Theoretical analysis of the hydration of fly ash cement

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In order to analysis the hydration reaction of fly ash cement, extended Tomozawa’s equation which considers the particle size distribution was applied to the reaction process of mixed system consisting of fly ash and ordinary Portland cement. By measuring the pozzolanic reaction of fly ash and the hydration reaction of ordinary Portland cement, the interaction between each reaction in fly ash cement was quantitatively analyzed. We also derived an equation to analyze the theoretical porosity of the fly ash cement based on the hydration reaction of the mixed system, and applied it to calculate the time dependence of porosity of the fly ash cement. Comparison of the simulated porosity with experimental values revealed that the porosity tend to increase with fly ash content, and after one year of aging, has almost no dependence on the vitrification rate of the fly ash cement.©2015 The Ceramic Society of Japan. All rights reserved.

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1. Introduction

In Japan, fly ash (FA) accounts for more than 85–95% of the coal ash produced by coal-fired power plants, with production reaching approximately 10 million tons per year.1 About 2/3 of this coal ash is used as substitute for manufacturing of cement, particularly in large and /or underwater structures. Here, FA offers the advantage of increasing the water density through a pozzolanic reaction, as well as providing a low exothermal heat of hydration by Ca(OH)2 generated by the hydration of alite (C3S) and belite (C2S) phases in ordinary Portland cement (OPC). Consequently, this coal ash is used as substitute for manufacturing of cement, reaction, as well as providing a low exothermal heat of hydration the advantage of increasing the water density through a pozzolanic interaction between the two. Hydration of OPC is also controlled by the vitrification of the FA, as it is typically only the glass components that react. It is therefore also necessary to clarify the relation between vitrification and hydration.

In this paper, the hydration reaction of an OPC-FA system is theoretically considered by deriving the hydration reaction and porosity of each component from their respective particle size distributions. For this, the pozzolanic reaction of FA in cement was measured at various FA ratios and with different OPC phases (C3S, C2S, C3A and C4AF) to determine the state of hydration. Experimental measurements of fly ash cement using FA with different degrees of vitrification were then used to measure the influence of the degrees of vitrification on both the pozzolanic reaction of FA and the hydration of OPC. Finally, the measured porosity of FA cements with different OPC-FA ratios was compared against the theoretical calculations.

2. Theoretical consideration

2.1 Quantity of residual water in a mixed particle system

We consider a mixed system consisting of cement particles (subscript: C) with a size distribution of \( f_C(r_C) \), density of \( \rho_C \) and a mass of \( M_C \), as well as an additive particle system (subscript: A) with its own size distribution \( f_A(r_A) \), density \( \rho_A \) and mass \( M_A \). As shown in Fig. 1, \( V \) and \( \delta \) are apparent volume and void fraction, respectively, of the mixed system. The net volume \( V_{\text{net}} \) is expressed as:

\[ V_{\text{net}} = (1 - \delta)V \]  

which can be rewritten as:

\[ V_{\text{net}} = \frac{M_C}{\rho_C} + \frac{M_A}{\rho_A} \]  

In Fig. 1(a), the apparent volume of the system is given as:

\[ V = \frac{1}{1 - \delta} \left( \frac{M_C}{\rho_C} + \frac{M_A}{\rho_A} \right) \]  

If it is assumed that the volume \( V' \) in Fig. 1(b) is the total volume of the mixed particle system, and that amount of water added is...
By substituting Eq. (3) into Eq. (4), we find the water-cement ratio is limited as:

\[
\frac{M_W}{M_C} \geq \frac{\delta}{1 - \delta} \left(1 + \frac{\rho_C}{\rho_A} \frac{M_A}{M_C}\right)
\]

By using an expression previously derived,\cite{3} the total volume of water absorbed over time \(t\) by particle systems \(C\) and \(A\) with size distributions of \(f_C(r_{AC})\) and \(f_A(r_{AA})\) is given as:

\[
V_{W(C)}(t) = \frac{k_{iC}C_{W\infty}}{\rho_w} N_C \sum_{i=1}^{N_C} 4\pi r_{iC}^2 f_C(r_{iC}) \left(1 + \frac{r_{iC}}{D_{iC}} \alpha_C^{2/3} \left[1 - \frac{\alpha_C}{n_C - (n_C - 1)\alpha_C}\right]^{1/3}\right) dt,
\]

\[
V_{W(A)}(t) = \frac{k_{iA}C_{W\infty}}{\rho_w} N_A \sum_{i=1}^{N_A} 4\pi r_{iA}^2 f_A(r_{iA}) \left(1 + \frac{r_{iA}}{D_{iA}} \alpha_A^{2/3} \left[1 - \frac{\alpha_A}{n_A - (n_A - 1)\alpha_A}\right]^{1/3}\right) dt,
\]

where,

\[
N_C = \frac{C_{W\infty}}{3\pi \sum_{i=1}^{N_C} r_{iC}^3 f_C(r_{iC})} \rho_C,
\]

\[
N_A = \frac{C_{W\infty}}{3\pi \sum_{i=1}^{N_A} r_{iA}^3 f_A(r_{iA})} \rho_A.
\]

Note that the hydration reaction of the mixed system will stop when the quantity of residual water reaches zero.

### 2.2 Porosity created by hydration in a mixed system

As shown in Fig. 2, the hydrate product formed on the parti-
The size distribution of the Portland cement and fly ashes reaction. In other words, it is assumed that the volume shown in Fig. 1(c) is the same as that in Fig. 1(d). Based on this, the porosity $\Delta$ of the cement at time $t$ is found using:

$$
\Delta = \delta' - \frac{\Delta V_C + \Delta V_A}{V''}
$$

$$
= \delta' - \frac{1 - \delta'}{1 + \frac{\rho_c M_A}{\rho_A M_C}} \times \left[ \sum_{i=1}^{N_C} \left( \frac{n_C}{1 - \alpha_C} \right) f_C(r_{i(C)}) r_{i(C)}^3(1 - \alpha_C) \right] ^{1/3} \left[ \sum_{i=1}^{N_A} \left( \frac{n_A}{1 - \alpha_A} \right) f_A(r_{i(A)}) r_{i(A)}^3(1 - \alpha_A) \right] ^{-1/3}
$$

(18)

2.3 Superposition of the rate equation of hydration

The rate equation for the hydration of cement is given by:

$$
- \sum_i f_C(r_{i(C)}) \frac{d\alpha_C}{dt},
$$

which is normalized by Eq. (20) to:

$$
\sum_i f_C(r_{i(C)}) = 1.
$$

Using the rate of reaction represented by Tomozawa’s equation:

$$
- \sum_i f_C(r_{i(C)}) \frac{d\alpha_C}{dt} = \frac{3C_{\infty}}{\nu \rho_c} \sum_i f_C(r_{i(C)}) r_{i(C)}^2 \frac{1}{r_{i(C)} \alpha_C^2 \left( \frac{1}{D_C} + \frac{1}{D_A} \right) + \left( \frac{\alpha_C}{D_C(1 - \alpha_C)} \right) \left( \frac{1}{D_A(1 - \alpha_A)} \right) \left( \frac{1}{D_D(1 - \alpha_D)} \right) \left( \frac{1}{D_E(1 - \alpha_E)} \right)^{1/3}}
$$

(21)

$$
k_{d(C)} = \frac{B_{d(C)}}{1 - \alpha_C} + C_{d(C)}(1 - \alpha_C)^2,
$$

$$
D_{d(C)} = D_{d(C)} \left( \frac{1}{1 - \alpha_C} \right)^2,
$$

(22) (23)

the rate of reaction for additional material is found as follows:

$$
- \sum_i f_A(r_{i(A)}) \frac{d\alpha_A}{dt} = \frac{3C_{\infty}}{\nu \rho_A} \sum_i f_A(r_{i(A)}) \frac{1}{r_{i(A)} \alpha_A^2 \left( \frac{1}{D_{d(A)}} \right) + \left( \frac{\alpha_A}{D_{d(A)}} \right) \left( \frac{1}{D_{d(A)}} \right) \left( \frac{1}{D_{d(A)}} \right) \left( \frac{1}{D_{d(A)}} \right) \left( \frac{1}{D_{d(A)}} \right) \left( \frac{1}{D_{d(A)}} \right)^{1/3}}
$$

(24)

$$
k_{d(A)} = \frac{B_{d(A)}}{1 - \alpha_A} + C_{d(A)}(1 - \alpha_A)^2,
$$

$$
D_{d(A)} = D_{d(A)} \left( \frac{1}{1 - \alpha_A} \right)^2,
$$

(25) (26)

3. Experimental procedure

The size distribution of the Portland cement and fly ashes
**Fig. 3.** Particle size distribution of Portland cement powder.

**Fig. 4.** Particle size distribution of fly ash powders with glass contents of 38.2% or 76.6%.

**Fig. 5.** Reaction ratio of fly ash in FA cement.

**Fig. 6.** Amount of Ca(OH)₂ produced by the OPC-FA series in Table 1.

**Fig. 7.** Fitting parameters for the (a) reaction rate ($k_r(A)$) (b) formation of a protective layer with no diffusion ($B_{d(A)}$) (c) destruction of the protective layer ($C_{d(A)}$), and (d) effective diffusion ($D_{E(A)}$) in Eq. (24).

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**Table 1.** OPC-FA mixing ratio of each sample type

<table>
<thead>
<tr>
<th>Glass content</th>
<th>Substitution ratio (mass %)</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>38.2% (F series)</td>
<td>0%</td>
<td>OPC</td>
</tr>
<tr>
<td>20%</td>
<td>F20</td>
<td></td>
</tr>
<tr>
<td>40%</td>
<td>F40</td>
<td></td>
</tr>
<tr>
<td>60%</td>
<td>F60</td>
<td></td>
</tr>
<tr>
<td>76.6% (F' series)</td>
<td>20%</td>
<td>F'20</td>
</tr>
<tr>
<td>40%</td>
<td>F'40</td>
<td></td>
</tr>
<tr>
<td>60%</td>
<td>F'60</td>
<td></td>
</tr>
</tbody>
</table>
with different glass contents used in this study are shown in Figs. 3 and 4, respectively. The ratios to which these were mixed, and the sample names these mixtures were given, are shown in Table 1. The composition of the OPC and FA used was that the same as that used in a previous study.6) The experimental method used to measure the reaction ratio of the fly ash and the individual components of the OPC were the same as those used in a previous study.6)

4. Results and discussion

4.1 Reaction ratio of fly ash in cement

Figure 5 shows the reaction ratio of FA when mixed at various ratios with OPC, as measured experimentally and calculated using Eq. (24). This reveals a tendency for the reaction ratio to decrease when the ratio of FA is increased, which can be attributed to a decrease in the relative supply of Ca(OH)₂ when...
FA changes to C–S–H by the pozzolan reaction. The amount of Ca(OH)₂ present at low and high FA glass content ratios of 38.2 and 76.6% are shown in Fig. 6, from which it is evident that as the hydration reaction is controlled by a decrease in Ca(OH)₂, the quantity of water needed for reaction also decreases.

Figure 7 shows the fitting parameters of Eq. (24) used to simulate the experimental data in Fig. 5, in which the decrease in effective diffusivity $D_i$ with FA content confirms that there is a decrease in the required water. The quantity of Ca(OH)₂ formed is also considered to be dependent on the degree of FA vitrification based on the data presented in Fig. 6. However, it is clear that the effective diffusivity is high with an FA that has a high degree of vitrification, as shown in Fig. 7. This suggests that the pozzolanic reaction of FA is promoted by the presence of numerous glass phases.

4.2 Film thickness generated by the hydration of fly ash

The thickness of the film generated on the surface of FA particles is determined by the difference in radius between the hydrate product and the non-reacted particle. Therefore, by using Eqs. (14) and (15), the film thickness is given as:

$$d_i = R_A(t) - r_{iA}(t)$$

$$= \left\{ [n_A - (n_A - 1)\alpha_A]^{1/3} - \alpha_A^{1/3} \right\} r_{iA}$$  (27)

If the particle size distribution is used, the mean value of the thickness of the film generated on the FA particles is expressed as:

$$\langle d_i \rangle = \sum f(r_i)d_i$$  (28)

Figure 8 provides a comparison between film thickness simulated by Eq. (28) and the experimentally obtained results, from which it is apparent that there is a good agreement between the two.

4.3 Hydration reaction of OPC in fly ash cement

In this section, we consider the influence of FA on the hydration reaction of OPC in cement. In order to observe the hydration reaction of OPC in FA cement, the reaction ratio of each ingredient (C₃S, C₂S, C₃A, C₄AF) of OPC was measured individually. Figure 9 shows the experimental data and simulated outputs (solid and dotted curves), the latter being obtained using Eq. (21). With the exception of $D_{E(C)}$, the reaction parameters $k_{E(C)}$, $B_{E(C)}$, and $C_{E(C)}$ remain almost constant when adding FA. This tendency is the same as that seen in Fig. 7. The simulated value $D_{E(C)}$ of each ingredient in OPC, F20, and F'20 are shown as black bars in Fig. 10.

In the case of C₃S, the reaction ratio was increased in the presence of FA over OPC alone, as shown in Fig. 9(a). For this reason, the film generated by hydration on the surface of C₃S decreases over 7 days, at which point the surface of the FA provides a site for additional precipitation of hydration products and promotes the hydration of C₃S. At the same time, however, it is believed that the lime saturation ratio of the liquid remains stable due to the fact that FA absorbs Ca(OH)₂ by the pozzolanic reaction, which also promotes the hydration of C₃S. Similarly, the effective diffusivity of the C₃S hydration reaction is increased in the presence of FA when compared to OPC alone, as shown in Fig. 10(a). In other words, the increase in Ca(OH)₂ consumption by the pozzolanic reaction of FA increases the effective diffusivity of C₃S.

The reaction of C₃S on the other hand, is inhibited for a long time when part of the OPC is replaced by FA, as is shown in Fig. 9(b). This is concordant with the results of Nagano et al., in which the quantity of water taken up by C₃S was found to be delayed by the addition of FA. This tendency for a delay in hydration is verified by the simulated results in Fig. 10(b), in which it is clear that the effective diffusivity of C₂S is lower in FA cement than in OPC alone. Furthermore, the effective diffusivity is reduced even more when the FA added has a lower degree of vitrification.

In the case of C₃A as is shown in Fig. 9(c), neither the presence of FA nor its degree of vitrification seems to have any effect. In contrast, the reaction rate of C₄AF in F20 and F'20 does increase slightly compared to OPC alone after 56 days of hydration, but unlike in OPC, the rate ceases to increase beyond this point, as shown in Fig. 9(d).

As it is almost impossible to measure the hydration reaction of each ingredient (C₃S, C₂S, C₃A, C₄AF) in samples F40,
F‘40, F‘60, results estimated by the least squares method (white bars) from the simulation values (black bars) shown in Figs. 10(a)–10(d) were used to discuss the $D_{\text{BC}}$ values. Figure 11 shows the rate of reaction and reaction ratio of “superposed OPC”, in which C3S, C2S, C3A, and C4AF were incorporated into FA cement. When compared to OPC alone, the reaction ratio of this “superposed OPC” is higher, but its reaction ratio gradually decreases with increasing FA content. The lime saturation ratio of the liquid phase does not rise by consuming Ca(OH)$_2$ at FA during the first half of the curing time; and as a result, the hydration of C3S is promoted. Moreover, increasing the percentage of FA has the effect of reducing the effective diffusivity as shown in Fig. 7. Consequently, although the consumption of Ca(OH)$_2$ is initially quite high, it gradually decreases over time. This is therefore believed to be responsible for the gradual decrease seen in the reaction ratio of the superposed OPC.

4.4 Time dependence of pore formation rate in fly ash cement

Having established the reaction rates of FA and OPC, it is now possible to calculate the time dependence of porosity in FA cement by treating it as a mixed system of FA and OPC using Eq. (18), the results of which are shown in Fig. 12. We see from this that although the experimentally obtained values are uniformly higher than the theoretical values by ~0.05, their similar tendencies are sufficient to provide a qualitative assessment. For instance, an increase in the ratio of FA or time reduces the influence of vitrification on both the theoretical and experimental values. However, the theoretical values indicate that the porosity should increase with a higher degree of vitrification, when in fact the opposite is seen in the experimental values. The reason for this is unclear and must be explored further in the future.

5. Conclusion

The reaction of FA in cement has been demonstrated to vary in accordance with the OPC-FA ratio. That is, when the FA ratio is lower, the effective diffusivity of FA increases and the pozzolanic reaction is promoted by an increase in the available quantity of Ca(OH)$_2$.

The reaction of FA cement also advances when the degree of FA vitrification is increased, on the basis of which it is considered that the glass content of FA contributes to the pozzolanic reaction. When the FA ratio is low, on the other hand, the reaction of OPC is initially promoted, but later slowed. This is believed to be caused by the consumption of Ca(OH)$_2$ by FA, with the pozzolanic reaction of FA directly interacting with the hydration of OPC through this transfer of Ca(OH)$_2$.

Taking these interactions into consideration, the porosity in cement produced from an FA-OPC was analyzed using a simulation based on hydration theory, the usefulness of which was confirmed by comparing against experimental data.

References