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KINETIC ANALYSIS OF THERMAL DECOMPOSITION OF $Ca(OH)_2$ FORMED DURING HYDRATION OF COMMERCIAL PORTLAND CEMENT BY DSC

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Abstract

In this paper, evaluation of kinetic parameters (the activation energy – *E*, the pre-exponential factor – *A* and the reaction order – *n*) with simultaneous determination of the possible reaction mechanism of thermal decomposition of calcium hydroxide (portlandite), $Ca(OH)_2$ formed during hydration of commercial Portland-slag cement, by means of differential scanning calorimetry (DSC) in non-isothermal conditions with a single heating–rate plot has been studied and discussed. The kinetic parameters and a mechanism function were calculated by fitting the experimental data to the integral, differential and rate equation methods.

To determine the most probable mechanism, 30 forms of the solid-state mechanism functions, $f(\alpha_c)$ have been tried. Having used the procedure developed and the appropriate program support, it has been established that the non-isothermal thermal decomposition of calcium hydroxide in the acceleratory period ($0.004<\alpha_c<0.554$) can be described by the rate equation: $d\alpha_c/dT=A/\beta\exp(-E/RT)f(\alpha_c)$, which is based on the concept of the mechanism reaction: $f(\alpha_c)=2(\alpha_c)^{1/2}$.

The mechanism functions as well as the values of the kinetic parameters are in good agreement with those given in literature.

Keywords: $Ca(OH)_2$–portlandite, DSC, kinetic parameters, non-isothermal kinetic, reaction mechanism, thermal decomposition

Introduction

Portland cement is a hydraulic binder, composed of a number of compounds that react with water, which leads to the setting and hardening of cement and formation of a compact solid state like stone. In Portland cement, tricalcium silicate (C_3S) is the main component of clinker. The hydration process of this compound may be represented as:

$$2C_3S+6H\rightarrow C_3S_2H_3+3CH \tag{1}$$

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where CH is the calcium hydroxide, and $C_3S_2H_3$ or the hydrated calcium silicate is the product that contributes to the strength and is related to the hydration properties.

Among the products of cement hydration, only calcium hydroxide, CH, is a compound of a precisely determined composition, so that its determination represents one of the ways to trace the development of the hydration process.

Various authors have shown thermal analysis techniques (TG/DTG, DTA, DSC) to be very reliable for estimating both the CH content of the set Portland cement [1–3], and the kinetic analysis of the hydration process [4, 5]. Recently, it has been shown that the activation energy of the decomposition of CH in isothermal and/or non-isothermal kinetics can be calculated by many methods that do not require knowledge of the reaction mechanism [4]. Numerous investigators have worked extensively on the kinetics of non-isothermal reaction due to the fact that both analytical and kinetic data can be obtained simultaneously from a single experiment in a short period of time [6]. Therefore, both the different mathematical methods and different approximation for the temperature integral have been developed and have often be used to obtain the kinetic parameters and the selection of the most possible mechanism function [7].

In [8] and [9], both Rongzu *et al.* and Jiaoqiang *et al.* have suggested that the kinetic parameters and the mechanism function of the thermal decomposition of organic materials can be obtained from the calculation of a single non-isothermal DSC curve by the integral, by the differential, and by the rate reaction methods. Validity and good applicability of the applied kinetic model, the authors have judged by estimating a linear correlation coefficient ($r>0.99$) and variance ($Q<0.1$).

Urbanovici *et al.* [10] have developed an improved iterative version of the Coats–Redfern method of evaluation non-isothermal kinetic parameters by introducing both a more accurate approximation for the temperature integral and a supplementary static criterion for the selection of the most probable mechanism function. The authors have applied a new method successfully on the non-isothermal dehydration of $Mg(OH)_2$.

The present paper describes the treatment of experimental data obtained by means of a single non-isothermal DSC curve in order to establish the kinetic parameters with simultaneous determination of the possible reaction mechanism of thermal decomposition CH, formed during the Portland cement hydration.

The method, given by Rongzu *et al.* [8], has been applied for the kinetic analysis of the CH dehydration.

In order to determine the possible reaction mechanisms of thermal decomposition of the CH, 30 different kinetic functions of the most common mechanisms in solid-state reactions have been tested. To obtain the kinetic parameters (values of E and A), the integral method, Eq. (2), the differential method, Eq. (3), and the change of enthalpy rate at time, t (or rate equation method), Eq. (4), were used [8, 9]:

$$\ln\left[\frac{G(\alpha_{\mathrm{i}})}{T_{\mathrm{i}}-T_0}\right]=ln\left[\frac{A}{\beta}\right]-\frac{E}{RT_{\mathrm{i}}} \tag{2}$$

$$\ln\left[\frac{(\mathrm{d}\alpha/\mathrm{d}T)_{\mathrm{i}}}{f(\alpha_{\mathrm{i}})[E(T_{\mathrm{i}}-T_0)/RT^2+1]}\right]=ln\left[\frac{A}{\beta}\right]-\frac{E}{RT_{\mathrm{i}}} \tag{3}$$

$$\ln\left[\frac{\mathrm{d}H_{\mathrm{t}}}{\mathrm{d}t}\right]_{\mathrm{i}}=\ln\left\{AH_0 f(\alpha_{\mathrm{i}})\left[1+\frac{E}{RT_{\mathrm{i}}}\left(1-\left[\frac{T_0}{T_{\mathrm{i}}}\right]\right)\right]\right\}-\frac{E}{RT_{\mathrm{i}}} \tag{4}$$

where $G(\alpha_{\mathrm{i}})$ is the integral mechanism function, T_{i} is the temperature (K) at time t, defined as: $T_{\mathrm{i}}=T_0+\beta t$; T_0 is the initial point at which the DSC curve deviates from the baseline; β is the linear heating rate ($\mathrm{d}T/\mathrm{d}t$); R is the gas constant; (α_{i}) is the conversion degree; $f(\alpha_{\mathrm{i}})$ is the differential mechanism function; $\mathrm{d}H_{\mathrm{t}}/\mathrm{d}t$ is the change of enthalpy rate at time, t from DSC curve; H_0 is the total enthalpy change of the substance (corresponding to the global area under the DSC curve); H_{t} is the reaction heat in a certain time (corresponding to the partial area under the DSC curve); E and A are the activation energy and pre-exponential factor of decomposition of materials, respectively.

Equation (2) has been derived on the basis of the assumption that kinetic law in isothermal kinetic analysis is also valid for non-isothermal cases [8, 9].

The present work has further developed and improved the applied method by introducing the standard deviation, SD as additional criteria for the evaluation of correspondence of theoretical equations with experimental data. The reaction kinetics was examined only for the acceleratory period of the CH decomposition. The analysis is derived on the basis of the assumption that most probably is a multi-step process that is controlled by the rate of the slowest step [11].

Experimental

A commercial, Portland-slag cement (supplied by the Dalmacijacement Coo., Croatian) was used to prepare the hydrated cement paste at water to cement ratio (W/C) of 0.5 and at a temperature of 293 K. After 11 h, the hydration process was stopped by crushing the samples, by washing them with acetone and by vacuum drying at room temperature. After drying, the sample was sieved. The grain size of sample was smaller than 0.060 mm.

DSC curves were obtained using about 5.20±0.05 mg of cement paste samples in a differential scanning calorimeter (DSC-4, Perkin Elmer Co., Norwalk, Connecticut, USA), which includes a thermal analysis microprocessor controller and model 3700 Data Station (TADS), and a graphics Plotter 2. The sample was heated at a rate of 20.0 K min^{-1} under a nitrogen flow of 20 cm^3 min^{-1} 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 693–783 K was computed. TADS, DSC-4 Kinetics Software Program was used for the calculation of the conversion degree, α_{c}. The value of α_{c} is defined as the ratio of change of the partial enthalpy, $\Delta H_{\mathrm{partial}}$ in temperature T and the total enthalpy change, $\Delta H_{\mathrm{total}}$. The values of $\Delta H_{\mathrm{partial}}$ and $\Delta H_{\mathrm{total}}$ are evaluated from the area under the DSC curve [12].

Due to the large amount of data produced for each experiment as well as the variety of available methods, computer programs were needed to carry out kinetic analysis. The commercial mathematical software MATHCAD 7, which had been used to create the model algorithm, was used for kinetic calculations and testing the models.

Results and discussion

Figure 1 shows the DSC curve of thermal decomposition of Ca(OH)$_2$, where T_0 is the temperature at the first deflection of the curve from the base line, T_m shows the maximum change of the enthalpy, and at T_f the curve has returned to the base line.

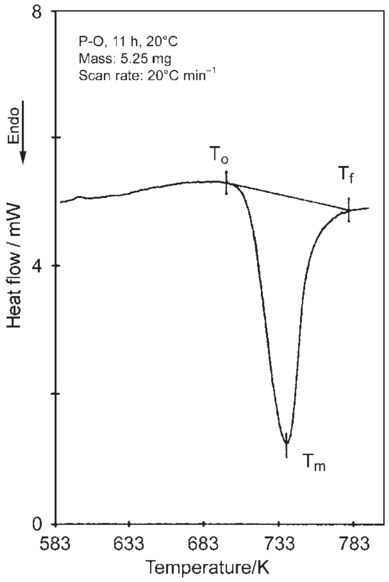

Fig. 1 DSC curve of thermal decomposition of Ca(OH)$_2$ in the temperature range of 697–783 K. The symbols are described in the text

Dependence of the change of enthalpy rate at time, t (dH/dt) on temperature, T, (from DSC curve, Fig. 1) was used to calculate variables needed to describe the reaction system kinetically, and to determine their dependence both on temperature, T, and on time, t. The original experimental data of thermal decomposition of Ca(OH)$_2$ determined by a single heating DSC curve in the temperature range of 693–783 K and heating rate of 20.0 K min^{-1} are presented in Table 1.

Figures 2 and 3 show the curves $\alpha_c=f(T)$ and $(d\alpha_c/dT)=f(\alpha_c)$ respectively. As can be seen from Fig. 2, the $\alpha_c=f(T)$ curve is a sigmoidal in shape which is characteristic for the reaction with zero-starting rate. The plot of the reaction rate $(d\alpha_c/dT)$ *vs.* α_c (Fig. 3) shows a maximum values of reaction rate, $(d\alpha_c/dT)_i$ for $(\alpha_c)_i$ values between 0.004 to 0.544.

Table 1 Data on thermal decomposition of $Ca(OH)_2$ determined by DSC

Data point, *N*	T_i/K	α_c/–	$(dH_t/dt)i$/mJ s^{-1}	$(d\alpha_c/dT)_i \cdot 10^3$/$K^{-1}$
1	711.25	0.004	0.148	1.230
2	719.87	0.045	1.037	8.630
3	727.06	0.154	2.420	20.140
4	734.24	0.349	4.050	33.700
5	739.99	0.554	4.590	38.200
6	747.03	0.792	2.810	23.380
7	754.22	0.908	1.430	11.900
8	761.40	0.961	0.590	4.910
9	768.59	0.987	0.250	2.080

T_0=704.06 K; H_0=360.8 mJ; β=0.333 K s^{-1}

The fact that the maximal rate of $Ca(OH)_2$ decomposition is achieved at a degree of conversion about of 0.50, may indicate that the overall decomposition process of $Ca(OH)_2$ may be viewed as a two- or more-stage reaction [11].

It is known that in the case of the solid phase reactions of the type solid→ solid+gas, a decomposition reaction often begins under kinetic control and then, as a surface layer of the solid products grows, the diffusion of a gaseous product becomes the rate-limiting step of the decomposition [11].

Generally speaking, thermal dehydration of hydrate is a reversible reaction and is influenced by the product phase, because such a residual material more or less, tends to diminish the rate of the water diffusion from the reaction interface. It means, that the rate of thermal dehydration of hydrate, as well as the course of the reaction

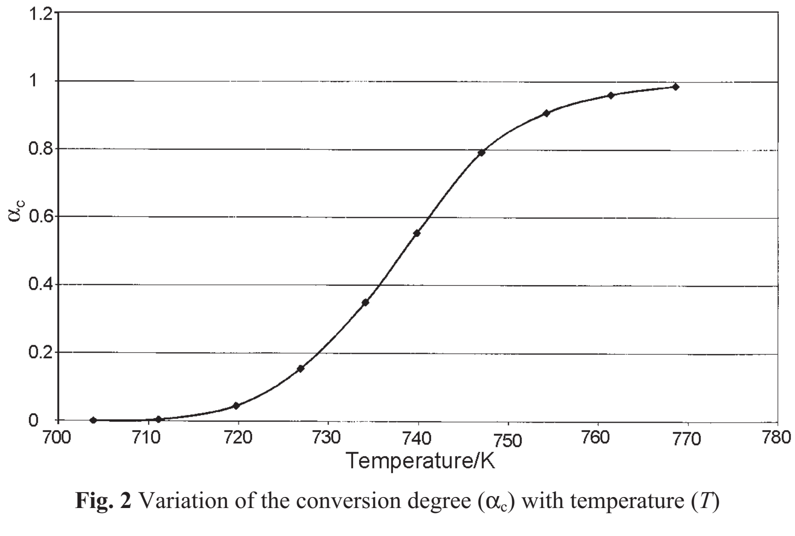

Fig. 2 Variation of the conversion degree (α_c) with temperature (*T*)

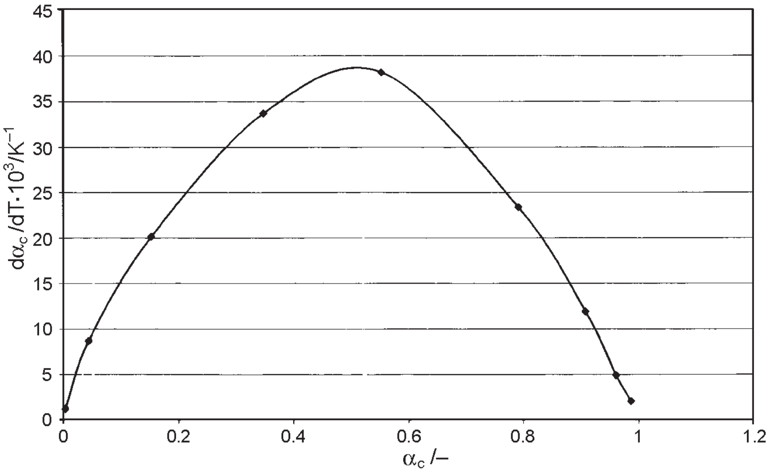

Fig. 3 Plot of the reaction rate $d\alpha_c/dT$ *vs.* α_c,

may be greatly affected by the experimental conditions, such as the sample size, the natural of atmosphere, the crucible shape and the heating rate [6].

In this study, the acceleratory period on the ($d\alpha_c/dT$) – T curve of the $Ca(OH)_2$ decomposition was kinetically analysed for checking the applied model [8]. Evolution of the kinetic parameters is made for N=5 data points (α_c, T) with the degree of conversion ranging from 0.004 to 0.544 (Table 1). The data were fitted to the integral and the differential equations, Eqs (2)–(3), by the linear least-squares and by the iterative methods, respectively.

The kinetic analysis data [13] showed that the calculated E and $\ln(A/\beta)$ values varied from 2934.00 to 57.60 kJ mol^{-1}, and from 473 to 5.59 K^{-1} respectively, depending on the solid-state mechanism functions that have been used. In order to select the most probable mechanism function, the linear correlation coefficient, r, and the variance, Q, were used as criteria for the validity and applicability of the considered kinetic models.

The results show when all conditions (the values of E and A are in the usual range of the thermal decomposition parameters for the $Ca(OH)_2$: E=127.54–155.05 kJ mol^{-1}; $\ln(A/\beta)$=16.95–21.58 K^{-1}, and the linear correlation coefficient, $r>0.99$ and the variance, $Q<0.1$) are satisfied at the same time, the most probable mechanism function is given by different kinetic functions, as follows: by the equations for diffusion – controlled, labelled D3 and Dn (for n=1/2); by the Avrami–Erofeev (growth of nuclei) for n=2, labelled A2; and by the Mampel power law for m=2, labelled P2 (Table 2).

By substituting the most probable mechanism functions (D3; Dn; A2 and P2) into Eq. (4), the proper values of E, and A are calculated by combined dichotomous and least-squares methods.

Table 2 Results of kinetic analysis of the CH thermal decomposition data calculated by Eqs (2), (3) and (4), which fit the applied criteria (r, Q) best

Function	Eq. (2)		Eq. (3)		Eq. (4)	
	E/kJ mol^{-1}	ln(A/β)/K^{-1}	E/kJ mol^{-1}	ln(A/β)/K^{-1}	E/kJ mol^{-1}	ln(A/β)/K^{-1}
D3	145.49	19.42	140.90	15.90	148.10	8.10
Dn	140.84	18.84	143.60	13.44	143.40	7.84
A2	155.05	21.58	151.80	20.93	155.90	8.90
P2	127.54	16.95	95.84	9.19	125.60	6.70

From the data presented in Table 2, it can be seen that very different kinetic models (D3; Dn; A2 and P2) provide the most approximate values for E and A. No significant differences were found between the activation energies calculated from the same kinetic function mechanisms by different mathematical approaches. The exception has shown only the E value of the P2 model obtained by differential method, Eq. (3). This result confirmed the problem of uniqueness and proves that it is impossible to select unambiguously the kinetic function obeyed by the reaction. An additional problem arises from the fact that in all cases different kinetic equations appear to fit the same set of kinetic data, and it is not possible to select the most appropriate one [6].

Consequently, we conclude that the applied criterion (r, Q) is not adequate for selecting the most possible mechanism reaction. From this reason we have further developed and improved this method, taken from [8], by introducing the standard deviation, SD as the additional criterion for validity and good applicability of kinetic models.

Table 3 Values of the standard deviation (SD) calculated by the least mean squares method according to Eqs (2) and (3) for the functions P2, D3, Dn (n=1/2) and A2

	Parameters/Functions	P2	D3	Dn	A2
Eq. (2)	E/kJ mol^{-1}	127.54	145.49	141.04	155.05
	A/s^{-1}	$7.58\cdot10^6$	$8.96\cdot10^7$	$5.01\cdot10^7$	$7.77\cdot10^8$
	SD	$1.0\cdot10^{-3}$	$3.0\cdot10^{-3}$	$2.0\cdot10^{-3}$	$3.0\cdot10^{-3}$
	r	0.970	0.986	0.982	0.991
	Q	0.094	0.118	0.112	0.113
Eq. (3)	E/kJ mol^{-1}	95.86	140.90	143.60	151.80
	A/s^{-1}	$3.23\cdot10^3$	$2.65\cdot10^6$	$2.26\cdot10^5$	$4.05\cdot10^8$
	SD	$6.0\cdot10^{-3}$	$7.0\cdot10^{-3}$	$7.0\cdot10^{-3}$	$3.0\cdot10^{-3}$
	r	0.721	0.933	0.936	0.967
	Q	0.072	0.124	0.091	0.133

From SD data presented in Table 3, the kinetic function P2 has been found to be the most appropriate one.

Therefore, the most appropriate rate equation for non-isothermal decomposition of $Ca(OH)_2$ in initial stage of reaction ($0.004<\alpha_c<0.554$), can be described by the following kinetic equation:

$$d\alpha_c/dT=A/\beta\exp(-E/RT)f(\alpha_c) \tag{5}$$

which is based on the concept of the reaction mechanism which can be described by a power law:

$$f(\alpha_c)=2(\alpha_c)^{1/2} \tag{6}$$

Those results are in agreement with literature data of the mechanism model of the calcium hydroxide decomposition [14]. The model includes both the processes in which the crystal lattice structure is destroyed and the chemical reactions, resulting in the formation of new reaction products. The rate-limiting step of the decomposition reaction is characterised by instantaneous nuclei product formation and its growth, which occurs in the area with enhanced reactivity, referred to as the reaction interface or the boundary between the reactant and the product.

On the other hand, taking SD values into account that were low and very close for the all appropriate kinetics models (Table 3), it may be suggested that the dehydration of $Ca(OH)_2$ involves all three different mechanisms controlling the reaction rate, i.e. different processes may act simultaneously but the slowest one is limiting or controlling [15]. Therefore, further research is certainly needed to fully elucidate the factors influencing our observation. Moreover, contribution to the kinetic analysis will be necessary to find both mechanistic models of the rate-controlling processes proceeds one after other, and a criterion for determination of the transition times of one process into other. Details will be given in our next publication.

Taking into account the calculated kinetic data of E=127.00 kJ mol^{-1} and A=7.58·10^{6} s^{-1}, given in Tables 2 and 3, it may be concluded that the values are in good agreement with literature data (the theoretical values of E=120.00 kJ mol $^{-1}$).

Chen *et al.* [4] have studied the kinetics of decomposition of commercial CH from the single heating-rate curve obtained by means non-isothermal thermogravimetric analysis by both differential and integral methods. Their calculated E and A values (E=152.42–98.90 kJ mol^{-1}, and A=5.2·10^{9}–3.13·10^{5} s^{-1}, and E=149.88–96.42 kJ mol^{-1}, and A=2.75·10^{9}–1.69·10^{5} s^{-1} respectively) agree perfectly with our results. But, they could not accurately describe the method that would lead to the selection of the correct reaction mechanism.

Chen and Dallimore [5] calculated the E value of CH formed in hydration of pure tricalcium silicate, C_3S by using simultaneously thermogravimetry and differential thermogravimetry (TG/DTG) employing the Kissinger method. Their E values are 139.68–159.04 and 135.84–146.85 kJ mol^{-1}, respectively. This is comparable with E=157.00 kJ mol^{-1}, calculated from non-isothermal thermogravimetric data (TG) in the cement–water system [13] obtained by Freeman and Carroll's method [16]. But, neither one of the above-mentioned methods [4, 5, 13, 16], which have been used in calculating the activation energy values, require knowledge of the reaction mechanism.

However, the described approach to the kinetic analysis of CH decomposition and the results obtained here may provide better insight into the range of these kinetic parameters, as well as the information on the reaction mechanisms.

It should also be mentioned when Eqs (2)–(4) are applied, no single mathematical method yields results that would be more exact (or the most correct) than those obtained by other methods, but those exact results are distributed over all the methods used. Therefore, after previous development of the accompanying mathematical software, we suggested that they be used simultaneously.

Conclusions

This study indicates that the non-isothermal decomposition of $Ca(OH)_2$ upon given experimental condition is initially kinetically controlled, and characterised by a maximum reaction rate values for $0.004<\alpha_c<0.544$. Kinetic parameters and mechanism functions were obtained by the integral, differential and rate equation methods.

Having used the procedure developed and the appropriate program support, it has been established that different kinetic functions (D3; Dn; A2 and P2) yield approximately the same values for the activation energy (E) and pre-exponential factor (A), and meet best the pre-defined criteria (the linear correlation coefficient, $r>0.99$ and variance, $Q<0.1$), so it is not possible to determine exactly which kinetic model is the most appropriate one to describe the possible reaction mechanism.

By introducing the mean standard deviation (SD) as the additional criterion for validity and good applicability of kinetic models, the kinetic function P2 has been found to be the most appropriate one.

That means that the initial, acceleratory period of the non-isothermal thermal decomposition of $Ca(OH)_2$ can be described by the rate equation of the form: $d\alpha_c/dT=A/\beta\exp(-E/RT)f(\alpha_c)$, which is based on the power-law reaction mechanism: $f(\alpha_c)=2(\alpha_c)^{1/2}$.

The values calculated for the activation energy, $E=127.00$ kJ mol^{-1}, and for the pre-exponential factor, $A=7.58\cdot10^6$ s^{-1}, as well as the reaction mechanism function obtained corresponded to literature data.

References

1 V. S. Ramachandran, Cem. Concr. Res., 9 (1979) 677.
2 H. G. Midgley, Cem. Concr. Res., 9 (1979) 77.
3 B. E. I. Abdelrazig, D. G. Bonner and D. V. Nowell, Thermochim. Acta, 145 (1989) 203.
4 D. Chen, X. Gao and D. Dollimore, Analytic Instrument., 20 (1992) 137.
5 D. Chen and D. Dollimore, J. Thermal Anal., 44 (1995) 1001.
6 A. Ortega, Thermochim. Acta, 298 (1997) 205.
7 K. N. Ninan, J. Thermal Anal., 35 (1989) 1267.
8 Hu Rongzu, Y. Zhengquan and L. Yanjun, Thermochim. Acta, 123 (1988) 135.
9 Z. Jiaoqiang, Hu Rongzu, Z. Chunhua, F. Guofu and L. Quihe, Thermochim. Acta, 298 (1997) 31.

10 E. Urbanovici, C. Popescu and E. Segal, J. Therm. Anal. Cal., 58 (1999) 683.
11 S. Vyazovkin and C. A. Wight, Annu. Rev. Phys. Chem., 48 (1997) 125.
12 Instruction for the TADS, DSC-4 Kinetics Software Kit, No. 0419-0332, Perkin Elmer, Norwalk, CT, 1986.
13 J. Zelić, PhD Thesis, University of Split, Split 1997.
14 M. Anić and N. Colović, Kinetics of a heterogeneous reaction, (Ed.) E. Kardelj Institute, Prosveta Press, Niš 1983, p. 364. (in Serbo-Croatian).
15 A. Bezjak, Cem. Concr. Res., 16 (1986) 605.
16 E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.