EVALUATION OF THE CEMENTING EFFICIENCY FACTOR OF LOW-CALCIUM FLY ASH FOR STRENGTH DEVELOPMENT AND CHLORIDE-PENETRATION RESISTANCE OF CONCRETES

（コンクリートの強度発現性および塩分浸透抵抗性に関するフライアッシュのセメント有効係数の評価）

March 2021

Huynh Tan Phat

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ABSTRACT

Fly ash which is a principal by-product of coal-fired power plants is used enormously due to its economic, environmental, and technical advantages. Besides the mitigation of the CO_2 emission, the use of fly ash to replace a part of cement in concrete leads to (1) a reduction in the construction cost, (2) an increase of the workability of fresh concretes, (3) improvement of the mechanical and durability properties of concretes, and so on. Fly ash is known as a pozzolanic material, which possesses a little or no cementitious value. When fly ash is used to replace part of the cement in the concrete, its cementing efficiency factor (*k*-value) that indicates its contribution to the mechanical and durability properties of concretes has been investigated by several studies. The quantity of the fly ash in concrete can be multiplied by the *k*-value to estimate the equivalent cement content, which can be added to the existing cement content for the determination of the water-to-cement ratio in the mixture. This leads to the more effective design of concrete mixture proportion that contains the fly ash as a supplementary cementitious material. Most of the proposed methods for determining the *k*-value of fly ash are for the compressive strength of concretes due to the simplicity and reliability of compression tests. Only a few studies have evaluated the *k*-value of fly ash for the durability of concretes, especially for the chloride-penetration resistances. Additionally, the effects of cement type and water-to-binder (W/B) ratio on the *k*-value of fly ash for strength development of concretes have not been evaluated in a chemical approach yet. There is a lack of research evaluating the effect of fly ash reaction degree on its *k*-value, and the correlation between the *k*-value of fly ash for strength development and that for chloride-penetration resistance of concretes has not been discussed in previous studies. Therefore, the three objectives of this research are the following: (1) evaluation of the effect of cement type and W/B ratio on the *k*-value of fly ash for the concrete-strength development for a long period, (2) investigation in a simple approach the *k*-value of fly ash for the chloride-penetration resistance of concretes using the chloride-

penetration depth as a concrete-durability property (3) experimental evaluation of the effect of fly ash reactions on its *k*-value for the concrete-strength development and chloride-penetration resistance of concretes. In addition to these, the correlation between the *k*-value of fly ash for the strength and durability of the concrete is obtained. The discussion on these evaluations would be shown by using the results of chemical analysis and/or pore structure analysis. To deal with these problems, this thesis is organized as follow:

Chapter 1 provides the background and motivation of this study.

Chapter 2 presents a brief review on fly ash and its *k*-value for the concrete-strength development and chloride-penetration resistance of concretes.

Chapter 3 describes the experimental program consisting of materials and mixture proportions, the mixing, casting, and curing condition for the paste and concrete specimens. The test procedures were conducted to evaluate the *k*-value of fly ash. This study uses a low-calcium fly ash which is one of the most popular fly ashes in Japan. Control concrete samples with W/B ratios of 0.30, 0.40, 0.50, and 0.60 by mass were prepared to experimentally evaluate the *k*-value of fly ash. Cement was partially replaced with fly ash at ratios of 20% to 40% by mass for the paste and concrete specimens with a W/B ratio of 0.50. To evaluate the *k*-value of fly ash for the strength development of concretes, two types of cement, namely, ordinary Portland cement (OPC) and high-early-strength Portland cement (HSPC) were used for making paste and concrete specimens. In addition, a W/B ratio of 0.30 was further used for making OPC specimens to investigate effect of W/B ratio on the *k*-value of fly ash for the concrete-strength development. For evaluation of the *k*-value of fly ash for the chloride-penetration resistance of concretes, only the OPC and two fly ash replacement ratios of 20% (F20) and 40% (F40) by mass for the paste and concrete specimens with a W/B ratio of 0.50 were investigated. A sodium chloride solution (10% NaCl) was used for the immersion test.

Chapter 4 investigates the effects of cement type and W/B ratio on the *k*-value of low-calcium fly ash for the concrete-strength development by (1) examining the degree of fly ash reaction in pastes and analyzing hydration product using the X-ray diffraction analysis, (2) evaluating the Portlandite (CH) content in pastes as well as calculating the CH consumption by the pozzolanic reaction of fly ash, and (3) determining the compressive strength of concretes. The obtained results indicate that the cement type strongly affects the *k*-value of fly ash for concrete-strength development because of the significant difference in the Blaine fineness between cement and fly ash as well as the difference in the relationships between cement-to-water ratio and compressive strength of the control concretes. With the presence of calcite (approximate 4% by mass) in the OPC, the stabilization of monocarbonate indirectly resulting in the stabilization of ettringite led to a more significant increase in the compressive strength of OPC concrete containing fly ash despite a low degree of fly ash reaction in OPC paste compared with HSPC paste. For OPC concrete, a lower W/B ratio has a higher *k*-value at the early ages mainly because of cement-hydration-enhancement effect of fly ash, and all *k*-values increased significantly after 28 days due to the pozzolanic reaction of fly ash. Further, a modified equation of the CH consumption taking the cement-hydration-enhancement effect into account was firstly proposed to evaluate precisely the CH consumption in fly-ash cement paste. This result is consistent well with the result of the degree of fly ash reaction, especially for OPC paste with a low W/B ratio of 0.30.

Chapter 5 aims at simply evaluating the *k*-value of low-calcium fly ash for the chloride-penetration resistance of concretes using the chloride-penetration depth (x_d). The chloride concentration profile and the x_d are examined, whereas the *k*-value of fly ash for the chloride-penetration resistance of concretes is evaluated by using the apparent diffusion coefficient (D_{app}) of chloride ion as well as the x_d. Additionally, the results of pore size distribution in pastes are presented in this chapter. Results indicate that x_d could be used as a concrete-durability property to obtain the *k*-value of fly ash in a simple approach compared to the D_{app}. The *k*-values of fly ash based on the x_d of the concrete after the immersion periods of 13, 26, and 39 weeks ranged from 2.75 to 3.94 and from 1.96 to 2.69 for F20 and F40 samples, respectively. The replacement of 40% or less cement by fly ash in the concretes with a W/B ratio of 0.50 yielded chloride-penetration resistance that is as good as that of plain cement concrete with a W/B ratio of 0.30 after 39 weeks of exposure to a 10% NaCl solution with regard to the chloride-diffusion coefficient. In addition, the results of pore size distribution in pastes indicated that the refinement effect of the fly ash reaction related to the significant reduction of the volume of pore in the diameter range of 0.02 to 0.33 μm could improve the chloride-penetration resistance of concretes.

Chapter 6 discusses (1) the relationship between the *k*-value of fly ash for concrete-strength development and the degree of fly ash reaction, (2) the effect of the degree of fly ash reaction on the *k*-value for the chloride-penetration resistance of concretes, and (3) the difference between the *k*-value for the compressive strength and that for the chloride-penetration resistance. Briefly, the *k*-value of fly ash for the strength development of concretes increased linearly with an increase in the degree of fly ash reaction regardless of cement type and W/B ratio. Also, the *k*-value of fly ash based on the x_d of concretes increased linearly with the increment in the degree of fly ash reaction subsequent to the start of immersion. For OPC concretes with a W/B ratio of 0.50, the *k*-value of fly ash for the chloride-penetration resistance of the concrete was approximately 2.5 higher than that for the concrete-strength development at each corresponding time.

Chapter 7 summaries the conclusions of this study. Recommendations for the future research are suggested as well.

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CHAPTER 1

INTRODUCTION

1.1 GENERAL

Supplementary cementitious materials that are mostly considered as industrial wastes or by-products have been widely used in concrete for developing sustainable building materials [1–6]. The use of supplementary cementitious materials yields a significant reduction in CO_2 emissions associated with the cement production [7,8]. Among the supplementary cementitious materials, fly ash which is a principal by-product of coal-fired power plants is used enormously due to its economic, environmental, and technical advantages. Besides the mitigation of the CO_2 emission, the use of fly ash to replace a part of cement in concrete leads to (1) a reduction in the construction cost, (2) an increase of the workability of fresh concretes, (3) improvement of the mechanical and durability properties of concretes, and so on. According to the American Society for Testing and Materials (ASTM) C618 [9], two classes of fly ash are defined as Class F (low-calcium) and Class C (high-calcium) fly ashes. The main difference between these classes is the contents of calcium, silica, alumina, and iron in the fly ash. The chemical properties of the fly ash are largely influenced by the chemical content of the burned coal (i.e., anthracite, bituminous, and lignite). Possessing pozzolanic properties, the glassy silica and alumina of Class F fly ash requires a cementing agent, such as Portland cement, quicklime, or hydrated lime mixed with water to react and produce cementitious compounds. Unlike Class F fly ash, in addition to having pozzolanic properties, Class C fly ash also has some self-cementing properties in the presence of water. Additionally, according to the ASTM C 595 [10], fly ash is known as a pozzolanic material, which possesses little or no cementitious value. Thus, when fly ash is used to replace part of the cement in the concrete, its cementing efficiency that contributes to the mechanical and durability properties of concretes should be examined accurately.

Among the durability properties of concretes, the chloride-penetration resistance is a critical durability property in determining the service life of steel-reinforced concrete structures exposed to marine environments and de-icing salts [11–14]. High chloride-penetration resistance of concretes results in long service life of the steel-reinforced concrete structures and low cost of concrete maintenance [15,16]. It is well known that concretes containing fly ash exhibit high chloride-penetration resistance [1,2,17,18]. The use of fly ash as a supplementary cementitious material yields the significant reduction in the rate of penetration of chloride ions into concretes and greatly prolong the time for initial corrosion of the reinforcing steels in concretes with the same cover depth and water-to-binder (W/B) ratio [19].

To quantitatively evaluate the contribution of fly ash to certain properties of concretes, the cementing efficiency factor (*k*-value) was introduced as a parameter for fly ash, which is considered as cement [20]. Most of the proposed methods for determining the *k*-value of fly ash are for the compressive strength of concretes [20–24]. Only a few studies have investigated the *k*-value of fly ash with regard to the durability of concretes such as the carbonation and/or chloride-penetration resistances [25–27]. The relationship between the chloride-diffusion coefficient and the water-to-cement ratio of the control concretes has been employed in the evaluation of the *k*-value based on the chloride-penetration resistance of concretes. However, knowledge of this evaluation is extremely limited [26].

Although rapid chloride-penetration [28] and chloride migration tests [29] can mitigate complicated procedures and prolonged test time in an immersion test [30] in which the amount of chloride ion is measured according to the distance from the concrete surface to calculate the chloride-diffusion coefficient, these accelerated approaches cannot address real diffusion problems [31]. Recently, chloride-penetration depth was introduced in some studies [31–34], which was employed in calculating the chloride-diffusion coefficient [31,35,36]. Hence, the chloride-penetration depth could be considered as a concrete-durability property for evaluating the *k*-value of fly ash in a simple approach.

Considering the fly ash reaction, some studies [37–41] have investigated the degree of fly ash reaction in fly-ash cement systems. A high degree of fly ash reaction results in a high contribution of fly ash to certain properties of concrete containing the same cement type. It is well known that the fly ash reaction degree mainly depends on the portlandite (CH) content as a by-product produced by the cement hydration. As a result, the rate of the cement hydration plays an important role in controlling the fly ash reaction degree and affects the *k*-value of fly ash. In fact, Bijen and Selst [21] have concluded that the *k*-value of fly ash for the compressive strength strongly depends on the cement type. However, the experimental explanation for the effect of cement type on the *k*-value of fly ash was limited and unclear. Moreover, the relationship between the degree of the fly ash reaction and the *k*-value has not been clarified under various conditions, such as cement type and W/B ratio, especially for a long period in which the pozzolanic reaction of fly ash is vital in contributing not only to the concrete-strength development but also to the chloride-penetration resistance of concretes. Therefore, in order to better utilize the fly ash as a supplementary cementitious material in the concrete industry and more effectively design the mixture proportions of concrete containing fly ash, it is necessary to understand how the *k*-value of fly ash for the concrete-strength development can be affected by the cement type and W/B ratio in considering the degree of fly ash reaction for each corresponding condition.

1.2 AIMS OF THE RESEARCH

The three objectives of this research are the following:

(1) Evaluation of the effect of cement type and W/B ratio on the *k*-value of fly ash for the concrete-strength development for a long period.

(2) Investigation in a simple approach the *k*-value of fly ash for the chloride-penetration resistance of concretes using the chloride-penetration depth as a concrete-durability property.

(3) Experimental evaluation of the effect of fly ash reactions on its *k*-value for the concrete-strength development and chloride-penetration resistance of concretes.

In addition to these, the correlation between the *k*-value of fly ash for the strength and durability of the concrete is obtained. The discussion on these evaluations would be shown by using the results of chemical analysis and/or pore structure analysis.

1.3 SCOPE OF THE RESEARCH

The present study uses a low-calcium fly ash classified as type II according to the Japanese Industrial Standard (JIS) A 6201 [42] because it is one of the most popular fly ashes as a mineral admixture in Japan. Control concrete samples with W/B ratios of 0.30, 0.40, 0.50, and 0.60 by mass were prepared to experimentally evaluate the *k*-value of fly ash for concrete-strength development as well as chloride-penetration resistance of concretes. Cement was partially replaced with fly ash at ratios of 20% to 40% by mass for the paste and concrete specimens with a W/B ratio of 0.50.

For evaluation of the *k*-value of fly ash for the concrete-strength development, two types of cement, namely, ordinary Portland cement (OPC) and high-early-strength Portland cement (HSPC) were used for making paste and concrete specimens. In addition, a W/B ratio of 0.30 was further used for making OPC specimens to investigate effect of W/B ratio on the *k*-value of fly ash for the concrete-strength development.

For evaluation of the *k*-value of fly ash for the chloride-penetration resistance of concretes, paste and concrete specimens at a W/B ratio of 0.50 with only OPC and fly ash at two replacement ratios of 20% and 40% by mass were investigated. A sodium chloride solution (10% NaCl) was used for the immersion test.

1.4 THESIS OUTLINE

This thesis is organized as follow:

Chapter 1 provides the background and motivation of this study.

Chapter 2 presents a brief review on fly ash and its cementing efficiency factor for the concrete-strength development and chloride-penetration resistance of concretes.

Chapter 3 describes the experimental program consisting of materials and mixture proportions, the mixing, casting, and curing condition for the paste and concrete specimens. The test procedures were conducted to evaluate the *k*-value of fly ash.

Chapter 4 investigates the effects of cement type and W/B ratio on the *k*-value of low-calcium fly ash for the concrete-strength development by (1) examining the degree of fly ash reaction in pastes and analyzing hydration product using the X-ray diffraction analysis, (2) evaluating the CH content in pastes as well as calculating the CH consumption by the pozzolanic reaction of fly ash, and (3) determining the compressive strength of concretes.

Chapter 5 aims at simply evaluating the *k*-value of low-calcium fly ash for the chloride-penetration resistance of concretes using the chloride-penetration depth as a concrete-durability property. The chloride concentration profile and evaluation of *k*-value for the chloride-penetration resistance of concretes using the apparent diffusion coefficient of chloride ion are first mentioned. Then, the chloride-penetration depth and evaluation of the *k*-value in a simple approach are reported and discussed. Additionally, the results of pore size distribution in pastes are presented in this chapter.

Chapter 6 discusses (1) the relationship between the *k*-value of fly ash for concrete-strength development and the degree of fly ash reaction, (2) the effect of the degree of fly ash reaction on the *k*-value for the chloride-penetration resistance of concretes, and (3) the difference between the *k*-value for the compressive strength and that for the chloride-penetration resistance.

Chapter 7 summaries the conclusions of this study. Recommendations for the future research are suggested as well.

The flow chart of thesis organization is shown in Fig. 1.1.

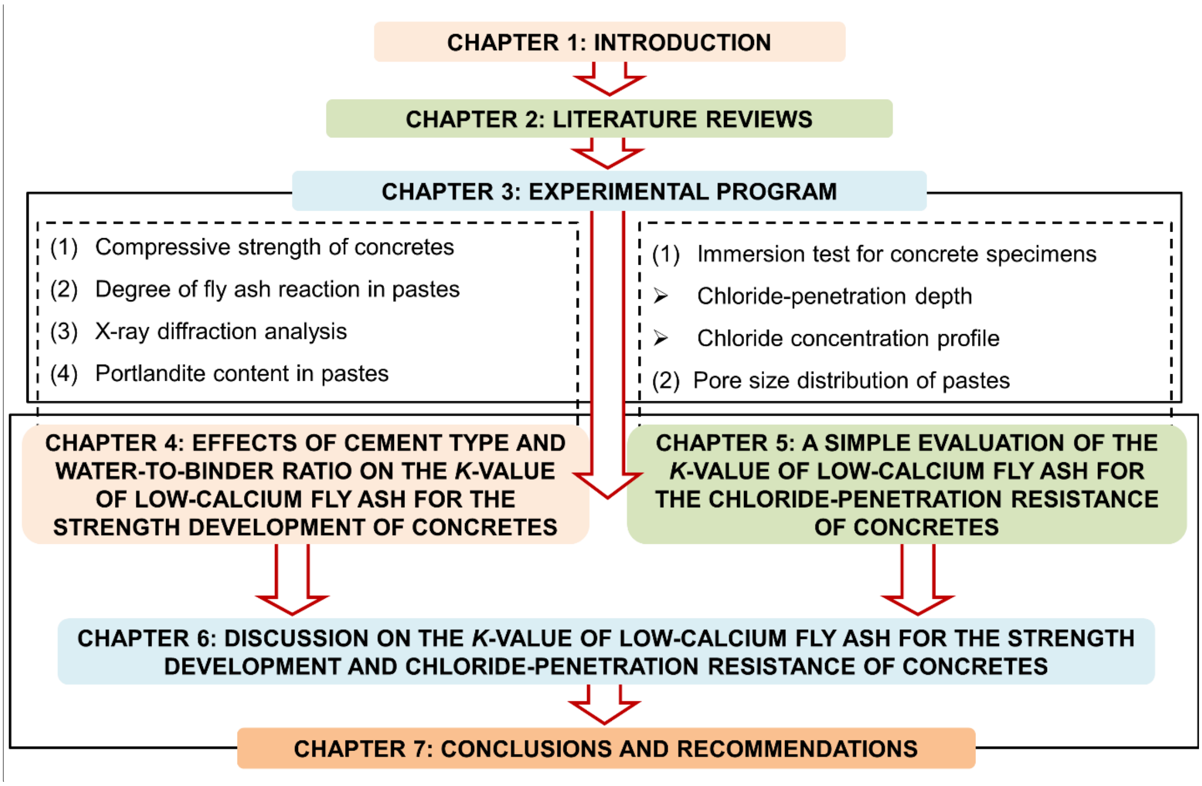

Fig. 1.1 Flow chart of thesis organization

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CHAPTER 2

LITERATURE REVIEWS

This chapter presents a brief review on properties of fly ash and fly-ash concrete in which the physical, chemical and pozzolanic properties of fly ash as well as compressive strength and chloride-penetration resistance of fly-ash concretes are mainly discussed. The cementing efficiency factor (*k*-value) of fly ash for the strength development and chloride-penetration resistance of concretes is briefly mentioned as well.

2.1 FLY ASH

As mentioned in Section 1.1, fly ash which is a principal by-product of coal-fired power plants has been used often as a supplementary cementitious material in the concrete industry because of its economic, environmental, and technical advantages. Besides, fly ash is utilized in other areas such as road basement material [1], cement clinkers [2], ceramic industry [3], zeolite synthesis [4], geopolymer concrete [5], and so on. In the past, fly ash was a waste material or by-product that the coal-fired power plants looked for an economically advantageous way to exploit it. In order to achieve this goal, numerous research works are being conducted in over the world. One of the most important areas of fly ash application can be the concrete production in which fly ash is utilized in mass, conventional and high performance concrete as a cement replacement material [6]. In the environmental aspect, this leads to a significant reduction in CO_2 emissions because the cement industry contributes to approximately 5%-8% of the global CO_2 emissions [7]. Hence, the more the utilization of fly ash as the cement replacement material, the more the reduction in the global CO_2 emissions related to the cement production. Additionally, fly ash is used in a technically advantageous way as a cement replacement material in the concrete production because of the following properties.

2.1.1 Properties of fly ash

The chemical properties of fly ash are strongly influenced by the properties of the coal burned and keep a vital role in classifying the fly ash. The main chemical compositions of fly ash are calcium (CaO), silica (SiO_2), alumina (Al_2O_3), and iron (Fe_2O_3), whereas the minor components of fly ash are magnesium, sulfur, sodium, potassium and loss on ignition (LOI). Based on the chemical compositions, fly ash is divided into two classes according to the American Society for Testing and Materials (ASTM) C618 [8]. Class F fly ash is mainly produced by burning anthracite or bituminous coal in which combination of SiO_2, Al_2O_3, and Fe_2O_3 content is exceeding 70% whereas Class C fly ash is produced by burning lignite or subbituminous coal that contains combination of aforementioned chemicals between 50% and 70%. In addition to having pozzolanic properties, Class C (high-calcium) fly ash may possess some cementitious properties (self-hardening when reacted with water) due to the high CaO content of more than 10%. Meanwhile, Class F fly ash is categorized as low-calcium fly ash or normal pozzolan because CaO content in Class F fly ash is less than 10%. In order to form calcium silicate hydrate (C-S-H) through pozzolanic reaction, it requires Portlandite (CH) formed from the cement hydration. Therefore, the chemical composition mainly affects the performance of fly ash in concrete.

In addition to the chemical properties of fly ash, its physical properties keep an important role in classifying the fly ash as well. According to the Japanese Industrial Standard (JIS) A 6201 [9], fly ash is divided into four types, as presented in Table 2.1. Type I is high quality fly ash with LOI less than 3.0% and Blaine fineness more than 5000 cm^2/g. Type II is fly ash with LOI less than 5.0% and Blaine fineness more than 2500 cm^2/g. Meanwhile, fly ash owning high LOI ranging from 5.0 to 8.0% or low Blaine fineness more than 1500 cm^2/g is classified as type III or type IV, respectively. Note that fly ash used in this study met the standard values of type II, which is generally used as a supplementary cementitious material in Japan, per JIS A 6201 [9] and was classified as class F (low-calcium) fly ash according to ASTM C618 [8].

Table 2.1 Quality of fly ash according to JIS A 6201 [9]

Properties	Type I	Type II	Type III	Type IV
Density (g/cm^3) (min.)	1.95			
Moisture content (%) (max.)	1.0			
SiO_2 (mass%) (min.)	45			
Loss on ignition (mass%) (max.)	3.0	5.0	8.0	5.0
Blaine fineness (cm^2/g) (min.)	5000	2500	2500	1500
Activity index (%) (min.)				
28 days	90	80	80	60
91 days	100	90	90	70

Blaine fineness of fly ash is one of the major physical properties of fly ash that determines the suitability of fly ash used in concrete because the size of fly ash particles significantly affects the properties of fly-ash cement systems. While cement particles have irregular polygonal shape, fly ash particles possess spherical shape as shown in Fig. 2.1 [10]. The spherical shape of fly ash particles enhances the workability of fresh concrete containing fly ash, especially at high fly ash replacement levels by ball bearing effect [6]. The density of fly ash usually ranges from 1.9 to 3.0 g/cm^3, whereas the Blaine fineness of fly ash varies from 1700 to 10000 cm^2/g [11]. The particle size of fly ash can be reduced through milling processes for obtaining a high Blaine fineness with different particle size distributions. Several studies [12–14] reported the advantage of using fine fly ash in improvement of compressive strength, mitigation of sulphate attack, enhancement of chloride-penetration resistance, reduction of drying shrinkage, and so on. Meanwhile, coarse fly ash is found to be less reactive and requires more water resulting in more porous structure of mortar/concrete. Briefly, the utilization of fine fly ash as supplementary cementitious materials could enhance the chemical and durability properties of concretes due to its higher pozzolanic activity than the coarse fly ash.

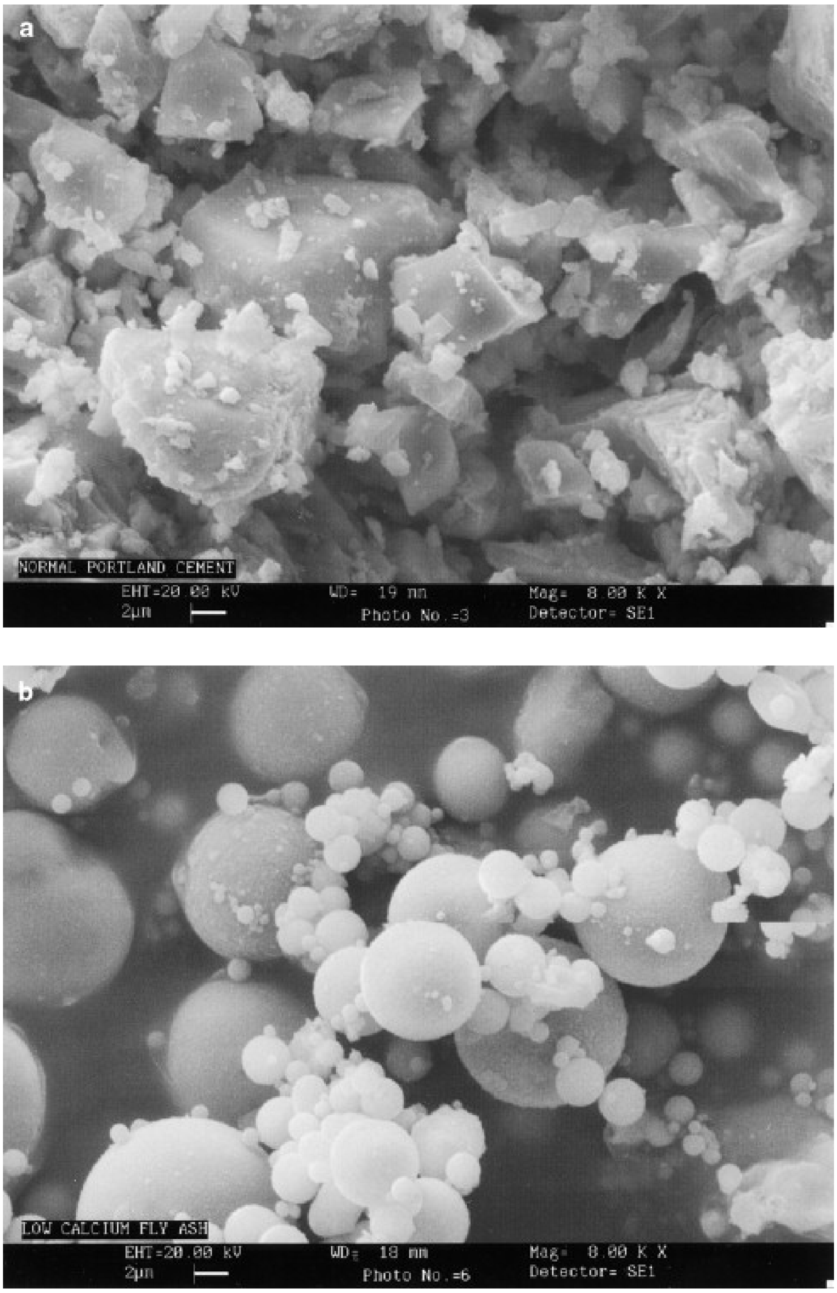

Fig. 2.1 Scanning electron microscope images (8000×) of (a) Portland cement and (b) low-calcium fly ash [10]

Fly ash mostly contains two principle constituents that are crystalline phases (i.e., quartz, mullite, hematite, ferrite, and so on) and amorphous phases (non-crystalline aluminosilicate glass). When used in concrete as a cement replacement material, fly ash possessing higher amorphous content is more effective in enhancing the pozzolanic reaction [15]. The reaction of active silica and alumina in fly ash with calcium hydroxide (CH) in the presence of water at normal temperature to form compounds possessing cementitious properties is defined as pozzolanic reaction. Papadakis described the pozzolanic reaction of fly ash, as shown in Eqs. (2.1) to (2.3) [10].

$$2S + 3CH \rightarrow C_3S_2H_3, \tag{2.1}$$

$$A + C\bar{S}H_2 + 3CH + 7H \rightarrow C_4A\bar{S}H_{12}, \tag{2.2}$$

$$A + 4CH + 9H \rightarrow C_4AH_{13}, \tag{2.3}$$

where S is SiO_2, C is CaO, H is H_2O, A is Al_2O_3, F is Fe_2O_3, and $\bar{S}$ is SO_3.

These reactions take place at different stages of curing to form various hydration products. Figure 2.2 shows the scanning electron microscope (SEM) images of cement paste specimen with 20% fly ash replacement ratio after (a) 3, (b) 14, (c) 49, and (d) 182 days of hydration [10]. It is interesting that fly ash particles are used as sites where cement hydration products (CH, ettringite) are grown at 3 days (Fig. 2.2a). This is because of their acidic character and thus they have great affinity for lime and alkalis. In the early hydration period of 0 to 21 days, no traces of reaction among fly ash particles can be detected, at least for the fly ash particle size that can be observed (Fig. 2.2b). After 28 days, the ash particles are extensively etched and surrounded by hydration products, while they retain their spherical shape (Fig. 2.2c). When pozzolanic reaction has significantly proceeded (6 months), fly ash particles are difficult to identify because they are covered by the reaction products (Fig. 2.2d). Few entirely round particles are still distinguished (nonreacted) [10]. This is well consistent the result of study by Ćojbašić et al. [16] in which the reaction mechanism in fly ash cement system is illustrated by the physical model, as illustrated in Fig. 2.3. Briefly, the pozzolanic reaction of fly ash only starts significantly after one or more weeks, as confirmed in several studies [10,15–18].

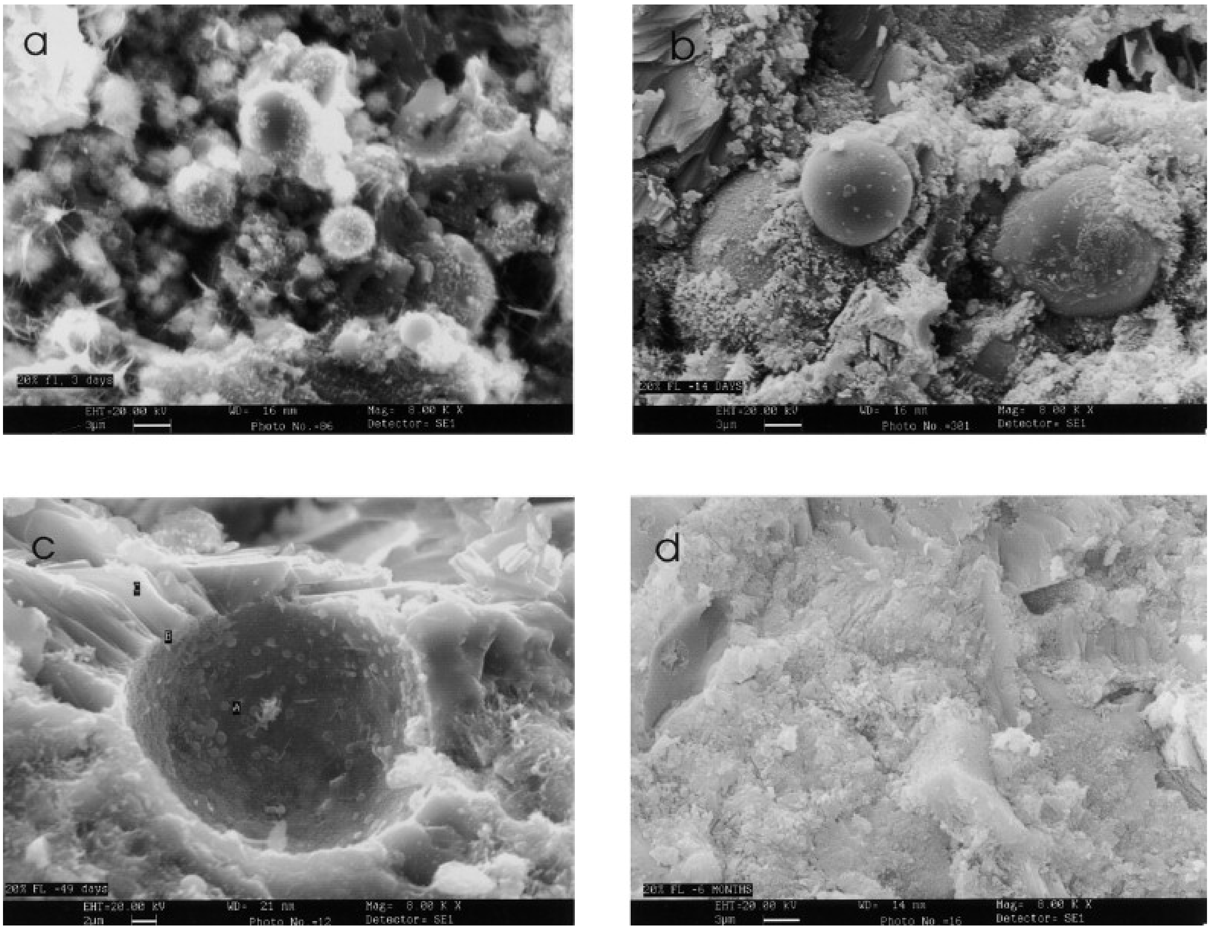

Fig. 2.2 SEM images (8000×) of cement paste specimen with 20% fly ash replacement ratio after (a) 3, (b) 14, (c) 49, and (d) 182 days of hydration

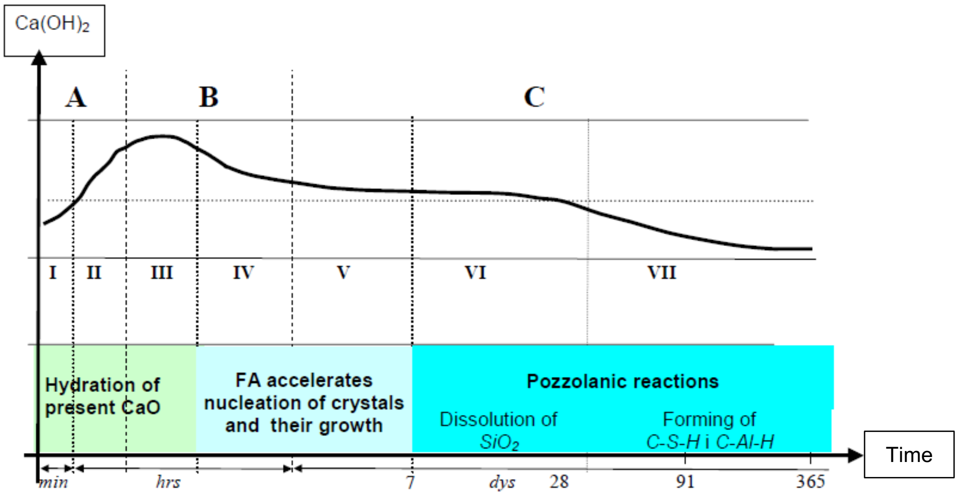

Fig. 2.3 Physical model of the reaction in fly ash cement system, A: the early stage; B: the medium stage; C: the late stage [16]

In addition to the properties of the fly ash, some external factors such as water-to-binder (W/B) ratio, replacement level, and curing temperature have been found to control the rate of pozzolanic reaction [20]. The high W/B ratio, low replacement level, and high curing temperature can result in the high degree of pozzolanic reaction of fly ash. To evaluate the degree of pozzolanic reaction of fly ash, CH content in fly-ash cement pastes is commonly examined and the CH consumption is generally used to indicate the degree of pozzolanic reaction. In other words, the pozzolanic reaction of fly ash leads to a reduction in CH content, as reported in previous studies [10,15,20,21]. While the pozzolanic reaction of low-calcium fly ash starts after 14 days of curing when the fly ash is used to replace fine aggregate (0%, 10%, 20%, and 30% addition by cement weight) as obviously seen in Fig. 2.4 [10], Poon et al. [21] found that the reduction in CH content relative to the cement content in Portland cement and fly-ash cement pastes with W/B ratio of 0.3 is significant after 28 days, as shown in Fig. 2.5.

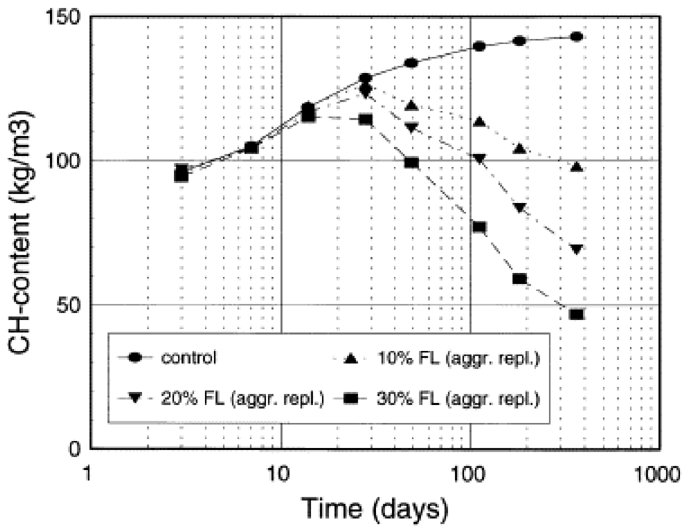

Fig. 2.4 Calcium hydroxide (CH) content in mortars with low-calcium fly ash to replace aggregate (0, 10, 20, and 30% addition by cement weight) as a function of time [10]

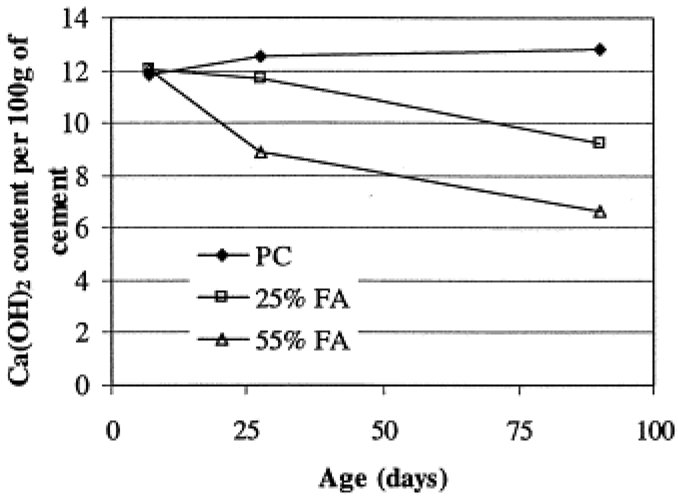

Fig. 2.5 CH content relative to the cement content in Portland cement (PC) and fly-ash (FA) cement pastes (based on ignited weight) with W/B ratio of 0.3 [21]

2.1.2 Properties of fly-ash concrete

Fly ash can improve workability of fresh concrete mainly due to the spherical shape of fly ash particles. When fly ash was used to replace a part of cement (by mass) in concrete, the volume of paste increases significantly owing to lower density of fly ash than that of cement. Moreover, the dilution effect of fly ash reduces the flocculation of the cement particles. Besides, the utilization of the fly ash as supplementary cementitious materials can reduce heat of hydration and thermal cracking in concrete at early ages [6].

Effects of fly ash on the compressive strength of hardened concrete are dependent on several factors such as physical and chemical properties of fly ash, W/B ratio, replacement level, curing condition. Because of the slow pozzolanic reaction, the compressive strength of low-calcium fly ash concrete is lower than that of specimen without fly ash at the early ages. However, it is improved significantly after 28 days due to the pozzolanic reaction of fly ash and becomes higher than that of the control specimen at the ages of 182 and 364 days, as shown in Fig. 2.6 [10]. The slow development in early-age strength of low-calcium fly ash concrete is often considered to be a major drawback [15,21], especially for high-volume fly ash concrete. In order to overcome this shortcoming, many methods including alkali activation have been explored to accelerate the early-age hydration of fly-ash cement systems. The use of nano-SiO_2 in fly-ash cement systems is one among them and more popular due to its advantages. The reasons for its popularity are (1) the accelerating effect on cement hydration, (2) its pozzolanic reaction, and (3) the improved particle packing of the matrix [6]. Li [22] found that addition of 4% nano-SiO_2 to high-volume fly ash concrete (HFAC) with 50% fly ash replacement ratio leads to an increase of both short-term strength and long-term strength. The concrete specimen that incorporates a combination of 50% fly ash and 4% nano-SiO_2 (SHFAC) has an increase in 3-day strength of 81% with respect to HFAC (containing 50% fly ash), and the 2-year strength was 115.9 MPa, higher than both of HFAC (about 108 MPa) and of Portland cement concrete (PCC) (about 103.7 MPa), as shown in Fig. 2.7.

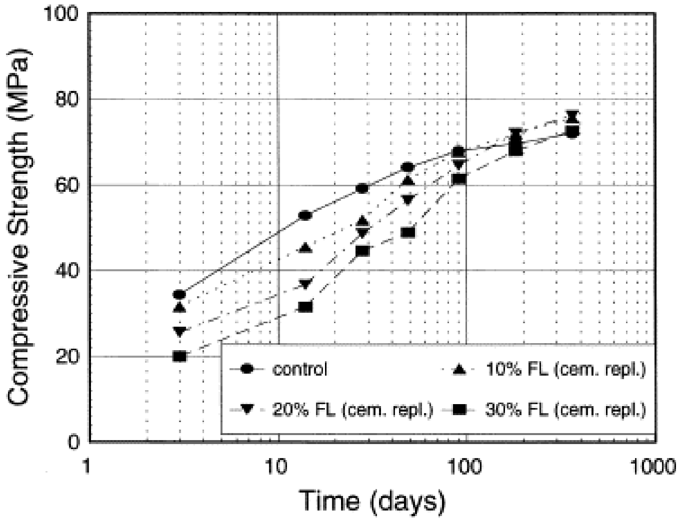

Fig. 2.6 Compressive strength development of mortars without and with low-calcium fly ash at 10, 20, and 30% cement replacement [10]

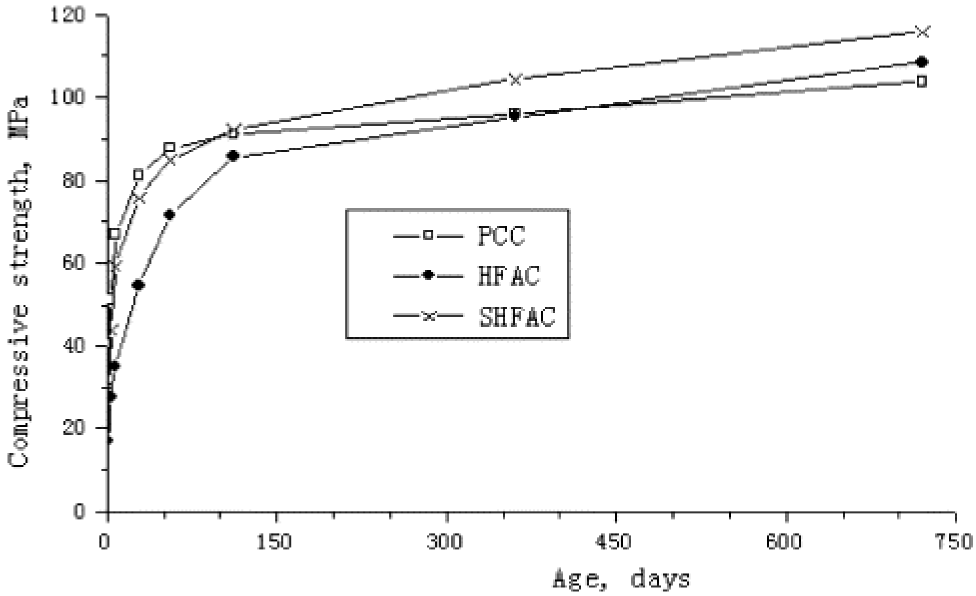

Fig. 2.7 Development of the compressive strength with time [22]

In addition, Li [22] reported that fly ash replacements in concrete increased both the pore size and the total porosity at 28 days. When high-volume fly ash cement systems incorporating nano-SiO_2, the cumulative mercury intrusion curve of SHFAC (containing 50% fly ash and 4% nano-SiO_2) lies on the finer side, and there is insignificant difference between SHFAC and PCC (Portland cement concrete) existing in the pores with diameter larger than 0.05 µm, as seen in Fig. 2.8. Meanwhile, the pore size distribution of SHFAC and HFAC (containing 50% fly ash) decreased significantly at the age of 2 years compared to that of PCC, as shown in Fig. 2.9.

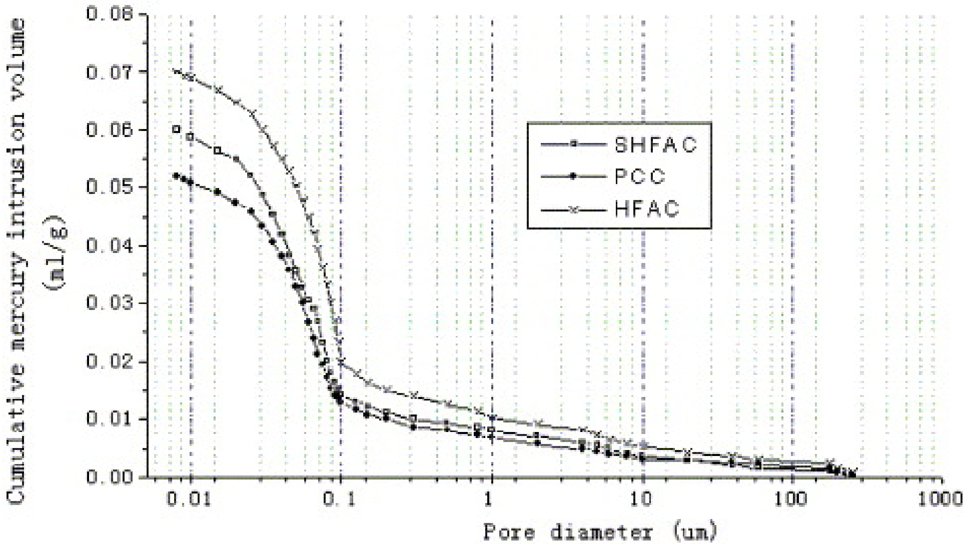

Fig. 2.8 Pore size distribution of concrete with a W/B ratio of 0.28 at 28 days [22]

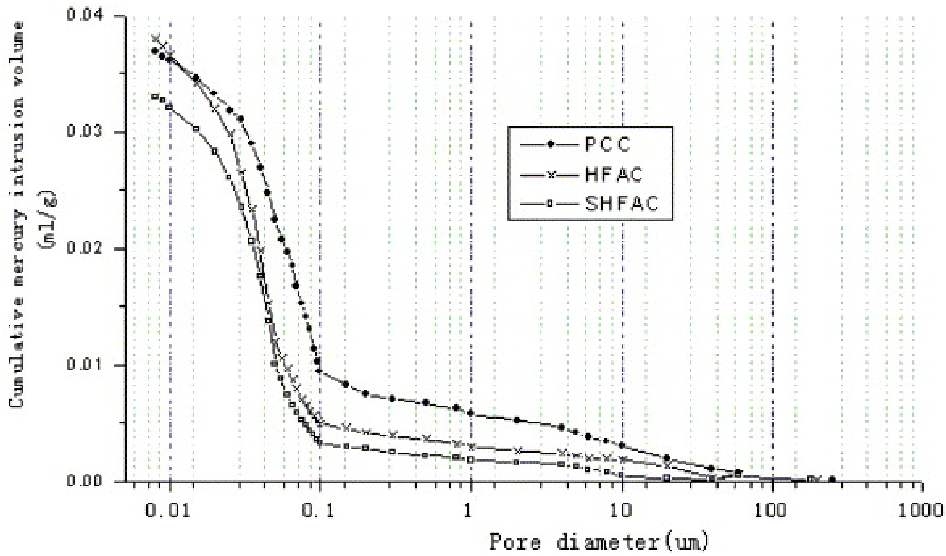

Fig. 2.9 Pore size distribution of concrete with a W/B ratio of 0.28 at 2 years [22]

The significant reduction in the pore structure yields the high resistance of fly ash concrete against the ingress of aggressive agents. The better quality of the interfacial transition zone (ITZ) between cement paste and coarse aggregates in fly-ash concretes may be another factor affecting the transport of aggressive agents in concrete [23]. Fly ash has some major beneficial effects on the performance of reinforced concrete structures. The most important one is the enormous reduction of the rate of penetration of chloride ions into concrete [23–26]. Generally, the time to initial corrosion of reinforcing steel is used to indicate the service life of a reinforced concrete structure in a marine environment [27]. Reinforced concrete with a shorter time to initial corrosion tends to have a shorter service life. Previous studies [27–29] found that a small amount of initial corrosion around the surface area of the reinforcing steel could lead to great damage of the reinforced concrete structure. This corrosion occurs when the amount of free chloride exceeds the chloride threshold level. As a result, the alkalinity around the reinforcing steel is reduced and the steel's protective film is destroyed. In the presence of sufficient amount of both moisture and oxygen, the corrosion of the steel begins and accelerates at an increasingly high rate. Designing marine reinforced concrete that is highly resistant to chloride not only prolongs its service life but also protects its reinforcing steel from other chemical attacks by specifying an appropriate concrete cover. This cover could be determined from the equivalent penetration depth of the chloride threshold. Fly ash has been found to reduce the chloride threshold in concrete because it gives concrete better protection against water and substantially lowers the rate of chloride penetration. Therefore, the use of fly ash in marine concrete could prolong the time to initial corrosion and reduce overall steel corrosion [26].

Additionally, fly ash improves the chloride binding capacity of the binder [30–32]. This can be attributed to both (1) more efficient chemical binding due to higher proportions of active alumina often present in fly ash and (2) better physical adsorption of chloride as the result of more gel produced in the course of hydration [31]. Dhir et al. [32] found that the chloride binding capacity of cement paste increases with the increase in fly ash replacement level up to 50%, and then declines at 67%.

2.2 CEMENTING EFFICIENCY FACTOR (*K*-VALUE)

The concept of *k*-value is firstly introduced by Smith [33] to develop a rational method for incorporation of fly ash in concrete. The mass F of fly ash can be considered as the equivalent mass *k*F of cement to determine its contribution to certain properties of concretes. This means the *k*-value concept can be applied to the mechanical and durability properties of concretes. Generally, the *k*-value concept is based on the comparison of certain properties of a concrete with fly ash against a reference concrete without fly ash. In other words, the *k*-value explains the ratio between the contribution of the Portland cement and that of fly ash to the mechanical and/or durability properties of concretes.

2.2.1 *K*-value of fly ash for the strength development of concretes

The *k*-value is generally determined through compressive strength test due to its simplicity and reliability. Babu and Rao [34] found that the *k*-value of fly ash increases with time and depends on physical and chemical properties of fly ash. In fact, fly ash exhibits a very little cementing efficiency at the early ages and acts rather like fine aggregate (filler), but at later ages, the pozzolanic property becomes effective leading to a considerable strength improvement. This obviously means that the cementing efficiency of fly ash improves with age due to the pozzolanic reaction [6]. Also, Papadakis and Tsimas [35] found that the *k*-value for equivalent strength is correlated with the active silica content of the fly ash which is mainly related to the pozzolanic reaction. Gopalan and Haque [36] reported that the other factors such as curing period, strength of concrete and class of fly ash affect the *k*-value as well. Furthermore, Bijen and Selst [37] found that the *k*-value also depends upon the external factors such as water-to-cement (W/C) ratio, cement type. It is reported that the *k*-value is a function of the W/C ratio and tends to decrease with an increase in the W/C ratio [37]. However, the effect of cement type on the *k*-value of fly ash has not been explained clearly. On the other hand, Smith suggested that the *k*-value of fly ash does not vary with W/C ratio. A constant *k*-value of 0.25

for fly ash in terms of the concrete-strength development was obtained in his study [33]. Also, the European Standard EN 206-1 [38] permits a constant *k*-value of 0.4 for fly ash. Therefore, it is necessary to quantitatively evaluate the contribution of the fly ash to the concrete-strength development under various conditions, such as a W/B ratio, replacement ratio of fly ash, and type of cement towards the better utilization of fly ash as supplementary cementitious materials in concrete.

The concrete-strength development has often been employed as a vital mechanical property for determining the *k*-value of fly ash by using the relationship between the compressive strength and the W/C ratio [34,36,37] or cement-to-water (C/W) ratio [39,40], as shown in Fig. 2.10. The equivalent C/W ratio, hereafter $(C/W)_{eq.}$, is calculated by substituting the compressive strength of the concrete containing fly ash into the relationship. Then, the *k*-value for the concrete-strength development is calculated using Eq. (2.5), which is derived from Eq. (2.4).

$$(C/W)_{eq.} = (C + kF)/W, \tag{2.4}$$

$$k_s = \{(C/W)_{eq.} /(C/W) - 1\} \times (C/F), \tag{2.5}$$

where C, F, and W are the unit contents (in kg/m^3) of cement, fly ash, and water, respectively, in the mixture and k_s is the *k*-value of the fly ash for the strength development of concrete (fraction).

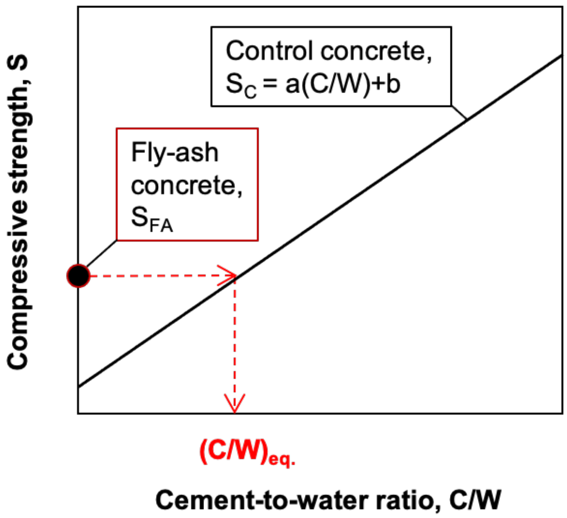

Fig. 2.10 Principle of calculating of the *k*-value of fly ash for the compressive strength of concretes

2.2.2 *K*-value of fly ash for the chloride-penetration resistance of concretes

For the chloride-penetration resistance of concretes, Aponte et al. [41] used a relationship between the chloride-diffusion coefficient and W/C ratio as a power function, as illustrated in Fig. 2.11, whereas Follini et al. [42] considered it as a linear correlation. Therefore, it is necessary to confirm the best fit for this relationship to evaluate the *k*-value of fly ash with regard to chloride-penetration resistance of concretes. The *k*-value for the durability of concretes is calculated using Eq. (2.6) as follows:

$$k_d = \{(W/C)/(W/C)_{eq.} - 1\} \times (C/F), \tag{2.6}$$

where $(W/C)_{eq.}$ is the equivalent water-to-cement ratio (fraction) and k_d is the *k*-value of fly ash for the chloride-penetration resistance of concrete (fraction).

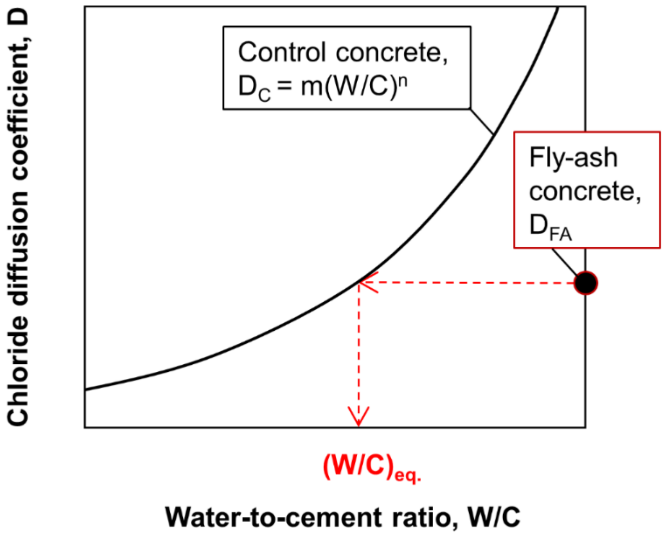

Fig. 2.11 Principle of calculating of the *k*-value of fly ash for the chloride-penetration resistance of concretes by using the chloride-diffusion coefficient

2.3 SUMMARY

In general, the *k*-value of fly ash for the strength development of concretes (i.e., k_s) depends mainly on the physical and chemical properties of fly ash, cement type, W/B ratio, curing condition, and so on. It includes not only the pozzolanic reactivity of fly ash but also the physical effect. The pozzolanic reactivity of fly ash significantly contributes to concrete-strength development at the later stage, especially after 28 days of curing for the low-calcium fly ash. Meanwhile, the physical effect of fly ash that consists of filling space and enhancing cement-hydration can contribute to the concrete-strength development at the early stage. Hence, the physical effect and chemical reaction of fly ash significantly influence the k_s.

For the *k*-value of fly ash for the chloride-penetration resistance of concretes (i.e., k_d), only a few studies have investigated the k_d. The relationship between the chloride-diffusion coefficient and the W/C ratio of the control concretes has been employed in the evaluation of the k_d. However, knowledge of this evaluation is extremely limited and unclear. In addition,

the k_d would be different from the k_s depending on the contribution of fly ash to the durability and mechanical properties of concretes and they should be investigated experimentally.

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CHAPTER 3

EXPERIMENTAL PROGRAM

This chapter describes the experimental program including (1) the materials, (2) the mixture proportions, (3) the mixing, casting and curing condition, and (4) the test procedures in this study.

3.1 MATERIALS

3.1.1 Cement

Two types of cement, namely, ordinary Portland cement (OPC) and high-early-strength Portland cement (HSPC) were used for making paste and concrete specimens. These cements meet the Japanese Industrial Standard (JIS) R 5210 [1]. The chemical compositions and physical properties of the cements, as provided by Taiheiyo Cement Corp. Tokyo, Japan, are shown in Table 3.1.

Table 3.1 Chemical compositions and physical properties of cements

	OPC	HSPC
CaO (mass%)	65.05	65.22
SiO_2 (mass%)	20.29	20.55
Al_2O_3 (mass%)	4.91	4.94
Fe_2O_3 (mass%)	2.96	2.50
MgO (mass%)	1.20	1.28
K_2O (mass%)	0.39	0.38
Na_2O (mass%)	0.26	0.26
SO_3 (mass%)	1.93	3.00
Loss on ignition (mass%)	2.44	0.73
Density (g/cm^3)	3.16	3.14
Blaine fineness (cm^2/g)	3290	4450
Compressive strength (N/mm^2)		
1 day	−	27.5

3 days	34.4	46.2
7 days	47.0	57.5
28 days	61.5	67.9

The mineralogical phase compositions of the binders determined by X-ray diffraction (XRD) analysis using Rietveld refinement are presented in Table 3.2. The HSPC contained high contents of C_3S and C_3A, and low contents of C_2S and C_4AF compared with the OPC. There was no significant difference in the total sulphate phase contents (i.e., gypsum, bassanite, and syngenite combined) for these cements. The OPC had higher amounts of calcite (4.2 mass%) than the HSPC (0.7 mass%), which may be due to the addition of admixture allowed at a maximum content of 5% by the JIS R 5210 [1].

Table 3.2 Mineralogical phase compositions of cements (mass%)

	OPC	HSPC
Alite, C_3S	58.3	63.4
Belite, C_2S	10.2	9.4
Aluminate, C_3A	6.5	8.9
Ferrite, C_4AF	12.8	9.5
Calcite	4.2	0.7
Gypsum	2.3	1.1
Bassanite	2.4	3.9
Syngenite	3.3	3.1

3.1.2 Fly ash

Fly ash (from Chugoku Electric Power Co. Inc., Hiroshima, Japan) used in this study met the standard values of type II per JIS A 6201 [2] and was classified as class F (low-calcium) according to ASTM C618 [3]. The measured chemical compositions and physical properties of fly ash are shown in Table 3.3. The XRD-Rietveld analysis of the fly ash indicates the presence of 12.3% mullite, 4.9% quartz, and 82.8% amorphous content by mass. Fly ash powder was mixed with 10% corundum as a reference to calculate the amorphous content.

Table 3.3 Chemical compositions and physical properties of fly ash

	Type II per JIS A 6201	Measured value
CaO (mass%)	-	3.12
SiO_2 (mass%)	more than 45	53.53
Al_2O_3 (mass%)	-	28.11
Fe_2O_3 (mass%)	-	5.17
MgO (mass%)	-	1.21
K_2O (mass%)	-	0.90
Na_2O (mass%)	-	0.79
SO_3 (mass%)	-	0.63
Loss on ignition (mass%)	less than 5.0	2.08
Density (g/cm^3)	more than 1.95	2.37
Blaine fineness (cm^2/g)	more than 2500	3530
Moisture content (%)	less than 1.0	0.1
Activity index (%)		
28 days	more than 80	82
91 days	more than 90	96

3.1.3 Aggregate

Crushed stone and manufactured sand that meet the JIS A 5005 [4] were used in the concrete as coarse and fine aggregates, respectively. The fine aggregate had a fineness modulus of 2.71, whereas the coarse aggregate had a maximum size of 20 mm. Note that the coarse aggregate has two types, which are 5–15 mm and 10–20 mm, and their mass ratio is 50:50. Moreover, the 5–15 mm coarse aggregate had a fineness modulus of 6.24, whereas the 10–20 mm coarse aggregate had a fineness modulus of 7.08. The physical properties of aggregates, as provided by Fukuhara Sangyo Co. Ltd., Japan, are listed in Table 3.4.

Table 3.4 Properties of aggregates

Aggregates	Type - Notation	Properties
Fine aggregate	Manufactured sand - S	Surface-dry specific gravity: 2.61 g/cm^3 Water absorption: 1.04%
Coarse aggregate	Crushed stone - G	Surface-dry specific gravity: 2.61 g/cm^3

	(50% type of 5–15 mm and 50% type of 10–20 mm)	Water absorption: 0.71%

3.1.4 Chemical admixtures

Chemical admixtures (from Flowric Co. Ltd., Japan), including a superplasticizer or water-reducing agent, and an air-entraining agent as per JIS A 6204 [5] were used to achieve the slump and air content of 10.0 ± 2.0 cm and 5.0 ± 0.5%, respectively, as the targets for all the fresh concretes in material designs.

Superplasticizer with a brand name of SF500S was used for the mixture of concrete with a low water-to-binder (W/B) ratio of 0.30, whereas water-reducing agent with a brand name of SV10L was used for the other mixtures to achieve the desired slump. Two brands of air-entraining agents with names AE-6 and AE-9B were alternatively employed in this study to achieve the desired air content in concrete mixture. The AE-6 is one of the usually-used agents, and the AE-9B is for fly-ash concretes. Details of the quantities of chemical admixtures are listed in Table 3.5.

3.2. MIXTURE PROPORTION

3.2.1 Concrete specimens

Table 3.5 shows the mixture proportion of concrete used in this study. Control concrete samples with water-to-binder (W/B) ratios of 0.30, 0.40, 0.50, and 0.60 were prepared to experimentally evaluate the *k*-value of fly ash for concrete-strength development as well as chloride-penetration resistance of concretes as mentioned in Chapter 2. Cement was partially replaced with fly ash at ratios of 20% (F20), 30% (F30), and 40% (F40) by mass for the concretes with a W/B ratio of 0.50, as shown in Table 3.5. In addition, a W/B ratio of 0.30 was further used for making OPC concrete specimens to investigate effect of W/B ratio on the *k*-value of fly ash for the concrete-strength development which will be discussed in Chapter 4.

A water content of 170 kg/m^3 and coarse aggregate content of 932 kg/m^3 were kept constant for seventeen concrete mixtures as listed in Table 3.5. All the concrete mixtures were designated following a code of C*x*-PF*y* which means concrete with W/B ratio of *x*, cement type of P (P = O means ordinary Portland cement; P = H means high-early-strength Portland cement), and fly ash replacement ratio of *y*%. For example, mixture named C50-OF20 means concrete with W/B ratio of 0.50, OPC as the cement, and fly ash replacement ratio of 20%. Details of seventeen mixture proportions and the measured properties of all the fresh concretes are listed in Tables 3.5 and 3.6, respectively. Note that casting temperature was recorded immediately after mixing.

Table 3.5 Mixture proportion of concrete

Group	Mixture	W/B	F/(C+F) (mass%)	Unit content (kg/m^3)					Chemical admixture (kg/m^3)		
				W	C	F	S	G	WR	SP	AE
Control HSPC concrete	C30-HF0	0.30	0	170	567	0	650	932	−	4.25	3.40*
	C40-HF0	0.40	0	170	425	0	767	932	5.10	−	5.10*
	C50-HF0	0.50	0	170	340	0	838	932	2.55	−	2.04*
	C60-HF0	0.60	0	170	283	0	885	932	1.84	−	1.13*
HSPC; W/B 0.50	C50-HF20	0.50	20	170	272	68	820	932	2.38	−	2.38*
	C50-HF30	0.50	30	170	238	102	810	932	2.55	−	2.04**
	C50-HF40	0.50	40	170	204	136	801	932	2.55	−	2.72**
Control OPC concrete	C30-OF0	0.30	0	170	567	0	653	932	−	3.97	2.27*
	C40-OF0	0.40	0	170	425	0	770	932	3.40	−	1.70*
	C50-OF0	0.50	0	170	340	0	840	932	1.53	−	1.36*
	C60-OF0	0.60	0	170	283	0	887	932	0.85	−	1.13*
OPC; W/B 0.50	C50-OF20	0.50	20	170	272	68	821	932	1.70	−	2.72*
	C50-OF30	0.50	30	170	238	102	812	932	2.55	−	1.70**
	C50-OF40	0.50	40	170	204	136	802	932	2.04	−	2.38**
OPC;	C30-OF20	0.30	20	170	453	113	621	932	−	4.82	6.80*

W/B	C30-OF30	0.30	30	170	397	170	606	932	−	5.10	3.40**
0.30	C30-OF40	0.30	40	170	340	227	590	932	−	5.10	4.54**

W/B = W/(C+F) is the water-to-binder ratio by mass, F/(C+F) is the replacement ratio of fly ash by mass, W is water, C is cement, F is fly ash, S is fine aggregate (manufactured sand), and G is coarse aggregate (crushed stone).

WR is the water-reducing agent (SV10L), SP is the superplasticizer (SF500S), and AE is the air-entraining agent. * denotes the AE-6 type, whereas ** denotes the AE-9B type.

Table 3.6 Properties of fresh concrete

Group	Mixture	W/B	F/(C+F) (mass%)	Properties of fresh concrete		
				Temperature (°C)	Slump (cm)	Air (%)
Control HSPC concrete	C30-HF0	0.30	0	16.2	15.0	5.1
	C40-HF0	0.40	0	15.2	9.0	4.5
	C50-HF0	0.50	0	15.3	8.5	5.1
	C60-HF0	0.60	0	15.3	7.5	5.0
HSPC; W/B 0.50	C50-HF20	0.50	20	15.3	11.5	5.0
	C50-HF30	0.50	30	16.7	11.0	5.4
	C50-HF40	0.50	40	15.6	14.0	5.1
Control OPC concrete	C30-OF0	0.30	0	18.6	11.0	5.2
	C40-OF0	0.40	0	14.3	7.0	5.2
	C50-OF0	0.50	0	17.5	11.5	5.3
	C60-OF0	0.60	0	13.7	8.5	5.2
OPC; W/B 0.50	C50-OF20	0.50	20	21.6	11.0	4.7
	C50-OF30	0.50	30	16.9	12.5	5.4
	C50-OF40	0.50	40	16.9	13.0	4.8
OPC; W/B 0.30	C30-OF20	0.30	20	23.6	9.5	5.1
	C30-OF30	0.30	30	23.7	13.0	4.7
	C30-OF40	0.30	40	23.8	12.0	4.8

3.2.2 Paste specimens

Paste specimens were prepared with the same W/B ratio as that of the concrete specimens. No chemical admixtures, as well as fine and coarse aggregates, were used in making the paste specimens. Low-calcium fly ash was used to partially replace cement at mass ratios of 0% (F0), 20% (F20), 30% (F30), and 40% (F40).

3.3 MIXING, CASTING AND CURING

The materials were prepared at an ambient temperature of 20 ºC. The concretes were mixed in the laboratory using a mechanical mixer. The concrete specimens used for the compressive strength test and the chloride-penetration test were cast in cylindrical molds of 100 mm diameter and 200 mm height, whereas the paste specimens used for chemical analyses and pore structure analysis were cast in 16 mL polypropylene bottles. All the concrete and paste specimens were cured under a sealed condition and stored at 20 ºC until the designated tests.

3.4 TEST PROCEDURE

3.4.1 Compressive strength of concretes

At the ages of 3, 7, 28, 91, 182, and 364 days, the compressive strength of concretes was determined according to JIS A 1108 [6] with the loading rate of 1.5 kN/s. Three specimens of each concrete mixture were examined, and the mean value of these measurements is reported.

3.4.2 Immersion test for concrete specimens

(1) Procedure

At the age of 91 days, the concrete specimens were fully immersed in a sodium chloride solution (10% NaCl). Prior to the immersion, the concrete specimens were demolded and cut into two parts, each of dimensions 100 mm height and 100 mm diameter. Then, all the surfaces of the specimens, except the cutting surface, were coated with epoxy resin. In addition, the specimens were submerged in water for at least 3 days before being immersed in the solution of 10% NaCl. The concentration of the solution was checked every three weeks in order to maintain the concentration range of 10 ± 0.5% for immersion periods of 13, 26, and 39 weeks at 20 ºC.

(2) Chloride-penetration depth

After the immersion periods of 13, 26, and 39 weeks, three specimens of each concrete mixture were removed from the solution and dried with paper towels. Thereafter, the dried specimens were split axially. Then, the chloride-penetration depth (x_d) was examined by spraying 0.1 M silver nitrate solution ($AgNO_3$) [7–10] and using an electronic caliper with an accuracy of 0.01 mm at ten points with 9 mm intervals, as illustrated in Fig. 3.1 (a). The mean values of the measurements were recorded for each mixture and for each immersion time. The white zone in Fig. 3.1 (a) represents an area in which free chloride ion penetrated, whereas the bronze-colored zone shows the area not penetrated by chloride ion.

(3) Concentration profile of chloride ion in concretes

After 39 weeks of immersion, the x_d of the concrete specimens was measured. Thereafter, the specimens were cut using an oil cutter at approximately 3 ± 0.5 mm intervals for each slice, as illustrated in Fig. 3.1 (b). The number of slices was dependent on the x_d of the concrete after immersion, but there should be at least four layers for the chloride-penetrated area and three layers for the non-chloride area. The slices were soaked in acetone for 30 min to remove the residual oil on the surfaces of the slices after cleaning with paper towels. This process was repeated two times, the acetone and paper towels were changed after each process, to completely remove the oil on the slices. The cleaned slices were cut into samples of cross section less than 5 mm x 5 mm and dried in a desiccator for at least 3 days. The samples were ground into powders of <150 μm in size prior to the measurement of the total chloride ion content.

One gram of the powder sample was mixed with 50 mL of a 2 M HNO_3 solution in a beaker covered with a watch glass. Then, the solution was heated to 120 ºC and stirred continuously at 300 rpm for 30 min to effectively extract all the chloride ions from the powder sample. In accordance with JIS A 1154 [11], 1 mL of H_2O_2 was further added into the beaker to eliminate possible contaminations in the powder samples containing fly ash. After cooling to the ambient temperature, the solution was filtered through a filter paper. Approximately 50 mL of deionized water was used to rinse the beaker as well as the filter paper so that the filtrate could reach a volume of 100 mL. Thereafter, the concentration of chloride ion in the filtrate was examined using a Dionex ICS-1000 ion chromatography system confirmed by JIS A 1154 [11].

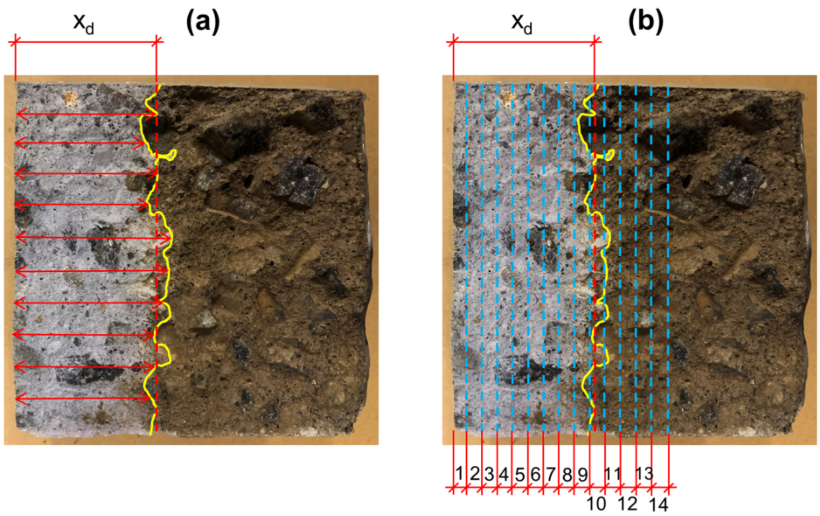

Fig. 3.1 Concrete sample after immersion test: (a) measurement of chloride-penetration depth (x_d) and (b) sampling of concrete specimens to examine the concentration profile of chloride ion

3.4.3 Degree of fly ash reaction in pastes

The degree of fly ash reaction in pastes was measured at the ages of 3, 7, 28, 91, 182, and 364 days by using selective dissolution method (SDM). The test samples were obtained by cutting the hardened pastes and selecting the materials in the size range of 2.5–5.0 mm. The samples were soaked in acetone under the pressure of –0.1 MPa for 30 min to stop further hydration.

This operation was repeated three times with the acetone being changed. Prior to the measurement, the samples were dried in a vacuum desiccator for 3 days after they were ground into powder of <150 μm.

To investigate the degree of fly ash reaction, Ohsawa et al. [12] proposed a method by using 2 M hydrochloric acid (HCl) and 5% sodium-carbonate aqueous solution (Na_2CO_3). The procedure for measuring the degree of fly ash reaction in paste specimens is illustrated in Fig. 3.2. Subsequently, the degree of fly ash reaction was calculated by using Eq. (3.1).

$$\alpha = 1 - \{X(1 - Ig')/a_2\}/\{(1 - Ig)a_1\} \quad (3.1)$$

where α is the degree of fly ash reaction (fraction), X is the extracted residue of the hydrated fly ash in a 1 g hydrated paste (fraction), a_1 is the original fraction of fly ash in the ignited base, a_2 is the extracted residue of a 1 g fly ash (fraction), Ig is the ignition loss of the hydrated paste (fraction), and Ig' is the ignition loss of the extracted residue (fraction).

It is noted that $\{X(1-Ig')/a_2\}$ is the amount (ignited base) of unreacted fly ash in a 1 g hydrated paste while $\{(1 - Ig)a_1\}$ is the total amount (ignited base) of reacted and unreacted fly ash in a 1 g hydrated paste. More details about this test could be found in the previous studies [13–15].

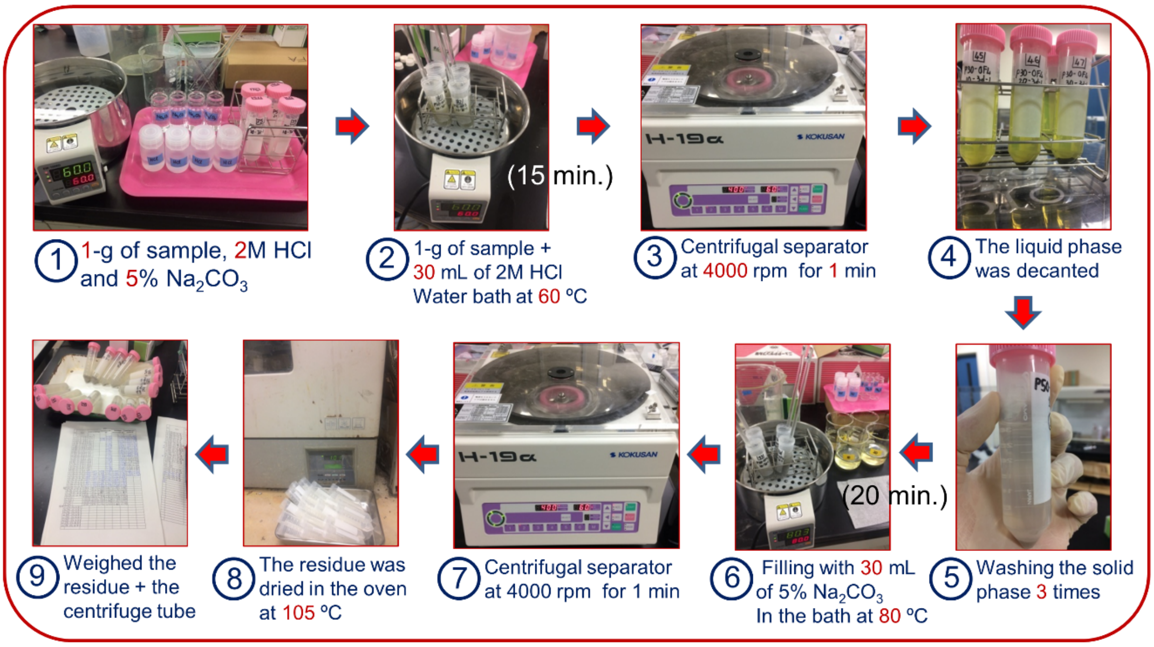

Fig. 3.2 Measurement of fly ash reaction degree by using SDM

3.4.4 X-ray diffraction (XRD) analysis

To identify differences between the hydration products of the cement and fly ash in the HSPC and OPC pastes, XRD patterns of the hydrated pastes (F0 and F40) were examined by using XRD equipment (D2 Phaser, Bruker, ARS K.K., Germany) at 3, 7, 28, and 364 days. The same samples were used for the XRD analysis and the degree of fly ash reaction. The measurement conditions of the XRD analysis were a scanning range of 2θ from 5° to 65° with CuKα radiation, voltage of 30 kV, electric current of 15 mA, a step width of 0.02°, and a scanning speed of 2°/min.

3.4.5 Portlandite content in pastes

The portlandite (CH) content in pastes were determined by thermogravimetry and differential thermal analysis (TG-DTA) (DTG-60H, Shimadzu Corporation, Japan) at the ages of 3, 7, 28, 91, 182, and 364 days. The same samples were used to examine the CH content and the degree of fly ash reaction. For the TG-DTA measurement, the temperature of a sample was increased at 20 °C/min and held at 100 °C for 30 min, before being increased at 20 °C/min to 1000 °C in a N_2 environment. The CH content was calculated from the mass loss between ~400 and 540 °C from dehydration of CH in a paste according to Eq. (3.2). The mass loss was calculated from the measured differential thermal-analysis curve between the initial and final temperatures of the corresponding peaks from the differential thermogravimetric curve [13,16].

$$CH_{\text{content}} = (m_1/m_0) \times (74/18) \times 100 \tag{3.2}$$

where CH_{content} is the CH content in pastes that consisted of plain cement and fly-ash cement pastes (%), m_1 is the mass loss from CH dehydration as determined by the TG-DTA apparatus (mg), and m_0 is the initial mass of paste which is ~45 ± 10 (mg).

3.4.6 Pore size distribution of pastes

The pore size distributions of OPC pastes at a W/B ratio of 0.50 without fly ash (F0) and with 20% fly ash (F20) were measured at the ages of 28 and 364 days using a mercury intrusion porosimeter (MIP) (POREMASTER 60, Quantachrome Instruments, USA) in order to evaluate the refinement effect of fly ash reaction on the pore structure of paste specimen during this period. The sample preparation process for the MIP was the same as that for the SDM, except the grinding step. The pore size distributions of paste samples were examined for the range from 0.0045 to 200 µm. The Washburn equation was used to calculate the porosity of the sample. The relationship between the pore diameter and the applied pressure is expressed in Eq. (3.3) [17,18].

$$D = -(4\sigma\cos\theta)/P \tag{3.3}$$

where D is the diameter of the intruded pore (µm), σ is surface tension of mercury (mN/m), θ is contact angle between mercury and the pore walls (°), and P is the applied pressure (mN/m^2).

3.5 SUMMARY

The experimental program in this work was conducted to (1) investigate the effect of cement type and W/B ratio on the *k*-value of fly ash for concrete-strength development and (2) evaluate in a simple approach the *k*-value of fly ash for the chloride-penetration resistance of concretes. The flow chart of experimental program is shown in Fig. 3.3.

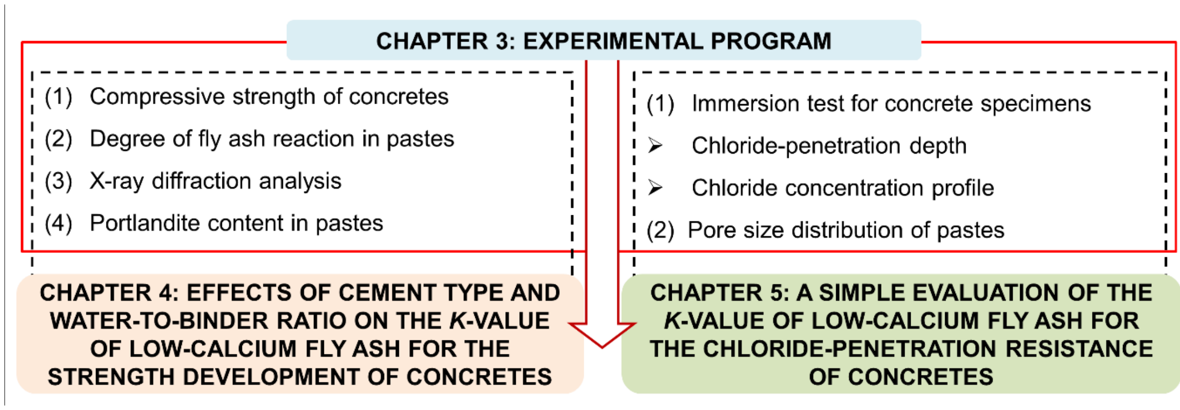

Fig. 3.3 Flow chart of experimental program

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CHAPTER 4

EFFECTS OF CEMENT TYPE AND WATER-TO-BINDER RATIO ON THE *K*-VALUE OF LOW-CALCIUM FLY ASH FOR THE STRENGTH DEVELOPMENT OF CONCRETES

Effects of cement type and water-to-binder (W/B) ratio on the cementing efficiency factor (*k*-value) of low-calcium fly ash for concrete-strength development are discussed in this chapter by (1) examining the degree of fly ash reaction in pastes and analyzing hydration product using the X-ray diffraction (XRD) analysis in Section 4.1, (2) determining the Portlandite (CH) content in pastes as well as calculating the CH consumption by the pozzolanic reaction of fly ash in Section 4.2, and (3) evaluating the *k*-value of fly ash for concrete-strength development in Section 4.3.

4.1 RESULTS OF DEGREE OF FLY ASH REACTION IN PASTES AND X-RAY DIFFRACTION ANALYSIS

4.1.1 Results of degree of fly ash reaction in pastes

The experimental results of the degree of fly ash reaction in paste specimens are shown in Fig. 4.1. Each value in Fig. 4.1 is a mean experimental value of at least two measurements with a standard deviation of less than 1.9%. Similar to previous studies [1–5], the degree of fly ash reaction in paste specimens increased with an increase in time and with a decrease in fly ash replacement ratio as well. The effects of cement type and W/B ratio on the degree of fly ash reaction were insignificant within 28 days for a sealed curing condition at 20 ºC. At 3 and 7 days, the degree of fly ash reaction in all the pastes was less than 10%. After 28 days, a higher W/B ratio resulted in a higher degree of fly ash reaction in the OPC pastes, and the degrees of fly ash reaction in the HSPC pastes were higher than those in the OPC pastes with the same W/B ratio of 0.50. In particular, during a period of 28 to 364 days, the increments of the fly ash reaction degree in F20, F30, and F40 were 29.0%, 22.4%, and 20.0%, respectively, for the HSPC pastes. Meanwhile, these values were 24.9%, 18.3%, and 16.7%, respectively, for the OPC pastes with a high W/B ratio of 0.50, and were 14.9%, 12.7%, and 9.0%, respectively, for the OPC pastes with a low W/B ratio of 0.30. The result for pastes with a W/B ratio of 0.30 agreed well with the results of the study by Termkhajornkit et al. [1]. The tendency showing the higher the W/B ratio, the higher the degree of fly ash reaction was also confirmed in the study by Hanehara et al. [2]. The reason for it will be explained in Section 4.2.

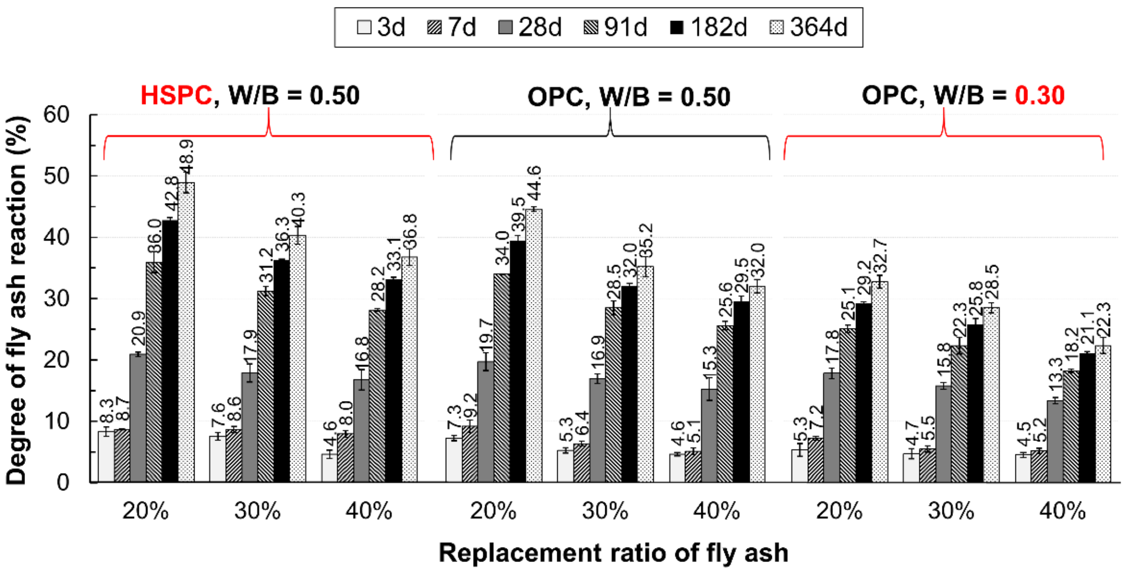

Fig. 4.1 Degrees of fly ash reaction in pastes with time: HSPC with a W/B ratio of 0.50, OPC with a W/B ratio of 0.50, and OPC with a W/B ratio of 0.30

4.1.2 Results of XRD analysis

Figure 4.2 shows the XRD patterns of hydrated pastes without fly ash (F0) and with 40% fly ash replacement (F40) at a W/B ratio of 0.50. There was an insignificant difference in the XRD patterns of these pastes at 3 days, except for the formation of monosulphate ($C_4A\bar{S}H_{12}$) in the HSPC paste. After 7 days, the monosulphate that was transferred from the ettringite ($C_6A\bar{S}_3H_{32}$)

still formed in the HSPC paste (see Fig. 4.2 (a)), whereas monocarbonate ($C_4A\bar{C}H_{11}$) formed in the OPC paste (see Fig. 4.2 (b)) as obviously seen at 28 days. Martin et al. [6] found that monosulphate can react with silica and alumina that are provided by the dissolved amorphous alumosilicates of the fly ash to produce additional strätlingite (C_2ASH_8) and ettringite. In this study, although the strätlingite was not detected in both HSPC and OPC pastes through XRD analysis, the high degree of fly ash reaction in the HSPC paste compared with that in the OPC paste may be related to the presence of monosulphate, which was not detected in the OPC paste. In fact, as shown in Fig. 4.2 (a), for F0, the ettringite peak decreased after 3 days, whereas that of the monosulphate increased gradually with time. A different tendency was observed in F40. The monosulphate peak in F40 became prominently high at 28 days, but it decreased as seen at 364 days. The peak of ettringite in F40 tended to increase with time. Thus, if the monosulphate can react with the silica and alumina of the fly ash to form additional ettringite as mentioned in a previous study [6], this reaction will lead to not only a destabilization of ettringite but also a high degree of fly ash reaction in the HSPC paste compared to the OPC paste.

As shown in Fig. 4.2 (b), hemicarbonate ($C_4A\bar{C}_{0.5}H_{12}$) was detected in OPC paste that contained fly ash (F40) at 28 days, whereas unreacted calcite remained in the OPC paste up to 364 days. As a result, the difference in hydration products that were formed in the HSPC and OPC pastes can be attributed to the presence of calcite in the raw cement. As listed in Table 3.2, the calcite content in the OPC was 4.2% by mass, whereas that in the HSPC was negligible. With calcite, the transformation of ettringite to monosulphate was suppressed, whereas monocarbonate and hemicarbonate (with the presence of fly ash in this study) formed instead. This tendency is more pronounced in the presence of fly ash because of a lower SO_3/Al_2O_3 ratio that is caused by replacing part of the cement by fly ash as demonstrated by De Weerdt et al. [7]. Many researchers [7–10] have found that in the presence of calcite, monocarbonate stabilization resulted in the indirect stabilization of ettringite and led to an increase in the later compressive strength. This indicated the compressive strength of the OPC concrete with fly ash increased much significantly at the later ages because of the presence of calcite when compared with that of the HSPC concrete with fly ash in this study (see Section 4.3).

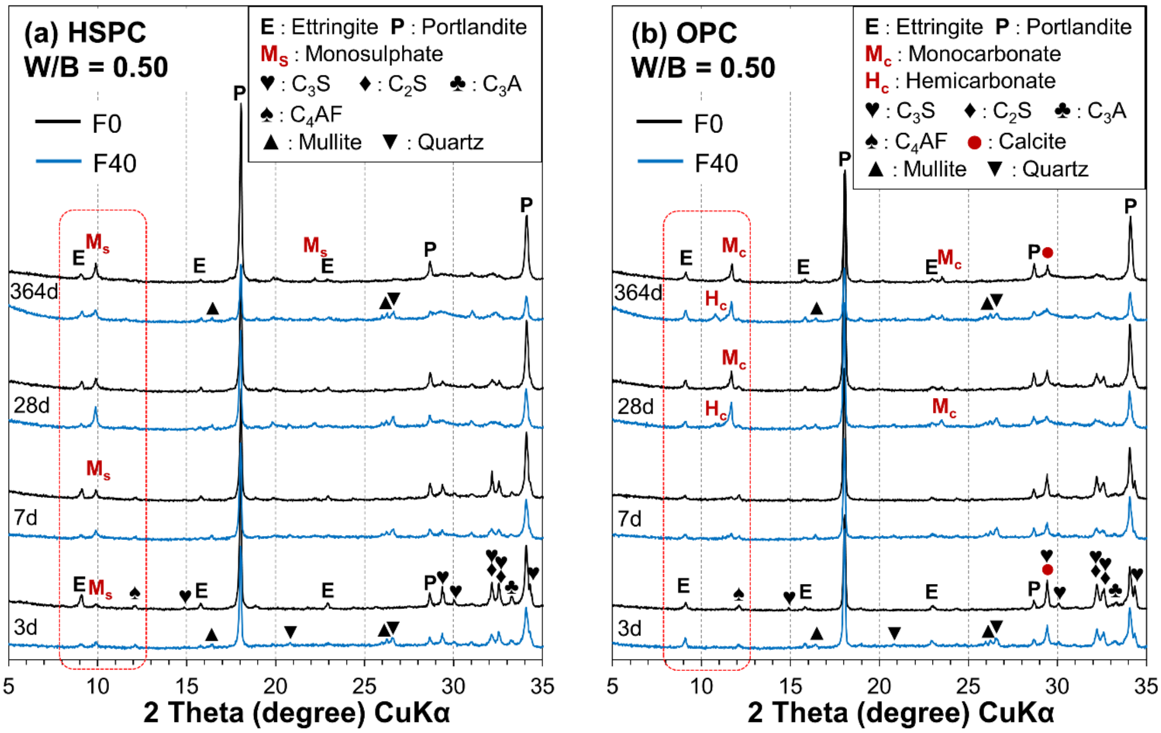

Fig. 4.2 XRD patterns of hydrated pastes without fly ash (F0) and with 40% fly ash replacement (F40): (a) HSPC and (b) OPC with a W/B ratio of 0.50

4.2 CH CONTENT AND EVALUATION OF CH CONSUMPTION IN PASTES

4.2.1 CH content in pastes

Figure 4.3 shows the CH content relative to the cement content (i.e., the relative CH content or CH content per 100 g of cement). For the plain cement paste without fly ash (F0), the CH content increased with time regardless of the cement type and W/B ratio. A higher W/B ratio yielded a higher CH content in the pastes because more space and water were available for cement hydration. It is well known that the more the CH content, the more the pozzolanic reaction of fly ash in pastes containing the same cement type. This means the higher W/B ratio can result in the higher degree of fly ash reaction, as reported in previous studies [1–4]. This result provides an obvious evidence for a higher degree of fly ash reaction in the OPC pastes with a higher W/B ratio as mentioned previously. The CH content in the plain HSPC pastes without fly ash increased rapidly at the early ages due to the rapid hydration of HSPC and was always higher than that in the plain OPC pastes without fly ash. This result can be considered as an additional reason for a higher degree of fly ash reaction in the HSPC pastes. For the fly-ash cement pastes, the CH content relative to the cement content increased slightly at the early ages but decreased subsequently because of the pozzolanic reaction of fly ash that consumed CH.

Compared with the plain cement paste without fly ash (F0), the high relative CH content in the fly-ash cement systems at the early ages can be attributed to a filler effect of the fly ash which enhances hydration of cement through providing additional nucleation sites for hydration products in the fly-ash cement pastes as confirmed in previous works [7,11–13]. Recently, De la Varga et al. [14] demonstrated that the filler effect of fly ash results in three factors: (1) larger separation among cement particles, which promotes more complete cement hydration because more space is available, (2) partial deflocculation of the cement particle 3-D network, providing increased exposed cement particle surface area, and (3) provision of new nucleation sites which can enhance the formation of more hydration products. In this study, the cement-hydration-enhancement effect of fly ash strongly depends on the cement type and W/B ratio as shown in Fig. 4.3. A lower W/B ratio yields a higher cement-hydration-enhancement effect of fly ash for the OPC pastes, whereas this effect became insignificant for the HSPC pastes. This can be explained due to a significant difference in Blaine fineness of the HSPC (4450 cm^2/g) and the fly ash (3530 cm^2/g), while the Blaine fineness of the OPC (3290 cm^2/g) is rather lower than that of the fly ash.

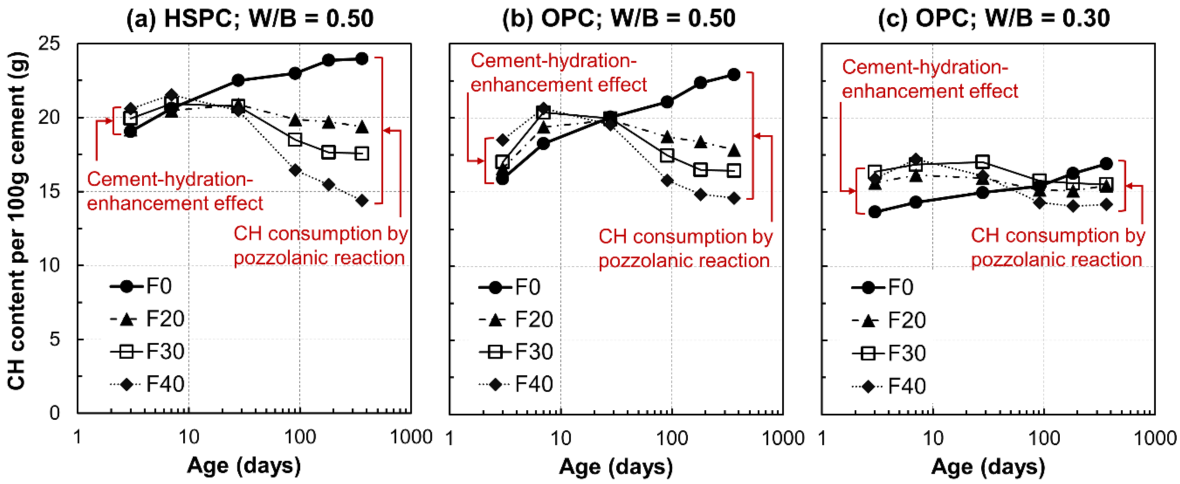

Fig. 4.3 CH content relative to cement content in pastes with time: HSPC paste with a W/B ratio of 0.50, OPC paste with a W/B ratio of 0.50, and OPC paste with a W/B ratio of 0.30

4.2.2 Evaluation of CH consumption in pastes

The CH consumptions by pozzolanic reaction of fly ash in the HSPC pastes were higher than in the OPC pastes with the same W/B ratio of 0.50. In contrast, the CH consumption in the OPC pastes with a W/B ratio of 0.30 was low as shown in Fig. 4.3 as well as listed in Table 4.1 with the values in the parenthesis. This result is consistent with that of Hanehara et al. [2] in which the CH consumption by the pozzolanic reaction of fly ash at 91 days was still low for a W/B ratio of 0.30. Generally, the CH consumption by pozzolanic reaction of fly ash is described by Eq. (4.1) [5]:

$$CH_{\text{consumption}} = CH_{\text{plain-cement,paste}} \times C/(C+F) - CH_{\text{flyash-cement,paste}} \quad (4.1)$$

Where $CH_{\text{consumption}}$ is the CH consumption (%), $CH_{\text{plain-cement, paste}}$ is the CH content in the plain cement paste (%), $CH_{\text{flyash-cement, paste}}$ is the CH content in the fly-ash cement paste (%), and $C/(C+F)$ is the mass ratio of cement in binder (fraction).

In this study, a modified equation shown in Eq. (4.2) is adopted to evaluate the CH consumption that considers the cement-hydration-enhancement effect of the fly ash.

$$CH_{consumption} = CH_{plain\text{-}cement,paste} \times C/(C+F) \times E - CH_{flyash\text{-}cement,paste} \quad (4.2)$$

where E is the CH enhancement ratio (fraction) because of the cement-hydration-enhancement effect at 3 days, which is described by Eq. (4.3). It is assumed that the formed CH has not yet been consumed by the pozzolanic reaction of fly ash at 3 days.

$$E = CH_{flyash\text{-}cement,paste\ at\ 3\ days} / \{CH_{plain\text{-}cement,paste\ at\ 3\ days} \times C/(C+F)\} \quad (4.3)$$

The pozzolanic reaction of fly ash only starts significantly after one or more weeks [3,4,12,13]. Moreover, it was found that little reaction of CH with fly ash occurred within 7 days, whereas approximately 8% by mass of fly ash reacted in the fly-ash cement system at 7 days [15].

Table 4.1 shows the CH enhancement ratio (i.e., E) and the CH consumption relative to the fly ash content in the HSPC and OPC pastes with considering the cement-hydration-enhancement effect. It is noted that the values in the parenthesis were calculated by Eq. (4.1) for comparison. A higher replacement ratio of fly ash or a lower W/B ratio leads to a higher E. The E in the HSPC pastes was lower than that in the OPC pastes with a W/B ratio of 0.50. Considering the cement-hydration-enhancement effect (with E), the CH consumption relative to the fly ash content in the HSPC pastes was lower than that in the OPC pastes with the same W/B ratio of 0.50 at the ages of 182 and 364 days.

Table 4.1 CH enhancement ratio, E, and CH consumption relative to fly ash content in HSPC and OPC pastes with considering the cement-hydration-enhancement effect

Mixture	E	CH consumption relative to fly ash content (%) with the E **					
		3 days	7 days	28 days	91 days	182 days	364 days
P50-HF20*	1.006	0.0 (-0.5)	1.1 (0.6)	7.0 (6.5)	13.0 (12.5)	17.2 (16.6)	18.5 (18.0)
P50-HF30	1.047	0.0 (-2.1)	1.5 (-0.7)	6.5 (4.1)	13.0 (10.5)	17.1 (14.5)	17.4 (14.8)
P50-HF40	1.081	0.0 (-2.3)	1.1 (-1.4)	5.8 (3.1)	12.6 (9.8)	15.5 (12.6)	17.2 (14.3)
P50-OF20	1.044	0.0 (-2.8)	-1.2 (-4.5)	4.3 (0.7)	13.1 (9.4)	19.9 (15.9)	22.6 (18.5)
P50-OF30	1.071	0.0 (-2.6)	-1.9 (-4.9)	3.5 (0.2)	11.9 (8.4)	17.4 (13.7)	18.0 (14.2)
P50-OF40	1.165	0.0 (-3.9)	1.0 (-3.6)	5.7 (0.8)	13.1 (7.9)	16.8 (11.3)	17.6 (11.9)

P30-OF20	1.143	0.0 (-7.8)	0.8 (-7.4)	4.6 (-3.9)	9.8 (1.0)	14.0 (4.7)	13.1 (3.4)
P30-OF30	1.198	0.0 (-6.3)	0.6 (-6.0)	2.1 (-4.8)	6.2 (-0.9)	9.0 (1.5)	9.6 (1.8)
P30-OF40	1.164	0.0 (-3.4)	-0.9 (-4.4)	2.0 (-1.7)	5.4 (1.6)	7.3 (3.3)	7.4 (3.3)

*P50-HF20 means paste with a W/B ratio of 0.50, high-early-strength Portland cement and fly ash replacement ratio of 20%

** The values in the parenthesis are the CH consumptions relative to fly ash content (%) without considering the *E* for comparison

Figure 4.4 illustrates a correlation between the CH consumption relative to the fly ash content and the degree of fly ash reaction in the HSPC or OPC paste without and with considering the *E*. The CH consumption relative to the fly ash content with *E* in Fig. 4.4 (b) is consistent with the result of the fly ash reaction degree, especially for pastes with a W/B ratio of 0.30 (solid circle) compared with those without *E* in Fig. 4.4 (a). This result confirmed the suitability of the proposed expression. For an HSPC paste (empty square), the higher degree of fly ash reaction did not result in a higher CH consumption compared with the OPC paste (empty circle) with a W/B ratio of 0.50 as presented in Fig. 4.4 (b). This result agreed well with the results of the fly ash reaction degree and XRD analysis as mentioned previously. This means the high degree of fly ash reaction in the HSPC paste compared with that in the OPC paste mainly related to the presence of monosulphate as also demonstrated in Section 4.1 rather than the high CH content.

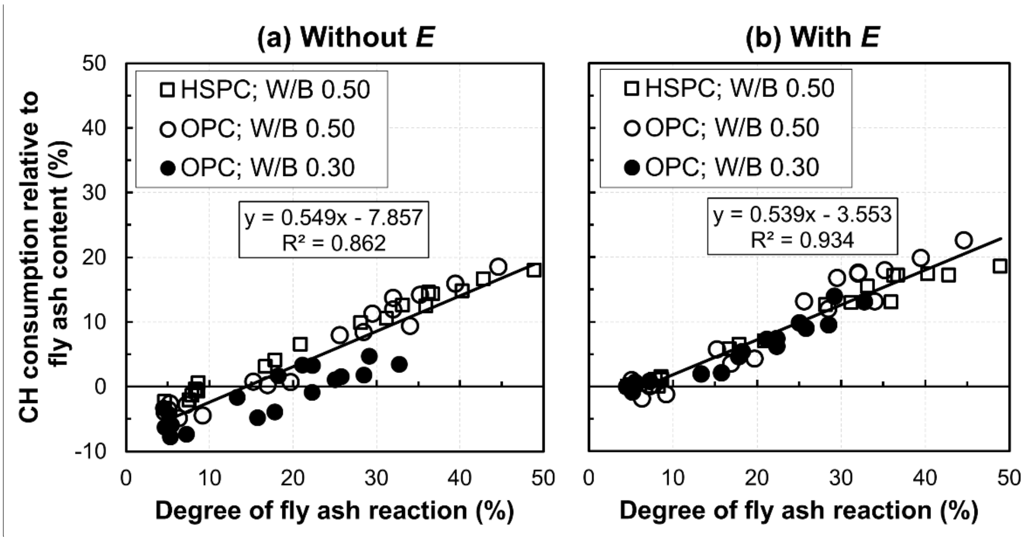

Fig. 4.4 CH consumption relative to the fly ash content in pastes (a) without and (b) with taking the cement-hydration-enhancement effect (*E*) into account

4.3. COMPRESSIVE STRENGTH OF CONCRETES AND EVALUATION OF *K*-VALUE OF FLY ASH FOR CONCRETE-STRENGTH DEVELOPMENT

4.3.1 Compressive strength of concretes

Compressive strengths of all the concretes are presented in Fig. 4.5. Each value of compressive strength shown in Fig. 4.5 is an average of three test results, the standard deviations of which ranged from 0.1 to 3.1 N/mm^2 with the coefficient of variation of less than 5% for all the mixtures.

For control concretes without fly ash as the references, the compressive strength of plain HSPC concretes increased quickly at early ages (i.e. 3 and 7 days) and was always higher than that of plain OPC concretes with the same mix proportion at each age as illustrated in Fig. 4.5 (a). The compressive strength of plain HSPC concrete increased slightly after 28 days, whereas that of plain OPC concrete still increased significantly up to 91 days. This different contribution of cement to strength development of concrete might play an important role and affect the evaluation of the *k*-value in terms of the relationship of control concrete, which will be discussed in Section 4.3.2.

On the other hand, the compressive strength of fly-ash concrete increased gradually with time regardless of cement type and W/B ratio as shown in Figs. 4.5 (b) and (c). Generally, the lower the replacement percentage of fly ash, the higher the compressive strength of fly-ash concrete. This tendency was also reported in some studies [16–19]. In addition, with a W/B ratio of 0.50 (see Fig. 4.5 (c)), the compressive strength of OPC concrete with fly ash was lower at 3 and 7 (except for C50-OF40) days but higher at 28 (except for C50-OF20), 91, 182, and 364 days than that of HSPC concrete (see Fig. 4.5 (b)). The higher compressive strength of HSPC concrete with fly ash at the ages of 3 and 7 days was mainly related to the better contribution of HSPC to strength at early ages as presented in Table 3.1. Meanwhile, the significant increase in compressive strength of OPC concrete in comparison with that of HSPC concrete at the later ages can be attributed to the presence of calcite which was mentioned in Section 4.1.

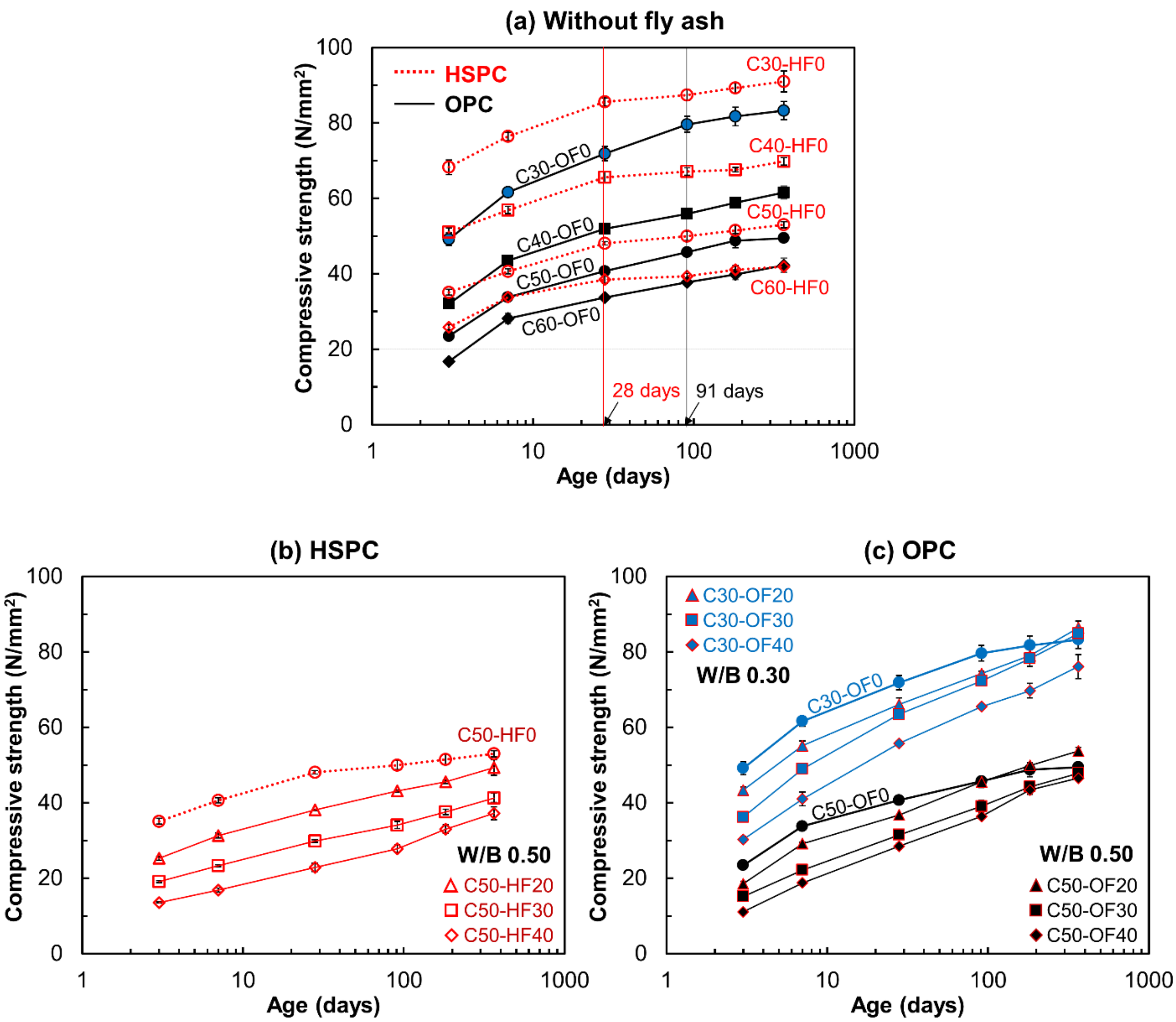

Fig. 4.5 Compressive strength of concretes: (a) without fly ash as the reference and with fly ash: (b) HSPC concretes and (c) OPC concretes

4.3.2. Evaluation of *k*-value of fly ash for the strength development of concretes

The relationship between the cement-to-water (C/W) ratio and compressive strength of the control concrete was obtained as shown in Fig. 4.6 with a very high correlation coefficient R^2 (equal to or higher than 0.990). These relationships of control HSPC concrete in Fig. 4.6 (a) had higher slopes than those of control OPC concrete in Fig. 4.6 (b). In the C/W range of the results in this study, the higher slope of the relationship can result in the lower *k*-value of fly ash due to the lower equivalent cement-to-water ratio (i.e., $(C/W)_{eq.}$) in the case of same compressive strength. In Fig. 4.7, if the value of compressive strength of fly-ash concrete reaches the relationship of the control concrete at corresponding age, the $(C/W)_{eq.}$ and the C/W ratio are the same. This means the *k*-value is equal to zero. Obviously, the higher the compressive strength of fly-ash concrete compared with the relationship, the higher the *k*-value of fly ash. The *k*-value of fly ash at each age and each replacement ratio is summarized in Table 4.2.

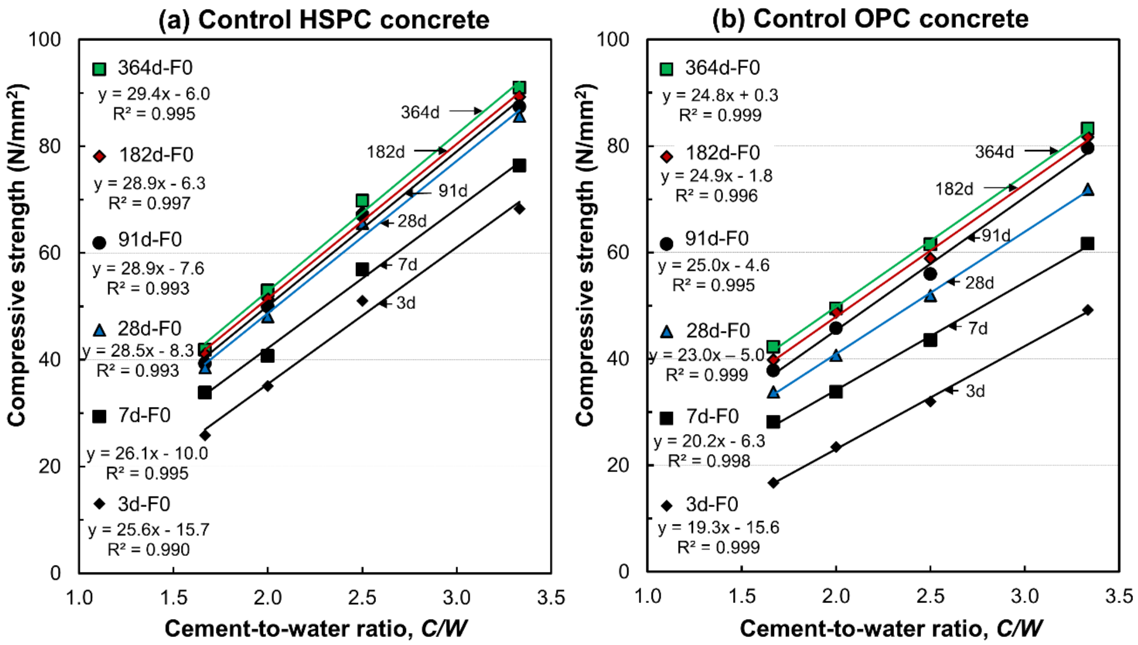

Fig. 4.6 Relationship between the C/W ratio and compressive strength of control concretes without fly ash: (a) plain HSPC concretes and (b) plain OPC concretes

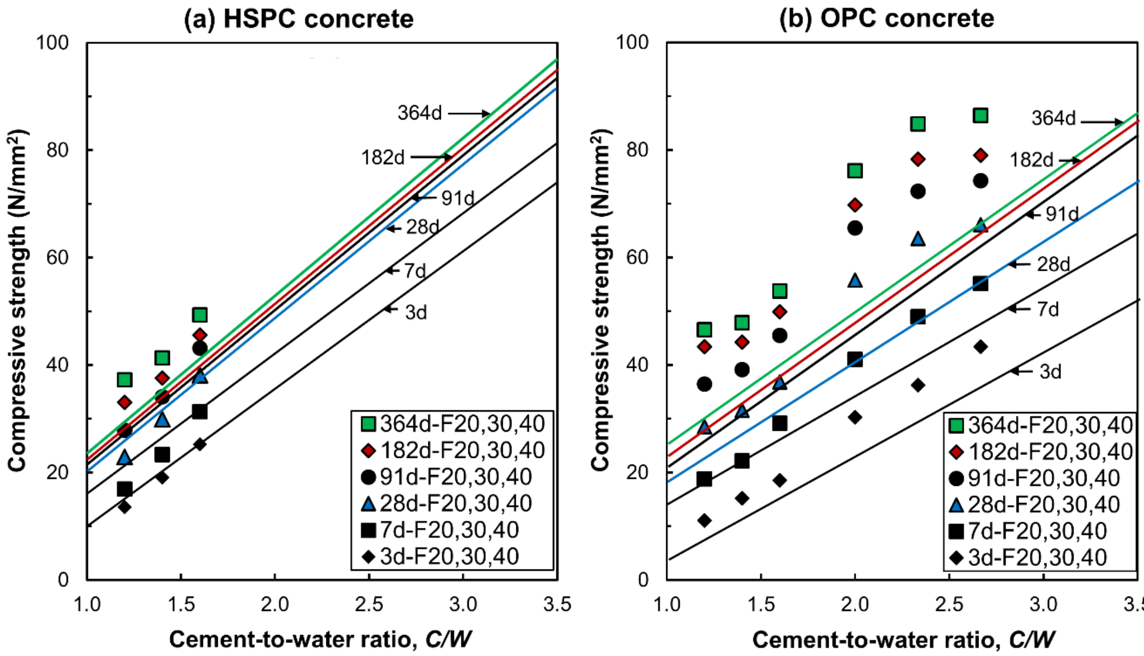

Fig. 4.7 Compressive strength of fly-ash concretes with relationships of (a) HSPC concretes and (b) OPC concretes

Table 4.2 *k*-value of fly ash in HSPC and OPC concretes

Group	Mixture	F/(C+F) (mass %)	*k*-value of fly ash for concrete-strength development					
			3 days	7 days	28 days	91 days	182 days	364 days
HSPC; W/B 0.50	C50-HF20	20	0.00	-0.04	0.07	0.40	0.49	0.70
	C50-HF30	30	-0.07	-0.20	-0.10	0.08	0.20	0.34
	C50-HF40	40	-0.07	-0.21	-0.14	0.03	0.20	0.33
OPC; W/B 0.50	C50-OF20	20	0.42	0.38	0.55	1.01	1.19	1.40
	C50-OF30	30	0.32	0.01	0.31	0.58	0.75	0.86
	C50-OF40	40	0.23	0.05	0.32	0.55	0.77	0.83
OPC; W/B 0.30	C30-OF20	20	0.57	0.55	0.64	0.73	0.87	1.22
	C30-OF30	30	0.35	0.40	0.65	0.74	0.88	1.08
	C30-OF40	40	0.28	0.25	0.48	0.60	0.66	0.80

Figure 4.8 shows the *k*-values of fly ash in each mixture proportion of concrete with time. Generally, the *k*-value of fly ash with regard to concrete-strength development increased with time regardless of cement type and W/B ratio. The relatively high *k*-value at 3 days for OPC concretes mainly related to the filler effect of the fly ash particles which may be ascribed to the cement-hydration-enhancement effect as mentioned in Section 4.2. A reduction of the *k*-value at 7 days indicated that the filler effect of the fly ash is less effective with an increase in the

curing time, especially for mixtures with a W/B ratio of 0.50. Additionally, the cement still hydrates prominently at the age of 7 days and this leads to the significant increase in compressive strength of control concretes. This reduction of *k*-value at early ages has been observed in previous studies [18,19]. After 28 days, the *k*-value increased considerably in all the mixtures because of the pozzolanic reaction of fly ash, which has also been discussed in Section 4.1.

For a W/B ratio of 0.50, the *k*-value of fly ash ranged from –0.21 to 0.70 for HSPC concretes and from 0.01 to 1.40 for OPC concretes up to 364 days as shown in Fig. 4.8 (a). These results indicated that the *k*-value of fly ash was strongly affected by the cement type. Nevertheless, a different trend was found in this work as compared with the result in a study by Bijen and Selst [20] in which a higher *k*-value was observed in the fly-ash concrete with rapid hardening Portland cement. This was explained that the hydration of rapid hardening Portland cement at the early ages provides not only a higher pH but also a higher temperature environment, which promoted the fly ash reaction, compared with that of OPC [20]. In this study, the rapid hydration of HSPC was also demonstrated in Section 4.2, but the degree of fly ash reaction in the HSPC paste was slightly higher than that in the OPC paste at the early ages. The rather higher fly ash reaction degree cannot lead to a higher *k*-value of fly ash in HSPC concrete. In the contrast, a negative *k*-value was found in the HSPC concrete within 7 days and can be attributed to (1) the less effective filler effect of fly ash as mentioned in Section 4.2 and (2) a slow pozzolanic reaction of the fly ash compared with the rapid hydration of HSPC. In general, it should be noted that the *k*-value of fly ash in the HSPC concrete was lower than that in the OPC concrete with the same W/B ratio even though the higher fly ash reaction degree in the HSPC paste was found. This finding agreed well with the result discussed in Section 4.1 in which the higher degree of fly ash reaction in the HSPC paste was related to the presence of monosulphate and led to the destabilization of ettringite at the later ages. Besides, the other factor affecting the *k*-value should be considered such as the difference in relationships of the control group. In fact, although the compressive strength of the C50-HF20 was higher than that of the C50-OF20 at the ages of 3, 7, and 28 days, the *k*-value of the C50-HF20 was always lower than that of the C50-OF20.

For OPC concrete, the *k*-value of fly ash increased significantly at 3 and 7 days for the low W/B ratio of 0.30 as shown in Fig. 4.8 (b). This indicated that the filler effect of the fly ash plays a vital role in improving the cement hydration in fly-ash cement systems with a low W/B ratio at the early ages as explained by the *E* in Section 4.2. After 28 days, the pozzolanic reaction of fly ash resulted in an increase in the *k*-value. In particular, the *k*-value ranged from 0.25 to 0.65 at a low W/B ratio of 0.30, whereas it ranged from 0.01 to 0.55 at a high W/B ratio of 0.50 within 28 days. After 28 days, the *k*-value ranged from 0.31 to 1.40 at a high W/B ratio of 0.50, whereas it ranged from 0.48 to 1.22 at a low W/B ratio of 0.30 up to 364 days.

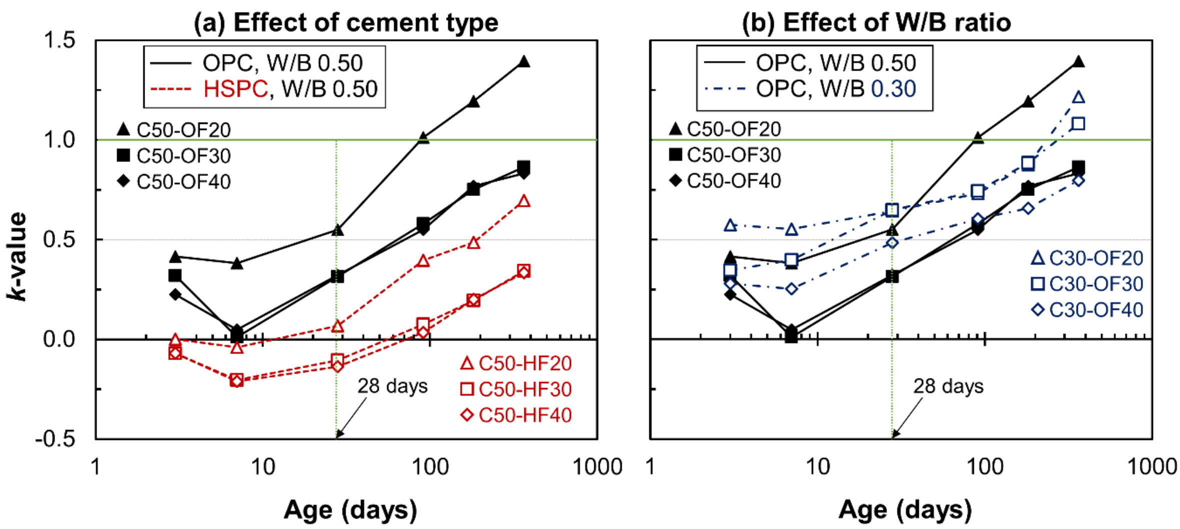

Fig. 4.8 *k*-values of fly ash in concrete with time: (a) effect of cement type and (b) effect of W/B ratio

4.4 SUMMARY

The following conclusions can be drawn within the limits of the present experiments:

a) The effect of cement type on the *k*-value of fly ash for concrete-strength development was obviously remarkable due to the difference in the relationships between cement-to-water ratio and compressive strength of the control concretes. With the presence of calcite (approximate 4% by mass) in the OPC, the stabilization of monocarbonate resulting in indirectly the stabilization of ettringite led to a more significant increase in the compressive strength of OPC concrete containing fly ash despite a low degree of fly ash reaction in OPC paste compared with HSPC paste.

b) With a W/B ratio of 0.50, the *k*-value ranged from –0.21 to 0.70 in HSPC concrete while it ranged from 0.01 to 1.40 in OPC concrete up to the age of 364 days.

c) For OPC concrete, the lower the W/B ratio, the higher the *k*-value of fly ash at the early ages mainly due to cement-hydration-enhancement effect of fly ash as explained by the CH enhancement ratio (i.e., *E*). The *k*-value ranged from 0.25 to 0.65 at a low W/B ratio of 0.30 while it ranged from 0.01 to 0.55 at a high W/B ratio of 0.50 within 28 days. Nevertheless, the *k*-value increased remarkably from 0.31 to 1.40 at the high W/B ratio of 0.50 while it increased from 0.48 to 1.22 at the low W/B ratio of 0.30 after 28 days up to 364 days due to mainly the pozzolanic reaction of fly ash.

d) A modified equation of the CH consumption taking the cement-hydration-enhancement effect into account was firstly proposed to evaluate the CH consumption in fly-ash cement paste. This result is consistent with the result of the degree of fly ash reaction, especially for OPC paste with a low W/B ratio of 0.30.

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CHAPTER 5

A SIMPLE EVALUATION OF THE *K*-VALUE OF LOW-CALCIUM FLY ASH FOR THE CHLORIDE-PENETRATION RESISTANCE OF CONCRETES

This chapter aims at simply evaluating the cementing efficiency factor (*k*-value) of low-calcium fly ash for the chloride-penetration resistance of concretes using the chloride-penetration depth. Because there are four mixtures of control OPC (ordinary Portland cement) concretes with water-to-binder (W/B) ratios of 0.30, 0.40, 0.50, and 0.60 and two mixtures of fly-ash OPC concretes with fly ash replacement ratios of 20% and 40% by mass at a W/B ratio of 0.50 which are presented in this chapter, the names of six mixtures are briefly revised from C30-OF0, C40-OF0, C50-OF0, C60-OF0, C50-OF20, and C50-OF40 to Ct30, Ct40, Ct50, Ct60, F20, and F40, respectively. First, chloride concentration profile and evaluation of *k*-value for the chloride-penetration resistance of concretes using the apparent diffusion coefficient (D_{app}) of chloride ion are mentioned in Section 5.1. Then, chloride-penetration depth (x_d) and evaluation of the *k*-value in a simple approach are reported and discussed in Section 5.2. Finally, the results of pore size distribution in pastes are presented in Section 5.3. Results indicate that the x_d could be used as a concrete-durability property to obtain the *k*-value of fly ash in a simpler way compared to the D_{app} of chloride ion.

5.1 CHLORIDE CONCENTRATION PROFILE AND EVALUATION OF *K*-VALUE FOR THE CHLORIDE-PENETRATION RESISTANCE OF CONCRETES

5.1.1 Chloride concentration profile

To confirm the result of the *k*-value based on the x_d which will be mentioned in Section 5.2, the D_{app} of chloride ion was determined, and the relationship between the D_{app} and the water-to-cement (W/C) ratio was used to evaluate the *k*-value based on the chloride-diffusion coefficient of the concretes after 39 weeks of exposure to a solution of 10% NaCl.

The total chloride concentration profiles obtained via chemical analysis are shown in Fig. 5.1. Additionally, the total chloride concentration at the average chloride-penetration depth (dashed line) can be derived from Fig. 5.1. The average content of total chloride corresponding to the color-change border is approximately 0.07% by mass of concrete for the control concretes without fly ash and the W/C ratio does not significantly affect the total chloride concentration at the average chloride-penetration depth. This is consistent with the finding in a study by Kim et al. [1]. It should be noted that the total chloride concentration in the first layer was eliminated while determining the D_{app}. Because of the influence of carbonation during the sample preparation process, the total chloride concentration in the first layer is lower than that in the other layers, especially for two mixtures of Ct60 and F40 as obviously seen in Fig. 5.1. Fitting the concentration profiles of chloride ion into Fick's second law (using non-linear regression analysis using the least square method), as shown in Eq. (5.1), the D_{app} of chloride ion was determined, as presented in Fig. 5.2.

$$C(x,t) = C_o + (C_s - C_o)[1 - erf\{x/(4D_{app}\, t)^{0.5}\}], \qquad (5.1)$$

where $C(x, t)$ is the chloride ion concentration at depth x and time t (mass%), C_o is the chloride ion concentration (mass%) of the concrete before immersion, C_s is the chloride ion concentration (mass%) at the surface, x is the depth (m), D_{app} is the apparent diffusion coefficient of chloride ion (m^2/s), t is time of immersion (s), and *erf* is the error function.

After 39 weeks of immersion in a solution of 10% NaCl, the D_{app} of chloride ion in the control concrete samples (i.e., Ct30, Ct40, Ct50, and Ct60) increased with an increase in the W/B ratio, as shown in Fig. 5.2. This is consistent with the study reported by Kim et al. [1]. In the fly-ash concretes, the D_{app} of chloride ion was low, which is also consistent with the study by Baroghel-Bouny et al. [2]. For concrete samples with a W/B ratio of 0.50, the D_{app} of chloride ion in F20 and F40 was significantly lower than that in Ct50. Meanwhile, it was nearly the same as that in Ct30. This indicates that replacing at least 40% of the cement with fly ash in concretes with a W/B ratio of 0.50 yield chloride-penetration resistance that is as good as that of the plain cement concrete with a W/B ratio of 0.30 after 39 weeks of exposure to a NaCl solution based on the chloride-diffusion coefficient.

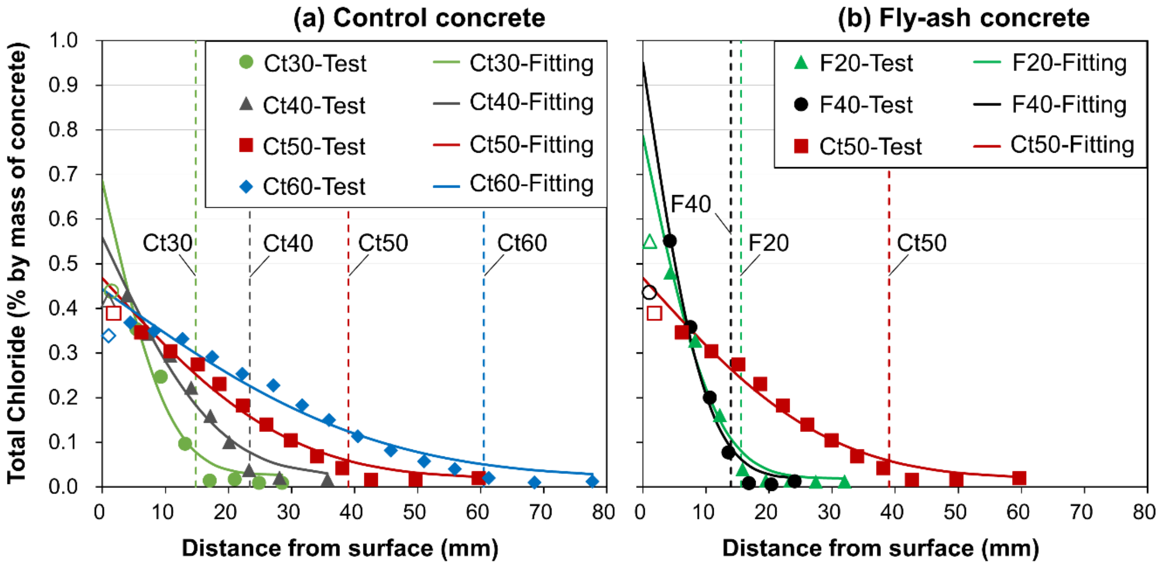

Fig. 5.1 Total chloride concentration profiles obtained via chemical analysis after 39 weeks of exposure to a 10% NaCl solution and the average chloride-penetration depth (dashed line) measured by spray test using 0.1 M $AgNO_3$

5.1.2 Evaluation of *k*-value of fly ash using the chloride-diffusion coefficient

To quantitatively evaluate the contribution of fly ash to the chloride-penetration resistance of concretes, the *k*-value of fly ash with regard to the D_{app} was obtained using the principle mentioned in Section 2.2.2, and the obtained values are listed in Table 5.1. The *k*-values of fly ash based on the D_{app} after 39 weeks of exposure to a 10% NaCl solution were obtained to be

4.03 and 2.78 for F20 and F40, respectively. This implies that the fly ash contributed significantly (over four and two times as much as cement) to the chloride-penetration resistance of concretes. Furthermore, the relationship between the D_{app} of chloride ion and the W/C ratio of the control concrete was established as a power function with an extremely high correlation coefficient (R^2) of 0.999, as shown in Fig. 5.2. This function is in good agreement with that reported by Aponte et al. [3].

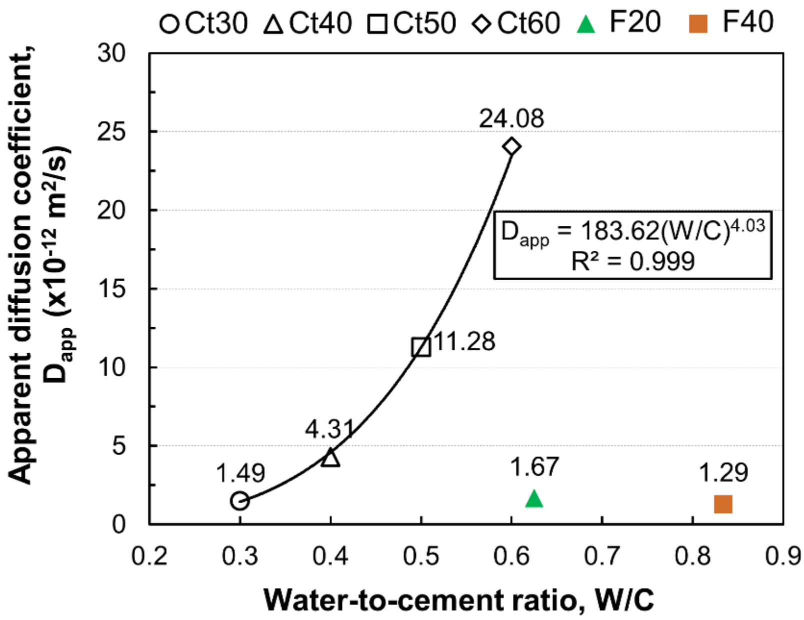

Fig. 5.2 Relationship between the D_{app} of chloride ion and W/C ratio of the control concrete after 39 weeks of exposure to a 10% NaCl solution obtained by the power function

Table 5.1 D_{app} of chloride ion in fly-ash concretes and *k*-values based on the D_{app} after 39 weeks of exposure to a 10% NaCl solution

Mixture	Apparent diffusion coefficient, D_{app} ($\times 10^{-12}$ m^2/s)	*k*-value of fly ash based on the D_{app} (fraction)
F20	1.67	4.03
F40	1.29	2.78

5.2 CHLORIDE-PENETRATION DEPTH AND EVALUATION OF THE *K*-VALUE IN A SIMPLE APPROACH

5.2.1 Chloride-penetration depth

Figure 5.3 shows the x_d of the concrete specimens after immersion periods of 13, 26, and 39 weeks. The relationship between the x_d and the W/C ratio for the control samples at each immersion period was established using the power function with a correlation coefficient greater than 0.989. The *k*-value of the fly ash with regard to the chloride-penetration resistance of the concrete based on the x_d was calculated using the established relationship and x_d of the concrete specimens containing fly ash. A low x_d of fly-ash concretes can result in a high *k*-value. At the same W/B ratio of 0.50, a different trend was obtained for the x_d of the concrete mixtures with and without fly ash, as shown in Fig. 5.3. The x_d of the control concrete (Ct50) increased gradually with an increase in the immersion time, whereas that of F20 and F40 increased slightly (almost constant) during the immersion process after 13 weeks of exposure to the 10% NaCl solution. Consistent with previous studies [4,5], these results indicate that the addition of fly ash yields much higher resistance to chloride-penetration in the concrete structures compared to the control concrete without fly ash. Hence, it is inferred that the fly ash reaction can significantly improve the chloride-penetration resistance of concretes for a long period. This is further discussed in Section 6.2.

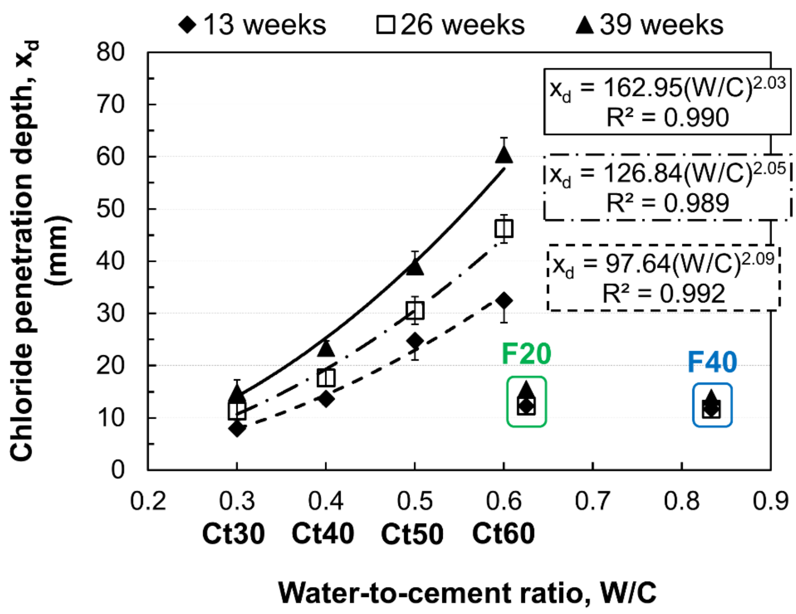

Fig. 5.3 The x_d of concrete specimens after immersion periods of 13, 26, and 39 weeks and the relationship between the x_d and the W/C ratio for the control concretes

Figure 5.4 shows the colorimetric pictures of the concrete specimens without (Ct50) and with fly ash (F20 and F40) at the same W/B ratio of 0.50 after 39 weeks of exposure to a 10% NaCl solution. The color change boundary, which shows the difference between the chloride-penetrated zone (white) and the chloride-free zone (bronze), is clearly observed in all the specimens. Although the addition of fly ash to the binder resulted in a lower pH and higher Cl^{-}/OH^{-} ratio in the pore solution [6], Kim et al. [1] demonstrated that the pH of concretes should not be lower than 11 in the colorimetric method. In addition, He et al. [7] explained the variation in the chloride ion concentration at the color change boundary and discovered that 0.1 M $AgNO_3$ solution yields the clearest boundary color. This is consistent with the results obtained herein as well as that reported in several studies [1,8–10].

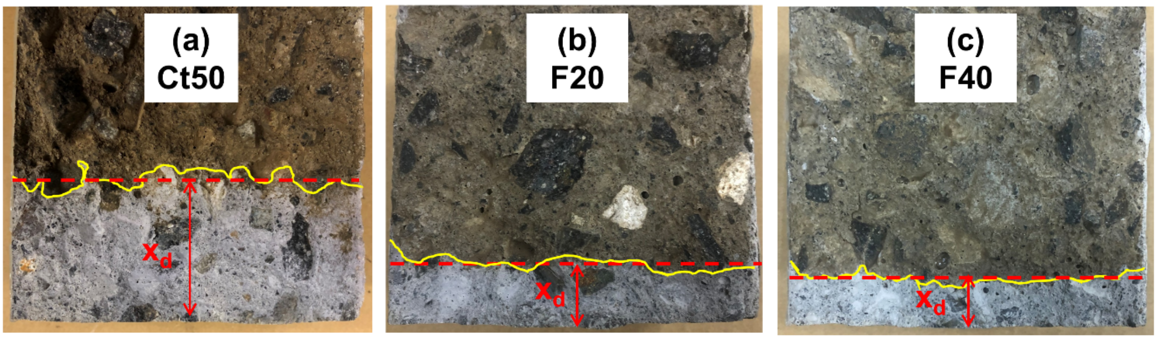

Fig. 5.4 Colorimetric pictures of concrete specimens without (Ct50) and with fly ash (F20 and F40) at the same W/B ratio of 0.50 after 39 weeks of exposure to a 10% NaCl solution

5.2.2 Evaluation of *k*-value of fly ash using the chloride-penetration depth

Figure 5.5 shows the *k*-value of the fly ash at immersion periods of 13, 26, and 39 weeks obtained using the x_d. Generally, the *k*-value increased with an increase in the immersion time. It ranged from 2.75 to 3.94 and from 1.96 to 2.69 for the F20 and F40, respectively. In previous studies, the *k*-value for the chloride-penetration resistance of concretes was reported to be 3 for low-calcium fly ash [11], whereas it was approximately 1.5 and 2 in refs [12] and [3], respectively. The difference in the *k*-value of the fly ash may be attributed to several factors such as the properties of fly ash (chemical composition and fineness), the proportion of the mixture, age of the specimen, and method of measurement. From the results of this study, the *k*-value of fly ash for the chloride-penetration resistance of the concrete is approximately higher than 2. In addition, the lower the replacement ratio of fly ash, the higher the *k*-value. This is attributed to the degree of fly ash reaction, which is discussed in Section 6.2.

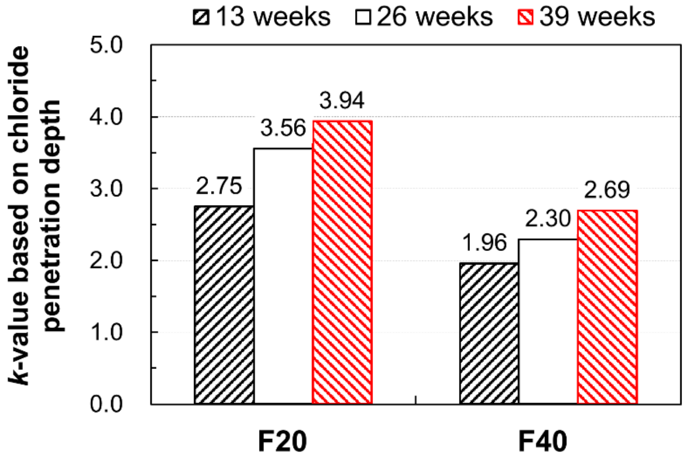

Fig. 5.5 *k*-value of fly ash for immersion periods of 13, 26, and 39 weeks obtained by using the x_d

The *k*-value based on x_d and that based on D_{app} were nearly the same after 39 weeks of exposure to a 10% NaCl solution, as shown in Fig. 5.6, which implies that x_d can be employed as a concrete-durability property to obtain the *k*-value of fly ash in a simpler way compared to D_{app}.

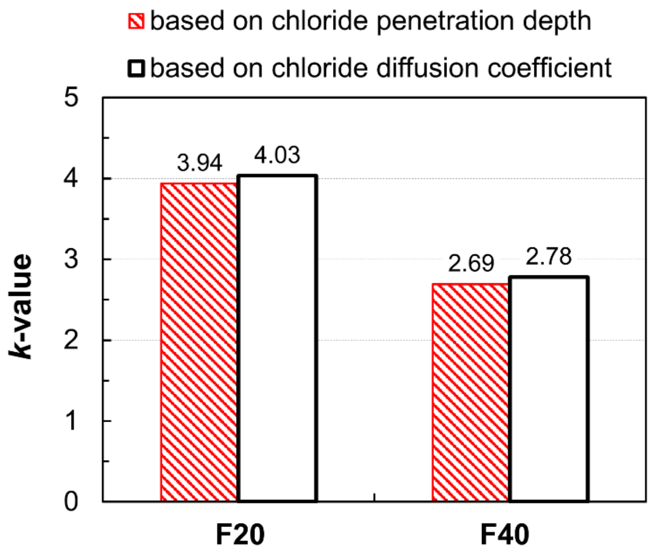

Fig. 5.6 Comparison of *k*-values using the chloride-penetration depth (x_d) and using the chloride-diffusion coefficient (D_{app}) after 39 weeks of exposure to a 10% NaCl solution

5.3 PORE SIZE DISTRIBUTION OF PASTES

The experimental results of the pore size distribution of paste specimens at a W/B ratio of 0.50 without fly ash (F0) and with 20% fly ash (F20) at 28 and 364 days are shown in Fig. 5.7. Although total pore volume of pastes with and without fly ash reduced with time, there was an obviously significant difference in the reduction of the total pore volume of both pastes. At 28 days, the total pore volume of F20 was higher than that of F0 because of a higher W/C ratio as well as the slower pozzolanic reaction of fly ash in the F20. However, the pozzolanic reaction of fly ash in F20 strongly occurred after 28 days and it resulted in a significant reduction of the total pore volume in the F20 compared with that in the F0 at 364 days, as plotted in Fig. 5.7 (a). These results are consistent well with those of a study by Sakai et al. [13]. In fact, the total pore volume of F0 decreased by approximately 12% whereas that of F20 significantly reduced by 29% from 28 to 364 days (see Fig. 5.7 (b)). The fly ash reaction degree in OPC pastes with a W/B ratio of 0.50 and 20% fly ash (F20) replacement ratio increased by 24.9% during period of 28 to 364 days, as illustrated in Fig. 5.8 which shows the correlation between the pore volume and the degree of fly ash reaction in F20 at the ages of 28 and 364 days. This increment of the degree of fly ash reaction resulted in the prominent refinement of the pore structure in the F20, especially for the pore diameter in 0.02 to 0.33 μm range. This was considered as an experimental evidence for the refinement effect of the fly ash reaction which could improve not only concrete-strength but also concrete-durability. In more detail, similar to previous studies [14,15], addition of fly ash yielded a significant reduction of the volume of pore in the diameter range of 0.02 to 0.33 μm and an increase of that of less than 0.02 μm for a long period caused by the pozolanic reaction of fly ash, as seen in Fig. 5.8. Briefly, it can be said that the reduction of 29% in the total pore volume of F20 during a period of 28 to 364 days was mainly attributed to the pore in the diameter range of 0.02 to 0.33 μm, as obviously illustrated in Fig. 5.7 (b). As a result, the refinement effect of the fly ash reaction related to the significant reduction of the volume of pore in the diameter range of 0.02 to 0.33 μm could improve the chloride-penetration resistance of concretes.

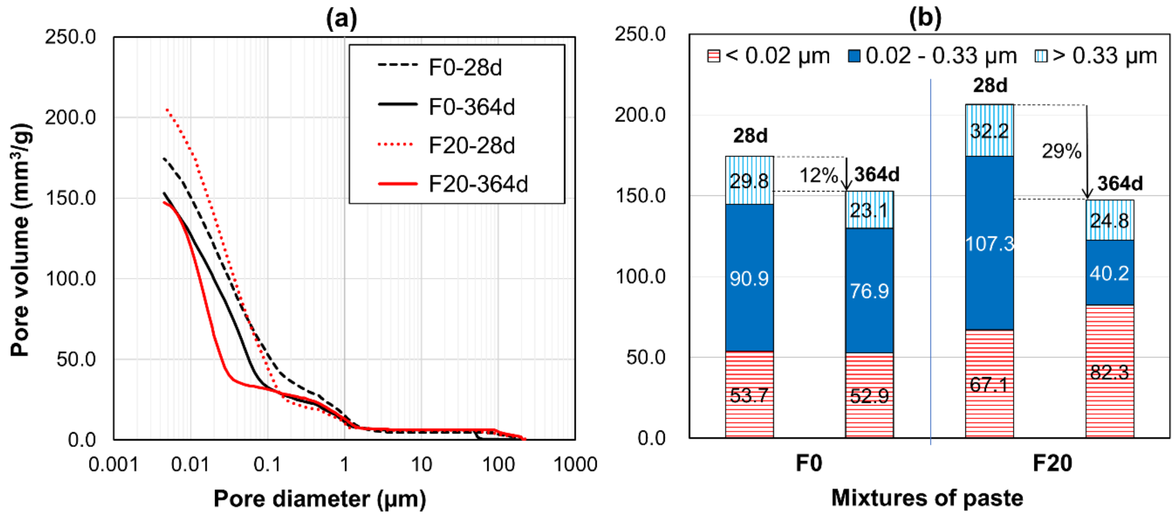

Fig. 5.7 Pore volume of paste specimens at a W/B ratio of 0.50 without fly ash (F0) and with 20% fly ash (F20) at 28 and 364 days: (a) cumulative intrusion curves and (b) pore size distributions

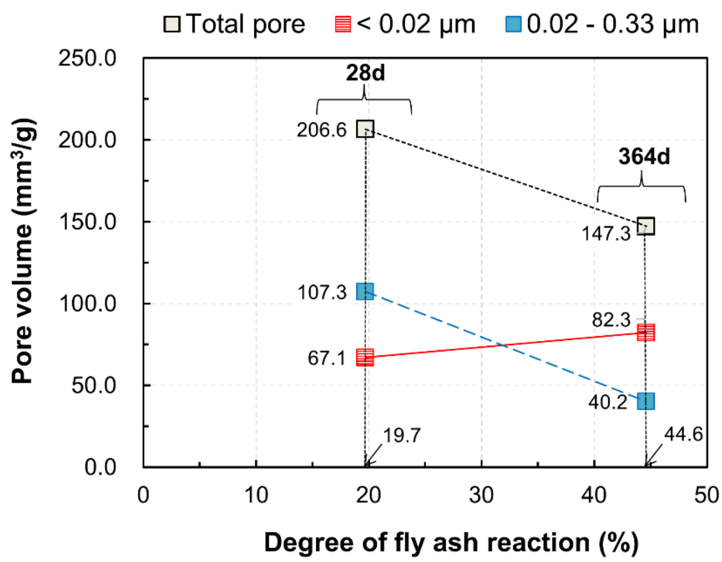

Fig. 5.8 Correlation between pore volume and degree of fly ash reaction in paste specimens at a W/B ratio of 0.50 with 20% fly ash (F20) at 28 and 364 days

5.4 SUMMARY

This chapter evaluated the *k*-value of low-calcium fly ash based on the chloride-penetration resistance of concretes in a simple approach. Four mixtures of control OPC concretes (i.e., Ct30, Ct40, Ct50, and Ct60) and two mixtures of fly-ash OPC concretes with fly ash replacement ratios of 20% (F20) and 40% (F40) by mass at a W/B ratio of 0.50 were investigated. Within the scope of this study, the following conclusions can be drawn:

a) The chloride-penetration depth (x_d) of concretes could be used as a concrete-durability property to obtain the *k*-value of fly ash for the chloride-penetration resistance of the concrete because the *k*-value using x_d was almost the same as that using the apparent diffusion coefficient (D_{app}) of chloride ion. Furthermore, with an extremely high correlation coefficient, the relationship between the x_d and W/C ratio of the control concretes should be used as the power function in determining the *k*-value of fly ash.
b) The *k*-values of fly ash based on the x_d of the concrete after the immersion periods of 13, 26, and 39 weeks ranged from 2.75 to 3.94 and from 1.96 to 2.69 for F20 and F40 samples, respectively. This indicates that the fly ash used in this study contributed significantly (over four and two times as much as the OPC) to the chloride-penetration resistance of concretes.
c) The replacement of 40% or less cement by fly ash in the concretes with a W/B ratio of 0.50 yielded chloride-penetration resistance that is as good as that of plain cement concrete with a W/B ratio of 0.30 after 39 weeks of exposure to a 10% NaCl solution with regard to the chloride-diffusion coefficient.
d) The results of pore size distribution in pastes indicated that the refinement effect of the fly ash reaction related to the significant reduction of the volume of pore in the diameter range of 0.02 to 0.33 μm could improve the chloride-penetration resistance of concretes.

With the experimental results of this investigation and the simplicity of the $AgNO_3$ spray test, we suggest that the x_d of concretes can be used to calculate the *k*-value of pozzolana (i.e., fly ash) based on the chloride-penetration resistance of the concrete. Moreover, the influence of the fly ash reaction degree on the *k*-value for durability of concrete would be addressed in next Chapter.

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CHAPTER 6

DISCUSSION ON THE *K*-VALUE OF LOW-CALCIUM FLY ASH FOR THE STRENGTH DEVELOPMENT AND CHLORIDE-PENETRATION RESISTANCE OF CONCRETES

This chapter discusses the effect of the degree of fly ash reaction on the cementing efficiency factor (*k*-value) of low-calcium fly ash for the strength development and chloride-penetration resistance of concretes. It consists of (1) the relationship between the *k*-value of fly ash for concrete-strength development and the degree of fly ash reaction, (2) the effect of the degree of fly ash reaction on the *k*-value for the chloride-penetration resistance of concretes, and (3) the difference between the *k*-value for the compressive strength and that for the chloride-penetration resistance for a purpose of comparison obtained in this study.

6.1 RELATIONSHIP BETWEEN THE *K*-VALUE OF FLY ASH FOR CONCRETE-STRENGTH DEVELOPMENT AND THE DEGREE OF FLY ASH REACTION

Figure 6.1 shows the relationship between the *k*-value of fly ash for concrete-strength development and the degree of fly ash reaction in HSPC (high-early-strength Portland cement) specimens with a W/B ratio of 0.50, and OPC (ordinary Portland cement) specimens with W/B ratios of 0.50 and 0.30. These relationships indicated that the *k*-value of fly ash with regard to concrete-strength development cannot be a constant value because it linearly increased with an increase in the fly ash reaction degree in each type of concrete, as obviously seen in Fig. 6.1. That is, fly ash reaction progresses with time, resulting in the increase in the fly ash contribution to the strength development of concrete. At the same degree of fly ash reaction, the *k*-value of fly ash is highest in the OPC concretes with a W/B ratio of 0.30, followed by that in the OPC concretes and HSPC concretes with a same W/B ratio of 0.50.

As presented in Fig 6.1, the *k*-value of fly ash for concrete-strength development is dependent not only on the degree of fly ash reaction but also on the physical effect of fly ash. Despite a lower degree of fly ash reaction in pastes with a W/B ratio of 0.30, the remarkable contribution of the fly ash to the strength development of concretes with a low W/B ratio of 0.30 at the early ages can be mainly attributed to the physical effect of fly ash that includes filler and cement-hydration enhancement effects, as mentioned in Section 4.3.2. Moreover, the efficiency of space filling due to fly ash reaction products, such as calcium silicate hydrate (C–S–H) and calcium alumino silicate hydrate (CASH), is also remarkable in pastes at a W/B ratio of 0.30 having a low initial capillary porosity. These reasons could lead to a difference between the *k*-value in OPC concretes with a W/B ratio of 0.30 and that in OPC concretes with a W/B ratio of 0.50. They could be used to explain why a significant improvement of compressive strength of concretes with lower W/B ratio even with high volume of fly ash has been obtained in previous studies [1–6].

It is revealed that the *k*-value of fly ash for the concrete-strength development is strongly dependent on the type of cement replaced partially by fly ash, as shown in Fig. 6.1. The lower the contribution of cement to strength development of concretes, the higher the *k*-value of fly ash. For the physical aspect, as fly ash possesses relatively smaller size particles compared to cement, it is capable of increasing the compressive strength of cement paste during early and later stages of hydration due to its efficient pore filling capacity [7,8]. Moreover, the cement-hydration-enhancement effect of fly ash determined by the CH enhancement ratio (i.e., *E*) in Section 4.2 is significant in the OPC pastes in comparison to the HSPC pastes because of the difference in the fineness between these cements and fly ash. These reasons confirmed that the fly ash used to replace a part of cement in concretes should have a higher Blaine fineness than the cement to reap more benefit.

For the chemical aspect, although the degree of fly ash reaction in OPC pastes is slightly lower than that in HSPC pastes with a W/B ratio of 0.50, the *k*-value of fly ash for the concrete-strength development in OPC concretes is much higher than that in HSPC concretes with a W/B ratio of 0.50 at the later ages. This can be explained due to the presence of calcium carbonate ($CaCO_3$) (approximately 4% by mass) which is incorporated as an admixture in the OPC. In fact, several studies [9–11] have pointed out the role of $CaCO_3$ in cement hydration. For example, Schöler et al. [11] concluded that a $CaCO_3$ content of 2–5% by mass leads to the stabilization of monocarbonate and ettringite, a maximum volume of hydrates, and thus to a higher compressive strength at the later ages. This is consistent well with the results of XRD analysis and compressive strength of concretes in this study.

Briefly, this study has experimentally demonstrated that the *k*-value of fly ash for the concrete-strength development increases linearly with an increase in the degree of fly ash reaction regardless of cement type and W/B ratio and it can be also affected by other factors, such as the physical effect of fly ash and presence of $CaCO_3$. The contribution of fly ash to strength development of concretes can be attributed to (1) the filler effect related to the difference in the particle size between cement and fly ash (at early age), (2) the cement-hydration-enhancement effect as explained by E (at early age) and (3) the fly ash reaction (over long period, especially after 28 days of curing).

Within the scope of this study, it is revealed that the contribution of fly ash to concrete-strength development can be partially evaluated in a chemical approach by a positive relationship between the *k*-value of fly ash and the degree of fly ash reaction. From these regression lines, to be considered the same as cement (k = 1.0), the fly ash reaction degree should reach to approximately 37.2% and 31.0% for OPC specimens with W/B ratios of 0.50 and 0.30, respectively, whereas it has to be around 79.9% for HSPC specimens with a W/B ratio of 0.50. Consequently, knowing the fly ash reaction degree in each paste, the quantity of the fly ash that considered as the cement in contributing to concrete-strength development can be estimated using this relationship. This leads to the more effective design of concrete mixture proportion that contains the fly ash as a supplementary cementitious material because the concrete technologist could select a suitable fly ash for use in concrete to achieve the desired concrete-strength. However, these relationships might vary due to various conditions, thus some further studies are necessary to have a more comprehensive evaluation of this relationship, such as the effects of physical properties as well as chemical compositions of fly ash and cement, W/B ratio, and curing condition on the *k*-value of fly ash for the concrete-strength development. Especially, the quantity of $CaCO_3$ added should be optimized to reap maximum benefit because the ideal amount of $CaCO_3$ depends on the composition and amounts of incorporated fly ash as well as the total SO_3. The amount of $CaCO_3$ that is already incorporated in cement has to be taken into account.

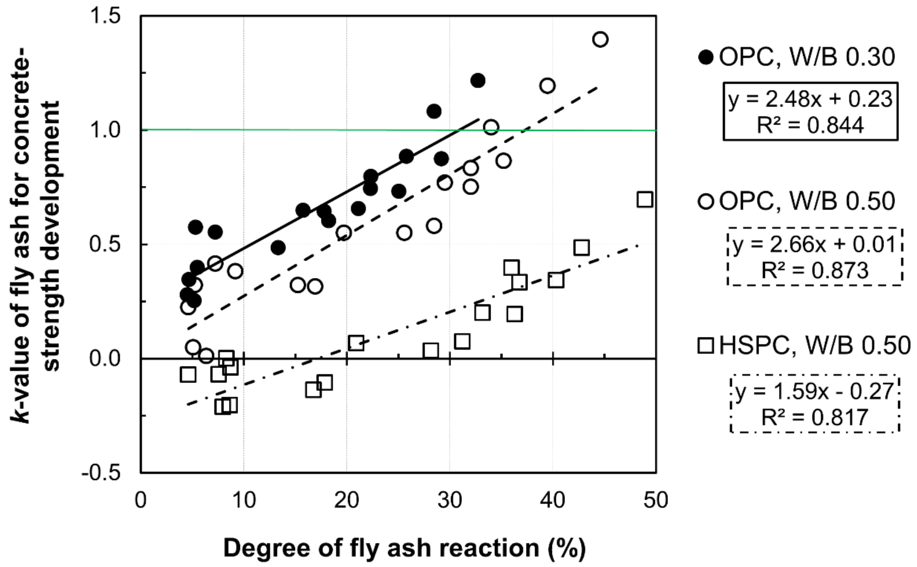

Fig. 6.1 Relationship between *k*-value of fly ash for concrete-strength development and the degree of fly ash reaction in HSPC specimens with a W/B ratio of 0.50, and OPC specimens with W/B ratios of 0.50 and 0.30

6.2. EFFECT OF THE DEGREE OF FLY ASH REACTION ON THE *K*-VALUE FOR THE CHLORIDE-PENETRATION RESISTANCE OF CONCRETES

Figure 6.2 shows the experimental results of the degree of fly ash reaction in OPC paste with fly ash replacement ratio of 20% (F20) and 40% (F40) at a W/B ratio of 0.50. This is a part of reported results in Section 4.1 and is used to get the easier understanding in this section. The rate of fly ash reaction before 91 days was significantly higher than that after 91 days, as shown in Fig. 6.2. This could clearly explain the reason for choosing 91 days as the starting time of immersion in the 10% NaCl solution, as mentioned in Section 3.4.6. For sample F20, the increments of fly ash reaction degree after 182 and 364 days were 5.5% and 10.6%, respectively, subsequent to 91 days. Meanwhile, they were 3.9% and 6.4%, respectively, for F40. These increments of the fly ash reaction degree could have a significant influence on the *k*-values regarding the chloride-penetration resistance of the concretes after the immersion periods of 13 and 39 weeks, as mentioned in Section 5.2.2. This can be explained due to (1) the improvement of chloride binding (chemical and physical) capacity of the pastes containing fly ash and (2) the significant reduction in the volume of pore in the diameter range of 0.02 to 0.33 μm as discussed in Section 5.3. Furthermore, the better quality of the interfacial transition zone (ITZ) between cement paste and coarse aggregates in fly-ash concretes may be another factor affecting the transport of chlorides in concrete, as reported in previous study [12]. The relationship between the *k*-values based on x_d and increment in the degree of fly ash reaction for each corresponding immersion period was established with an extremely high R^2 of 0.960, as shown in Fig. 6.3. From this relationship, it is determined that the *k*-value of low-calcium fly ash for the chloride-penetration resistance of concrete increases linearly with the increment in the degree of fly ash reaction for all the immersion periods. This indicates that although the increase in the degree of fly ash reaction was small after 91 days, it played a vital role in improving the chloride-penetration resistance of the fly-ash concretes, which is good experimental evidence for the enhancement of the fly ash contribution to the chloride-penetration resistance of concretes.

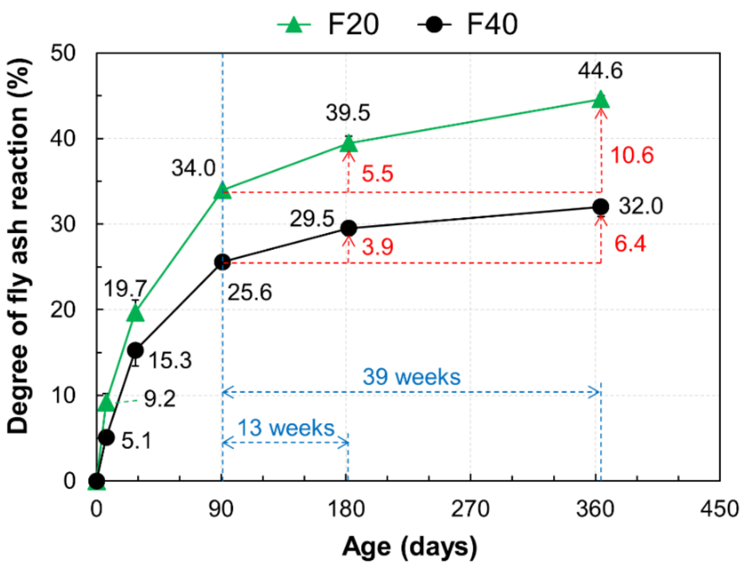

Fig. 6.2 Degrees of fly ash reaction in the pastes with time

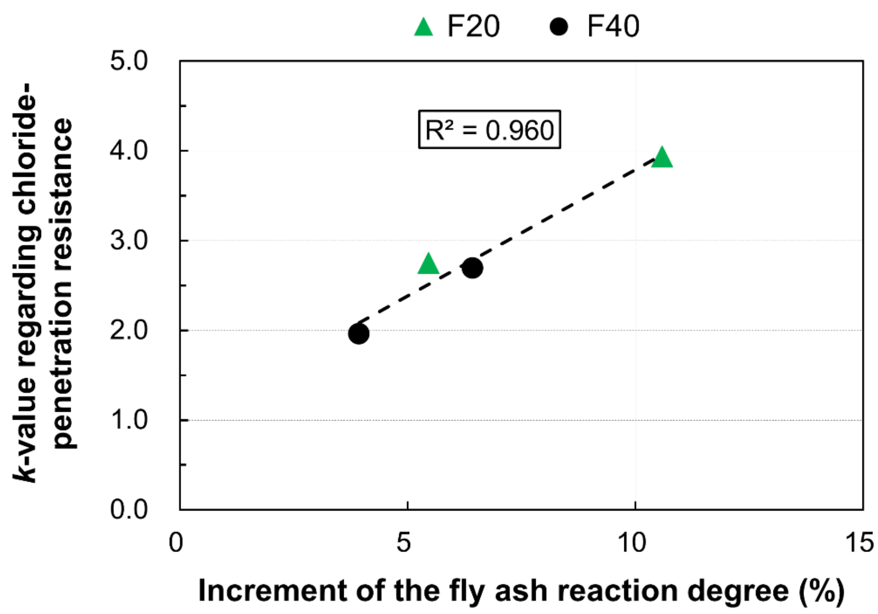

Fig. 6.3 Relationship between the *k*-value of fly ash for the chloride-penetration resistance of concrete based on x_d and the increment of the degree of fly ash reaction for each corresponding period

6.3 DIFFERENCE BETWEEN THE *K*-VALUE FOR THE COMPRESSIVE STRENGTH AND THAT FOR THE CHLORIDE-PENETRATION RESISTANCE

For the purpose of comparison, Fig. 6.4 shows a correlation between the *k*-value for the chloride-penetration resistance and that for the compressive strength at 13 and 39 weeks of exposures after 91 days of curing for the chloride-penetration test, corresponding to the ages of 182 and 364 days of curing for the compressive strength test. Generally, this correlation might vary due to various properties of fly ash, but the contribution of fly ash to the chloride-penetration resistance of concretes was more significant than that to the concrete-strength development. Within the scope of this study, although the value of R^2 for this correlation was not extremely high, at a W/B ratio of 0.50, the *k*-value of the low-calcium fly ash for the chloride-penetration resistance was approximately 2.5 higher than that for the strength of the concrete. Thus, the fly ash reaction at the later ages contributed not only to the denser pore structure but also to the formation of additional C–S–H, which has a strong physical chloride binding ability because of its very large surface area, as reported by Hirao et al. [13] and Angst et al. [14]. The chemical chloride binding through the formation of Friedel's salt between chloride and the AFm phases significantly increased since the addition of fly ash that contains a higher amount of Al_2O_3 yielded the formation of more AFm phases [14]. Additionally, as mentioned above, the replacement of cement with fly ash resulted in a lower pH and higher Cl^-/OH^- ratio in the pore solution [14]. These reasons could result in a difference between the *k*-value based on the chloride-penetration resistance and that based on the strength development. This is because the concrete-strength development is dependent mainly on the macropore refinement via fly ash reactions. This is consistent with the finding reported by Aponte et al. [15], in which higher efficiencies with regard to the durability of concrete were obtained as compared to those based on the compressive strength.

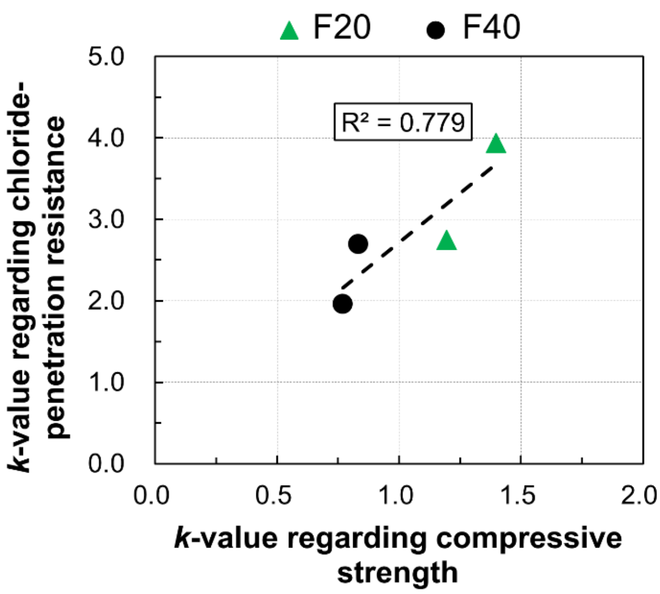

Fig. 6.4 Correlation between the *k*-value regarding the chloride-penetration resistance based on x_d and that regarding the compressive strength of the concrete at a W/B ratio of 0.50 for each corresponding time

Moreover, to reap a more comprehensive evaluation, the effects of fly ash type, cement type, W/B ratio, and curing condition on the correlation between the *k*-value regarding the chloride-penetration resistance and that regarding the compressive strength of the concrete should be investigated. The influence of the free chloride content and the chloride binding ability of fly ash on the *k*-value for the chloride-penetration resistance of concretes should be addressed in the future works as well.

6.4 SUMMARY

Within the scope of this study, it is revealed that the *k*-value of fly ash for the concrete-strength development increases linearly with an increase in the degree of fly ash reaction regardless of cement type and W/B ratio and it can be also affected by other factors, such as the physical effect of fly ash and presence of $CaCO_3$. The contribution of fly ash to strength development of concretes can be attributed to (1) the filler effect related to the difference in the particle size between cement and fly ash (at early age), (2) the cement-hydration-enhancement effect as explained by E (at early age) and (3) the fly ash reaction (over long period, especially after 28 days of curing).

The relationship between the *k*-value fly ash for the chloride-penetration resistance of concretes based on x_d and increment in the degree of fly ash reaction for each corresponding immersion period has been evaluated in this study. It is determined that the *k*-value of fly ash based on x_d increases linearly with the increment in the degree of fly ash reaction for all the immersion periods. The contribution of fly ash to the chloride-penetration resistance of concretes was much more significant (approximately 2.5 higher) than that to the strength development of concretes mainly because of the chemical and physical chloride binding ability in pastes incorporating fly ash.

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CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

This chapter shows the conclusions and the recommendations from this study.

7.1 CONCLUSIONS

The present study uses a low-calcium fly ash and two types of cement, namely, ordinary Portland cement (OPC) and high-early-strength Portland cement (HSPC) as binders. Control concrete samples with water-to-binder (W/B) ratios of 0.30, 0.40, 0.50, and 0.60 by mass were investigated and cement was partially replaced with fly ash at ratios of 20% to 40% by mass for the paste and concrete specimens with a W/B ratio of 0.50. Additionally, a W/B ratio of 0.30 was further used for making OPC specimens to investigate effect of W/B ratio on the *k*-value of fly ash for the concrete-strength development. For evaluation of the *k*-value of fly ash for the chloride-penetration resistance of concretes, only the OPC and two fly ash replacement ratios of 20% (F20) and 40% (F40) by mass for the paste and concrete specimens with a W/B ratio of 0.50 were evaluated. Within the scope of the present study, the following conclusions can be drawn:

(1) For the *k*-value of fly ash for concrete-strength development

a) The contribution of fly ash to strength development of concrete can be attributed to the filler effect related to the difference in the particle size between cement and fly ash (at early age), the cement-hydration-enhancement effect (at early age), and the fly ash reaction (over long period). Additionally, the *k*-value of fly ash for the strength development of concretes linearly increased with an increase in the degree of fly ash reaction regardless of cement type and W/B ratio.

b) The effect of cement type on the *k*-value of fly ash for concrete-strength development was obviously remarkable due to the difference in the relationships between cement-to-water ratio and compressive strength of the control concretes. With the presence of $CaCO_3$ (approximate 4% by mass) in the OPC, the stabilization of monocarbonate resulting indirectly in the stabilization of ettringite led to a more significant increase in the compressive strength of OPC concrete containing fly ash despite a low degree of fly ash reaction in OPC paste compared with HSPC paste. With a W/B ratio of 0.50, the *k*-value ranged from –0.21 to 0.70 in HSPC concrete while it ranged from 0.01 to 1.40 in OPC concrete up to the age of 364 days.

c) For OPC concrete, the lower the W/B ratio, the higher the *k*-value of fly ash at the early ages mainly due to cement-hydration-enhancement effect of fly ash as explained by the CH enhancement ratio (i.e., *E*). The *k*-value ranged from 0.25 to 0.65 at a low W/B ratio of 0.30 while it ranged from 0.01 to 0.55 at a high W/B ratio of 0.50 within 28 days. Nevertheless, the *k*-value increased remarkably from 0.31 to 1.40 at the high W/B ratio of 0.50 while it increased from 0.48 to 1.22 at the low W/B ratio of 0.30 after 28 days up to 364 days due to mainly the pozzolanic reaction of fly ash.

d) A modified equation of the CH consumption, taking the cement-hydration-enhancement effect into account, was firstly proposed to evaluate the CH consumption in fly-ash cement paste. This result is consistent with the result of the degree of fly ash reaction, especially for OPC paste with a low W/B ratio of 0.30.

e) It is confirmed that the contribution of fly ash to concrete-strength development can be partially evaluated in a chemical approach by a positive relationship between the *k*-value of fly ash and the degree of fly ash reaction. Consequently, knowing the fly ash reaction degree in each paste, the quantity of the fly ash that is considered as the cement in contributing to concrete-strength development can be estimated using this relationship.

(2) For the *k*-value of fly ash for the chloride-penetration resistance of concretes

a) The chloride-penetration depth (x_d) of concretes could be used as a concrete-durability property to obtain the *k*-value of fly ash for the chloride-penetration resistance of the concrete because the *k*-value using x_d was almost the same as that using the apparent diffusion coefficient (D_{app}) of chloride ion. Furthermore, with an extremely high correlation coefficient, the relationship between the x_d and water-to-cement ratio of the control concretes should be used as the power function in determining the *k*-value of fly ash.

b) The *k*-values of fly ash based on the x_d of the concrete after the immersion periods of 13, 26, and 39 weeks ranged from 2.75 to 3.94 and from 1.96 to 2.69 for F20 and F40 samples, respectively. This indicates that the fly ash used in this study contributed to the chloride-penetration resistance of concretes approximately twice more than cement.

c) The replacement of 40% or less cement by fly ash in the concretes with a W/B ratio of 0.50 yielded chloride-penetration resistance that is as good as that of plain cement concrete with a W/B ratio of 0.30 after 39 weeks of exposure to a 10% NaCl solution with regard to the chloride-diffusion coefficient.

d) The results of pore size distribution in pastes indicated that the refinement effect of the fly ash reaction related to the significant reduction of the volume of pore in the diameter range of 0.02 to 0.33 μm could improve the chloride-penetration resistance of concretes.

e) The *k*-value of fly ash based on the x_d of concretes increased linearly with the increment in the degree of fly ash reaction subsequent to the start of immersion. For the concretes with a W/B ratio of 0.50, the *k*-value of fly ash for the chloride-penetration resistance of the concrete was approximately 2.5 higher than that for the concrete-strength development at each corresponding time.

Briefly, with the experimental results of this investigation and the simplicity of the $AgNO_3$ spray test, it was suggested that the x_d of concretes can be used to calculate in a simple approach the *k*-value of pozzolana (i.e., fly ash) for the chloride-penetration resistance of the concrete. On the other hand, the effect of cement type and W/B ratio on the *k*-value of fly ash for the concrete-strength development was evaluated for a long period. Furthermore, the significant effect of fly ash reactions on its *k*-value for the strength development and chloride-penetration resistance of concretes was addressed through considering the results of phase identification, CH content, and pore size distribution in pastes. In addition, the correlation between the *k*-value of fly ash for the strength and durability of the concrete was obtained in this study.

7.2. RECOMMENDATIONS

Based on the results in this study, some recommendations for the future work can be drawn as follows:

1) The relationship between the *k*-value of fly ash and the degree of fly ash reaction might vary due to various conditions, thus the further studies are necessary to have some guidelines of how to make use of the *k*-value of fly ash to optimize the concrete mixture proportion. Especially, fly ashes from various sources should be investigated to related the *k*-value to their chemical compositions and amorphous content.
2) The effect of $CaCO_3$ on the *k*-value of fly ash should be evaluated quantitatively in the future work. The quantity of $CaCO_3$ added should be optimized to reap maximum benefit because the ideal amount of $CaCO_3$ depends on the composition and amounts of incorporated fly ash as well as the total SO_3. The amount of $CaCO_3$ that is already incorporated in cement has to be taken into account before a further addition.
3) With the experimental results of this investigation and the simplicity of the $AgNO_3$ spray test, it is indicated that the x_d of concretes can be used to calculate the *k*-value of fly ash

based on the chloride-penetration resistance of the concrete. Moreover, some further studies are necessary to have a more comprehensive evaluation, such as the effects of physical properties as well as chemical compositions of fly ash, cement type, W/B ratio, and curing condition on the *k*-value for the chloride-penetration resistance of concretes.

4) The influence of the free chloride content and the chloride binding ability of fly ash on the *k*-value for durability of concrete should be addressed in the future works as well.
5) In addition to fly ash, the x_d of concretes used to calculate the *k*-value for the durability property of concretes should be carried out on the other pozzolan materials, such as ground granulated slag, metakaolin, silica fume, and so on.
6) Additionally, the *k*-values of fly ash for the other properties of concretes (i.e., carbonation resistance, sulphate attack, mitigation of alkali silicate reaction, and shrinkage) should be investigated and compared with those of other pozzolan materials to reap a more comprehensive evaluation in the future.