

EXPERIMENTAL STUDY OF DRY DESULPHURIZATION PROCESS WITH CALCIUM OXIDE. CHARACTERIZATION OF CALCIUM OXIDE STRUCTURE

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ABSTRACT. Since the micro structure of the adsorbant has an important influence upon its reactivity, this paper presents the - in situ - generation of calcium oxide process from limestone. The calcium oxide obtained by calcination of limestone at temperatures of 973-1273 K and $p=0,3404$ bar was characterised by BET surface area, porosity and pore size distribution. The obtained surface areas are in the range between 18,9107 - 55,1966 m²/g and a porosity in the range of mesopores as a function of the particles size and the decomposition temperatures.

INTRODUCTION

Due to the important sulphur dioxide quantities emitted in the atmosphere, the flue gas desulfurization from the power plants, represents a strictly actual field of research.

Environmental pollution are consequences of the economic development and most of the industrial one. The energetic sector is one of the main pollutants of the atmosphere: SO₂ from the coal-burned power plant is one of the main sources. Coal contains a certain amount of sulfur, depending on its origin. During combustion, the sulfur reacts with the oxygen in the air and forms SO₂, which flows along with the flue gas into the atmosphere and contributes to the acid rains.

Romania registers pollutant emissions about 10-12% higher in comparison with some of the european countries, like: Holland, Belgium, Denmark or Germany. The energetic industry contributes to this situation, thus for producing of 1 kWh energy, the emissions are more higher in Romania as in Holland (about 40 – for sulphur oxide, 2 – for NO_x and 870 – for dust) [1].

Although the "international pollutant", character of sulphur oxide has been recognized at various international meetings and urgent and radical measures have been claimed, actually very little has been done so far.

Due to the important sulphur dioxide quantities emitted in the atmosphere, the flue gas desulphurization from the power plants, represents a strictly actual field of research [2 - 5].

From the great number of desulphurization methods (wet, semidry, dry) the practice confirms only the utilisation of alkaline, alkaline-earth, especially of limestone, and ammonia compounds. For the reactive dry adsorption of sulphur dioxide of flue gas, the most used adsorbants are: limestone, dolomite, lime and dolomitic lime.

Under identical experimental conditions, the reactivity of this adsorbants is significantly influenced of its chemical structure and composition [6].

If the limestone is utilised as adsorbant, its chemical composition may be a factor which contributes significantly to its reactivity.

In the case of dolomite, magnesium doesn't react in a significant manner but it has a favourable influence about the utilisation of calcium fraction. Silicium constitutes the most undesirable impurity because it reduces the reactivity of the particle in the interaction with sulphur dioxide.

The high content of iron in the adsorbant, through its catalitical oxidation action, seems to enhance the reactivity but sodium constitutes an impurity which determines diffusivity modifications in the reaction product layer (CaSO_4). However these hypotheses are not confirmed yet. Several researchers [5, 6] made estimations of the influence of particle size about the desulphurization degree and confirm a reverse correlation.

The optimal temperature of the dry injection of the adsorbant is a function of its origin, the particle size and reaction type, which always necessitates experimental determinations.

Since the micro structure of the adsorbant has an important influence about its reactivity, in this paper it would be presented the - in situ - generating of calcium oxide process from limestone. The generated calcium oxide was characterised by BET surface area, porosity and pore size distribution.

For this purpose, the calcination process were conducted in the temperature range 973-1273 K and the pressure in the system was $p=0,3404$ bar.

In the first stage it was established the evolution of the decarbonate degree in the heating and calcination period of the sample for the four used granulometric class.

EXPERIMENTAL

The experimental equipment used in our measurements was a CAHN TG-121 system presented in a previous paper [7].

It consisted of two sections: the main frame and the Data Acquisition and Control Station (DACS) which controls the system. The microbalance, the furnace, the cooling fan, the thermocouple, the gas and vacuum ports were the components of the main frame. The CAHN microbalance included in the TG-121 system is considered the finest apparatus available today for this application. Its sensitivity is of 0.1 g and the maximum capacity of 1.5 g. Each sample of limestone has been primarily calcinated for 40 minutes between 973 K- 1273 K, $P=0.3403$ bar and under a nitrogen stream. The probes belongs to one of the following average particle diameter: 25 μm , 90 μm , 450 μm and 900 μm . After the complete calcination, each sample has been characterised by BET surface area, porosity and pore size distribution. The operation parameters of the system are shown in Table 1.

Table 1.

Operate parameters of the system

Crt. Nr.	Parameter	Value
1	Calcination temperature	973 K, 1023 K, 1123 K, 1173 K, 1273 K
2	Calcination time	40 min
3	Pressure	0,3403 bar
4	Particle size of CaO	0-50; 80-100; 400-500; 800-1000 μm

Materials

The adsorbant was obtained “in situ” through calcination of limestone with the following chemical composition: CaCO_3 (97 %), Fe_2O_3 (1,8 %), Al_2O_3 (0,88 %), SiO_2 (0,3 %).

The granulometric class of the particles were obtained through volumetric sizing of limestone with a Retzsch set of sieves mesh between 0-1000 μm .

Each sample of calcium carbonate belonging to one granulometric class was subdue in a first stage to complete calcintion. After the calcination each sample has been characterised by BET surface area, porosity and pore size distribution through the sorption method.

RESULTS AND DISCUSSION

The evolution of the decomposition of limestone for all granulosities was followed through the decomposition degree η_D . On the basis of the material balance, one can write:

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

where: m_s^0, m_s – initial mass and at a moment of the sample [mg];

\bar{x}_{PC}^0 – mass fraction of the calcination losses (0,4397) determined as a arithmetical mean of four values obtained for four limestone samples submitted to calcination at 1323 K for two hours.

The obtained results are presented in figures 1, 2 and 3.

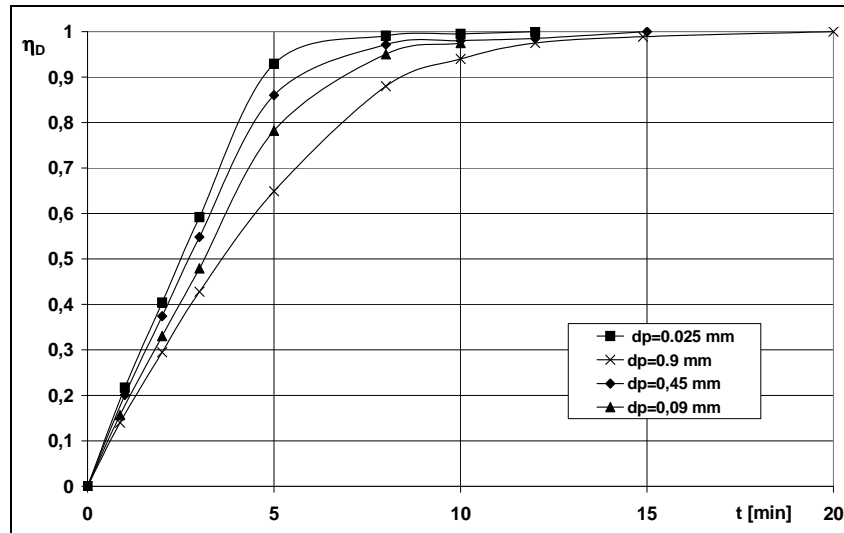


Fig. 1. Influence of particles sizes on the decomposition degree of CaCO_3 at $T_c=1173$ K

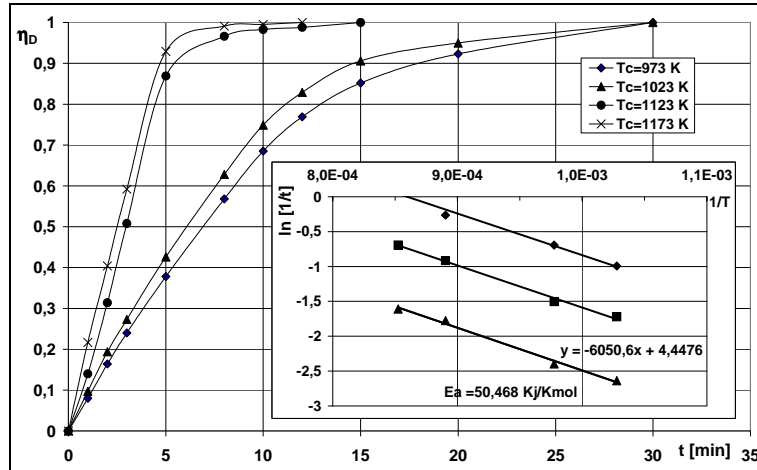


Fig. 2. Influence of temperature on the decomposition degree of CaCO_3 particles with $d_p=0,025\text{mm}$

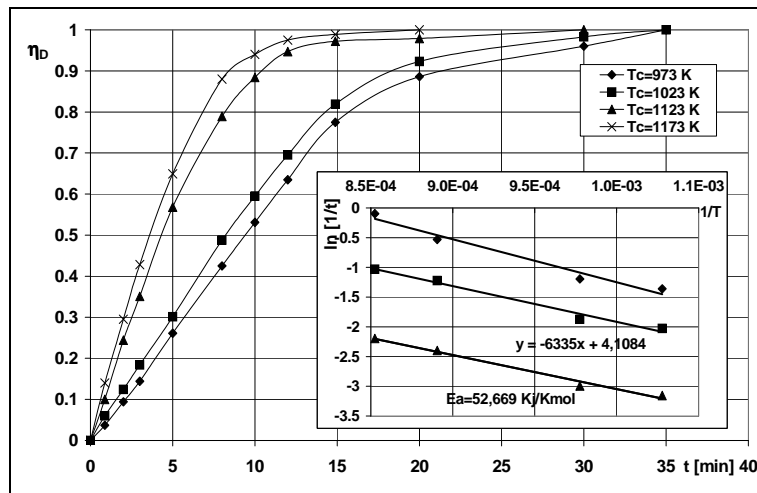


Fig. 3. Influence of temperature on the decomposition degree of CaCO_3 particles with $d_p=0,9\text{mm}$

The kinetic curves, show an insignificant influence of the particle size on the degree of decomposition. The difference that appears, is due to the different thermal conductivity of the particles layer from the examined samples. In all cases there would be reached the maximal decarbonation degree.

The calculated activation energy for both cases shown in figures 2 and 3 is about 50 – 53 KJ/mol and indicates that the calcination of limestone is generally kinetically controlled while the gas film resistance and pore diffusion limitation are negligible.

From the experimental data obtained in the sorption method the desorption isotherms shown in figure 4 are obtained.

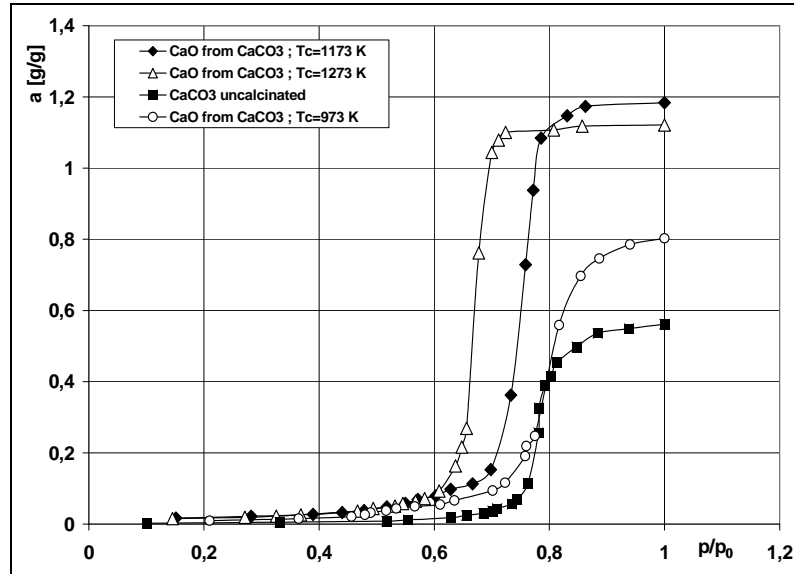


Fig. 4. Desorption isotherms for CaO particles with $d_p=0,025$ mm

In order to calculate the specific surface area there the Brunner, Emmet & Teller equation for the adsorption of benzen in polymolecular layers [8] was used:

$$\frac{x}{a(1-x)} = \frac{1}{a_m \cdot C} + \frac{C-1}{a_m \cdot C} \cdot x \quad (2)$$

Where: a – quantity of adsorbed benzen [g benzen/g CaO] at any value of the relative equilibrium pressure $x = p/p_0 = t_0/t$;

a_m - monomolecular load [g benzene /g CaO];

C – BET- parameter.

The BET – isotherm represented by equation (2) is a straight line given by:

$$y = m \cdot x + n \quad (3)$$

$$\text{Where: } y = \frac{x}{a(1-x)}; \quad m = \frac{(C-1)}{a_m \cdot C}; \quad n = \frac{1}{a_m \cdot C}$$

In the range of relative low pressures, the BET – equation is rigorous by linear and allows for the evaluation of a_m and C from the slope “ m ” and the ordinate intersection “ n ” of the line given by equation (3) (figure 5).

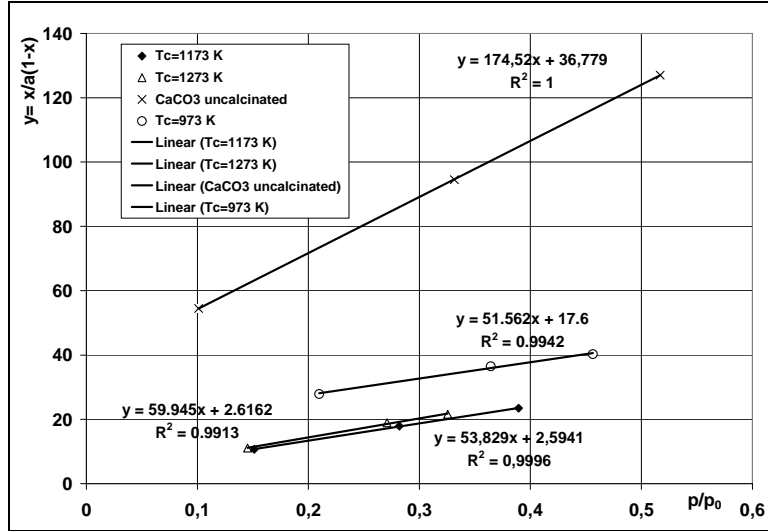


Fig. 5. BET-isotherms for CaO particles with $d_p=0,025$ mm

Considering that the covering is in monomolecular layer with compact and tangent arranged molecules and knowing the covering surface of one benzene molecule $s_0 = 40,3 \text{ \AA}^2$ at 293 K the specific surface can be calculated with following equation:

$$S_{sp} = \frac{a_m}{M_b} \cdot N_A \cdot s_0 \quad (4)$$

where: S_{sp} - BET specific surface area [m^2/g];

a_m - monomolecular load [g benzen/g CaO];

M_b - Molecular mass of the adsorbate (benzen) [g/mol];

N_A - Avogadro number [$6,023 \cdot 10^{23} \text{ mol}^{-1}$];

s_0 - covering surface of one benzene molecule [\AA^2].

The specific surfaces area calculated from the BET isotherms similar to those shown in figure 5 are presented in table 2.

Table 2.

Specific area of used adsorbant [m^2/g]

$\bar{d}_p \downarrow$ [μm]	Uncalcinated	T [K]				
		973	1023	1123	1173	1273
25	14,7274	44,9941	47,4971	53,4127	55,1966	49,7292
90	11,3384	35,9535	38,0421	42,3875	44,0020	39,3590
450	-	29,8988	33,2475	40,1042	41,8644	36,8775
900	6,8443	18,9107	25,0107	36,6412	40,1346	35,0438

The values of the specific area increase with the temperature until 1173 K. At higher temperatures the surface area decreases due to the sinterisation effect. Using the desorption isotherms there was calculated the mean pores radius and the pores size distribution. The vertical portion of the desorption isotherms were attributed to the capillary condensation-vaporisation phenomenon. The relation between the relative pressure x and the pore radius when condensation-vaporisation occurs is given by the Kelvin equation [9]:

$$x = \frac{p}{p_0} = \frac{t_0}{t} = e^{-\frac{2 \cdot \sigma \cdot M}{r \cdot \rho \cdot R \cdot T}} \quad (5)$$

where: $x = p/p_0$ - relative equilibrium vapours pressure;

σ - superficial tension of the liquid adsorbate (benzen) at the isotherm temperature [dyn/cm];

ρ - adsorbate density (benzen) at the isotherm temperature [g/cm³];

r - pore radius , equal with the menisc radius curvature [m];

M – molar mass of the adsorbate (benzen) [g/mol];

R –general gases constant;

T - temperatura isotherm [K].

From the equality between the pore radius and menisc curvature radius the pore size can be evaluated [8-11]. The distribution function versus radius was calculated with following equation:

$$\frac{\Delta a}{\Delta r} = f(r_p) \quad (6)$$

which reproduced the variation of the evacuated adsorbant amount in successively stages Δa as a function of the pore radius Δr shown in the figure 6.

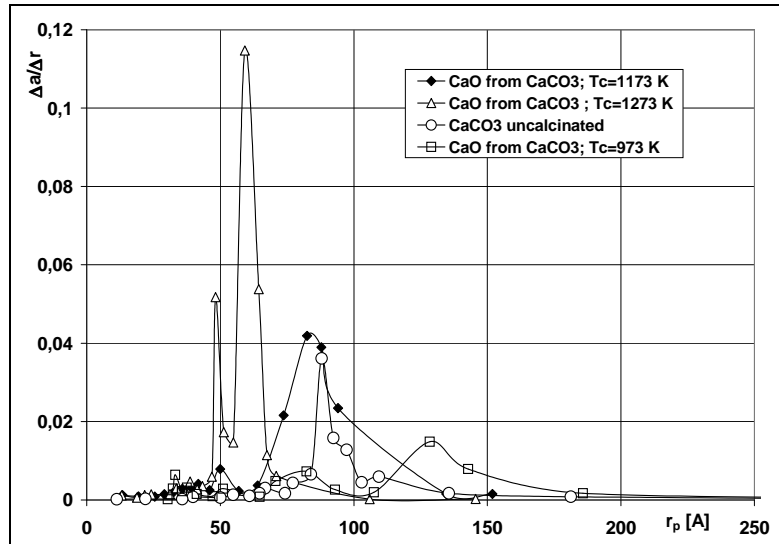


Fig. 6. Pore size distribution for CaO particles with $dp=0,025$ mm

Figure 6 shows a modest proportion of micropores, predominant is the mesopores category.

CONCLUSIONS

1. The structure and the chemical composition of the adsorbant has a significant importance on the calcium oxide reactivity in the flue gas desulphurization processes;
2. The obtained surface areas for calcium oxide are in the range between 18,9107 - 55,1966 m²/g and a porosity in the range of mesopores as a function of the particles size and the decomposition temperatures;
3. The high specific surface area increased the degree of utilisation of calcium oxide because the sulfation reaction is initially a surface reaction.
4. The large range in which the surface area of calcium oxide is included showed the necessity of its correlation with the kinetic of the sulphatation process

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