

*In memoriam prof. dr. Ioan A. Silberg*

## KINETIC STUDY OF CALCINATION FOR PRECIPITATE CALCIUM CARBONATE

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**ABSTRACT:** In this paper, the calcination reaction of precipitate calcium carbonate (PCC) was investigated, using thermogravimetric analysis technique. All experiments were performed in isothermal conditions, within a temperature range of 1073-1223 K, with main diameters of granules between 0.063 mm and 0.45 mm. Two models were applied to the experimental results and it was found that the Avraami-Erofeev-Kolmogorov is the best model which has fitted the experimental data.

The equation of mathematical model is  $\eta_D = 1 - e^{-k(T) \cdot \tau^{n(T)}}$  where  $\ln k(T) = 5.674 - \frac{68226.3}{R \cdot T}$  and  $n(T) = 0.0034 \cdot T - 2.4803$ .

### INTRODUCTION

Thermal decomposition of limestone has been the subject of many studies over the years due to its importance in the cement industry and in the flue gas desulphurization processes [1, 2]. For the reactive dry adsorption of sulfur dioxide from flue gases, the most used adsorbents are different assortments of natural and synthetic calcium carbonate: limestone, dolomite, lime, dolomitic lime and precipitate calcium carbonate. Under identical experimental conditions, the reactivity of these adsorbents is significantly influenced by their chemical structure and composition [3]. The optimal temperature for the dry injection of the adsorbent is a function of its origin, particle size and reaction type. Experimental determinations are always necessary in order to establish the optimal work conditions.

The mechanisms and the rate expression for the calcination reactions were analyzed 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 reaction, were tested [4].

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Since the microstructure of the solid adsorbent has an important influence over its reactivity, a kinetic study of precipitate calcium carbonate (PCC) decomposition will be presented in this paper. The decomposition process was realized at temperatures between 1073 -1223 K and atmospheric pressure. Evolution of the decomposition degree during the heating and calcination intervals of the (PCC) sample for three granulometric classes was established.

## RESULTS AND DISCUSSION

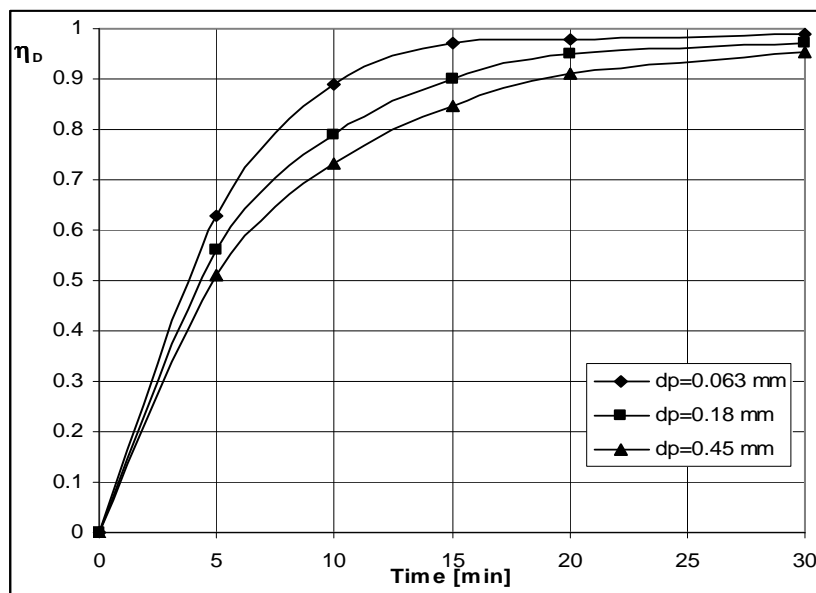
Evolution of the PCC decomposition for all grain sizes was followed by means of decomposition degree  $\eta_D$ . On the basis of the material balance, the decomposition degree  $\eta_D$  can be described by equation (1):

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

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 (0,41427) determined as arithmetical average of four values obtained for four PCC samples subjected to calcination at 1323 K for two hours.

The obtained results are presented in figures 2, 3 and 4.



**Fig. 2.** Particles sizes influence over the decomposition degree of PCC  $\text{CaCO}_3$  at  $T_c=1173$  K.

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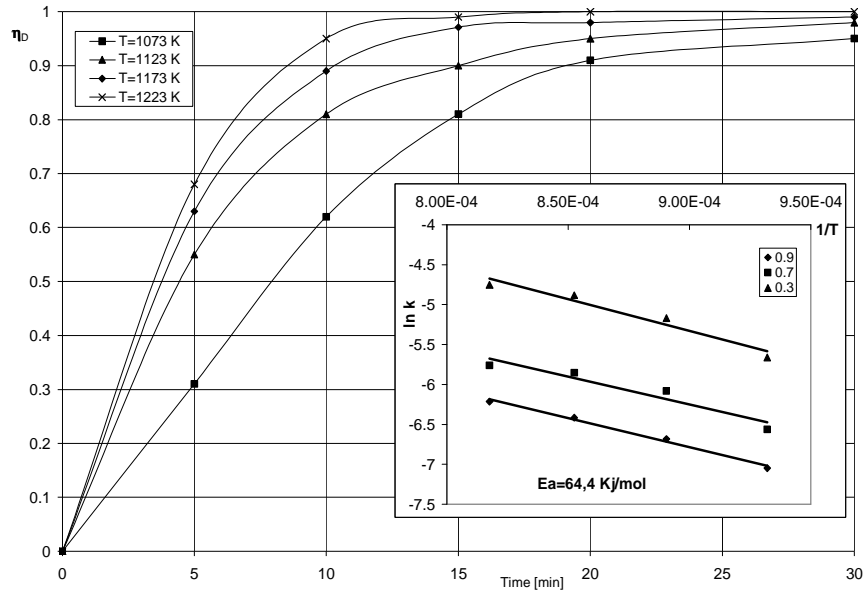


Fig. 3. Temperature influence over the decomposition degree of PCC granules with  $d_p=0.063$ mm.

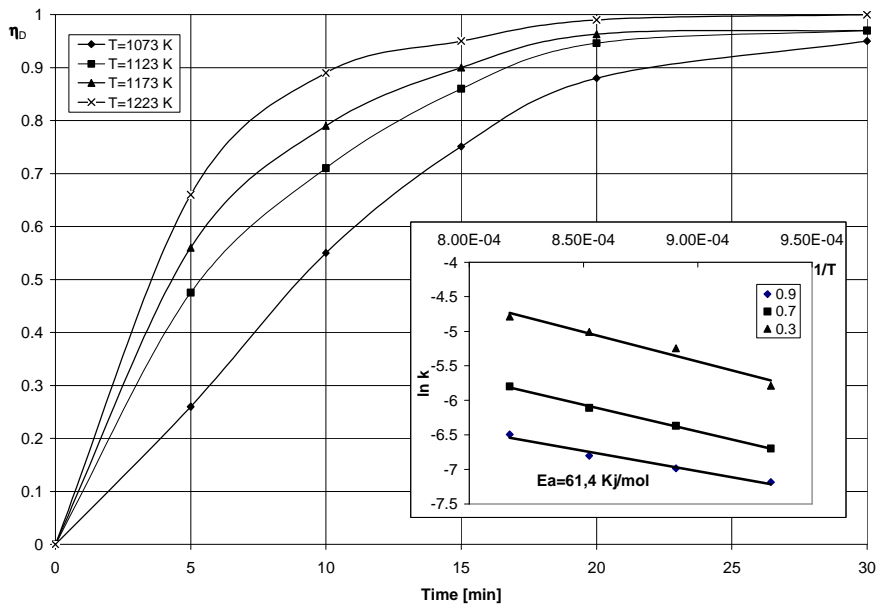


Fig. 4. Temperature influence over the decomposition degree of PCC granules with  $d_p=0.18$ mm.

The kinetic curves  $\eta_D$ - $\tau$ , plotted in figure 2 have shown a small influence of the grain size on the decomposition degree. The difference which appears between the studied samples was attributed to the different thermal conductivity of the granules layer in the nacelle. In all cases the decarbonation degree reached was higher than 0.95 at 30 minutes.

The results presented in figures 3 and 4 have shown significant influence on the decomposition degree for low temperature and large granule size. With an increase in temperature, the decomposition degree increases also, reaching values higher than 0.95.

The kinetic curves plotted in  $\ln \tau^{-1}-1/T$  coordinates, figures 3 and 4 as picture in picture, led to linear Arrhenius dependences at different decomposition degrees for granules with  $dp=0.063$  mm and  $dp=0.180$  mm. The apparent activation energies evaluated from the slopes are between 61.4 and 64.4 kJ/mol, and indicate that decomposition of precipitate calcium carbonate is generally kinetically controlled.

**Model of the real decomposition process.** In order to establish the appropriate model which describes better the PCC decomposition process we used the unreacted shrinking core model and Avraami-Erofeev-Kolmogorov equation [5].

By processing experimental data obtained for granules with 0.063 mm in diameter, within the same experimental set, in specific coordinates for unreacted shrinking core model :  $F(\eta_D)-\tau$  were  $F(\eta_D)=1-(1-\eta_D)^{1/3}$  and in specific coordinate  $\ln[-\ln(1-\eta_D)]-\ln \tau$  for Avraami-Erofeev-Kolmogorov (AEK) model  $\eta_D = 1 - e^{-k(T) \cdot \tau^{n(T)}}$ , we obtained the dependencies presented in figures 5 and 6.

In the figure 5 it is easy to see that the graphic dependences are not linear. This means that the transformation model was not validated by the experimental data, which demonstrates that the macrokinetic model, unreacted shrinking core, do not describes the process in the entire variation range of the decarbonation degree.

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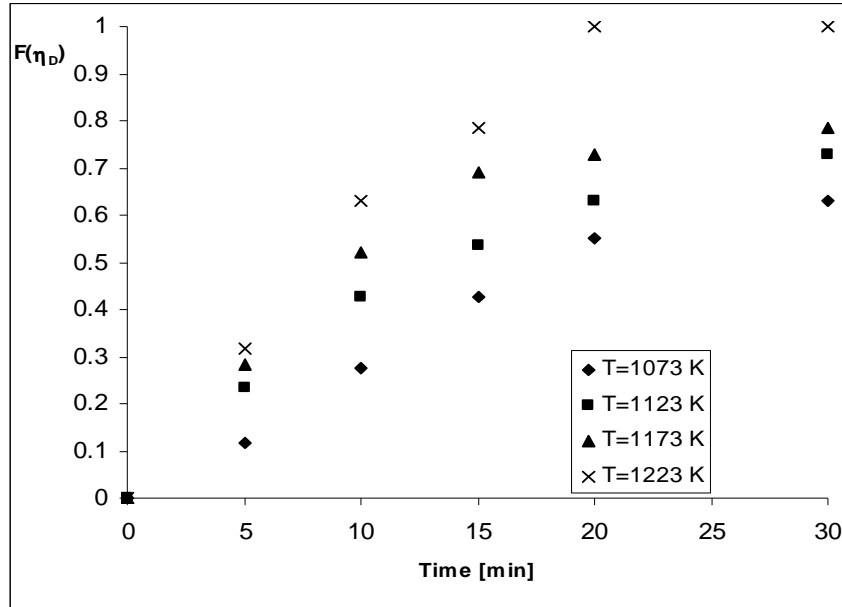


Fig. 5.  $F(\eta_D)$ -time dependence for the unreacted shrinking core model for granules with  $d_p = 0.063$  mm.

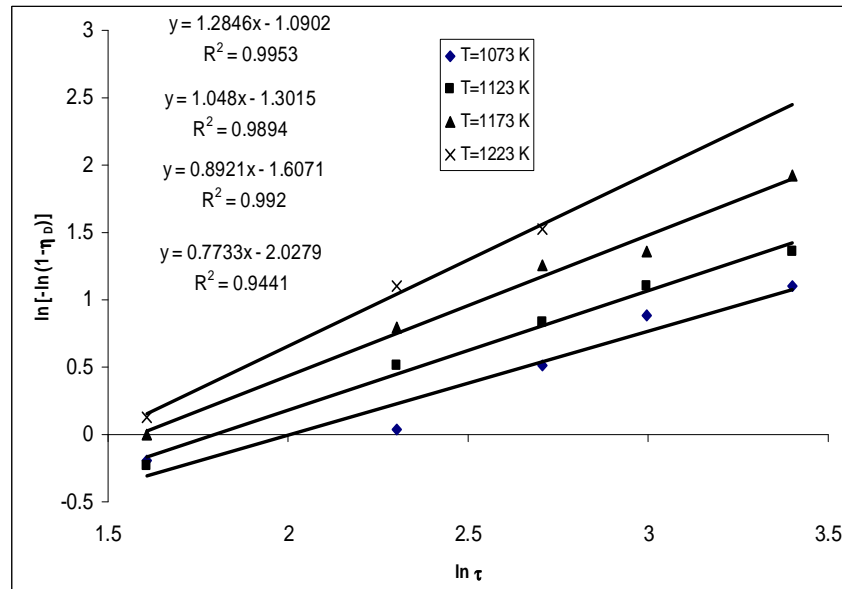
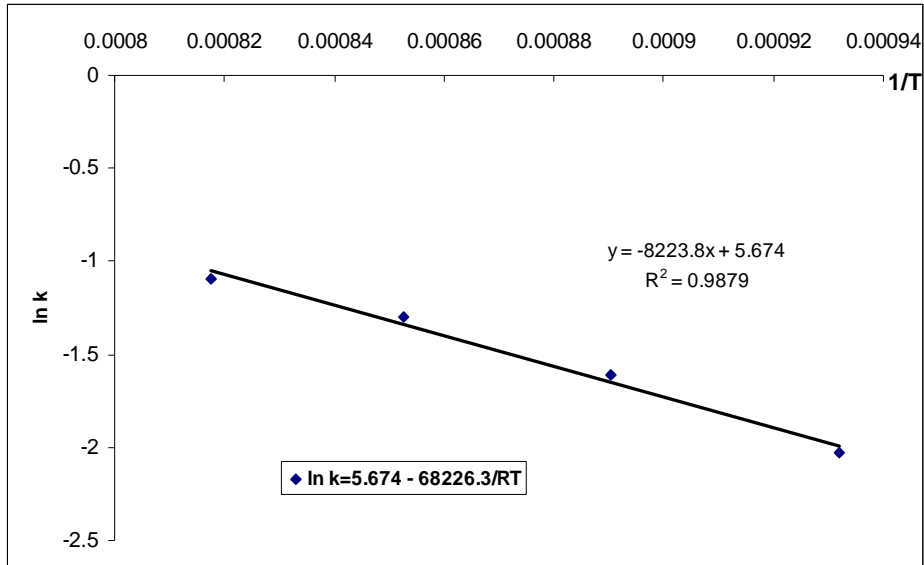
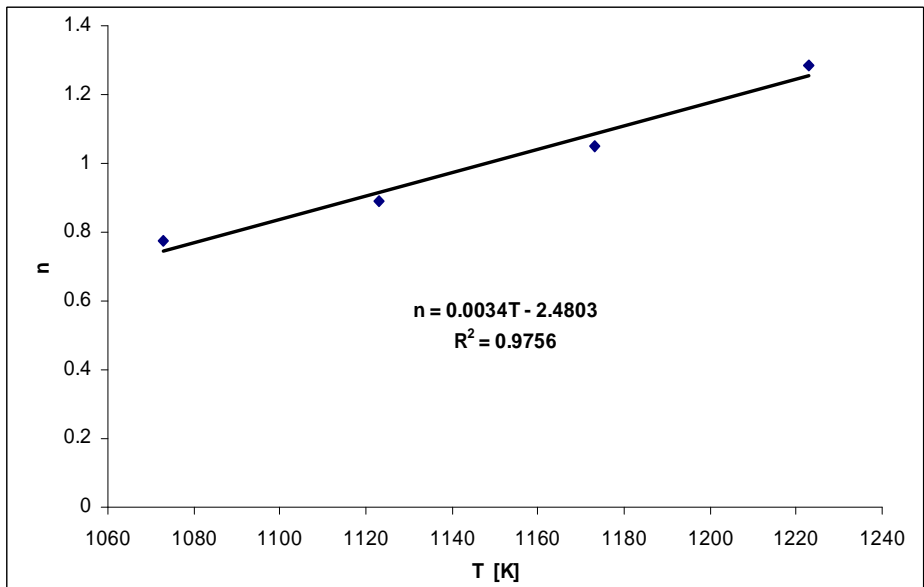


Fig. 6.  $\ln[-\ln(1-\eta_D)]$ - $\ln \tau$  dependence for the PCC granules with  $d_p = 0.063$  mm at different temperatures (AEK model equation).

Using graphical method to process the experimental results ( $\eta_D$ - $\tau$ ), the dependence of the process rate constant  $k(T)$  and of the kinetic order on temperature  $n(T)$  with the temperature was established, figure 7 and figure 8:



**Fig. 7.**  $\ln k$  versus  $1/T$  variation for PCC granules with  $d_p=0.063$  mm.



**Fig. 8.**  $n$  versus  $T$  dependence for PCC granules with  $d_p=0.063$  mm.

For the decomposition of PCC granules having 0.063 mm in diameter, the mathematical equation model (2) was obtained:

$$\eta_D = 1 - e^{-k(T)\tau^{n(T)}} \quad (2)$$

where :  $\ln k(T) = 5.674 - 68226.3/RT$  and  $n(T) = 0.0034 T - 2.4803$

In figure 9 is presented the validation of the model with experimental data.

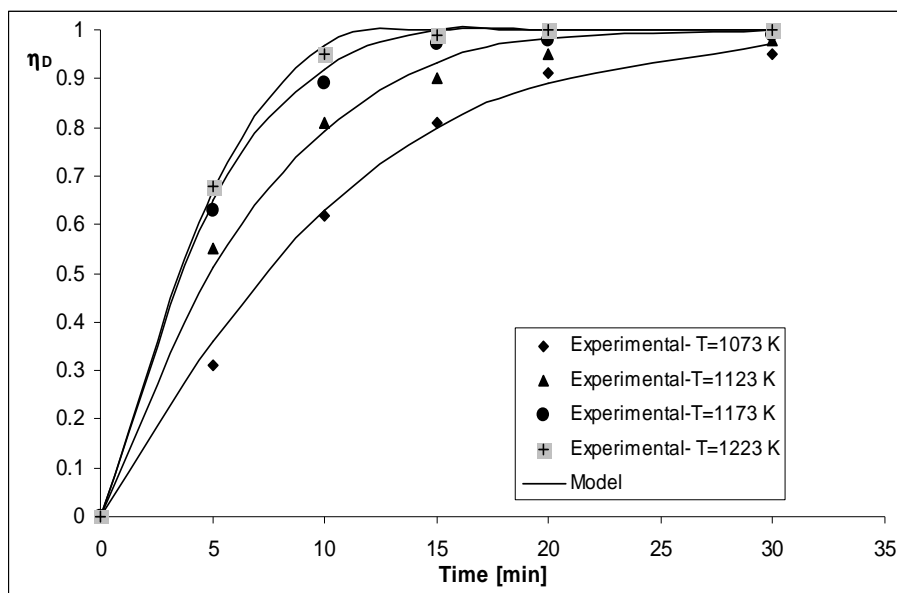


Fig. 9. AEK model validation.

The results given in figure 9 have shown that Avraami-Erofeev-Kolmogorov model describes the decomposition of precipitate  $\text{CaCO}_3$  granules with  $d_p=0.063$  mm in good agreement with experimental data. Standard deviation was in all cases less than 10%.

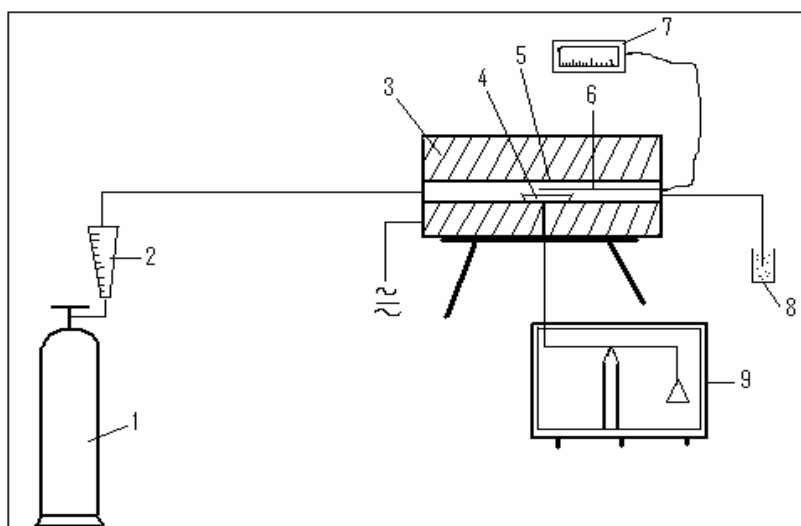
## CONCLUSIONS

1. The results obtained have indicated that the effect of temperature in the case of PCC calcination is more significant than the grain size.
2. Apparent activation energy obtained, over 61.4 kJ/mol suggested that the global process of decomposition is kinetically controlled.
3. The results obtained during the calcinations process of PCC showed that the unreacted core model is not valid for the entire domain of the decarbonation degree values.

- The equation of Avraami-Erofeev-Kolmogorov model can describe the real process of PCC decomposition with good precision; the standard deviations were less than 10%.

## 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 experiments were carried out on an experimental installation presented in figure 1.



**Fig. 1.** Experimental set-up for PCC calcination  
1-Gas cylinder with  $N_2$ ; 2- Gas flow meter; 3- Electric Furnace; 4- Nacelle with solid sample; 5-Tubular reactor; 6- Thermocouple; 7- Temperature controller; 8- Absorbing vessel for gas ; 9- Thermo balance

This installation contains a hand-made thermo balance, having a 30 mm diameter tubular reactor placed in a tubular electric furnace, with possibilities to operate in temperature range of 373-1473 K. The solid reactant placed in thin layer on a ceramic nacelle, was introduced in the tubular reactor and the experiments were carried out isothermally within the temperature range of 1073-1223 K. We used samples of 0.4-0.5g (PCC) with main diameter of 0.063 mm, 0.18 mm and 0.45 mm. The granulometric classes of the particles in the considered samples were obtained by sizing of precipitate calcium carbonate with a Retzsch set of sieves, mesh between 0-1000  $\mu\text{m}$ .

To evaluate the decomposition process in the time the variation of sample mass was determined every five minute.

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