

Technical Note

Kinetic study of the thermal decomposition of calcium carbonate by isothermal methods of analysis

I. Halikia*, L. Zoumpoulakis, E. Christodoulou, D. Prattis

National Technical University of Athens (NTUA), Department of Mining and Metallurgical Engineering, Section of Metallurgy and Materials Technology, Laboratory of Metallurgy, 9 Heroon Polytechniou Str., Zografou Campus, 15780 Athens, Greece

Received 12 June 2001; accepted 15 November 2001

ABSTRACT

In the present study, isothermal methods of kinetic analysis are used to investigate the kinetics of the thermal decomposition of calcium carbonate. Thermogravimetric analyzer experiments were carried out in standard temperature values. In order to determine the decomposition mechanism and the conversion function form that governs it, four different methods of isothermal kinetic analysis were used. The kinetic model that was found to better fit the experimental results was that of phase boundary controlled reaction. The activation energy was evaluated from the Arrhenius plots, as well as by applying an alternative method, and the results confirmed the predominance of the chemical mechanism. © 2001 SDU. All rights reserved.

Keywords: Calcium carbonate; Thermal decomposition; Isothermal methods; Kinetic analysis; Decarbonisation

1. INTRODUCTION

The general eq. (1) demonstrates the kinetics of many solid-state reactions:

$$f(\alpha) = k t, \quad (1)$$

where α is the fraction reacted in time t and the function $f(\alpha)$ depends on the reaction mechanism and the geometry of the reactive particles.

Two alternative methods (Tang et al., 1980; Jerez et al., 1987) have been used in kinetic investigations of the thermal decomposition and other reactions of solids: In one, yield-time ($a-t$) measurements are made while the reactant is maintained at a constant (known) temperature (isothermal method) while in the second, the sample is subjected to a controlled rising temperature (nonisothermal method). Measurements using both techniques have been used widely for the determination of kinetic characteristics and parameters.

The rate-determining step in any solid-phase reaction (Bamford and Tipper, 1980) can be either (i) diffusion, i.e. the transportation of participants to, or from, a zone of preferred reaction, or (ii) a chemical reaction, i.e. one or more bond redistribution steps, generally occurring at a reaction interface. Intermediate behavior and transition regions from one type to the other, are also known. These two fundamental processes are based on the assumption that, initially, surface diffusion rapidly coats the surface of the reacting particle with a continuous product layer. There is, however, another approach that considers the nucleation of products at active sites and the rate at which the nucleated particles grow (Bamford and Tipper, 1980; Garner, 1955).

* Corresponding author. E-mail: halikia@metal.ntua.gr

According to this state, the known kinetic functions $f(\alpha)$ have been classified into three groups: the diffusion, the chemical reaction, and the nucleation model. Features of yield-time curves for reactions of solids are of characteristic sigmoid shape, as can be seen from Figure 1 (Bamford and Tipper, 1980), a generalised reduced-time plot in which time values have been scaled to $t_{0.5} = 1.00$ when $\alpha = 0.50$. A refers to the initial reaction, sometimes with the decomposition of impurities or unstable superficial material. B represents the induction period, usually regarded as being terminated by the development of stable nuclei (often completed at low value of α). C is the acceleratory period of growth of such nuclei, perhaps accompanied by further nucleation, and which extends to the maximum rate of reaction at D. Thereafter, the continued expansion of nuclei is no longer possible, due to the impingement and consumption of reactant and this leads to the deceleratory or decay period, E, which continues until completion of reaction, F. One or more of these stages (except D) may be absent or negligible; variations in their relative importance results in the appearance of a wide variety of different types of kinetic behavior.

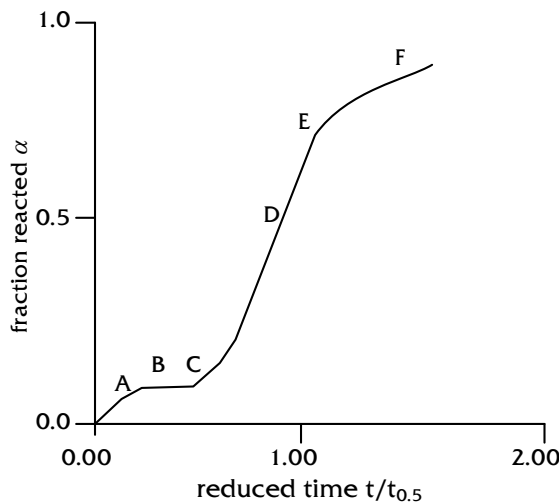


Figure 1. Generalized α - t plot summarizing characteristic kinetic behavior observed for isothermal decomposition of solids. There are wide variations in the relative significance of the various stages (distinguished with the letters above). Some stages may be negligible or even, absent and many reactions of solids are deceleratory throughout. A, initial reaction (often deceleratory); B, induction period; C, acceleratory period; D, point of inflection at maximum rate (in some reactions there is an appreciable period of constant rate); E, deceleratory (or decay) period; and F, completion of reaction

In isothermal techniques many methods of kinetic analysis have been used for determining the reaction mechanism, i.e. the kinetic model $f(\alpha)$. In this paper, the most commonly methods for isothermal kinetic analysis are used in order to determine the mechanism of CaCO_3 decomposition using thermogravimetric analyzer, and evaluate the activation energy.

2. LITERATURE REVIEW

Calcium carbonate is a widely known raw material for the metallurgical industry, ceramics and refractories. It is an industrial mineral being used in a variety of applications. A lot of studies have been performed in various experimental conditions regarding the CaCO_3 thermal decomposition. Critical factors that are known to influence the kinetic parameters are: the sample weight, the applying pressure and inert atmosphere, the impurities content, the use of isothermal or non-isothermal method and the rate of temperature increase.

Ninan et al. (1991) using thermogravimetric data found the equation: $1-(1-\alpha)^{1/2} = kt$ to be representative of the kinetics of CaCO_3 thermal decomposition, although they have reported values of activation energy E varying between 167.5 and 3768 kJ/mol depending on the experimental conditions.

Zcako and Arz (1974) have proposed a relationship between the activation energy E and A valid for specific thermal decomposition conditions and they have evaluated E between 113 and 204 kJ/mol. Guler et al. (1982) proposed also the relationship $A = f(E)$, while Gorbachev (1976) correlated the sample weight with the prediction of A and E .

Ray (1982) determined the activation energy between 100 and 4000 kJ/mol and A varying between 10^2 and 10^{69}s^{-1} , while Altortter (1978) estimated E between 220 and 348 kJ/mol.

Criado et al. (1995) studied the influence of carbon dioxide pressure on the thermal decomposition kinetics of calcium carbonate and determined the Arrhenius parameters using a correcting factor that takes into account the CO_2 pressure. Criado et al. (1977) in another study, suggested the phase boundary contacting volume (R_3) model $f(\alpha) = (1-\alpha)^{2/3}$ for the CaCO_3 decomposition under vacuum. Perez-Maqueda et al. (1996) proposed a new method for discriminating between kinetic models for solid-state reactions using a single constant-rate thermal analysis (CRTA) experiment. Finally, Maciejewski (2000) introduced computational methods for kinetic analysis.

3. EXPERIMENTAL

A Perkin-Elmer, TG₂, thermogravimetric analyzer was used to carry out the isothermal CaCO_3 decomposition experiments. The thermogravimetric analyzer consisted of the following units: a furnace with an inert atmosphere, a microprocessor controller, a heat and balance controller and an interface that connected the furnace with a computer and a plotter. The CaCO_3 material used was of high purity grade, with impurities lower than 0.3%. In order to determine the temperature values for the study of the decomposition kinetics, a thermogravimetric experiment was made in a CaCO_3 sample, as a function of temperature (Figure 2). It was apparent, that decomposition takes place between 635°C and 865°C. So, the temperatures of 637°, 650°, 700°, 750°, 800°, 850° and 870°C were selected for the tests, with initial sample weight of 14.9696, 19.3014, 19.3014, 18.5352, 20.2720, 19.2728 and 18.7154 mg, respectively. The applying atmosphere was nitrogen.

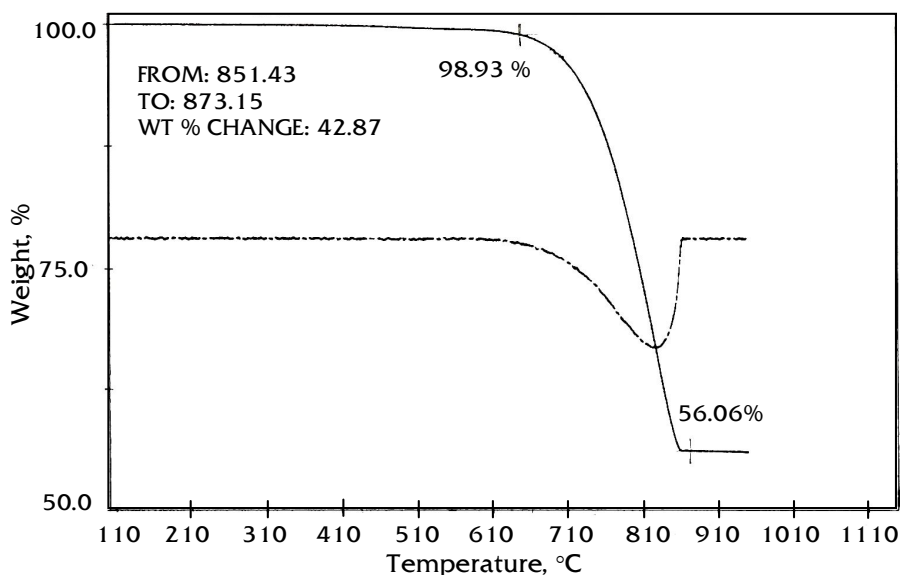


Figure 2. Weight loss versus temperature for the thermal decomposition of CaCO_3

4. RESULTS AND DISCUSSION

CaCO₃ decomposes to CaO and CO₂ according to the following eq. (2):



The data of percent weight loss vs. time, produced by the analyzer for the temperatures examined were used as the basis, for the calculation of the fraction reacted (α) in time t , according to eq. (3):

$$a = \frac{m_t}{m_0} \quad (3)$$

where m_t is the percent weight loss in time t and m_0 the theoretical total weight loss (44%).

The plots of fraction reacted α vs. t for the temperature values examined are presented in Figure 3.

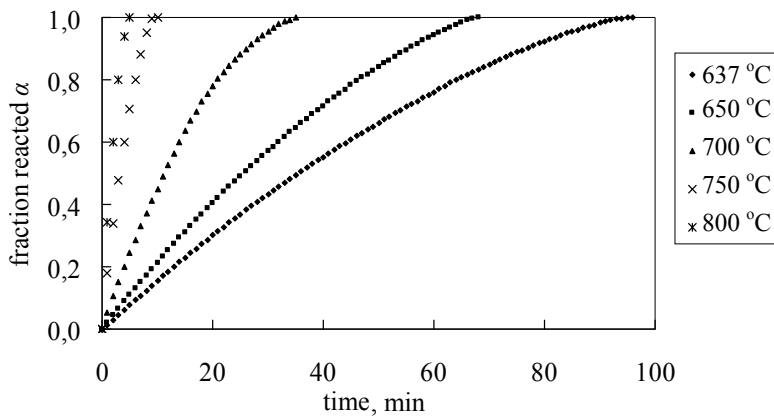


Figure 3. Fraction reacted (α) vs. time for the thermal decomposition of CaCO₃ at various temperature values

The rate of reaction ($d\alpha/dt$), given by eq. (4):

$$da / dt = \frac{m_t / \text{min}}{m_0} \quad (4)$$

was determined as a function of time for each temperature value. In Figure 4, a typical graphical representation of da/dt vs. time t is given for $T=637^\circ\text{C}$.

These experimental data were further kinetically treated and analysed in order to determine the controlling mechanism and the underlying equations.

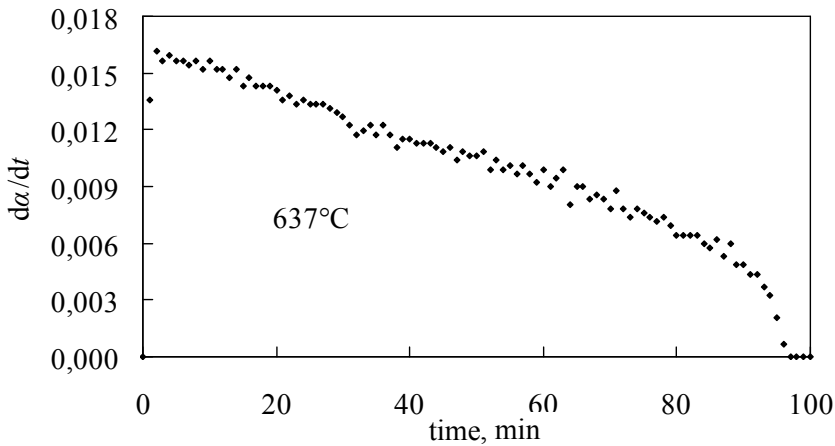


Figure 4. Rate of reaction ($d\alpha/dt$) vs. time for the thermal decomposition of CaCO₃ at $T=637^\circ\text{C}$

4.1. Kinetic analysis

In order to proceed with the kinetic analysis of the experimental data, the following methods were used (Halikia et al., 1998):

First method: This method compares the experimental data, in the form of fraction reacted α vs. time $t/t_{0.5}$ (Table 3) at definite α levels, with well-known calculated data for the most commonly used solid-state reaction equations (Table 1), as presented in Table 2 by Sharp et al. (1996).

Table 1
 Values of "n" for the most commonly used solid-state reaction equations

Kinetic equation	Values of "n" *
D ₁ : $\alpha^2 = kt$	0.62
D ₂ : $(1-\alpha)\ln(1-\alpha) + \alpha = kt$	0.57
D ₃ : $[1-(1-\alpha)^{1/3}]^2 = kt$	0.54
D ₄ : $1-(2/3)\alpha-(1-\alpha)^{2/3} = kt$	0.57
F ₁ : $-\ln(1-\alpha) = kt$	1.00
R ₂ : $1-(1-\alpha)^{1/2} = kt$	1.11
R ₃ : $1-(1-\alpha)^{1/3} = kt$	1.07
Zero order: $\alpha = kt$	1.24
A ₂ : $[-\ln(1-\alpha)]^{1/2} = kt$	2.00
A ₃ : $[-\ln(1-\alpha)]^{1/3} = kt$	3.00
Prout: $-\ln(\alpha/1-\alpha) = kt$	
Tompkins: $\ln(\alpha/1-\alpha) = k \ln t$	

* "n" is the slope of the line described by Eq. 5

Table 2
 Values of α and $t/t_{0.5}$ for the most commonly used solid-state equations

α	D ₁ (α)	D ₂ (α)	D ₃ (α)	D ₄ (α)	F ₁ (α)	R ₂ (α)	R ₃ (α)	A ₂ (α)	A ₃ (α)
0.1	0.040	0.033	0.028	0.032	0.152	0.174	0.165	0.390	0.533
0.2	0.160	0.140	0.121	0.135	0.322	0.362	0.349	0.567	0.685
0.3	0.360	0.328	0.395	0.324	0.515	0.556	0.544	0.717	0.801
0.4	0.640	0.609	0.576	0.595	0.737	0.768	0.762	0.858	0.903
0.5	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.6	1.440	1.521	1.628	1.541	1.332	1.253	1.277	1.150	1.097
0.7	1.960	2.207	2.568	2.297	1.737	1.543	1.607	1.318	1.198
0.8	2.560	3.115	4.051	3.378	2.322	1.887	2.014	1.524	1.322
0.9	3.240	4.363	6.747	5.028	3.322	2.334	2.062	1.822	1.492

Table 3
 Experimental values of α vs. $t/t_{0.5}$ for the thermal decomposition of CaCO₃ at definite α levels

Temperature, °C									
637		650		700		750		800	
α	$t/t_{0.5}$	α	$t/t_{0.5}$	α	$t/t_{0.5}$	α	$t/t_{0.5}$	α	$t/t_{0.5}$
0.093	0.169	0.109	0.195	0.105	0.179	0.599	1.250	0.600	1.250
0.108	0.197	0.193	0.350	0.199	0.357	0.705	1.563	0.798	1.875
0.200	0.366	0.214	0.389	0.287	0.536	0.799	1.875		
0.301	0.563	0.293	0.545	0.411	0.804				
0.395	0.761	0.312	0.584	0.490	0.982				
0.409	0.789	0.404	0.778	0.600	1.250				
0.494	0.986	0.506	1.012	0.699	1.518				
0.506	1.014	0.601	1.245	0.803	1.875				
0.597	1.239	0.703	1.518	0.900	2.321				
0.608	1.268	0.794	1.790						
0.693	1.493	0.807	1.829						
0.702	1.521	0.895	2.140						
0.798	1.803	0.905	2.179						
0.807	1.831								
0.895	2.141								
0.903	2.169								

Table 4
 Results of the comparison between $(t/t_{0.5})_{exp}$ and $(t/t_{0.5})_{theor}$ as obtained by the least-squares method

Kinetic Equation	Temperature, °C														
	637			650			700			750			800		
	R ²	Slope	Intercept	R ²	Slope	Intercept	R ²	Slope	Intercept	R ²	Slope	Intercept	R ²	Slope	Intercept
D ₁ (a)	0.9850	0.5963	0.3087	0.9836	0.5924	0.3177	0.9904	0.6349	0.2871	0.9982	0.5571	0.4560	1	0.5580	0.4464
D ₂ (a)	0.9525	0.4425	0.4093	0.9478	0.4388	0.4187	0.9669	0.4724	0.3908	0.9934	0.3895	0.6741	1	0.3921	0.6536
D ₃ (a)	0.8802	0.2827	0.5266	0.8708	0.2795	0.5365	0.9052	0.3044	0.5126	0.9833	0.2537	0.8653	1	0.2579	0.8301
D ₄ (a)	0.9295	0.3837	0.4532	0.9231	0.3801	0.4628	0.9482	0.4115	0.4362	0.9895	0.3367	0.7528	1	0.3402	0.7257
F ₁ (a)	0.9610	0.6375	0.2538	0.9550	0.6318	0.2650	0.9753	0.6819	0.2246	0.9889	0.6244	0.4407	1	0.6313	0.4091
R ₂ (a)	0.9982	0.9328	0.0404	0.9966	0.9265	0.0512	0.9994	0.9911	0.0037	0.9975	0.9834	0.0276	1	0.9858	0.0148
R ₃ (a)	0.9852	0.9517	0.0241	0.9892	0.9533	0.0321	0.9765	1.0117	-0.0080	0.9963	0.8449	0.1832	1	0.8480	0.1671
A ₂ (a)	0.9971	1.4532	-0.4449	0.9947	1.4428	-0.4303	0.9962	1.5423	-0.5102	0.9965	1.6653	0.6533	1	1.6711	-0.6718
A ₃ (a)	0.9895	2.1773	-1.1207	0.9879	2.1626	-1.1020	0.9835	2.3048	-1.2214	0.9964	2.7680	-1.77460	1	2.7778	-1.7972

To compare the experimental with the theoretical values, the linear relation of $(t/t_{0.5})_{exp}$ with $(t/t_{0.5})_{theor}$ was examined. The parameters slope, intercept and least square coefficient were calculated and are given in Table 4. The experimental values approximate better the theoretical ones in cases where the slope, intercept and regression coefficient values are close to one, zero and one respectively.

As it can be seen from Table 4, equations of chemical reaction group (R_2 , R_3) best fit the experimental results for 637°, 650°, 700°, 750° and 800°C and mainly that of R_2 .

For 850° and 870°C, the decomposition phenomenon is extremely fast and no attempt was made to proceed with the kinetic analysis of the results as this would probably lead to false results.

Finally, it should be stated that the aim of this method was to rule out a reaction-controlling mechanism rather than discovering the exact underlying equation, since for each separate group of equations the values of $t/t_{0.5}$ were too similar to each other.

Second method: From the widely applied eq. (5)

$$\ln [-\ln(1-\alpha)] = n \ln t + \ln k \quad (5)$$

characteristic values of "n", that represents the slope of the lines produced, have been established for the most commonly used solid-state reaction equations and are represented in Table 1 (Hancock and Sharp, 1972). For values of the experimentally calculated fraction reacted (α) ranging from 0.15 to 0.50 the following values of "n" have been found and the linearity of the diagrams obtained was ensured by the least-squares method:

- For 637° and 650°C, and for α varying between 0.15 and 0.5, "n" had a value of 1.12 and 1.10 respectively, denoting that chemical reaction was the CaCO_3 decomposition controlling mechanism while equation R_2 best fit the results.
- For 700° and 750°C, "n" had a value of 1.07 and 1.08 respectively, that implies the chemical reaction as the controlling mechanism and equation R_3 most likely to fit.
- For the experiments in 800°, 850° and 870°C, this method cannot be applied since the reaction of the CaCO_3 thermal decomposition takes place too fast. In addition to that, for 800°C, only one value of α can be taken in the interval $0.1 \leq \alpha \leq 0.9$, while for 850° and 870°C, no values were obtained.

Third method: For the equations of chemical reaction mechanism (F_1 , R_2 , R_3 , Table 1) indicated by the previous methods to control the decomposition reaction, the correlation coefficient R (obtained by substituting in those the fraction reacted α), is an indicator of the equation most likely to represent the decomposition process; the closer to unity, the more suitable the equation.

The resulted values of α and the respective time t from the experiments in various temperatures were substituted in the above equations and the linearity was examined by the least-squares method.

Table 5
 Correlation coefficients resulted by the application of the least-squares method to the experimentally obtained data for the most commonly used solid-state reaction equations and rate constants for the R_2 kinetic model

α	F_1	R_2	K	R_3
T=637°C				
70 points	0.998			
80 points	0.978			
93 points		0.996	0.0054	0.984
96 points		0.994	0.0053	0.973
T=650°C				
50 points	0.989			
60 points	0.972			
66 points		0.996	0.0075	0.985
68 points		0.993	0.0074	0.971
T=700°C				
25 points	0.990			
34 points	0.944	0.999	0.0146	0.994
35 points		0.999	0.0143	0.983

Continued (Table 5)

α	F_1	R_2	K	R_3
T=750°C				
8 points	0.968	0.998	0.0588	0.993
9 points	0.875	0.994	0.0550	0.974
10 points		0.996	0.0506	0.974
T=800°C				
3 points	0.996			
4 points	0.979	0.999	0.1169	0.996
5 points		0.997	0.0999	0.971

As it can be seen from Table 5, for all the temperature values examined, the R_2 chemical reaction appears the best fitting of the experimental data, because it exhibits the best values of correlation coefficients, for all the cases studied. This method was not applied for 850° and 870°C because the decomposition was very fast and there were only 3 and 2 α -t couple points respectively, for the application of the least-squares method.

Fourth method: According to this method proposed by Tang and Chaudri (1979), there are three cases in the kinetic analysis procedure, based on the differential form of the kinetic equation, depending on the value of “n”, already obtained in the preceding procedure (second method).

(a) $n \geq 2$. In this case:

$$d\alpha/dt = k\alpha^p(1-\alpha)^q \quad (6)$$

and, by the least-squares method, fit on the graph of $\alpha \log(d\alpha/dt) / \alpha \log \alpha$ against $\alpha \log(1-\alpha) / \alpha \log \alpha$, p and q can be calculated.

(b) $n \approx 1$. In this case:

$$d\alpha/dt = k(1-\alpha)^s \quad (7)$$

and from the graph of $\log(d\alpha/dt)$ against $\log(1-\alpha)$, the slope s is determined.

(c) $n \approx 0.5$. In this case:

$$-(d\alpha/dt)\ln(1-\alpha)^s = k(1-\alpha)^s \quad (8)$$

is the basic equation, with $s = 0$ (diffusion in two dimensions) or $s = 1/3$ (diffusion in three dimensions).

From the second method of kinetic analysis, the value of “n” was determined to be from 1.12 to 1.07, for the experiments at temperature values from 637° to 750°C, so it approaches that of $n=1$ (case b). Therefore, by plotting the diagrams $\log(d\alpha/dt)$ against $\log(1-\alpha)$ for each temperature value (Figures 5-8) and for “ α ” to be between 0.15-0.50, the slope “s” was determined by the least-squares method. The results are presented in Table 6. As it can be seen from this table, the slope “s” of the linear portion approaches well the 0.50 value, except for 700°C, meaning that the differential reaction equation is: $d\alpha/dt = k(1-\alpha)^{0.5}$ and the respective kinetic equation is R_2 . For higher temperature values this method could not be employed, due to the high rate of the reaction, since there are no data for $0.15 < \alpha < 0.50$.

Table 6
 Results of the least-squares method application to the diagrams of $\log(d\alpha/dt)$ vs. $\log(1-\alpha)$

Temperature, °C	637	650	700	750
Value of “n”	1.12	1.10	1.07	1.08
Number of points	26	19	9	3
Slope (value of “s”)	0.51	0.49	0.38	0.55
Correlation coefficient	0.977	0.968	0.980	0.999

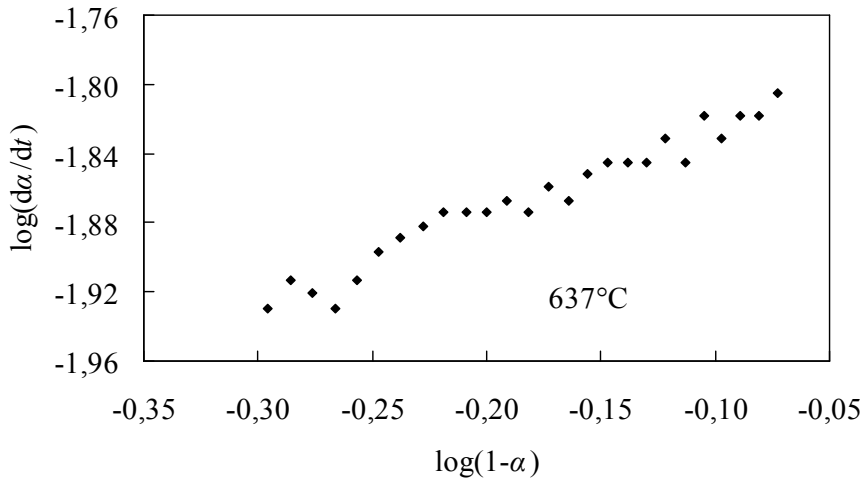


Figure 5. Log $(d\alpha/dt)$ vs. log $(1-\alpha)$ for the differential equation form: $\log(d\alpha/dt)=\log k+r \log(1-\alpha)$ at $T=637^\circ\text{C}$

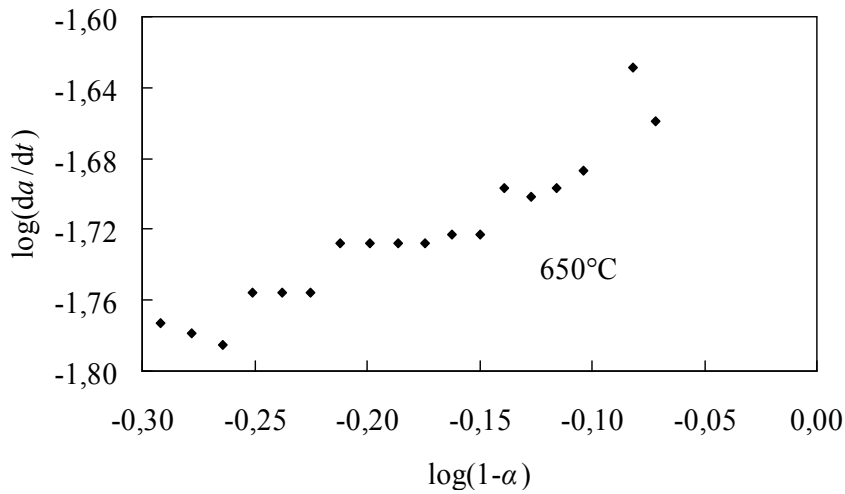


Figure 6. Log $(d\alpha/dt)$ vs. log $(1-\alpha)$ for the differential equation form: $\log(d\alpha/dt)=\log k+r \log(1-\alpha)$ at $T=650^\circ\text{C}$

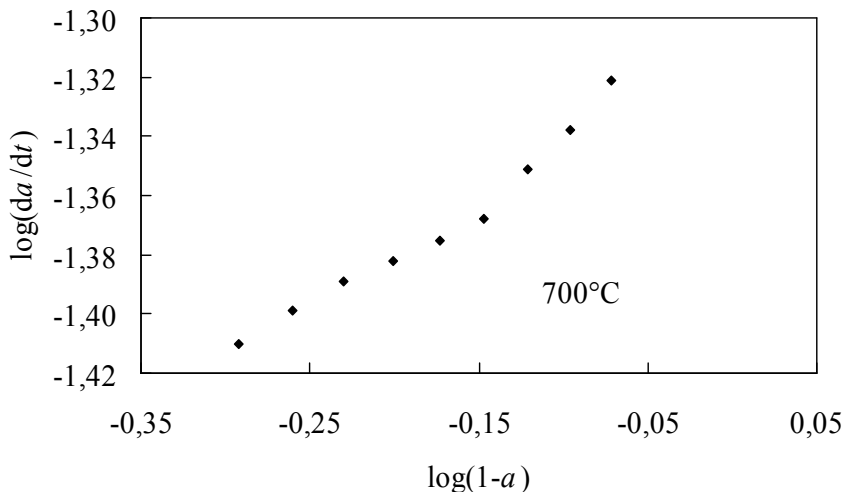


Figure 7. Log $(d\alpha/dt)$ vs. log $(1-\alpha)$ for the differential equation form: $\log(d\alpha/dt)=\log k+r \log(1-\alpha)$ at $T=700^\circ\text{C}$

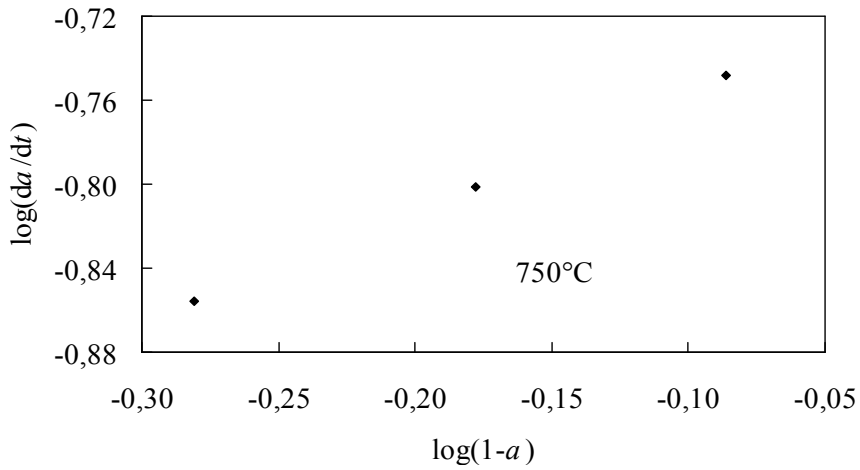


Figure 8. Log $(d\alpha/dt)$ vs. $\log(1-\alpha)$ for the differential equation form: $\log(d\alpha/dt) = \log k + r \log(1-\alpha)$ at $T=750^\circ\text{C}$

4.2. Determination of activation energy

For activation energy determination, two alternative methods were used:

1. In one method, the Arrhenius equation has been used directly; for this purpose, first, the maximum rates were evaluated from the $d\alpha/dt$ vs. time diagrams for the four values of temperature. The Arrhenius plot of $\ln(d\alpha/dt)_{\max}$ vs. $1/T$ is shown in Figure 9. The activation energy determined from the slope of the straight line was 162.45kJ/mol.

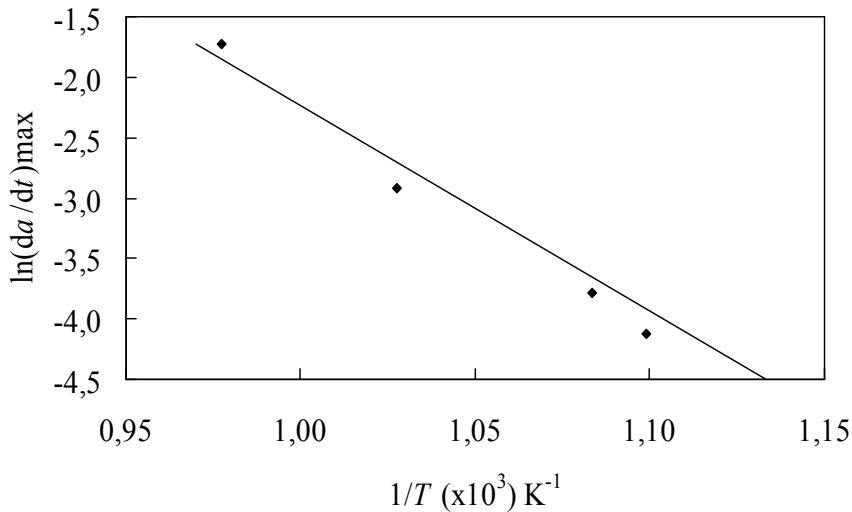


Figure 9. Arrhenius plot with the use of maximum rates

Secondly, the usual way for the activation energy estimation was used by means of kinetic constants from the kinetic model equation best fitted to the experimental data. The K values are given in Table 5. The Arrhenius line was constructed by plotting $\ln K$ vs. $1/T$ values (Figure 10). The activation energy estimated from the slope of the straight line is 152.6kJ/mol and is characterized as a more representative value for the whole reaction. The estimated values of activation energy confirm the chemical mechanism predominance.

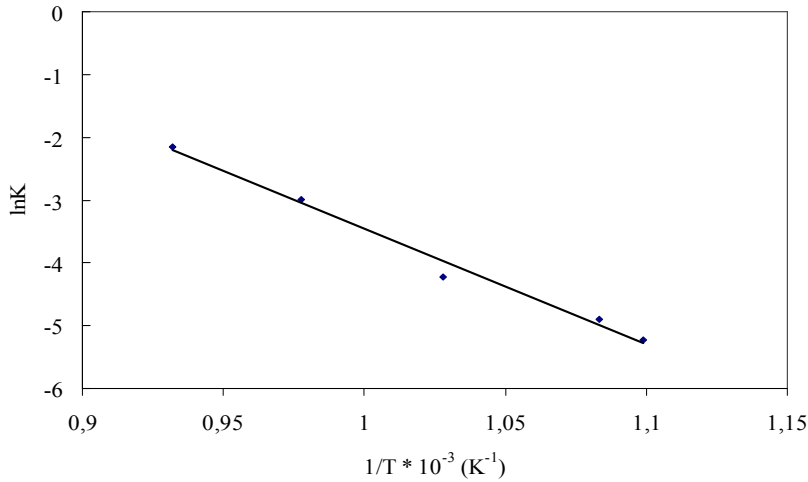


Figure 10. Arrhenius plot using rate constants

2. An alternative method was used for the activation energy determination, proposed by Haynes and Young (1961). According to this method, the experimental curves (α_1, t_1) , (α_2, t_2) , (α_3, t_3) and (α_4, t_4) , in different temperatures T_1, T_2, T_3 and T_4 are selected, having the same shape. It can be written that (Eqs. 9-12)

$$F(\alpha_1) = t_1 A e^{[-E/RT_1]} \quad (9)$$

$$F(\alpha_2) = t_2 A e^{[-E/RT_2]} \quad (10)$$

$$F(\alpha_3) = t_3 A e^{[-E/RT_3]} \quad (11)$$

$$F(\alpha_4) = t_4 A e^{[-E/RT_4]} \quad (12)$$

For points corresponding to the same α on these curves we have $F(\alpha_1) = F(\alpha_2)$ and $F(\alpha_3) = F(\alpha_4)$. So E can be calculated from the plot of $\ln t$ vs. $1/T$. This method was applied to the experimentally obtained curves of $637^\circ, 650^\circ, 700^\circ$ and 750°C , for three values of α (0.25, 0.50, 0.75), and the corresponding time t in each temperature was determined. By plotting $\ln t$ vs. $1/T$, straight lines were resulted with correlation coefficients very close to unity, and the activation energy was calculated from the slope of the lines for each value of α (Figure 11). The results are presented in Table 7 from which it is observed that the values of E for the three above values of α are 160.23, 160.56 and 158.09kJ/mol, respectively. As it is seen from the results, these estimated values are in accordance with the previous one, determined by the Arrhenius method.

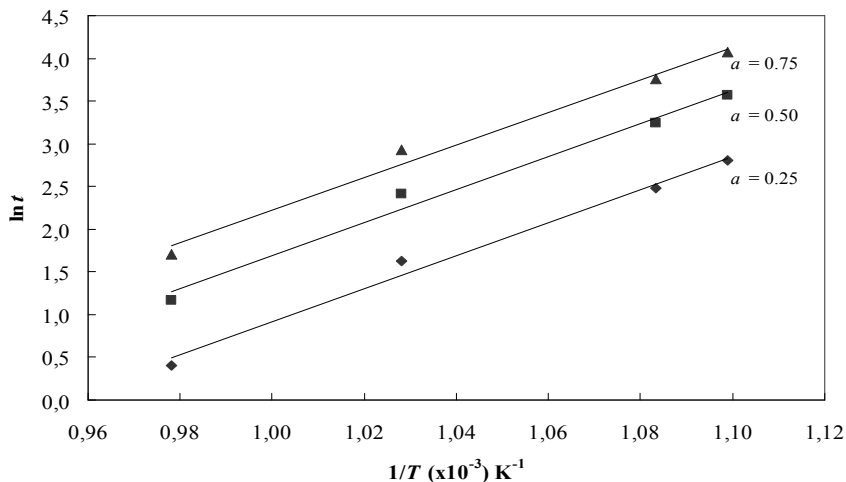


Figure 11. Plots of $\ln t$ vs. $(1/T)$ for various " α "

Table 7
 Values of $\ln t$ and $1/T$ for the determination of the activation energy with the alternative method and the resulted values of E

T, °C	α	t	$\ln t$	1/T	E, kJ/mole
637	0.25	16.5	2.8034	0.0010989	160.23
650	0.25	11.9	2.4765	0.0010834	
700	0.25	5.1	1.6292	0.0010280	
750	0.25	1.5	0.4055	0.0009780	
637	0.50	35.5	3.5695	0.0010989	160.56
650	0.50	25.7	3.2465	0.0010834	
700	0.50	11.2	2.4159	0.0010280	
750	0.50	3.2	1.1632	0.0009780	
637	0.75	58.8	4.0741	0.0010989	158.09
650	0.75	42.7	3.7542	0.0010834	
700	0.75	18.8	2.9339	0.0010280	
750	0.75	5.5	1.7047	0.0009780	

5. CONCLUSIONS

From the thermogravimetric data of the CaCO_3 thermal decomposition, the graphs of α vs. t and $d\alpha/dt$ vs. t were determined. For the evaluation of the experimental results, four methods were used. The first and second method helped in the determination of the reaction mechanism. These two methods did not reveal with accuracy the underlying kinetic equation that represents the experimental data.

The first method was based in the comparison of the experimental results with well-known calculated data for the most commonly used solid-state reaction equations. The method derived that the equations of chemical reaction group (R_2 , R_3) best fit the experimental results for 637°, 650°, 700°, 750° and 800°C and mainly that of R_2 . Regarding the 850° and 870°C, the decomposition was extremely fast and no attempt was made to proceed with the kinetic analysis of the results that would probably led to false results.

The second method involved the use of a diagnostic equation for the reveal of the kinetic mechanism. The implementation of this method led to the conclusion that the most probable controlling mechanism for the decomposition of CaCO_3 is the chemical reaction mechanism. This method was not applied for 800°, 850° and 870°C due to the lack of enough experimental data for α values between 0.15 and 0.50.

By the third method, the adaptation of the experimental results to the three theoretical equations that described the chemical reaction mechanism was verified. The use of the least-squares method checked the linearity of $f(\alpha)$ vs. t plot, through the determination of the correlation coefficient. This resulted to the verification that for 637°, 650°, 700°, 750° and 800°C the R_2 kinetic equation was followed. The method was not applied for the 850° and 870°C due to the lack of experimental data.

With the fourth method, an attempt was made to distinguish which kinetic equation represents better each examined temperature. Using the slope of the diagnostic equation (second method) as an indicator, it was concluded that for 637°, 650° and 750°C, the R_2 equation was followed. Uncertainty concerns the case of 700°, 800°, 850° and 870°C.

As a conclusion it can be stated that the governing kinetic model for the isothermal decomposition of CaCO_3 in temperatures varying between 637° and 750°C, is the chemical reaction model represented by the equation:

$$1 - (1 - \alpha)^{1/2} = k t \quad (13)$$

By comparing the various methods of kinetic analysis that were used in the present study to predict the model underlying the CaCO_3 thermal decomposition, the following separate groups can be recognized: that, involving the determination of the linearity; such was the case in the second, third and fourth method. On the other hand, the first method consisted in comparison with master curves and data. Therefore, the first method has the drawback that the data used

was derived from the reduced time curves, meaning that it was not real one. So, it seems that the remaining methods are more reliable in order to draw conclusions.

Another point that has to be stressed out is that the first two methods made it possible to find out only the controlling mechanism and not to discriminate the exact equation. It was the fourth method that enabled us to determine which of the kinetic equations of the already predicted controlling mechanisms truly represents the CaCO_3 decomposition process.

Concerning the activation energy of the process, this was determined by the Arrhenius plots using maximum rates, $(da/dt)_{\max}$, as well as the kinetic constants K from the prevailing model equation, at various temperatures. The activation energy values evaluated were 162.5 and 152.6 kJ/mol respectively. An alternative method was applied to the data based on plots of $\ln t$ vs. $1/T$ (corresponding to the same value of α). The resulted activation energy values were 160.23, 160.56 and 158.09 kJ/mol, for α values of 0.25, 0.50 and 0.75 respectively. The results showed that the values determined by the two methods are in accordance; besides, the predominance of the chemical mechanism is confirmed.

The observations made in the present study about the controlling mechanism, the kinetic equation and activation energy values, are in accordance with the conclusions of other investigators (Ninan et al., 1991; Zsako and Arz, 1974; Gorbachev, 1976; Gleixner and Chang, 1985; Zernov et al., 1982). However, some investigations have indicated that kinetic mechanism varies under different experimental conditions (Maciejewski and Reller, 1987).

The present study was focused on kinetic analysis; this alone cannot be regarded as indisputable evidence of the predominance of a particular mechanism. It has to be further supplemented from other independent evidence such as microscopic observations regarding the geometry of the interface development.

REFERENCES

- Altorfer R., Estimation of kinetic parameters from conversion curves, determined at constant heating rate. *Thermochimica Acta*, 1978, **24**, 17.
- Bamford C.H., Tipper C.F.H., (Eds.), *Comprehensive chemical kinetics*. Elsevier Scientific Publishing Corporation, 1980, Vol.22, Chap.22.
- Criado J.M., Gonzalez M., Malek J., and Ortega A., The effect of the CO_2 pressure on the thermal decomposition kinetics of calcium carbonate. *Thermochimica Acta*, 1995, **254**, 121.
- Criado J.M. and Morales J., Thermal decomposition reactions of solids controlled by diffusion and phase-boundary processes: possible misinterpretation of the mechanism from thermogravimetric data. *Thermochimica Acta*, 1977, **19**, 305.
- Garner W.E., (Ed.), *Chemistry of the solid state*, Butterworth Scientific Publications, 1955, London.
- Gleixner R.A., and Chang Y.A., Cyclic thermogravimetric methods for the study of the decomposition of carbonates- CaCO_3 . *Metallurgical Transactions B*, 1985, **16B**, 743.
- Gorbachev V.M., The compensation effect in the kinetics of the thermal decomposition of calcium carbonate. *Journal of Thermal Analysis*, 1976, **9**, 121.
- Guler I., Dollimore D., and Heal G.R., The investigation of the decomposition kinetics of calcium carbonate alone and in the presence of some clays using the rising temperature technique. *Thermochimica Acta*, 1982, **54**, 187.
- Halikia I., Neou-Syngouna P., and Kolitsa D., Isothermal kinetic analysis of the thermal decomposition of magnesium hydroxide using thermogravimetric data. *Thermochimica Acta*, 1998, **320**, 75.
- Hancock J.D., and Sharp J.H., Method of comparing solid state kinetic data and its application to the decomposition of kaolinite, brucite and BaCO_3 . *Journal of the American Ceramic Society*, 1972, **55**, 74.
- Haynes R.M., and Young, *Discussions of the Faraday Society*, 1961, 31, 229.
- Jerez A., Ramos E., Gaitan M., Veiga M.L., and Pico C., A method for the kinetic analysis of nonisothermal decomposition reactions of solids. *Thermochimica Acta*, 1987, **115**, 175.
- Maciejewski M., Computational aspects of kinetic analysis. Part B: The ICTAC kinetics project- the decomposition kinetics of calcium carbonate revisited, or some tips on survival in the kinetic minefield. *Thermochimica Acta*, 2000, **355**, 145.
- Maciejewski M., and Reller A., How (un)reliable are kinetic data of reversible solid state decomposition processes?. *Thermochimica Acta*, 1987, **110**, 145.
- Ninan K.N., Krishnan K., and Krishnamurthy V.N., Kinetics and mechanism of thermal decomposition of in-situ generated calcium carbonate. *Journal of Thermal Analysis*, 1991, **37**, 1533.

- Perez-Maqueda L.A., Ortega A., and Criado J.M., The use of master plots for discriminating the kinetic model of solid state reactions from a single constant-rate thermal analysis (CRTA) experiment. *Thermochimica Acta*, 1996, **277**, 165.
- Ray H.S., The kinetic compensation effect in the kinetics of the thermal decomposition of calcium carbonate. *Journal of Thermal Analysis*, 1982, **24**, 35.
- Sharp J.H., Brindley G.W., and Narahari B.N., Numerical data for some commonly used solid state reaction equations. *Journal of the American Ceramic Society*, 1996, **49**, 379.
- Tang, T.B., and Chaudri M.M., Analysis of isothermal kinetic data from solid state reactions. *Journal of Thermal Analysis*, 1980, **18**, 247.
- Tang T.B., and Chaudri M.M., Analysis of isothermal kinetic data from solid state reactions. *Journal of Thermal Analysis*, 1979, **17**, 359.
- Zernov V.N., Gropyanov V.M., and Abbakumov V.G., Application of methods of nonisothermal kinetics to thermal decomposition of CaCO_3 at constant rate, *Zh. Prikl. Khim.*, 1982, **55**, 1493.
- Zsako I., and Arz H.E., Thermal decomposition of calcium carbonate. *Journal of Thermal Analysis*, 1974, **6**, 651.