Effect of Curing Temperature on Pozzolanic Reaction of Fly Ash in Blended Cement Paste

Mongkhon Narmluk and Toyoharu Nawa

***Abstract*—In this research, the degree of pozzolanic reaction of fly ash in blended Portland cement pastes cured at different temperatures was determined by the selective dissolution method. The effect of curing temperature on pozzolanic reaction was then investigated using the modified Jander's model. The results confirm that the pozzolanic reaction of fly ash is strongly influenced by curing temperature and replacement ratio of fly ash. The higher the curing temperature and the lower the fly ash replacement ratio, the higher is the degree of pozzolanic reaction of fly ash. The rate and mechanism of pozzolanic reaction of fly ash vary with curing temperature. Elevated curing temperatures lead to faster the onset and accelerated the rate of the main reaction linearly.**

***Index Terms*—Fly ash, pozzolanic reaction, cement paste, curing temperature, hydration.**

I. INTRODUCTION

Fly ash, a by-product from coal combustion process, is widely used as a supplementary cementitious material (SCM) in high performance concrete (HPC). Partially replacing the Portland cement with fly ash has been reported to increase long-term strength and durability of the resulting concrete [1], [2]. This can be attributed to the pozzolanic reaction between fly ash and calcium hydroxide ($Ca(OH)_2$) produced by hydration of the cement. The pozzolanic reaction produces additional calcium silicate hydrate (C-S-H) product to fill up capillary pores, making the fly ash concrete denser in microstructure as compared to normal concrete [1], [3]. Therefore, the kinetics of pozzolanic reaction of fly ash is crucial information to understand the microstructure development and to predict the long-term performances of the fly ash concrete.

The kinetics of pozzolanic reaction of fly ash is known to be influenced by numerous factors, such as chemical and physical properties of the fly ash particles, water to binder ratio, replacement ratio of fly ash, and curing temperature. Previously, the effect of these factors has been investigated by researchers [3], [5]-[7]. However, the effect of curing temperature is relatively unclear.

In real application, the hydrating fly ash concrete might be subjected to temperature variations in various situations. For example, the core of large fly ash concrete element is subjected to a couple of days of temperature rise due to heat of hydration. In such situations, the early age kinetics of pozzolanic reaction of fly ash can be remarkably different from that at room temperature. Therefore, in modeling of fly ash concrete performances, the effect of temperature on the pozzolanic reaction of fly ash should be taken into account.

However, at present, a clear understanding regarding the quantitative effect of temperature on the reaction rate and mechanism of pozzolanic reaction of fly ash has not been well established, especially in HPC with low w/b ratio. There is very limited research work describing the effect of curing temperature on the kinetics of pozzolanic reaction of fly ash in actual fly ash-cement paste [7], [8]. Hanehara *et al*. [7] reported that the onset of the pozzolanic reaction of fly ash at the curing temperature of 20 ^{o}C is at 28 days or longer, and the pozzolanic reaction of fly ash in cement paste highly depends upon the curing temperature. Although, this work provided a perspective view, it focused on long-term kinetics and no kinetics analysis has been presented.

The main objective of this paper is to provide experimental evidences of the temperature dependency of the reaction kinetics of fly ash in low water to binder (w/b) fly ash-cement paste. The degree of pozzolanic reaction of fly ash was measured as a function of curing ages by means of the selective dissolution. Two volumetric replacement ratios of fly ash were studied. The modified Jander's model was used as a tool to quantify the kinetic coefficients of the pozzolanic reaction at different temperatures.

II. MATERIALS AND METHODS

A. Materials

Ordinary Portland cement (OPC) and fly ash with the chemical and mineralogical composition in Table I and Table II were used in this study. As can be seen from Table I, the fly ash contains 3.36% CaO and 88.15% of (SiO_2+Al_2O_3+Fe_2O_3), classifying this fly ash as a low calcium fly ash (ASTM C618-05, 2005). The mineralogical compositions in Table II show that the fly ash consists of 82% of amorphous phases and the remaining portions consist of mulite, quartz, and hematite.

B. Sample Preparations

Two fly ash-cement pastes with different fly ash volume fractions were produced with a constant w/b ratio of 25 % (by weight). In the following, these two mixtures will be referred to as FA25, and FA50, respectively. Details of mixture proportions are shown in Table III.

To prepare test specimens, cement and fly ash powders were mixed at room temperature until homogeneity of the mixture was obtained. Then mixing water containing

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superplasticizer was added while mixing with low speed for 90 seconds, followed by a further mixing stage with high speed mixing for 120 seconds to ensure uniform dispersion of the cementitious particles. After the mixing, the fly ash-cement slurry was cast into cylindrical steel molds of 5 cm in diameter and 10 cm in height. The molds were carefully sealed to prevent evaporation of water. After the casting process, the paste specimens were cured at 20 ^oC, 35 ^oC, and 50 ^oC until the required ages were achieved.

When the required ages were reached, the hydration reaction in the fly ash-cement pastes was stopped by crushing the hardened specimens into pieces of about 3-5 mm, and then immersing them in acetone for 24 h. After that the samples were dried at 40 ^oC for 3 h, and placed in vacuum desiccators for 2 days. The samples were then pulverized to be used in the selective dissolution and the powder X-Ray diffraction (XRD) measurements.

TABLE I: CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF PORTLAND CEMENT AND FLY ASH

Oxide (%)	Portland Cement	Fly Ash
SiO_2	21.06	59.10
Al_2O_3	5.77	20.20
Fe_2O_3	2.67	8.85
CaO	63.55	3.36
MgO	1.85	1.17
SO_3	2.28	0.12
TiO_2	0.29	1.90
MnO	0.07	0.14
P_2O_5	0.25	2.58
Na_2O	0.26	0.34
K_2O	0.38	1.87
Blaine (cm^2/g)	3,400	3,740
Density (g/cm^3)	3.16	2.33
LOI (%)	0.614	0.960

TABLE II: MINERALOGICAL COMPONENTS OF PORTLAND CEMENT AND FLY ASH USED IN THIS STUDY (OBTAINED BY THE XRD-RIETVELD METHOD)

Mineral (%)	Portland Cement	Fly Ash
C_3S	64.54	-
C_2S	14.04	-
C_3A	4.40	-
C_4AF	9.16	-
Mulite	-	7.09
Quartz	-	8.02
Hematite	-	1.23
Glass content	-	81.97

TABLE III: MIXTURE PROPORTIONS

Mix	w/b (mass fraction)	Fly ash/Cement (vol. fraction)	Superplasticizer [a)] (% of binder weight)
FA25	0.25	25/75	1.30
FA50	0.25	50/50	0.65

[a)] Content of superplasticizer that controls the flow diameter of paste at 200 mm

C. Method for Quantifying the Degree of Pozzolanic Reaction of Fly Ash

The selective dissolution method was used in quantifying the degree of pozzolanic reaction (d.o.p.) of fly ash. One gram of hydrated fly ash-cement power was dissolved in 30 cm^3 of an acid solution of 2N HCl at 60 ^oC for 15 min. The undissolved portion was washed with hot water 3 times before it was further dissolved in a base solution of 5% $NaCO_3$ at 80 ^oC for 20 min. The final residue was again washed with hot water 3 times and then dried at 105 ^oC for 24 hours. The degree of fly ash reaction was calculated from weight fraction of the reacted fly ash. Calculation details and accuracies of this method can been seen in Termkhajornkit et al. [9], which reported the above measurement conditions to give a high accuracy of the amount of the reacted fly ash.

D. Method for Quantifying the $Ca(OH)_2$ Content

The content of calcium hydroxide ($Ca(OH)_2$) can be used as an indicator for monitoring the progress of the pozzolanic reaction of fly ash. The $Ca(OH)_2$ content in hydrated fly ash-cement sample was measured by the powder XRD-Rietveld method. Samples used in the measurements were the hydrated paste powder mixed with 10 wt. % of corundum as a reference compound. The measurement conditions of the XRD were a scanning range of 2θ from 5^o to 70^o at 40kV, 20mA, step width 0.02^o, and a scanning speed of 2^o/min. The measured XRD data were further analyzed using the Seroquant software which works based on the Rietveld quantitative phase analysis.

III. RESULTS AND DISCUSSIONS

A. Effect of Curing Temperature

The degree of pozzolanic reaction (d. o. p.) of fly ash and the $Ca(OH)_2$ content at different curing temperatures are plotted as a function of time in Fig. 1(a) for FA25 and Fig. 1 (b) for FA50. Small fluctuation in the progress of the d. o. p. data may be observed, when the reaction rate is slow. This demonstrates difficulties of the selective dissolution method in detecting small change of a slow chemical reaction. However, the overall kinetic tendency is the main focus in this study. Each data point represents an average value of three replicated samples. The maximum standard deviations are found to be lower than 0.005 for the d. o. p. and below 0.032 for the content of $Ca(OH)_2$. To avoid a chaotic presentation, error bars are not included in the Figs.

At 20 ^oC, the d. o. p of fly ash reported by Lam *et al*. [3] (solid rhombus marks) are also plotted for comparisons. These data were measured from fly ash cement pastes with w/b ratio of 24 wt.%, and at fly ash replacement ratios of 25 vol.% in Fig. 1(a) and 45 wt.% in Fig. 1(b)), which were slightly different from the test condition used in this work. It can be seen that the development trend of the pozzolanic reaction of fly ash obtained by [3] are closed to the results of this study, although the former is higher at some point. This is basically due to differences in mix proportions, and qualities of fly ashes and cements used. Nevertheless, it may be deduced from this comparison that the d. o. p. of fly ash obtained in this study is in a reliable tendency.

Regarding the effect of curing temperatures in FA25 pastes, the pozzolanic reaction of fly ash is strongly temperature-dependent (Fig. 1(a)). The onsets of the reaction appear early at elevated curing temperatures. These points are approximately 12 hr at 50 ^oC, 72 hr at 35 ^oC, and 672 hr at 20 ^oC curing, corresponding well with the peak of $Ca(OH)_2$ evolution curves. After the onset, the pozzolanic reaction of fly ash in pastes at different temperatures proceeds with asimilar reaction rate. However, at 50 ℃, the reaction rate tends to slow down at later aging times. On the other hand, the $Ca(OH)_2$ contents decrease continuously after their peaks. This indicates that the $Ca(OH)_2$ is consumed by the pozzolanic reaction of fly ash [10]. The final d. o. p. at the end of observation (2160 hours or 90 days) are 0.22, 0.37, and 0.43 for pastes cured at 20 ℃, 35 ℃, and 50 ℃, respectively. It is interesting to note that the d. o. p. in the sample cured at 50 ℃ for 72 h (3 days) is almost the same as that in the sample cured at 20 ℃ for 2160 h (90 days).

For FA50 pastes in Fig. 1(b), a similar temperature dependency of the onset of the pozzolanic reaction, as found in FA25 pastes, is observed. The peaks of the $Ca(OH)_2$ curves are also closed to the onsets of reaction. However, the rate and the extent of reaction at the same curing period are lower. These are consistent with previous reports [3], [5], [6], [10], which found that the d. o. p. of fly ash in pastes containing high volume fly ash replacement is lower than that in pastes with low fly ash content. Here, the final degree of pozzolanic reaction in FA50 are 0.15, 0.23, and 0.27 for paste cured at 20 ℃, 35 ℃, and 50 ℃, respectively.

In both FA25 and FA50 pastes at 35 ℃ and 50 ℃ curing, the rises of $Ca(OH)_2$ evolutions at early stage occur earlier than that at 20 ℃. This can be attributed to the accelerated hydration reaction of the cement due to an increased curing temperature. The higher the curing temperature, the faster the hydration of cement accelerates, and the faster the $Ca(OH)_2$ is produced.

Based on the presented experimental results, it can be confirmed that the early kinetics of pozzolanic reaction of fly ash is strongly temperature-dependent. In particular, the onset of the reaction is activated earlier at high curing temperatures. The higher the curing temperature and the lower the fly ash replacement ratio, the higher is the d. o. p. at the same ages. This suggests that at high curing temperatures the pozzolanic reaction of fly ash plays a crucial role on the microstructure development of fly ash concrete since early age.

B. Kinetics Analysis

In this paper, a fly ash particle is modeled as a sphere covered with product layer (C-S-H). The thickness of the product layer increases with the d. o. p. Base on this assumption, the pozzolanic reaction of fly ash is assumed to be controlled by diffusion of reactants through the product layer. The modified Jander's equation in Eq.(1) can be used to analyze this behavior [11]-[13].

$$\left(1-\sqrt[3]{1-\alpha_f}\right)^N = K.t \qquad (1)$$

$$log(t) = N\,log\left(1-\sqrt[3]{1-\alpha_f}\right) - log(K) \qquad (2)$$

where K is the reaction rate constant; N is the constant describing the reaction mechanism; α_f is the degree of pozzolanic reaction (d. o. p) obtained from experiment, and t is the reaction time.

This equation is capable of classifying reaction processes by considering on values of the exponent N. According to [11]-[13], if $N \leq 1$; the reaction is controlled by dissolution processes, or by the immediate reaction at the surface of the grains. If $N > 1$; the reaction is controlled by the diffusion of reactants through a layer of reaction products. This layer is porous if $N \leq 2$ and dense if $N > 2$.

Eq.(1) can be written in an alternative form as shown in Eq.(2). Based on the experimental $\alpha_f - t$ data, Eq.(2) is plotted as shown in Fig. 2(a) and Fig. 2(b). It can be seen that the plot appears to be several linear portions with various slopes, suggesting that the mechanism of pozzolanic reaction varies with time and temperature. Thus, the coefficients K and N in Eq.(2) are determined for each reaction stage and they are listed in Table IV.

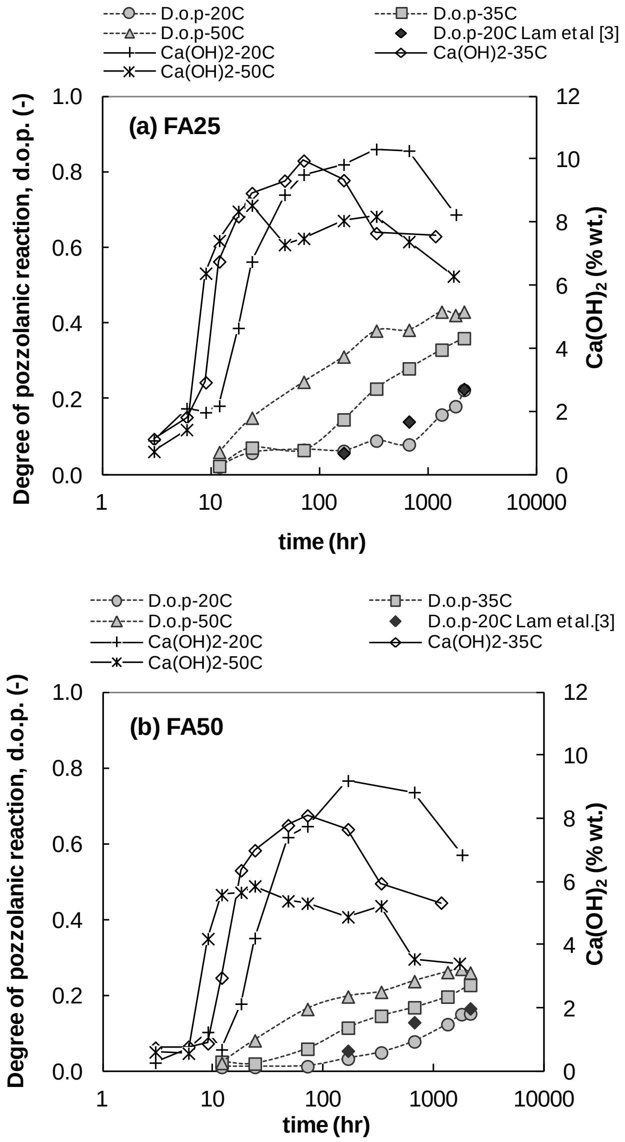

Fig. 1. Kinetics of pozzolanic reaction of fly ash at different curing temperatures; (a) FA25 paste, (b) FA 50 paste (d. o. p = degree of pozzolanic reaction)

C. Effect of Curing Temperature on Reaction Mechanisms

The results in Table III show that the exponent N of Eq.(2) changes with time and curing temperature. In general, the reaction kinetics can be divided into 3 stages: stage I with $N > 2.0$, stage II with $1.0 < N < 2.0$, and stage III with $N > 2.0$.

The reaction kinetics in stage I is found as the initial period of 20 ^oC and 35 ^oC curing with $N = 2.62$ and 2.81 in FA25 paste, and with $N = 5.10$ and 2.60 in FA50 paste, respectively.

The higher the curing temperature, the shorter is the duration of this stage. For 50 °C curing, it is expected that the reaction has already progressed to the more advanced stage, therefore the reaction kinetics in stage I is not observed. According to criteria defined previously [11]-[13], the mechanism of pozzolanic reaction in stage I should be controlled by diffusion of ions through a dense product layer around fly ash particle. However, Fig. 1 shows that at early period the main pozzolanic reaction of fly ash in paste cured at 20 °C and 35 °C has not started. According to Fraay *et al.* [4], a long dormant period of pozzolanic reaction of fly ash is because the glass structure of the fly ash particle has probably not yet dissolved. Therefore, the high N value in this case indicates a slow diffusion of reactants (ions) through the dense glass wall of the fresh fly ash particles rather than the dense C-S-H product.

TABLE IV: KINETIC COEFFICIENTS OF THE MODIFIED JANDER'S MODEL

Mixture	Temperature	Exponent N			Reaction rate constant K [day^{-1}]		
		Stage I	Stage II	Stage III	Stage I	Stage II	Stage III
FA25	20 °C	2.62	1.10	-	4.83 E-06	1.00E-03	-
	35 °C	2.81	1.16	3.31	6.20E-05	4.18E-03	1.87E-05
	50 °C	-	1.58	7.38	-	6.10E-03	2.89E-08
FA50	20 °C	5.10	1.75	-	3.81E-05	1.37E-04	-
	35 °C	2.60	1.56	3.64	5.22E-05	2.80E-03	1.21E-06
	50 °C	-	1.49	6.50	-	4.82E-03	3.68E-09

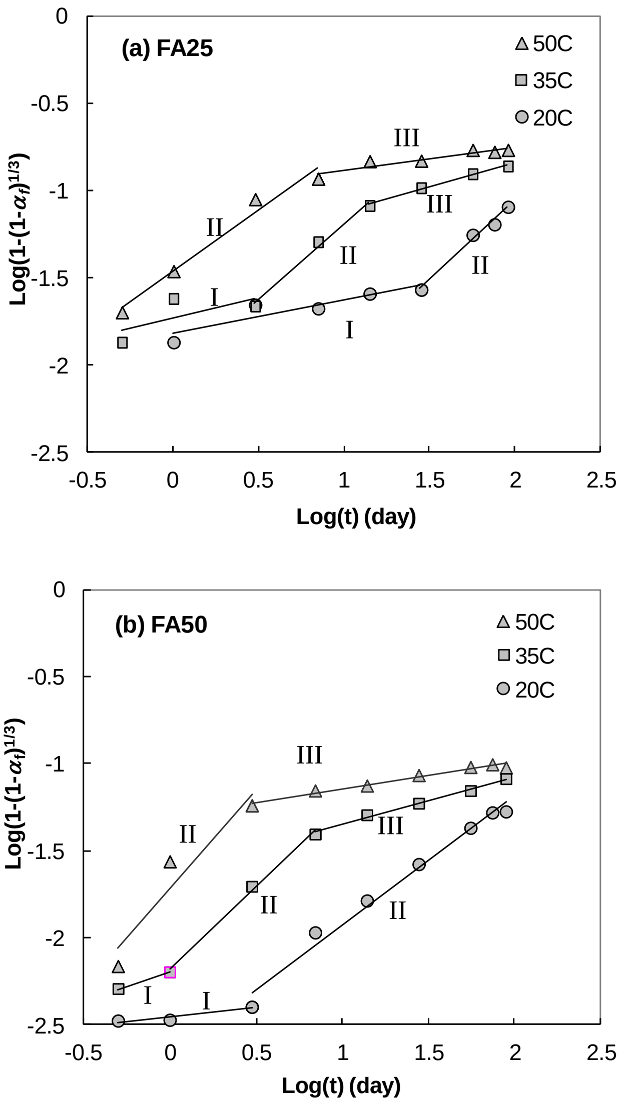

Fig. 2. Illustration of the plots of the kinetic function in Eq.(2) ; (a) FA25 paste, (b) FA50 paste

The reaction kinetics in stage II is observed for the initial period of 50 °C and the middle period of 20 °C and 35 °C curing in both pastes, as indicated by 1.0< N <2.0. According to [11], the product layer around the fly ash particle is still porous, and the pozzolanic reaction is, therefore, controlled by diffusion of ions through porous product layer. The degree of pozzolanic reaction increases largely with rapid reaction rate, considering as the main stage of pozzolanic reaction.

The reaction kinetics in stage III is found at the last period of 35 °C and 50 °C curing in both pastes, as shown by N >2.0. The diffusion of ions through the dense C-S-H layer becomes the rate controlling mechanism. This implies that at elevated curing temperatures the product layer becomes denser compared with 20 °C curing. As a result, the rate of pozzolanic reaction is slowed down at later age. The dense reaction product has also been found around the cement grain when it hydrates at high curing temperatures [14], [15].

D. Effect of Curing Temperature on Reaction Rate

Table IV shows that the reaction rate constants (K) generally increase with curing temperatures, and decrease with fly ash replacement ratios. Furthermore, the reaction rate constant varies with reaction stages. The reaction in stage II is the most active, showing the highest rate constant. In stage I and stage III, the rates of reaction are relatively low. This is a result of difference in reaction mechanisms, as discussed in previous section.

The effect of curing temperature on the reaction rate constant (K) in stage II is illustrated in Fig. 3. It can be seen that the reaction rate increases linearly with increasing curing temperatures. Similar tendency is observed in both FA25 and FA50 pastes.

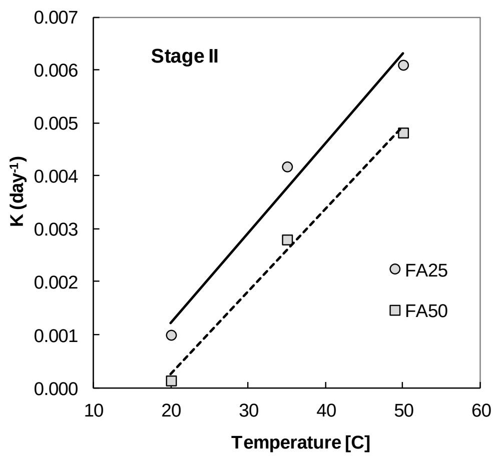

Fig. 3. Variations of the reaction rate constant with curing temperatures

IV. Conclusions

From the results of this study, the following conclusions can be drawn.

1) The kinetics of pozzolanic reaction of fly ash in low w/b fly ash-cement pastes can be divided into 3 stages: First, a slow diffusion through the dense glass wall of the fresh fly ash particles, Second, a rapid diffusion through porous product layer, and Third, a slow diffusion through a dense product layer.
2) At a specific age, the degree of pozzolanic reaction of fly ash depends on replacement ratio of fly ash and curing temperature. The lower the fly ash replacement ratio and the higher the curing temperature, the higher is the degree of pozzolanic reaction of fly ash.
3) The rate and mechanism of pozzolanic reaction of fly ash are strongly temperature-dependent. Elevating curing temperature from 20 ^{o}C to 50 ^{o}C shortens the dormant period and brings about faster the onset of the main reaction from 28 days to 12 hr. The rate constant of the main reaction (stage II) increases linearly with temperature. However, the reaction rate in the later period is retarded.
4) In future research, microstructural characteristics and mechanical properties of hardened fly ash cement pastes cured at different temperatures and different ages should be measured and verified with the degree of pozzolanic reaction of fly ash.

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