



# Prediction of compressive strength of fly ash concrete by new apparent activation energy function

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## Abstract

A new prediction model using apparent activation energy is proposed to estimate the variation of compressive strength of fly ash concrete with aging. After analyzing the experimental result with the model, fly ash replacement content and water–binder ratio influence on apparent activation energy was investigated.

According to the analysis, the model provides a good estimation of compressive strength development of fly ash concrete with aging. As the fly ash replacement content increases, limiting relative compressive strength and initial apparent activation energy increase. Concrete with water–binder ratio smaller than 0.40 gives nearly constant limiting relative compressive strength and initial apparent activation energy when analyzed with various water–binder ratios. However, concrete with water–binder ratio larger than 0.40 increases limiting relative compressive strength and initial apparent activation energy.

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## 1. Introduction

New trends in environmental regulations related to disposal of wastes such as fly ash or granulated blast furnace slag have initiated increasing interests in using the wastes as construction materials partially replacing Portland cement in concrete. Especially, fly ash, the ash precipitated electrostatically or mechanically from the exhaust gases of coal-fired power stations, has been used in mass concrete to reduce the heat of hydration and cracking at early ages. Also, fly ash concrete increases long-term compressive strength and durability of concrete structures. More recently, fly ash has become a necessary component of high-strength concrete.

When manufacturing fly ash concrete or constructing fly ash concrete structures, it is necessary to estimate the mechanical properties of fly ash concrete such as compressive strength, splitting tensile strength, elastic modulus, creep, shrinkage, etc. Among the mechanical properties

used in design, compressive strength is most important since other properties can be estimated on the basis of compressive strength.

The objectives of this study are to produce a data inventory of fly ash concrete for various water–binder and fly ash replacement ratios and to propose a new prediction model estimating compressive strength development of fly ash concrete.

## 2. Experimental program

### 2.1. Experimental variables

Experimental variables are water–binder ratio and fly ash replacement ratio. Details of these ratios are tabulated in [Table 1](#).

### 2.2. Materials

Physical properties of cement are shown in [Table 2](#). The type of fly ash is class F. [Table 3](#) shows the chemical

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Table 1  
Test variables

Cement type	w/b	Fly ash replacement ratio (%)
Type II	0.60	0, 10, 20, 30
	0.55	0, 10, 20, 30
	0.40	0, 10, 20, 30
	0.35	0, 10, 20, 30
	0.32	0, 10, 20, 30
	0.27	0, 10, 20, 30

composition and physical properties of fly ash. Table 4 shows the physical properties of aggregates.

### 2.3. Mixture proportions

Table 5 tabulates basic mixture proportions. Cement content ranges from 231 to 600 kgf/m<sup>3</sup> according to water–binder ratio and water content ranges from 162 to 198 kgf/m<sup>3</sup>. The quantities of superplasticizer (naphthalene polymer) are presented as the ratio with binder content.

### 2.4. Test methods

After casting fly ash concrete in molds of  $\phi 100 \times 200$  mm cylinders, the cylinders wrapped with plastic film were cured in the chamber at  $98 \pm 1\%$  humidity and  $20 \pm 3$  °C. Molds were removed after 48 h and specimens were wet cured at  $21 \pm 2$  °C. The test ages of specimens were 3, 7, 28, 90, 180, and 365 days. The upper and lower surfaces of specimens were capped with sulfur mortar before testing and the experimental values of three identical specimens were averaged. Compressive strength was tested according to ASTM C 39.

## 3. Experimental results

Table 6 tabulates the experimental results and Fig. 1 shows the relative compressive strength. Previous researches [1,2] reported that the early-age compressive strength of fly ash concrete is smaller than that of ordinary concrete but the long-term compressive strength of fly ash concrete is larger than that of ordinary concrete. As shown in Table 6, the 90-day compressive strengths of concrete with 10% fly ash replacement ratio were larger than concrete without fly ash. For concrete with 20% and 30% fly ash replacement ratios, the trend described above appeared

Table 2  
Physical properties of cement

Cement type	Specific gravity	Specific surface (cm <sup>2</sup> /g)	Setting time (min)		Compressive strength (MPa)		
			Initial set	Final set	3 days	7 days	28 days
Type II	3.15	3700	250	370	24.5	31.4	42.1

Table 3  
Chemical composition and physical properties of fly ash

SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	CaO (%)	MgO (%)	Na <sub>2</sub> O (%)	K <sub>2</sub> O (%)	Specific gravity	Specific surface (cm <sup>2</sup> /g)
55.1	34.9	3.7	3.6	1.2	0.44	0.73	2.06	3318

at 180 and 365 days, respectively. Therefore, it is safe to conclude that the fly ash replacement increases the long-term compressive strength. Also, the crossover effect of compressive strength of fly ash concrete becoming larger than that of ordinary concrete with aging is delayed as the fly ash replacement ratio increases.

In Fig. 1, a graph of the relative compressive strength as a function of age clearly shows the trend of fly ash significantly increasing the long-term compressive strength. As shown in Fig. 1, compressive strength gain of early-age concrete increased with decreasing fly ash replacement ratio, but the tendency was reversed with aging. In other words, the increasing rate of compressive strength at later ages increases as the fly ash replacement ratio increases.

## 4. Application of prediction model

Authors previously proposed a new prediction model to estimate compressive strength development with temperature and aging [3]. The model reduced the shortcomings of previous models and reasonably estimated the experimental results of compressive strength of Type I cement concrete. This paper investigates the applicability of the model as a tool in predicting compressive strength of fly ash concrete. The proposed model can be expressed as follows [3]:

$$\frac{S}{S_{28}} = R_u \left\{ 1 - \frac{1}{\sqrt{1 + A \left[ e^{-\frac{E_0}{RT}} e^{-\alpha t} + e^{-\frac{E_0}{RT}} e^{-\alpha t_0} (t - t_0) \right]}} \right\} \quad (1)$$

where  $S$  is the compressive strength,  $S_{28}$  is the 28-day compressive strength at each curing temperature,  $R_u$  is the limiting relative compressive strength with  $R_u = S_u/S_{28}$ ,  $S_u$  is the limiting compressive strength,  $A$  is a constant,  $R$  is gas constant and equal to 8.3144 J/K mol,  $T$  is curing

Table 4  
Physical properties of aggregates

	Type	Specific gravity	Fineness modulus	Water absorption rate (%)
Fine aggregate	River sand	2.58	2.89	1.61
Coarse aggregate	Crushed stone	2.66	6.38	0.96

Table 5  
Basic mixture proportions

Type	w/b	s/a	Unit weight (kgf/m <sup>3</sup> )						Slump (cm)
			w	b		s	g	Super plasticizer (b × %)	
				c	FA				
WC60-0	0.60	0.45	198	330	0	788	963	0	7.4
WC60-10				297	33	781	955	0	4.9
WC60-20				264	66	775	947	0	5.3
WC60-30				231	99	768	938	0	5.0
WC55-0	0.55	0.45	193	350	0	787	962	0	5.5
WC55-10				315	35	780	953	0	3.8
WC55-20				280	70	773	945	0	3.5
WC55-30				254	100	766	936	0	3.4
WC40-0	0.40	0.40	168	420	0	703	1054	1.2	20.9
WC40-10				378	42	696	1044	1.2	18.2
WC40-20				336	84	688	1032	1.5	19.7
WC40-30				294	126	680	1020	1.7	18.9
WC35-0	0.35	0.40	168	480	0	683	1025	1.5	19.3
WC35-10				432	48	675	1012	1.5	21.8
WC35-20				384	96	666	999	1.5	19.0
WC35-30				336	144	657	986	1.8	17.9
WC32-0	0.32	0.38	166	520	0	638	1042	1.8	21.5
WC32-10				468	52	629	1027	1.8	21.6
WC32-20				416	104	621	1013	2.0	21.4
WC32-30				364	156	612	998	2.3	20.7
WC27-0	0.27	0.35	162	600	0	569	1056	2.0	21.7
WC27-10				540	60	560	1039	2.0	17.9
WC27-20				480	120	550	1022	2.3	17.5
WC27-30				420	180	541	1005	3.0	17.1

temperature (K),  $E_0$  is initial apparent activation energy (J/mol),  $\alpha$  is a constant,  $t$  is age (days), and  $t_0$  is age when the strength development is assumed to begin (days). This equation involves five unknown parameters,  $R_u$ ,  $t_0$ ,  $E_0$ ,  $\alpha$ , and  $A$ .

The experimental results of Table 6 were analyzed by Eq. (1). Table 7 tabulates the regression results. Because the preliminary regression results showed that  $t_0$  was estimated as nearly 0, it is assumed that  $t_0$  is 0. Because a constant  $A$  was not a function of age and mixture proportion, the value of  $10^7$  proposed in Ref. [3] was used. Therefore, Table 7 shows the regression results of the three unknown parameters,  $R_u$ ,  $E_0$ , and  $\alpha$ .

Fig. 1 shows the regression curves and experimental results according to the water–binder ratio. As shown in Fig. 1, the prediction model gives good estimates of compressive strengths of concrete with water–binder ratios more than 0.35. The difference between predicted and experimental compressive strengths of concrete with 0.32 and 0.27 water–binder ratio increases with increasing fly ash replacement content. The compressive strength gain for concrete with water–binder ratio less than 0.32 and superplasticizer content more than 2.0% varies considerably at early ages (less than 7 days) and later ages (more than 180 days). However, the difference is not large and the prediction model properly estimates the relative compressive strength in an error range of  $\pm 10\%$  as shown in Fig. 2.

## 5. Suggestion of functions estimating variables

Figs. 3, 4, and 5 show the regression results of Table 7 according to fly ash replacement ratio and water–binder ratio. The limiting relative compressive strength of Fig. 3(a) increases with fly ash replacement ratio. This trend arises since the long-term compressive strength increases with fly ash replacement ratio as mentioned previously [1,2]. In terms of microscopic viewpoint, this tendency can be explained as follows. Pozzolanic reactions do not start until the pH value of pore water reaches at least about 13.2. The increase in alkalinity of pore water requires a condition that a certain amount of hydration of cement has taken place. When the pH of the pore water becomes high enough, the products of reacted fly ash are formed on the fly ash particles and in their vicinity. With aging, further products diffuse away and precipitate within the capillary pore system. This precipitation results in a reduction in the capillary porosity, consequently leading to a finer pore structure [2]. As shown in the research of Beaudoin and Ramachandran [4], the decreased capillary porosity increases compressive strength. Fig. 3(b) shows limiting relative compressive strength with water–binder ratio. The limiting relative compressive strengths of concrete with water–binder ratios less than 0.35 are nearly constant, but those of concrete with water–binder ratios more than 0.40 increase with increasing water–binder ratios. The increase in limiting relative compressive strengths with increasing

Table 6  
Experimental results

Type	Compressive strength (MPa)					
	3 days	7 days	28 days	90 days	180 days	365 days
WC60-0	15.4	23.6	32.9	38.6	41.6	42.5
WC60-10	13.1	21.8	33.8	40.3	45.4	47.6
WC60-20	10.2	18.0	28.0	37.2	41.6	44.8
WC60-30	7.2	13.5	25.0	36.0	40.1	43.2
WC55-0	18.7	26.6	36.1	40.2	46.3	46.5
WC55-10	16.0	25.4	38.3	45.8	49.6	51.8
WC55-20	14.6	22.6	33.8	43.5	50.0	52.1
WC55-30	12.7	18.3	30.9	39.3	47.0	48.2
WC40-0	34.0	43.6	49.7	56.3	60.4	61.9
WC40-10	31.5	42.1	50.3	57.5	62.8	66.5
WC40-20	29.4	38.0	48.0	56.5	61.4	65.4
WC40-30	24.2	33.7	42.8	53.5	57.6	61.3
WC35-0	45.0	49.1	56.3	59.7	66.6	68.8
WC35-10	39.5	50.2	55.7	64.3	72.4	74.8
WC35-20	34.1	44.9	56.0	61.3	71.4	75.3
WC35-30	27.0	39.1	51.8	59.5	68.9	73.9
WC32-0	45.9	52.2	62.1	63.3	71.2	71.4
WC32-10	43.4	51.9	61.7	65.3	75.4	77.6
WC32-20	39.6	46.6	58.6	66.1	78.1	78.9
WC32-30	28.8	36.5	44.2	57.7	67.5	72.8
WC27-0	56.5	61.2	71.8	73.8	82.0	83.4
WC27-10	49.9	56.6	67.7	75.4	85.2	87.4
WC27-20	44.0	50.5	65.0	72.8	81.3	85.2
WC27-30	34.5	40.0	51.9	60.4	70.8	78.6

WC a-b: a is water cement ratio and b is fly ash replacement ratio.

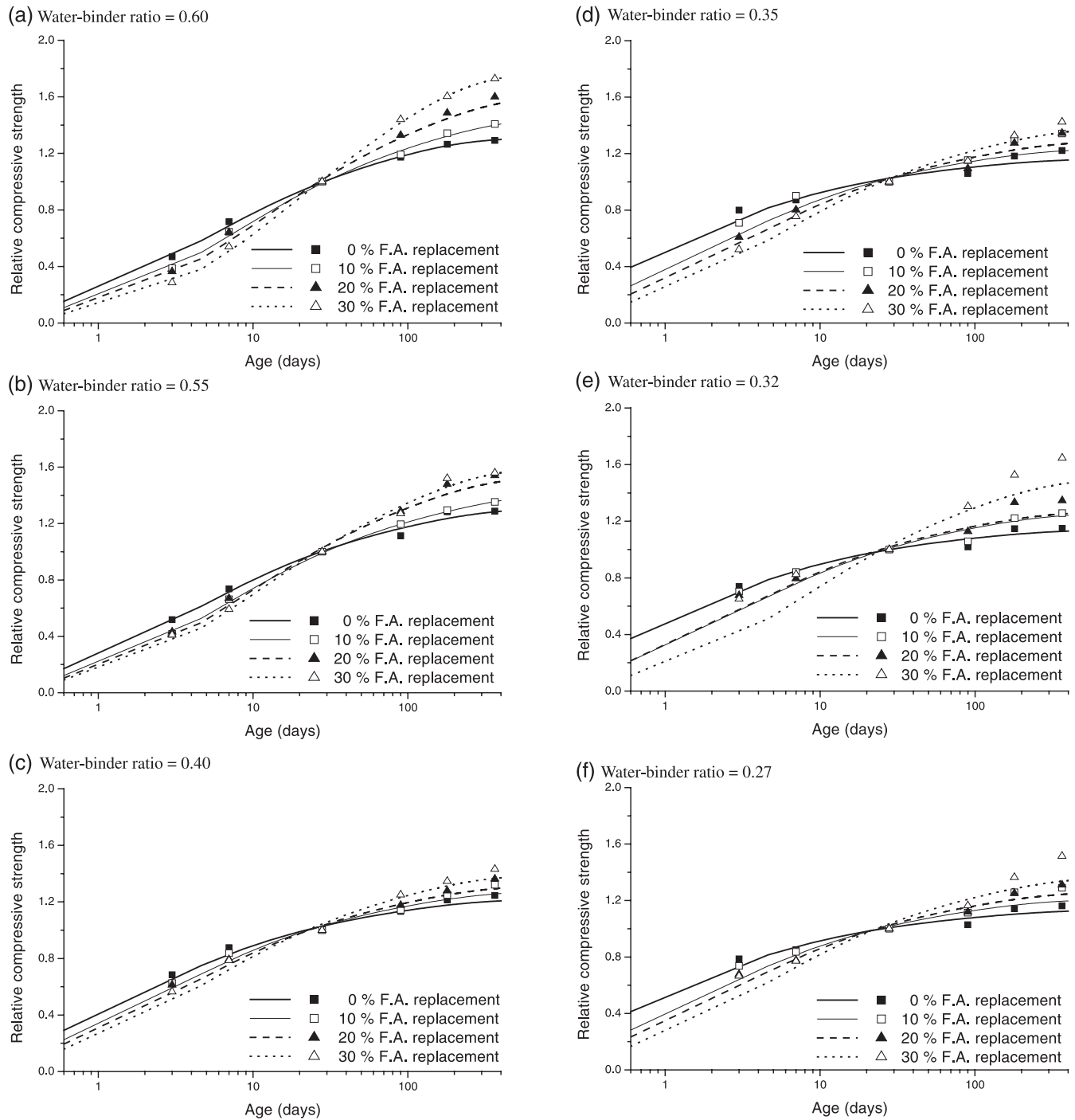


Fig. 1. Experimental and calculated relative compressive strength.

water–binder ratio arises because the cement grains become more distant to one another and a continuous system of gel is established more slowly. Mindess and Young [5] stated that concrete with water–cement ratio less than 0.36 hardly has the capillary porosity. Therefore, concrete with 0.27, 0.32, and 0.35 water–cement ratios of Fig. 3(b) hardly has the capillary porosity degrading strength development with aging and may have a similar

limiting relative compressive strength. The limiting relative compressive strengths were divided into two groups according to 0.40 water–binder ratio. The following estimation functions were proposed.

$$\text{Water–binder ratio} \leq 0.40$$

$$R_u = 1.166 + 0.008 \text{ FA} \quad (2)$$

Table 7  
Regression results

Water–binder ratio	Fly ash replacement ratio	$E_0$ (J/mol)	$\alpha$	$R_u$
0.60	0	42,953	0.000855	1.309
	10	44,205	0.000428	1.453
	20	45,036	0.000471	1.640
	30	46,061	0.000698	1.767
0.55	0	42,611	0.000609	1.306
	10	43,816	0.000335	1.417
	20	44,470	0.000568	1.563
	30	44,979	0.000594	1.596
0.40	0	40,626	0.000720	1.217
	10	41,661	0.000615	1.275
	20	42,226	0.000612	1.315
	30	43,017	0.000638	1.391
0.35	0	39,215	0.000709	1.162
	10	41,031	0.000691	1.271
	20	42,008	0.000570	1.291
	30	43,190	0.000527	1.383
0.32	0	39,403	0.000655	1.139
	10	41,811	0.000653	1.295
	20	41,811	0.000653	1.295
	30	44,254	0.000597	1.530
0.27	0	38,898	0.000634	1.133
	10	40,709	0.000712	1.232
	20	41,515	0.000645	1.260
	30	42,798	0.000566	1.392

Water–binder ratio > 0.40

$$R_u = 1.313 + 0.013 \text{ FA} \quad (3)$$

where FA is the fly ash replacement ratio (%).

Ref. [3] suggested the limiting relative compressive strength of 1.16 for Type I cement concrete with 0.35 to 0.55 water–cement ratio. The limiting relative compressive strengths of Type II cement concrete without fly ash with 0.35 to 0.55 water–cement ratio tested in this study are 1.16 to 1.31. This difference can be explained by the variation of the rate of hydration according to cement type. As the gain rate of the early-age compressive strength of Type II cement

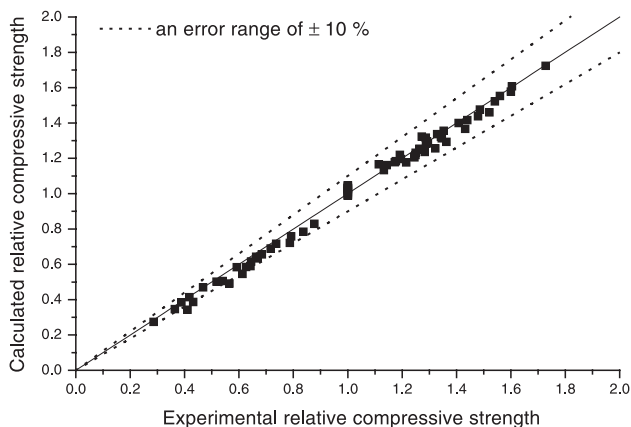


Fig. 2. Comparison of experimental and calculated relative compressive strength.

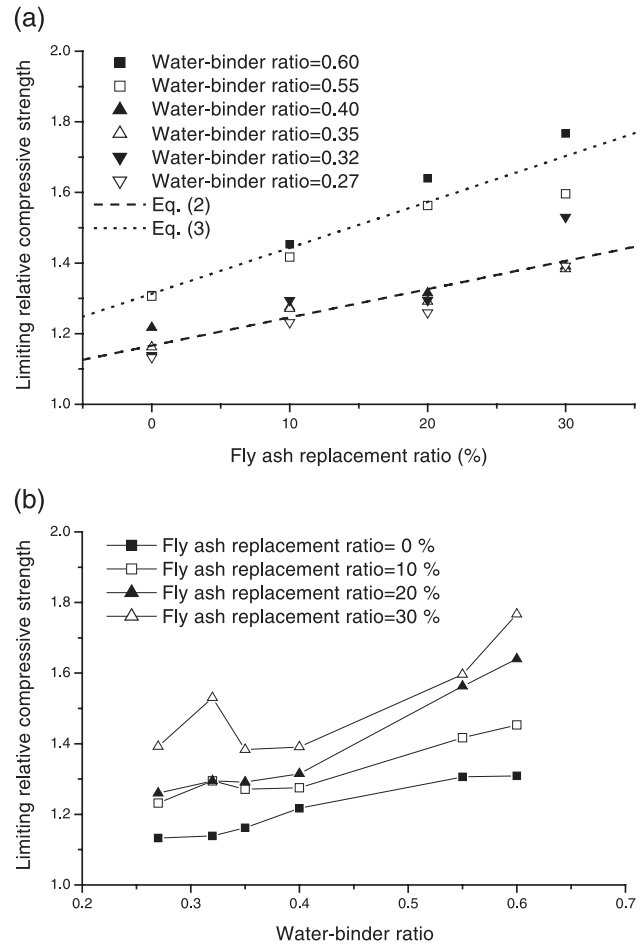


Fig. 3. Limiting relative compressive strength.

concrete with slow rate of hydration is smaller than that of Type I cement concrete, the limiting relative strength of Type II cement concrete can be larger than that of Type I cement concrete.

Fig. 4 shows the variation of initial apparent activation energy according to water–binder ratio and fly ash replacement ratio. As shown in Fig. 4(a), initial apparent activation energy increases with increasing fly ash replacement ratio. Also, the initial apparent activation energy of concrete with water–binder ratio more than 0.40 increases with increasing water–binder ratio as shown in Fig. 4(b). But the initial apparent activation energy of concrete with water–binder ratio less than 0.35 is nearly constant and this tendency is the same as that of limiting relative strength. The cause of increase in initial apparent activation energy with water–binder ratio and fly ash replacement ratio can be interpreted as follows. The previous researches [3,7] adopted the apparent activation energy to estimate the effect of temperature on cement hydration or compressive strength. In the researches [3,7], the apparent activation energy decreased as temperature increased. In other words, the acceleration of cement hydration reduced the apparent activation energy. Therefore, the decrease in fly ash replacement ratio or



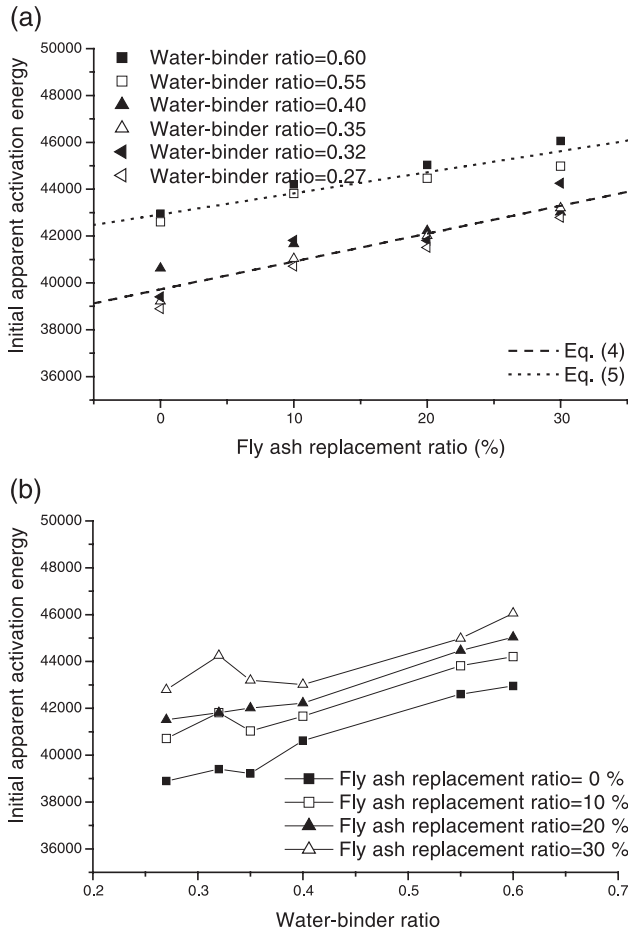


Fig. 4. Initial apparent activation energy.

water–binder ratio accelerates the binder hydration and reduces the initial apparent activation energy. The experimental results were divided into two groups and the following estimation curves were proposed.

$$\text{Water–binder ratio} \leq 0.40$$

$$E_0 = 39,720 + 119 \text{ FA} \quad (4)$$

$$\text{Water–binder ratio} > 0.40$$

$$E_0 = 42,920 + 90 \text{ FA} \quad (5)$$

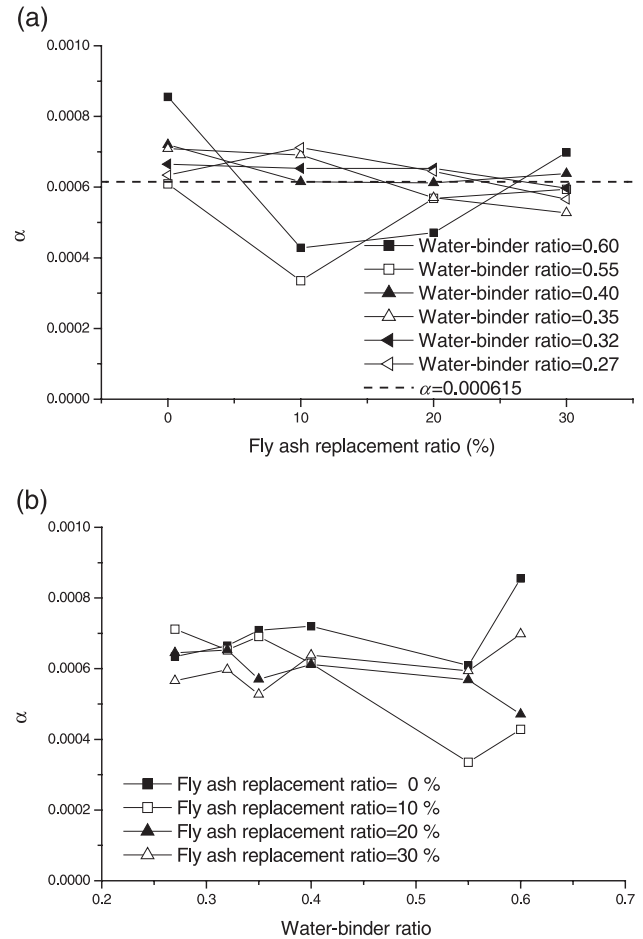
where FA is the fly ash replacement ratio (%).

Fig. 5 presents the variation of  $\alpha$ , which is a constant of the following function estimating apparent activation energy.

$$E = E_0 e^{-\alpha t} \quad (6)$$

where  $t$  is age (days). As shown in Fig. 5,  $\alpha$  does not show a strong trend as fly ash replacement and water–binder ratios vary. Therefore, all data were averaged and presented as follows:

$$\alpha = 0.000615 \quad (7)$$

Fig. 5. Variable  $\alpha$ .

This value is slightly different than that proposed in Ref. [3]. It is estimated that the deviation is due to the difference in cement type.

Eq. (1) estimates the ratio of compressive strength to 28-day compressive strength, but it does not propose the compressive strength. Therefore, it is necessary to estimate

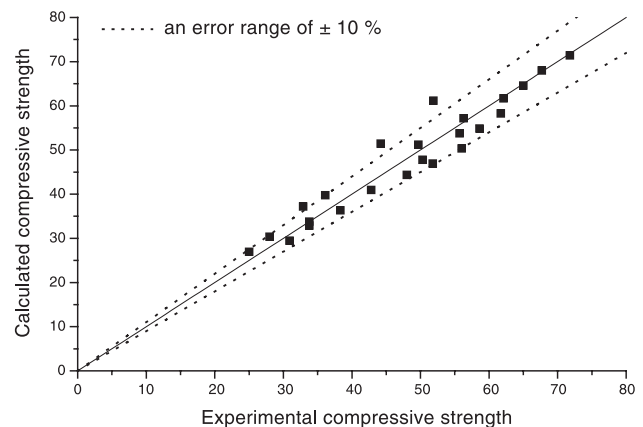


Fig. 6. Comparison of experimental and calculated 28-day compressive strength.

the 28-day compressive strength according to fly ash replacement ratio and water–binder ratio. The following equation was proposed using Bolomey's model to analyze the 28-day compressive strength [6].

$$\begin{aligned} S_{28} &= X \frac{c}{w} + Y \frac{f}{w} + Z = X \left( \frac{c}{w} + k_s \frac{f}{w} \right) + Z \\ &= 16.8 \frac{c}{w} - 34.2 \frac{f}{w} + 9.20 \\ &= 16.8 \left( \frac{c}{w} - 2.04 \frac{f}{w} \right) + 9.20 \end{aligned} \quad (8)$$

where  $c$  is cement content ( $\text{kgf/m}^3$ ),  $w$  is water content ( $\text{kgf/m}^3$ ), and  $f$  is fly ash content ( $\text{kgf/m}^3$ ). As shown in Fig. 6, Eq. (8) reasonably estimates 28-day compressive strength in an error range of  $\pm 10\%$ .  $k_s$  of Eq. (8) takes into account the reactivity of fly ash with respect to strength compared to the reactivity of cement. For example,  $k_s$  equal to 0.20 means that it needs five times as much fly ash by weight to replace cement in order to obtain the same compressive strength [6]. However,  $k_s$  of this paper has the minus value, because the increase in fly ash replacement ratio reduces the compressive strength. If finer fly ash is used or estimation age becomes greater than 28 days, compressive strength of concrete with increasing fly ash replacement ratio increases and  $k_s$  will have the plus value.

## 6. Conclusions

In this study, compressive strengths of fly ash concrete varying fly ash replacement ratio and water–binder ratio were experimentally obtained. Also, the variation of compressive strength of fly ash concrete with aging was esti-

mated using a new prediction model. The following conclusions can be made from the results.

1. The fly ash replacement increases the long-term compressive strength. Also, the crossover effect of compressive strength of fly ash concrete becoming greater than that of ordinary concrete with aging is delayed as the fly ash replacement ratio increases.
2. The prediction model properly estimates the relative compressive strength in an error range of  $\pm 10\%$ . The limiting relative compressive strengths of concrete with water–binder ratios less than 0.35 are nearly constant, but those of concrete with water–binder ratios more than 0.40 increase with increasing water–binder ratios.
3. The decrease of fly ash replacement ratio or water–binder ratio reduces the initial apparent activation energy. But,  $\alpha$ , a constant of function estimating the apparent activation energy, does not show a strong trend as fly ash replacement and water–binder ratios vary.

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