Theoretical analysis of the hydration dependence of low heat Portland cements with or without silica fume on their packing fractions

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The reaction process between components in mixed systems consisting of silica fume and low-heat Portland cement was studied by using an extended version of the Tomozawa's equation that considers particle size distributions. In addition, the relationship between the hydration reaction of the cement and the pozzolanic reaction of silica fume was quantitatively analyzed. In order to determine theoretical porosity of the silica fume containing cements, a special equation including the hydration reaction of the mixed system was described and used to quantify cement porosity as a function of time. The comparison of the simulated porosity results with the measured values revealed that the silica fume reactivity was similar to that of alite.

Key-words: Silica fume, Low heat Portland cement, Silica fume cement, Ordinary Portland cement, Size distribution, Hydration reaction, Pozzolanic reaction, Rate of reaction, Reaction ratio, Porosity

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1. Introduction

Low heat Portland cement (LHC) is a component for high-strength and ultra-high strength cement/concretes which are widely used in construction especially for high-rise buildings due to their ability to prevent thermal cracking caused by the heat of hydration and reduce autogenous shrinkage, which severely damages building structures. The main components of this cement contain high amounts of a belite phase (C₂S), in contrast with ordinary Portland cement having alite (C₃S) as a main component, and extremely low contents of aluminate (C₃A) and ferrite (C₄AF) phases. In order to manufacture ultra-high strength concretes with compressive strengths of 100 N/mm² or higher, it is necessary to reduce the water-to-powder (W/P) ratio below 0.25 while ensuring that cement workability is maintained.¹,² In addition, in ultra-high strength fiber concretes such as reactive powder concretes, the required W/P ratio is less than 0.2.³,⁴ Generally, cements mixed with silica fume (SF) are used to obtain ultra-high strength concretes. Increasing the fluidity of a cement paste is very important for improving the performance of high-strength concretes with or without SF. It has been reported elsewhere that fluidity may be improved by increasing the packing fraction through the use of cements mixed with early-strength clinkers classified into various particle sizes.⁵,⁶ Many researchers have studied the packing density of cementitious materials to improve the cement performances and proposed various packing models and simulation methods. For example, De Larrard and Sedran have investigated the packing density of high-strength concrete by using linear packing density and solid suspension simulation methods. For example, De Larrard and Sedran have investigated the packing density of high-strength concrete by using linear packing density and solid suspension models.⁷ Bentz and Haecker showed that coarse cement was important for producing high-strength concretes using a microstructure model developed at the National Institute of Standards and Technology (NIST).⁸ Wang Aiqin et al. suggested that, according to the Rosin-Ramler-Benutzer equation, wider particle size distributions are advantageous for increasing the packing density of a system and decreasing the water demand.⁹ Wong and Kwan proposed a new wet method of packing density and water demand.¹⁰ In our previous reports, a new packing simulation method that takes into account particle size distribution has been developed.¹¹,¹² The resulting program was capable of calculating material packing fractions with particle size distributions by utilizing a statistical method and three-dimensional geometries of particles with given particle size distributions. This software calculates the void fraction and the average coordination number of particle systems with arbitrary particle size distribution based on the original theory.¹¹ The authors have previously reported that fluidity of cement pastes containing lime stone Portland cement with low W/P ratios is significantly affected by packing fractions calculated from powder particle shapes by using this method.¹³,¹⁴ Several studies discussing the mechanical properties of high-belite cements related to SF replacement by curing condition and/or packing fraction con-

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ditions have been reported.\textsuperscript{15)–18) However, the dependence of LHC properties on the packing fraction ratio at different curing conditions of SF containing systems has not been investigated in detail. The aim of this study was to explore the properties of LHC, taking into account packing fraction ratios, at different percentages of SF replacement and various curing conditions. The obtained results were discussed in terms of the hydration reaction that occurred in the system, while total pore volumes were measured at laboratory conditions and compared with the LHC standard. This work also provides a theoretical analysis of the LHC hydration as a function of the packing fraction of powder particles with or without SF at low W/P ratios.

2. Experimental procedure

2.1 Preparation of samples

The particle size distribution as well as Brunauer-Emmett-Teller (BET) specific surface areas of LHC and SF were analyzed by a laser diffraction particle size analyzer (SALD-2300; SHIMADZU) and surface area and pore size analyzer (Micromeritics Gemini V; SHIMADZU), respectively. The mineral composition of LHC is listed in Table 1. An LHC clinker was ground using a small ball mill to obtain ground clinkers with different particle fineness (BL1190, BL3640, and BL5670), the numbers after “BL” represent Blain’s values of fineness, as shown in Table 2. BL3640 had a particle size distribution comparable to that for the commercially available LHC (referred to as BL0SF in these abbreviations). Reagent-grade CaSO₄·2H₂O was added at 2 mass % to the ground clinkers on the basis of SO₃. Proportions and void fraction ratios of the coarse and fine LHC used in this experiment were obtained using a packing simulation program, which provided optimum packing fraction conditions.\textsuperscript{11)\textsuperscript{12)} A polycarboxylic acid-based superplasticizer was utilized for controlling the bleeding effect, we used two-liquid type Visco-top BASF Japan Ltd. for the bleeding control.

The constituents of LHC are listed in Table 1. To control the bleeding effect, we used two-liquid type Visco-top 100 (Kao) as a thickener. The LHC powder was kneaded with water-powder ratios to form a paste. Water was added to 1 mass % of the powder, simultaneously the undiluted solution of the thickener comprising two types of liquids was added to the powder for the solution mass conversion of LHC. Gradually, the paste was hardened, and sealed in a styrene pot for a predetermined period. Then, we arrested the hydration of the hardened material using a large quantity of acetone.

2.2 Measurement of fluidity and early hydration studies

The obtained pastes were mixed using a hybrid defoaming mixer for one minute,\textsuperscript{14)} left untouched for two minutes, mixed by hand for one minute, and afterwards were subjected to testing procedures. Strain rates for the prepared pastes at shear stresses ranging from zero to 200 Pa were measured using a double-cylinder rotational viscometer of a stress-control type. The obtained fluidity curves exhibited Newtonian characters, while apparent viscosities of fluids were calculated using the corresponding Newtonian viscosities. Measurements were conducted at a temperature of 20°C, and early hydration of samples was measured by a conduction calorimeter. The curing temperature was equal to 20°C.

2.3 Measurements of reaction ratios and porosities of the hardened samples

The cement pastes were casted using a 1 cm × 1 cm × 8 cm mold. Pre-curing conditions of 20°C and 100% humidity were applied to the molded samples for 2 days before demolding. After that, the samples were placed at 20 and 80°C wet curing conditions for 3, 7, 14, and 28 days (including pre-curing times). After the required curing period, the samples were ground and sieved using a 90μm sieve, immersed in acetone to arrest the hydration of samples, and dried in an aspirator for 24 h. The hydrated cement powder was mixed with 10 mass % of MgO (utilized an internal standard).

The hydration reaction was analyzed by an XRD instrument (Bruker XIS). XRD patterns were measured using Cu-Kα, a tube voltage of 45 kV, a tube current of 200 mA, scan range of 2θ = 5°–70°, a step width of 0.02°, and a scan rate of 5°/min, while the specific peaks for the alite, belite and MgO phases were 51.78 and 51.97, 36.63, and 42.91 degrees respectively. Peak areas were obtained using PeakFit software program and subsequently compared with those for non-hydrated materials. When calculating the reaction ratios using residual function, corrections for ignition losses (estimated by using the ignited base) were added. The residual function is given as

\[ \alpha = \frac{I}{k} \frac{m/M}{I_0/k_0 m_0/M_0} \frac{1 - (Ig)_0}{1 - Ig} \]

where, \( I \) is the peak intensity of hydration sample, \( k \) is the peak intensity of MgO, \( M \) is the mass of the hydration sample, \( m \) is the mass of MgO, \( Ig \) is the ignition loss of hydration sample. The subscript 0 indicates each quantity of non-hydration state.

Pore volumes of the hardened specimens were measured using a mercury porosimeter. After cutting out the hard-
ened specimens having a thickness of 5 mm at the corners, and performing D-Dry drying for 24 h, we measured the volume of pores.

2.4 Calculations of void fractions

Table 3 lists the packing and void fractions for BL3640 (BLOSF) and the mixtures of BL1190 and BL5670 with or without SF. The maximum packing fraction value was obtained when 73 mass % of BL1190 was mixed with 27 mass % of BL5670 by packing simulations,1,11,12 while their corresponding particle size distributions are shown in Fig. 1. This mixture was selected as base cement. The cements with adjusted particle size distributions were blended with 0, 3, 5, and 10% of SF and denoted as PKnSF (PK and n correspond to BL1190:BL5690 = 73:27, and n% of SF, respectively). Remarkably, packing fractions of particles were increased by adjusting packing fraction of cement. After adding SF, the packing fraction of PKnSF increased, while the corresponding void fraction slightly decreased.

3. Theoretical simulations

3.1 Cement hydration reaction that has the related size distribution

The particle size distribution of a mixed system consisting of multiple components characterized by particle size distributions \( f_j(r_j) \), volumes \( V_j \), and packing rate \( p_j \) \((j = 1, 2, \ldots)\) can be expressed as11)

\[
F(r) = \sum_j \frac{p_j V_j f_j(r)}{\sum_k p_k V_k}.
\]

We can calculate the particle size distribution of the mixed system PKnSF \((n = 0, 3, 5, 10)\) described in Table 3 by applying this theory using the data representing the particle size distributions of the raw materials (Fig. 1).

Tomoawa suggested a hydration rate equation for Portland cement form an industrial point of view. Several parameters for the hydration rate equation were determined by comparing the hydration rate equation and experimental data for the heat liberation rate.19,20 The Tomosawa equation can be written as follows:21)

\[
\frac{-\frac{d\alpha(r)}{dt}}{1-\alpha} = \frac{3C_{\infty}}{V \rho c^2} \frac{1}{r c} \left( \frac{1}{k_d} + \frac{1}{k_f} \right) + \frac{1}{D_e} \left[ \frac{\alpha(r, t) - \alpha(r, t)}{1} - \frac{\alpha(r, t)}{1} \right]^{1/3},
\]

where \(-\frac{d\alpha}{dt}\) is the rate of reaction, \(\alpha\) is the residual fraction \((1 - \alpha)\) is the degree of hydration), \(r_{ci}\) is the particle radius, \(C_{\infty}\) is the concentration of water around the particle, \(v\) is the water mass ratio consumed by water-cement reaction, \(\rho_c\) is the density of cement, \(n\) is the volume ratio of hydration product to reacted cement, \(k_d\) is the coefficient of the velocity of the reaction, and \(k_f\) is the coefficient of the mass transfer. The latter is written as a function of \(\alpha\), as given by Eq. (3), where \(B_d\) is the coefficient describing the formation of a protective layer that permits diffusion, and \(C_d\) is the coefficient expressing the destruction of the protective layer. The effective diffusion coefficient \(D_e\) is written as a function of degree of hydration \(1 - \alpha\) and diffusion coefficient \(D_{ei}\):

\[
D_e = D_{ei} \left[ \ln \frac{1}{1 - \alpha} \right]^2,
\]

where the degree of hydration arrived at \(1/\epsilon\), \(D_e\) takes \(D_{ei}\). Eq. (4) is used to modify the expression for the rate of hydration. In the case that using the effective diffusion coefficient \(D_e\) instead of the diffusion coefficient \(D_{ei}\), the rate of hydration after the most rapid reaction tends to be more increased than experimental values. By using \(D_e\) as the diffusion coefficient, revised calculation results are in the tendency of experimental values. The parameters \(v\) and \(C_{\infty}\) typically have values of 0.25 and 1, respectively. The temperature dependence of each parameter is given as follows:

\[
B_d(T) = B_d \sqrt{\frac{T}{\theta}},
\]

\[
C_d(T) = C_d \exp \left[ -\beta_1 \left( \frac{1}{T} - \frac{1}{\theta} \right) \right],
\]

\[
k_r(T) = k_r \exp \left[ -\beta_2 \left( \frac{1}{T} - \frac{1}{\theta} \right) \right],
\]

\[
D_e(T) = D_e \exp \left[ -\beta_3 \left( \frac{1}{T} - \frac{1}{\theta} \right) \right].
\]

where \(\theta\) and \(T\) are the environmental temperature and the temperature of curing, respectively, while the values of 3000 [deg], 4200 [deg], and 4000 [deg] are typically used for the respective empirical constants \(\beta_1, \beta_2, \text{ and } \beta_3\).

Equation (2) is valid only for single-particle radii and must be generalized in order to be used for systems containing cement particles with various sizes. Such particles can be described by the general particle size distribution equation reported in our previous papers.22,23

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Table 3. Mixture compositions, SF contents, and packing properties of various mixed LHCs

<table>
<thead>
<tr>
<th>LHC</th>
<th>BL3640</th>
<th>LHC</th>
<th>BL1190</th>
<th>LHC</th>
<th>BL5670</th>
<th>SF</th>
<th>packing ratio</th>
<th>void fraction</th>
</tr>
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<tr>
<td>BLOSF</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>0.809</td>
<td>0.191</td>
</tr>
<tr>
<td>PK0SF</td>
<td>73</td>
<td>27</td>
<td>0</td>
<td>0.818</td>
<td>0.182</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PK3SF</td>
<td>70.8</td>
<td>26.2</td>
<td>3</td>
<td>0.821</td>
<td>0.179</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PK5SF</td>
<td>69.4</td>
<td>25.6</td>
<td>5</td>
<td>0.824</td>
<td>0.176</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PK10SF</td>
<td>65.7</td>
<td>24.3</td>
<td>10</td>
<td>0.830</td>
<td>0.170</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
where $F(r_i)$ is defined by Eq. (1).

### 3.2 Porosity of the hydrated samples

The hydration of SF-consisting cement with particle size distribution $F(r_i)$ was investigated. In Fig. 2(b), we assumed that the volume $V'$ corresponded to the total volume of the LHC, SF, and added water, that is larger than $V_{LHC} + V_{SF}$ in (a). The difference between $V'$ and the net volume of the cement ($V_{LHC} + V_{SF}$) is equal to:

$$V' - (V_{LHC} + V_{SF}) = \frac{M_w}{\rho_w}$$

where $\rho_w$ and $M_w$ are the density and mass of the added water, respectively. The void fraction $\delta'$ is given as follows:

$$- \sum F(r_i) \frac{d\omega(r_i, t)}{dt} \quad (6)$$

where $F(r_i)$ is defined by Eq. (1).

### Fig. 2

(a) A total volume of particles ($V_{LHC} + V_{SF}$), and the corresponding void fraction $\delta$. (b) A total volume of cement particles ($V'$) with added water that exceeds the total volume ($V_{LHC} + V_{SF}$) in (a). $\delta'$ denotes the water ratio in $V'$. (c) A colloid or paste described in (b) after sufficient stirring. (d) Porosity ($\Delta'$) of cement at time $t$ after the beginning of hydration.
\[ \delta' = \frac{V_W}{V_{\text{LHC}} + V_{\text{SF}} + V_W} = 1 - \frac{M_w \rho_{\text{LHC}}}{M_{\text{LHC}} \rho_w} \left( \frac{1}{1 + \frac{M_{\text{SF}} \rho_{\text{LHC}}}{M_{\text{LHC}} \rho_{\text{SF}}}} \right) \]

where \( V_w \) is the volume of the added water, and \( \rho_i \) and \( M_i \) are the density and mass of the substance \( i \), respectively. This equation is based on the assumption that the hydration reaction (Fig. 2) in system (c) does not begin immediately after stirring, and that the volume \( V' \) remains unchanged during the reaction. In addition the pore volume ratio decreases with reaction time, because hydrate species are formed on the surface of each particle as the reaction advances. The time dependence of the pore volume ratio of the mixed system consisting of LHC and SF can be expressed as:\(^{24}\)

\[ \Delta = \delta' - (1 - \delta') \sum_j M_j \left( n_j - 1 \right) \frac{f_j(r_{i,j})r_{i,j}^3(1 - \alpha_j)}{\sum_i f_j(r_{i,j})r_{i,j}^3} \]

where, \( j = \text{BL1190, BL5670, SF} \). The reaction completion time \( t_m \) can be determined by solving Eq. (10) as:\(^{24}\)

\[ 1 - \sum_j \frac{3k_{r,j}C_{\text{Wix}}}{\rho_j} \left( \frac{M_w}{M_j} \sum_i r_{i,j}^3 f_j(r_{i,j}) \right)^{-1} \times \sum_i r_{i,j}^2 f_j(r_{i,j}) \int_0^{\alpha_j} \left( \frac{k_{r,j}}{k_{i,j}} + \frac{r_{i,j}^3 k_{r,j}^3 \alpha_j^3}{D_{i,j}} \right) \left( 1 - \frac{\alpha_j}{n_j - (n_j - 1) \alpha_j} \right)^{1/3} \text{d}r = 0 \]  

4. Results and discussion

4.1 Fluidity of the SF-containing and SF-free LHCs with adjusted packing fractions

Table 4 lists the fluidities of the BL0SF and PKnSF series. At the same apparent paste viscosity, the W/P ratio of the paste can be reduced by adjusting the PKnSF packing fraction. When the SF replacement ratio was 0 or 3% (PK0SF,PK3SF), the corresponding W/P ratio was reduced to 0.15. When SF was used to replace between 5 and 10% of the base cement (PK5SF, PK10SF), the W/P ratio was reduced to 0.14 at the same apparent viscosity of the paste. For BL0SF, the W/P ratio could not be reduced to less than 0.2 simply by increasing the cement of superplasticizer (SP).

4.2 Early hydration of LHC

Figure 3 describes the early hydration process for the BL0SF and PKnSF series measured by using a conduction calorimeter. The hydration of the PKnSF series was retarded compared to that of BL0SF. The observed heat liberation for the PKnSF series was smaller than the corresponding value for BL0SF because the PKnSF samples contained larger amounts of coarse cement (BL1190).\(^{22}\) In addition, the W/P ratio and packing fractions were also affected by the early hydration of PKnSF series. For the PKnSF series, maximum hydration rate was decreased by increasing the SP content as compared to that for the BL0SF. In addition, the hydration of PK3SF, PK5SF and PK10SF was retarded compared with the case of PK0SF. Packing fractions also affected hydration reactions for the SF-containing cements. It was reported that early hydration of a 50:50 mixture of coarse LHC and fine LHC was identical to that of LHC with standard particle size distributions. Therefore, both packing fractions and early hydration are important factors that should be considered when choosing a suitable material design for high-strength cement.\(^{15}\)

5. Simulations of the hydration process

In this section, we discuss the influence of SF addition on the hydration reaction of the alite and blite phases in BL0SF and PKnSF \( (n = 0, 3, 5, 10) \).

![Fig. 3. Experimental heat liberation rates for the BL0SF and PKnSF series (n = 0, 3, 5, and 10).](image-url)
5.1 Reaction ratios of the C₃S and C₂S phases

The hydration reaction rates of alite (C₃S) and belite (C₂S) studied in this experiment were calculated from the areas under the C₃S and C₂S peaks of XRD measurements, respectively. In general, a hydration reaction progresses with hydration time; however, it can be accelerated by high temperatures. Figures 4–6 show the reaction rates for the C₃S and C₂S phases cured at 20 and 80°C by a wet curing. The reaction ratios for each ingredient (C₃S and C₂S) in BLOSF were measured individually as the first step. Figure 4 shows the experimental data (circles) and the simulation output (solid curves) generated by using Eq. (6). The fitting parameters from Eq. (2) are listed in Table 5.

The reaction ratios for each ingredient (C₃S and C₂S) of the PKₙSF series listed in Table 4 were also individually measured. Each ratio (such as W/P) was determined in order to equate the coefficients of viscosity of the samples. Figure 5 and 6 show the experimental data and simulated results (circles and solid curves) for the reaction ratio of C₃S and C₂S phases, respectively; the fitting parameters used in the simulation are listed in Table 6. In the presence of SF, C₃S and C₂S in the PK series have almost constant reaction ratios as shown in Figs. 5 and 6, respectively.

The hydration reaction of PKₙSF was decreased around 20% for the C₃S phase and by 10% for the C₂S phase, as compared to that for BLOSF. BLOSF did not contain coarse cement (B1190) and its W/P ratio was higher than that...
for the PK\(n\)SF series, the SP content in PK\(n\)SF had to be increased (although, SP addition had no effect on cement hydration during the late stages). Therefore, coarse cement contents and lower W/P ratios mainly affect the rate of PK\(n\)SF hydration during early stages as compared to BL0SF. These results indicate that the reduction in total surface area due to the increase in packing fraction decreased the reactivity of the C3S and C2S phases. The packing fractions of the PK\(n\)SF series were increased with increasing SF content; however, the reaction rates of the C3S and C2S exhibited the same tendency across the PK\(n\)SF series because the W/P ratios for the samples of the PK\(n\)SF series were almost identical.

### 5.2 Porosity of the hardened samples

Figure 7 shows the time-dependence of the porosity [Eq. (9)] of the LHC (SF = 0\%), BL0SF and PK0SF samples, at curing temperatures 20 and 80°C. The porosity of the hardened PK0SF was smaller than that of BL0SF. The reason why 6\% difference between BL0F and PK0F of the early porosity decreased to 2\% three days later is that the hydration reactions for the C3S and C2S phases in BL0SF were stronger than the corresponding reactions in PK0SF. A close correspondence between the theoretical and experimental values was obtained at both temperatures. In contrast, Fig. 8(a) reveals that, except for SF = 0\%, the observed correspondence is worse for the PK series due to zero reactivity of SF [1 – \(\alpha\) SF = 0 in Eq. (9)]. In fact, the differences between the theoretical and experimental values measured at 20 and 80°C increased with increasing SF content assuming the absence of any SF reactions in SF-containing cements [Fig. 8(a)]. Therefore, we assumed that the reaction ratio of SF after 3 days of hardening could be described by the behavior specified in Table 7, which resulted in an improved correspondence between the corresponding porosity values as indicated in Fig. 8(b) which shows a comparison between the theoretical and the experimental data corresponding to the \(n\)-dependence of the porosity for the PK series. These results were obtained using the assumptions that SF (a) did not react and (b) reacted as described in Table 7. Figure 8(b) confirms that an excellent correspondence is obtained if SF reacts as specified in Table 7. In other words, the reaction ratio for SF becomes approximately equal to that for C3S in the SF-containing cements.

### Table 5. Fitting parameters for Eq. (2) used to obtain the reaction ratios for C3S and C2S phases in BL0SF (via simulations)

<table>
<thead>
<tr>
<th></th>
<th>C3S</th>
<th>C2S</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_r) [cm/h]</td>
<td>(1 \times 10^{-7})</td>
<td>(1 \times 10^{-6})</td>
</tr>
<tr>
<td>(B_d) [cm/h]</td>
<td>(1 \times 10^{-9})</td>
<td>(1 \times 10^{-9})</td>
</tr>
<tr>
<td>(C_d) [cm²/h]</td>
<td>(5 \times 10^{-4})</td>
<td>(5 \times 10^{-4})</td>
</tr>
<tr>
<td>(D_d) [cm²/h]</td>
<td>(3 \times 10^{-14})</td>
<td>(5 \times 10^{-14})</td>
</tr>
</tbody>
</table>

### Table 6. Fitting parameters for Eq. (2) used to obtain the reaction ratios for the C3S and C2S phases in PK\(n\)SF \((n = 0, 3, 5, \text{and} 10)\) (via simulations)

<table>
<thead>
<tr>
<th></th>
<th>C3S</th>
<th>C2S</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_r) [cm/h]</td>
<td>(1 \times 10^{-7})</td>
<td>(1 \times 10^{-6})</td>
</tr>
<tr>
<td>(B_d) [cm/h]</td>
<td>(1 \times 10^{-9})</td>
<td>(1 \times 10^{-9})</td>
</tr>
<tr>
<td>(C_d) [cm²/h]</td>
<td>(5 \times 10^{-4})</td>
<td>(5 \times 10^{-4})</td>
</tr>
<tr>
<td>(D_d) [cm²/h]</td>
<td>(2 \times 10^{-14})</td>
<td>(2 \times 10^{-14})</td>
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### Table 7. Postulated values of the SF reaction ratios obtained after 3 days of hardening at 20 and 80°C

<table>
<thead>
<tr>
<th></th>
<th>20°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction ratio</td>
<td>50%</td>
<td>70%</td>
</tr>
</tbody>
</table>
6. Summary

LHCs are characterized by particle size distribution comparable to those for commercially available LHC (BL0SF). By adjusting LHC packing fractions, the W/C of PK$n$SF can be reduced while maintaining the same apparent viscosity of the paste as compared with BL0SF. The hydration reaction of the SF-containing and SF-free LHCs with adjusted packing fractions (PK$n$SF series) was investigated and compared with commercially available LHC (BL0SF). As a result, the following conclusions were obtained:

1) The presence of coarse particles (BL1190) in the PK$n$SF series with and without SF can reduce the cement heat of hydration, as observed from the calorimetry measurements.
2) Both the increase in SP content and lower W/P ratios decreases the rate of cement hydration.
3) The maximum rate of cement hydration is retarded by the increase in cement packing fraction due to larger SF contents.
4) In order to determine hydration reaction parameters, the reaction ratio of each ingredient can be simulated by using the extended version of the Tomozawa’s equation of hydration, which takes into account the particle size distribution.
5) A close correspondence between the theoretical and experimental porosity values was observed from the calorimetry measurements.
6) The reaction ratios for C$_3$S and C$_2$S phases exhibited the same tendency for various PK$n$SF ($n = 0, 3, 5, 10$) samples, whereas the PK$n$SF packing fractions increased with SF addition.
7) An excellent correspondence between the theoretical and experimental porosity data for the PK$n$SF ($n = 3, 5, 10$) series was obtained assuming that the SF reaction ratio was equal to that for C$_3$S in SF-containing cements.

References