



A mathematical model for prediction of compressive strength in cement–silica fume blends

J. Zelić*, D. Rušić, R. Krstulović

Faculty of Chemical Technology, Department of Engineering and Technology, University of Split, Teslina 10/V, HR-21000 Split, Croatia

Received 30 January 2003; accepted 9 April 2004

Abstract

In the present study, a mathematical model has been developed to predict cement properties from the description of hydration kinetics in Portland-slag cement–silica fume blends containing up to 15 mass % of silica fume. Knudsen's dispersion models were applied in fitting both the degree of hydration and the compressive strength experimental data as a function of time. It was found that the “mixed (linear/parabolic) dispersion model” fits the cement–silica fume blend systems well, as both the rate constants k_1 and k_2 of the Knudsen expressions are significant in the systems to which they are referring. With respect to the fact that there is a relationship between parameters as defined by Knudsen, this study has attempted to establish the direct functional dependence between the degree of hydration and the compressive strength by means of the time variable. It was found that the degree of hydration—the compressive strength dependence, for replacement levels varying from 0 to 15 mass % of silica fume, indicates a linear mathematical function. There are good agreements between the model and the experimentally obtained results. The proposed model provides the opportunity to predict the compressive strength development based on measuring the heat release during the 48-h cement hydration if the infinitely (ultimate) achievable compressive strength value is known. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Cement–silica fume blends; Hydration; Heat of hydration; Strength development; Modelling

1. Introduction

The development of strength of concrete is affected by many factors, such as cement composition and fineness, water-to-cement ratio, aggregate, age and temperature of curing. There is as yet no such formula (mathematical model) that could reproduce the effects of all these factors adequately in a quantitative manner, primarily due to a high number of variables [1].

The first studies carried out to predict and program the final strengths of cement mortars have been based on the assumption that each constituent of the clinker mineral independently affects the mechanical properties of hydrated products [2]. The attempt was made to explain this effect by means of a multiple linear correlation that examined the effect of each of the constituents. This linear correlation has undergone a series of improvements. Thus, Popovics [1] has introduced “the exponential cement model,” probably the

first nonlinear cement model for representation of hardening, which is much simpler conceptually than most linear models. However, a more direct approach in describing the effect of the compound composition on porosity and strength of Portland cement was used by Joens and Osbaeck [3]. According to these authors, the development of microstructure in cement pastes should be quantitatively interpreted from the kinetic point of view. More recently, Tsvilis and Parissakis [4] showed that cement fineness is an important factor influencing the early strength while the chemical and mineralogical properties of cement contribute to the strength development at later ages.

Knudsen made a first attempt to develop an analytical model of hydration. He was considering a linear hydration mechanism and was using a Rosin–Rammler particle size distribution (with $n=1$) [5]; he later presented a simple analytical model for development of hydration of Portland cement (the dispersion model), which covered linear, parabolic and joint kinetics of hydration [6]. This model was tested on experimental hydration curves, mainly obtained by chemical shrinkage and the degree of hydration as a function of time and temperature [7].

* Corresponding author. Tel.: +385-21-385-633; fax: +385-21-384-770.

E-mail address: jelica.zelic@st.htnet.hr (J. Zelić).

According to Knudsen [6], an analytical model for development of hydration of Portland cement may be represented by:

$$k_1 \left(\frac{P}{P_\infty - P} \right) + k_2 \left(\frac{P}{P_\infty - P} \right)^2 = t - t_0 \quad (1)$$

where P is the represented property of interest (heat evolution, amount of chemically bound water, chemical shrinkage, etc.), P_∞ is the property measured after an infinitely long time, t_0 is the length of the dormant period, t is the time from mixing with water and k_1 and k_2 are rate constants.

Eq. (1) represents the best expression so far to relate a cement paste property with time, as it is based on the fundamental criteria of hydration kinetics, taking into account the polydispersion of the system, and yet being simple enough to be used in practice.

According to Knudsen [6], the parameter $[P/(P_\infty - P)]$ is related to the hydration ratio, $[\alpha/(1 - \alpha)]$, so that Eq. (1) can assume the following form:

$$k_1 \left(\frac{\alpha}{1 - \alpha} \right) + k_2 \left(\frac{\alpha}{1 - \alpha} \right)^2 = t - t_0 \quad (2)$$

where α is the degree of cement hydration, k_1 and k_2 are rate constants, t_0 is the length of dormant period and t is the time from mixing cement with water.

By substituting the Knudsen's parameter P from Eq. (1) with the compressive strength, fc values, the following equation can be obtained:

$$k_{k1} \left(\frac{fc}{fc_\infty - fc} \right) + k_{k2} \left(\frac{fc}{fc_\infty - fc} \right)^2 = t - t'_0 \quad (3)$$

where fc is the compressive strength of mortar at time t , (MPa); fc_∞ is the compressive strength after very long proper curing (MPa), that is, the 360-day compressive strength of mortars given in Table 1; t'_0 is the age at start of strength development (h); and k_{k1} and k_{k2} are rate constants (h).

Bentz [8,9] has applied Knudsen's kinetic (dispersion) models and shown the importance of the physical microstructure of the initial cement powder in influencing the cement paste hydration kinetics. The three-dimensional computer model developed by Bentz has provided quantitative predictions of the effects of cement composition, water-to-cement ratio and curing environment on resultant hydration and physical properties (heat release and mortar cube compressive strength), suggesting that the model may be applicable in designing new materials. The model has been successfully applied to predict the percolation and diffusion properties of cement pastes with no mineral admixtures [10], as well as to determine the effect of silica fume on the microstructure and diffusivity of cement paste [11].

The purpose of the research presented here was to develop a mathematical model that would describe reliably

Table 1

The properties and mix proportional of the cement–silica fume blend mortars

Systems	MP0	MP2	MP5	MP8	MP11	MP15
Silica fume replacement (mass %)	0	2	5	8	11	15
<i>Mix proportional (g/dm³)</i>						
Aggregate	1350	1350	1350	1350	1350	1350
Cement	450.0	437.4	419.0	401.0	383.3	360.5
Silica fume	–	8.9	22.0	34.8	47.4	63.6
Water	225	222	223	225	231	244
Fresh mortar density (g/cm ³)	2.158	2.156	2.165	2.161	2.147	2.135
Air content (%)	6.07	6.00	5.35	5.32	5.30	5.50
Flow table (mm)	131	127	128	128	129	130
Heat released (J/g, 90 days)	326	310	312	320	290	273
<i>Compressive strength (MPa)</i>						
3 days	23.20	26.60	27.20	25.40	24.70	18.20
7 days	30.20	32.50	37.00	35.50	38.80	29.00
28 days	42.45	47.95	53.95	53.00	53.20	49.10
360 days	53.60	58.60	66.60	64.20	61.20	58.40

the effect of early hydration on properties of Portland-slag cement containing various silica fume replacements (2, 5, 8, 11 and 15 mass %), as reflected by their developed strength.

The mathematical program package MathCad 2000 has been used in model development and testing.

2. Experimental procedure

2.1. Materials

The commercial Portland-slag cement (Dalmacijacement RMC Group, Solin, Croatia), produced by grinding of cement clinker and mixing up to 5 mass % of gypsum and 20–30 mass % of the blast furnace slag, conforming to the European cement standard EN 197.1: type CEM II-S 42.5, was used. The value of 42.5 refers to the minimal normalised mortar strength at 28 days, expressed in MPa. The Bogue composition of the cement clinker was (in mass %) as follows: $C_3S = 70.0$; $C_2S = 15.0$; $C_3A = 6.0$; $C_4AF = 8.0$; $CaO (free) = 1.0$. The Blaine fineness of cement used was 353 m²/kg.

Silica fume was obtained from filters used in production of ferrosilicon (Carbide and Ferroalloys Works Dalmacija, Dugi Rat, Croatia), containing about 90 mass % SiO_2 and having a surface area of 18,000 m²/kg as measured by the BET nitrogen sorption method.

2.2. Hydration kinetics

The hydration kinetics was measured by means of heat evolution from hydrating cement under the temperature conditions of 293 K using a differential microcalorimeter,

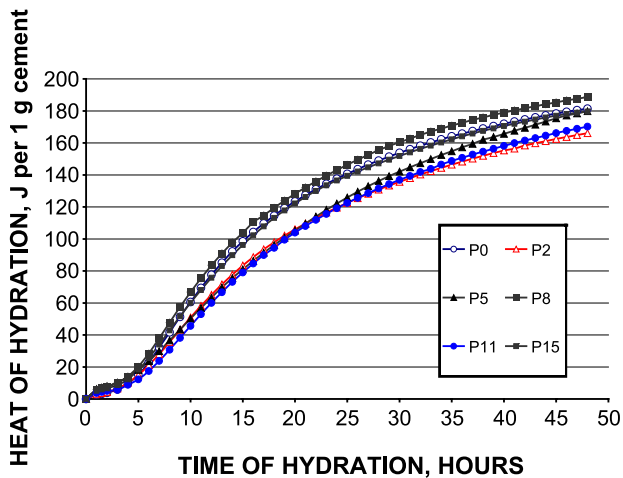


Fig. 1. Heat development curves normalized by the mass of cement used in cement-silica fume-blended systems.

DMC (constructed at the Faculty of Civil Engineering in Budapest, Hungary). The details of the experimental method are described elsewhere [12,13]. Cement pastes with mass samples of 4.00 g were prepared by using the water-to-solid ratio (W/S) of 0.5, including both cement and silica fume as solids. Silica fume was added as a partial replacement of cement at levels of (0, 2, 5, 8, 11 and 15) % by mass of cement. The samples were designated as follows: P0, P2, P5, P8, P11 and P15, respectively. The hydration heat output was continually monitored for up to 48 h by a computer, which was interfaced with the DMC.

To calculate the $\alpha - t$ data, the signal formed due to the difference in potentials on the microcalorimeter thermocouples in the referent part and in the part with the hydrating sample which has been analysed by the PC software program. The heat released, Q_t , has been calculated first, and then it was converted to the degree of hydration, α_t , by the values of the heat of hydration achieved experimentally for each of the cement-silica fume blends at 90 days measured using the heat of solution method, according to the Croatian standard [14]. Because mixing of samples for the standard heat of solution method may be more complete than that achieved in small microcalorimeter cells, higher heat release values could be expected [8].

2.3. Preparation of mortars

Mortar samples were prepared from a mixture of Portland-slag cement, type CEM II-S 42.5 and standardized siliceous sand as aggregate with the 1:3 ratio by mass according to the standard HRN.B.C8. 022 [15]. The aggregate fractions falling in the ranges 0.125–0.25, 0.25–0.5, 0.5–1.0 and 1.0–2.0 mm were used at 1:2:3:3 ratio. Silica fume in the amount of (0, 2, 5, 8, 11 and 15) mass % on the cement basis was used as a replacement for cement. The samples were designated as follows: MP0, MP2, MP5,

MP8, MP11 and MP15, respectively. No water-reducing agents were used for improving the workability of mortar in this program. However, the experiment has been conducted at constant flow conditions. The mortars have been prepared to have the constant flow-table consistency, according to the Croatian standard, HRN.B.C8. 042 [16]. According to this standard, the mortars were formed into pats of 127–131 mm in diameter. The air content of freshly mixed mortars was determined by the pressure method according to HRN.B.C8. 050 [17]. The specific gravities of Portland cement, aggregate and silica fume used were 3.18, 2.62 and 2.26 g/cm³, respectively. Because volume of binders (cement+silica fume) into the cement-silica fume mortars was kept constant, the mass ratios of mixture composition were calculated into the volumetric ratio [18]. The properties and mix proportional (in g/dm³) of the cement-silica fume blends are given in Table 1.

Mortars were moulded into the 4 × 4 × 16 cm prisms and were vibrated for 1 min to remove air bubbles and voids. After moulding, the specimens were immediately cured in a humidity cabinet at 293 K and 95% relative humidity for 24 h. Then, they were demoulded and placed in a water-filled tank, where the temperature of 293 K was held constant by a thermostat. When mortar samples reached the prescribed age, they were taken out of the curing tank. Compressive strengths of mortars were measured in accordance with the Croatian standard, HRN.B.C8. 022 [15] from triplicate specimens at 3, 7, 28, 120 and 360 days. However, several samples were tested after 1, 4 and 14 days. All the reported results are the averages of three measurements. The test results are given in Table 1.

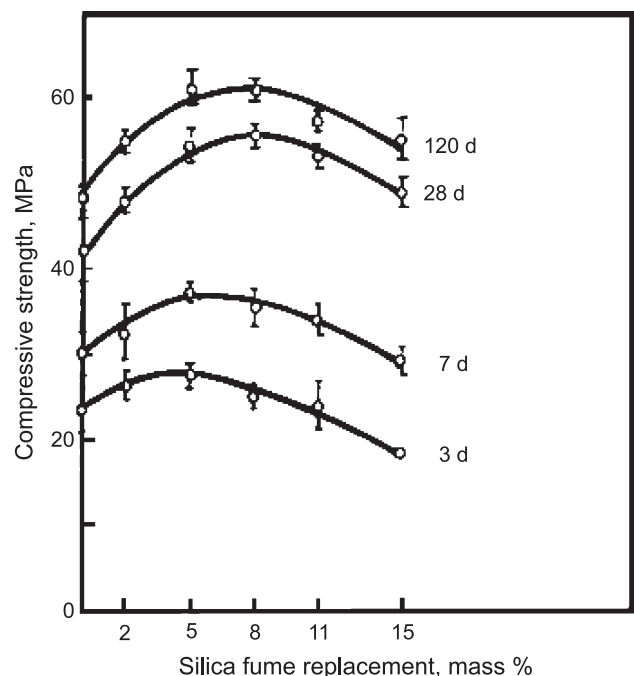


Fig. 2. Compressive strength developments vs. silica fume replacement.

3. Results and discussion

3.1. Hydration

Fig. 1 shows the curves of the normalized experimental results of heat release for pastes containing up to 15 mass % of silica fume replacement ($W/S = 0.5$; $T = 293$ K) during the 48-h hydration. An experimentally determined value of heat hydration has been normalized by the mass of cement used in different replacements of silica fume blends and converted to the degree of hydration by the values of heat release after 90 days of hydration measured using the heat of solution technique [14]. By normalizing the heat release ($J\ g^{-1}$) by the mass of cement in the sample, the heat hydration per gram of initial cement ($J\ g^{-1}/1\ g\ cement$) could be determined. Thus, heat development values could be compared with one another and the contributions from silica fume can be separated.

The time-dependent courses of the heat of hydration (Fig. 1) show that 8 mass % of silica fume replacement causes a significant acceleration of cement hydration in comparison to the control cement paste (sample P0). These results agree with previous research [19,20] which has shown that the presence of silica fume slightly increases the rate of the early cement hydration when it still exists as a chemically inert filler. The increased rate of hydration is believed to be due to enhanced precipitation of hydration products on submicroscopic silica fume particles that possibly serve as nucleation sites for crystallisation of hydrated products [21]. However, no correlation has been observed between the increase of the mass % of silica fume and hydration acceleration. This might be partly due to the variability of the experimental technique. The possible sources of errors may be due to nonuniform composition in the samples (in the range of mass up to 4.00 g) of the cement used, as well as due to nonuniform distribution of silica fume in the

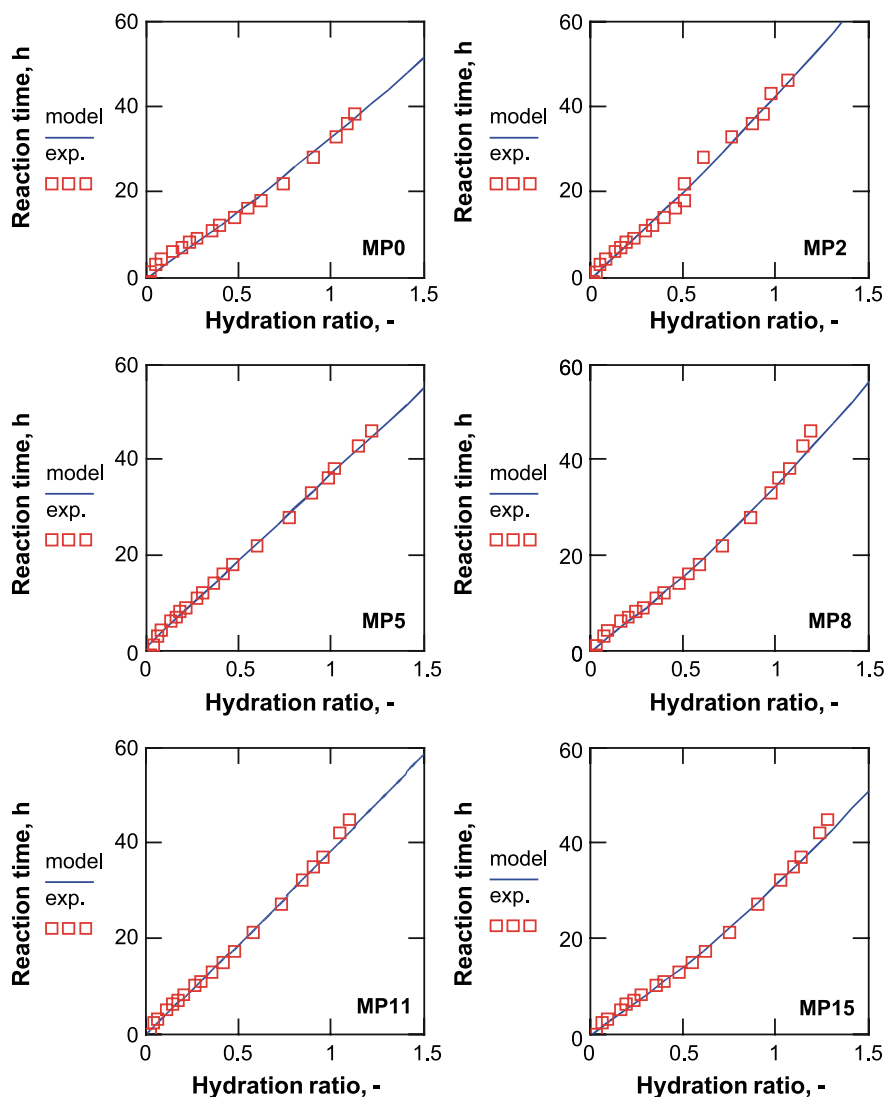


Fig. 3. Comparison of experimental measurements (data points) and the model predictions by Eq. (2) (solid line) for all cement–silica fume blends, where the hydration ratio is $[\alpha/(1 - \alpha)]$, and the reaction time is $(t - t_0)$.

cement silica fume blends, because no plasticizer is used to ensure proper dispersion of the silica fume. However, care has been taken to avoid all such errors while experimenting with the present program. The deviation of the heat development of individual paste specimens from the mean of two or three specimens has been small [12,13,20]. Use of a large number of test specimens to obtain better average heat of hydration development could elucidate the factors influencing our observation.

3.2. Compressive strength

Fig. 2 shows the effect of the silica fume replacement on cement mortar compressive strength development at different hydration ages (3, 7, 28 and 120 days). Mortars containing 5 and 8 mass % of silica fume replacement show the higher compressive strength. They were also characterized by a better sulphate resistance than a control sulphate-resisting mortar, as has been reported previously [22]. The samples with higher silica fume replacement evidently attain their final strengths later. This behaviour can be attributed to the twofold effect of silica fume that acts as a pozzolan and as a microfiller. Over time, the ratio of these two effects changes, leading to the shift of maximum strengths to higher silica fume contents as time passes. Fig. 2 also indicates that early strengths (up to 7 days) of the mortar containing 15 mass % of silica fume replacement are lower than those of cement mortar not containing silica fume (sample MP0). After 28 days, however, when new hydration products are formed by the pozzolanic reaction between silica fume and calcium hydroxide, the compressive strength of this mortar (sample MP15) increases noticeably and is higher than that in the control mortar (sample MP0). This implies that the pozzolanic reaction is responsible for development of strength in samples of mortar containing silica fume. Obviously, in the earlier ages of hydration, a pozzolanic reaction took place later than the reaction of hydration and therefore mortars containing silica fume replacement show lower strength values than the control mortar (MP0).

3.3. Mathematical modelling: the effect of early hydration on compressive strength development of cement mortars containing silica fume

The present study stresses the importance of kinetic analysis of the cement hydration process for predicting the compressive strengths. The mathematical modelling, based on the dispersion models of Knudsen, has been carried out to establish a direct relationship between the kinetic analysis of the hydration process and strength as the final property of the cement stone.

To develop the model, experimental studies have been conducted both of the compressive strength development of standard mortars up to 360 days and of the heat of hydration release of cement pastes up to 48 h for each of the cement–silica fume blends. Both cement paste and mortar not

containing silica fume replacement (samples P0 and MP0) were used as control samples.

The Knudsen's dispersion models have been applied in fitting both the degree of hydration and compressive strength data as a function of time.

Eq. (2) has been fitted to the experimental reaction time, $(t - t_0)$, vs. hydration ratio, $[\alpha/(1 - \alpha)]$, data using nonlinear regression analysis. Heat release results indicate that the length of the dormant period is about 2 h for blends without and with up to 8 mass % of silica fume replacement and about 3 h for blends containing more than 8 mass % of silica fume replacement.

Fig. 3 compares the experimental measurements and the model prediction of Eq. (2). The values of parameters k_1 and k_2 for both the cement–silica fume blends and control sample are presented in Table 2.

The relationship between the reaction time, $(t - t_0')$, and the strength ratio, $[fc/(fc_\infty - fc)]$, was used to determine the values of constants k_{k1} and k_{k2} of the Knudsen expression, according to Eq. (3), by means of nonlinear regression analysis. Fig. 4 shows the fit of Eq. (3) to the experimental data. The values of constants k_{k1} and k_{k2} of Eq. (3) are presented in Table 2.

The values of the rate constant (k_1 and k_2) of the Knudsen expressions in Eqs. (2) and (3), presented in Table 2, indicate that the “mixed (linear/parabolic) dispersion model” fits the cement–silica fume blends data well, as both the rate constants of the Knudsen expressions (i.e., k_1 and k_2 in Eq. (2) and k_{k1} and k_{k2} in Eq. (3)) are significant in the systems to which they are referring.

However, neither Eq. (2) nor Eq. (3) establishes a direct relationship between the compressive strength and the degree of hydration (the $fc - \alpha$ data), but both the degree of hydration and strength development are a function of age.

With respect to the fact that there is a relationship between parameters as defined by Knudsen, this study has attempted to establish the degree of hydration–compressive strength function.

Table 2

Numeric values of the rate constants from Eqs. (2)–(5) for cement–silica fume blends (MP0, MP2, MP5, MP8, MP11 and MP15)

Systems	MP0	MP2	MP5	MP8	MP11	MP15
Eq. (2)						
k_1	29.27	38.32	36.34	28.37	37.01	25.40
k_2	3.52	4.39	0.00	6.29	1.56	5.87
Eq. (3)						
k_{k1}	135.13	135.13	194.55	133.13	126.42	125.42
k_{k2}	0.21	0.13	0.15	0.00	0.21	0.25
Eq. (4)						
k_t	0.0074	0.0074	0.0051	0.0075	0.0079	0.0079
Eq. (5)						
k_{fc2}	4.14	3.34	4.32	4.28	3.38	3.88
k_{fc3}	0.099	0.056	0.073	0.014	0.064	0.099

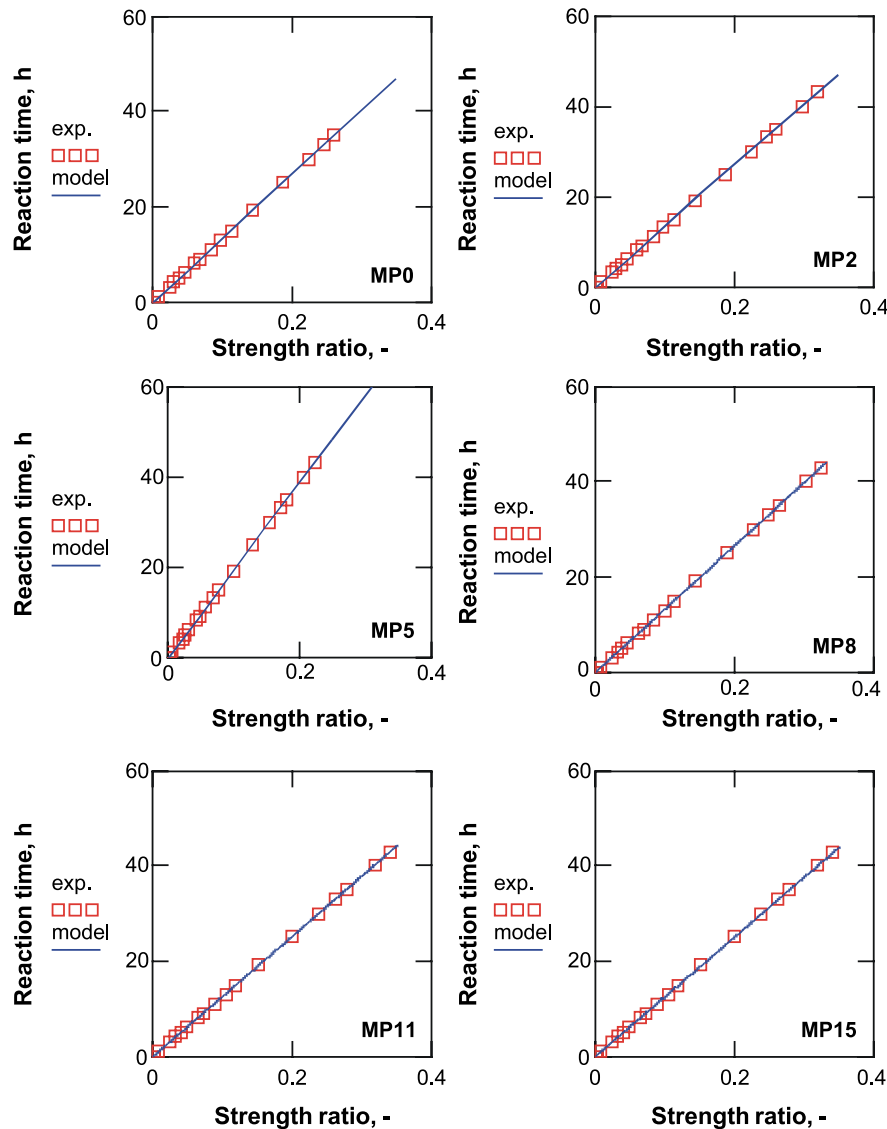


Fig. 4. Correspondence of the empirical expression given by Eq. (3) (solid line) to the experimentally determined values (data points) for all cement–silica fume blends, where the strength ratio is $[f_c/(f_{c\infty} - f_c)]$, and the reaction time is $(t - t'_0)$.

The relationship between the degree of hydration, α , and the corresponding compressive strength, f_c , is established by means of the time variable, t .

As no experimental degrees of hydration–compressive strength development data at the equivalent age ($t = \text{constant}$) were available, the following linear hyperbolic function for strength development of mortars vs. age was used [5,23]:

$$f_c = f_{c\infty} \frac{k_t(t - t'_0)}{1 + k_t(t - t'_0)} \quad (4)$$

where f_c = strength at age t , MPa; $f_{c\infty}$ = the actual long-term strength, MPa; k_t = rate constant, $1/h$ and t'_0 = age at start of strength development.

An average value of t'_0 , determined by the final time of set measured for all cement–silica fume blends using Vicat needle techniques, was found to be of the order of 5 h.

Fig. 5 compares the experimental measurements and the model predictions by Eq. (4) for compressive strength versus age for standard mortars with (2–15 mass %) and without silica fume replacement. As can be seen, the agreement between the model and the experimental data is very good. Table 2 summarizes the results of the regression analysis for the values of the rate constant k_t of Eq. (4) for each of cement–silica fume blends, as well as for the control cement sample (MP0).

We find it important to stress, that Eq. (4) is equivalent to Eq. (3) (rearranged) with a value of the zero for the rate constant of k_{k2} in Eq. (3). This is supported by the fact that the values for the rate constant k_t in Eq. (4) are basically equivalent to one over the values of the rate constant k_{k1} in

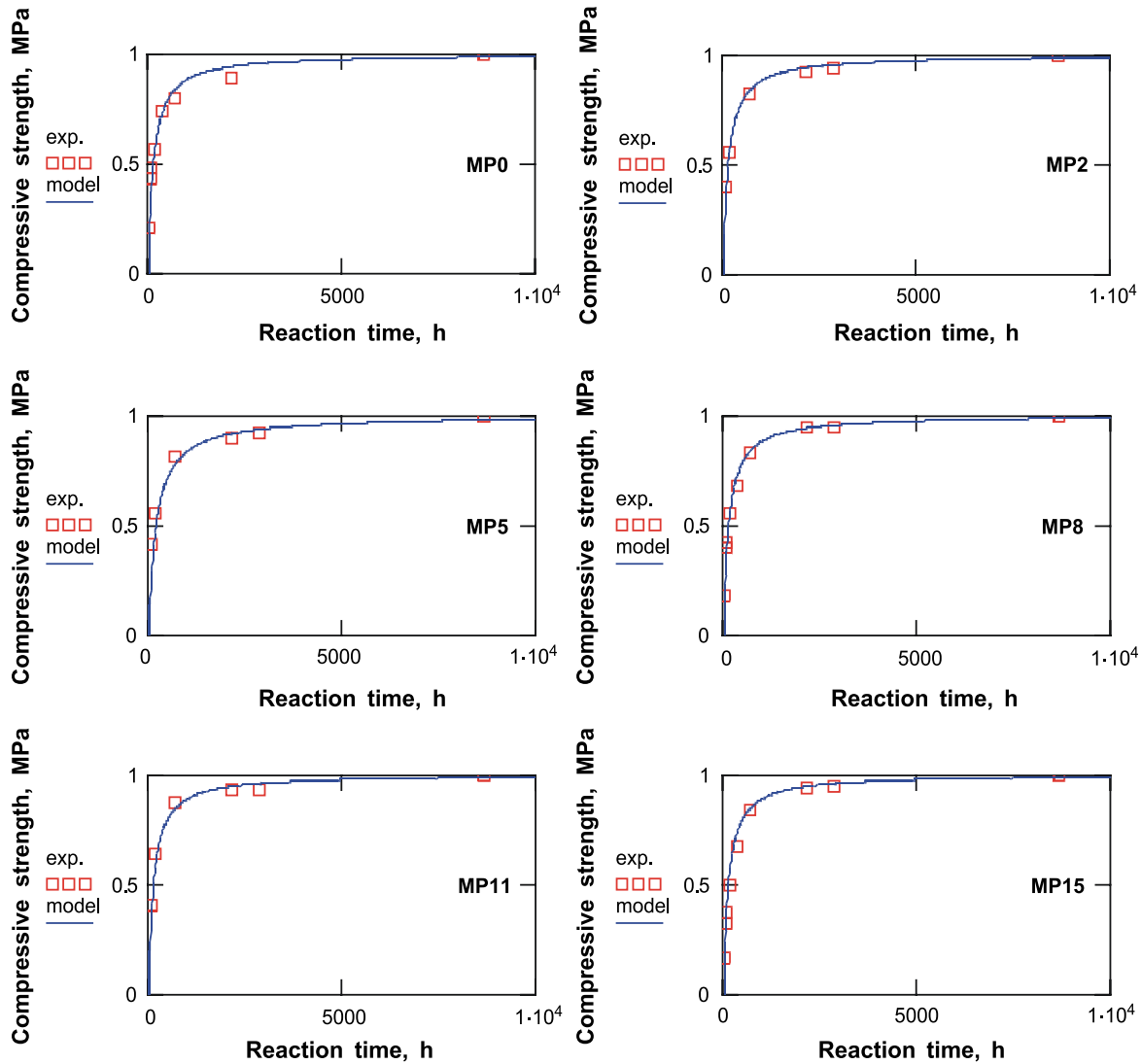


Fig. 5. Comparison of experimental measurements (data points) and the model predictions by Eq. (4) (dotted lines) for all cement–silica fume blends, where the reaction time is $(t - t'_0)$.

Eq. (3). In other words, if we set $k_{k2} = 0$ in Eq. (3) and solve for fc , we will arrive at Eq. (4) with k_t of Eq. (4) = $1/k_{k1}$ of Eq. (3). Thus, the linear hyperbolic function [23] and the linear dispersion model [5] are simply equivalent.

The same equation in only a different form was also used by Knudsen [5] and by Knudsen and Geiker [7] to represent the degree of hydration and development of chemical shrinkage as a function of age.

The values of corresponding strengths, calculated from Eq. (4), were joined to the experimentally determined values of degree of hydration vs. time. Thus, a set of the $fc - \alpha$ data at the equivalent age could be obtained, and the values of Knudsen's parameters: the hydration ratio, $[\alpha / (1 - \alpha)]$, and the strength ratio, $[fc / (fc_\infty - fc)]$, could be calculated.

As t_0 in Eq. (2) is not the same as t'_0 in Eq. (3), both the strength development data during setting and the degree of hydration data during the early period (up to 5 h from

mixing) are not considered in Eq. (5). This step is necessary because the degrees of hydration values are not evenly distributed with compressive strength development (that is, after cement and water are mixed together, there is a time delay before strength development begins, but more hydration heat is released during the early period than during the later ones).

Based on these considerations, the corresponding relationships between Knudsen's parameters were found to be provided by the empirical expression:

$$\frac{\alpha}{(1 - \alpha)} = k_{fc2} \left(\frac{fc}{fc_\infty - fc} \right) + k_{fc3} \quad (5)$$

where k_{fc2} and k_{fc3} are constants. Other symbols are identical with the symbols of Eqs. (2) and (3).

Eq. (5) represents the linear function, and provides a direct mathematical relationship between the degree of hydration (a kinetic parameter of the early cement hydration process) and the compressive strength (a final mechanical property of hardened cement mortar/stone).

The suitability of the linear model was also demonstrated in a recent study on the applicability of the maturity method to mortar mixtures with low water–cementitious materials ratios, typical of those in high-performance concrete [24]. Knudsen [6] has also suggested that numerous hydration curves modelled could in practice be considered to be 100% linear. According to Knudsen [6], a change

from linear to parabolic kinetics, as pictured by Eq. (1), may come so late (small values of k_2) as to have no practical implication.

Table 2 summarizes the numeric values of the k_{fc2} and k_{fc3} constants of Eq. (5). Fig. 6 presents the correspondence of the empirical expression according to Eq. (5) to the experimentally determined values of Knudsen's parameters for all samples (MP0–MP15). The model applied is well supported by experimentally obtained results for each of the cement–silica fume blends and the control sample examined. This suggests that the model, given by Eq. (5), could be used to predict the compressive strength development

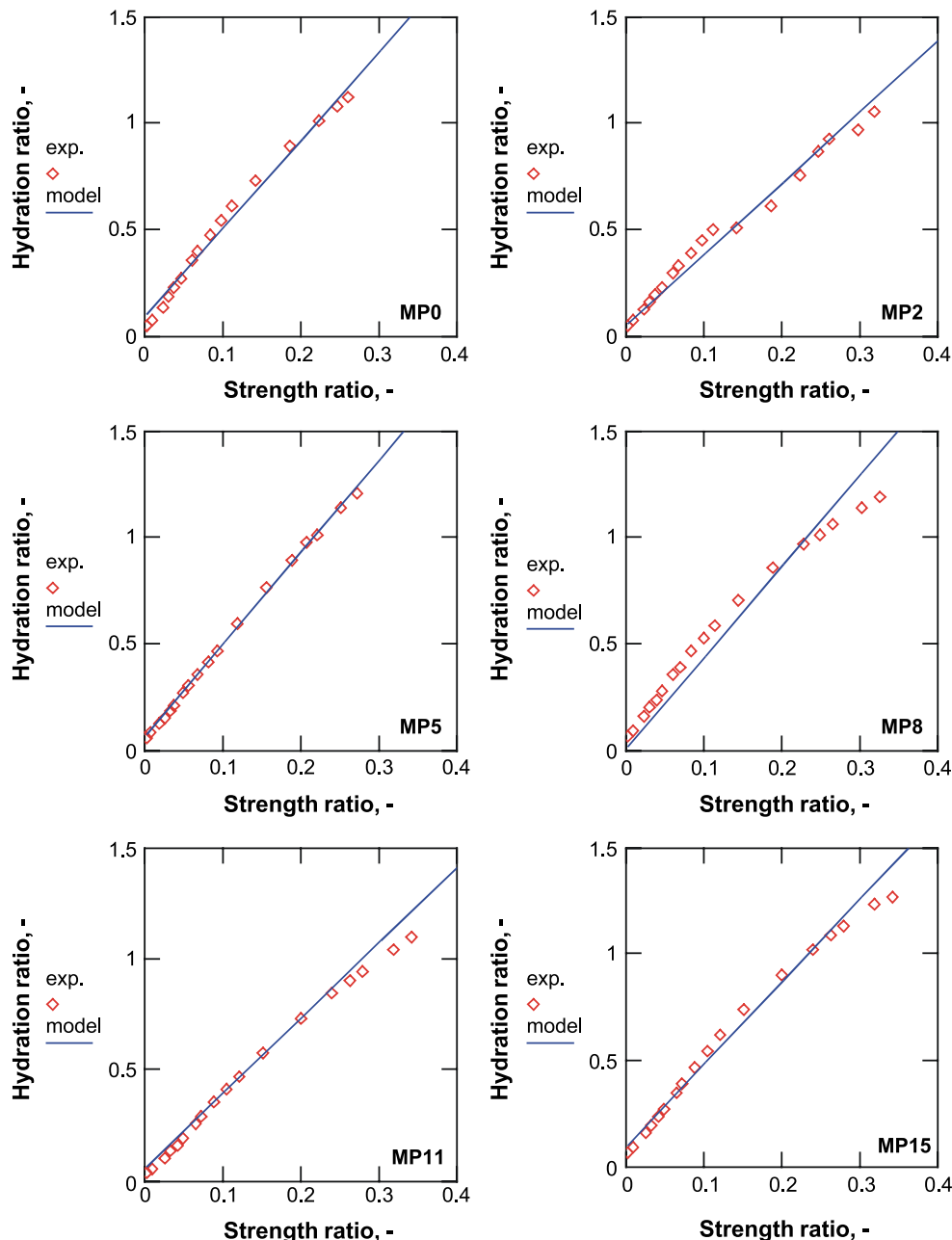


Fig. 6. Correspondence of the empirical expression given by Eq. (5) (solid line) to the experimentally determined values (data points) for all cement–silica fume blends where the strength ratio is $[f_c/(f_{c\infty} - f_c)]$, and the hydration ratio is $[\alpha/(1 - \alpha)]$.

based on measuring the heat release during the 48-h cement hydration in the case that the infinitely compressive strength value (fc_{∞}) is known.

The values of coefficients k_{fc2} and k_{fc3} in Eq. (5) suggest that the efficiency of silica fume in the cement–silica fume blends depends on the percentage of silica fume replacement. Therefore, each of the cement–silica fume systems has to be calibrated separately.

Thus, the calibration performed for one cement–silica fume blend (Fig. 6) can be used to predict the hydration behaviour of other cement-blended system of reasonably similar properties, such as cement phase composition, percentage of silica fume replacement, W/S and temperature conditions.

The usefulness of the proposed model is based on its ability to make predictions about the compressive strength at later ages only, 48 h after mixing of cement or cement–silica fume blends with water.

As no plasticizer was used to ensure complete dispersion of the silica fume, further studies would include the addition of plasticizer that could serve to better justify the model proposed.

4. Conclusion

This paper stresses the importance of kinetic analysis of the cement hydration process in predicting the compressive strength development of cement mortars containing up to 15 mass % of silica fume replacement, and describes a mathematical model developed.

The Knudsen's dispersion models have been applied in fitting both the experimental degree of hydration and the strength development data as a function of time using the nonlinear regression analysis. It has been found that the “mixed (linear/parabolic) dispersion model” fits the cement–silica fume blend systems data well, as both the rate constants (k_1 and k_2) in the Knudsen expressions are significant in the systems to which they are referring.

With respect to the fact that there is a relationship between parameters as defined by Knudsen, this study has attempted to establish the direct relationship between the degree of hydration and compressive strength. Their functional dependence has been determined by means of the time variable.

Examinations have indicated a linear dependence between these variables according to the relation:

$$\frac{\alpha}{(1-\alpha)} = k_{fc2} \left(\frac{fc}{fc_{\infty} - fc} \right) + k_{fc3}$$

The values of coefficients k_{fc2} and k_{fc3} suggest that the efficiency of silica fume in mortar depends on the percentage of silica fume replacement. Therefore, each cement–silica fume blend system has to be calibrated separately.

Thus, calibration performed for one cement-blended system could be used to predict the hydration behaviour of other ones of reasonably similar cement phase composition, silica fume replacement percentage, W/S and curing conditions.

The proposed model provides the opportunity to predict the compressive strength development based on measuring the heat release during the 48-h cement hydration if the infinite compressive strength value is known.

Further efforts will be directed to further justification of the model developed by including other properties of interest into the model proposed.

Acknowledgements

This work was supported by the Ministry of Science and Technology, Croatia under the Project No. 0011012. The authors are grateful to the reviewers for their valuable contribution to improvement of this paper.

References

- [1] S. Popovics, A model for the quantitative description of the kinetics of hardening of Portland cement, *Cem. Concr. Res.* 17 (1987) 821–838.
- [2] K.M. Alexander, The relationship between strength and the composition and fineness of cement, *Cem. Concr. Res.* 2 (1972) 663–680.
- [3] E.S. Joens, B. Osbaeck, The effect of cement composition on strength described by a strength–porosity model, *Cem. Concr. Res.* 12 (1982) 167–178.
- [4] S. Tsivilis, G. Parissakis, A mathematical model for the prediction of cement strength, *Cem. Concr. Res.* 25 (1995) 9–14.
- [5] T. Knudsen, On particle size distribution in cement hydration, 7th Inter. Congress on Chemistry of Cement, Paris, vol. II, 1980, pp. I-170–I-175.
- [6] T. Knudsen, The dispersion model for hydration of Portland cement: I. General concepts, *Cem. Concr. Res.* 14 (1984) 622–630.
- [7] T. Knudsen, M. Geiker, Chemical shrinkage as an indicator of the stage of hardening, *Proceedings, RILEM International Conference on Concrete at Early Ages*, Paris, vol. 1, 1982, pp. 163–165.
- [8] D.P. Bentz, A Three-Dimensional Cement Hydration and Microstructure Program: I. Hydration Rate, Heat of Hydration and Chemical Shrinkage, U.S. Dept. of Commerce, Gaithersburg, MD, 1995, pp. 1–47 (NISTIR No. 5756).
- [9] D.P. Bentz, Three-dimensional computer simulation of Portland cement hydration and microstructure development, *J. Am. Ceram. Soc.* 80 (1997) 3–21.
- [10] D.P. Bentz, Modelling cement microstructure: pixels, particles and property prediction, *Mat. Struct.* 32 (1999) 187–195.
- [11] D.P. Bentz, O.M. Jensen, A.M. Coats, F.P. Glasser, Influence of silica fume on diffusivity in cement-based materials: I. Experimental and computer modelling studies on cement pastes, *Cem. Concr. Res.* 30 (2000) 953–962.
- [12] R. Krstulović, P. Krolo, T. Ferić, Microcalorimetry in the cement hydration process, *Period Polytech* 33 (1989) 315–321.
- [13] R. Krstulović, P. Dabić, A conceptual model of the cement hydration process, *Cem. Concr. Res.* 30 (2000) 693–698.
- [14] HRN. B.C8. 028-75, Determination of heat of hydration of Portland cement and cement with additions by method of solution.
- [15] HRN. B.C8. 022-81, Bending and compressive strength of hydraulic cement mortars.

- [16] HRN. B.C8. 042-81. Building lime. Methods of physical and mechanical testing.
- [17] HRN. B.C8. 050-81, Air content of hydraulic cement mortar.
- [18] A.M. Neville, *Properties of Concrete*, 3rd ed., Pitman Publishing, London, 1981.
- [19] P. Lu, G. Sun, J.F. Young, Phase composition of hydrated DSP cement pastes, *J. Am. Ceram. Soc.* 76 (1993) 1003–1007.
- [20] J. Zelić, D. Rušić, D. Veža, R. Krstulović, The role of silica fume in the kinetics and mechanisms during the early stage of cement hydration, *Cem. Concr. Res.* 10 (2000) 1655–1662.
- [21] A. Larbi, A.L.A. Fraay, J.M.J.M. Bijen, The chemistry of the pore fluid of silica fume-blended cement systems, *Cem. Concr. Res.* 10 (2000) 1655–1662.
- [22] E. Tkalčec, J. Zelić, Influence of amorphous silica (silica dust) on the properties of Portland cement mortars, *ZKG Int* 11 (1987) 574–579.
- [23] N.J. Carino, The maturity method: theory and application, *J. Cem., Concr. Aggreg.* 6 (1984) 61–73.
- [24] N.J. Carino, R.C. Tank, Maturity functions for concrete made with various cements and admixtures, *ACI. Mater. J.* 89 (1992) 188–196.