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The role of silica fume in the kinetics and mechanisms during the early stage of cement hydration

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Abstract

The role of silica fume in the reaction kinetics and mechanisms of the early stage hydration of Portland-slag cement–silica fume pastes (W/S = 0.5 at 20°C) has been studied. Using differential scanning calorimetry (DSC), the rate of calcium hydroxide (CH) formed during hydration has been determined quantitatively and the percentage of reaction of hydration has been calculated. The kinetic analysis was used to obtain parameters, which were employed to find out the influence of the silica fume content on the reaction rate constant value. The reaction stages have been analysed and explained by kinetic terms. The delay in CH formed during hydration between 8 and 10 h from the beginning of hydration has been noticed and a mechanism has also been discussed. The investigations have shown that the addition of silica fume of more than 8 mass% reduces the duration of the phase boundary interaction as a rate-determined process resulting in the fast diffusion rate-determining process. The results of this study have also revealed evidence of the accelerator effect of silica fume during the first 8 h of hydration when it still exists as chemically inert filler. The pozzolanic reaction between silica fume and CH formed during hydration is occurring after three days of hydration. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Cement hydration; Kinetic analysis; Silica fume; $Ca(OH)_2$; Paste

1. Introduction

Calcium hydroxide (CH) is one of the major phases formed in set Portland cements. Among the products of cement hydration, only CH is a compound of precisely determined composition, hence, its determination represents one of the ways to trace the development of the hydration process. The formation of CH in hydrating Portland cement not only determines the percentage of reaction of hydration, but may also influence its mechanical properties, especially in the presence of reactive pozzolanic materials such as silica fume. When silica fume is added to cement/concrete, it acts both as a chemical inert filler, improving the physical structure, and as a pozzolan, reacting chemically with CH formed during hydration of cement. The starting time of the pozzolanic reaction varied with the properties of pozzolana from 1 day to 28 days [1–3].

Previous studies [3–6] have shown that the addition of amorphous silica and natural pozzolana accelerates the early stage of hydration of Portland cement and its individual compounds. The authors propose that the increased rate of hydration may be due to enhanced precipitation of hydration products on the surface of pozzolana, which possibly serves as a nucleation site during the early hours when it exists as a chemically inert filler. It has been suggested that the surface of pozzolana can adsorb many Ca^{2+} ions and that lowering of the concentration of calcium ions accelerates the rate of dissolution of C_3S [3,6].

The purpose of the investigation in the present work, preliminary in nature, has been to determine under what circumstances silica fume would act as an accelerator during the early stage of hydration in the Portland-slag cement–silica fume paste system.

Various models for solid reactions have been proposed to quantify and describe the hydration process in cement or its constituents [7–14]. By applying the kinetic models, which involve calculation of the kinetic parameters according to different rate equations [11–13], we have investi-

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gated the effect of different additions of silica fume (2–15 mass%) on the rate-determining mechanisms. The kinetic model observes hydration rate relative to time of hydration, $d\alpha/dt = f(T,t)$.

In the early stage of Portland cement hydration, mainly the clinker minerals C_3S and C_3A react. Though slag hydration takes place simultaneously with the hydration of Portland cement, major acceleration of the slag component hydration occurs later [15]. Moreover, the alkalis and lime released by Portland cement are retained in hydration products of the slag fraction and do not seem to contribute to the hydration of slag [16]. According to De Schutter and Taerwe [17], a general hydration model in the early stage of hydration is valid both for Portland cement and Portland-slag cement.

The start of the pozzolanic reaction of silica fume can be estimated by the reduction of CH in cement paste. As the pozzolanic reaction has not been observed during 72 h of hydration in the examined cement–silica fume system, the quantitative estimation of formed CH is therefore useful in determining the percentage of hydration. CH can exist in both crystalline and amorphous form during hydration of cement minerals. Various authors have shown thermal analysis techniques to be very reliable for estimating the CH content of set Portland cement [18–21]. In the present study, differential scanning calorimetry (DSC) has been employed to estimate the CH content. Based on the analyses of DSC curves, the rate of CH formed during hydration has been determined quantitatively and the percentage of reaction of hydration has been calculated [21].

The mathematical program package MATHCAD 7 has been used in the development and testing of the models applied. Conclusions have been reached about validity of each of the kinetic models and their applicability in quantitative evaluation of the hydration process and mechanism.

2. Theoretical part

According to numerous data obtained by several investigators [9–14], the hydration process involves three basically different mechanisms controlling the reaction rate: nucleation and growth (NG), phase–boundary interaction (I), and diffusion (D). The conceptual model including changes in rate control implies that different processes may act simultaneously as limiting ones in the course of hydration of polysize, polymineral and heterogeneous system such as cement–water. The applied model [12] presupposes that the rate-determining processes proceed one after other according to the following scheme:

$$\mathrm{NG} \rightarrow \mathrm{I} \rightarrow \mathrm{D} \tag{1}$$

According to Bezjak and Jelenić [11], the following basic relations can represent the described course of the hydration process in cement pastes [Eq. (1)]:

$$G_{\mathrm{NG}}(\alpha) = [-\ln(1-\alpha)]^{1/n} = K'_{\mathrm{NG}}t \tag{2}$$

$$G_{\mathrm{I}}(\alpha) = -1 - (1-\alpha)^{1/3} = K'_{\mathrm{I}}R^{-1}t \tag{3}$$

$$G_{\mathrm{D}}(\alpha) = [-1 - (1-\alpha)^{1/3}]^2 = K'_{\mathrm{D}}R^{-2}t \tag{4}$$

The kinetic differential functions $d\alpha/dt = f(T,t)$ have been derived from the basic $\alpha - t$ functions [Eqs. (2)–(4)], and the hydration rate has been observed relative to time, not relative to the reaction percentage [13]:

$$F_{\mathrm{NG}}(\alpha) = \left(\frac{d\alpha}{dt}\right)_{\mathrm{NG}} = nk_{\mathrm{NG}}^{n}t^{n-1}e^{-(k_{\mathrm{NG}}t)^n} \tag{5}$$

$$F_{\mathrm{I}}(\alpha) = \left(\frac{d\alpha}{dt}\right)_{\mathrm{I}} = 3k_{\mathrm{I}}(1 - k_{\mathrm{I}}t)^2 \tag{6}$$

$$F_{\mathrm{D}}(\alpha) = \left(\frac{d\alpha}{dt}\right)_{\mathrm{D}} = \frac{3}{2}k_{\mathrm{D}}\frac{\left[1 - (k_{\mathrm{D}}t)^{\frac{1}{2}}\right]^2}{(k_{\mathrm{D}}t)^{\frac{1}{2}}} \tag{7}$$

R in Eqs. (3) and (4) represent the radius of the reacting particle. The values of K_{I}'/R [Eq. (3)] and K'_{D}/R^2 [Eq. (4)] are included in the values of the relative rate constants k_{I} and k_{D} in Eqs. (6) and (7), respectively [13]. Eqs. (2) and (5) refer to the process of nucleation and growth of hydration products (NG), Eqs. (3) and (6) to the phase–boundary interaction (I), and Eqs. (4) and (7) to the diffusion process (D) through the layer of hydration coating. In the above equations, k_{NG}, k_{I}, and k_{D} denote the reaction rate constants for the nuclei growth controlled process, for the phase–boundary interaction and for the diffusion process, respectively. In Eqs. (2) and (5), the n value is the Avrami exponent that reflects the details of the nucleation and growth mechanisms. The n value depends on the reaction mechanism, growth dimension, and nucleation rate [14].

When one rate-determining process substitutes for the other, their rates ($d\alpha/dt$) have to be equal. Therefore, the transitional times of one process into another are determined from the conditions [Eqs. (8) and (9)] [12,13]:

$$\left(\frac{d\alpha}{dt}\right)_{\mathrm{NG}} = \left(\frac{d\alpha}{dt}\right)_{\mathrm{I}} \tag{8}$$

$$\left(\frac{d\alpha}{dt}\right)_{\mathrm{I}} = \left(\frac{d\alpha}{dt}\right)_{\mathrm{D}} \tag{9}$$

where, $t_{\mathrm{NG-I}}$ is the time when I takes control after NG, and $t_{\mathrm{I-D}}$ is the time when D takes control after I.

The mathematical derivation for the representation of cement hydration development according to Eqs. (5)–(7) makes it possible to calculate the kinetic parameters (k and n values) and the transitional time (t_i) of one process into another.

3. Experimental procedure

3.1. Materials

A commercial, blended Portland cement (Dalmacijacement, K. Sućurac, Croatia) was produced by grinding of cement clinker and mixing up to 5 mass% of gypsum and 30 mass% of the blast furnace slag, marked PC30z45s according to the Croatian standard HRN. B. C1. 011 — conforming to the European cement standard EN 197.1: type CE II-S 32,5 (Portland-slag cement). The Blaine specific surface was 3530 cm^2/g. The Bogue composition of cement clinker was: 64.7% C_3S, 9.6% C_2S, 7.5% C_3A, 10.1% C_4AF. The silica fume was collected from the production of ferrosilicon (Ferroalloys Works Dalmacija, Dugi Rat, Croatia), containing about 90 mass% SiO_2 and having a surface of 18 m^2/g as measured by BET nitrogen sorption.

3.2. Hydration procedure

Six series of cement paste samples were prepared at water to solid (cement + silica fume) ratio (W/S) of 0.5. One was made with 10 g Portland-slag cement, PC30z45s only (marked P0). The others were made with mixture of 10 g Portland-slag cement and 2–15 mass% silica fume added by mass of cement (marked P2, P5, P8, P11, and P15). After casting into plastic bottles, the samples were allowed to hydrate at a temperature of 20°C. At a specific time of hydration (1, 3, 5, 6, 8, 9, 10, 11, 14, 18, 24, and 72 h), the particular sample was demoulded. Grinding of the crushed samples in acetone and filtering quenched the hydration. The dried samples were then passed through a 200 μm nylon sieve and finally stored in a desiccator kept under vacuum.

3.3. Methods of investigation

The DSC curves were obtained using about 5,0 mg samples in a differential scanning calorimeter (DSC-4, Perkin Elmer, Norwalk, CT, USA), which includes a thermal analysis microprocessor controller, model 3700 Data Station and a graphics Plotter 2. The samples were heated at 20°C/min in a nitrogen atmosphere with crimped aluminium crucibles as the reference material. The amount of energy absorbed by the endothermic reaction due to dehydration of CH in the temperature range of 420–510°C was computed for each sample. The quantity of CH present in each sample was then calculated using the energy absorbed by the 480°C DSC peak and that of CH, analytic grade chemical. The level of CH formed in a sample can be used as an estimate of the percentage of reaction [21]. The results obtained may be a slight exaggeration of the level present as an endothermic peak at around 445°C was noted in studies of the anhydrous cement and may overlap with the CH peak in the hydrated samples. The decomposition of amorphous CH present during the early stages of hydration could also be responsible for the double endothermic peak [21].

The percentage of hydration, $\alpha(t)$ is defined as the ratio of the amount of CH that has formed at time, t, to the total amount of CH formed after 28 days in hydrated cement paste not containing silica fume.

3.4. Testing the model

The model has been tested by means of experimental $\alpha-t$ data obtained from DSC plots by quantifying the content of CH formed during hydration time, t. From the representation graphs of $\alpha=f(t)$, translating the tangent to the designated point of the abscissa, the derivative functions of $d\alpha/dt-t$ have been calculated. The $d\alpha/dt-t$ curve was thus resolved into component parts, each representing an individual process according to the applied kinetic model [Eq. (1)]. The experimental data were then fitted to the kinetic equations [Eqs. (5)–(7)] and by means of linear and nonlinear regression analysis, the kinetic parameters for different hydration periods were determined. Validity and good applicability of the applied kinetic model was judged by estimating the standard deviation (S.D.) as a criterion for evaluation of the correspondence of theoretical equations and experimental data [Eq. (10)]:

$$\text{S.D.} = \frac{1}{m}\sqrt{\sum_{i=1}^{m}\left[(d\alpha/dt)_i - F(\alpha)_i\right]^2} \tag{10}$$

where, S.D. is the standard deviation, m the number of measurement point, $(d\alpha/dt)_i$ the rate of i time, $F(\alpha)_i$ represents Eqs. (5)–(7).

4. Results and discussion

The curves in Fig. 1 show the changes in the relative amounts of CH formed throughout the 7-day hydration for cement pastes without and with silica fume addition (2–15

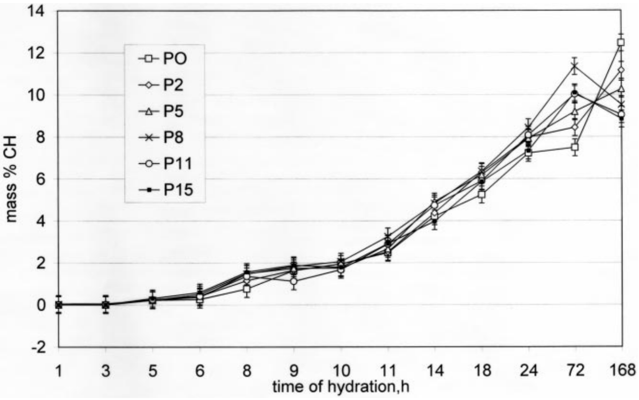


Fig. 1. The CH content as a function of curing time.

mass%). It is clear that the trend for cement pastes containing silica fume was that of increasing CH especially during the first 72 h, suggesting an acceleration of the hydration of cement components. At longer time of cement hydration (between 3 and 28 days), the CH content decreases with increasing silica fume content (sample P8, P11, and P15). For paste not containing silica fume, the CH content increased from 7.46 mass% at 3 days to 13.71 mass% after 28 days, while for paste with 15 mass% silica fume, it decreased from 10.09 mass% at 3 days to 3.56 mass% after 28 days [22]. The observed CH content is the result of a combined cement hydration, which generates CH, and a pozzolanic reaction, which consumes CH. These test results imply that the pozzolanic reaction starts after three days of hydration and continued up to 28 days depending both on silica fume content and on the hydration time. The results also show that silica fume has a slight retarding effect on the rate of release of free CH. In fact, no substantial changes in the CH content are observed between 8 and 10 h of hydration for pastes made with 2–15 mass% of silica fume when compared with the silica fume-free paste.

From kinetic curves $\alpha = f(t)$ in Fig. 2, it can be seen that the presence of silica fume slightly increases the percentage of hydration during the first hours of hydration when compared with the silica fume-free cement paste (if cement content in all samples is the same). The reason for the increased rate in the first few hours of hydration is believed to be the enhanced precipitation of hydration products on the surface of silica fume particles, which possibly serve as nucleation sites. Thereafter, lowering of the concentration of calcium ions accelerates the rates of dissolution of cement grains [3]. Although not specified here, the concentration of calcium ions in the solution rises very rapidly within the first minutes and withdraws from the solution at the end of 1 h after the formation of the silica fume–cement suspension. It is believed to be attributable to the nucleating effects of the silica fume particles. Details will be given in our next publication. A slight retarding effect on the rate of liberation of CH (Fig. 1), as well as on the percentage of reaction (Fig. 2) is clearly distinguished between 8 and 10 h. The inflexion point, between 8 and 10 h, corresponds to the time from which the reaction of liberation of the CH becomes limited. However, the reaction cannot be related to the lime–pozzolana reaction, which is slower and occurs later. In contrast to the CH content, investigation of the non-evaporable water content have shown a slightly but continuously increasing in the same time of hydration [22]. These results perhaps indicate an enhancement of both C_3S hydration (the liberation of CH) and the hydration of C_3A, as well as C_4AF (the consumption of CH for their reaction to produce hydrated phases). As a result, the non-evaporable water content is increased, whereas the content of CH remains unchanged. A similar phenomenon of the consumption of CH in the pozzolana–C_3A–lime–gypsum system before the start of pozzolanic reaction was observed by Collepardi et al. [23]. Authors suggested that some other reaction between pozzolana and hydration products could occur in the cement–pozzolana system.

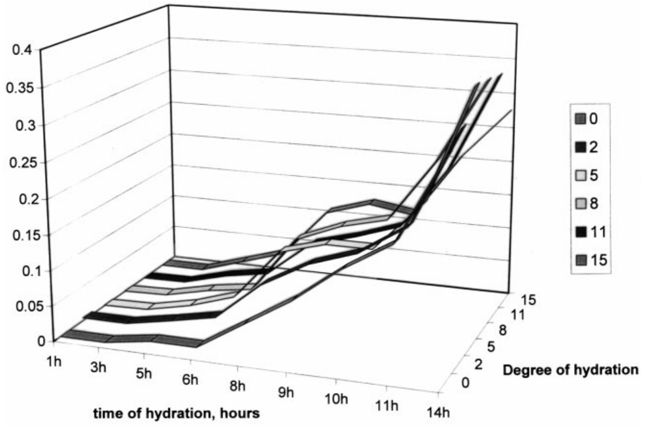


Fig. 2. α–t curves.

The representative $d\alpha/dt$–t curves for all paste samples are shown in Fig. 3. The results clearly show that there are two stages of acceleration: the first in the period up to 8.5 h, and the second in the period between 9 and 11.5 h of hydration. Though such a two-stage acceleration is rare in cement hydration, it may appear in certain systems under certain circumstances [12]. They have been observed so far in hydrothermally treated C_2S–quartz mixtures, as well as during hydration of C_2S and C_3A. However, according to the same authors [12], in the case of polysize specimens the differences in the registered $d\alpha/dt$–t curves could be the consequence of different particle size distribution and overlapped reaction mechanisms rather than the modified nucleation and growth process.

The kinetic analysis was used to obtain parameters, which were employed to find out the influence of silica fume on the reaction rate constant values. The kinetic parameters were calculated according to Eqs. (5)–(7).

Knowing the parameters n, k_{NG}, k_I, and k_D, the time of process transition NG → I and I → D [Eqs. (8) and (9)], marked as t_{NG-I} and t_{I-D}, could be determined, respectively. The calculation of the reaction rate constant k_{NG} at transition points between two adjacent intervals (points corresponding to 8–10.5 h) has been neglected in the present work, but full elucidation of this phenomenon of limiting hydration rate requires additional theoretical and experimental research.

The values obtained for kinetic parameters by the above-mentioned mechanistic models, as well as the time of transition from one interval to another are listed in Table 1.

Fitting the theoretical curves to the experimental data is illustrated in Fig. 3. It can be seen that the kinetic model applied [Eq. (1)] makes it possible to describe the mechanical concept used by the proposed procedure as the following: the nucleation and growth process during the first 8 h of hydration, the phase boundary interaction process between 15 and 30 h, and the diffusion process for all the duration.

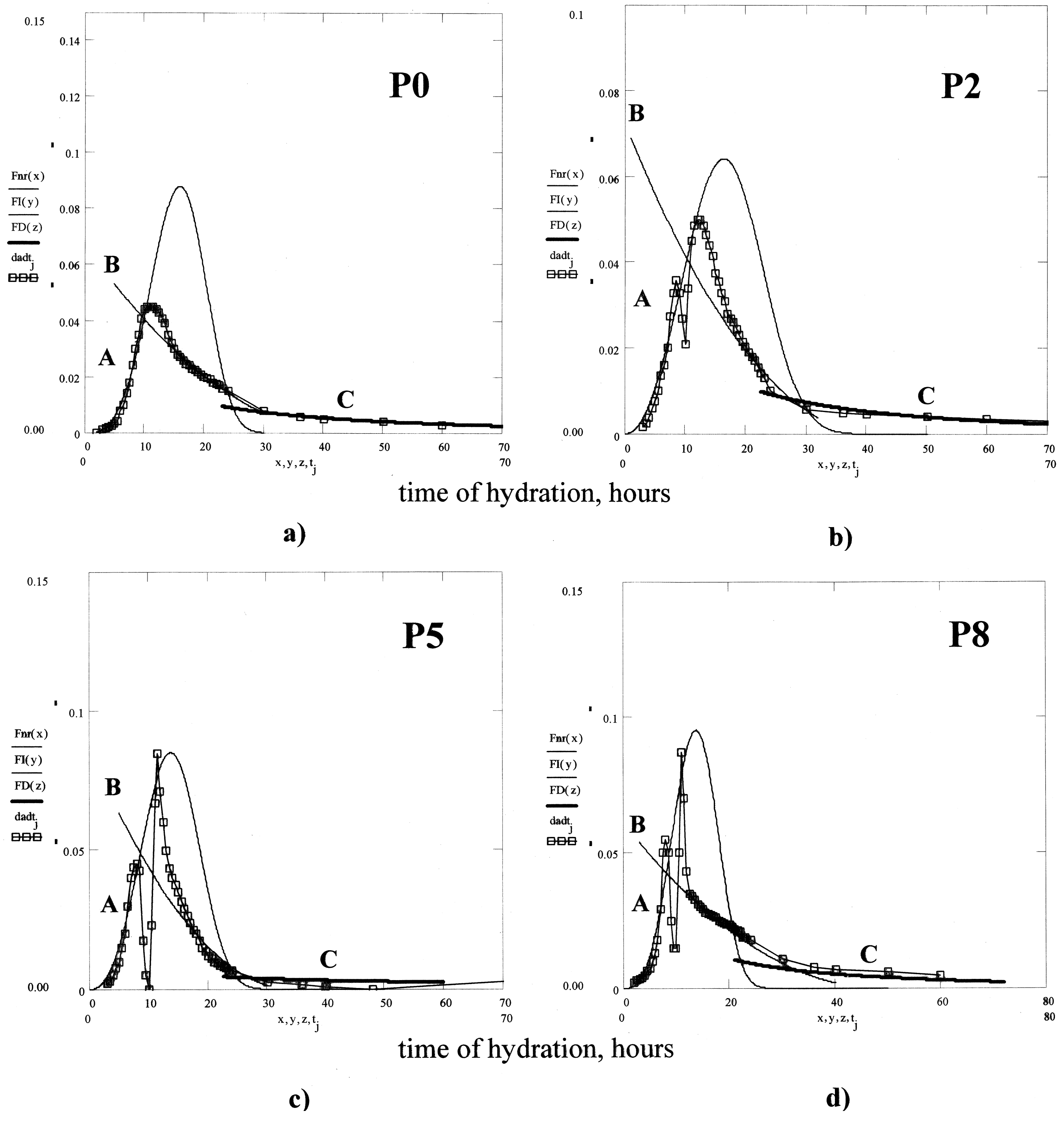
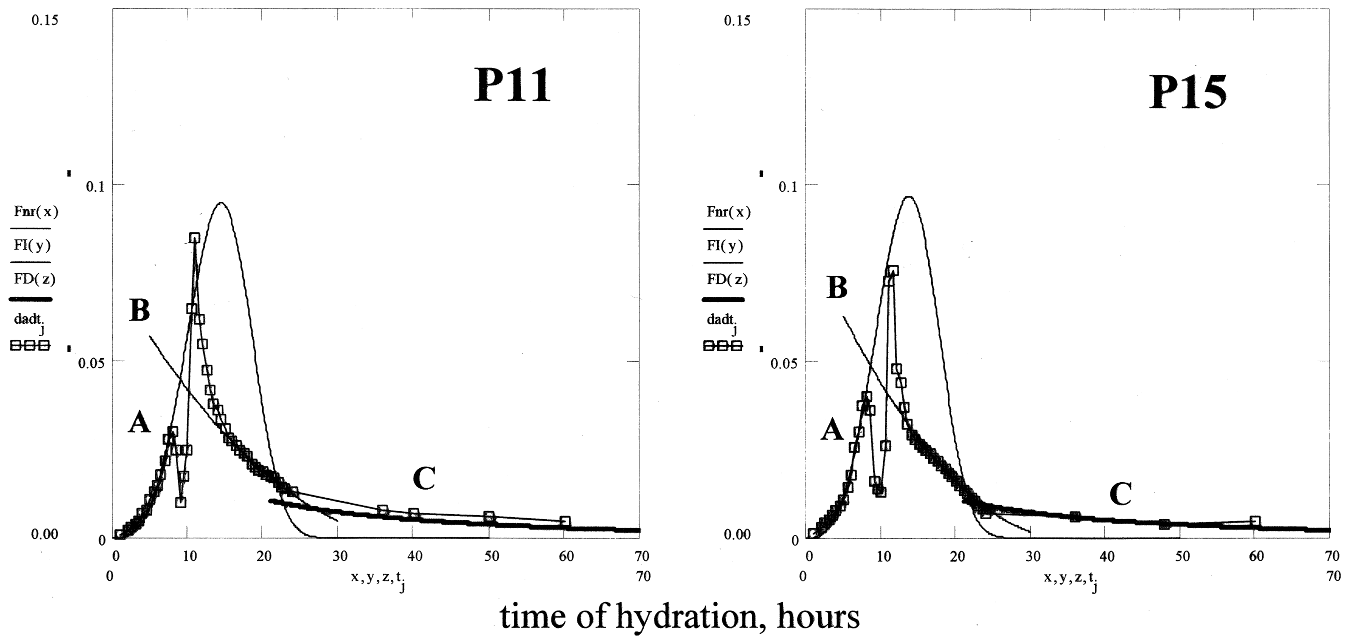


Fig. 3. (a–f) Comparison of experimental data to the mathematical model for cement–silica fume systems. Plot A [Eq. (5)] corresponds to the NG process, plot B [Eq. (6)] corresponds to the I process, plot C [Eq. (7)] corresponds to the D process. Symbols (□) denote experimental curves dα/dt–t.

Further research is needed to describe the period of hydration between 8 and 15 h.

As shown in Table 1, the values obtained for the rate constant of the nucleation and growth process, k_{NG}, range between 0.058 h^{-1} for cement paste only (sample P0) and 0.054–0.067 h^{-1} for cement pastes containing silica fume (samples P2–P15). Compared to the k_{NG} data, the increased rate of the NG process for pastes containing more than 5 mass% of silica fume is evident, indicating that the inclusion of silica fume in cement systems accelerates hydration (Fig. 4). Thereafter, additions of silica fume of more than 5 mass% reduce time intervals of the phase boundary interaction as the control process, resulting in diffusion taking control sooner.

The values obtained for the Avrami exponent, n (Table 1) are 3.96 for PC paste only, and in the range of 3.06–3.88 for



e)

f)

Fig. 3. (*continued*)

cement containing silica fume. In the literature [24], different *n* values can be found. As the *n* value depends on the reaction mechanism, growth dimensions and nucleation rate, the same *n* value can be interpreted ambiguously. Therefore, the relationship between the *n* values and growth dimensions (two- or three-dimensional), even in the case of a monophase system, is usually debatable if not supported by other evidence, i.e. electron microscopy [25].

As seen from the distribution of the rate-control processes (Table 1), higher diffusion rate constants are found in cement–silica fume systems than in the cement–silica fume free system. It may be assumed that the observed changes of kinetic parameters in the presence of silica fume can be attributed to changes of mechanism of forming of hydrated products, i.e. to changes in structural properties of hydration coatings and thus the permeability of the diffusion barrier in the presence of silica fume [4].

When experimental data are summarised and compared with theoretical research, it seems that large surfaces of silica fume particles increase the number of CH nuclei [6,26], but, initially, the crystal growth is slower than the dissolution of cement grains. A similar effect of large surfaces of silica fume particles is observed in the nucleation and growth of portlandite: the reduction of crystal size by increasing the number of nuclei has been obtained by Vernet and Noworyta [26]. When CH nuclei reach their critical size, they are ready to grow according to the well-known acceleration process ruled by the Avrami's nucleation kinetic equation [27]. According to Bentz and Stutzman [28], silica fume addition affects both the amount and size of the

Table 1
The kinetic parameter values of the model [Eqs. (2)–(4)] and the transitional time of one process into another (t_{NG-I}, t_{I-D}) in the cement–silica fume system, W/S = 0.5, T = 20°C, $0 = t \leq 72$ h

	P0	P2	P5	P8	P11	P15
n	3.9644	3.0625	3.3665	3.7263	3.8890	3.7585
k_{NG}, h^{-1}	0.0581	0.0537	0.0654	0.0668	0.0640	0.0675
S.D.	0.0006	0.0011	0.0054	0.0071	0.0038	0.0040
k_{I}, h^{-1}	0.0223	0.0241	0.0290	0.0204	0.0247	0.0284
S.D.	0.0065	0.0015	0.0043	0.0013	0.0053	0.0018
k_{D}, h^{-1}	0.0038	0.0044	0.0003	0.0044	0.0048	0.0048
S.D.	0.0012	0.0043	0.0036	0.0018	0.0013	0.0047
t_{NG-I}, h	10.13	10.26	8.61	8.14	8.98	8.54
t_{I-D}, h	29.61	27.65	26.95	32.75	26.94	23.40

S.D.: standard deviation.

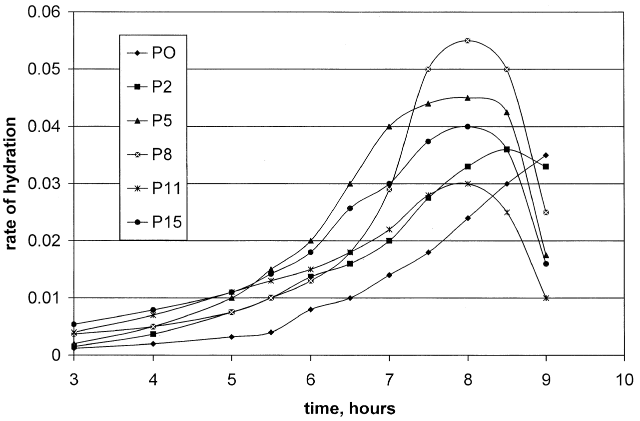


Fig. 4. The changes of the hydration rate during the first hours of hydration in the cement–silica fume systems.

CH crystals. The large crystals of CH increase with time of hydration and continue to grow at the expense of smaller ones in the system of Portland cement paste only. In contrast, their values decrease in the systems with 10 and 20 mass% of silica fume.

In the literature, there is evidence that silicate species retard the growth of CH and possibly poison the nucleation of CH, and a silicate rich surface causes the same effect, known as "the silicate poisoning theory" [5,29,30]. This theory proposes that CH nuclei are "poisoned" by the adsorbed silicate species, and can only grow spontaneously from a solution supersaturated with respect to pure CH.

These observations suggest that the short induction period observed in the dα*dt*–*t* curves (Fig. 3) between 8 and 10 h of hydration in the cement–silica fume systems represents the time required to overcome the poisoning effect of adsorbed silicates and to form the growth surfaces for pure CH crystals. Therefore, the growth of CH is predicted throughout the course of subsequent crystallisation.

Bearing these analyses in mind, the following early hydration mechanism through CH crystallisation in cement–silica fume systems has been proposed:

1. rapid sorption of calcium ions on the surface of silica fume particles which serve as nucleation sites, therefore the rate of dissolution of cement grains is accelerated;
2. simultaneous formation of CH nuclei on the sites and outside of the original grain boundaries in the water-filled space;
3. large surfaces of silica fume particles increase the number of CH nuclei, but the crystal growth is initially slower than the dissolution of cement grains;
4. as the growth of CH is controlled by supersaturation of the liquid phase, CH nuclei can only grow spontaneously from solution supersaturated with respect to pure CH;
5. the delay in formation of stable CH nuclei and crystals in the short induction period between 8 and 10 h of hydration has been attributed to poisoning by the sorption of silica species; and
6. after 10 h of hydration, CH nuclei reach their critical size and start growing according to the laws of nucleation kinetics.

As this study is preliminary in nature, to fully elucidate the factors affecting the kinetic behaviour during hydration in the presence of silica fume, further investigation is needed, accompanied by monitoring changes in the liquid phase.

5. Conclusions

The experimental data in this study show that the pozzolanic reaction between silica fume and lime formed during cement hydration begins to occur after 3 days of hydration. Therefore, the pozzolanic reaction has no affect on reaction mechanisms during the early stage of hydration in Portland cement–silica fume systems.

The results also indicate that the presence of silica fume slightly increases the rate of cement hydration during the first few hours of hydration, indicating that silica fume affects hydration by the nucleating effect of its surface when it still exists as a chemically inert filler. However, no substantial changes in the CH content were observed in the period between 8 and 10 h of hydration process. This effect cannot be related to the pozzolanic reaction, which is much slower. It is probable that the formation of CH is limited by some aspect of the silica fume addition. Either the large surface of silica fume increases the number of nuclei, but crystal growth is slower, or the poisoning effect of adsorbed silicates retard the nucleation and growth of CH, and CH nuclei can only grow spontaneously from a solution supersaturated with respect to pure CH.

The differences in the registered dα/d*t*–*t* curves in the cement system containing silica fume (2–15 mass%) have suggested the modified nucleation and growth process with a two-stage acceleration period.

The obtained values of rate constants are generally higher in cement–silica fume systems than in cement–silica fume free ones. High rate constants are predominantly responsible for the accelerator effect observed in the system containing silica fume during the first 8 h.

Addition of more than 8 mass% silica fume shortens the time interval of duration of the phase boundary interaction as a control process, which results in diffusion taking control sooner.

The results reported here are only preliminary, but they may provide some insight into the role of silica fume in hydration kinetics and mechanisms during the early stage of cement hydration. Structure investigations, accompanied by monitoring the changes in the liquid phase (Ca^{2+}, OH^-, and silicon concentration) at the transition points between two adjacent intervals, will certainly also contribute to better understanding of the kinetic behaviour of silica fume in the course of the hydration process. The described approach to the kinetic study can be improved by introducing the effect of particle radii into the calculation procedure, too. Therefore, further research is certainly needed to fully elucidate the factors influencing our observation.

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