TEXTURE OF A LIMESTONE CALCINE AND ITS REACTIVITY WITH SULPHUR DIOXIDE

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A micro-grained limestone was used to study the effects of such variables as temperature and time of exposure to the gas on surface area, pore size distribution and porosity of calcined particles under the conditions applicable to a practical unit for fluidized-bed combustion and desulphurization. The mean pore size was correlated as a function of the temperature of calcination. An optimum temperature was found for the sulphation reaction of the carbonate.

Temperature at which a contactor with a fluidized bed of limestone will be operated should be selected by consideration of a number of technical and economical factors. The present state of knowledge on the fluidized-bed combustion and desulphurization does not allow to analyze them in detail. One of the key factors is the effect of temperature on the rate at which sulphur dioxide reacts with particles of calcium oxide.

In once-through limestone process it would be impractical to use the precalcined sorbent. At high temperature, the limestone rock is usually calcined immediately, and in the presence of excess oxygen, sulphur dioxide combines with calcium oxide to form calcium sulphate[1,2]. As follows from the equilibrium data[3], in flue gas containing 10% of carbon dioxide by vol., calcium carbonate starts to decompose at 1 023—1 033 K. Physico-chemical properties of the formed calcine are strongly affected by the nature of the original carbonate rock and conditions of the calcination process.

A general survey on problems and the reaction kinetics of thermal decomposition of calcium carbonate was published by Hyatt and coworkers[4]. Fisher[5,6] presented in his study data on the size of crystallites and porosity of calcines prepared under various conditions. These studies of calcination were made under the conditions used in the lime industry where relatively large particles are heated in kilns at high temperature for considerable lengths of time. A mathematical model of the shock calcination of micron-size particles in time intervals of seconds or less, as it would occur in an limestone injection process, was recently developed by Biba and coworkers[7]. The said investigations were made at 1 223—1 673 K which is well above practical temperatures of the considered desulphurization process (1 073—1 173 K). None of the published works dealt with changes in the physical characteristics of the lime caused by the different temperature of calcination and corresponding differences of its reactivity with sulphur dioxide.

The purpose of this study was to determine an optimum temperature for the sulphation reaction of a commercial limestone and find the effect of temperature on the texture of its calcine.

EXPERIMENTAL

Reactor. A differential, single-pass reactor with a thin, fixed bed of the solid was employed. The flue gas fed to the reactor was generated by combustion of propane. Further details on the apparatus and the analyses can be found elsewhere[8].

Material. The present study was conducted with a commercial, reactive limestone from the quarry located at Čížkovice near Lovosice. This natural carbonate was chosen because of its high attainable conversion to calcium sulphate found in our previous comparative studies[9,10] of a number of carbonate rocks. The limestone from Čížkovice will probably be used as an additive in studies of fluidized-bed combustion and desulphurization on a larger sized unit in near future. This rock contains a considerable amount of silica (15% by weight), and aluminum oxide (3·6% by weight), and is classified as a calcareous marl with 42·4% of calcium oxide. The crushed and sieved particles were of irregular shapes and mostly without sharp edges. Majority of the particles were grey, some of them with a green or yellow shade. Microscopic examination revealed a very fine-grained structure of the rock. It contains numerous organic residues frequently filled with crystallized calcite. The fraction of particles used in this work comprised a size range 0·50 to 0·63 mm ($\overline{D}_p = 0{\cdot}565$ mm).

Measurement. Having steadied the whole apparatus (the flow rates of gases and the temperature) the weighed sample of dried limestone was placed into the reactor and exposed to the flue gas. The sample removed from the reactor was partially cooled and transferred immediately from the hot cup into an air-tight bottle to prevent hydration and recarbonation. In the samples calcined in the flue containing no sulphur dioxide (about 5 g) physical properties such as pore volume, pore size distribution and BET surface area were determined. Pore volumes of the calcined particles were measured by helium and mercury displacement. Pore size distributions were determined by measuring the volume of mercury penetrating the pore volume at increasing pressure using the Carlo Erba Porosimeter. The amount of sulphate in the particles exposed to the flue gas containing sulphur dioxide was determined by titration.

The experimental program was divided into two parts: *1*) Experiments were made to determine the effects of the temperature and time of calcination on the surface area, pore size distribution and pore volume of the prepared calcines. *2*) Uncalcined particles of the limestone were exposed to the flue gas containing sulphur dioxide at different temperatures and their conversions were measured. A range of the experimental conditions was chosen with respect to the assumed operational regime of a fluidized-bed boiler with desulphurization: temperature about 1123 K, particles of limestone as large as 0·2—0·8 mm, a mean residence time of the solid in the bed on the order of hours[11].

RESULTS AND DISCUSSION

The Effect of Calcination Temperature on the Specific Surface Area

In the previous study[10] we have found out that at 1023 K the thermal decomposition of limestone proceeds very slowly and is incomplete even after long times of exposure. As the equilibrium data show the partial pressure of carbon dioxide is too low at this temperature and, therefore, a driving force of the dissociation process is too small. That was why the lowest temperature was chosen 1073 K for experiments. An upper limit of 1223 K was given by the heat-resistance of the material of the reactor.

Values of the BET surface area of the particles calcined 1073, 1123, 1173 and 1223 K are shown in Fig. 1. From the course of the curve in this figure a considerable effect of the calcination temperature can be seen on the surface area of calcined particles. Raising the temperature of calcination from 1073 to 1223 K caused a decrease in surface area from 3·8 to 1·9 m^2/g.

These values are in general agreement with data reported in the literature. Borgwardt and Harvey[10] determined surface areas of calcines produced from different types of carbonate rocks at 1253 K. Their values vary broadly from 0·6 to 38 m^2/g, most of them amount to 1 – 3 m^2 per gram of calcine. Borgwardt and Harvey also measured the rate of sulphation of different limestones and found a direct relationship between the initial reaction rate and the BET surface area.

The grain model proved to be very useful in analysis of the sulphation reaction[13–15]. The mean size of spherical grains composing macroscopic particles can be calculated from their surface area by the equation

$$r_g = 3/S_g \varrho_{He} \,. \qquad (1)$$

The calculated radii of the grains decrease with increasing surface areas and thus increase with temperature from 2·87 . 10^{-5} to 5·83 . 10^{-5} cm. The broadening of

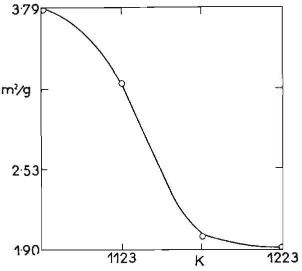

FIG. 1

Effect of the Temperature of Calcination on the Surface Area of a Calcine

Limestone Čížkovice, particle size 0·565 mm, exposure time 240 min.

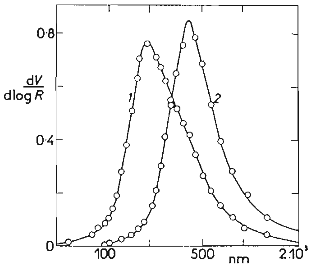

FIG. 2

Pore Size Distribution of the Particles Calcined at 1123 K (curve *1*) and 1223 K (curve *2*)

Limestone Čížkovice, particle size 0·565 mm, exposure time 240 min.

X-ray diffraction lines was used to determine the mean grain size of the calcined samples in our work with the grain model[13]. Such values were about $1 . 10^{-5}$ cm. The model described well the effect of principal variables on the course of reaction and predicts considerably slower sorption of sulphur dioxide by the calcined particles made up of larger grains.

It can be seen that the particles produced by calcination at lower temperatures have higher surface area, which is desirable for the sulphation reaction.

The Effect of Calcination Temperature on the Pore Size Distribution

The effect of temperature on the pore size distribution is shown in Fig. 2. Whereas in the particles calcined at 1123 K the pore radii are in the range 30 to 2500 nm, those in the particles calcined at 1223 K vary from 90 to 7500 nm. The mean pore sizes for the two temperatures are about 200 nm (1123 K) and 440 nm (1223 K). These values and those determined for 1073 and 1173 K are plotted in Fig. 3. It is seen in this figure that raising the temperature of calcination causes a rapid increase in the mean pore size. The increase of the calcination temperature from 1073 K by 150 K results in formation of pores the diameter of which is doubled.

The effect of calcination temperature on the mean pore size was correlated by a simple empirical function

$$\log_{10} \bar{R} = -3304{\cdot}15/T + 5{\cdot}33812 . \qquad (2)$$

As shown in Fig. 3 the mean pore sizes computed by Eq. (*2*) are in good agreement with the values determined by experiment. Deviations from the experimental values vary in the range −12·6 to +1·5% rel.

TABLE I

Effect of the Temperature of Calcination and Length of Exposure on the Texture of Calcines

Calcination		Annealing		Mean pore size nm	Surface area m²/g	Porosity
temperature K	exposure min	temperature K	exposure min			
1 073	240	—	—	195	3·80	0·524
1 073	240	1 173	240	388	2·05	0·542
1 173	240	—	—	337	1·95	0·509
1 073	240	1 223	240	515	1·94	0·560
1 223	240	—	—	447	1·87	0·509

To find out whether the texture of calcines is determined exclusively by the temperature of calcination, *i.e.* the temperature of the process when carbon dioxide is released, the following experiments were made. The particles calcined at 1073 K were further exposed to the flue gas (annealed) at 1173 K in one case and at 1223 K in the other case. Their textural characteristics are given and compared in Table I and in Fig. 4 with the parameters of calcines produced in one-stage operation. Although the comparison is made more difficult by the fact that the overall times of exposure are not the same, it can clearly be seen that the texture of the calcines, annealed at the temperature higher that of calcination, is different. Such differences are more expressive when a difference between the temperature of calcination and that of adsitional annealing is greater.

The obtained results suggest that the transformations in structure are not completed immediately after release of carbon dioxide from the lattice of calcite belonging to the hexagonal (rhombohedral) crystal system. Calcium oxide occurs in the face centered cubic structure and the course of its recrystallization depends on the conditions of annealing. Besides the nature of the parent limestone the state of the texture of calcined particles is determined by their overall temperature-time history.

From the standpoint of capacity of the calcines to react with sulphur dioxide, *i.e.* with respect to their attainable conversion, larger pores are desirable. The reacting

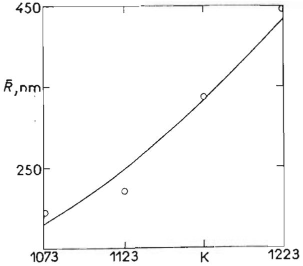

FIG. 3

Dependence of the Mean Pore Size on the Temperature of Calcination

The solid line shows the values of mean pore size predicted by Eq. (*2*). Limestone Čížkovice, particle size 0·565 mm, exposure time 240 min.

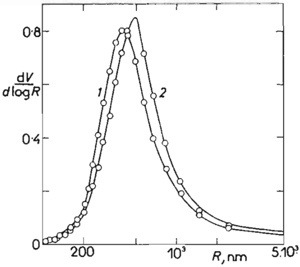

FIG. 4

Effect of the Conditions of Calcination on the Pore Size Distribution in Calcined Particles

Calcination at 1223 K, exposure time 240 min (curve *1*); calcination at 1073 K, exposure time 240 min and annealing for 240 min at 1223 K (curve 2).

gases diffuse easily into the centre of particles by such pores. From the calcined particles of the same pore volume, Potter[14] found higher conversions of the particles containing larger pores.

An effect of the temperature of calcination on the porosity of particles is illustrated in Fig. 5. It is seen that, in the applied range, the effect of the calcination temperature on the porosity is not expressive. The measured values are near 0·51 – 0·52. It is of interest to note that the calcined and further annealed particles are somewhat more porous than those nonannealed. Our results[15] and also findings of other authors[14] show a close relation between the sulphur dioxide sorption capacity and the pore volume of reacting particles.

The Effect of Temperature on the Course of the Sulphation Reaction

The effect of temperature on the degree of conversion was investigated using the dried, noncalcined particles of mean size 0·282 mm. The amount of sulphate in the reacted particles was determined after 20, 30, 45 and 60 min of exposure to the flue gas. The experimental results are plotted in Fig. 6.

From the curves in this figure it is obvious that the conversion increases with increasing length of the exposure. The family of curves is limited by the isotherms

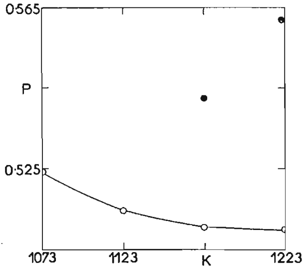

FIG. 5

Effect of the Calcination Conditions on the Porosity of Particles

○ Calcination, exposure time 240 min; ● calcination at 1 073 K (240 min) and annealing at 1 173 K (240 min); ◓ calcination at 1 073 K (240 min) and annealing at 1 223 K (240 min). Limestone Čížkovice, particle size 0·565 mm.

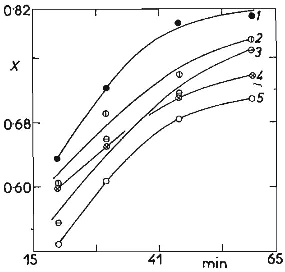

FIG. 6

Dependence of the Conversion of Calcium Oxide tu Sulphate on the Exposure Time and Temperature

○ 1 023 K, ⦶ 1 073 K, ● 1 123 K, ⊖ 1 173 K, ⊗ 1 223 K. Limestone Čížkovice, particle size 0·282 mm, concentration of SO_2 0·3% by vol.

1023 and 1123 K. The lowest conversions were attained at 1023 K, the highest ones were found at 1123 K over the whole time interval. The first temperature is clearly too low for the sulphation reaction. The X-ray analyses revealed the presence of undecomposed calcium carbonate in the particles sulphated at 1023 K.

Although the experimental data are considerably scattered, the effect of temperature on the rate of reaction can be seen well in Fig. 7. From smoothed graphs of conversion *vs* time of exposure, the times required to attain a conversion of 70% were obtained and plotted in figure 7. It is seen that the sulphation is accelerated when temperature is raised in the range 1023–1213 K. The reaction proceeds most rapidly at temperatures near 1123 K; at higher temperatures the rate of the sulphation reaction is lower.

This optimum temperature is by about 50 K lower than the optimum temperature determined for the limestone from the quarry in Štramberk in our earlier work[13]. Unlike the rock used in this study, the limestone from Štramberk is a high-grade and rather coarse-grained mineral. Hoke and coworkers[16] used a natural limestone for removal of sulfur dioxide from flue gas in a fluidized bed and found that the bed was most efficient at 1143 K.

Working with precalcined particles at 1253 K, Borgwardt[17] found that the rate of sulphation increased with temperature in the whole measured range 923–1253 K. The chemical equilibrium remains favourable up to 1343 K (ref. [1]). McClellan[18] found beginning thermal decomposition of calcium sulphate at 1473 K.

The rate of the sulphation reaction itself increases with temperature until equilibrium constraints become evident. The results of Reid[1], Borgwadt[17] and McClellan[18] indicate that the equilibrium constraints can become evident at temperatures much higher than the optimum temperature found as high as 1123 K. Since both calcination and sulphation occurred simultaneously, the optimum temperature can be

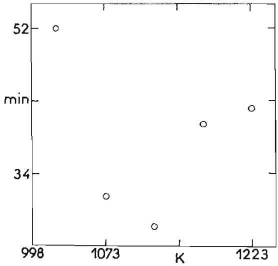

FIG. 7

Effect of the Temperature on the Reaction Rate.

Exposure time to reach 70% conversion plotted *vs* temperature. Limestone Čížkovice, particle size 0·282 mm, concentration of SO_2 0·3% by vol.

expected to result from the two opposing tendencies: from the favourable effect of temperature on the reaction rate itself and its adverse effect on surface area, grain size and activity of calcium oxide which is produced before the sulphation starts and the texture of which changes in the course of the reaction.

As reported in our previous studies[8,9] the reactivity of calcines, aside from the conditions of reaction, is influenced markedly by the nature and origin of the parent rock. In general, the optimum temperature is likely to be different for various types of limestones and its value should be always found for each rock by experiment.

It should be mentioned that in the results plotted in figures 6 and 7 a possible influence of temperature on the texture of the sulphation product is included which may be worth of further consideration.

The textural measurements were made on the facilities generously provided by Department of Heterogeneous Reactions, Institute of Chemical Process Fundamentals. We are grateful to Mr J. Jež for his assistance in obtaining the experimental data.

LIST OF SYMBOLS

P	porosity
r_g	radius of micrograins (m)
R	radius of pores (nm)
$\bar{R}$	mean radius of pores (nm)
S_g	BET surface area (m^2/g)
T	temperature (K)
V	pore volume (cm^3/g)
X	conversion of calcium oxide to sulphate
ϱ_{He}	true density of solid reactant (g/m^3)
τ	time of exposure (min)

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