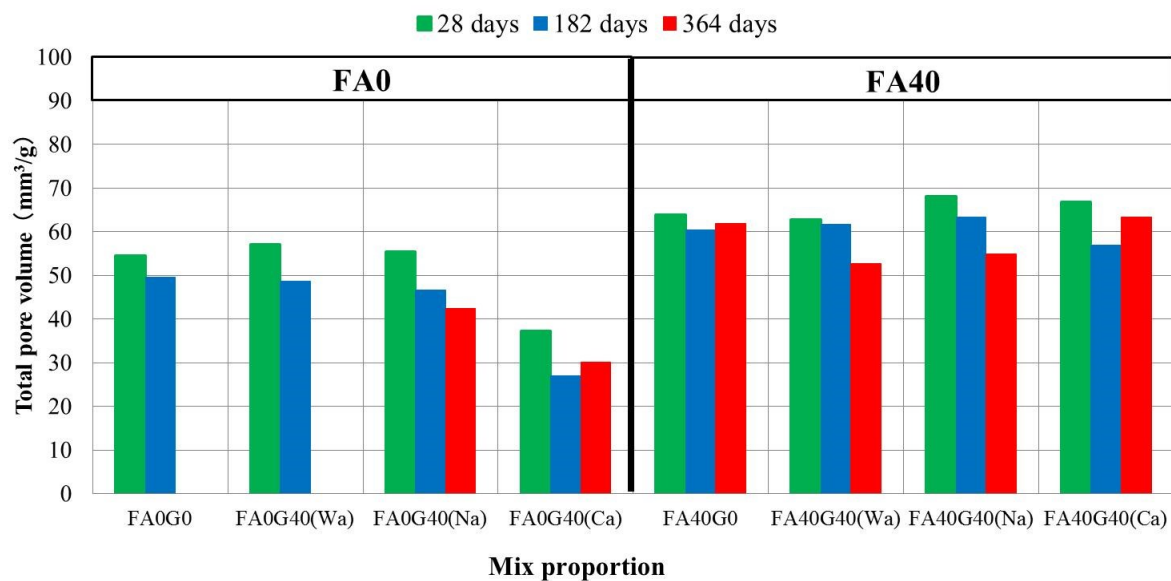


Figure 5.18 Total pore volumes of concretes over time

In addition, the pores larger than 0.05 μm (i.e. macro pore) are also considered as one of factors which affect the compressive strength of concrete [6]. The total pore volumes of macro pores obtained from the porosity measurement of the broken concrete specimens at the ages of 28, 182, and 364 days are shown in Figure 5.19. The effects of PCWA in reducing the macro pores volume of the concrete with 40% replacement of fly ash (FA40) was more

significant than that of concrete without fly ash (FA0). It is considered that 40% replacement of PCWA supplied enough internal alkali solution for the acceleration of the pozzolanic reaction as well as the promotion of the cement hydration to densify the pore structure in the systems although their strengths were not improved (see Figure 5.19). Perhaps, this can be due to the high replacement of PCWA and the lower strength of PCWA than the normal aggregate [7].

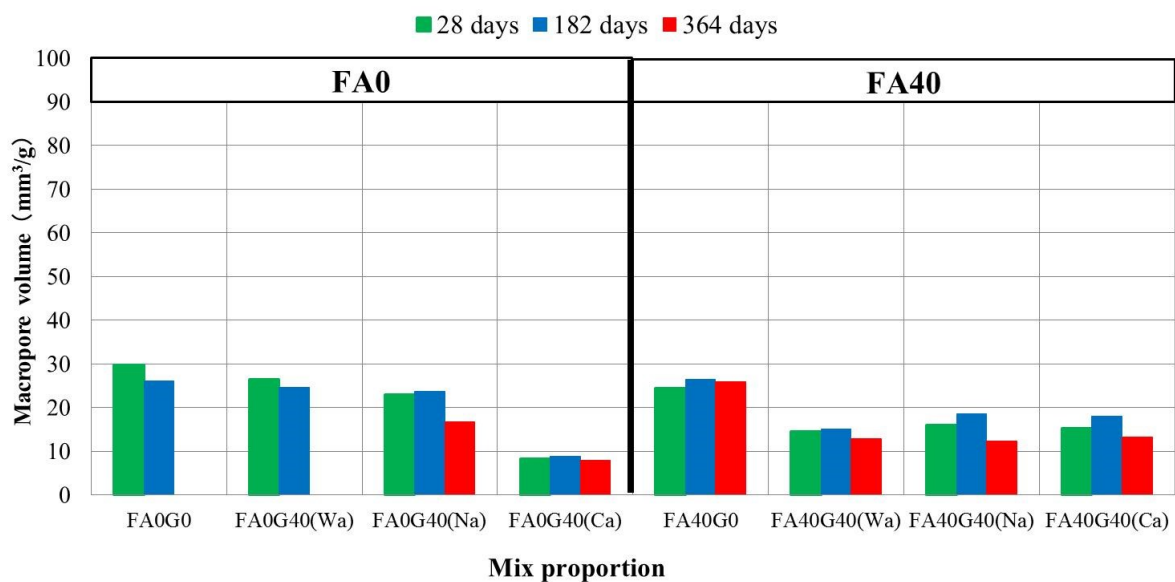


Figure 5.19 Total pore volumes of macro pores (ranging 0.05 - 50 μ m in diameter) of concretes over time

In order to estimate the effects of IAA on promoting the cement hydration and accelerating the pozzolanic reaction in fly ash concrete (FA40), the volume ratio of 20-330 nm pores to the total pore and the volume ratio of 3-20 nm pores to the total pore of fly ash concrete are also shown in Figure 5.20. When using 40% replacement of PCWA, the decrease in the volume ratio of 20-330 nm pores to the total pore and increase in the volume ratio of 3-20 nm pores to the total pore due to IAA (NaOH solution and saturated Ca(OH)₂ solution) were

observed at the ages of 182 and 364 days. It confirms that IAA was effective on accelerating the pozzolanic reaction of the fly ash concrete. Although the decrease in the volume ratio of 20-330 nm pores to the total pore were not observed at the age of 28 days, the volume ratio of 3-20 nm pores to the total pore increased. In addition, it appears the effects of internal curing water from 40% replacement of PCWA in decreasing the volume of 20-330 nm pores and increasing the voume of 3-20 m pores. It demonstrates internal curing water accelerated the pozzolanic reaction of the fly ash concrete. Nevertheless, these tendencies in the case of fly ash concrete with PCWA imbibing NaOH solution or saturated $\text{Ca}(\text{OH})_2$ solution were less than those in the case of fly ash concrete with PCWA imbibing water. Perhaps, it is due to the cement hydration which was prevented by the alkali solution in FA40 at the early age discussed in the section 4.1.1 (Chapter 4).

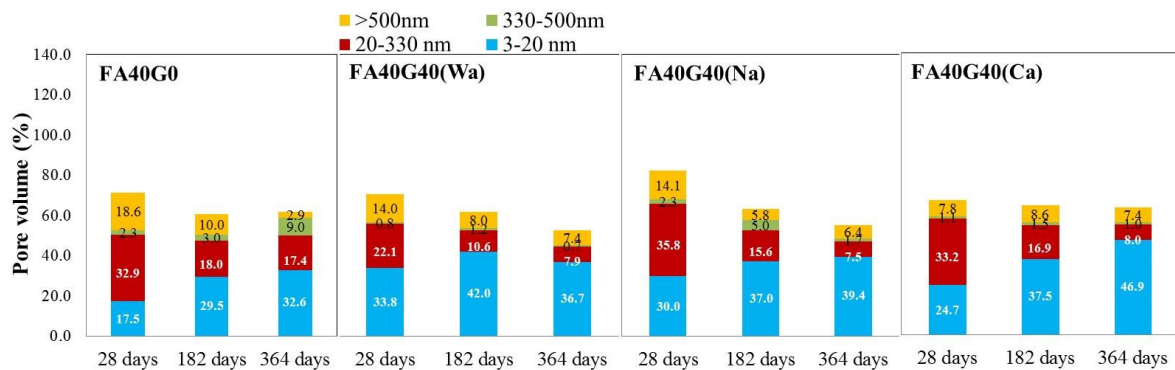


Figure 5.20 Effect of IAA on pore volumes of fly ash concrete at the ages of 28, 182, and 364 days

5.3.3 Relationship between compressive strength and porosity

The relationship between the volume of macro pores and the compressive strength at the ages of 28, 182, and 364 days is shown in Figure 5.21. Generally, the linear relationship between the macro pore volume and the strength is found. It implies that pore structure is densified, resulting in improved compressive strength and enhanced durability of concrete. However, it

appears no relationship between the compressive strength and the macro pore volume in all eight mixture proportions. It is confirmed again that their compressive strengths attributed partially the high amount of PCWA replacement due to possessing the lower strength of PCWA than the normal aggregate.

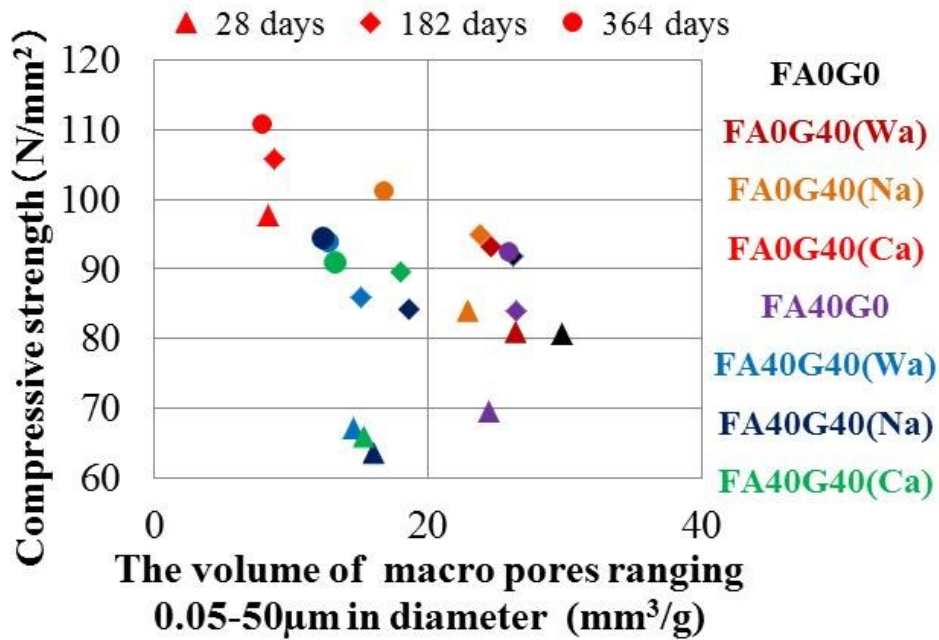


Figure 5.21 Relationship between compressive strength and macro pore volume (pores ranging from 0.05 to 50 µm) of specimens

5.4 SUMMARY

Based on some previous studies and experimental results in this chapter, the following conclusions can be drawn:

5.4.1 Fly ash cement paste

(1) Effects of IAA

IAA decreased the total pore volume in the fly ash cement paste (FA40) as well as the plain cement paste (FA0). Moreover, pore size distribution in FA40 was altered by IAA, with the

volume ratio of 20–330-nm pores to the total pore decreasing and that of 3–20-nm pores increasing.

(2) Effects of types of IAA

The internal saturated $\text{Ca}(\text{OH})_2$ solution activation was more effective in accelerating the pozzolanic reaction of the fly ash cement paste than the internal water injection or NaOH solution activation regardless of starting time of IAA.

(3) Effects of starting time of IAA

(a) An injection of solution at 3 months reduced total pore volume in FA0 more than an injection of solution at 1 month.

(b) An injection of water at 1 month reduced the volume of 20–330-nm pores in diameter in FA40 more than an injection of water at 3 months due to the longer period of injection.

(c) An injection of alkali solution at 3 months reduced the volume of 20–330-nm pores in diameter in FA40 more than an injection of alkali solution at 1 month because the pozzolanic reaction was accelerated more by alkali solution activation 3 months after casting than by the alkali solution activation 1 month after casting.

5.4.2 Fly ash cement paste with one PCWA

(1) The thickness of ITZ between PCWA and bulk paste could be 200 μm .

(2) The hardness of ITZ and bulk paste in FA40 was smaller than that in FA0 at the ages of 1 day and 1 month, while the hardness of ITZ and bulk paste in FA40 was nearly the same as that in FA0 at the age of 6 months. It indicates that the internal saturated $\text{Ca}(\text{OH})_2$ solution supplied from PCWA accelerated the pozzolanic reaction in FA40 significantly at the ages of 6 months.

(3) The effects of water, NaOH solution, or saturated $\text{Ca}(\text{OH})_2$ solution supplied from one PCWA on the hardness of ITZ and bulk paste were nearly same in FA0 at the ages of 1 day

and 6 months.

(4) Alkali solution (NaOH solution and saturated $\text{Ca}(\text{OH})_2$ solution) supplied from one PCWA increased the hardness value of ITZ and bulk paste in FA40 more at the age of 6 months than water supplied from one PCWA. It indicates that alkali solution supplied from one PCWA improved the microstructure of ITZ and bulk paste in FA40 more than water supplied from one PCWA at the age of 6 months.

5.4.3 Fly ash concrete

Although the effects of IAA in improving the compressive strength of the fly ash concrete were not observed, it can be concluded that IAA promoted the cement hydration and accelerated the pozzolanic reaction of the fly ash concrete, with the volume ratio of 20–330 nm pores to the total pore decreasing and that of 3–20 nm pores increasing.

References

1. Mehta PK, Monteiro PJM, 1993. Concrete: Structure, Properties, and Materials. Second Edition. Prentice Hall. Englewoods Cliffs, NJ.
2. Yamamoto T, Kanazu T, 2007. Experimental explanation of compacting effect on hydration phases and strength development mechanism derived from pozzolanic reaction of fly ash. *J JSCE* 63-1:52-65.
3. Bentz DP, 2009. Influence of internal curing lightweight aggregates on interfacial transition zone percolation and chloride ingress in mortars. *Cem Concr Compos* 31:285-289.
4. Zheng-jun W, Qiong W, Yong-feng W, 2012. Effects of Mineral Admixtures and Superplasticizers on Micro Hardness of Aggregate-Paste Interface in Cement Concrete. *J. Shanghai Jiaotong Univ.* 17(5): 629-634.
5. JSCE, 'Standard Specification for Concrete Structures', (2012) 314-315.

6.Mehta PK, Monteiro PJM, 2006. Concrete: Microstructure, Properties, and Materials, Third Edition. McGraw-Hill Publisher, USA.

7. Suzuki M, Meddah MS, Sato R, 2009.Use of porous ceramic waste aggregate for internal curing of high performance concrete. Cem Concr Res 39:373-381.

CHAPTER 6

DISCUSSIONS OF MECHANISM OF INTERNAL ALKALI ACTIVATION

Based on the experimental results in the study obtained by TGA, MIP, and SEM in the Chapters 4 and 5, and some previous studies in Chapter 2, the mechanism of IAA on the microstructure of plain cement paste (FA0) and the microstructure of fly ash cement paste (FA40) were discussed in the sections 6.1 and 6.2, respectively. In addition, the differences of the starting times in IAA mechanism on FA40 and the differences of types of alkali solution in the activation mechanism of pozzolanic reaction in fly ash particles are also described in the sections 6.3 and 6.4, respectively.

6.1 MECHANISM OF IAA ON MICROSTRUCTURE DEVELOPMENT OF PLAIN CEMENT PASTE

Dissolution of anhydrous cement grains and dissolution of water occur first in the plain cement paste when they start to contact with water as shown in Figure 6.1 (a1). It is known that the hydration products (calcium hydroxide (CH), and calcium silica hydrate (C-S-H)) are formed by the reaction between the cement grains and water, called cement hydration, after some hours and even after some early ages (as shown in Figure 6.1 (a2 and a3)). Later, the cement hydration becomes limited owing to the outer C-S-H covering the surface of cement grains [1]. On the other hand, if the paste has a water to cement ratio less than about 0.4, there will be not enough water for cement to hydrate fully [2]. As a result, there are a lot of anhydrous cement grains still remaining in the plain cement paste (as shown in Figure 6.1 (a4)).

Therefore, IAA performed 1 or 3 months after casting would become effective in promoting the cement grains to hydrate at later ages as the plain cement paste with a low water to cement ratio did not have enough water to hydrate at that time (as shown in Figure 6.1 (b) and (c)). This is due to water in alkali solution may promote the cement hydration. As a result, the microstructure in the plain cement paste with IAA could be improved at the later ages more than that without IAA (as shown in Figure 6.1 (b4 and c4)) although alkali in alkali solution supplied 1 month after casting may affect the production of CH adversely at the early ages (as shown in Figure 6.1 (b3)). This was confirmed by the reduction of the total pore volume of the plain cement paste which IAA was applied to when compared with that of the paste without IAA, as mentioned in Chapter 5.

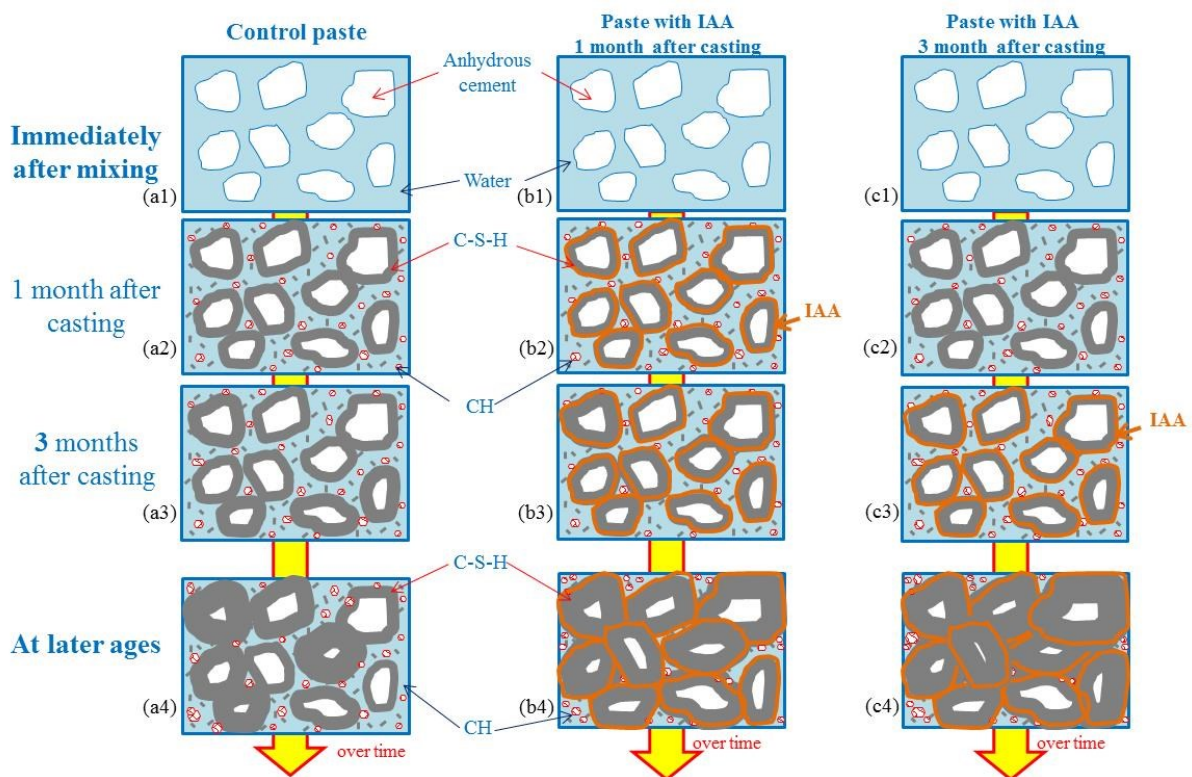


Figure 6.1 Illustration of the difference in microstructure development between the plain cement paste without (left) and with IAA (right) over time

6.2 MECHANISM OF IAA ON MICROSTRUCTURE DEVELOPMENT IN FLY ASH CEMENT PASTE

In the case of fly ash cement paste, the dissolution of the cement grains and dissolution of water also occurs at early ages and forms the hydration products – CH and C-S-H. After some hours or some ages, the CH content formed from cement hydration and high alkalinity provided by NaOH and KOH in pore solution play a role as an alkali environment for fly ash particles to dissolve and release reactive silica and alumina [3]. Then, the pozzolanic reaction, which is chemical reaction between reactive silica and alumina in fly ash particles and CH formed from cement hydration in the presence of water at normal temperature, starts to occur at a very slow degree at the age of 1 month (as shown in Figure 6.2 (a2)) [4]. As a result, the decrease of CH is shown as the pozzolanic reaction of fly ash occurs [5]. The pozzolanic reaction keeps at a constant degree at the later ages [6] (as shown in Figure 6.2 (a3)) because a large amount of C-S-H covers fly ash particles and prevents them to contact with CH formed from cement hydration at that time [7].

The reduction of CH along with the insufficient water content in the fly ash cement system at early ages would be overcome if there were IAA 1 or 3 months after casting (as shown in Figure 6.2 (b2)). IAA supplies not only water for the cement grains to hydrate but also alkalinity for fly ash particles to dissolve and react with CH so that the hydration products are formed from the cement hydration and pozzolanic reaction completely and fill up the pores in the fly ash cement system (as shown in Figure 6.2 (b3)). This was confirmed by SEM examination described in Chapter 4. Furthermore, the pozzolanic reaction of fly ash is accelerated more by IAA with the pore size distribution altered [8]. The decrease in the volume ratio of 20–330 nm pores to the total pore and the increase in the volume ratio of 3–20 nm pores are shown significantly in the presence of IAA discussed in Chapter 5. These result in the improvement of pore structure for the fly ash cement systems at the later ages.

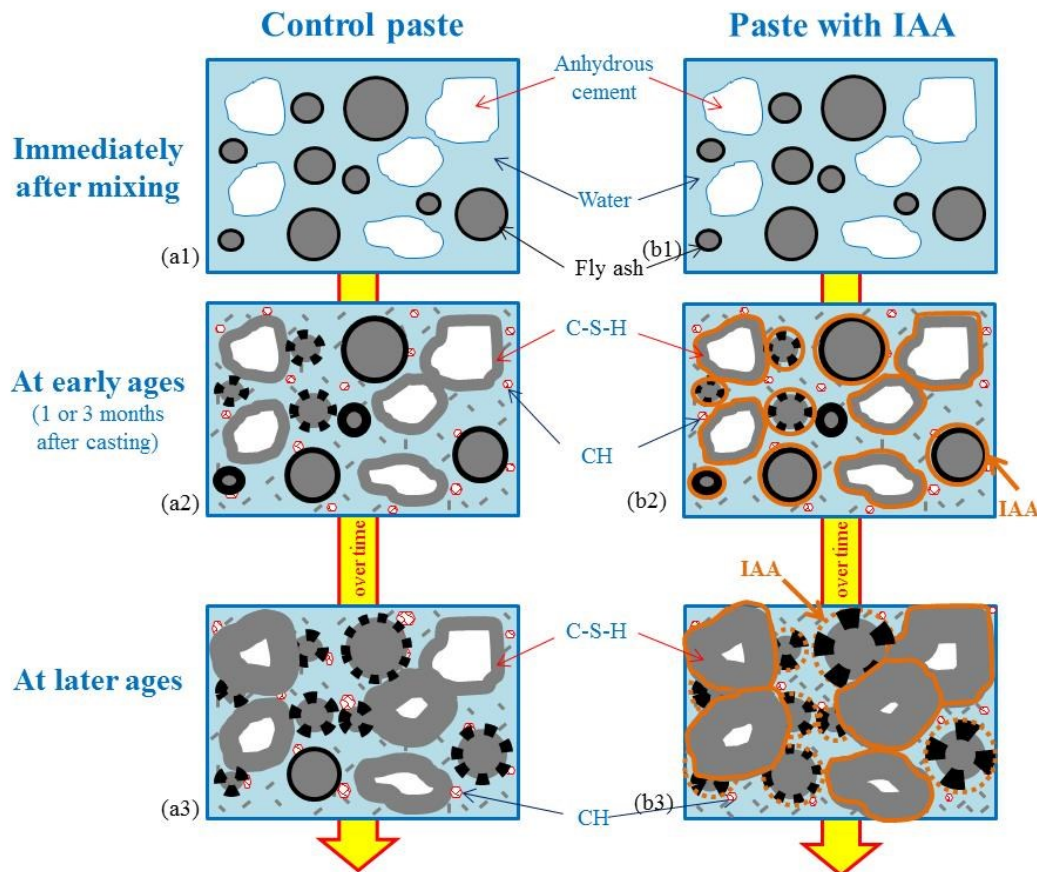


Figure 6.2 Illustration of the difference in microstructure development between the fly ash cement paste without (left) and with IAA (right) over time

6.3 DIFFERENCES OF STARTING TIME IN IAA MACHANISM ON MICROSTRUCTURE DEVELOPMENT IN FLY ASH CEMENT PASTE

The differences in the microstructure among the fly ash cement paste without IAA (a), with alkali activation (AA) at mixing (b), with IAA 1 month after casting (c), and with IAA 3 months after casting (d) over time are shown in Figure 6.3. According to Jariyathitipong et al., the alkali activation on the fly ash cement systems was investigated by combining alkali activators (i.e. alkali solution and additional mixture of calcium hydroxide) with mixing water before casting. It can be said that this activation was carried out on the fly ash particles at mixing together with the high amount of alkali activator, as shown in Figure 6.3 (b1). It was also reported that the microstructure of specimens at the early age (Figure 6.3 (b2)) is not

improved although the addition of high concentration of alkali ion and that of calcium hydroxide can accelerate the pozzolanic reaction and reduce the volume of 0.1-1.0 μm pores [9]. Meanwhile, IAA at 1 or 3 months after casting (as shown in Figure 6.3 (c2) and (d3)) could accelerate the pozzolanic reaction and promote the cement hydration in the fly ash cement systems as shown in Figure 6.3 (c3), (c4), and (d4).

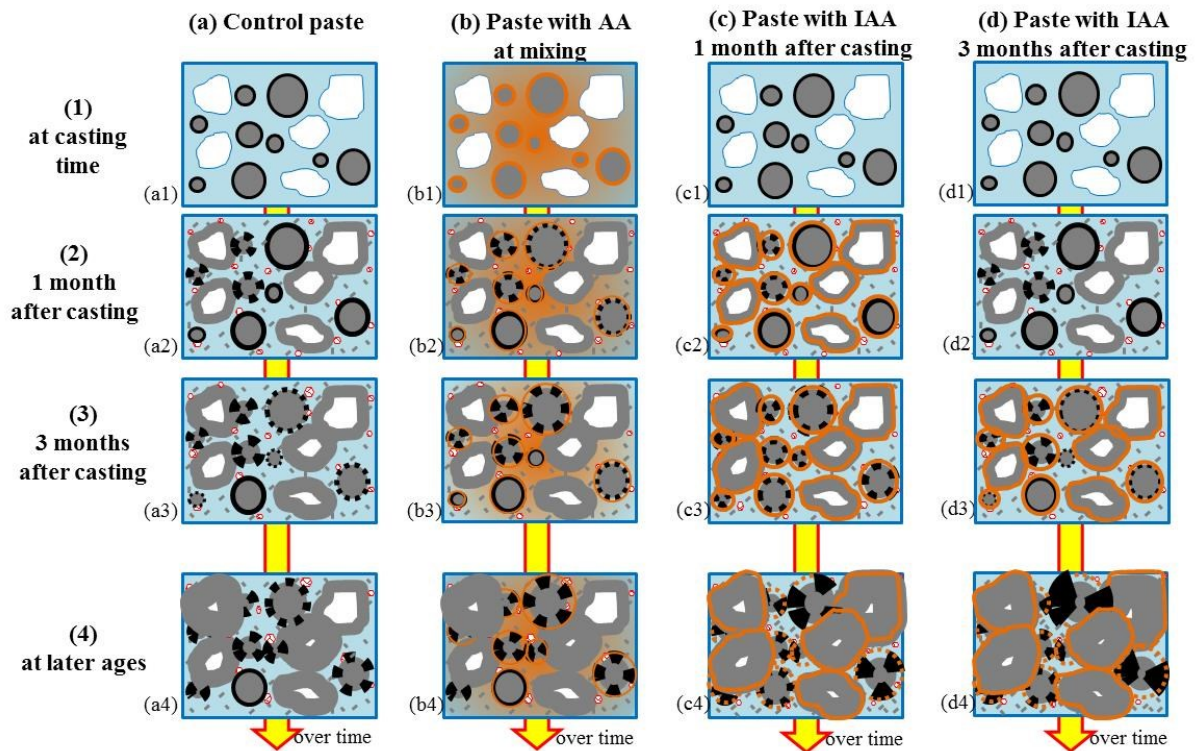


Figure 6.3 Illustration of the differences in microstructure development between the fly ash cement paste without IAA (a), with AA at mixing (b), with IAA 1 month after casting (c), and with IAA 3 months after casting (d) over time

Furthermore, the more effects of IAA 3 months after casting on the acceleration of the pozzolanic reaction and the promotion of the cement hydration at the late ages than that 1 month after casting are also shown in Figure 6.3 (c4) and (d4). Therefore, IAA conducted through PCWA 3 months after casting would be effective in accelerating the pozzolanic

reaction and the cement hydration of the fly ash cement systems so that the mechanical properties and durability of the fly ash concrete could be improved. An application of IAA 3 months after casting by using PCWA as an internal alkali activating agent is also suggested. It is known that if the fly ash cement systems have the lower alkalinity or less water, the alkali solution or water will start to transfer from PCWA to the fly ash cement systems at that time. IAA conducted through PCWA could start 3 months after casting as the alkalinity or water in the fly ash cement systems could be lower or less than that in PCWA at that time. It means the alkalinity or water in the fly ash cement systems should be higher or more than that in PCWA before the age of 3 months so that the alkali solution or water could be kept in PCWA.

6.4 DIFFERENCES OF TYPES OF ALKALI SOLUTION IN ACTIVATION MECHANISM OF POZZOLANIC REACTION IN FLY ASH PARTICLE

The mechanism of pozzolanic reaction in fly ash particles in some previous studies as mentioned in Chapter 2 is shown in Figure 6.4. When the fly ash cement system has sufficient alkali (OH^-) or $\text{Ca}(\text{OH})_2$ formed from the cement hydration, the corrosion at the surface of fly ash particles starts to occur (i.e. the cross-linked silica-tetrahedral (Si-O-Si) and cross-linked alumina-tetrahedral (Al-O-Al) in the fly ash particles are broken) as shown in Figure 6.4 (b)). Then, they release reactive silica and alumina which react with Ca^{2+} and OH^- ions from the cement hydration at normal temperature to form the reaction products (as shown in Figure 6.4 (c)). This reaction is known as the pozzolanic reaction of fly ash particles.

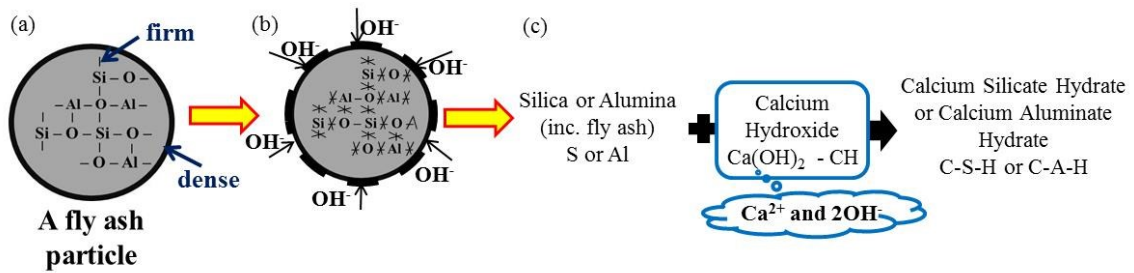


Figure 6.4 Mechanism of pozzolanic reaction in fly ash particle

Combining the above mechanism of pozzolanic reaction in fly ash particle and the experimental results in this study, the differences of each type of alkali solution in the activation mechanism of the pozzolanic reaction of the fly ash particles are shown in Figure 6.5. The content of Ca(OH)₂ formed from the cement hydration in the fly ash cement system was increased by water, NaOH solution, and saturated Ca(OH)₂ solution injection as shown in Figure 6.5 (b2) and (c2). In addition to the amount of OH⁻ formed from cement hydration promoted more by water, NaOH solution, and saturated Ca(OH)₂ solution injection, NaOH solution or saturated Ca(OH)₂ solution supplied the content of OH⁻ ion more than water. NaOH solution or saturated Ca(OH)₂ solution could play a role as the activating agent for the corrosion of fly ash surface to occur at very extensive rate. As a result, the pozzolanic reaction of fly ash particles was accelerated in the alkali activation more than water activation.

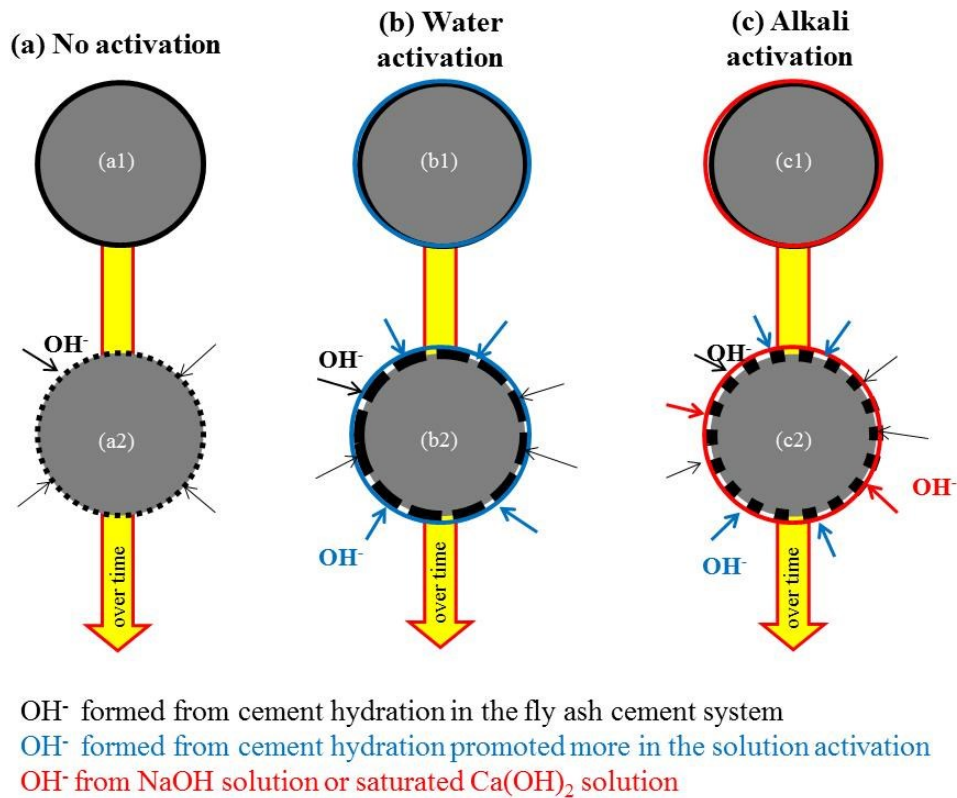


Figure 6.5 Illustration of the differences in activation mechanism among (a) no activation, (b) water activation, (c) NaOH solution or saturated Ca(OH)₂ solution activation

A comparison of activation mechanism between 0.1mol/L NaOH solution (pH = 13.0) and saturated Ca(OH)₂ solution (pH = 12.6) is also proposed in this chapter. It is demonstrated that the disruptions of the Si-O-Si links (or Al-O-Al) in the fly ash particles occur at a pH of 12.5 at room temperature [10] and more than 13 at 20°C in NaOH solution [11] as mentioned in the chapter 2. Therefore, these disruptions could depend on the concentration of each alkali solution although the pH of NaOH solution selected for an internal activation was higher than that of saturated Ca(OH)₂ solution. In addition, the presence of saturated Ca(OH)₂ solution supplied the small amount of Ca²⁺ ion to participate in the fly ash reaction (as shown in Figure 6.4 (c)). Therefore, the saturated Ca(OH)₂ solution activation was more effective in accelerating the pozzolanic reaction of fly ash than the NaOH solution activation. This was also confirmed in Chapters 4 and 5.

References

1. Barron AR. Hydration of Portland cement.

Available from:

<http://cnx.org/contents/2dbbf7c5-c045-4d8b-b07b-ee668a02223a@11/Hydration_of_Portland_Cement>

2. Available from <http://iti.northwestern.edu/cement/monograph/Monograph5_1.html>

3. Mehta PK (1987) Natural pozzolans: Supplementary cementing materials in concrete. CANMET Special Publication 1-33.

4. Sakai E, Miyahara S, Ohsawa S, Lee SH, Daimon M (2005) Hydration of fly ash cement. *Cem Concr Res* 35:1135-1140.

5. Feldman RF, Carette GG, Malhotra VM (1990) Studies on of development of physical and mechanical properties of high-volume fly ash-cement paste. *Cem Concr Compos* 12:245-251.

6. Termkhajornkit P, Nawa T, Nakai M, Saito T (2005) Effect of fly ash on autogenous shrinkage. *Cem Concr Res* 35:473-482.

7. Wang Q, Feng J, Yan P (2012) The microstructure of 4-year-old hardened cement-fly ash paste. *Constr Build Mater* 29:114-119.

8. Yamamoto T, Kanazu T (2007) Experimental explanation of compacting effect on hydration phases and strength development mechanism derived from pozzolanic reaction of fly ash. *J JSCE* 63-1:52-65.

9. Jariyathitipong P, Kawai K, Sato R, Tsuchida S, 2002. Experimental study on acceleration of pozzolanic reaction of fly ash. *Proceed of JCI* 24:105-110.

10. Tang M, Han S, 1981. Effect of $\text{Ca}(\text{OH})_2$ on alkali-silica reaction. *J. of Chinese Silicate Society* 9:160-166.

11. Bijen J, 1996. Benefits of slag and fly ash. *Constr Build Mater* 10:309-314.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

This study combined the replacement of cement with fly ash to mitigate the huge CO₂ emission into the atmosphere, the replacement of coarse aggregate with porous ceramic waste aggregate (PCWA) in order to utilize this waste material as an internal curing agent, and an alkali activation on the pozzolanic reaction of fly ash particles for the future pre-stressed pre-cast concrete manufacturing. The experiments by using two fundamental models with an installed syringe and one PCWA in the fly ash cement systems were carried out to investigate the effects of internal alkali activation (IAA) on the chemical and mechanical properties of the fly ash cement systems. In addition to these two models, the short term and long term mechanical properties of fly ash concrete were studied by using 40% replacement of PCWA with absorption of alkali solution. A quantitative analysis of the Ca(OH)₂ (CH) content, a calculation of CH consumption by the pozzolanic reaction, the porosity and hardness measurements of specimens from these two models, and a test of compressive strength as well as the measurement of porosity of the fly ash concrete were carried out. As a result, the following conclusions can be drawn:

(1) Effects of IAA

(a) An increase in the CH content and a reduction of the total pore volume by applying IAA were observed in the plain cement paste (FA0). Although IAA in FA0 has an effect on the cement hydration adversely at the early ages (i.e. at the ages of 2 and 4 months), it was effective in promoting the cement hydration at the late ages (i.e. at the ages of 6, 8, 10, and 12 months).

(b) IAA not only decreased slightly the CH content but also increased the CH consumption by the pozzolanic reaction in the fly ash cement systems. In addition, the volume ratio of pores ranging 20-330 nm in diameter to the total pores of the paste was decreased, while that of pores ranging 3-20 nm in diameter was increased in the presence of IAA. It demonstrates IAA was effective in accelerating the pozzolanic reaction of the cement paste with 40% replacement of fly ash (FA40). This was confirmed by SEM examination.

Furthermore, an injection of saturated $\text{Ca}(\text{OH})_2$ solution was more effective in decreasing the CH content and increasing the CH consumption in FA40 than that of water or NaOH solution. It indicates that the pozzolanic reaction of the fly ash particles was accelerated by the saturated $\text{Ca}(\text{OH})_2$ solution activation more than by water or NaOH solution activation.

(c) There were the correlations between the CH consumption and the volume ratio of 20-330nm pores to the total pore, and between the CH consumption and the volume ratio of 3-20 nm pores to the total pore in FA40.

(d) The hardness values of ITZ and bulk paste in FA40 were observed smaller at the ages of 1 day and 1 month than that in FA0 and nearly the same at the age of 6 months when IAA was applied from the model of internal activation by using one PCWA. It indicates that IAA also improved the ITZ microstructure between PCWA and bulk paste, and increased the hardness values of ITZ and bulk paste in FA40.

(e) Although the short term and long term compressive strength in the fly ash concrete using 40% replacement of PCWA with the alkali absorption was nearly the same as that without PCWA, the macropore volume (pores ranging 0.05 – 50 μm) was reduced in the presence of IAA at the ages of 28, 182, and 364 days. Moreover, pore size distribution was altered by IAA, with the volume ratio of 20-330 nm pores to the total pore decreasing and that of 3-20 nm pores increasing.

(2) Effects of starting time of IAA

(a) IAA 3 months after casting promoted the cement hydration in FA0 more than that 1 month after casting.

(b) Internal saturated $\text{Ca}(\text{OH})_2$ solution activation 3 months after casting accelerated the pozzolanic reaction in FA40 more than that 1 month after casting.

Meanwhile internal water or NaOH solution activation 1 month after casting accelerated the pozzolanic reaction in FA40 before 12 months more than that 3 months after casting due to the longer period of activation. However, internal water or NaOH solution activation 3 months after casting was effective in accelerating the pozzolanic reaction in FA40 at the age of 12 months more than that 1 month after casting.

In general, it can be concluded that IAA shows its potential effects on the chemical and mechanical properties of fly ash cement systems. Furthermore, these findings of the present study clarify the effects of starting time of IAA on the pozzolanic reaction of the fly ash cement paste cured at normal temperature.

7.2 RECOMMENDATIONS

Based on the previous studies and the present study, some recommendations for the future work can be made as follows:

(1) It has been known that IAA affected the cement hydration adversely at the early age. In addition, IAA 3 months after casting was effective in accelerating the pozzolanic reaction of the fly ash cement systems more than that 1 month after casting. Therefore, a new method for keeping the alkali solution inside PCWA should be suggested to release alkali solution into the fly ash cement paste only 3 months after casting.

- (2) In addition to two starting times of IAA (i.e. 1 and 3 months after casting), the starting time of IAA 6 and 12 months after casting should be studied for a comparison.
- (3) Only two types of alkali activators used in the present study were 0.1 mol/L NaOH solution and saturated $\text{Ca}(\text{OH})_2$ solution. It is recommended that more types of alkali activators as well as their higher concentrations should be used for IAA in the future work.
- (4) The replacements of cement with fly ash at the ratios of 0% and 40% were used in the present study. It is recommended that higher replacement of fly ash should be investigated such as 60% and 80% replacement of fly ash.
- (5) This study only focuses on the effects of IAA on the CH content, CH consumption, and porosity of the fly ash cement systems with one model of installed syringe. The effects of IAA on some different properties (such as the degree of fly ash reaction, hardness of area around the needle of the syringe, and so on) should be investigated in the future work.
- (6) Effects of IAA in improving the ITZ microstructure were only compared between the plain cement systems and fly ash cement systems by using one PCWA which was prepared in the alkali or water immersion for 7 days. Comparison of ITZ hardness of specimens prepared without and with one normal aggregate, and with one PCWA has not been reported yet. Therefore, this comparison should be shown in the future. In addition to hardness measurement, the movements of ions from these models should be studied in the future.
- (7) Effects of IAA in increasing the compressive strength of fly ash concrete using 40% replacement of PCWA were still limited in this study due to the high replacement of PCWA. The effects of IAA by using the lower replacement of coarse aggregate with PCWA on the strength of the fly ash concrete should be investigated in the future.
- (8) Some tests of durability in the fly ash concrete using many replacement ratios of PCWA should be conducted in the future.

(9) In addition to fly ash, the effects of IAA should be studied on the other pozzolanic materials.

APPENDIX

Ca(OH)₂ CONTENT AND CONSUMPTION OF Ca(OH)₂ AT EACH 4MM-SECTION OF SPECIMEN

1. Ca(OH)₂ content

The Ca(OH)₂ – CH contents of samples under each condition ((1) no injection – control, (2) water injection, (3) 0.1mol/L NaOH solution injection (pH = 13.0), and (4) saturated Ca(OH)₂ solution injection (pH = 12.6)) were measured at each 4mm-section of the samples (as shown in Figure 1) at the designated months (i.e. 2, 4, 6, 8, 10, and 12 months).

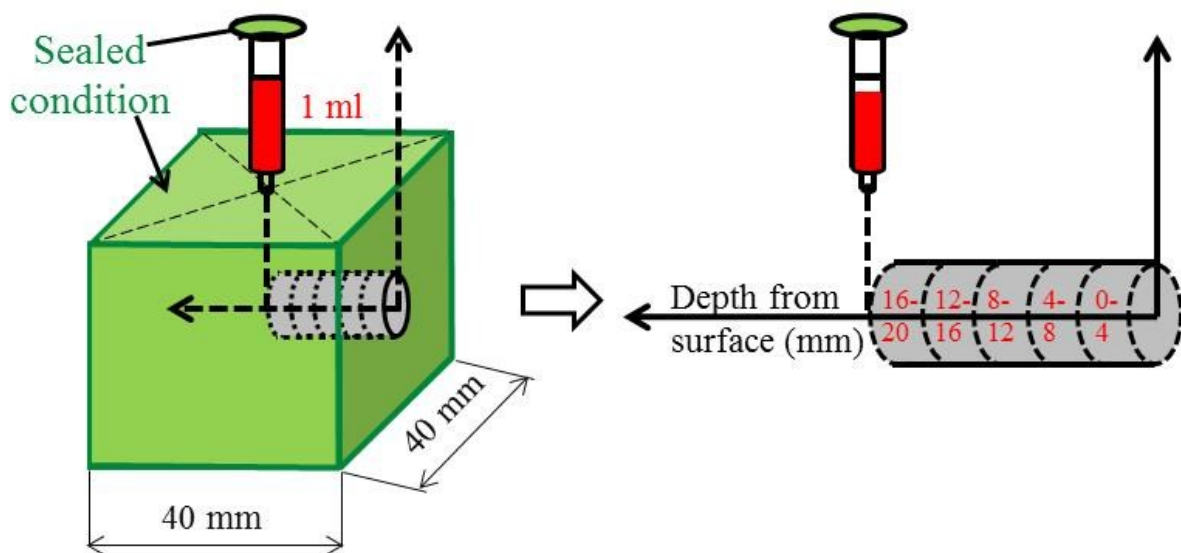


Figure 1 Sample preparation and measurement of CH content at each 4mm-section of the samples at the designated months

A combination of the injection time and testing time is listed in Table 1.

Table Combination of the injection time and testing time

Conditions	Designation	Fly ash replacement (mass %)	Designated ages (months)							
			1M	2M	3M	4M	6M	8M	10M	12M
No injection	FA0	0	○	○	○	○	○	○	○	○
	FA20	20	○	○	○	○	○	○	○	○
	FA40	40	○	○	○	○	○	○	○	○
Injection at 1 month	FA0	0	*	○		○	○	○	○	○
	FA20	20	*	○						
	FA40	40	*	○		○	○	○	○	○
Injection at 3 months	FA0	0			*	○	○	○	○	○
	FA40	40			*	○	○	○	○	○

Where, ○ : testing time for the measurement of the Ca(OH)₂ content

* : starting time of the injection

1.1 No solution injection

CH contents of the FA0 and FA40 control samples without solution injection at each 4mm-section of samples are shown in Figures 2 and 3.

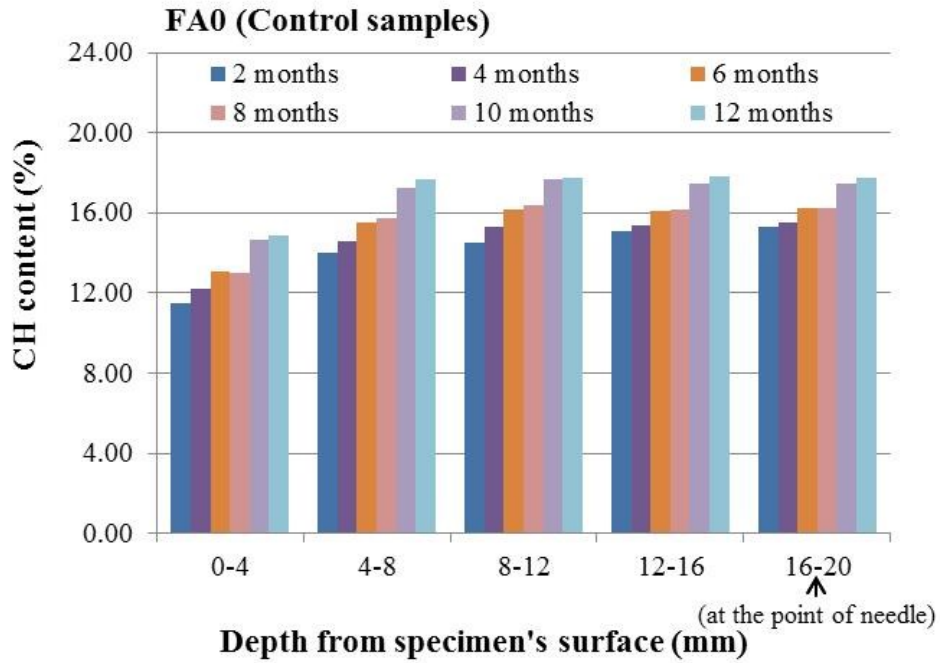


Figure 2 CH content of FA0 control samples without injection at each 4mm-section of samples over time

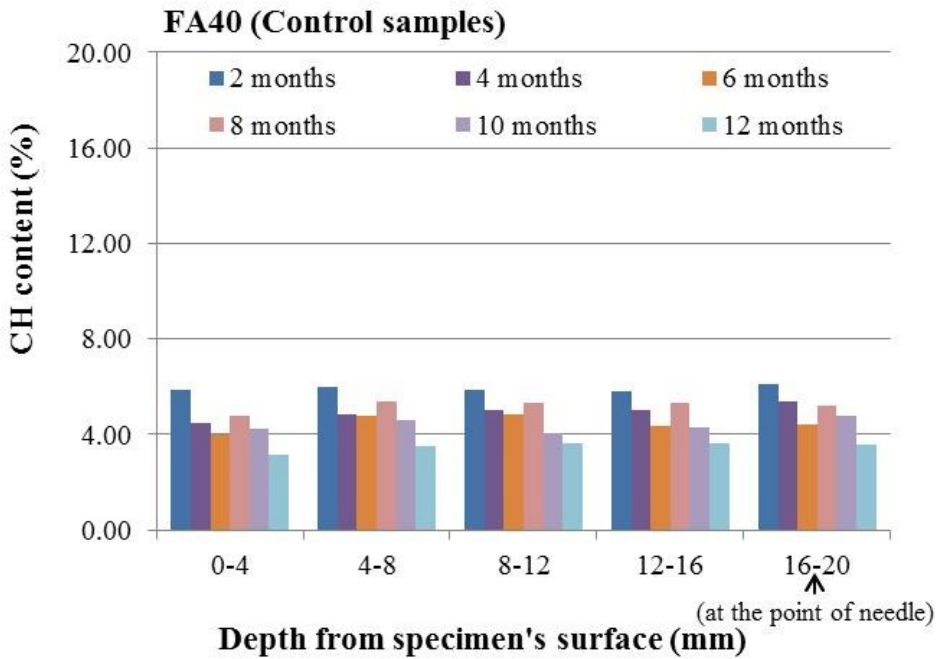


Figure 3 CH content of FA40 control samples without injection at each 4mm-section of samples over time

1.2 IAA 1 month after casting

1.2.1 FA0

CH contents of the FA0 samples into which water, NaOH solution, or saturated $\text{Ca}(\text{OH})_2$ solution was injected 1 month after casting at each 4mm-section of samples over time are shown in Figures 4, 5, 6, 7, 8, and 9.

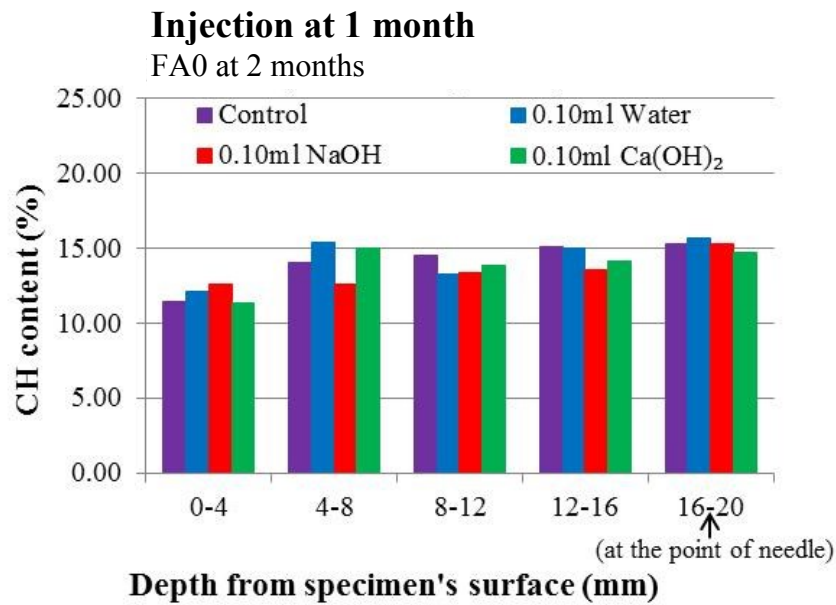


Figure 4 CH content of FA0 samples into which water, NaOH solution, or saturated $\text{Ca}(\text{OH})_2$ solution was injected 1 month after casting at each 4mm-section of samples at the age of 2 months

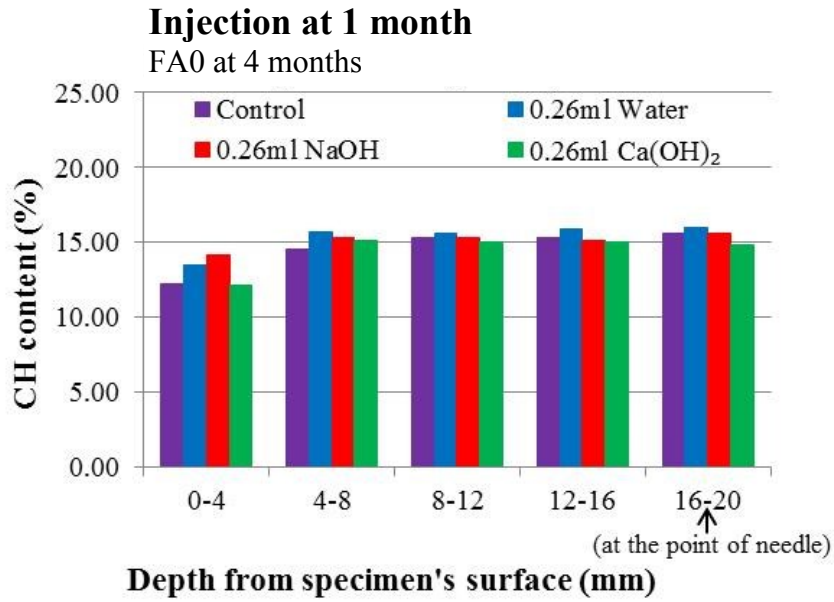


Figure 5 CH content of FA0 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 1 month after casting at each 4mm-section of samples at the age of 4 months

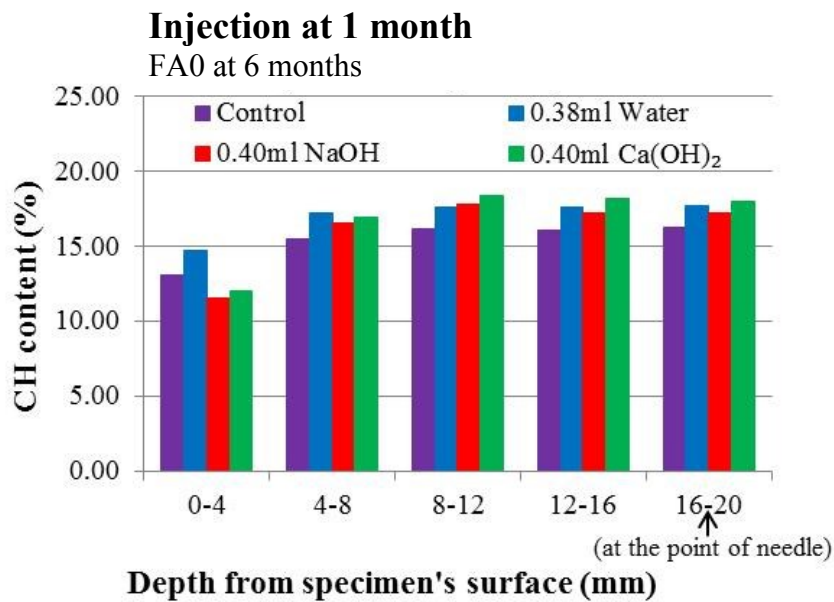


Figure 6 CH content of FA0 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 1 month after casting at each 4mm-section of samples at the age of 6 months

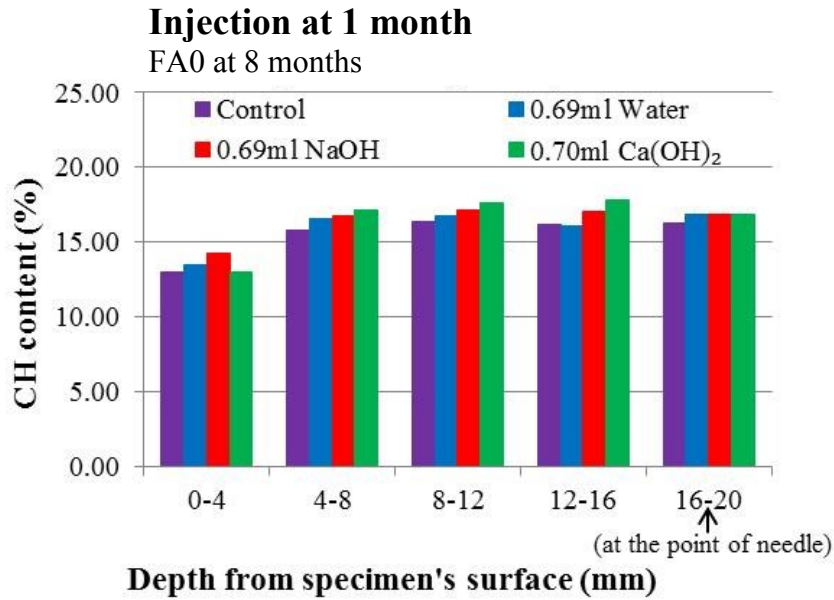


Figure 7 CH content of FA0 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 1 month after casting at each 4mm-section of samples at the age of 8 months

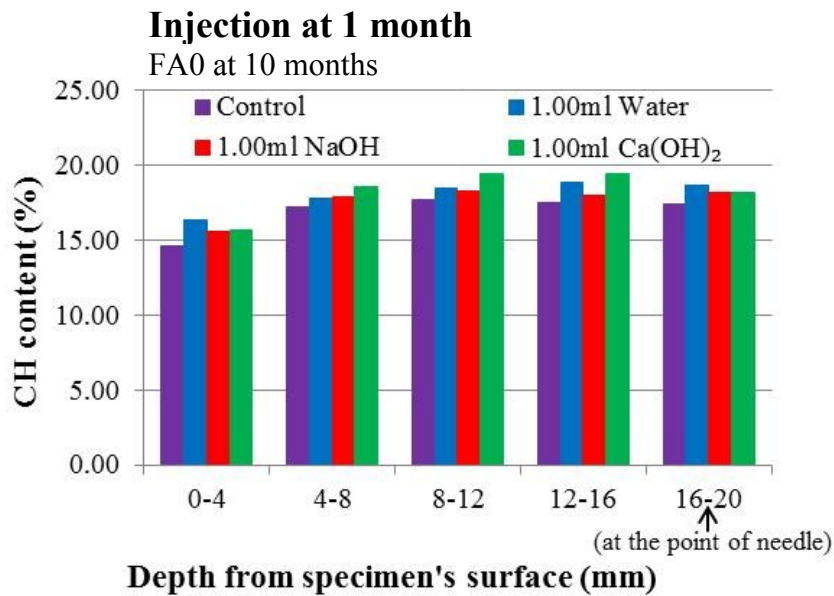


Figure 8 CH content of FA0 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 1 month after casting at each 4mm-section of samples at the age of 10 months

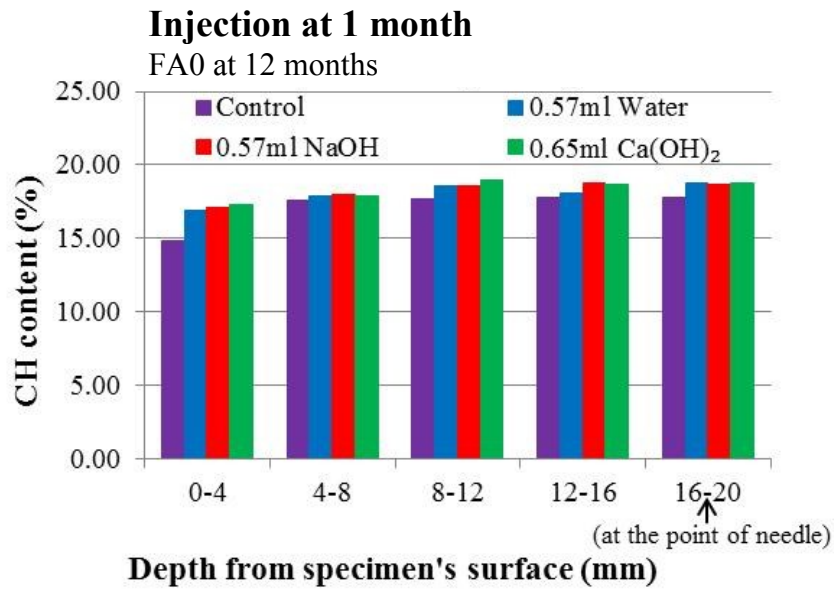


Figure 9 CH content of FA0 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 1 month after casting at each 4mm-section of samples at the age of 12 months

1.2.2 FA40

CH contents of the FA40 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 1 month after casting at each 4mm-section of samples over time are shown in Figures 10, 11, 12, 13, 14, and 15.

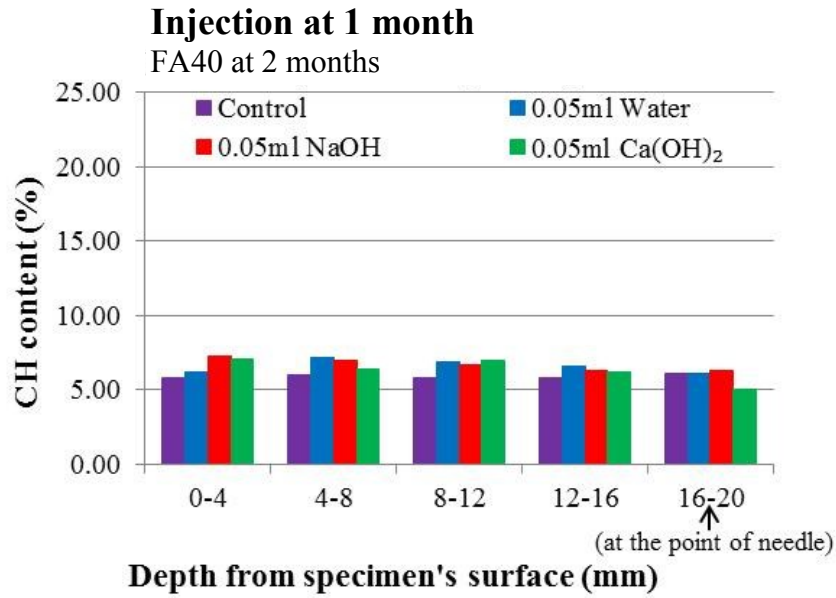


Figure 10 CH content of FA40 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 1 month after casting at each 4mm-section of samples at the age of 2 months

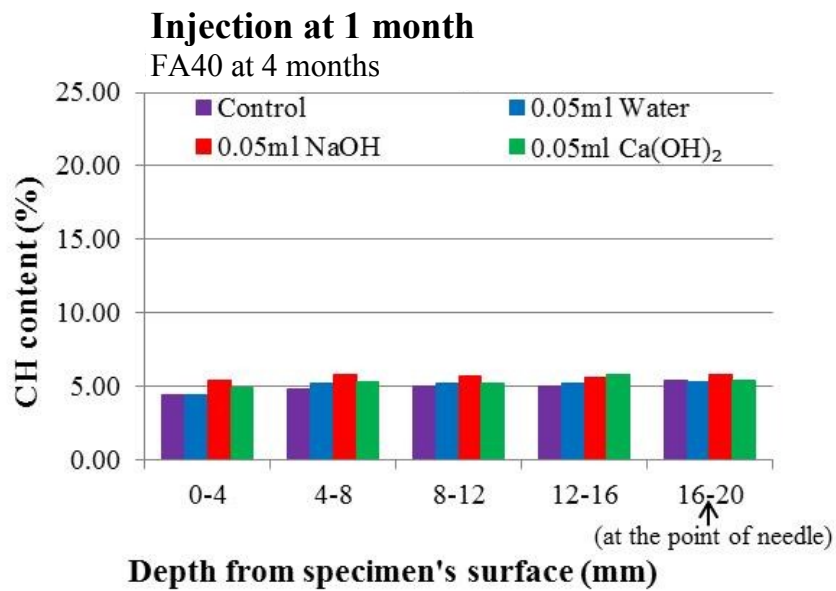


Figure 11 CH content of FA40 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 1 month after casting at each 4mm-section of samples at the age of 4 months

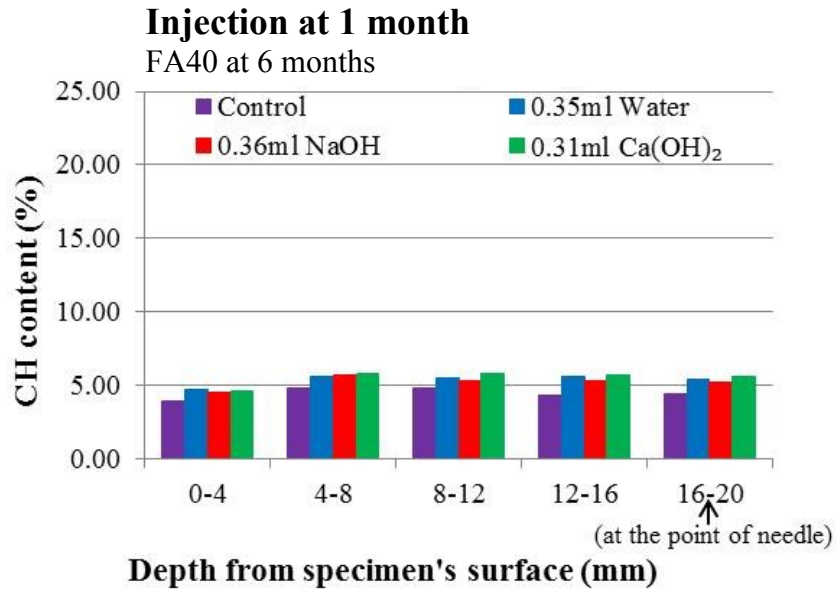


Figure 12 CH content of FA40 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 1 month after casting at each 4mm-section of samples at the age of 6 months

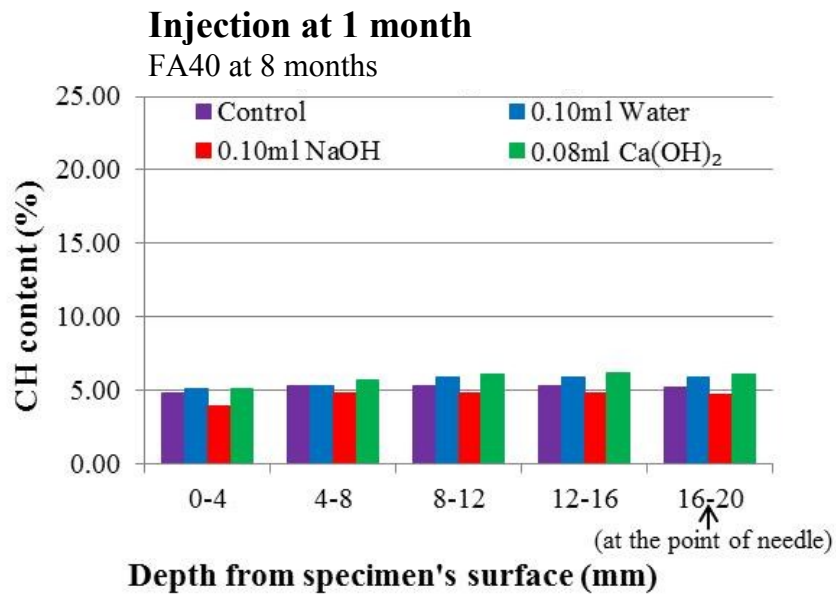


Figure 13 CH content of FA40 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 1 month after casting at each 4mm-section of samples at the age of 8 months

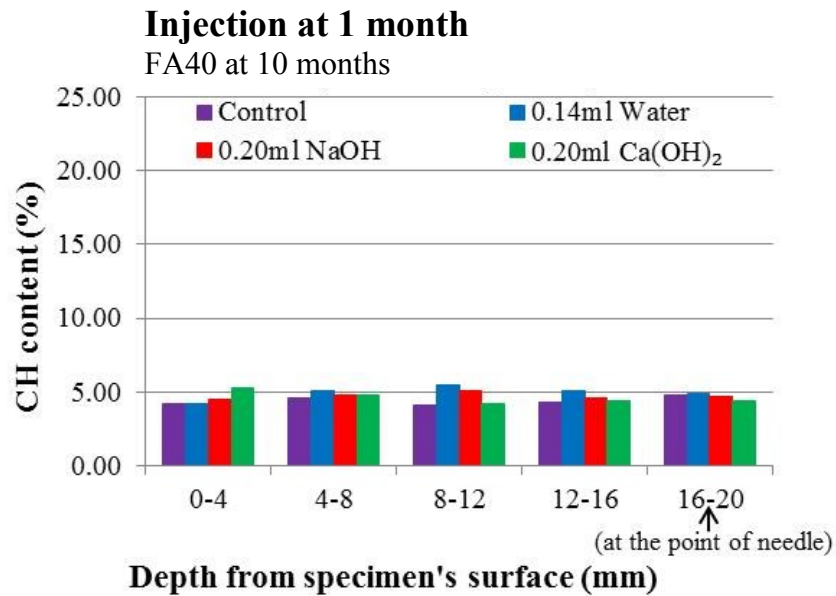


Figure 14 CH content of FA40 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 1 month after casting at each 4mm-section of samples at the age of 10 months

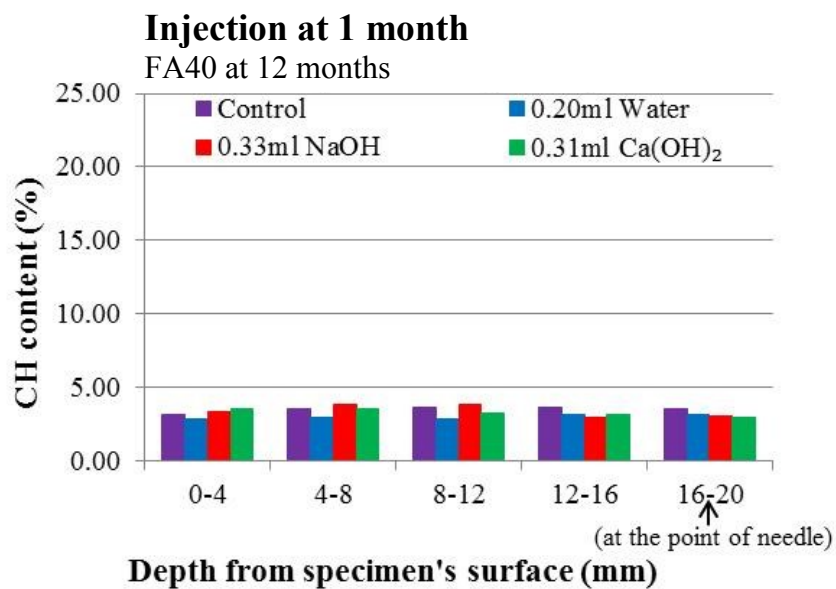


Figure 15 CH content of FA40 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 1 month after casting at each 4mm-section of samples at the age of 12 months

1.3 IAA at 3 month after casting

1.3.1 FA0

CH contents of the FA0 samples into which water, NaOH solution, or saturated $\text{Ca}(\text{OH})_2$ solution was injected at 3 month after casting at each 4mm-section of samples over time are shown in Figures 16, 17, 18, 19, and 20.

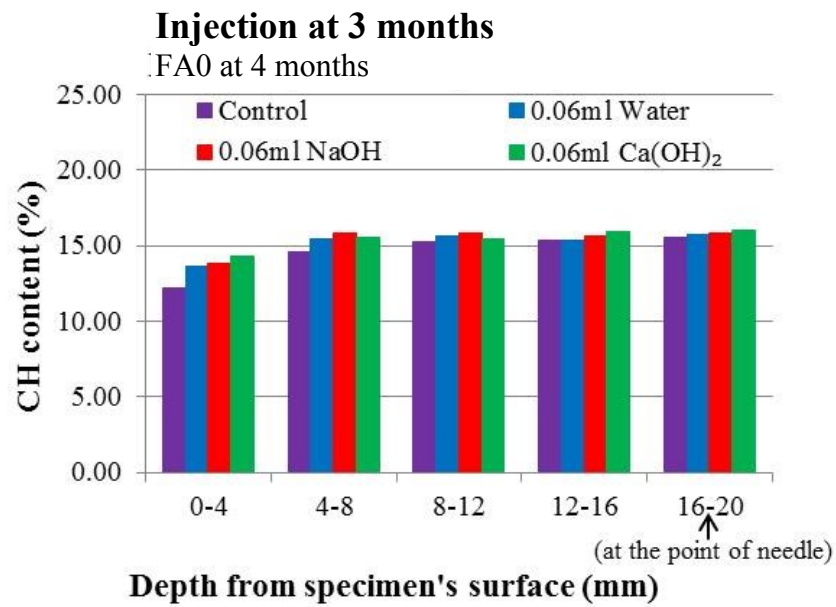


Figure 16 CH content of FA0 samples into which water, NaOH solution, or saturated $\text{Ca}(\text{OH})_2$ solution was injected 3 months after casting at each 4mm-section of samples at the age of 4 months

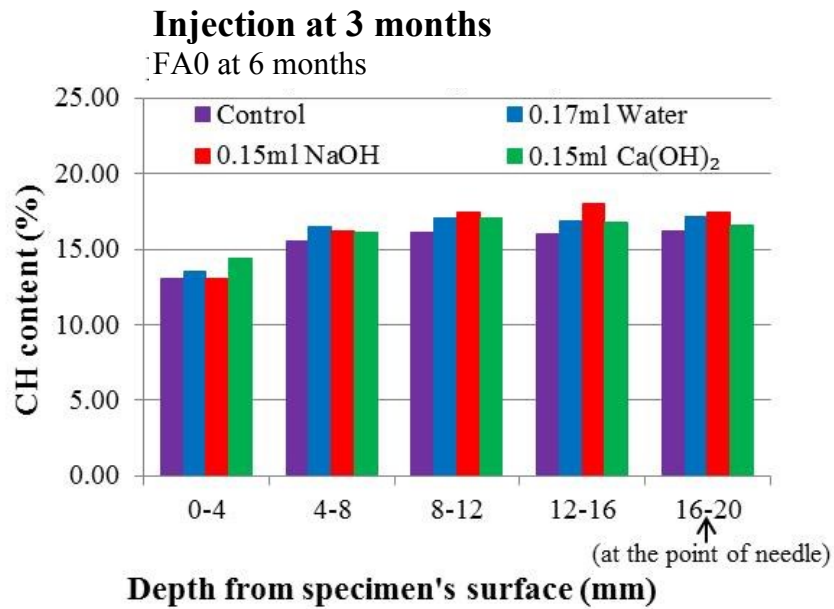


Figure 17 CH content of FA0 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 3 months after casting at each 4mm-section of samples at the age of 6 months

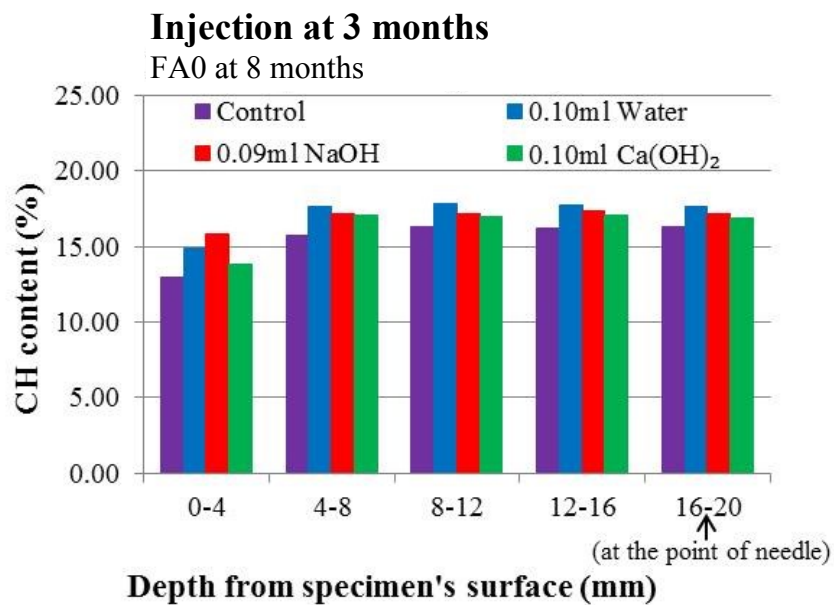


Figure 18 CH content of FA0 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 3 months after casting at each 4mm-section of samples at the age of 8 months

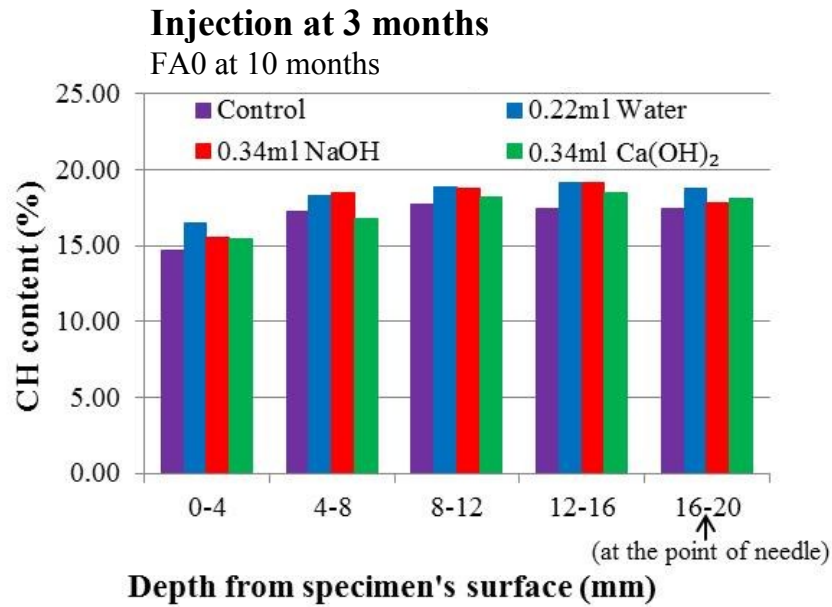


Figure 19 CH content of FA0 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 3 months after casting at each 4mm-section of samples at the age of 10 months

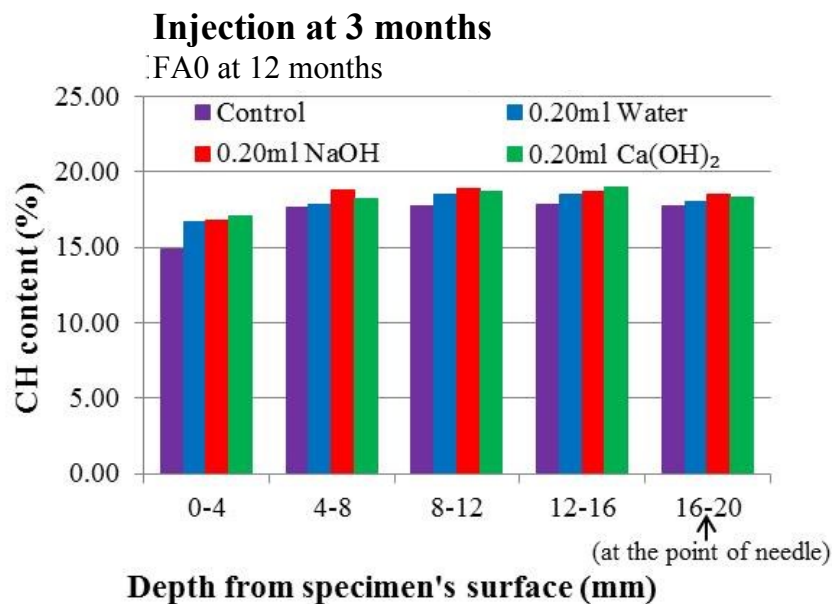


Figure 20 CH content of FA0 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 3 months after casting at each 4mm-section of samples at the age of 12 months

1.3.2 FA40

CH contents of the FA40 samples into which water, NaOH solution, or saturated $\text{Ca}(\text{OH})_2$ solution was injected at 3 month after casting at each 4mm-section of samples over time are shown in Figures 21, 22, 23, 24, and 25.

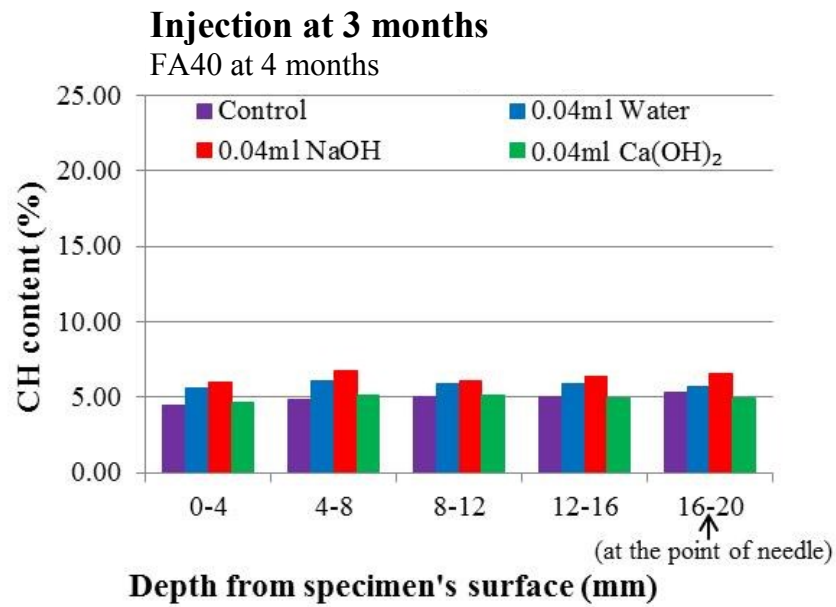


Figure 21 CH content of FA40 samples into which water, NaOH solution, or saturated $\text{Ca}(\text{OH})_2$ solution was injected 3 months after casting at each 4mm-section of samples at the age of 4 months

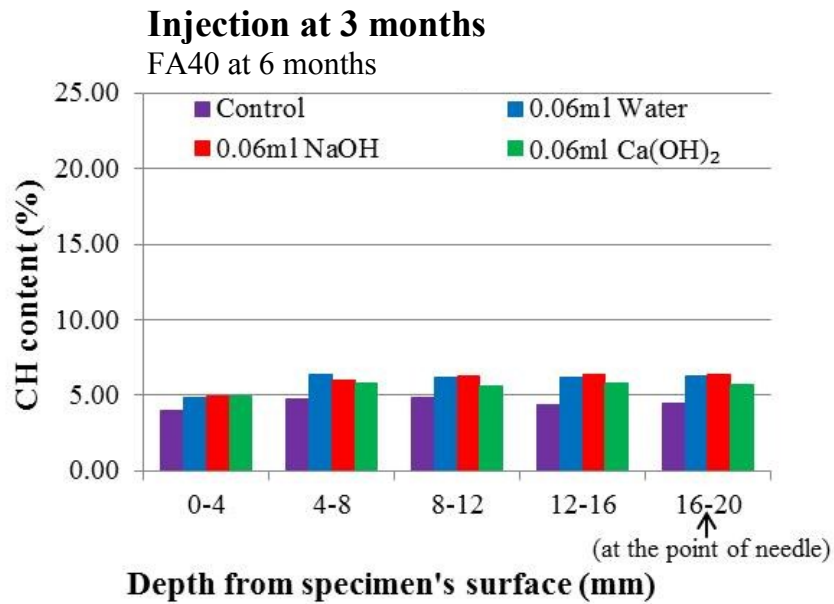


Figure 22 CH content of FA40 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 3 months after casting at each 4mm-section of samples at the age of 6 months

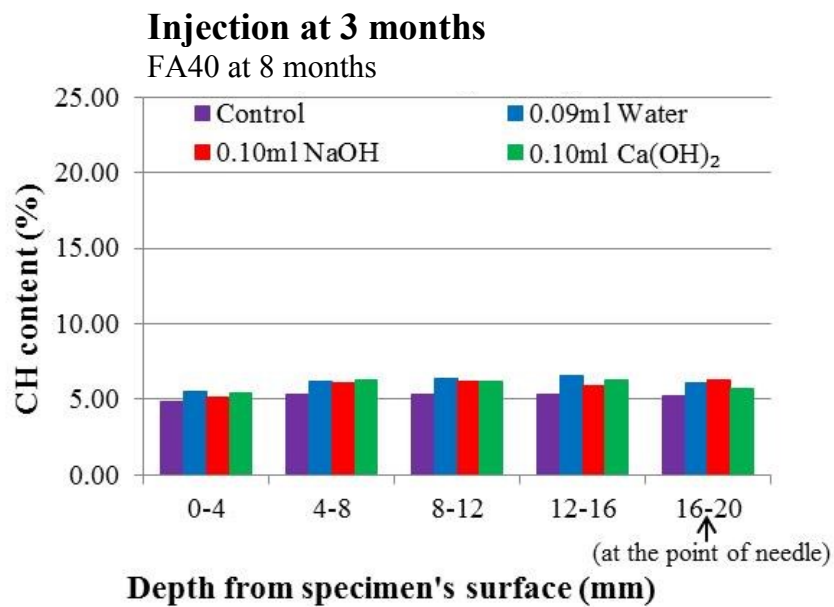


Figure 23 CH content of FA40 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 3 months after casting at each 4mm-section of samples at the age of 8 months

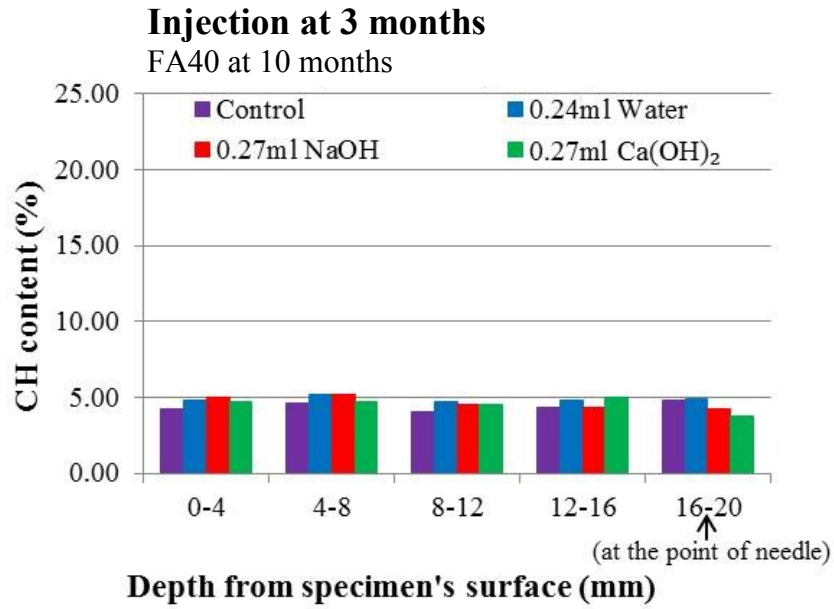


Figure 24 CH content of FA40 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 3 months after casting at each 4mm-section of samples at the age of 10 months

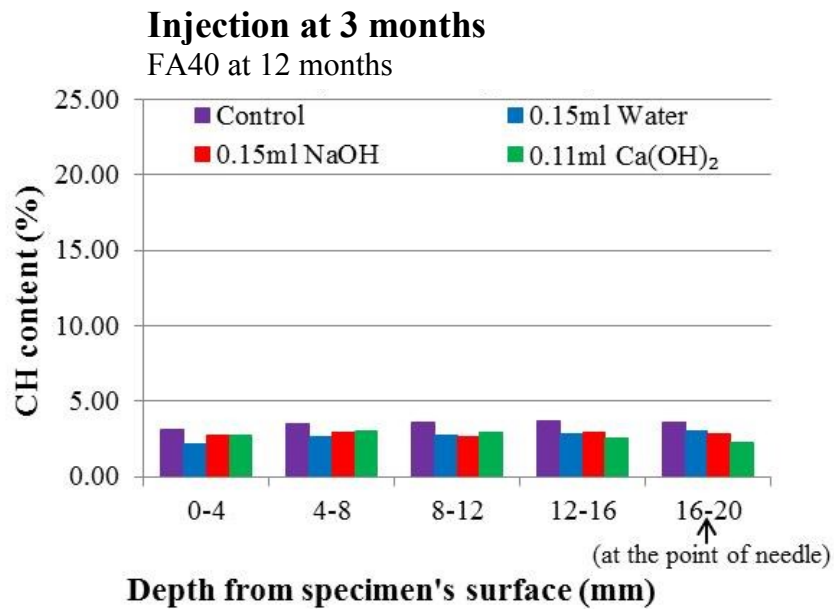


Figure 25 CH content of FA40 samples into which water, NaOH solution, or saturated Ca(OH)₂ solution was injected 3 months after casting at each 4mm-section of samples at the age of 12 months

2. Consumption of Ca(OH)₂

Supposed that the CH content formed by cement in FA40 is almost the same as that in FA0, the consumption of CH by the pozzolanic reaction is described by Equation 1:

$$CH_{\text{cons}} = CH_{\text{FA0}} (c/(c+f)) - CH_{\text{FA40}}, \quad (1)$$

where CH_{cons} is the consumption of CH by the pozzolanic reaction (%), CH_{FA0} is the CH content of FA0 (%), CH_{FA40} is the CH content of FA40 (%), and $(c/(c+f)) = 0.6$ is the mass ratio of cement in the binder (cement + fly ash).

The consumptions of CH by the pozzolanic reaction in the samples into which water, or NaOH, or saturated Ca(OH)₂ solution was injected at 1 or 3 months after casting were also calculated by Equation 1.

2.1 IAA 1 month after casting

The consumptions of CH by the pozzolanic reaction in the samples into which water, or NaOH solution, or saturated Ca(OH)₂ solution was injected 1 month after casting are compared with the untreated control samples at 4mm-section of specimens as shown in Figures 26, 27, 28, 29, and 30.

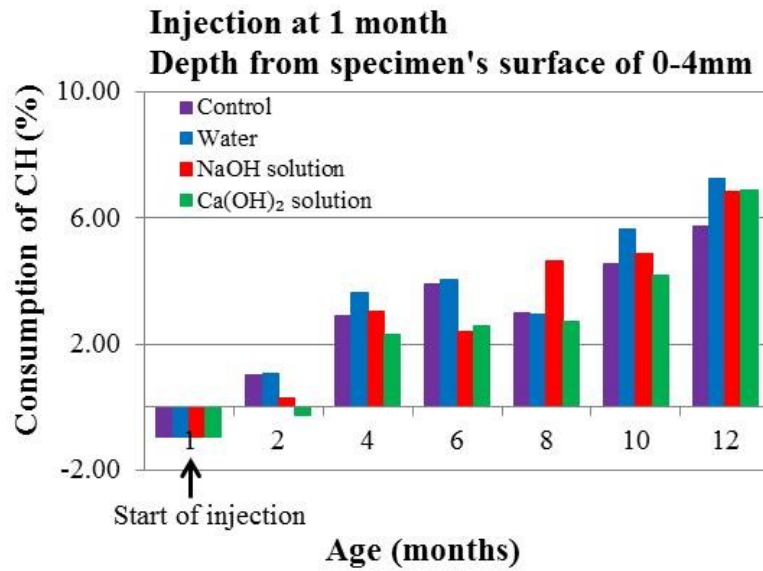


Figure 26 Consumption of CH under each condition ((1) control, (2) water, (3) NaOH solution, and (4) Ca(OH)₂ solution) when IAA was applied 1 month after casting at depth from specimen's surface of 0-4 mm

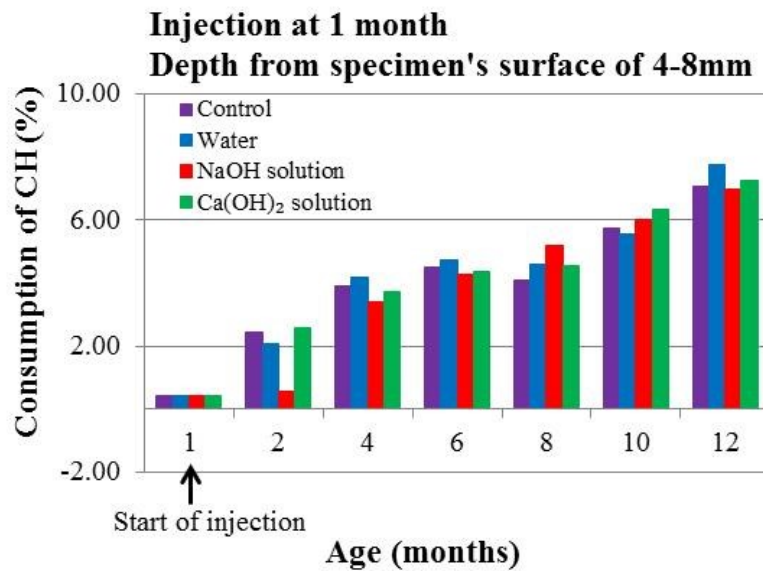


Figure 27 Consumption of CH under each condition ((1) control, (2) water, (3) NaOH solution, and (4) Ca(OH)₂ solution) when IAA was applied 1 month after casting at depth from specimen's surface of 4-8 mm

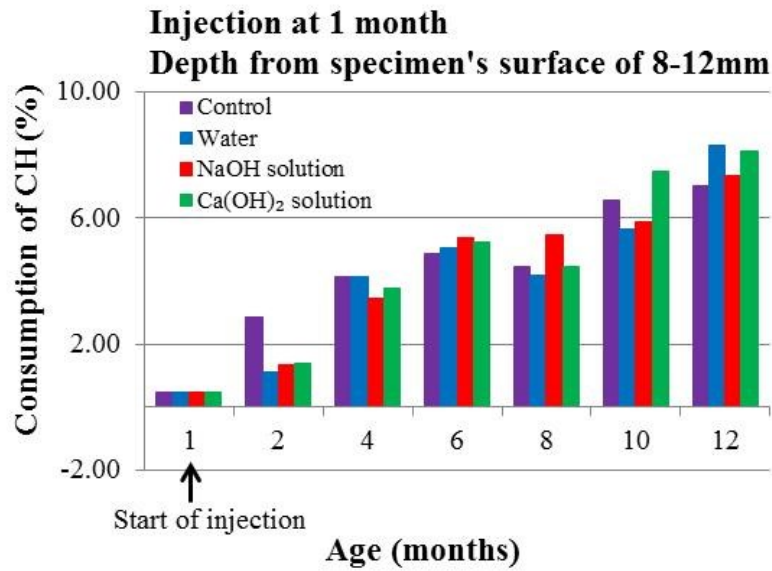


Figure 28 Consumption of CH under each condition ((1) control, (2) water, (3) NaOH solution, and (4) Ca(OH)₂ solution) when IAA was applied 1 month after casting at depth from specimen's surface of 8-12 mm

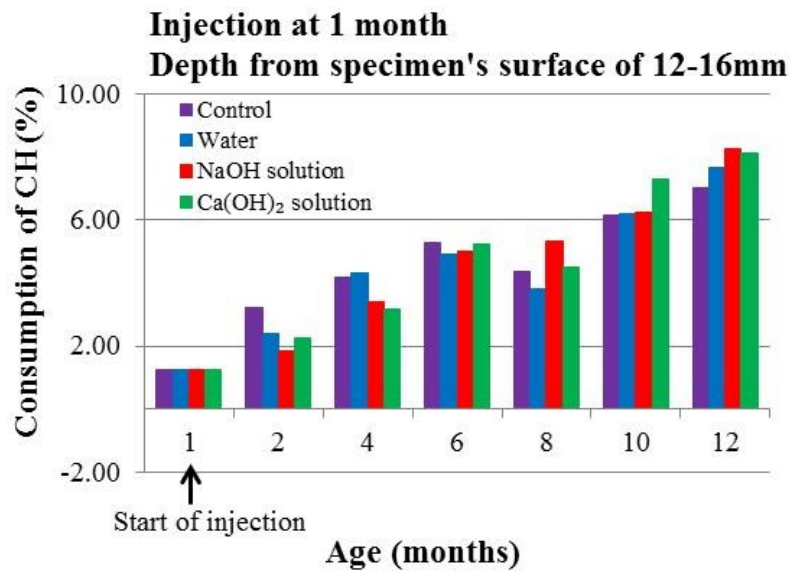


Figure 29 Consumption of CH under each condition ((1) control, (2) water, (3) NaOH solution, and (4) Ca(OH)₂ solution) when IAA was applied 1 month after casting at depth from specimen's surface of 12-16 mm

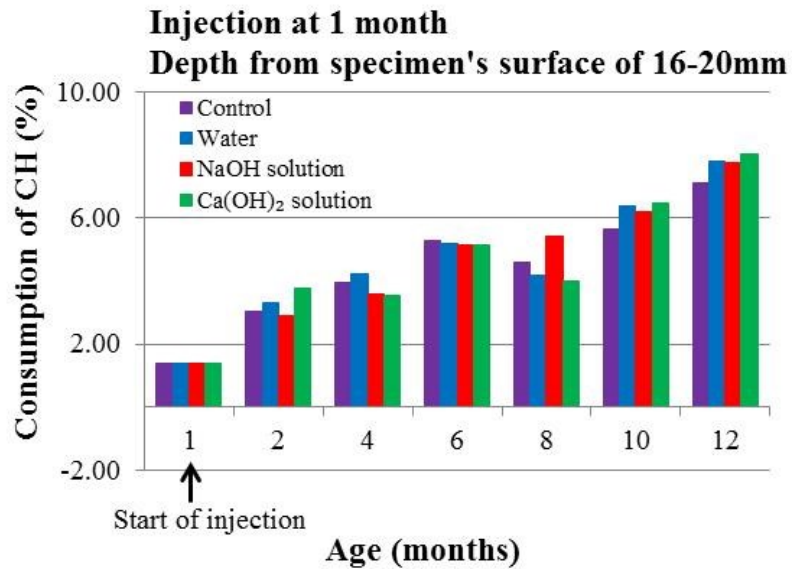


Figure 30 Consumption of CH under each condition ((1) control, (2) water, (3) NaOH solution, and (4) Ca(OH)₂ solution) when IAA was applied 1 month after casting at depth from specimen's surface of 16-20 mm (i.e. at the point of the needle)

2.2 IAA 3 months after casting

The consumptions of CH by the pozzolanic reaction in the samples into which water, or NaOH solution, or saturated Ca(OH)₂ solution was injected 3 months after casting are compared with the untreated control samples at 4mm-section of specimens as shown in Figures 31, 32, 33, 34, and 35.

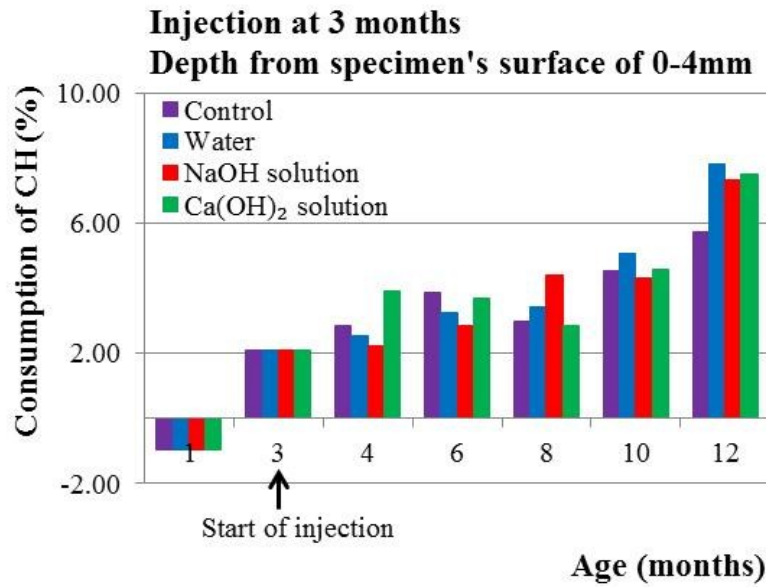


Figure 31 Consumption of CH under each condition ((1) control, (2) water, (3) NaOH solution, and (4) Ca(OH)₂ solution) when IAA was applied 3 months after casting at depth from specimen's surface of 0-4 mm

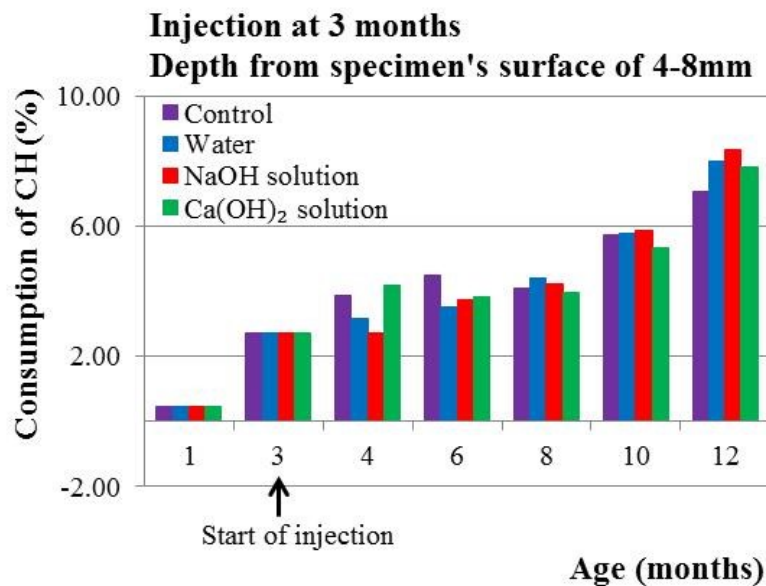


Figure 32 Consumption of CH under each condition ((1) control, (2) water, (3) NaOH solution, and (4) Ca(OH)₂ solution) when IAA was applied 3 months after casting at depth from specimen's surface of 4-8 mm

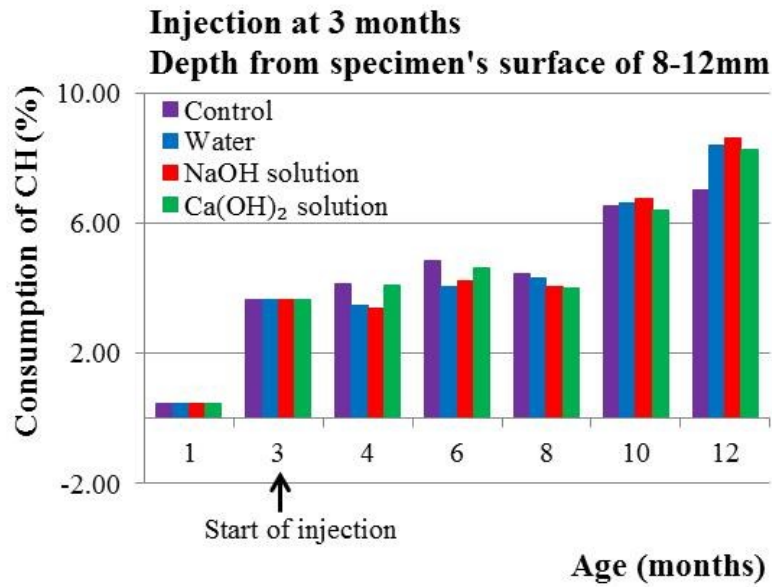


Figure 33 Consumption of CH under each condition ((1) control, (2) water, (3) NaOH solution, and (4) Ca(OH)₂ solution) when IAA was applied 3 months after casting at depth from specimen's surface of 8-12 mm

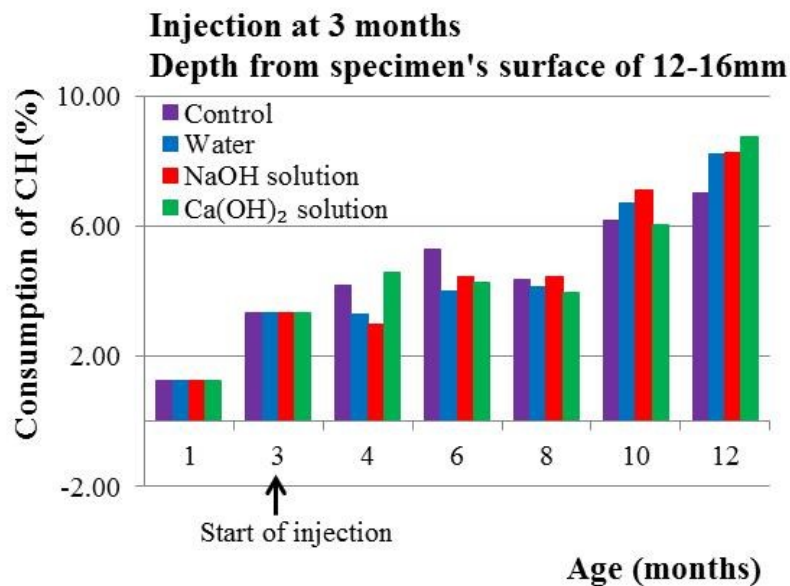


Figure 34 Consumption of CH under each condition ((1) control, (2) water, (3) NaOH solution, and (4) Ca(OH)₂ solution) when IAA was applied 3 months after casting at depth from specimen's surface of 12-16 mm

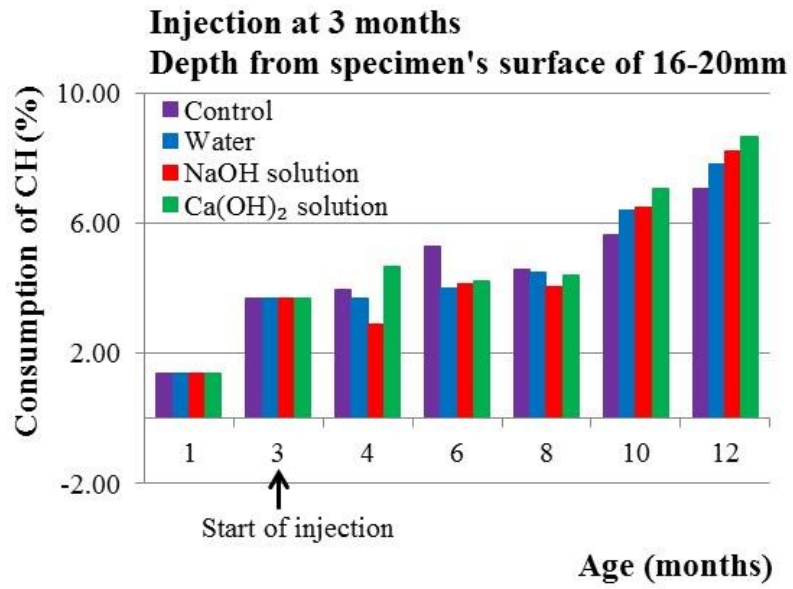


Figure 35 Consumption of CH under each condition ((1) control, (2) water, (3) NaOH solution, and (4) Ca(OH)₂ solution) when IAA was applied 3 months after casting at depth from specimen's surface of 16-20 mm (i.e. at the point of the needle)