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A conceptual model of the cement hydration process

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Abstract

Cement hydration development has been analyzed on the basis of measured data obtained by the microcalorimetrical method. Based on the most appropriate model assumed, thermokinetic analysis has been carried out for the polymineral and polysize system tested on industrial cement samples. A computer program has been developed to determine specific kinetic parameters describing individual hydration processes. The program makes it possible to determine the controlling processes during hydration and their share. Certain kinetic parameters make it possible to observe differences in hydration of pure clinker minerals and of Portland cement in a subtler way. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Portland cement; Hydration; Kinetics; Modeling

1. Introduction

Cement hydration has been examined from different points of view, one of which is very often the kinetic analysis of the hydration process development, which can be analyzed by different methods [1–8]. Bearing in mind the complexity of the hydration mechanism in polymineral and polysize systems, and the absence of a universal theoretical hypothesis in the study of heterogeneous systems, it is necessary to take into account the methods of formal and conceptual mathematical modeling [9].

This means that the mathematical analysis of data measured during hydration is performed at several levels: data representation and forecast (the formal model), separation of hydration stages, and the thermokinetic analysis (the conceptual model). The first analysis of data measured is carried out in order to provide data necessary for the thermokinetic analysis ($\alpha - t$ data). The conceptual model is used to carry out the thermokinetic analysis of the hydration system in order to obtain parameters that finally describe hydration of pure clinker minerals, as well as the actual cement samples. Apart from the purely mathematical approach to modeling the hydration kinetics, subtle methods have been recently developed which make it possible to trace hydration of cement systems directly by means of sophisticated techniques that provide an image of the system, such as SEM and ESEM [10,11]. A huge progress in description of hydration processes has been achieved by digital image analysis and by development of hydration models based on quantitative shares of individual minerals in the image [12], such as two-dimensional and three-dimensional NIST cement hydration model [13,14]. In this way, it is possible to directly observe the development of hydrated particle microstructure, and to determine the reaction degree for individual constituents of the cement paste.

This article outlines the relevant theoretical basis and the experimental thermokinetic analysis of the hydration process in the example of industrial cement according to the hypothetical mathematical model, which provides for the fact that the process takes place in a heterogeneous system according to characteristic laws of reactions taking place (nucleation and growth, interaction at phase boundaries, and diffusion).

2. Theoretical principle for solving cement hydration kinetics

The kinetic model assumes three basic processes taking place: nucleation and crystal growth (NG), interactions at phase boundaries (I) and diffusion (D). All three processes are assumed to take place simultaneously but the slowest one dominates the hydration process as a whole, so that it is necessary to determine their rates. Based on studies carried

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out so far, it has been established that the slowest process at the beginning is NG, which is later replaced by I or D, as can be concluded from the rate of these processes [15,16]. The basic kinetic equations describing heterogeneous systems are based on the change in the reaction degree relative to time elapsed ($\alpha - t$ data).

Microcalorimetry [17] is characterized by continuous determination of heat released during hydration of cement constituents, primarily clinker minerals, added gypsum, free CaO and MgO. By means of the heat released, it is possible to determine the degree of hydration relative to hydration duration according to the equation:

$$\alpha_{(t)} = Q_{(t)}/Q_{\max} \tag{1}$$

where $Q_{(t)}$ is heat released by time t, and $Q_{\max}$ represents the total heat a sample can release. For pure minerals, $\alpha_{(t)}$ is the mineral reaction degree, while for cement it is a consequence of the combined effect of heat released by all constituents present [18].

2.1. Development of a mathematical model for kinetic analysis of cement hydration

The basic Avrami–Erofeev equation describing hydration kinetics during the dominant nucleation and growth process is often used for spherical particles:

$$[-\ln(1-\alpha)]^{\frac{1}{3}} = K_{\mathrm{NG}}t \tag{2}$$

However, for a real system, the fixed exponent 1/3 is usually replaced by $1/n$ where it is necessary to determine the most appropriate n. The value for the exponent n describes geometrical crystal growth [15] and its value usually ranges from 1 to 3, and can be determined graphically as a slope of the straight line from the log–log diagram of the relation $-\ln(1-\alpha)$ and elapsed time t. The method is illustrated by Fig. 1.

For interactions at phase boundaries, the following equation is usually used:

$$1-(1-\alpha)^{\frac{1}{3}} = K_{\mathrm{I}}t \tag{3}$$

where K_{I} is the rate constant for the reaction at phase boundaries, and is equal to k_{I}/R. R represents the radius of the reacting particle. In microcalorimetry, the hydration degree α depends on the heat released as a consequence of the total hydration effect, so that the effect of the change of radius of reacting particles during hydration is not examined.

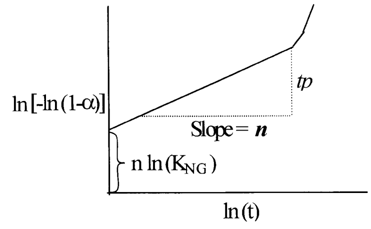


Fig. 1. Graphical determination of the values for the exponent n from $\alpha - t$ data, t_{p} is the time up to which $\alpha - t$ data are dominated by the NG process.

The diffusion process is defined by the expression:

$$[1-(1-\alpha)^{\frac{1}{3}}]^2 = K_{\mathrm{D}}t \tag{4}$$

where $K_{\mathrm{D}} = k_{\mathrm{D}}/R^2$ and represents the diffusion process rate. The particle radius has not been considered further.

Fig. 1 shows that $\alpha - t$ data up to time t_{p} are dominated by the NG process, i.e. it can be said for each $\alpha < \alpha_{\mathrm{p}}$ and $t < t_{\mathrm{p}}$ that they are dominated by the NG process. To determine the dominant process after t_{p}, the rates of these processes should be equated. If NG → I or NG → D, the following expressions are used:

$$\left[\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right]_{\mathrm{NG}} = \left[\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right]_{\mathrm{I}} \quad \textit{or} \quad \left[\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right]_{\mathrm{NG}} = \left[\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right]_{\mathrm{D}} \tag{5}$$

The basic Eqs. 2–4 should now be written in the differential form, so that they become Eqs. (6–8):

$$\left[\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right]_{\mathrm{NG}} = K_{\mathrm{NG}}n(1-\alpha)[-\ln(1-\alpha)]^{\frac{(n-1)}{n}} \tag{6}$$

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

$$\left[\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right]_{\mathrm{D}} = \frac{3}{2}K_{\mathrm{D}}(1-\alpha)^{\frac{2}{3}}/[1-(1-\alpha)^{\frac{1}{3}}]. \tag{8}$$

If expressions are equated according to Eq. 5, the calculation constants K_{I0} and K_{D0} can be determined. These are control values to be compared to the experimental constants K_{I} and K_{D}. The condition is that the difference between the calculation and the experimental constants should be as small as possible. Value of the standard deviation, sd, represents the mean deviation of the experimental points in the interval chosen from the straight line drawn through these points, determined by the least square method. sd is calculated according to the Eq. (9):

$$\mathrm{sd} = \sqrt{\frac{\sum_{i=1}^{m}(y_i - Y_i)^2}{N}} \tag{9}$$

where y_{i} is the value of the experimental point, Y_{i} represents the corresponding value on the straight line. N is the number of degrees of freedom on the interval observed, while the coefficients i and m represent the initial and final point of the interval observed.

3. Experimental

A referent alite (A) sample prepared in laboratory, and two types of commercial cement, a neat Portland cement, PC55 designated as sample (B), and a blended Portland cement PC30t45s designated as sample (C) have been used

Table 1
Mineralogical composition of clinkers used to produce cements B and C calculated according to Bogue [R.H. Bogue, The chemistry of portland cement, 2nd. ed., Reinhold, New York (1955)]

Sample	C_3S	C_2S	C_3A	C_4AF	CaO_{free}
B	71.50	22.70	3.02	1.75	1.00
C	62.10	17.60	11.20	8.20	0.90

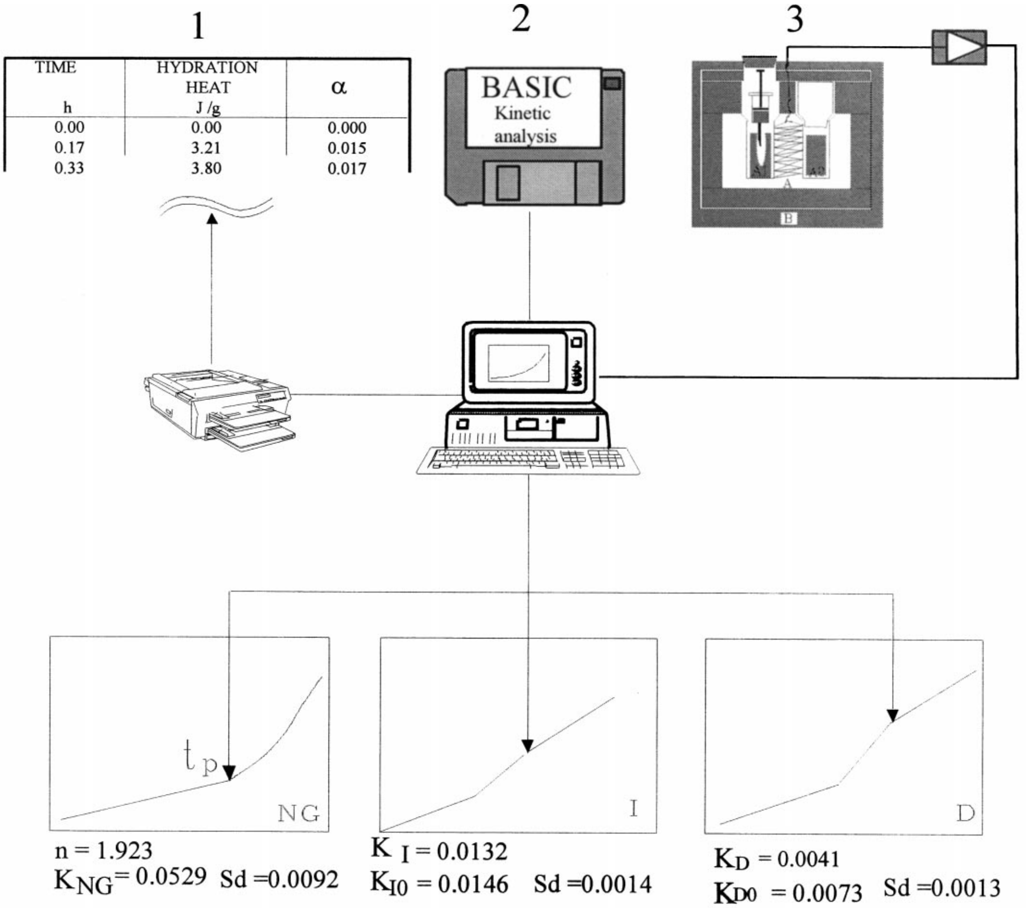
in this study. Cement samples B and C conform to the HRN B.C1-011 standard. Sample B is actually cement with a compressive strength of 55 MPa after 28 days, while the C sample is blended Portland cement with 30% slag, with compressive strength of 45 MPa after 28 days. The mineralogical composition of clinkers is shown in Table 1.

Measurements of hydration heat have been carried out in a differential microcalorimeter for all samples under the following conditions: mass sample = 4 g, $W/C = 0.5$, $T = 25°C$.

4. Result analysis

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, has been analysed by the PC software program [19] where the heat released $Q_{(t)}$ is calculated first, and then $\alpha_{(t)}$ is determined according to the Eq. 1. Fig. 2 shows the process of determining the transition time t_p when hydration control is taken over by another process. Values K_I and K_{I0} show a high deviation, which means it is necessary to find the time for which a satisfactory correspondence is achieved. The precision of determination of the time interval I directly affects the values of the rate constant for the subsequent process, i.e. K_D and K_{D0}, as can be immediately seen on the graphic display at the computer screen, so that a compromise solution is searched for. The most appropriate transition time is determined by inputting a series of values for time in the vicinity of the assumed t_p into the software program loop, and determining the most appropriate t_p on the basis of correspondence between the theoretical constants and constants determined from the experimental data.

Calculation of kinetic parameters based on the mathematical model starts with the determination of the time interval up to the point t_p where the NG process is the dominant one, according to Fig. 1. The control in choosing the optimum time for the t_p point is the standard deviation



TIME h	HYDRATION HEAT J /g	α
0.00	0.00	0.000
0.17	3.21	0.015
0.33	3.80	0.017

Fig. 2. Diagram of determination of kinetic parameters from microcalorimetrical measurements: (1) calculated $\alpha - t$ data, (2) kinetic analysis software, (3) differential microcalorimeter.

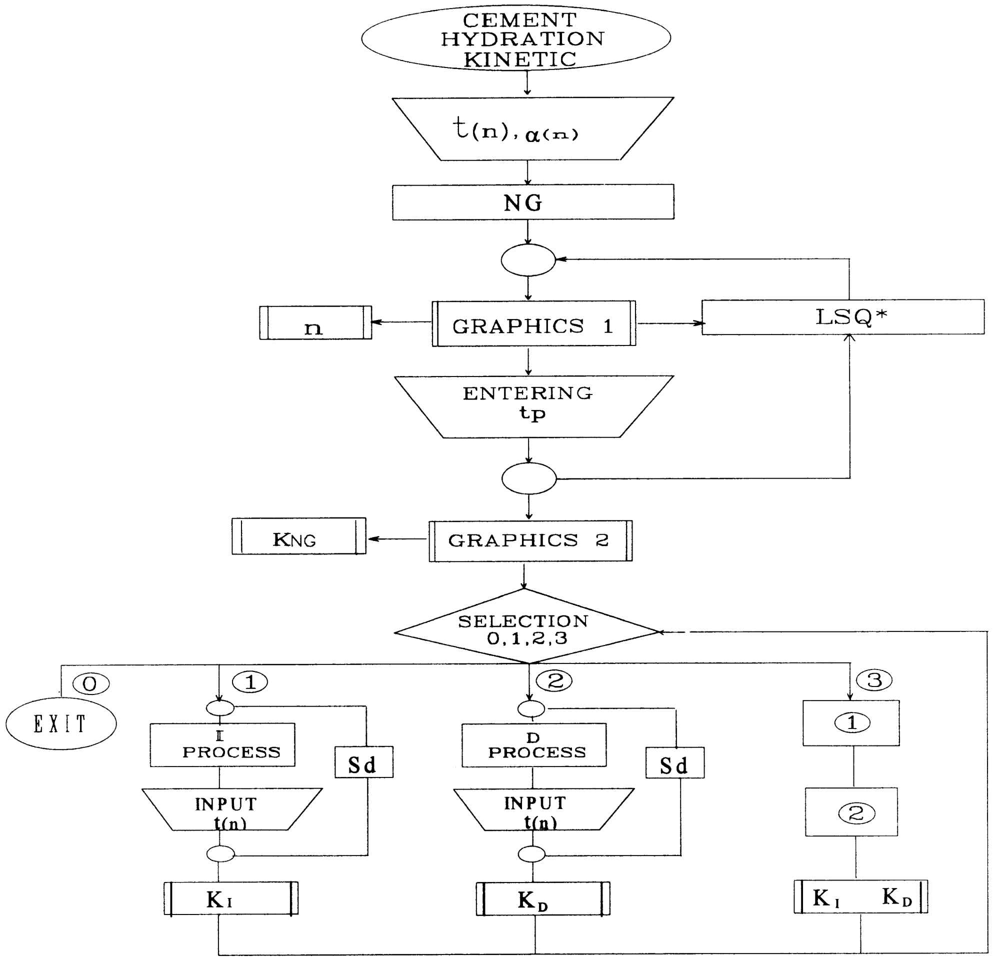


Fig. 3. A block diagram of the Q-BASIC program to determine kinetic parameters for the cement hydration process. *LSQ—a subroutine for the least square method. It is also included in the calculation of processes I and D, which has not been shown here for greater clarity.

which shows how precisely the data line on the straight line is drawn through the experimental data by means of the least square method. Once the t_p point has been determined, the program calculates the value of the exponent n and the rate constant K_{NG}. Now, a menu makes it possible to test the remaining $\alpha-t$ data after t_p, whereby determining the direction of the process according to data obtained for sd. In other words, selection is carried out for individual processes assumed and their domination is ascertained. The procedure can be seen in the flow diagram of the Basic "Kinetic Analysis" program shown in Fig. 3.

The kinetic parameters determined for samples A, B, and C are shown in Table 2. Three measurements were made for the sample C, so that the marks C1, C2, and C3 are used.

5. Discussion

Kinetic analysis of the early cement hydration stage is based on the mathematical model encompassing three basic dominant processes, NG, I, and D. The developed computer program [19] presents a determination of kinetic parameters

Table 2
Kinetic parameters determined by means of the mathematical hydration model "Kinetic Analysis"

	NG			I		D	
Sample	n	K_{NG} (h^{-1})	sd	K_I ($\mu m\ h^{-1}$)	sd	K_D ($\mu m^2\ h^{-1}$)	sd
A	1.7960	0.0313	0.0004	0.0190	0.0014	0.0002	0.0002
B	1.7510	0.0504	0.0058	0.0138	0.0015	0.0061	0.0014
C1	1.9230	0.0529	0.0092	0.0132	0.0014	0.0041	0.0013
C2	1.9680	0.0550	0.0077	0.0143	0.0013	0.0041	0.0066
C3	1.9240	0.0561	0.0010	0.0130	0.0021	0.0032	0.0013

for cement hydration by means of values obtained for hydration heat on alite and Portland cement samples of different compositions. The hydration heat has been determined by a differential microcalorimeter and the data have been gathered and processed up to 48 h. The computer software provided relevant kinetic data on all the parameters needed to define time intervals in which individual processes prevail. Values for kinetic parameters indicate that the first hours of hydration are dominated by the NG process. After that, the I process becomes the dominant process, followed by the D process.

A comparison of kinetic parameters for the examined cement samples from Table 2, with the clinker mineral alite as a referent sample, indicates essential differences in the systems examined. The values for the exponent n for alite and neat Portland cement (B) are relatively close, while the sample containing slag (C) has a much higher value of this exponent. This indicates that addition of slag to Portland cement greatly affects the crystal growth geometry. Values for K_{NG} for cement samples B and C are very similar, while this value for sample A differs to a great degree. This indicates that the polymineral composition of commercial cements greatly affects the nucleation and growth process. The standard deviation shows best agreement with the experimental data obtained for sample A, which could be expected, this being the pure clinker mineral. The values for the constants K_I indicate similarity in samples B and C as compared to sample A. The diffusion process is most indicative with regard to the values of the parameter K_D, the differences among individual samples being the largest there. A very low constant value up to 48 h characterizes alite, as well as a very small value of sd. For Portland cement samples, the constants are higher, but experimental data agree with the theoretical ones to a lesser degree as regards sd. Three measurements of the same cements samples marked C1, C2, and C3 indicate satisfactory reproducibility of values for all kinetic parameters observed, as well as the share of individual processes up to 48 h hydration (Fig. 4).

Initial hydration time has not been covered by the mathematical analysis because of measuring problems caused by small temperature differences between the cement paste and the water bath in the calorimeter [18]. The contribution of heat developed due to wetting and dissolving cement particles in contact with water or to reactions of the free CaO, MgO, and gypsum with water has not been provided for either. If Refs. [15,20,21] are considered, which had been obtained by mathematical analysis and the model for describing the process changes in hydration, which refer to individual clinker minerals, usually alite, a conclusion can be reached that the values in a real system such as cement show great differences relative to the composition and conditions for processing of data measured. Comparisons of values for all kinetic parameters calculated according to the hydration model presented indicate that the data are within the boundaries obtained by different techniques for determination of the reaction degree [1,20]. If parameters obtained for alite are compared to data according to Bezjak [15], where different exponents are considered for R ($R^{2/3}$, R, R^2) in the modified Eq. 4, the closest values for the constant K_D are for R^2. This indicates that although the radius of reacting particles is not taken into consideration, the value of $1/R^2$ is included in the value of the relative rate constant K_D, as has been assumed at the beginning $K_D = k_D/R^2$. It can be said that the results obtained, shown in Table 2, agree with the literature data if measuring conditions are taken into account.

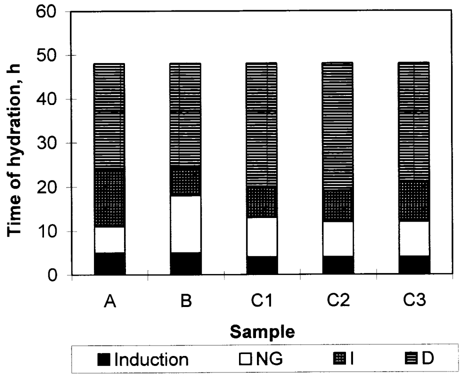


Fig. 4. Share of individual processes up to 48 h of hydration.

The comparison of measurements of different cement samples clearly indicates the difference in the share of individual processes (Fig. 4). The graphical representation adds to the kinetic data in Table 2 with regard to changes in individual hydration processes with time relative to the cement type and some of its properties. Individual processes take place simultaneously, but affect hydration rate and particles of different sizes in a different manner. The model presented has been simplified; only the possibility of determination of basic kinetic parameters by mathematical analysis of the resultant plot for heat released during hydration of commercial cement has been considered. Flexibility of the model provides for further extensions by addition of mathematical modules for various factors affecting cement hydration, such as particle size and distribution, addition of admixtures, etc.

A simple and relatively cheap technique that can be found in most cement production plants offers a perspective for research related to designing cement systems according to the requirements for the hydration process development based on a global experimental $Q-t$ plot, i.e. $\alpha-t$, which makes it possible to select the cement needed for specific purposes in a more exact way.

6. Conclusions

The method developed makes it possible to calculate kinetic parameters from microcalorimetrical measurements of cement hydration and to clearly differentiate the three basic hydration processes and separate them by their share in time.

The thermokinetic analysis can provide certain guidelines for further study of the hydration process development and changes in the values of kinetic parameters in individual periods.

For samples B and C, the most probable process sequence is NG → I → D. Reproducibility of measurements has been confirmed, and satisfactory agreement of kinetic parameters (n, K_{NG}, K_I, and K_D) has been obtained. The model used with cement samples in comparison to alite indicates that the results obtained are acceptable within certain limits.

The kinetic analysis described and the software program developed provide for a rapid and easy approach to modeling and determining individual development stages in early hydration periods and for cement samples, especially if factors affecting the early hydration are studied, which has been planned for supplementary research.

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