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Experimental Investigation on Reaction Rate and Self-healing Ability in Fly Ash Blended Cement Mixtures

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Abstract

This paper investigates the hydration rate in fly ash blended cement paste and self-healing ability in mortar incorporating fly ash for long-term period. The hydration rate of fly ash and consumption of calcium hydroxide in fly ash paste containing calcium hydroxide reagents were examined at different ages and curing temperatures. Five types of fly ash blended cement paste, each of which with 10% by mass fly ash replacement ratio, were prepared for the acceleration test at 80°C. Four fly ash cement pastes, with two types of fly ash and with fly ash replacement ratios by mass 10% and 30%, were tested to measure the rate of reaction of fly ash in the mixtures. Ten mixtures were tested to evaluate the self-healing ability of mortar incorporating fly ash, considering different types of cement and fly ash. Compressive strength, bending strength, accelerated carbonation depth, after applying freeze/thaw cycling until 60% and 80% relative dynamic modulus of elasticity, and porosity were examined. The experimental results revealed that incorporating fly ash in cement paste would affect the hydration rate of fly ash and consumption of calcium hydroxide. Curing temperature can affect hydration rate, acceleration rate and velocity of reaction rate in fly ash cement paste. Moreover, it is confirmed that self-healing ability, carbonation rate coefficient and the pore volume modification in mortar incorporating fly ash rely on the curing conditions. Finally, it is suggested that the practical fly ash replacement ratio in concrete could be 10% to 15% and 11% to 20% for water to cement ratios 0.50 to 0.55 and 0.55 to 0.60, respectively.

1. Introduction

Durability of concrete would be adversely degraded by micro cracks due to freezing/thawing cycles and drying/wetting cycles. Hence, it is necessary to repair appropriately the cracks in order to extend the service life of concrete structures. On the other hand, it has been well known that concrete has originally self-healing function due to rehydration of cementitious materials such as anhydrous cement in the microstructure. Self-healing of concrete is a phenomenon that micro cracks in a concrete structure naturally close under an environment with

water supply. To restore the original performance of damaged concrete, self-healing ability is quite needed since it is a relatively cost-effective solution compared to conventional repair methods. Fly ash, which has been increasingly used as a concrete admixture in last decades, has such kind of appropriate self-healing ability in the presence of calcium hydroxide. The filling of micro cracks, with hydrated products of fly ash and cement, can decrease the transfer of substances into damaged concrete, and hence, longer life span of concrete structures can be achieved appropriately.

In 2009, the Japan Concrete Institute committee has reported the definition of self-healing such as autogenous healing, natural healing, autonomic healing, engineered healing and activated repairing (JCI 2009). It was concluded that in the case of low water to cement ratio and high fly ash replacement ratio, the additional hydration would be caused easily by water supply around the micro cracks because of the pozzolanic reaction of fly ash. This pozzolanic reaction produces C-S-H gel that may heal micro cracks and result in better performance of cement mixtures. However, it is not sufficient to understand the self-healing mechanism in long-term period, to explain the hydration process of fly ash blended cement mixtures.

There are many studies in the literatures that have dealt with hydration property of cement based on X-ray diffraction (XRD)-Reitveld analysis. They showed that XRD-Reitveld analysis is able to investigate the hydration characteristics of cement, considering the quantitative technique, curing condition and particle size distri-

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bution in cement and amorphous admixtures (Yamaguchi *et al.* 1960; Asaga *et al.* 1992; Itoh *et al.* 2002; Whitfield and Mitchell 2003; Sagawa *et al.* 2004; Scrivener *et al.* 2004; Hoshino *et al.* 2005). Additionally, the reaction model of cement paste has been developed by Sagawa *et al.* (2005); this model considers the thickness of hydrated products.

Takei *et al.* (1997, 2004) performed a fundamental study on the reaction between fly ash and calcium hydroxide to measure the calcium hydroxide and hydration water using thermogravimetry and differential thermal analysis (TG-DTA). To calculate the reaction rate and unhydrated products of fly ash, the selective dissolution method has been reported (Ohsawa *et al.* 1999; Matsui and Ikabata 1999; Yamamoto and Kanazu 2004; Termkhajornkit *et al.* 2005).

Based on the above literatures, there is lack of information about long-term behavior of hydration process, hydrated products and self-healing ability in fly ash blended cement mixtures for different types of fly ash and cement. The objective of this study is to investigate the hydration process of fly ash and consumption of calcium hydroxide and self-healing performance in fly ash cement mixtures for long-term examination period, taking into consideration effect of cement types, fly ash types, fly ash replacement ratio and curing conditions. The observation of hydration rate of fly ash and calcium hydroxide was conducted by the combination of selective dissolution and XRD-Rietveld analysis. Thermogravimetry and differential thermal analysis (TG-DTA) was applied to quantify amount of calcium hydroxide in hardened paste. In order to introduce the micro cracks in sample, the freeze/thaw cycling test was applied to pose damage in mortar incorporating fly ash, and then, self-healing effect on accelerated carbonation tests, compressive strength, bending strength, relative dynamic modulus (RDM) of elasticity, point count test and modification of pore volume were evaluated. The porosity and pore structure modification were measured by mercury intrusion porosimetry (MIP). Finally, the obtained results from this study are valuable information for practical design codes in which the understanding of

self-healing ability of fly ash is quite needed to prolong the service life of concrete structures.

2. Experiment

The experimental work in this study consists of three parts. The first part deals with reaction rate of fly ash and consumption of calcium hydroxide. The second part concerns with reaction rate of fly ash cement paste based on acceleration test at 80°C, and the velocity of fly ash reaction rate. While the last part of this study concerns with self-healing effect in mortars incorporating fly ash, which exposed damage by freezing/thawing cycles, based on mechanical tests such as compressive and bending strengths, relative dynamic modulus of elasticity, accelerated carbonation test, point count test and porosity. Details of the experimental plan and investigated fly ash blended cement samples are given below.

2.1 Reaction of fly ash and calcium hydroxide reagents

The physical properties and chemical composition of ordinary Portland cement (OPC) and fly ash are shown in **Tables 1** and **2**; mineral composition and glass phase for all investigated types of fly ash are shown in **Table 3**. The experimental plan for fly ash samples 4A and 2B is shown in **Table 4**. The materials were mixed 2 minutes and then casted in cubic mould with dimension of 50×50×50 mm. After casting, 4A and 2B samples were cured in water at 60°C and 40°C, respectively, for 1 day. After 1 day, they were demoulded and then moved into water till the planned ages at 60°C and 40°C for 4A and 2B samples, respectively. At the required ages, samples were soaked in acetone to stop the hydration, dried at 105°C, and then ground by ball mill. The amount of unhydrated fly ash was estimated based on the selective dissolution method (Ohsawa *et al.* 1999; Matsui and Ikabata 1999; Yamamoto and Kanazu 2004; Termkhajornkit *et al.* 2005).

The rate of hydration of cement minerals was calculated by the results obtained by the XRD-Rietveld analysis. The XRD-Rietveld analysis was performed

Table 1 Characteristics of cement.

Types of cement	Density (g/cm ³)	Blain (cm ² /g)	Chemical composition(%)							Mineral composition (%)			
			SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃		C ₃ S	C ₂ S	C ₃ A	C ₄ AF
N	3.16	3250	21.5	5.4	2.9	64.3	1.9	1.8		52	23	10	9
H	3.13	4650	20.4	4.8	2.5	64.4	2.3	3.2		62	12	9	7
L	3.24	3330	25.9	3.2	3.7	63.1	0.1	2.4		27	54	2	11

Table 2 Properties of fly ash used for reaction rate tests.

Types of Fly ash	Blain fineness (cm ² /g)	Chemical composition(%)										Density (g/cm ³)	Insoluble matter(%)
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	TiO ₂	MnO		
4A	3900	73.1	16.9	3.0	1.6	1.2	0.3	1.0	0.2	0.7	0.0	2.11	93.4
4B	4120	59.4	24.9	6.0	3.2	1.0	0.6	1.2	0.1	1.0	0.1	2.19	89.1
4C	4060	52.7	24.2	12.4	3.2	1.0	0.4	1.4	0.4	0.8	0.1	2.41	84.4
2A	3300	62.0	22.3	4.7	2.8	1.9	1.2	0.3	1.1	1.1	0.0	2.21	91.3
2B	4240	46.9	23.9	11.0	2.8	4.1	1.2	0.2	3.3	1.2	0.1	2.39	87.5

Table 3 Mineral composition and glass phase for fly ash determined by XRD-Rietveld analysis.

Types of fly ash	Mullite	Quartz	Magnetite	Glass phase	Ignition loss(%)
4A	4.6	7.8	0.5	85.1	2.0
4B	10.0	6.7	2.4	78.5	2.5
4C	10.5	8.8	4.4	73.0	3.4
2A	11.3	9.2	0.6	76.3	2.6
2B	8.9	2.8	2.2	80.7	5.4

Table 4 Experimental plan for hydration rate test.

Types of fly ash	Ca(OH) ₂ : Fly ash	W/B (%)	Curing Temperature(°C)	Curing age (days)
4A	1:1	50	60	7,14,21,28 and 56
2B			40	1,4,5,7 and 28

Note: W/B = Water / (Fly ash + Calcium hydroxide reagent).

after adding 10% of Al₂O₃, as internal reference, to the sample. The sample and internal reference were blended uniformly till becoming a harmonized texture. Cu K α X-ray diffraction system was used for conducting XRD-Rietveld analysis, with 45 kV tube electric voltage, 40mA tube current, 20-70° scanning range of 2 θ with scan width step of 0.02°. The Rietveld analysis program used in this study was Rietan-2000 software developed by Izumi and Ikeda (2000). Target minerals for analysis were C₃S, C₂S, C₃A, C₄AF, Mullite, Quartz and Magnetite. In addition, the thermogravimetry and differential thermal analysis (TG-DTA) was performed to obtain the amount of calcium hydroxide in hardened paste. An ignition loss was measured according to JIS R5202.

2.2 Acceleration test for fly ash cement paste

2.2.1 Acceleration test of fly ash reaction

In order to investigate the insoluble residue contents (unhydrated amount fly ash) until the final reaction in fly ash cement paste, the acceleration test at 80°C of five fly ash blended cement samples, which are 4A, 4B, 4C, 2A and 2B in addition to N sample as a reference mixture, was conducted. Each sample includes different type of

fly ash and with 10% by mass fly ash replacement ratio. The experimental plan is given in **Table 5**. All samples mixed according to JIS R5201 before they were casted into 40×40×160 mm prisms, and then cured in water at 20°C for 1 day. After 1 day, the samples were cut as 3 mm thick, and cured in water at 80°C. At the testing age, the samples were soaked in acetone to stop the hydration reaction, dried at 105°C and further ground by ball mill until particles became smaller than 75 μ m.

2.2.2 Measurement of velocity of fly ash reaction rate

Four fly ash cement paste samples, which are 4A1, 4A3, 2B1 and 2B3 with two types of fly ash and with fly ash replacement ratios by mass 10% and 30% in addition to N sample as a reference mixture, were tested to measure the reaction rate in the mixtures. The experimental plan is shown in **Table 6**. Moreover, the effect of different curing conditions was also considered. All samples mixed according to JIS R5201, and then cured in water at 20°C for 7 days. After 7 days, the samples were cut as 3 mm thick, and cured in water at 5°C, 20°C and 40°C. At the testing age, the samples were soaked in acetone to stop

Table 5 Experimental plan for acceleration test.

Designation	Fly ash (mass %)	W/C (%)	W/B (%)	Curing Temperature(°C)	Curing age (days)
4A	10	50	45	80 in water	5hr, 1, 2, 3, 4, 7, 14, 28, 56 and 94
4B					
4C					
2A					
2B					
N	0		-		

Note: W = water, C = Cement, W/B = Water / (Fly ash + Cement).

Table 6 Experimental plan for reaction rate test.

Designation	Types of fly ash	Fly ash (mass %)	W/C (%)	W/B (%)	Curing Temperature(°C)	Curing age (days)
4A1	4A	10	50	45.5	5, 20 and 40 in water	14, 21, 35, 63 and 198
4A3		30		38.5		
2B1	2B	10		45.5		
2B3		30		38.5		
N	-	0		0		

Note: W/B = Water / (Fly ash + Cement).

the hydration reaction, dried at 105°C and further ground by ball mill until 75 μm . The amount of unhydrated fly ash was estimated based on the selective dissolution method, and the rate of hydration of cement minerals was calculated by the results obtained by the XRD-Rietveld analysis; both methods apply the same procedures explained in section 2.1. TG-DTA was conducted to observe the amount of the calcium hydroxide and calcium carbonate in hardened paste (Ohsawa *et al.* 1999). An ignition loss was tested according to JIS R5202.

2.3 Self-healing of fly ash

Ten mixtures were tested to evaluate the self-healing ability of mortar incorporating fly ash, considering different types of cement, fly ash, fly ash replacement ratio and curing conditions. The experiments used ordinary Portland cement (N), high early strength Portland cement (H) and low heat Portland cement (L). The fly ash characteristic properties, such as blain fineness, ignition loss and glass phase, were given in **Table 7**. The mortar mixtures were prepared with the proportions summarized in **Table 8**. It is well known that the reaction rate of fly ash is late, in fact that may cause a decrease of the compressive strength at early age. This drawback can be improved by using high early strength Portland cement type, therefore, the high early strength Portland cement type (H) was chosen in order to avoid the decrease of compressive strength at early ages. In addition, low heat Portland cement has a large amount of C_2S (belite), unlike ordinary Portland cement and that may improve the long-term reaction. The physical properties and chemical composition of ordinary Portland cement (N), high early strength Portland cement (H) and low heat

Portland cement (L) are shown in **Table 1**. The cement replacement ratio of these two types cement could be calculated from mineral composition. The ten mortar mixtures consist of one OPC mortar sample (N) without fly ash replacement and eight fly ash cement mortar samples with mixing ratio 7 to 3 for high early strength Portland cement to low heat Portland cement, respectively, and with fly ash replacement ratio as 10%, 20% and 30% by volume. The water to cement ratio (W/C) in this experiment varied as 45%, 55% and 65%. After casting, samples were cured under a condition of 20°C for 4 weeks in water. In order to introduce the micro cracks in the sample, the freeze/thaw test was performed until relative dynamic modulus of elasticity (RDM) 60% and 80%, in accordance with JIS A 1127. The relative dynamic modulus of elasticity was determined by measuring the resonant frequency and was calculated as the percentage fraction of square transverse frequency after n cycles of freeze/thaw test to square transverse frequency at 0 cycle of freeze/thaw test. After deterioration of samples, different curing conditions were applied as 20°C for 1 week and 40°C for 4 weeks in water. Then, tests for physical properties, which are compressive test, bending test, accelerated carbonation depth test and point count procedure, of samples at testing ages were performed.

In the point count test, which was used to quantify the change of the number of cracks after deterioration, the number of cracks in sample was analyzed using a modified point count procedure which was suggested by T. Matsumura *et al.* (2003) who investigated experimentally the relationship between the number of cracks and degree of frost damage by means of image analysing microscope (with 100 $\times$ magnification). It was inferred that the decrease of relative dynamic modulus can increase the number of cracks in concrete sample after the frost damage has taken place. In the accelerated carbonation test, at condition of 20°C and 60% RH, after 4 weeks the samples were dried in advance, and then this test was carried out with 5% CO_2 concentration at 1, 4 and 13 weeks. Finally, the PoreMaster 33 mercury intrusion porosimetry (MIP) was used to measure the pore

Table 7 Properties of the fly ash used for self-healing ability tests.

Types of fly ash	Blain fineness (cm^2/g)	Ignition loss (%)	Glass Phase (%)
A	4090	1.5	88.8
B	4040	2.1	86.2
C	3160	1.9	88.4
D	2830	1.7	80.6

Table 8 Mortar mix proportion.

Designation	W/C (%)	Types of fly ash	F/ (S+F) (vol.%)	Degree of deterioration (%)	Curing age and temperature after deterioration (°C)	Unit weight (kg/m³)					
						W	cement			F	S
							N	H	L		
N	55	-	-	60 and 80	20 at 1 week and 40 at 4 weeks in water	342	621	-	-	-	1241
HL		-	-			342	-	434	187	-	1241
FA20		A	20			342	-	434	187	97	1119
FA10			10	342		-	434	187	195	994	
FA30			30	342		-	434	187	293	870	
FAX	45	20	60%	316		-	492	211	221	1125	
FAY	65			380		-	409	175	183	937	
FB	55			B		342	-	434	187	195	994
FC				C		342	-	434	187	207	994
FD				D		342	-	434	187	205	994

Note: W = water, N = Ordinary Portland cement, H = High early strength Portland cement,

structure distribution and its modification in the mortar samples, so that the influence of fly ash and the curing condition on the change of pore structure volume in studied samples can be examined. In order to determine the hydration rate of fly ash for normal slab concrete in Asahikawa, Japan, the natural temperature and humidity were investigated for 2 years. The water to cement ratio (W/C) of normal concrete in this experiment was 50%.

3. Results and discussion

3.1 Reaction of fly ash and calcium hydroxide reagent

The methods based on selective dissolution (Ohsawa *et al.* 1999; Matsui *et al.* 1999) can be adopted as the calculation method of reaction rate of unhydrated fly ash. The phase constitution of fly ash in both unreacted process and reaction process is considered in **Fig. 1**. Glass contents in the unreacted process can be calculated by deducting the amount of crystalline phase and ignition loss from unreacted fly ash amount. The glass contents can be divided into two parts which are acid soluble amount (*As*) and acid insoluble matter (*Au*). As for the crystal phase part, assuming that it does not dissolve in acid, acid insoluble matter can be obtained by excluding the amount of crystal phase from the test results for the insoluble residue quantity. Thus, the calculation method of reaction ratio by selective dissolution method can be explained as follows. When fly ash reacts, it becomes the substance where portion of insoluble matter dissolves in acid. Here, selective dissolution test is carried out, and the unreacted part of acid insoluble matter is measured as an insoluble residue. Then, the dissolved contents can be estimated from reacted weights of paste. The following patterns are considered for the calculation method.

Pattern 1: it is related to the melting ratio of glass phase and crystal phase (*Cr*). This pattern (*Rec*) is calculated as follows:

$$Rec = (As + Ar) / (Au + As + Cr) \quad (1)$$

Pattern 2: it is related to the melting ratio for glass phase. This pattern (*Rg*) is expressed as follows:

$$Rg = (As + Ar) / (Au + As) \quad (2)$$

Pattern 3: it can be estimated from the melting ratio for acid insoluble matter. This pattern (*Rus*) is given as shown in Eq. (3):

$$Rus = Ar / (Au + Cr) \quad (3)$$

Pattern 4: It can be obtained from the melting ratio for the acid insoluble matter in the glass phase. This pattern (*Rau*) is calculated as in Eq. (4):

$$Rau = Ar / Au \quad (4)$$

Figure 2 shows the comparison of the consumption of calcium hydroxide contents and reaction rate of fly ash for each pattern. Relationship between the reaction rate and the calcium hydroxide consumption for fly ash cement paste can be expressed as given in Eq. (5):

$$\text{Ca(OH)}_2 \text{ consumption contents} = W_0 - \frac{W_{cc} + (W_{cc} \times 74.09 / 100.09)}{(100 - R_w) \times 0.01} \quad (5)$$

Where, W_0 is calcium hydroxide contents within 1g of unreacted sample (g/g), W_{ch} is the calcium hydroxide weights which include in unreacted sample 1g (g/g), W_{cc} is calcium carbonate weights in hydrated sample 1g (g/g) and R_w is the amount of bound water in 1 g within hydration sample (%).

By observing **Figs. 2 (a)** and **(b)**, which represent patterns 1 and 2, respectively, it can be inferred that, although calcium hydroxide consumption is almost zero, the reaction rate is not identical to zero. This is due to the fact that pozzolanic reaction exists in fly ash and calcium hydroxide. However, it cannot be determined which part of fly ash that reacting with calcium hydroxide. The data plotted in **Figs. 2(c)** and **(d)**, which explains behavior of patterns 3 and 4, respectively, reveals that when the consumption of calcium is almost zero, there is no contribution of calcium to reaction rate. It is obvious from the comparison given in **Fig. 2** that pattern 4 gives the best response for reaction rate of fly ash compared to other patterns 1, 2 and 3. The reason for this response is due to the assumption of pattern 4, in which the reaction rate is calculated based on the melting ratio for the acid insoluble matter in the glass phase, meaning that there is no contribution of crystalline phase (*Cr*) to reaction rate. From the results above, the reaction of fly ash with calcium hydroxide can be considered, when acid insoluble

Fig. 1 Schematic reaction models.

Fig. 2 Comparison of the consumption of CH contents and reaction rate of fly ash.

matter in the glass phase exists, as given by Eq. (4).

3.2 Fly ash cement paste acceleration reaction test at 80°C

Figure 3 presents the comparison of the pozzolanic reaction rate and curing age (days) for 5 types of fly ash cement paste. It can be inferred from the figure that the reaction rate for sample 4C, at early age, is higher than other samples. At 94 days, the reaction rate for sample 2A is increased to 100 %, while samples 4C and 2B almost have the same reaction rate. The results shown in Fig. 3 reveal that acid insoluble matter of the glass phase of fly ash (FA) reacts almost 100%, for all types of fly ash in the study at 94 days. In Fig. 4, the relationship between remaining contents of calcium hydroxide and curing ages (days) is described. The amount of calcium hydroxide in the hardened paste can be calculated as shown in Eq. (6):

$$\text{Calcium hydroxide contents} = \frac{W_{ch} + (W_{cc} \times 74.09 / 100.09)}{(100 - R_w) \times 0.01} \quad (6)$$

Where, W_{ch} is the calcium hydroxide weight which includes in unreacted sample 1g (g/g), W_{cc} is calcium carbonate weights in hydrated sample 1g (g/g) and R_w is the amount of bound water in 1 g within hydration sample (%)

In comparison with N sample, the remaining contents of calcium hydroxide in fly ash cement samples after 2

Fig. 3 Comparison of the pozzolanic reaction rate of different fly ash types versus curing age (days).

days decrease because of its pozzolanic reaction. For the remaining calcium hydroxide contents at each age, it is found that there is no significant difference among the types of fly ash. Although the pozzolanic reaction rate is almost 100%, the calcium hydroxide in paste remains after 56 days. Therefore, in case of cement paste with 10% by mass fly ash replacement ratio, it can be considered that the glass phase and insoluble residue contents in fly ash could react with the calcium hydroxide.

Fig. 4 Remaining contents of calcium hydroxide versus curing age (days).

3.3 The reaction rate of fly ash cement paste

3.3.1 Amount of calcium hydroxide

In Fig. 5, the amount of remaining calcium hydroxide in hardened fly ash paste based on the XRD-Rietveld analysis is plotted versus testing age for different curing conditions. From the figure, it can be revealed that in the case of cement paste incorporating fly ash (samples 4A and 2B), the amount of remaining calcium hydroxide is lower than N sample which is the case of OPC paste without fly ash. Also, it is obvious that fly ash cement samples with fly ash replacement ratio by mass 30%, and with high curing temperature in water (samples 4A3-40°C and 2B3-40°C), yielded smaller remaining amount of calcium hydroxide compared to other samples with smaller fly ash replacement ratio (samples 4A1-40°C and 2B1-40°C). This observation confirms that large amount of fly ash as 30% replacement ratio and high curing temperature in water can increase the consumption amount of calcium hydroxide. The reason for this behavior is due to the pozzolanic reaction of fly ash, which increases with increasing the amount of fly ash and curing temperature, and thus consumes more calcium hydroxide that comes from cement.

3.3.2 Prediction equation of reaction rate

For the hydration reaction of cement, the reaction rate for each cement minerals calculated by Sagawa *et al.* (2004, 2005) equation can be expressed as Eq. (7):

$$dx/dt = k(1/x) \quad (7)$$

Where, x is reaction thickness to inner particle, k is a constant represent the reaction rate, and t is reaction time. The hydration rate (k) can be derived from the following equation:

$$k = A \exp(-Ea/RT) \quad (8)$$

Where, A is experimental constant, Ea is apparent activation energy (J/mol), R is universal gas constant

Fig. 5 Remaining contents of $\text{Ca}(\text{OH})_2$ versus curing age(days).

Fig. 6 Rate of reaction of cement in fly ash cement mixture.

and T is temperature. In addition, an average particle size of fly ash in radius (r) can be expressed as in Eq. (9):

$$r = 3/(\rho \times s) \quad (9)$$

Where, s is blaine fineness of fly ash (cm^2/g) and ρ is the density of fly ash (g/cm^3).

The above equation can applied in the case of $x \geq r$, however, if $x < r$ the following equation can be used:

$$Fr(\%) = (1 - (r - x)^3 / r^3) \times 100 \quad (10)$$

3.3.3 Reaction of cement in fly ash blended paste

The rate of reaction of cement for fly ash paste sample 4A1 with curing temperature varies as 5°C, 20°C and 40°C is given in Fig. 6. This data is calculated by the

unreacted mineral composite based on the XRD-Rietveld analysis. Although the cement, which was blended with fly ash, could not react fully as 100%, the reaction rate is almost 85%, containing C_2S and C_4AF . The figure shows that there is influence of the curing temperature on the cement reaction rate for different ages; this is obvious when comparing the response for reaction rate of sample 4A1-20 °C with sample 4A1-5 °C.

3.3.4 Reaction of fly ash

For the rate of fly ash reaction, the dissolved ratio can be estimated by the insoluble matter contents in glass phase. The apparent activation energy (E_a) can be calculated by Eq. (8) and was obtained based on a nonlinear regression analysis applied to the experimental results; its value is given in **Table 9**. Both two types of fly ash have the same apparent activation energy (E_a), but the experimental constant (A) is slightly different. **Figure 7** shows the actual and predicted hydration rate (straight line) of fly ash in fly ash cement samples for different curing conditions and fly ash replacement ratios. In the case of 4A1 and 2B1 samples (10% by mass replacement ratio of fly ash), the actual and predicted hydrations at the final reaction in paste have the same tendency for all curing condition cases. However, in the case of 4A3 and 2B3 samples (30% by mass replacement ratio of fly ash), there is no identical tendency at the final reaction for all

Table 9 Velocity coefficient of reaction rate.

	4A	2B
E_a (kJ/mol)	67.1	67.1
A ($\times 10^8$)	10.1	9.2

Note: E_a = Apparent activation energy,
 A = Experimental constant

curing conditions. It can be inferred from **Fig. 7** that the reaction rate of fly ash depends on the curing temperature, curing age and fly ash replacement ratio.

3.4 Self-healing effects

Figures 8, 9 and 10 show the results of compressive strength, bending strength and relative dynamic modulus of elasticity for fly ash blended cement mortar samples with four fly ash types, replacement ratios vary as 10%, 20%, and 30% by volume and three types of cement. Ten mortar mixtures were prepared with the proportions summarized in **Table 8** and section 2.3. The examined mortar samples consist of N sample using OPC without fly ash replacement, nine samples using combination of high early strength Portland cement and low heat Portland cement. It can be seen that the investigation of each mortar sample includes four cases which are no cracking case, after deterioration case, cured in water 20 °C at

Fig. 7 Predicted results of fly ash reaction rate versus experimental values.

Fig. 8 Self-healing effects on compressive strength for different mixtures and curing conditions.

Fig. 9 Self-healing effects on bending strength for different mixtures and curing conditions.

Fig. 10 Self-healing effects on relative dynamic modulus of elasticity for different mixtures and different curing conditions.

1 week case and cured in water 40°C at 4 weeks case; the results of each case are shown in Figs. 8 through 10. After deterioration, it can be seen from the figures that most of the investigated samples can heal the compressive strength, bending strength and RDM. However, degree of healing in mortar samples incorporating fly ash is higher compared to N sample, which is the case of

Fig. 11 Change of carbonation depth for FA30 sample.

OPC mortar without fly ash, especially for the case of curing in water 40°C at 4 weeks. Also, it is evident that the curing condition in water 20°C at 1 week is not enough to heal the deterioration compared to the curing condition in water 40°C at 4 weeks, implying that high temperature in curing deteriorated fly ash cement mortar samples is efficient for self-healing performance. The fly ash has a pozzolanic reaction that reacts with calcium hydroxide from cement hydration and produces C-S-H gel, which may heal micro cracks under high temperature curing condition. Consequently, it is expected that the mortar made with cement and fly ash may improve various properties such as compressive strength, bending strength and RDM, showing self-healing ability. These results agree with the findings in the previous work (Pipat *et al.* 2009).

Figure 11 shows the relationship between accelerated carbonation time and carbonation depth for specimens FA30, which include 30% by volume fly ash replacement ratio, considering the four studied cases. It is clear from the figure that the carbonation depth of sample FA30 in the case of curing in water 20°C at 1 week shows almost the same response as the case after deterioration. However, the sample carbonation depth, in the case that it is cured in water 40°C at 4 weeks, is less than 1 mm. Also, it is found that the carbonation depth for the case cured in water 40°C at 4 weeks is smaller than no cracking case, at any time of accelerated carbonation test, implying that the curing condition of mortar with fly ash would affect the carbonation depth and self-healing. The fact that curing in water at high temperature would result in continuing the hydration of both unhydrated cement and fly ash, which can fill micro cracks is the cause of the observed performance in FA30 mortar sample for carbonation test.

The carbonation coefficient for each studied case of the designated mixtures is given in Fig. 12. It can be inferred from the figure that mixtures incorporating fly ash show smaller carbonation coefficient and better performance compared to the mixtures without fly ash

under curing condition of 40°C at 4 weeks. The reason that incorporating fly ash in mortar would result in higher resistance to carbonation effect is because of the pozzolanic reaction of fly ash. The pozzolanic reaction of fly ash may continue after the full hydration of cement, and consequently, micro cracks can be filled by hydrated products of fly ash resulting in higher resistance to carbonation test.

Figure 13 shows the effect of water to cement ratio on the carbonation coefficient in fly ash mortar samples FAX, FA20 and FAY, which are with same condition of type and content of fly ash but water to cement ratios, for different curing conditions. It is found that the fly ash mortar samples with lower water to cement ratio lead to smaller carbonation coefficient and better self-healing performance for the studied cases. The fact that smaller water to cement ratio may cause smaller volume of micro cracks and pores in mortar sample, which is enough to be sealed by hydration products of cement and fly ash, is the reason for this better self-healing ability and carbonation resistance. On the other hand, larger water to cement ratio may contribute into a large volume of micro cracks and pores in mortar sample, which requires more hydration products of cement and fly ash to be filled in order to have more resistance for carbonation test.

The values of carbonation coefficient for two mortar mixes, which are N (OPC mortar mix), FA20 (fly ash cement mortar mix with 20% by volume replacement ratio), are given in **Fig. 14**. Also, the figure shows the results of carbonation coefficient for seven cases of each examined mortar mixes, which are no cracking case, after deterioration (RDM 60%) case, cured in water 20°C at 1 week (RDM 60%) case and cured in water 40°C at 4 weeks (RDM 60%) case, after deterioration (RDM 80%) case, cured in water 20°C at 1 week (RDM 80%) case and cured in water 40°C at 4 weeks (RDM 80%) case. It can be seen from the figure that fly ash mortar sample FA20 shows smaller carbonation coefficient under curing condition 40°C in water at 4 weeks for both deterioration indexes 60% and 80% compared to OPC mortar mix N for the same curing condition. This behavior can be attributed to the fact that fly ash is a pozzolanic active material that reacts with calcium hydroxide in cement producing C-S-H gel efficiently under high temperature curing condition in water, which may fill micro cracks in the fly ash mortar mixtures, and thus, improve the self-healing performance and resistance to carbonation.

3.5 Pore structure investigation and point count

Figures 15 (a), (b) and (c) show the change in relative pore volume with respect to pore size for three mortar samples N, HL and FA20, respectively. These results which were obtained by mercury intrusion porosimetry (MIP) technique, for four different cases which are no cracking case, after deterioration case, cured in water 20°C at 1 week case and cured in water 40°C at 4 weeks

Fig. 12 Self-healing effects on carbonation coefficient for different mixtures and curing conditions.

Fig. 13 Change of carbonation coefficient for fly ash mortar samples with different water to cement ratio subjected to CO₂ for 13 weeks after drying.

Fig. 14 Change of carbonation coefficient for different damage degrees and curing conditions.

Fig. 15 Change of pore volume of mortar mixtures for different curing conditions.

case are given in the figure. It should be noticed that mortar samples HL and FA20 incorporate a combination of high early strength Portland cement type (H) and low heat Portland cement (L), while mortar sample N incorporates OPC cement. In addition, mortar sample FA20 incorporates fly ash with 20% replacement ratio. Pore size distributions were examined; the pore sizes were divided into two ranges, 6 to 50 nm of meso pores

Fig. 16 Change of the number of cracks with mortar mixtures for different curing conditions.

and larger than 50 nm to 10 µm of micro pores. (F. de Larrard 2002 and M.M.Y. Delmi 2004). It is obvious from Fig. 15 that the change in ratio of pore volume for 6 to 50 nm pore size is almost the same between N, HL and FA20 mortar mixes. While after deterioration, the rate of pore volume for 50 nm to 10 µm pore size for N mortar sample increased in comparison to HL and FA20 mortar samples, this is due to using of a combination of H and L cement types. A notable reduction of pore volume rate for 50 nm to 10 µm pore size in fly ash mortar sample FA20 was obtained for 40°C curing condition in water at 4 weeks case. The reason for this performance is that the fly ash has a pozzolanic ability that produces C-S-H gel, which may fill 50 nm to 10 µm pore size under high temperature curing condition.

Figure 16 shows change of the number of cracks per unit length obtained by point count test for N, HL and FA10 mortar samples for different curing conditions after 80% deterioration of relative dynamic modulus of elasticity. It is clear that FA10 sample, in comparison with N and HL samples, experienced greater reduction in the number of cracks for 40°C curing condition in water at 4 weeks case with respect to the number of cracks for after deterioration case (RDM 80%). This observation implies that products of fly ash can fill micro cracks under high temperature curing condition, as an evidence for self-healing phenomena and self-healing effect on micro cracks.

3.6 Optimization of fly ash replacement ratio

The above results clarified that the behavior of fly ash is attributed to the pozzolanic reaction due to the glass content of acid insoluble. This glass content can be obtained by deducting the amount of crystalline from the acid insoluble matter in the fly ash. The pozzolanic reaction may continue after the full hydration of cement, and consequently, remaining pores can be filled by this pozzolanic reaction. Figure 17 shows the calculated values of reaction rate of fly ash and cement minerals in fly ash blended cement paste (as discussed in section 3.3.2) for which the temperature and relative humidity

Fig. 17 Calculating reaction rate of fly ash and cement minerals based on measurement of environment temperature and humidity until 2 years.

Fig. 18 Relationship between fly ash replacement ratio and water cement ratio for different damage degrees.

have been measured for 2 years. It is obvious that the hydration rate of fly ash and C_2S continues, even, after full hydration of C_3S at the time of 360 days. It is known that when the relative dynamic modulus of elasticity was about 60%, the relative length change was about 1×10^{-3} due to fact that internal cracking in the concrete sample took place for the rapid freezing and throwing test (Koh and Hasegawa 1981). Therefore, to obtain optimization of fly ash replacement ratio in concrete, it is assumed that the relative dynamic modulus of elasticity for concrete structure deteriorates until 60% and micro cracks in concrete are about 0.3 % (by volume). An increase of volume by 0.3% is typical to 3 liters, and the amount of fly ash can be calculated as shown in Eqs. (12), (13) and (14).

$$V = V_{FA} (R_{winter} - R_{spring}) / 100 \times G \quad (12)$$

Where;

V = increase of volume by 3 liters due to micro cracks

V_{FA} = increase of volume by fly ash reaction, equals to 2.4 which was determined based on the current experi-

ment)

R_{winter} = percentage of fly ash reaction in start of winter (see Fig. 17), and it is equal to 25.6%

R_{spring} = percentage of fly ash reaction in start of spring (see Fig. 17), and it is equal to 13.1%

G = glass phase of fly ash and it can be expressed as $[Fw(Fins - Fcry) / (100 \rho_f)]$

Hence, Eq. (12) can be rewritten as follows,

$$3 = 2.4(25.6 - 13.1) / 100 \times Fw(Fins - Fcry) / (100 \rho_f) \quad (13)$$

$$Fw = 3 / (2.4 \cdot 0.124(Fins - Fcry) / (100 \rho_f)) \quad (14)$$

Where, Fw is the fly ash content (kg/m^3), $Fins$ is insoluble residue of fly ash (%), $Fcry$ is the crystal content in fly ash (%) and ρ_f is density of fly ash (g/cm^3), the fly ash substitution ratio F/B can be calculated from Eq. (15).

$$F/B(\%) = Fw / (Cw + Fw) \times 100 \quad (15)$$

Where, Fw is fly ash content (kg/m^3) and Cw is cement unit weight (kg/m^3). The fly ash reaction volume, Frv can be calculated as shown in Eq. (16).

$$Frv = Fw(Fins - Fcry) / (100 \rho_f) \quad (16)$$

In addition, to avoid filling pores in concrete, the maximum fly ash contents can be determined based on a concrete unit that can be represented as water unit, cement unit, density of cement and the fly ash reaction as follows:

$$Ww - (1.06 \cdot Cw / \rho_c + 2.4 \cdot Frv) > 0 \quad (17)$$

$$Fw < (Ww - 1.06 \cdot Cw / \rho_c) / 2.4 \quad (18)$$

Where, Ww is unit water weight (kg/m^3), ρ_c is density of cement (g/cm^3), and Frv is fly ash reaction volume.

From the above equations, the fly ash replacement ratio determines the glass content and water cement ratio which are needed to both heal the deteriorated concrete until RDM 60% and to fill pore for long periods. Figure 17 shows the hydration rate with C_3S and C_2S fly ash based on the natural temperature and humidity in internal slab specimens in Asahikawa, Japan. This hydration rate for the mineral composite was calculated by using reaction rate equation (chapter 3.3.2). From the figure, the hydration rate for C_3S increased until 360 days and was also constant after 360 days, however, the hydration rate of C_2S and fly ash did not completely hydrated at 720 days. Figure 18 represents the relationship between the fly ash replacement ratio and water to cement ratio in deteriorated concrete for relative dynamic modulus of elasticity (RDM) 60%, 70% and 80%, which were derived from the above equations. This relationship has upper and lower limits for calculation of fly ash replacement ratio at different water to cement ratio as

shown in the figure to ensure proper self-healing performance. Accordingly, it can be suggested that the practical fly ash replacement ratios in fly ash concrete mix could be 10% to 15% and 11% to 20% for water to cement ratios (W/C) 0.50 to 0.55 and 0.55 to 0.60, respectively.

4. Conclusion

The purpose of this study is to investigate the hydration process, reaction rate of cement and fly ash in fly ash blended cement paste, and self-healing ability in mortar incorporating fly ash for long-term performance. First, the experiment examined the reaction rate of fly ash and consumption of calcium hydroxide by adding calcium hydroxide reagents to fly ash. Then, reaction rate of fly ash and remaining contents of $\text{Ca}(\text{OH})_2$ were measured based on acceleration reaction test and rate of reaction test in fly ash cement paste taking into consideration different types of fly ash, fly ash replacement ratios, curing conditions. The performance of self-healing ability of mortar samples incorporating fly ash was evaluated using ten mixtures with different types of cement, fly ash, fly ash replacement ratio, water to cement ratio and curing conditions. Mortar samples were deteriorated by freeze/thaw cycling until 60% and 80% relative dynamic modulus of elasticity to examine their characteristics properties such as compressive strength, bending strength, accelerated carbonation depth, and pore structure modification. Based on experiment results, the following conclusions can be derived, which are valuable information to enhance the existing design codes with long-term performance of self-healing ability of fly ash that is quite needed to prolong the service life of concrete structures:

- (1) From the hydration performance of calcium hydroxide reagent and fly ash, the calculation of reaction rate of fly ash using pattern 4 was found to have better response to experimental results compared to other patterns. The reason for this response is due to the assumption of pattern 4, in which the reaction rate is calculated based on the melting ratio for the acid insoluble matter in the glass phase, meaning that there is no contribution of crystalline phase to reaction rate.
- (2) Incorporating fly ash in cement paste would affect the hydration reaction rate and consumption of calcium hydroxide. In comparison with N sample, which is the case of OPC sample without fly ash replacement, the remaining contents of calcium hydroxide in fly ash cement samples after 2 days decreased because of its pozzolanic reaction. For the remaining calcium hydroxide contents at each age, it was found that there is no significant difference among the types of fly ash.
- (3) Fly ash cement samples with fly ash replacement ratio by mass 30%, and with high curing temperature, showed smaller remaining amount of calcium hy-

droxide compared to other samples with smaller fly ash replacement ratio. This implies that large amount of fly ash as 30% replacement ratio and high curing temperature in water can increase the consumption amount of calcium hydroxide. The reason for this behavior is due to the pozzolanic reaction of fly ash, which increases with increasing the amount of fly ash and curing temperature, and thus consumes more calcium hydroxide that comes from cement.

- (4) It was found that reaction rate of fly ash depends on curing temperature, curing age and fly ash replacement ratio.
- (5) The investigated mortar samples can heal the bending strength, compressive strength, crack density and relative dynamic modulus of elasticity after deterioration. However, degree of recovering in mortar samples incorporating fly ash was higher compared to OPC mortar sample without fly ash, especially for the case of curing in water 40°C at 4 weeks. Also, it was clarified that the curing condition in water 20°C at 1 week was not enough to heal the micro cracks compared to the curing condition in water 40°C at 4 weeks. The fly ash has a pozzolanic reaction that reacts with calcium hydroxide from cement hydration and produces C-S-H gel, which may heal micro cracks under high temperature curing condition.
- (6) It was confirmed that the carbonation depth for the case cured in water 40°C at 4 weeks is less than 1 mm and smaller than the no cracking case at any time of accelerated carbonation test for fly ash mortar samples, concluding that the curing condition of mortar with fly ash would affect the carbonation depth and self-healing due to continuing the hydration of both unhydrated cement and fly ash. Incorporating fly ash in mortar would result in higher resistance to carbonation effect is because of the pozzolanic reaction of fly ash. The pozzolanic reaction of fly ash may continue after the full hydration of cement, and consequently, micro cracks can be filled by hydrated products of fly ash resulting in higher resistance to carbonation test.
- (7) The fly ash mortar samples with lower water to cement ratio resulted in smaller carbonation coefficient and better self-healing performance for the studied cases. The fact that smaller water to cement ratio may cause smaller volume of micro cracks and pores in mortar sample, which is enough to be sealed by hydration products of cement and fly ash, is the reason for this better self-healing ability and carbonation resistance. On the other hand, larger water to cement ratio may contribute into a large volume of micro cracks and pores in mortar sample, which requires more hydration products of cement and fly ash to be filled in order to have more resistance for carbonation test.
- (8) The reductions of pore volume rate 50 nm to 10 μm

in fly ash mortar sample FA20 were higher than those in ordinary Portland cement sample N, for 40°C curing condition in water at 4 weeks case. The reason for this behaviour is that the fly ash has a pozzolanic ability that produces C-S-H gel, which may fill 50 nm to 10 µm pore size under high temperature curing condition. All the above results show the potential performance of fly ash as a pozzolanic material that can improve the self-healing ability.

- (9) Based on the practical assumption and to ensure proper self-healing performance, practical fly ash replacement ratios in fly ash concrete could be 10% to 15% and 11% to 20% for water to cement ratios 0.50 to 0.55 and 0.55 to 0.60, respectively.

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