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Dedicated to Professor Liviu Literat
On the occasion of his 85th birthday

KINETIC ANALYSIS OF THERMAL DECOMPOSITION OF THE LIMESTONE AND PRECIPITATE CALCIUM CARBONATE

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ABSTRACT. In this paper, decomposition reaction of limestone and precipitate calcium carbonate (PCC) was investigated, using thermo gravimetric analysis technique. All experiments were performed in isothermal conditions, within a temperature range of 973-1173 K, with main diameters of granules: 63µm, 180µm, and 450µm. The temperature influence was found using Arrhenius law. The reaction rate constant k and activation energy E_a have been determined. The values were found to be between: $k=1.8 \times 10^{-3}$ -4.4×10^{-3} s^{-1}, Ea=139,9 Kj/mol for limestone and $k=2.1 \times 10^{-3}$ - 6.5×10^{-3} s^{-1}, Ea=124,9 Kj/mol for PCC, according to the values reported in the literature.

Keywords: *Ca-looping process, calcium oxide as adsorbent of the CO_2, decomposition reaction, rate constant,* activation energy.

INTRODUCTION

Increasing atmospheric CO_2 emissions from fossil fuel combustion systems is responsible for the effect on global warming. Calcium oxide (CaO) is recognized as an efficient carbon dioxide adsorbent and separation of CO_2 from gas stream [1,2].

The Ca-looping process is a promising technique for reducing CO_2 emissions from the power generation sector. The basic idea of the calcium looping process is to use calcium oxide as sorbent of the CO_2 to form $CaCO_3$, and regeneration of the sorbent (calcination of $CaCO_3$). Utilization of calcium-based adsorbent in a process based on chemical looping from the gas stream through the calcination and carbonation process is extensively applied in the gas purification process [2,3,4].

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Thermal decomposition of limestone has been the subject of many studies over the years due to its importance in the industry and lately it is well known that calcium carbonate is used in calcium looping CO_2 capture systems [5,6,7,8].

The most used adsorbents are different assortments of natural and synthetic calcium carbonate: limestone, dolomite, precipitate calcium carbonate, etc. Under identical experimental conditions, the reactivity of these adsorbents is significantly influenced by their chemical structure and composition.

The kinetics of calcination is complicated by several factors which are: decomposition temperature, concentration of CO_2, sizes of the solids particle and also impurities. Calcination is favored by the high temperature as it is an endothermic reaction which needs low decomposition pressure of $CaCO_3$ in order to drive the equilibrium reaction forward [10].

Calcium oxide is an efficient carbon dioxide adsorbent, especially at high temperature. The temperature for decomposition of the adsorbent is a function of its origin, particle size and chemical reactivity.

Kinetic studies of different limestones have been investigated by many researchers [6,7,10,11,12] but there has not been reported work on that of precipitate calcium carbonate which is abundantly present in waste deposits of NP fertilizer industry.

In this research study, the potential of waste precipitate calcium carbonate, sources for CaO adsorbent compared with natural limestone was investigated. Since the microstructure of the solid adsorbent has an important influence over its reactivity, the main objectives of this work are the kinetic analysis of the process of natural and precipitate calcium carbonate (PCC) decomposition.

The decomposition process was realized at temperatures between 973-1173 K and atmospheric pressure in a TGA. Evolution of the decomposition degree during the heating and calcination intervals of the limestone and PCC sample for three particle size was established.

RESULTS AND DISCUSSION

The chemical composition of the limestone and precipitate calcium carbonate (PCC) has been determined and is summarized in Table 1.

Table 1. Composition of limestone and precipitate calcium carbonate

Carbonate source	Composition			
Limestone Sănduleşti - Turda	$CaCO_3$ [%] 97	Fe_2O_3 [%] 1,8	Al_2O_3 [%] 0,88	SiO_2 [%] 0,3
Precipitate Carbonate (waste) PCC	$CaCO_3$ [%] 96,7	Fe_2O_3 [%] 0,8	NH_4NO_3 [%] 1,2	humidity[%] 0,7

To determine the crystallographic structure and to compare the two types of carbonates has been carried out the structure analysis. IR spectra are shown in Figure 1.

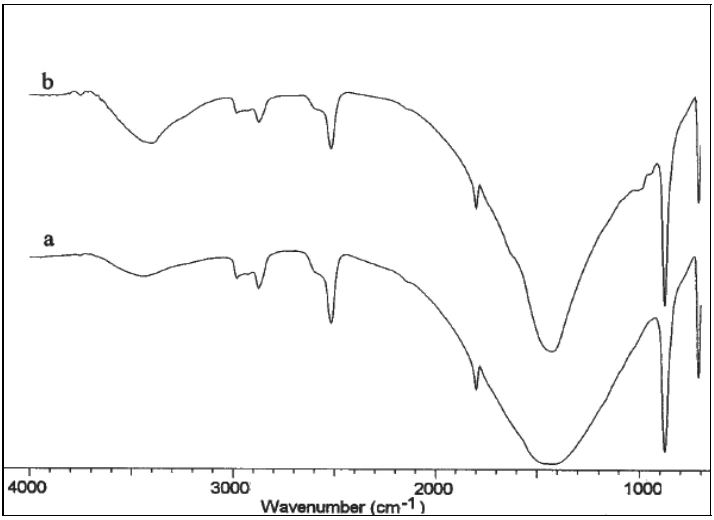

Figure 1. IR spectra of calcium carbonate. a.) - precipitated calcium carbonate (waste) of NP fertilizer industry; b) – natural limestone from Sănduleşti-Turda

IR spectra shows that chemical and crystallographic structure of the two types of carbonates are not significantly different. They presented same maximum and minimum absorbance curve, precipitated calcium carbonate wider band corresponding wavelength 1450 cm $^{-1}$ can be attributed to the degree of crystallinity lower than that derived its rock.

Evolution of the limestone and PCC decomposition for all grain sizes was followed by means of decomposition degree η_D. On the basis of the material balance, the decomposition degree η_D can be described by equation (1):

$$\eta_D = \frac{m_S^0 - m_S}{m_S^0 \cdot \bar{x}_{PC}^0} = \frac{1}{\bar{x}_{PC}^0}\left(1 - \frac{m_S}{m_S^0}\right) \qquad (1)$$

where: m_S^0, m_S – initial and at a given moment sample mass [mg];

$\bar{x}_{PC}^0$ – mass fraction of the calcination losses (0,4397-limestone and 0,41427PCC) was determined as arithmetical average in four values obtained samples subjected to calcination at 1323 K for two hours.

The particle sizes and temperature influence on the decomposition degree are presented in figures 2, 3, 4, 5.

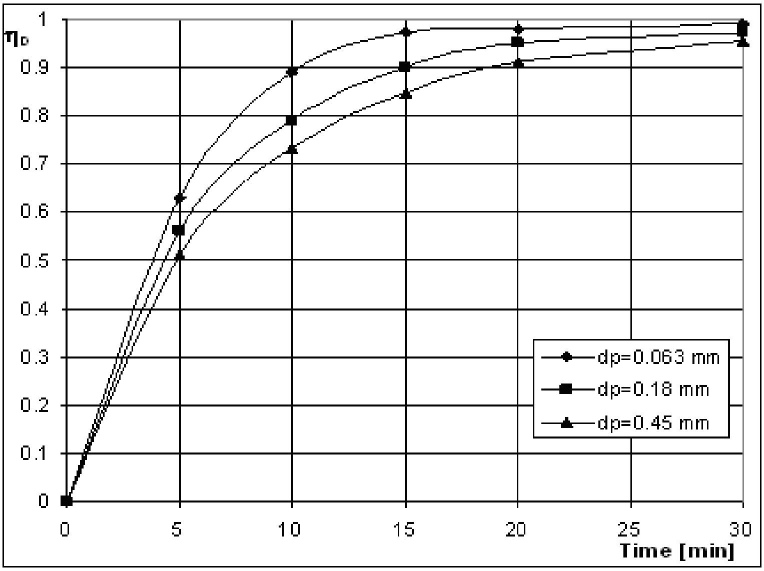

Figure 2. Effect of particles sizes on the decomposition degree of limestone at T_c=1173 K.

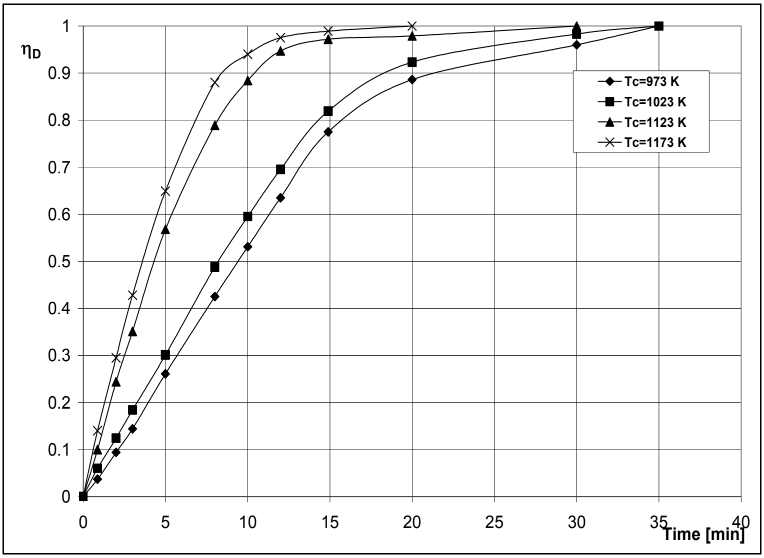

Figure 3. Effect of temperature on the decomposition degree of limestone granules with d_p=0.063mm

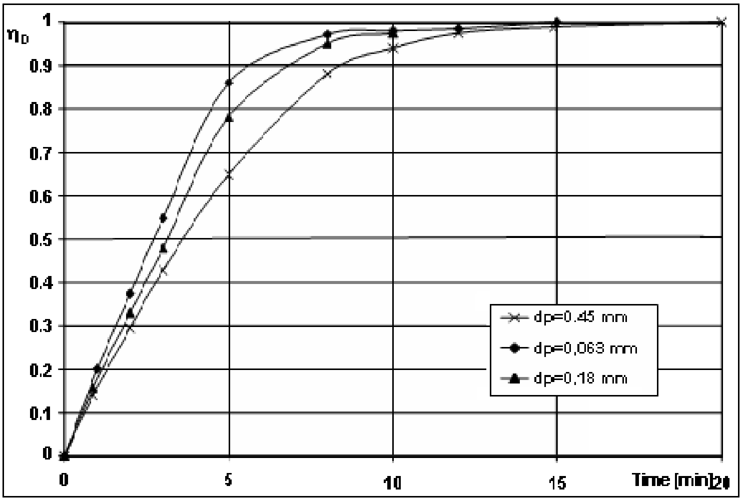

Figure 4. Effect of particles sizes on the decomposition degree of PCC at T_c=1173 K

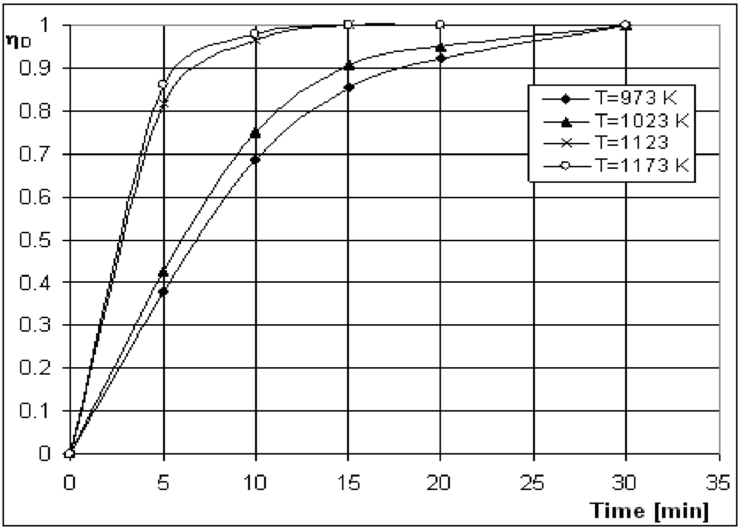

Figure 5. Effect of temperature on the decomposition degree of PCC granules with d_p=0.063mm

The kinetic curves η_D-τ presented in figures 2 and 4, shown a influence of the grain size on the decomposition degree. Decomposition degree increased as the particle size is smaller. It is also observed that the time taken for maximum decomposition degree of the smallest particle size is shorter compared to the sample with larger particle size. Particle sizes become a factor to the thermal decomposition process as it determines the surface area of the sample. Smaller particles size has large surface area that contributes to high efficiency of heat transfer.

The results presented in figures 3 and 5 shown significant temperature influence on the decomposition degree for both carbonate samples. With an increase in temperature, the decomposition degree increases rapidly at temperature over T=1123 K, reaching values higher than 0.90 in the first ten minutes. The difference which appears between two types of carbonates samples was attributed to the different structure of the granules. In all cases the reached decarbonation degree was higher than 0.95 at 30 minutes.

It can accelerate the process by reducing the thermal or heat resistance and other resistance such as mass transfer or gas diffusion.

Kinetics analysis is important as the process involves thermal effect to the sample. The process takes place once the heat supplied is enough. Thus, the kinetic energy needs to be analyzed so that best operating condition by controlling particle size and operating temperature can be implemented.

In this work, kinetic analysis of thermal decomposition was described using Arrhenius law.

For irreversible decomposition reaction:

$$CaCO_3 \rightarrow CaO + CO_2$$

the rate of disappearance of $CaCO_3$ can be represented by equation:

$$r_{CaCO_3} = -\frac{dc_{CaCO_3}}{d\tau} = k \cdot c_{CaCO_3}^{n} \qquad (2)$$

where k is the reaction rate constant and n reaction order.

For a first order irreversible type reaction the integrated form of equation 2 is given in equation 3:

$$-\int_{C_{CaCO_3}^{0}}^{C_{CaCO_3}} \frac{dc_{CaCO_3}}{c_{CaCO_3}} = k \cdot \int_{\tau=0}^{\tau} d\tau \text{ or } -\ln\frac{c_{CaCO_3}}{c_{CaCO_3}^{0}} = k \cdot \tau \qquad (3)$$

In terms of decomposition degree η_D we can write:

$$\ln(1-\eta_D) = -k\,\tau \qquad (4)$$

where k is the reaction rate constant and has a unit of s^{-1} for first order reaction

The kinetic curves plotted in $\ln(1-\eta_D)$□-τ coordinates, figures 6 and 7, gives a straight line graph with slope equal to k. The values obtained are presented in the Table 2.

Table 2. Effect of temperature on reaction rate constant

Temperature, K	Rate constant k x10^3, s^{-1}	
	Limestone	PCC
973	1.8	2.1
1023	2.1	2.5
1123	3.3	5.4
1173	4.4	6.5

The values of k increase with temperature due to increase the porosity of solid particles due to diffusion of CO_2 from the interior to surface of solids, so increase the heat transfer to the interior of particles.

The linear relationship of figure 6 and 7 having average regression coefficient R^2 higher than 0,97, confirmed than the decomposition of Sandulesti limestone and precipitated calcium carbonate (waste) of NP fertilizer industry at temperature range studied followed a first order reaction [13].

The temperature influence on the reaction rate constant has been found to be well described by Arrhenius equation:

$$k = k_0 \cdot e^{-\frac{E_a}{RT}} \qquad (5)$$

where: k_0 –pre-exponential or frequency factor;
E_a -the activation energy;
R –gas constant;
T- absolute temperature.

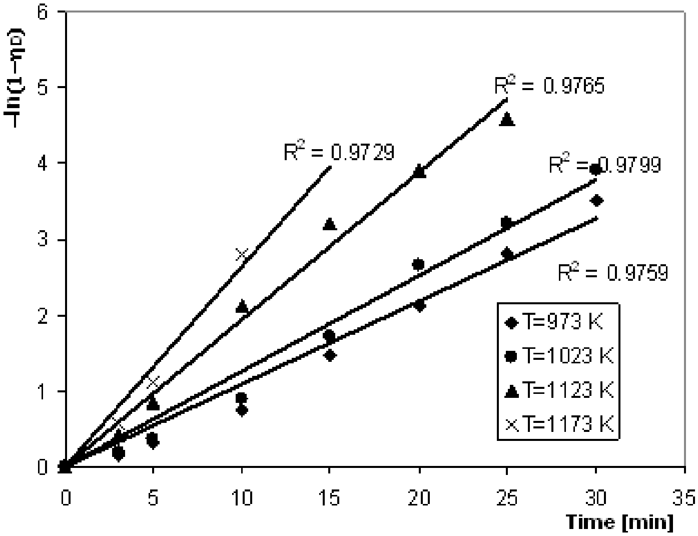

Figure 6. Determination of reaction rate constant at various temperature of limestone decomposition

The value of activation energy E_a is a good measure sensitivity of a given reaction to temperature changes. A plot of ln k-1/T coordinate yields values of frequency factor k_0 and activation energy E_a, by taking the natural logarithm of equation 5:

$$\ln k = \ln k_0 - \frac{E_a}{R} \cdot T^{-1} \tag{6}$$

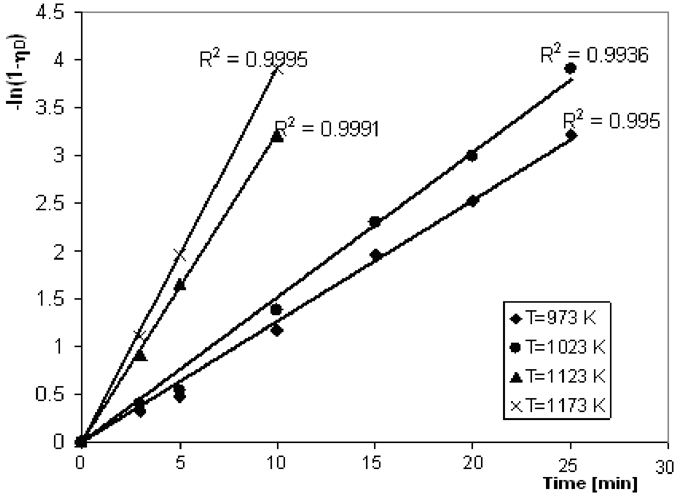

Figure 7. Determination of reaction rate constant at various temperature of PCC decomposition

The values of activation energy were estimated from the figure 8.

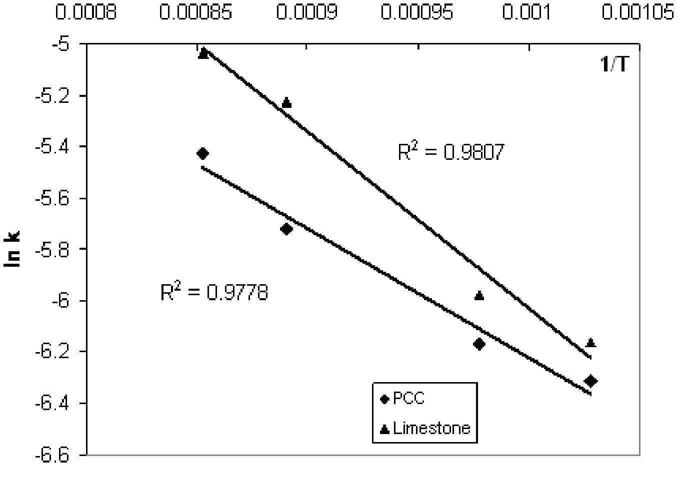

Figure 8. Dependence of reaction rate constant on temperature for granules with d_p=0.063 mm

The slope of the plotted graph in ln k versus 1/T, indicates the activation energies E_a of the process. The values of Ea are 124,9 Kj/mol for PCC decomposition and 139,9 Kj/mol for limestone, in agreement with the values reported in the literature [7,8,14].

These values indicate that decomposition of precipitate calcium carbonate and Sandulesti limestone is generally kinetically controlled. At constant heating rate, activation energy is higher for limestone compared with PCC, thus the limestone consumed more energy to initiate the decomposition process.

CONCLUSIONS

The chemical composition of the two types of carbonate is very similar as they both have a content exceeding 96% $CaCO_3$. IR analysis shows a very good analogy between the two sorts of carbonate. Chemical reactivity is the main parameter to validate or not to use the PCC in Ca-looping process for reducing CO_2 emissions.

The results obtained have indicated that the effect of temperature in the decomposition process of PCC and limestone is more significant than the grain size of the solid particles. Apparent activation energy obtained, E_a=124,9 Kj/mol for PCC decomposition and E_a =139,9 Kj/mol for limestone, suggested that the global process of decomposition is kinetically controlled. Activation energy is higher for limestone compared with PCC, thus the limestone consumed more energy to initiate the decomposition process. The results obtained during the decomposition process of precipitated calcium carbonate (waste) of NP fertilizer industry (PCC) and Sandulesti limestone showed that at temperature range studied followed a first order reaction.

The experimental research shows that the waste precipitate calcium carbonate (PCC) from NP fertilizers industry has a similar behavior in the decomposition process with natural limestone. PCC testing is recommended in the Ca-looping for CO_2 reduction in competition with limestone because both energy consumption for grinding and thermal decomposition process is less energy.

EXPERIMENTAL

In order to elucidate the effect of the temperature and grain size on the rate of the decomposition process, the isothermal gravimetric method was employed. The characterization of the two carbonate sources was carried out by crystallographic structure analysis. IR spectra were determined with a Digilab FTS 2000 spectrophotometer. The decomposition experiments were carried out isothermally on an experimental equipment presented in a previous paper [10].The parameters of the system are shown in Table 3.

Table 3. Operate parameters of the system

Crt. Nr.	Parameter	Value
1	Calcination temperature	973 K, 1023 K, 1123 K, 1173 K
2	Heating rate	10°C/min
3	Calcination time	30 min
4	Pressure	1 atm.
5	Particle size of calcium carbonate	0,063 mm; 0,18 mm; 0.45 mm

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