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CHANGES IN TEXTURAL PROPERTIES OF LIMESTONE AND DOLOMITE DURING CALCINATION

F. RUBIERA, A.B. FUERTES, J.J. PIS, V. ARTOS and G. MARBÀN

Instituto Nacional del Carbòn (C.S.I.C.), Apdo. 73, 33080 Oviedo (Spain)

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ABSTRACT

The effect of the conversion degree, calcination conditions (temperature and CO_2 concentration) and retention time at high temperature on textural evolution in limestone and dolomite has been studied. A lower porous development was observed during calcination than was theoretically expected. An increase in CO_2 concentration during limestone calcination results in considerably wider pores provided that the specific surface area decreases; The formation of wider pores is not related to a further increase in conversion of CaO to $CaSO_4$.

INTRODUCTION

The combustion of coal in fluidised bed reactors provides a suitable means of reducing sulphur dioxide emissions. This reduction can be achieved by adding limestone ($CaCO_3$) or dolomite ($CaCO_3 \cdot MgCO_3$) particles. Under operating conditions in the reactor these carbonates are rapidly transformed into their oxides. Later on, the CaO thus obtained reacts with sulphur dioxide according to the equation

$$CaO + SO_2 + 1/2O_2 \rightarrow CaSO_4 \quad (1)$$

As $MgSO_4$ is unstable above 1073 K, MgO is inactive towards sulphation under these conditions [1].

Limestone and dolomite particles usually show very low porosity. Some porosity is generated during calcination due to the marked difference between the molar volume of $CaCO_3$ (36.9 cm^3 mol^{-1}) and CaO (16.9 cm^3 mol^{-1}). The CaO thus formed has a porosity of $\sim 54\%$ and a pore volume of ~ 0.36 cm^3 g^{-1} [2]. Because the molar volume of $CaSO_4$ (52.2 cm^3 mol^{-1}) is bigger than that of calcium carbonate, during sulphation the CaO pores will be full before complete conversion has been reached. Thus the maximum possible conversion is, in theory, 57% and the (Ca/S) molar ratio required to achieve total desulphuration is 1.75. However when using 1 mm limestone particles, a higher (Ca/S) molar ratio is needed in order to reach 90% desulphuration.

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Hartman and Trnka [3] consider that the reaction rate of sulphation is governed by three individual processes: diffusion of SO_2 through the pores, diffusion of SO_2 through the $CaSO_4$ layer formed, and chemical reaction. The diffusion of SO_2 through the pores controls the overall reaction when a 1 mm particle size is used (the standard size used in atmospheric fluidized bed boilers). This leads to a sharp decrease in SO_2 concentration from the outer surface to the centre of the particle. In this case, the sulphation mainly occurs in the outermost zone and stops when no further occlusion of the outer pores is possible [4]. In this way, the maximum possible conversion reached during sulphation is considerably lower than the 57% mentioned and greatly depends on the porous evolution of CaO and the size of the particles. Consequently, any improvement in the access of SO_2 through the particle will result in a higher degree of SO_2 capture.

Smaller limestone particle sizes could provide higher degrees of conversion, so that diffusion through the pores is not important for a particle size below 100 μm [5]. In this case the whole process is controlled by the diffusion of SO_2 through the $CaSO_4$ layer, as Borgwardt and Bruce have proved [6]. However, a decrease in the particle size increases elutriation loss in a fluidised bed combustor, making it advisable to use particles above 500 μm. In consequence, a good way of improving the applicability of sorbent particles bigger than 500 μm would be by the control of textural development during calcination.

In fact, whereas the specific pore volume is little affected by the normal FBC calcination conditions, the pore size is closely related to CO_2 concentration, retention time and the temperature of calcination [7,8]. Wide pores obviously allow a better diffusion of SO_2 through the particle.

The scope of this work is to evaluate the effect of different factors (calcination degree, retention time, CO_2 concentration, temperature) on the textural evolution of limestone and dolomite particles during calcination. The influence of pore development on sulphation is also discussed.

EXPERIMENTAL

Experiments were carried out in a quartz reactor, with an inner diameter of 20 mm, placed vertically in a tubular furnace. A thermocouple in contact with the bed was used to control the temperature. A 2 g sample was used for the calcination. The sample was fed quickly into the reactor. The conversion of $CaCO_3$ to CaO was calculated as

$$X = (m_o - m)/(m_o - m_\infty) \tag{2}$$

where m_o is the weight of the resulting sample from the process at the operation temperature in a CO_2 atmosphere and m_∞ is the weight of the resulting sample from total calcination.

TABLE 1

Chemical analysis of the samples

	$CaCO_3$	$MgCO_3$	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	Na_2O	K_2O
Limestone	95.84	1.04	1.75	0.08	0.16	0.04	0.05	0.04
Dolomite	53.71	40.02	0.20	0.14	0.08	0.45	0.02	0.02

A 1 g sample was used in the sulphation experiments. The samples were fed suddenly into the preheated reactor at the operation temperature. In these experiments, a gas flow of 3 l min^{-1} (STP) during calcination and 5 l min^{-1} (STP) during sulphation were used. The gas composition (%vol.) was: 5% O_2, 12% CO_2, 0.3% SO_2; the balance was N_2. The time of exposure was 1 hour.

All experiments were carried out using a particle size ranging from 0.71 to 1 mm. The chemical analysis of the materials is given in Table 1.

The raw and calcined samples were characterized texturally (pore volume, porosity, specific surface area and pore size distribution) by mercury porosimetry. The specific surface was determined using the Roostare and Prenzlow method [9] for powders with areas below 100 m^2 g^{-1}. A Carlo Erba mercury porosimeter (Macropore Unit 120 and Porosimeter 2000) was used.

RESULTS AND DISCUSSION

The evolution of pore volume during calcination may be described by the equation

$$V_p = \frac{V_{po} + 0.454(1-P)X}{1-(1-P)X} \tag{3}$$

where $P = m_\infty / m_o$ (0.564 for limestone and 0.674 for dolomite), X is the fraction of calcined $CaCO_3$ and V_{po} the pore volume of the initial sample (cm^3 g^{-1}).

The pore volume obviously depends on the porosity of the initial material and the pores generated during thermal treatment in the CO_2 atmosphere. These pores are not related to the decomposition of calcium carbonate but contribute to the intake of $CaSO_4$. As a general rule, every kind of limestone rock has very low porosity, the initial pore volume of limestone used in this experiment being 0.014 cm^3 g^{-1}. Untreated dolomite also has low porosity (the initial pore volume of dolomite is 0.015 cm^3 g^{-1}). However, dolomite is semi-calcined at 800 °C and $P_{CO_2} = 1$ atm because the dissociation temperature of $MgCO_3$ is about 400 °C in these conditions. The pore volume of the semi-calcined dolomite is 0.120 cm^3 g^{-1}.

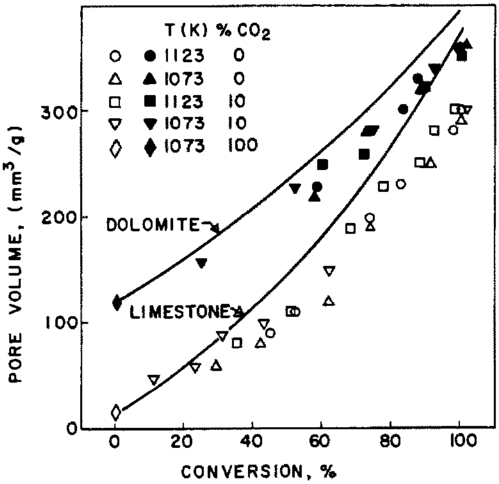

Fig. 1. Variation of pore volume during calcination of limestone (open symbols) and dolomite (closed symbols). Continuous lines correspond to eqn. (3).

Figure 1 shows the variation in the pore volume of limestone and dolomite with the conversion degree. The continuous lines represent the change in the pore volume predicted by eqn. (3). This equation predicts values a little higher than those obtained experimentally. This is probably due to shrinkage during calcination [10]. Appreciable differences between the evolution of pore volume and the degree of conversion under different calcination conditions (temperature and CO_2 concentration) were not observed.

Figure 1 shows greater pore development in dolomite compared with limestone. Thus fully calcined dolomite has a pore volume of 0.360 cm^3 g^{-1} whereas the pore volume in calcined limestone is 0.300 cm^3 g^{-1}.

The pore volume developed during calcination determines the maximum conversion attainable during sulphation. This conversion may be evaluated by the equation

$$X_m = 125 \frac{P}{1-P} V_{po} \qquad (4)$$

where V_{po} is the pore volume of the wholly calcined sample. Equation (4) predicts a maximum achievable conversion of 49% during sulphation for limestone and 93% for dolomite. Thus dolomite appears to be much more efficient than limestone but the lower percentage of $CaCO_3$ in dolomite must be considered. In fact 213 g of limestone is necessary to retain 1 mol of SO_2, compared with 200 g of dolomite. Under these circumstances, the difference is not appreciable.

Other textural properties of limestone and dolomite under different conditions of calcination are given in Table 2. The samples treated with CO_2 concentrations below 100% were completely calcined. Table 2 shows that

TABLE 2

Textural properties of limestone and dolomite samples under different conditions

Sample	T (K)	CO_2 (%)	Porosity (%)	Specific surface area (m^2 g^{-1})	Pore radius (Å)
Limestone	Raw		3	0.2	–
	1073	0	44	30	147
	1073	10	49	3	2451
	1123	0	45	25	163
	1123	10	44	7	865
	1173	0	47	22	204
	1173	10	46	9	460
Dolomite	Raw		4	0.2	–
	1073	100	25	10	147
	1073	0	55	24	264
	1073	10	46	19	306
	1123	100	22	7	263
	1123	0	55	22	334
	1123	10	51	17	268

both the surface area and the pore radius of limestone are considerably affected by changes in the calcination conditions. The effect of CO_2 on limestone is remarkable. Thus, samples calcined in N_2 at 1123 K have a surface area of 25 cm^2 g^{-1} whereas those calcined in 10% CO_2 have an area of 7 m^2 g^{-1}. The pore radius is affected in the same way, being 865 Å in 10% CO_2 and 163 Å in N_2. This difference decreases as the temperature increases. Thus, whilst the pore radius increases from 147 Å in N_2 to 2451 Å in 10% CO_2 at 1073 K, this variation is only from 204 to 460 Å at 1173 K. However, in the case of dolomite no significant change in textural development under the different calcination conditions was observed.

The increase both in temperature and in CO_2 concentration enhances the sintering of CaO [11,12] which results in a decrease in the specific surface area and an increase in the pore radius. On the other hand, the surface area of the CaO particles resulting from calcination in N_2 is considerably lower than that found by Borgwardt [13] for CaO particles originating from 2 μm limestone particles (104 m^2 g^{-1}). The reason for this difference is due to the CaO sintering during calcination. The CO_2 produced at the $CaCO_3$–CaO interface diffuses to the outer layer of the particle. While the gas is diffusing the CO_2 accelerates the sintering of the CaO formed. In consequence, at the end of calcination the specific surface area of CaO particles is lower than that of the nascent CaO.

The pore volume generated during calcination limits sulphation, but in practice maximum conversion is reached when pore plugging occurs (diffusion control). This obviously depends on the pore size. Several authors [14–16] have noticed the strong relation between the pore radius and

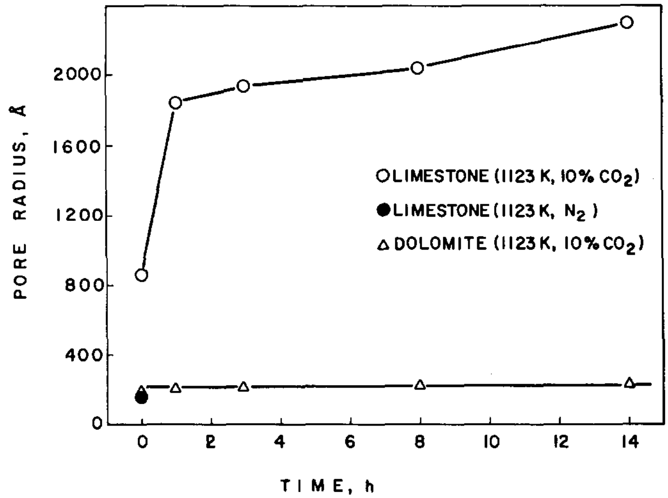

Fig. 2. Variation of pore radius with retention time (after overall calcination).

sulphation capability. The pore size generated during calcination is influenced by a number of parameters as has already been shown. In particular, CO_2 concentration during the calcination and the retention time of the calcined sample at high temperature is of great importance.

Figure 2 shows the evolution of the pore radius in relation to the retention time (after calcination) for limestone and dolomite at 1123 K and 10% CO_2. The difference between the behaviours of dolomite and limestone is remarkable. Thus, the dolomite pore radius does not change with retention time and remains at ~ 200 Å. However, in the case of limestone there is a rapid initial increase from 865 to 1840 Å for the first hour. This increase slows down and after 14 hours the pore radius is 2300 Å. In connection with this, the surface area diminishes from 7 $m^2\ g^{-1}$ for the initial time to about 2 $m^2\ g^{-1}$ for a retention time of 14 h. Once the limestone calcination has finished, the sintering of the CaO goes on [12,13,17]. This enables the textural properties of calcined particles to evolve under certain conditions, namely, high temperature, and the presence of CO_2 and H_2O. As these conditions arise during fluidised bed combustion, it can be assumed that sulphation and sintering occur simultaneously in the reactor. This means that the pore radius will continue increasing, impeding fast pore closure, and the degree of sulphation will also increase.

The effect of the concentration of CO_2 used during calcination on the evolution of the pore radius and the specific surface area is shown in Figs. 3 and 4. The behaviour of the dolomite is similar to that seen in Fig. 2. The pore radius hardly changes, ranging from 200 to 250 Å. Ulerich et al. [7] also found that the pore size distribution for dolomite was little affected by the calcination conditions. However, in the case of limestone, the pore radius increases from 150 Å for samples calcined at 1123 K in N_2 to 6700 Å for

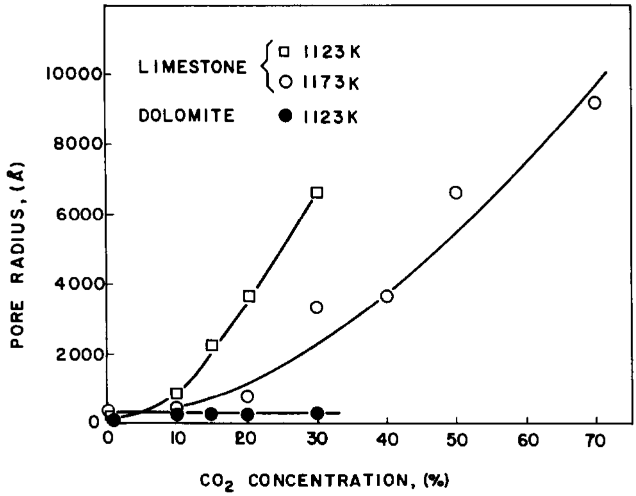

Fig. 3. Pore radius evolution for samples calcined at several CO_2 concentrations.

samples calcined in 30% CO_2. At 1173 K, the pore radius increases from 200 Å (N_2) to 9200 Å (70% CO_2).

Figure 3 shows, again, that higher operating temperatures during calcination reduce the pore radius. The specific surface area of the calcined samples strongly decreases when the CO_2 concentration is increased. At 1123 K, the specific surface falls from 25 m^2 g^{-1} in N_2 to 3 m^2 g^{-1} for calcination in 30% CO_2. At 1173 K, this decrease ranges from 22 m^2 g^{-1} in N_2 to about 1 m^2 g^{-1} in 70% CO_2. The CO_2 clearly enhances the sintering of CaO powders. The mechanism of this process is not well understood, although Borgwardt et al. [17] and Beruto et al. [11] suggest a catalytic effect from the CO_2.

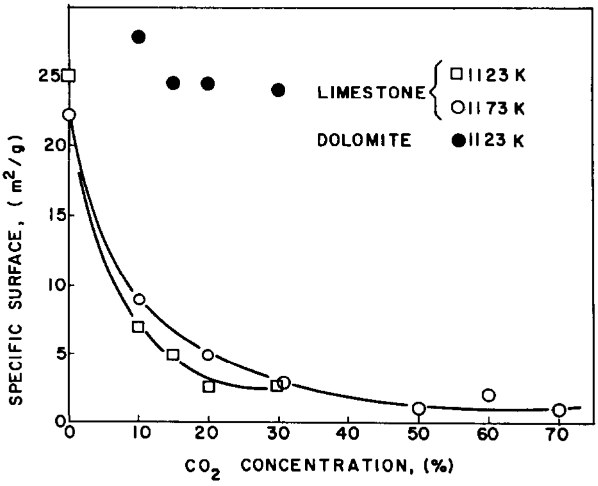

Fig. 4. Variation of specific surface area with CO_2 concentration.

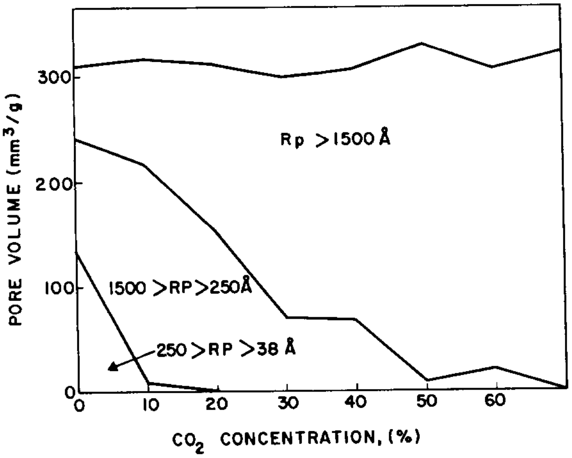

Fig. 5. Changes in pore size distribution for samples of limestone calcined under different CO_2 concentrations.

Changes in pore size distribution as a consequence of this effect are shown in Fig. 5. It should be noted that the total pore volume stays at 0.300–0.330 cm^3 g^{-1}. However, the volume whose pore radius is above 1500 Å changes from 22% total volume for calcination in N_2, to 77% for calcination in 30% CO_2 and 100% in 70% CO_2. On the other hand, a decrease in the pore volume due to shrinkage under several CO_2 concentrations was not observed.

The textural properties which develop under different calcination conditions determine the sulphation of calcined particles. Thus, it has been proved that calcination under certain conditions (high CO_2 concentrations and retention times) produces a notable increase in pore radius. This should

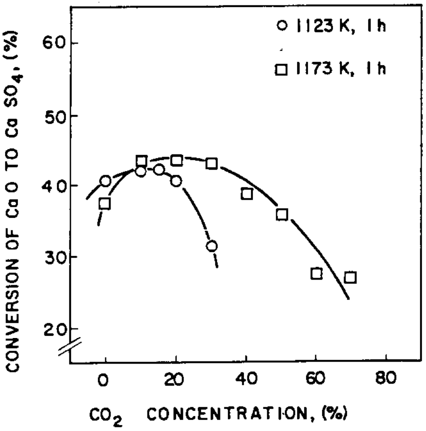

Fig. 6. Dependence of the sulphation conversion of calcium oxide on CO_2 concentration during calcination.

obviously enhance the diffusion of SO_2 into the particle and in consequence enhance sulphation. However, the results shown in Fig. 6 are not in agreement with this hypothesis. Figure 6 gives the conversion from CaO to $CaSO_4$ for several CO_2 concentrations in the calcined limestone samples whose textural characteristics are correlative with those shown in Figs. 3–5. A slight increase in conversion was noted when the concentration of CO_2 changes from 0 to 10–15% at 1123 K and up to 20–25% at 1173 K. At 1173 K, the maximum in sulphation appears at 20–25% CO_2. Both maximum points belong to calcined samples with pore radius ranging between 1000 and 2000 Å. This behaviour can be understood if one takes into account the fact that although an increase in the pore radius enhances the diffusion of SO_2 into the particle and retards pore closure, the decrease in the specific surface area reduces reactivity. These opposing effects lead to a maximum conversion which is correlative with the pore radius ranging between 1000 and 2000 Å.

CONCLUSIONS

Changes in limestone and dolomite pore volume during calcination are lower than expected due to shrinkage. Calcination conditions have a strong effect on the textural evolution of limestone but not of dolomite. In the case of limestone the pore radius is notably increased by the presence of CO_2 during the calcination, with values as high as 9200 Å in 70% CO_2 at 1173 K. Once the calcination was completed, the textural characteristics of the calcined particles of limestone continue evolving due to sintering. A big increase in the pore radius of calcined limestone during the first hour of sintering was observed.

The increase in the pore radius during calcination does not lead to an increase in the degree of sulphation. This reaches maximum values for the calcined samples with pore radius ranging from 1000 to 2000 Å.

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