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A new approach in mathematical modelling of cement hydration development

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Abstract

This paper describes development of a kinetic cement hydration model, which observes hydration rate relative to time $d\alpha/dt = f(T,t)$. The model established makes it possible to observe hydration rate relative to time and not relative to the reaction degree α, $d\alpha/dt = f(T,\alpha)$, which offers a new approach to solving the cement hydration kinetics. The model assumes several simultaneous processes sequentially governing individual hydration segments. The model has been tested by means of experimental $\alpha-t$ data obtained from the DSC plots by quantifying the content of $Ca(OH)_2$ from the cement–water system. The results indicate that the model established is valid and can be applied well. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Based on our experimental research and theoretical insight into the development of cement hydration process, this article describes a new approach to solving individual processes through mathematical modelling of this complex heterogeneous system. A large number of equations have been studied and applied to heterogeneous systems to describe their characteristic physical and chemical properties and processes [1–4]. With actual materials, these equations are frequently not exact, as they primarily relate to analysis of idealised models, so that the equations suggested can be considered as engineering approximations. Although subject to criticism from the viewpoint of mathematical formulations or practical applicability, they are very instructive in understanding interdependencies in the studies of processes. However, practice and theory, being two halves of the same whole, cannot be taken separately, which forms the basis for process engineering [5–8].

Our purpose was to propose and test mathematical models that would describe individual basic processes determined from experimental plots of hydration development in cement samples. Kinetic laws for heterogeneous processes have provided the basis for a mathematical model of cement hydration kinetics that observes the hydration rate relative to time, which is a new approach, as the hydration rate of this heterogeneous system had been previously defined relative to the reaction degree (α).

Furthermore, the model links several simultaneous processes that sequentially govern hydration segments [9,10].

2. Theoretical

The basis for development of a cement hydration model is $\alpha-t$ functions derived under the assumption that only one of several simultaneous processes controls the hydration rate [9–13]. If nucleation and growth govern the hydration process, the $\alpha-t$ function has the form:

$$[-\ln(1-\alpha)]^{\frac{1}{n}} = k_{NG}t, \qquad 0 = t \leq \infty \tag{1}$$

where n is the value of the Avrami exponent that reflects the details of the nucleation and growth mechanism [11,12].

The derived differential equation is:

$$\frac{d\alpha}{dt} = nk_{NG}^{n}t^{n-1}e^{-(k_{NG}t)^{n}}, \qquad 0 = t \leq \infty \tag{2}$$

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Table 1
Mineralogical composition of the PC45B and PC30T45S[a] cements

Sample	C_3S	C_2S	C_3A	C_4AF	CaO_{free}
PC45B	72.09	9.82	11.18	6.35	0.56
PC30T45S	62.10	17.60	11.20	8.20	0.90

[a] Calculated according to Bogue for the initial cement clinker.

If the process is governed by the phase boundary reactions, the function and the differential equations are:

$$1-(1-\alpha)^{\frac{1}{3}}=k_1 t, \qquad 0=t\leq\infty \tag{3}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=3k_1(1-k_1 t)^2, \qquad 0=t\leq\infty \tag{4}$$

while if diffusion governs the process, the starting and the derived expression will be:

$$\left(1-(1-\alpha)^{\frac{1}{3}}\right)^2=k_\mathrm{D}t, \qquad 0=t\leq\infty \tag{5}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{3}{2}k_\mathrm{D}\frac{\left(1-(k_\mathrm{D}t)^{\frac{1}{2}}\right)^2}{(k_\mathrm{D}t)^{\frac{1}{2}}}, \qquad 0=t\leq\infty \tag{6}$$

The functions $\alpha = f(t)$ [Eqs. (1), (3), and (5)], as well as the derived kinetic functions $\mathrm{d}\alpha/\mathrm{d}t = f(t)$ [Eqs. (2), (4), and (6)], are defined in the range $0-\infty$.

If two or three processes sequentially governing the hydration process segment rate take place simultaneously on a particle, the total hydration time is divided:

(a) for two processes: $t = t_\mathrm{NG} + t_\mathrm{I}$; $t = t_\mathrm{NG} + t_\mathrm{D}$; and
(b) for three processes, bearing in mind the assumption that hydration control starts with the nucleation and growth process, proceeds with the phase boundary interaction and ends with diffusion: $t = t_\mathrm{NG} + t_\mathrm{I} + t_\mathrm{D}$.

Kinetic equations [Eqs. (2), (4), and (6)] can be applied successfully in modelling the hydration kinetics [14,15] for cases where individual segments are sequentially governed by several processes.

Namely, the $\alpha-t$ functions, [Eqs. (1), (3), and (5)], are partial solutions to differential equations, [Eqs. (2), (4), and (6)], respectively, and are obtained for initial conditions $t = 0$ and $\mathrm{d}\alpha/\mathrm{d}t = 0$ [16–18].

In case of more than one governing process, the $\alpha-t$ functions will be defined by conditions at transition of one process into another. The development of the kinetic model will be illustrated by example (b), which takes place according to the pattern: NG→I→D.

At the beginning, the NG process is the slowest one, so that the initial time $t_\mathrm{NG} = 0$, while takeover of control by interaction and diffusion processes will be defined by times of transition of one process into another. If the interaction process takes control after the nucleation and growth process, the transition time is denoted as $t_{\mathrm{NG-I}}$; if diffusion takes control after interaction, the transition time is $t_{\mathrm{I-D}}$. Transition times $t_{\mathrm{NG-I}}$ and $t_{\mathrm{I-D}}$ are determined from the conditions:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_\mathrm{NG}=\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_\mathrm{I} \tag{7}$$

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

Thereby, the prerequisites have been established for development of the model.

The kinetic equation of the NG process, while it is the governing one, is:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_\mathrm{NG}=nk_\mathrm{NG}^n t_\mathrm{NG}^{n-1}\mathrm{e}^{-(k_\mathrm{NG}t_\mathrm{NG})^n}, \qquad 0=t_\mathrm{NG}\leq t_{\mathrm{NG-1}} \tag{9}$$

and the corresponding $\alpha-t$ function for NG is

$$\alpha_\mathrm{NG}=1-\mathrm{e}^{-k_\mathrm{NG}t_\mathrm{NG}}, \qquad 0=t_\mathrm{NG}\leq t_{\mathrm{NG-1}} \tag{10}$$

Eq. (10) represents a particular solution of the differential equation, Eq. (9), for initial conditions $t_\mathrm{NG} = 0$, $\alpha_\mathrm{NG} = 0$.

When the I process takes control over hydration, the kinetic and $\alpha-t$ functions are:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_\mathrm{I}=3k_\mathrm{I}(1-k_\mathrm{I}t_\mathrm{I})^2, \qquad t_{\mathrm{NG-1}}\leq t_\mathrm{I}\leq t_{\mathrm{I-D}} \tag{11}$$

$$\alpha_\mathrm{I}=C_\mathrm{I}-(1-k_\mathrm{I}t_\mathrm{I})^3, \qquad t_{\mathrm{NG-I}}\leq t_\mathrm{I}\leq t_{\mathrm{I-D}} \tag{12}$$

where C_I is the integration constant, defined from the conditions at the transition NG→I ($t_{\mathrm{NG-I}}$, $\alpha_{\mathrm{NG-I}}$), i.e.

$$C_\mathrm{I}=\alpha_{\mathrm{NG-1}}+(1-k_\mathrm{I}t_{\mathrm{NG-I}})^3 \tag{13}$$

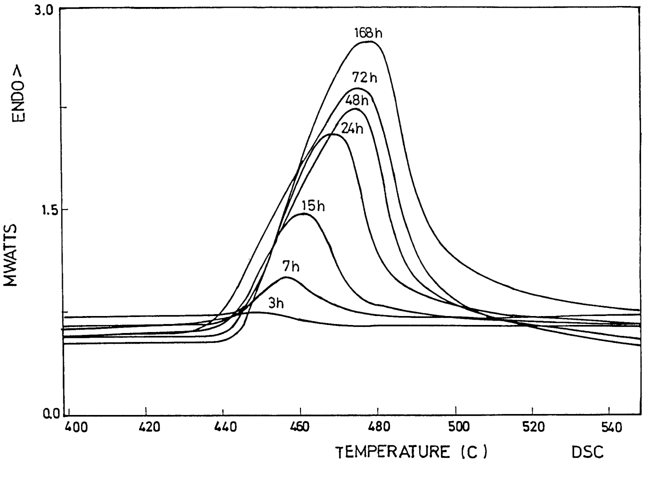

Fig. 1. DSC plots for the PC45B sample showing peaks of decomposition of $Ca(OH)_2$ formed in hydrated cement samples for specific hydration times.

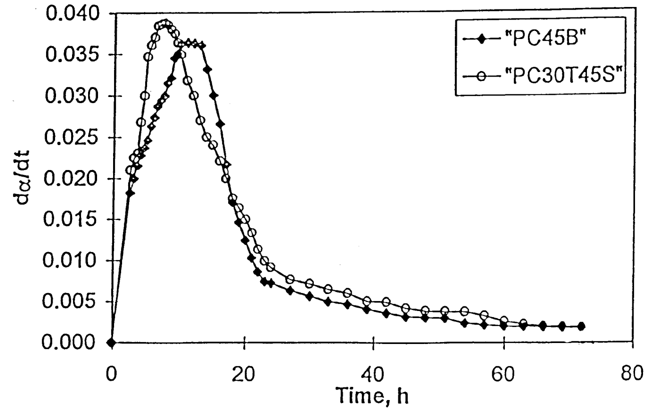

Fig. 2. Relationships between hydration rate and hydration times for hydrated PC45B and PC30T45S cement samples calculated from the data on the $Ca(OH)_2$ content.

Mathematically speaking, the values t_{NG-I} and α_{NG-I} represent initial conditions for the differential equation that determine the particular solution, Eq. (12).

The value α_{NG-I} is calculated from Eq. (10), i.e.

$$\alpha_{NG-I} = 1 - e^{k_{NG}t_{NG-I}} \tag{14}$$

When the D process takes control, the corresponding kinetic and $\alpha-t$ functions are:

$$\left(\frac{d\alpha}{dt}\right)_D = \frac{3}{2}k_D\frac{\left(1-(k_Dt_D)^{\frac{1}{2}}\right)^2}{(k_Dt_D)^{\frac{1}{2}}}, \qquad t_{I-D} \le t_D \le \infty \tag{15}$$

$$\alpha_D = C_D - [(1-k_Dt_D)^3]^2, \qquad t_{I-D} \le t_D \le \infty \tag{16}$$

while the integration constant C_D is calculated from Eq. (16) for initial conditions t_{I-D} and α_{I-D}, i.e.

$$C_D = \alpha_{I-D} + [(1-k_Dt_{I-D})^3]^2 \tag{17}$$

while α_{I-D} is calculated from Eq. (12), i.e.

$$\alpha_{I-D} = C_I - (1-kit_{I-D})^3 \tag{18}$$

The functions $\alpha-t$ are given in their explicit form in (Eqs. (10), (12), and (16)). Mathematical derivation for the representation of cement hydration development according to Eqs. (1)–(18) makes it possible to model the hydration process and test it against the experimental data.

3. Experimental

Portland cements PC45B and PC30T45S whose properties are described by the Croatian standard HRN B. C1-011 were used. These Portland cements achieve compression strength of 45 MPa after 28 days of hydration. The PC30T45S cement contains up to 30% slag. Its mineralogical and chemical composition is shown in Table 1.

Sample preparation:

Doubly distilled water was added to cement samples at the ratio W/C = 0.5 to obtain cement paste. The paste was then divided and placed into a large number of polyethylene test tubes, sealed hermetically, and stored in the thermostat at a constant temperature of 35°C.

Hydration was blocked in individual samples at specified time intervals (1, 2, 3, ..., 168 h) by addition of 2-propanol. This was done by grinding and mudding the sample with 2-propanol, transferring it to the funnel according to Büchner, and having the liquid part sucked out. The solid residue at the funnel was well rinsed with the newly added 2-propanol, the liquid part was filtered, while the solid, partly hydrated sample was transferred to the vacuum drier. Drying took place for 4 h at a constant temperature of 40°C. After drying, the samples were sieved on a 0.06-mesh sieve. Thus prepared, the samples were sealed hermetically in their containers and stored in the exsiccator [19].

Differential scanning calorimetry (Perkin-Elmer DSC model 4) was used to determine the content of $Ca(OH)_2$ at non-isothermal conditions in partly hydrated cement samples thus prepared. The scanning experiments were run with the heating rate 10°C/min using nitrogen flow. The amount of energy absorbed by endothermic reaction due to dehydration of CH in the temperature range 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 calcium hydroxide, analytic grade chemical [20].

The hydration degree $\alpha(t)$ is defined as the ratio of the amount of $Ca(OH)_2$ formed at time t to the total amount of $Ca(OH)_2$ formed after 28 days in hydrated cement paste without slag. The measured hydration degree (α) is the average value, averaged over all chemical species in the cement, all of which may not hydrate at the same rate. Fig. 1 shows some individual DSC plots.

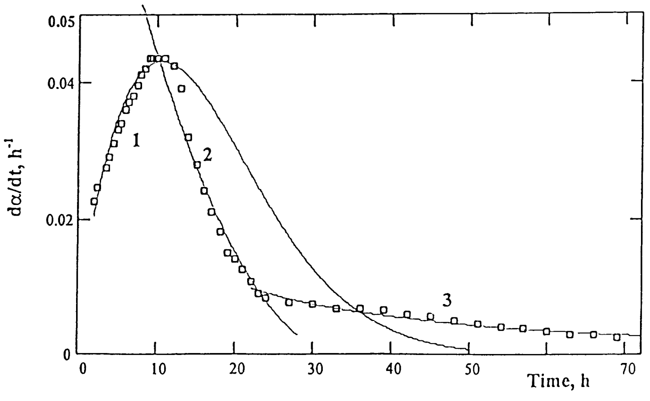

Fig. 3. Hydration rate relative to process duration for the PC45B sample. Plot 1 [Eq. (9)] corresponds to the NG process, plot 2 [Eq. (11)] corresponds to the I process, plot 3 [Eq. (15)] corresponds to the D process. Symbols (□) denote experimental data.

Table 2
Kinetic parameters for hydration of cements PC45B and PC30T45S at W/C=0.5 and T=35°C, determined by the model

Kinetic parameter	PC45B	PC30T45S
n	1.781	1.710
k_{NG}	0.0465	0.0554
k_I	0.0315	0.0286
k_D	0.0086	0.0058

These data have served to calculate the hydration duration ($d\alpha/dt-t$). Fig. 2 shows the experimental plot obtained for the hydration rate.

4. Testing of the model and discussion

The measured data from the DSC plots and calculated changes in hydration heat relative to time ($d\alpha/dt-t$) according to Fig. 2 were used to test the model derived in the theoretical part. The $d\alpha/dt-t$ plot was thus resolved into component parts, each representing an individual process with known kinetic parameters. The commercial mathematical software MATHCAD7, which had been used to create the model algorithm, was used in testing the model [10].

The first step was to show graphically the experimentally determined $d\alpha/dt-t$ functions. Then, it was necessary to determine optimum parameters n, k_{NG}, k_I, and k_D from the kinetic models, [Eqs. (9), (11), and (15)], which would best fit the experimental data. Fig. 3 shows the procedure used. It can be seen that the theoretical kinetic function $(d\alpha/dt)_{NG}-t$ [Eq. (9)], used to describe the kinetics of the nucleation and growth process at the beginning of hydration, shows best correspondence with the experimental data until the moment when the experimental function $d\alpha/dt-t$ achieves its maximum, after which significant deviations are observed. This indicates that the nucleation and growth process is no longer the governing process. Literature [9,10,15] indicates that the control should be taken over by the phase boundary interaction process. The model confirms this: after the nucleation and growth process, best correspondence with the experimental data, $d\alpha/dt-t$, is observed in the theoretical kinetic function, $(d\alpha/dt)_I-t$ [Eq. (11)], which is used to describe the kinetics of the interaction at the phase boundary. The estimated parameters n, k_{NG}, and k_I, make it possible to determine the time of process transition NG→I, t_{NG-I} from the conditions of Eq. (7).

Fig. 3 shows that the function $(d\alpha/dt)-t$ [Eq. (11)], does not follow the experimental data to the end of the hydration process. Literature [9,10,15] indicates that the control should be taken over by the diffusion process. The model confirms this: the theoretical kinetic function $(d\alpha/dt)_D-t$ [Eq. (15)], shows best correspondence with the experimental data. Estimation of parameters makes it possible to determine the process transition time I→D, t_{I-D}, from the conditions of Eq. (8). The transition points t_{NG-I} and t_{I-D} make it possible to determine the period during which each of these processes has control. Table 2 lists the kinetic parameters determined for the cement samples examined.

The reaction degree, α_{NG-I}, is calculated for the time t_{NG-I}, according to Eq. (14), in order to determine the C_I constant according to Eq. (13). It is now possible to calculate the reaction degree, α_I, for the region governed by the I process according to Eq. (12). The reaction degree after the t_{I-D} transition time is calculated by means of Eq. (16). Eqs. (17) and (18) help calculate the integrating constant C_D for the reaction degree α_{I-D}. Fig. 4 shows a comparison of experimental $\alpha-t$ data with the data determined by the model.

Fig. 4a and b shows good correspondence between the experimental $\alpha-t$ plot and the mathematical model. Cor-

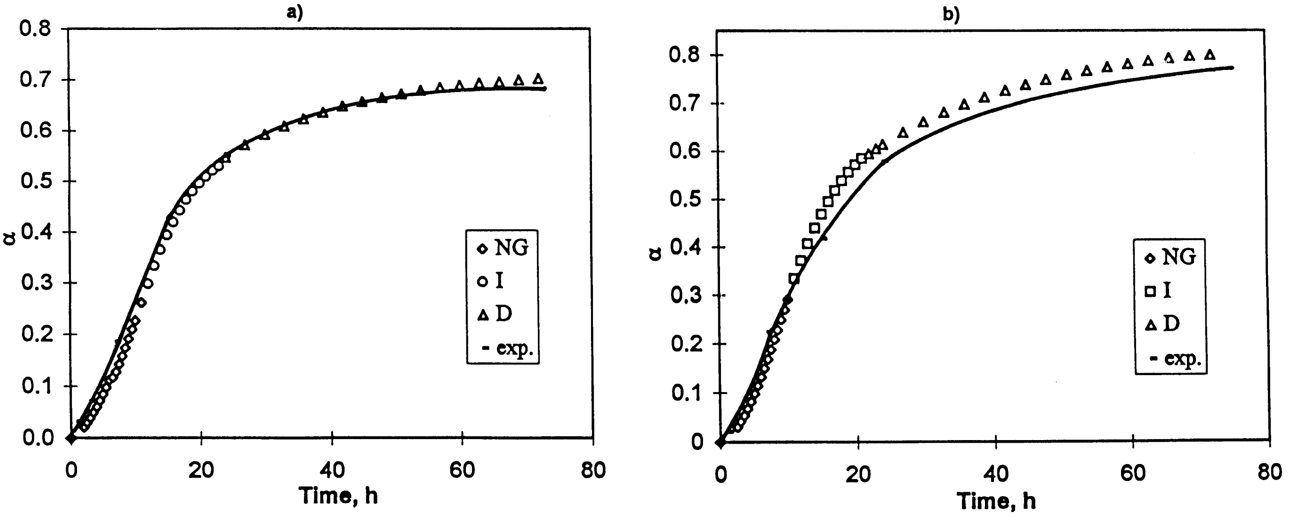

Fig. 4. Experimental and model-determined $\alpha-t$ values for the PC45B (a) and PC30T45S (b) cements.

respondence is very good in the case of pure cement (Fig. 4a), while a deviation is observed after 18 h in the case of cement with addition of 30% slag (Fig. 4b). The deviation from the model is attributed to the pozzolanic reaction between slag and $Ca(OH)_2$ produced from cement, which takes place during hydration. Therefore, in cases of cement systems where the pozzolanic reaction takes place, mathematical modelling of the phase boundary interaction process and the diffusion process requires further corrections in order to describe better the effect of additions to cement on the hydration process. This will be a subject of further theoretic research that will be tested against experimental results.

5. Conclusions

Kinetic functions $d\alpha/dt = f(T,t)$, which have been derived from the basic $\alpha - t$ functions for the case of only one process governing hydration, can be successfully applied to the case when two or three processes take place at the same time, but govern the hydration process rate sequentially.

Being particular solutions of differential equations, the $\alpha - t$ functions' form will be determined by conditions at transition of one process into another.

The functions derived for the hydration rate $d\alpha/dt = f(T,t)$ can determine kinetic parameters for actual cement samples. These functions are not affected by the reaction degree α, which reduces errors relative to precision of experimental determination of the reaction rate α for actual cement samples.

The mathematical model developed describes well the pure cement systems, but shows deviations with cement systems containing 30% slag in periods when phase boundary interactions and diffusion control the kinetics of the hydration process, which requires additional theoretical and further experimental research.

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