Short communication

Calcination kinetics of high purity limestones

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Abstract

In this study, the calcination reaction of 10 different limestone samples which were taken from different regions of Turkey was investigated by using thermogravimetric analysis (TGA) technique. Various models were applied to the experimental results and it was found that the shrinking core model with surface reaction rate controlling mechanism is the best model fitting the experimental data. Application of this model to the experimental data showed that the calcination activation energies of various limestone samples change in the range 40–50 kcal/gmol. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Limestone; Calcination kinetics; Calcination rate

1. Introduction

The uncertainty in predicting the behaviour of a particular limestone in a calcination process is due to the complexity of the calcination process which involves a five-step mechanism [1]. Heat transfer resistances as well as pore diffusion resistance of the CO_2 evolved might have significant effects on the calcination rate. As it is reported by Doğu [2], changes in pore structure also play a significant role on the calcination mechanism and the reactivity of a calcined limestone is strongly dependent on its physical and structural properties which in turn are highly dependent on calcination conditions.

On the other hand, limestone can be obtained from a huge variety of sources and various limestones differ considerably in their chemical composition and physical structure. The chemical reactivity of different limestones shows a large variation due to their differences in crystalline structure and also because of the nature of impurities such as silicon, iron, magnesium, manganese, sodium and potassium [3].

Thermal decomposition of limestone has been the subject of intensive study over the years due to its importance in the flue gas desulfurization and in the hydration of cement industry. The mechanisms and the rate expressions for the calcination reactions were analysed extensively by many investigators and several models, such as shrinking core model, homogeneous reaction model, and structural models which include grain models proposed for gas–solid reactions were tested. The models for non catalytic gas–solid reactions are summarized in number of studies [4–6]. McKewan [7], Satterfield and Feaks [8] and Ingraham and Marrier [9] have reported that the rate is controlled by chemical reaction at the interface whereas Koloberdin et al. [10] and Narsimhan [11] reported that the rate is controlled by the heat transfer at the interface. On the other hand, Shen and Smith [12] and Scrivner and Manning [13] considered three rate controlling steps, i.e., chemical reaction, gas film diffusion, and product layer diffusion with allowance for shrinking or swelling of particle size.

Khraisha and Dugwell [14] studied the thermal decomposition of a Couldon limestone in a thermogravimetric analyser at heating rates up to $80 \, K \, min^{-1}$ up to temperatures of 1223 K. They interpreted the experimental data in terms of an apparent activation energy and frequency factor. They also reported very wide range of data quoted by other workers. The activation energy and frequency factor values quoted varied between 23.9 and 956 kcal/gmol and 10^2 and $10^{69} \, s^{-1}$, respectively. Authors concluded that the kinetic parameters measured are in the region reported in the literature. Their own values of activation energy varied between ∼98 and 351 kcal/gmol depending on heating rate and composition of atmosphere in TGA. In another study [15], they also investigated the effect of water vapour on the calcination process and found that the injection of water vapour at the 2.22% level enhanced the conversion achieved in the calcination process, whereas injection at the 6.09% level produced a retarding effect.

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Nomenclature

C_{CO_2}	concentration of CO_2 in the pores of the particle ($gmol/cm^3$)
D_e	effective diffusivity of CO_2 (cm^2/s)
E_a	activation energy of calcination reaction (kcal/gmol)
k_s	surface reaction rate constant (cm/s)
k_{s0}	pre-exponential factor in Arrhenius equation
M_{CC}	molecular weight of $CaCO_3$ (g/gmol)
M_{CO_2}	molecular weight of CO_2 (g/gmol)
R	radius of limestone particle at any time t (cm)
R_0	initial radius of particle (cm)
R_C	radius of unreacted core (cm)
W_0	initial weight of limestone sample (mg)
W_t	weight of limestone sample at any time t (mg)
x_k	conversion ratio of limestone at any calcination reaction time t
y_{CC}	weight fraction of $CaCO_3$ in limestone sample

Greek letters

ρ_{CC}	density of $CaCO_3$ (g/cm^3)

In a more recent study, Khraisha and Dugwell [16] studied the calcination of limestone and cement raw meal in a suspension reactor simulating dynamic and thermal conditions within a commercial precalciner. They measured the combustion and calcination rates by on-line monitoring of the CO_2, CO and O_2 content in the exit gas stream by a quadruple mass spectrometer. As a result of this study they found that the limestone calcination is a shrinking core process and the rate of calcination is proportional to the carbon dioxide concentration, difference between the reaction interface and the bulk atmosphere surrounding the particle.

Rao et al. [17] studied the decomposition of calcium carbonate by using a thermobalance. They used the grain model together with a modified Prater relationship accounting for nonisothermality to explain the reaction phenomena. They found that the model predictions for the conversions and temperatures in the solid during the reactions are in good agreement with all the experimental results. In a later study, Rao [18] determined the intrinsic reaction rate constant for calcium carbonate decomposition by using a structural model (grain model). Investigator tried to determine the effective diffusivity, effective thermal conductivity, and heat and mass transfer coefficients taking the temperature variations in the solid into consideration.

Murthy et al. [19] also investigated the kinetics of thermal decomposition of calcium carbonate and they applied grain model for cylindrical pellets with transient heat and mass transfer equations assuming spherical grains. They experimentally found that additives like Al, W, Zn increase the rate of reaction. Authors stated that small amount of additives enhance conversion but quantities greater than 15% are ineffective in further improving the rates of reaction.

Khinast et al. [20] investigated the decomposition of limestone by means of a TGA. They investigated three different size fractions isothermally in different percentages of CO_2/N_2 mixtures. They reported an exponential decrease in the reaction rate with increasing CO_2 partial pressure and an induction period at low conversion. Authors tried to explain this period by the evolution of the reacting surface area which is described by random pore model. They suggested that both chemical kinetics and mass transport in the particle are reaction limiting factors. Their relative importance is dependent upon the particle texture, the initial particle size and CO_2 partial pressure. In another study, Ülkütan [21] showed that a two-stage model explained the calcination mechanism of limestones.

Under the light of the above theoretical considerations, in this study calcination reaction mechanism is investigated by using 10 limestone samples taken from different regions of Turkey. After the determination of the sample weight range in which interparticle heat and mass transfer resistances can be neglected, calcination experiments were performed in TGA and various kinetic models were tested.

2. Experimental studies

Chemical compositions of limestone samples which were taken from 10 different regions of Turkey were determined by volumetric and gravimetric methods [22]. Chemical compositions of limestones used in this study are given in Table 1. Calcination reactions of limestones were performed by using Linseis L81 TGA. Its block diagram is given in Fig. 1.

Since it is very important to minimize the interparticle heat and mass transfer, resistance effects in gas–solid reactions, it is required to work with sample weights as small as possible. On the other hand, the amount of sample should be sufficient so that it should be representative of its origin. Therefore, in preliminary experiments it was tried to determine the sample weight range by keeping all the parameters constant except the sample weight. These experiments were performed by using arbitrarily chosen Göynük limestone (Sample No. 10).

Göynük limestones were crushed, screened and classified according to their particle size. All size groups were dried in an electrically heated furnace at 110°C for 90 min to remove their moisture. After drying, a 50 mg sample having average particle size of 1.015 mm was taken. This sample was placed into the sample holder of TGA and heated up to 900°C with 20 K/min heating rate in an inert atmosphere (N_2). To ensure the completion of calcination reaction, sample was held at this temperature for further about

Table 1
Chemical compositions of limestones used

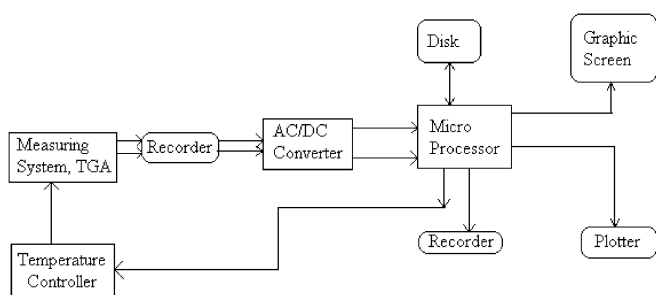| No.	Limestone type	CaO (%)	MgO (%)	R_2O_3 (%)	SiO_2 (%)	Ignition loss (%)
1	Bağlum	42.7	2.5	4.1	16.8	33.9
2	Köserelik	44.0	1.2	1.3	19.3	34.2
3	Polatlı Y.	51.4	2.5	0.1	1.8	44.2
4	Ayaş	51.8	1.1	0.3	4.5	42.3
5	Kınık T.	47.9	1.5	1.0	8.4	41.2
6	Alacaatlı	47.8	1.2	0.6	10.9	39.5
9	Kurucaşile	51.8	1.4	0.1	3.1	43.6
10	Göynük	53.1	1.1	0.2	2.2	43.6
11	Çeşme	51.8	1.5	0.2	3.2	43.3
12	Dikmen	52.8	2.0	0.5	1.7	43.3

Fig. 1. Block diagram of Linseis L81 TGA.

10 min. Experiments were repeated with different sample weights (40, 50, ..., 125, 150 mg) by keeping all the experimental parameters constant. As it is seen in Fig. 2, weight loss vs. temperature curves obtained with sample weights of 65.3, 59.2, 50.0 and 40.7 mg are quite close. Based on the experimental results illustrated in Fig. 2, it

was decided to use 50 mg of sample in further calcination experiments.

Calcination experiments were performed by using 50 mg samples from different limestones which were crushed, classified according to their particle size and dried previously. Calcination of limestones of different regions were carried out at 20 K/min heating rate and 12 l/h gas velocity. Maximum experimental measuring temperature was 900°C. In this group of experiments, 1.015 mm average particle size was used. Carbon dioxide which arises from decomposition of $CaCO_3$ during the reaction was swept by the nitrogen stream. Therefore, its equilibrium partial pressure was not reached and there was no film resistance.

After the calcination experiments, porosity of the calcined samples were measured in a Quantochroma Autoscan 60 mercury intrusion porosimeter. Results are given in Table 2. In order to see the effect of the particle size, a set of experiments were performed by using Göynük limestone
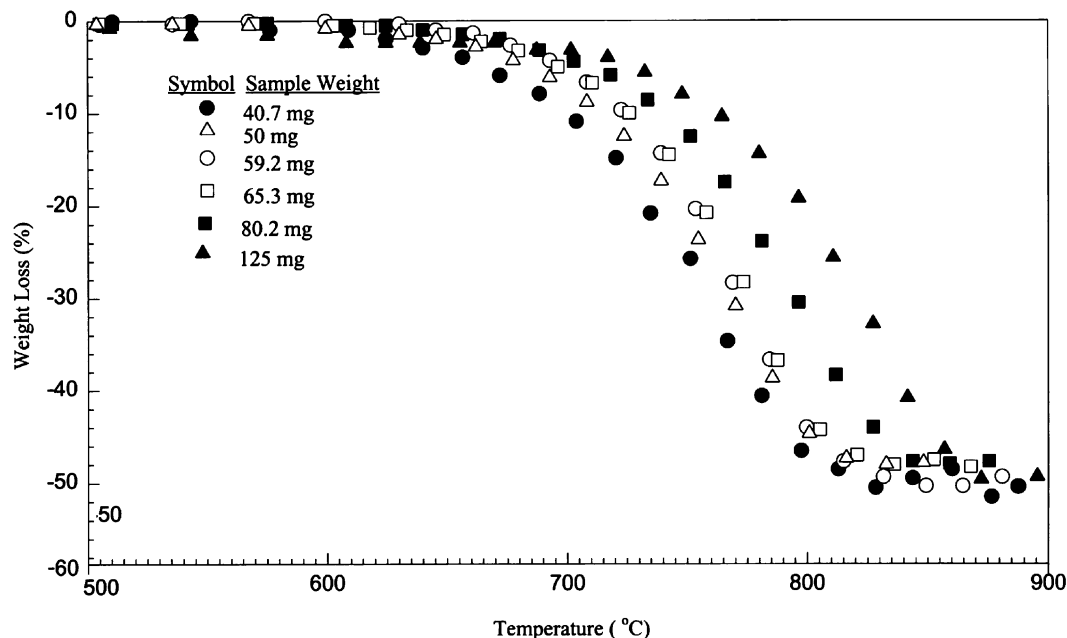

Fig. 2. Effect of sample weight on the calcination reaction rate ($d_{av} = 1.015$ mm, heating rate = 20 K/min, atmosphere: inert, sample: Göynük limestone).

Table 2
Physical properties of the calcined samples

Sample No.	Limestone type	Average pore radius (nm)	Porosity, ε	Solid density, ρ
1	Köserelik, Bağlum	102.53	0.47	3.38
2	Köserelik	131.08	0.36	2.93
3	Polatlı Yolu	62.98	0.51	2.52
4	Ayaş	37.93	0.35	2.56
5	Kınık Tüneli	125.30	0.44	2.57
6	Alacaatlı	56.73	0.35	2.80
9	Kurucaşile	43.27	0.37	2.66
10	Göynük	61.91	0.39	2.55
11	Çeşme-İzmir	45.31	0.32	2.45
12	Dikmen	23.21	0.32	2.25

with four different particle sizes. Results of the experiments performed were presented in the following section.

3. Results and interpretation

Results of sample weight determination experiments showed that increase in sample weight caused a significant decrease in the calcination reaction rate. This phenomena can be easily observed from Fig. 2. Calcination reaction was completed in 39 min (approximately at 830°C) when 40.7 mg sample was used whereas it was completed in about 43 min, which corresponds to 870°C, when sample weight was increased to 125 mg. These results indicate that change in sample weight does not have any significant effect on calcination reaction rate in 40–60 mg sample weight range. But in the case of further increase in sample weight interparticle heat and mass transfer resistances gain impor-

tance. Therefore, it was decided to use 50 mg samples in the calcination experiments in this work. In order to check the reproducibility and repeatability of the experimental data experiments for 40.7 mg samples and 65.3 mg samples were repeated three times. Results were quite reproducible and standard deviation values were found as 0.52% for 65.3 mg samples and 0.63% for 40.7 mg samples.

Results of calcination experiments which were carried out under identical experimental conditions and by using limestones of different regions showed that weight loss of limestones differed from each other depending on their $CaCO_3$ content. Since $MgCO_3$ content of limestones was in negligible amount with respect to their $CaCO_3$ content, weight loss of samples considered were wholly result of decomposition of their $CaCO_3$ content. Results of these experiments were given in Fig. 3. It was also observed that for almost all limestone samples used, calcination reaction started at around 620°C and was completed at about 820°C.
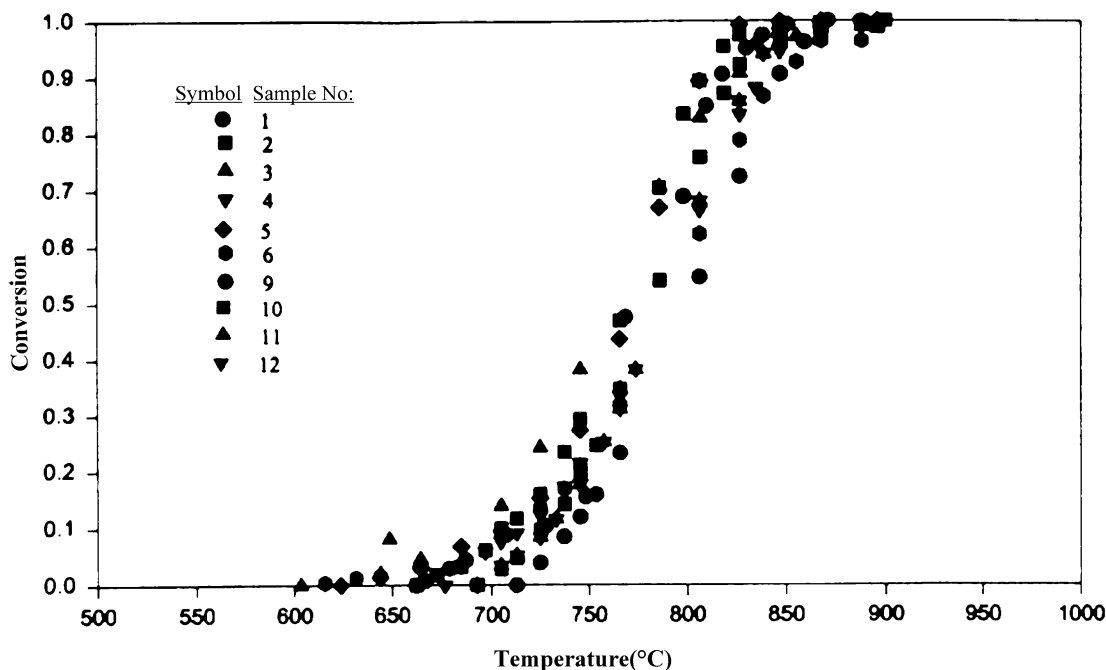

Fig. 3. Results of calcination reaction experiments of limestones of different origin ($d_{av} = 1.015$ mm, heating rate = 20 K/min, atmosphere: inert).

It was intended to find out kinetic parameters such as reaction rate constant and activation energy of calcination reaction of limestone samples. In order to achieve this goal various models were applied to the data obtained from TGA for the calcination reaction of samples.

Fractional conversion of limestone samples was defined as

$$x_k = \frac{M_{cc}}{y_{cc} M_{CO_2}} \frac{W_0 - W_t}{W_0} \tag{1}$$

and this definition was used in the analysis of the data.

3.1. Shrinking core model with surface reaction rate control

In the shrinking core model with the surface reaction rate controlling mechanism, it is assumed that the reaction initially takes place at the outer surface of the particle and while reaction proceeds, exterior surface of the particle is covered by a porous product layer and an unreacted core remains in the interior region of the particle. Particle size remains constant while the diameter of the unreacted core decreases with time. Other assumptions used in this model are: calcination reaction is zeroth order and the surface reaction is the controlling mechanism. If mass balance for the solid reactant ($CaCO_3$) is written and the simplifications depending on the above assumptions are made, governing equations are as follows:

$$-\frac{\rho_{cc}}{M_{cc}} \left(\frac{dR_c}{dt} \right) = k_s = k_{s0} e^{-E_a/RT} \tag{2}$$

Since

$$x_k = 1 - \left(\frac{R_c}{R} \right)^3 \tag{3}$$

then Eq. (2) will become

$$\frac{dx_k}{dt} = 3(1 - x_k)^{2/3} k_{s0} e^{-E_a/RT} \frac{M_{cc}}{\rho_{cc} R} \tag{4}$$

Since the temperature changes during the reaction, the evaluation of surface reaction rate constant was carried out by using differential method.

In order to check the conformity of the model with the experimental data, natural logarithm of surface reaction rate constant values which were calculated from the application of Eq. (4) to the experimental conversion time data, were plotted against inverse of reaction temperature. Results obtained are given in Fig. 4.

Since $\ln k_s$ vs. $1/T$ plots for all limestone samples gave straight lines it has been concluded that this model confirms very well with the experimental results. Calcination activation energies (E_a) and k_{s0} values for all limestone samples were calculated from the slope and intercept of their $\ln k_s$ vs. $1/T$ plots, respectively. E_a and k_{s0} values evaluated in this manner are shown in Table 3.

Calcination activation energies of different limestones changed between 22 and 50 kcal/gmol [23,24]. Difference between their activation energies may be explained by the differences in their chemical compositions and operational conditions [17]. Wernick [25] tried to explain the difference between the activation energy values of limestones with the difference in calcination temperatures. He proposed that the calcination reaction has higher activation energy at low temperatures. On the other hand, Bischoff [26] found the activation energy as 44.2 kcal/gmol in the temperature range between 550 and 800°C in the moist or dry sweeping air. The results of Bischoff's work seem to contradict with the results of Wernick's study. All the limestones used
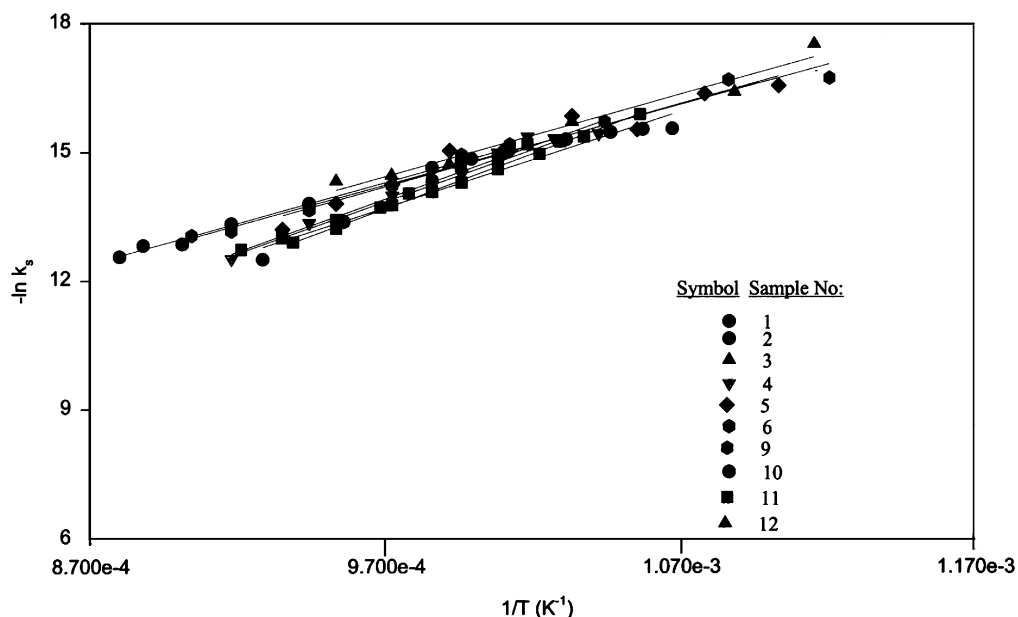

Fig. 4. Application of shrinking core model with surface reaction rate controlling mechanism to the calcination reaction data of various limestone.

Table 3
E_a and k_{s0} values obtained from the application of shrinking core model with surface reaction rate controlling mechanism to the experimental result of calcination of limestones

Sample No.	E_a (kcal/gmol)	$k_{s0} \times 10^6$ (gmol/(cm^2 s))
1	44.5	10.20
2	46.1	9.67
3	38.1	3.65
4	49.0	10.70
5	41.0	6.05
6	37.2	4.19
9	37.9	4.09
10	50.8	14.30
11	45.3	8.47
12	42.1	5.95

in our study were calcined under the identical experimental conditions. Our results agree well with the results of Bischoff [26]. In this study, experimental conditions were carefully chosen to eliminate heat and mass transfer effects. In number of previous publications, such transport effects have significant contributions on the calcination rate, consequently, the observed activation energies differ.

3.2. Other models tested

Besides shrinking core model with surface reaction rate control, film mass transfer control and product layer diffusion control models and the volume reaction model were also tested. In the volume reaction model, a first-order calcination reaction with respect to the solid reactant was assumed. All these models gave poor agreement with the experimental data [6] and they were discarded.

3.3. Particle size effect

In order to see the particle size effect on the calcination reaction, a set of experiments were performed by using Göynük limestone with different particle sizes. Results obtained were given in Fig. 5. The results obtained indicate that the time required to achieve the same conversion in cal-
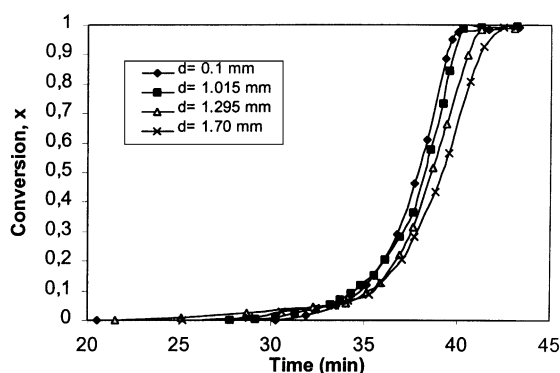
cination reaction is slightly longer for the larger particles (diameter of 1.7 mm) than that of small particles. For large particle sizes diffusional effects might have some contribution to the calcination rate. Results obtained with particles having 1.015 and 0.1 mm diameter were found to be very close. This result also supported the agreement of unreacted core model with surface reaction rate control with our experimental data obtained with particles of 1.015 mm diameter.

4. Conclusions

Results of sample weight determination experiments showed that sample weight did not have significant effect on the calcination reaction rate in 40–65 mg range. This may be explained by the insignificance of external heat and mass transfer resistances, in this sample weight range.

The calcination results of 10 different limestones of different origin and composition showed that unreacted core model with surface reaction control gave good fit with the experimental data. Other models tested, i.e., volume reaction model, shrinking core model with gas film mass transfer controlled mechanism and shrinking core model with diffusion control through the product layer failed in representing the experimental data. Results of the experiments performed with different particle sizes supported the unreacted core model with surface reaction control. Activation energy of calcination was found to be rather close for these 10 samples (between 40 and 50 kcal/gmol). However, the porosities of calcined samples change in a wide range ($\varepsilon = 0.32$–0.51) depending upon the origin of the limestone used.

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Fig. 5. Effect of particle size on calcination reaction rate.

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