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INFLUENCE OF SPECIFIC SURFACE AREA ON THE REACTION OF LIME WITH SO_2. I.EXPERIMENTAL DATA

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ABSTRACT. Experimental measurements concerning the influence of calcinated and particles size on the specific surface area and reactivity CaO in the capture of SO_2 were performed. The paper presents data about the study of the SO_2/CaO reaction which includes specific surface area as an experimental variable. The obtained values of specific surface area are in the range of 19 – 55 m^2/g coresponding to particles size of 25 to 900µm. The CaO-reactivity increases significantly with the specific surface area, calcinated temperature and SO_2 concentration in the gas mixture.

INTRODUCTION

Reactions of acidic gases with calcined limestone have received much experimental study due to their industrial importance. They have also received extensive theoretical analysis as a class of gas-solid reaction because of the fact that the high porosity of the CaO (54%) makes them well suited for tests of the numerous grain – and pore – reaction models that have been formulated during the past decade.

A particular case is the reaction CaO-SO_2. The porous solid CaO, produced by calcining limestone:

$$CaCO_3 = CaO + CO_2 \tag{1}$$

can then react with SO_2 in the presence of oxygen to give calcium sulphat:

$$CaO + SO_2 + ½\, O_2 = CaSO_4 \tag{2}$$

A lot of experimental data have been achieved in modeling, but the rate-limiting step are still not understood [1].

The high temperature sensitivity of reaction (2) to has led some researchers to conclude that chemical reaction is rate controlling [2,3], while different features of the same data have been interpreted by others as evidence that the process is controlled by either:

- diffusion of the reactive gas through the product layer on the CaO grains that comprise the interior of the particles [4], or
- combinations of diffusion and chemical reaction on the grains.

Maybe for these reasons the process has been extensively studied both by scientists involved in the environmental protection [5 -6] and by academics interested in solid-gas reactions [7-9].

The aim of the present paper is to present data about the study of the SO_2/CaO reaction which included specific surface area as an experimental variable. Because of the importance of such data to an elucidation of the rate controlling mechanism of the process, this study was carried out with the objective of quantifying the surface area effect using the experimental techniques recently developed for producing CaO *in situ*.

EXPERIMENTAL

The experimental equipment used in our kinetic measurements was a CAHN TG-121 system (Figure 1).

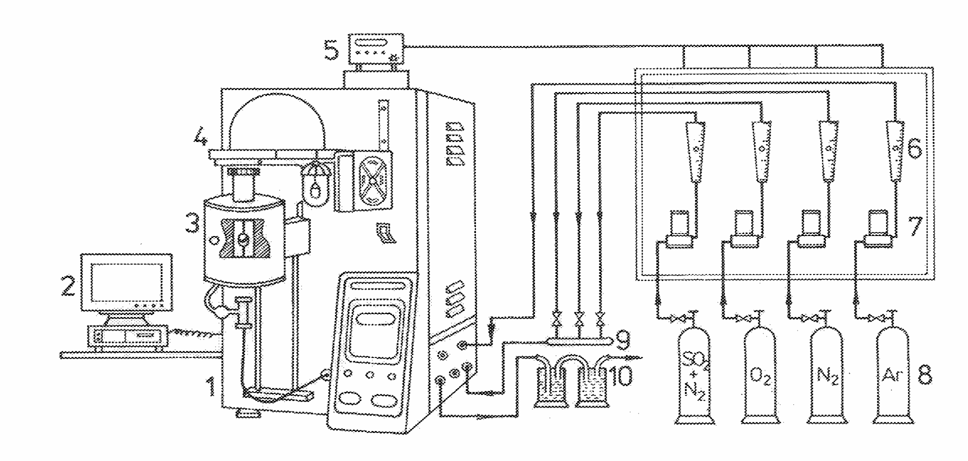

Figure 1. Experimental equipment: 1.Main frame; 2.Data Acquisition Control Station (DACS);3.Electric Furnace; 4. Microbalance and cooling fan; 5.Flow-gas-regulator; 6.Gasrotameter; 7.Massflowcontroller; 8. Gas cylinders; 9.Gas-mixture room; 10.Absorbing vessel for unreacted gas.

It consisted of two main sections: the main frame and the Data Acquisition and Control Station (DACS) which controlled 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 0.1µg and the maximum capacity of 1.5 g. Each sample of limestone has been primarily calcinated for 40 minutes at 973 K;1023 K; 1123 K; 1173 K; 1273K and 0.3403 bar. The thirty probes belonged to one of the following average particle diameter: 25µm, 90µm,180µm and 900µm. After the complete calcination, each sample has been sulfated in a gas mixture containing 0,3 % and 0,9% (vol.) SO_2, 20 % (vol.) O_2, and nitrogen for the balance. The gas mixture was prepared from pure gases measured with rotameters.

The temperature in the sulfation process was kept constant at 973K, and 1173K. The solid weight has been continuously registered. Specific surface areas were measured by nitrogen adsorbtion at –195 ˚C using the BET method.

RESULTS AND DISCUSSION

The principal variables that are expected to determine the rate of SO_2 capture by a given limestone are reaction temperature, specific surface area of the CaO and the SO_2 concentration in the gas mixture. The results of experimental evaluation of these variables are shown in Figure 2-7.

The effect of particles size and calcination temperature on the specific surface area is shown in Figure 2 and Figure 3.

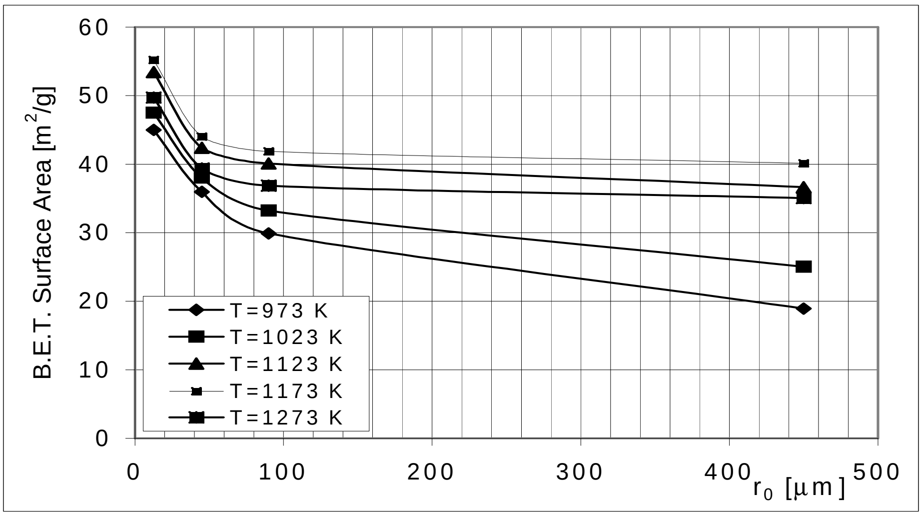

Figure 2. Effect of particles size on the specific surface area of CaO

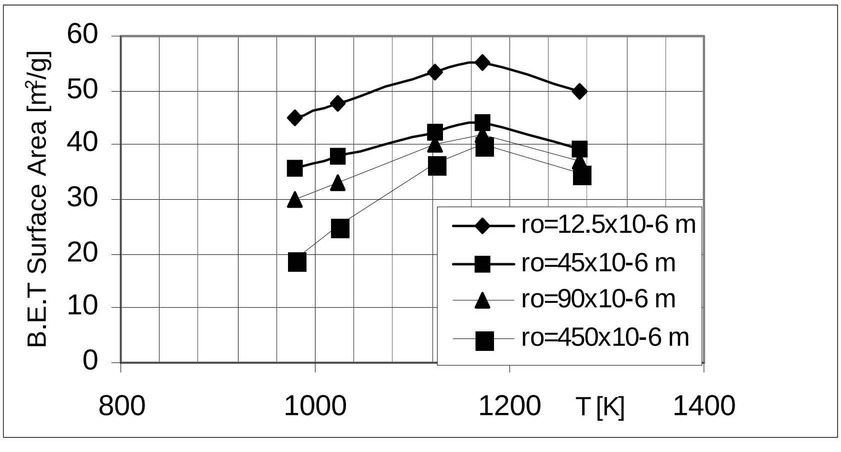

Figure 3. Effect of calcination temperature on the specific surface area of CaO

Figure 2 shows that the higer BET surface area belonged to smaller particles of CaO at 1173 K. For our limestone particles calcined in the TGA reactor at temperatures of 973 K-1273 K these are in the range of 19 to 55 m^2/g and this range is also similar to the CaO surface area found by Beruto et.al. [10].

Figure 3 shows that the surface area for constant particles size increases with the calcination temperature.The highest surface area was obtained by calcination in situ at 1173 K, and the lowest was obtained at 973 K.

At temperatures above 1173 K, while the sintering process begins the specific surface area decrease continuosly.

The effect of specific surface area on the reaction rate was determined at a constant temperature of 973 K and 1173 K with the results shown in Figure 4 and Figure 5. The reaction (2) is accompanied by an important solid weight increase, and the effects of side reactions are negligible. On the basis of materials balance equations (3):

$$
\begin{aligned}
m_{Cao} &= m^0{}_{CaO} - m^0{}_{CaO}.\eta_{CaO} \\
m_{CaSO_4} &= \frac{136}{56} m^0{}_{CaO}.\eta_{CaO} \\
m_{A''} &= m^0{}_{A''} \qquad (3) \\
m_S &= m^0{}_S \left(1 + \frac{80}{56} \bar{x}_{CaO}.\eta_{CaO}\right)
\end{aligned}
$$

the relation between the solid mass increase (Δm_S) and the fractional conversion of lime (η_{CaO}) can be derived:

$$\eta_{CaO} = \frac{56}{80} \frac{\Delta m_S}{x^0{}_{CaO}.m^0{}_S} \qquad (4)$$

According to the equation (4), at an average conversion of 50 %, a sample of 100 mg pure lime increase in weight with 71.42 mg because of sulfation reaction (2).

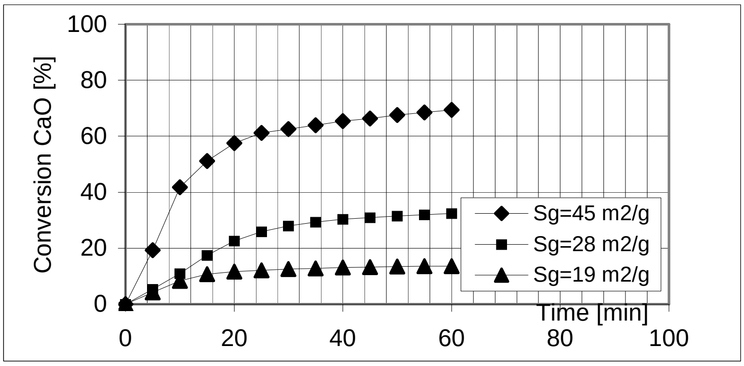

Figure 4. Reactivity of CaO as a function of its specific surface area T=973 K; C_{SO2}=0,9% vol ;Gv=50 cm^3/min

Figures 4 and 5 shown that the reactivity of CaO is strongly influenced by the specific surface area. The highest reactivity was obtained for the greatest specific surface area either at the reaction temperature of 973 K or 1173 K.

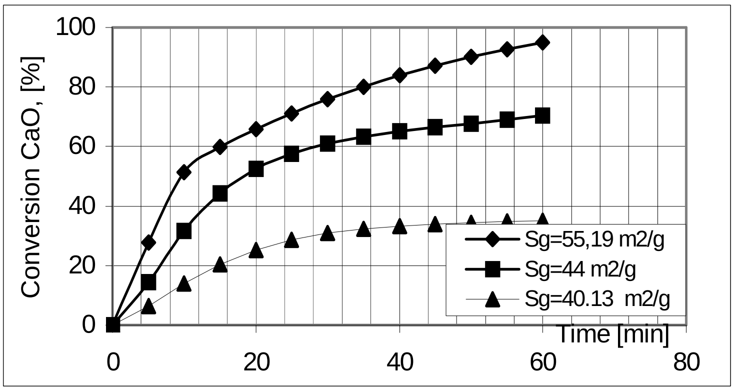

Figure 5. Reactivity of CaO as a function of its specific surface area $T=1173$ K; $C_{SO2}=0,9\%$ vol;Gv=50 cm^3/min

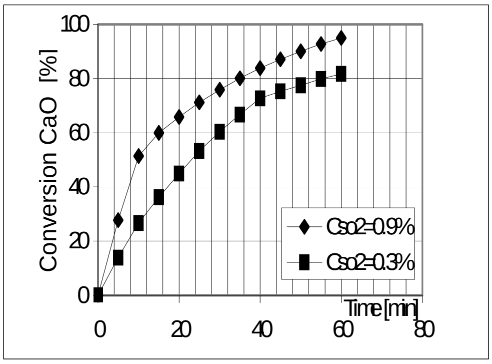

Figure 6. Effect of SO_2 concentration on CaO reactivity at $T=1173$ K; $S_g=55$ m^2/g

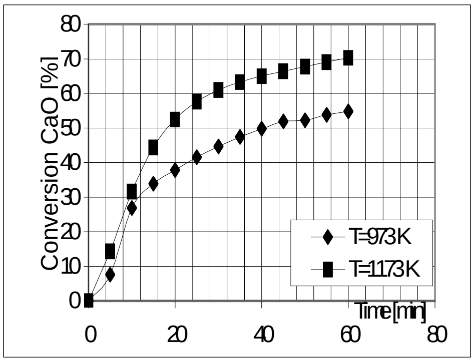

Figure 7. Effect of temperature on CaO reactivity at $C_{SO2}=0,9\%$; $S_g=36$ m^2/g

Figures 6 and 7 illustrates a significant influence of SO_2-concentration on the CaO reactivity at constant temperature (1173 K) and specific surface area respectively at constant sulfure dioxide concentration in the gas mixture and two different temperatures. Higher reactivities were obtained for greater sulfure dioxide concentrations at constant temperatures (fig. 6) and for greater temperature at constant sulfure dioxide concentration.

When the SO_2-concentration is uniform within the pore structure, which can be assumed to particles of low surface area, the reactivity versus time will be expected to follow one of five possible responses depending on the rate-controlling processes at the grain surfaces. These influences as described [11], can be written for constant temperature and constant grain size as follows:

- if chemical reaction controls at the surface of a shrinking core of unreacted CaO within the grain:

$$1-(1-\eta_{CaO})^{1/n} = k_c \cdot t \qquad n = 1,2,3 \qquad (5)$$

- if homogeneous first-order reaction occurs within the grains:

$$-\ln(1-\eta_{CaO}) = k_h \cdot t \qquad (6)$$

- for power law reaction within the grains:

$$(1-\eta_{CaO})^{-n} = k_p \cdot t \qquad n>0 \qquad (7)$$

- for product nucleation and growth on grain surfaces:

$$[-\ln(1-\eta_{CaO})]^{1/n} = k_g \cdot t \qquad n = 1,2,3,4 \qquad (8)$$

- for diffusion through the product layer surrounding unreacted cores of (spherical) grains:

$$1-3(1-\eta_{CaO})^{2/3} + 2(1-\eta_{CaO}) = k_d \cdot t \qquad (9)$$

Using the above equations, in the second part of the paper it should be presented the results for the establishment of the rate – controlling processes.

CONCLUSIONS

The limestone is quickly converted to lime which further reacts with sulfur dioxide. New studies have been carried out on the sulfation reaction using a CAHN TG –121 system for experimental measurements.

The experimental data shown that the reactivity of CaO are strongly influenced by three factors: calcined temperature, specific surface area and SO_2 concentration in the gas mixture.

Higher reactivities were obtained for greater sulfure dioxide concentrations at constant temperatures (fig. 6) and for greater temperature at constant sulfure dioxide concentration.

When the SO_2-concentration is uniform within the pore structure, which can be assumed to particles of low surface area, the reactivity versus time will be expected to follow one of five possible responses depending on the rate-controlling processes at the grain surfaces.

NOTATIONS

A'' – inert substances in the solid, - ;

m_i - mass of component , kg ;

P – pressure, Pa ;

S_g– specific surface area, m^2/g ;

T – temperature, K;

k_c, k_h, k_p, k_g, k_d – Constants defined by equations (5-9) for a given temperature, grain size, and SO_2-concentration relating conversion and time for grain reactions controlled, respectively by: c-chemical reaction; h-homogeneous reaction; p-power law reaction; g- product nucleation; d- product layer diffusion;

$\overline{x_{CaO}}^{0}$ - mass fraction of CaO in the lime, -;

Δm_s - thermogravimetric mass increase, kg ;

η_{caO} - fractional conversion of CaO.

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