Hydration Kinetics of Fly Ash-Portland Cement Paste with Low Water to Cementitious Powder Ratio

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Introduction

Fly ash is widely used as a supplementary cementitious material in high performance concrete because of its benefits in enhancing both fresh and long-term concrete properties and as it promotes eco-friendly construction. In the past, many investigations have been carried out mainly to elucidate the pozzolanic reaction of fly ash and its effect on the microstructure of the fly ash-cement paste. Although the effect of fly ash on hydration has been established experimentally, the quantitative influence of fly ash on the kinetics of cement hydration is not well understood. In particular, for modern high-performance concretes with low w/b ratios, the effect of the fly ash on the cement hydration may be different. To predict the performance of fly ash concrete accurately throughout its service life, a more quantitative understanding of the effect of fly ash on cement hydration in low w/b ratio cementitious mixtures is needed.

In this study, the degree of cement hydration and fly ash reactions can be measured separately by using the XRD-Rietveld analysis and the selective dissolution methods. The shrinking-core model is then used to determine the kinetic parameters of individual hydration processes. These model parameters represent the apparent hydration kinetics of multiple cement components. The results of experiments conducted at three different curing temperatures will be reported.

Theoretical backgrounds

Kinetic model for cement hydration

The shrinking-core model is used in this study to simulate the development of cement hydration. This model is expressed as a single equation consisting of three coefficients: \( k_d \) the reaction coefficient in the induction period; \( D_e \) the effective diffusion coefficient of water through the C-S-H gel; and \( k_r \), a coefficient of the reaction rate of cement as shown in Eq.(1) below. These coefficients determine the rate of mass transport through the initial shell layer (a layer of semipermeable, metastable C-S-H product that forms initially when water comes in contact with the cement), the rate of chemical reaction processes, and the rate of diffusion controlled processes. The modeled cement particles are assumed to be spheres surrounded by an initial shell layer. External water diffuses through this layer and reacts with the unhydrated cement at the surface of the core, and then some dissolved ions diffuse outward to the exterior to form new hydration products (C-S-H gel) on the surface of hydrating particles while some take part in forming products locally. Based on this theory, the rate of cement hydration is derived as shown in Eq.(1), where \( \alpha \) is the degree of cement hydration; \( \nu \) is the stoichiometric ratio by mass of water to cement; \( w_s \) is the physically bound water in C-S-H gel; \( \rho_c \) is the density of the unhydrated cement; \( C_{w-free} \) is the amount of water at the exterior of the C-S-H gel; and \( r_0 \) is the radius of unhydrated cement particles.

In Eq. (1), the cement particles are assumed to have a uniform size with an average radius of \( r_0 = 3/5(3S_B\rho_c) \) [1]. The terms \( S_B \) and \( \rho_c \) stand for the Blaine surface area and density of the cement, respectively. As the hydration progresses, the hydration rate decreases with a reduction in the contact area between cement particles and the surrounding water because of the increase in interconnections among cement particles. This effect is accounted for by the term \( S_w/S_0 \) in Eq. (1) where \( S_w \) is the effective surface area of the cement particles in contact with water and \( S_0 \) is the total surface area if the surface area develops unconstrained [1].

The reaction coefficient \( k_d \) is assumed to be a function of the degree of hydration as shown in Eq.(2) where \( B \) and \( C \) are the coefficients determining this factor [1]; \( B \) controls the rate of the initial shell formation and \( C \) controls the rate of the initial shell decay.

\[
\frac{\alpha}{1 - \alpha} = B \left[ \frac{1}{(1 - \alpha)^{1/3}} + \frac{1}{k_r (1 - \alpha)^{2/3}} \right]
\]
In [2-3], the effective diffusion coefficient $D_e$ is assumed to be affected by the tortuosity and pore size of the C-S-H gel and it is expressed in a term for the degree of hydration as shown in Eq.(3). If the C-S-H gel is very porous and has low tortuosity of the pore network, the value of $D_e$ will be high and ions easily diffuse through the gel. The $D_{e0}$ is the initial effective diffusion coefficient of water when C-S-H gel is still only loosely formed at the early period after mixing. With the progress of hydration, the thickness of the C-S-H layer increases, and the diffusivity of water through this layer becomes lower. In [2-3] this effect was expressed by the term $\ln(1/\alpha)$ in Eq. (3) and this term is also included in the model presented here.

\[
D_e = D_{e0} \ln(1/\alpha) \tag{3}
\]

In addition, free water in the capillary pores is depleted as hydration of cement minerals progresses. Some water is bound in the gel pores, and this water is not available for further hydration, an effect that must be taken into consideration in every step of the progress of the hydration [4]. Therefore, the amount of water in the capillary pores $C_{w-free}$ is expressed as a function of the degree of hydration in the previous step as shown in Eq. (4).

\[
C_{w-free} = \frac{(W_0 - 0.38 \times 10^{-3} C_a)}{W_0} \tag{4}
\]

where $C_a$ and $W_0$ are the mass fractions of cement and water in the mix proportion.

The effect of temperature on these reaction coefficients is assumed to follow Arrhenius’s law as shown in Eqs.(5a)-(5d) [1].

\[
B = B_{293} \exp(-\beta_1(1/T-1/293)) \tag{5a}
\]
\[
C = C_{293} \exp(-\beta_2(1/T-1/293)) \tag{5b}
\]
\[
D_e = D_{e20} \exp(-\beta_3(1/T-1/293)) \tag{5c}
\]
\[
k_s = k_s{20} \exp(-E/R(1/T-1/293)) \tag{5d}
\]

where $\beta_1$, $\beta_2$, $\beta_3$, and $E/R$ are temperature sensitivity coefficients and $B_{293}$, $C_{293}$, $D_{e20}$, and $k_s{20}$ are the values of $B$, $C$, $D_e$, and $k_s$ at 20 °C.

**Working hypothesis of the deposition mechanism**

A reduction in $D_e$ is assumed to take place in concert with the increases in the degree of hydration as suggested by Eq.(3). The physical meaning of this phenomenon can be related to the changes in C-S-H gel tortuosity and gel pore diameters [2-3] but no fully explanatory mechanism for this has been established.

Recently, Bishnoi and Scrivener [5] has proposed that C-S-H is loosely packed in the beginning and that its packing density increase with hydration.

This allows the proposition that the diffusive properties of the C-S-H layer would decrease due to increases in the packing density of the gel as the hydration progresses. The cause of the increase in packing density as considered in the model here is assumed to be due to the deposition of small C-S-H particles/nuclei on the interior pores of the C-S-H layer.

The diameter of the large gel pores range from 3 to 12 nm (Jennings [6]), and it is possible that some C-S-H particles deposit on the walls of large gel pores, potentially narrowing the diffusion path diameter or completely blocking it, as suggested in Figure 1.

![Figure 1 Illustration of the C-S-H particle deposition blocking the pore system](image)

In this study, it was assumed that the resistance of the C-S-H layers to ion diffusion is due to both the thickness of the C-S-H layers and the deposition of C-S-H particles in gel pores. At the beginning, C-S-H is loose and porous and contains a range of sizes of small and large gel pores. Deposition of C-S-H particles can occur only in the large gel pores, which can accommodate the C-S-H particles. Ionic diffusion can occur in both small and large gel pores. As a result, when large gel pores are narrowed or blocked, there are small gel pores available for ions to diffuse through. Therefore, it is possible for the deposition of C-S-H particles on the pore walls to occur in parallel with the diffusion of ions through the C-S-H layer. The deposition of C-S-H particles induces more turning and forking (increases tortuosity), resulting in a longer paths for ions to diffuse through the C-S-H layers as the hydration progresses.

**Model modifications based on the working hypothesis**

Assuming that the kinetics of the deposition of the C-S-H particles/nuclei in the interior gel pores is similar to the kinetics of the nucleation and growth of the hydration product on the exterior surface of the cement particles, a function analogous to the Avrami-type function (Eq.(6)) is proposed to describe the deposition behavior of the C-S-H particles. With this, the fraction
of the deposited C-S-H relative to a unit gel porosity is given by Eq.(6).

\[ f = 1 - \exp(-k_1 \cdot t^n) \]  

(6)

Further, the volume of the gel pores, which is high at the beginning, is reduced because it becomes increasingly more occupied by deposited C-S-H. Ions can still diffuse through the remaining path ways which however become increasingly more complex (tortuous) and narrower. The volume fraction of the space available for diffusion in the C-S-H gel may be estimated from Eq.(7).

\[ 1 - f = \exp(-k_1 \cdot t^n) \]  

(7)

With Eq.(6), it is suggested that the rate of deposition increases with time. A high rate of deposition of C-S-H particles/nuclei results in lower ionic diffusion rates despite the thickness of the C-S-H layer around the unreacted core. Further, the degree of hydration \( \alpha(t) \) at the initial stage, where the rate of hydration is controlled by the rate of nucleation and growth of nuclei, can be represented as [7]:

\[ \alpha = k \cdot t^n \]  

(8)

Assuming that the effect of deposition of C-S-H particles on the ion diffusion is proportional to the available space for diffusion in the C-S-H gel, from Eqs.(7) and (8), the coefficient of reduction in available space, C, can be expressed by Eq.(9),

\[ C = \exp(-\lambda \cdot \alpha^n) \]  

(9)

Here \( n = \kappa / m \) and \( \lambda = k_1 / k^n \) are kinetic parameters that control the rate and amount of the C-S-H deposition. This study established best values of 4.87 for \( \lambda \) and 5 for \( n \).

Finally, the effective diffusion coefficient \( D_e \) in Eq.(3) is modified by coefficient C in Eq.(9) giving

\[ D_e = D_0 \ln(1/\alpha) \exp(-\lambda \cdot \alpha^n) \]  

(10)

The pozzolanic reaction between fly ash and calcium hydroxide in cement pastes consumes some amount of water, and to complete the pozzolanic reaction of 1 g of fly ash, the following assumes that 0.1 g of water is bound chemically and that another 0.15 g of water is bound physically as gel water [8]. Therefore, the reduction of the amount of free water at the outer boundary of a hydrating particle must be adjusted by subtracting the amount of water consumed by the pozzolanic reaction of fly ash as suggested in Eq.(11).

\[ C_{w-free} = \left( W_0 - 0.38aC_0 - 0.28a_F F_0 \right) / W_0 \]  

(11)

where \( F_0 \) is the mass fraction of the fly ash in the mixed in proportion and \( a_F \) is the degree of fly ash hydration obtained experimentally with the selective dissolution method.

**Experimental program**

**Materials**

Ordinary Portland cement and fly ash which comply with Japanese standard JIS R5210 and JIS A6201 were used in this study. The chemical compositions and physical properties are shown in Table 1 and the mineralogical compositions obtained by the XRD-Rietveld method are given in Table 2.

**Mixing procedure**

Cement and fly ash powders were mixed at room temperature until homogeneity of the mixture was obtained. After the mixing, the fresh cement paste was cast in cylindrical 5 cm diameter and 10 cm high molds. The molds were carefully sealed to prevent evaporation of water. The mix proportions of the cement pastes are shown in Table 3.

**Curing conditions**

After the casting process, which took about 30 min for each mix, the paste specimens were cured at 20 °C, 35 °C, or 50 °C.

**Method for quantifying the degree of cement hydration**

When the required curing ages were reached, the hydration reaction of the cement paste was stopped by crushing the paste specimens into pieces of about 3-5 mm size, and then immersing them in acetone for 24 h. After that the paste sample was dried at 40 °C for 3 h, and next placed in a vacuum desiccator for 2 days. The specimens were then pulverized to be used in powder X-Ray diffraction (XRD) measurements.

The degree of hydration of the cement was measured by the powder XRD equipment. The measurement conditions of the XRD were a scanning range of 20 from 5 to 70 degree at 40kV, 20mA, step width 0.02 degrees, and a scanning speed of 2 degree/min. The measured XRD data were further analyzed using the Seroquant software which is based on the Rietveld quantitative phase analysis. The overall degree of hydration of the cement can be calculated based on a weighted summation of the degree of hydration of the individual cement components.

**Method for quantifying the degree of fly ash hydration**

A selective dissolution method was used in quantifying the degree of fly ash hydration. Hydrated fly ash – cement powder was dissolved by an acid solution of 2N HCl at 60 °C for 15 min and subsequently dissolved by a base solution of 5% NaCO₃ at 80 °C for 20 min.

**Determination of model parameters**

The overall degree of cement hydration was determined by the XRD-Rietveld method at various times after
mixing the water and cement. By fitting the model simulation with the experimental results, model parameters were systematically determined using commercial software. The effect of the fly ash was then characterized based on these parameters.

Table 1: Chemical composition of the Portland cement and fly ash used in this study

<table>
<thead>
<tr>
<th>Oxide (%)</th>
<th>OPC</th>
<th>Fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>21.06</td>
<td>59.10</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.77</td>
<td>20.20</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.67</td>
<td>8.85</td>
</tr>
<tr>
<td>CaO</td>
<td>63.55</td>
<td>3.36</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.28</td>
<td>0.12</td>
</tr>
<tr>
<td>Blaine (cm³/g)</td>
<td>3.400</td>
<td>3.740</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>3.16</td>
<td>2.33</td>
</tr>
<tr>
<td>LOI (%)</td>
<td>0.614</td>
<td>0.960</td>
</tr>
</tbody>
</table>

Table 2: Mineralogical components of the Portland cement and fly ash used in this study

<table>
<thead>
<tr>
<th>Mineral (%)</th>
<th>OPC</th>
<th>Fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>64.54</td>
<td>-</td>
</tr>
<tr>
<td>C₃S</td>
<td>14.04</td>
<td>-</td>
</tr>
<tr>
<td>C₃A</td>
<td>4.40</td>
<td>-</td>
</tr>
<tr>
<td>C₆AF</td>
<td>9.16</td>
<td>-</td>
</tr>
<tr>
<td>Gypsum</td>
<td>0.19</td>
<td>-</td>
</tr>
<tr>
<td>Mullite</td>
<td>-</td>
<td>7.09</td>
</tr>
<tr>
<td>Quartz</td>
<td>-</td>
<td>8.02</td>
</tr>
<tr>
<td>Hematite</td>
<td>-</td>
<td>1.23</td>
</tr>
<tr>
<td>Amorphous</td>
<td>-</td>
<td>81.97</td>
</tr>
</tbody>
</table>

Table 3: Mixture proportions of the fly ash-cement mixtures used here

<table>
<thead>
<tr>
<th>Mix</th>
<th>w/b (mass fraction)</th>
<th>Fly ash/Cement (vol. fraction)</th>
<th>Superplasticizer (%) of binder weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>0.25</td>
<td>0/100</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>0/100</td>
<td>0.65</td>
</tr>
<tr>
<td>FA25</td>
<td>0.25</td>
<td>25/75</td>
<td>1.30</td>
</tr>
<tr>
<td>FA50</td>
<td>0.25</td>
<td>50/50</td>
<td>0.65</td>
</tr>
</tbody>
</table>

a) To control the flow diameter of paste at 200 mm

Results and discussions

Model evaluation
To evaluate the applicability of our model, a comparison of the degree of cement hydration in OPC paste with a w/b of 0.35, obtained from 1) our model, 2) the Park model, and 3) the experiments, is illustrated in Figure 4. Figure 4 shows the effect of the C-S-H particle deposition on the hydration kinetics. It is clear that our model, which considers the effect of C-S-H particle deposition, exhibits a better agreement with the experimental data than the Park model. The Park model shows overestimated degrees of cement hydration for hydration values above 0.65. From the ideas used in the model modification (Section 2.3 above), the deviations between the results are mainly due to differences in the effective diffusion coefficient. Our model has a lower effective diffusion coefficient at a later age because of the deposition of C-S-H particles blocking the diffusion paths. Therefore, it can be concluded here that the key mechanism leading to differences between our model and the Park model is the deposition of C-S-H particles blocking the diffusion paths.

Effect of fly ash on the overall hydration kinetics of Portland cement
In this section, our model is used to simulate the experimental results of the cement hydration in fly ash cement pastes with a w/b of 0.25. The simulated results are presented by curves in Figure 5 (a) - (d). As can be seen, the simulated results are generally in good agreement with the experimental data for all fly ash cement pastes and all curing temperatures. This demonstrates that our model is valid throughout the period of hydration starting from the onset of the acceleration period to the deceleration period of hydration.

For OPC paste (Figure 5(a)), the curing temperature shows the acceleration effect on the early hydration rates. The higher curing temperatures lead to faster hydration rates at an early age. However, the degrees of hydration converge to the same level, approximately 0.65, at 1000 hours of hydration for all the curing temperatures here. This is consistent with the conclusion of Schindler [9] where there was little or no reduction in the final degree of hydration of Portland cement as a result of curing at different temperatures. Cervera et al. [10] used model simulation to establish that the final degree of hydration of the same sample cured at any temperature only depends on the initial water content of the mixture.

For FA25 paste, a similar effect of curing temperature as found in the OPC paste here is also
observed, as shown in Figure 5(b). Overall, the early hydration rates are very similar to those for OPC paste (Fig. 5(a)). For 20 °C curing, the acceleration period of FA25 paste starts at around 10 hours which is later than that of the OPC paste. The degree of hydration at 1000 hours of all FA25 pastes converges to about 0.75, which is slightly higher than with the OPC pastes.

For FA50 pastes as seen in Figure 5(c), retardation of the cement hydration at the early period is more pronounced than that found in FA25 pastes. A longer induction period is observed at all curing temperatures. The degree of hydration at 1000 hours reaches a level higher than 0.80 for pastes cured at 20 °C and 35 °C. However, for the paste cured at 50 °C, the degree of cement hydration levels off below 0.80 after 100 hours of curing. These observed phenomena are related to the effects of fly ash replacement. According to [3] the effect of fly ash on the hydration of the cement includes a dilution effect, an early age physical effect, and a chemical effect.

1) The dilution effect

Incorporation of fly ash results in increasing the effective water to cement ratio (w/c), thus enhancing the long-term hydration of cement with what has been termed a "dilution" effect [11]. To show this more clearly, the hydration kinetics of the cement in pastes containing different replacement ratios of fly ash at 20 °C are compared in Figure 5(d). The figure shows a clear increase in the long-term degree of hydration with higher replacement ratios of fly ash, especially at the high fly ash replacement condition (FA50).

2) The physical effect

The effect of fly ash replacement is also related to the physical properties of fine fly ash particles. There are two kinds of physical effects of fly ash on cement hydration: early retardation of hydration and an increase in available nucleation sites. The early slowing down of hydration in the presence of fly ash is related to the condition of the fly ash surface. Calcium ions adsorb on the fly ash surface, thus lowering the [Ca²⁺] in the bulk solution. It may be that the reduction of [Ca²⁺] could lead to a lower Ca/Si ratio in the solution and also in the initial shell of the fly ash-cement pastes.

It could be hypothesized that the initial shell with a lower Ca/Si ratio in fly ash-cement pastes would transform to a more stable C-S-H at a slower rate than that with higher the Ca/Si ratio in OPC paste. This could partly explain the extended induction period of hydration in fly ash-OPC paste. The retardation effect, early slowing down, is compensated by a physical acceleration effect in that the fly ash surface provides additional nucleation sites for hydration products to precipitate on [3]. This is indicated in Figure 5(d) where the cement hydration in fly ash-cement paste shows a longer induction period and a higher hydration rate thereafter for the fly ash containing samples.

3) The chemical effect

Fly ash is chemically involved in the cement hydration in two ways. First, cement produces Ca(OH)₂ in the hydration while fly ash consumes Ca(OH)₂ in the pozzolanic reaction. Second, both cement and fly ash consume water in their hydration reactions [3].

Figures 6(a) and (b) show the development of the pozzolanic reaction of fly ash in FA25 and FA50 pastes at different curing temperatures. The results for both mixtures show that at 50 °C the pozzolanic reaction of fly ash starts with a high rate of increase as early as 12 hours after mixing, while at 35 °C and 20 °C the high rate of increase starts after 72 hours and 336 hours, respectively. The early high pozzolanic reaction of fly ash in FA50 paste at 50 °C confirms that the contribution of fly ash in consuming water and producing C-S-H to fill the capillary pores is the main factor that impedes the hydration of the cement phase.

![Figure 6 Progress of the degree of pozzolanic reaction of fly ash at three (20 °C, 35 °C, and 50 °C) curing temperatures: (a) FA25 paste, (b) FA50 paste](image)

**Conclusions**

In this paper, the effect of fly ash on the hydration kinetics of Portland cement in fly ash–Portland cement mixtures of low w/b ratios were studied at three curing temperatures. The shrinking-core model was used in a modified form in quantifying the kinetics parameters of the cement hydration. Based on the results, the following conclusions may be drawn.
1) With the concept of densification of C-S-H gel due to deposition of C-S-H particles in gel pores, the model can better simulate the hydration kinetics of cement in the later hydration period than the Park model.

2) The effect of fly ash on hydration of the cement depends on the fly ash replacement ratio and the timing of the onset of the pozzolanic reaction, not on the extent of pozzolanic reaction. Also, the results suggest that, in low w/b pastes containing high replacement volumes of fly ash and subjected to curing at high temperatures, the hydration of the cement is more likely to become retarded because of insufficient water and/or insufficient space for the C-S-H gel from the cement hydration to grow.

References


Figure 5 Simulation of the progress of the degree of cement hydration of fly ash-cement paste with w/b = 0.25: (a) OPC paste, (b) FA25 paste, (c) FA50 paste, (d) different fly ash-cement pastes at 20 °C