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MODIFICATION OF SURFACE TEXTURE OF LIMESTONES AS ACTIVE SO_2 SORBENTS BY HEAT TREATMENT AND ADDITIVES

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Abstract

Properties of limestone related to SO_2/SO_3 reactivity were investigated. Limestone calcined under different conditions (temperature, time and with/without additives) yield calcines of distinctly different physical structures. The amount of pores and the size of the pores formed during calcination is important.

The main purpose of the present work was to gain a better understanding and more reliable explanation of the temperature regime for gas desulphurization using Ca-based sorbents in atmospheric fluidized-bed combustors.

Pore size, surface area and pore volume of each calcine were determined by mercury porosimetry and BET methods. At higher calcination temperature and during longer time, sintering became significant and the obtained calcine had a smaller internal surface area and thereby the average pore radius increased. The additives such as NaCl also accelerated sintering thus increasing the pore size. The measurements of porosity were supplemented by scanning electron microscopic observations employed for qualitative description of the pore structure. SEM micrographs are presented.

Keywords: additives, calcination, limestone, mercury porosimetry, morphology, particle structure change, pore size distribution, surface area

Introduction

Natural limestone is attractive as SO_2 sorbent during the fluidized bed combustion of coal because of its low cost and widespread availability throughout Poland and many other places. However the major disadvantage of using it is disposing of large quantities of solid waste material which is magnified by the fact that only part of $CaCO_3$ is converted into Ca–S compounds. The absorption of SO_2 by $CaCO_3/CaO$ is a rather complex gas-solid reaction. Laboratory tests on a large number of carbonate rocks showed no relationship between chemical composition and SO_2 reactivity, e.g. [1]. Previous work has shown [2, 3] that the use of chemical additive, NaCl in particular, may enhance the SO_2 reactivity

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of limestones and can affect the reaction rate. However, there are also some contradictory data [4]. It is important to bear in mind that the effect of NaCl on sulphation depends on the manner in which the salt is introduced into the system [5].

Limestone calcined porosity is one of the essential factors that have been found to impact the rate and gives quantity of sulphur uptake. Sulphur oxides must diffuse into the particle and react with the available CaO. Adequate porosity must exist to accommodate the products sulphation which have higher molar volume than the reactant. Thus the physical structure of the sorbent is critically important to the sulphation behaviour. However, the importance of pore size distribution is as yet not well understood. In reality, one can say that the data on the sintering meaning are still collected, e.g. [6–11]. As the surface area in the description of the sorbent properties is dependent on the variations in the particle pore structure, it was decided to study in this paper the comparison of pore size distribution including pore volume and pore surface distribution of uncalcined and calcined state of limestone with and without NaCl using one of the best sorbents chosen on the basis of the laboratory tests under atmospheric fluidized combustion of coal [12]. Visual analysis on surface particle morphology of the specimens after heat treatment, with and without additives, using scanning electron microscopy, were performed and some of SEM micrographs are presented below.

Experimental

Materials

Natural limestone, quarried in Zabierzow near Cracow (Poland) was used. It had been studied before, during fluidized bed combustion experiments [12] and using TG [13]. Samples were crushed and sieved to the desired size range (0.5–0.6 mm). TG curves for calcination indicated that the weight loss was 43.70±0.09% and chemical analyses carried out with a Philips PW 1400 X-ray fluorescence spectrometer showed their average composition to be CaO 57.4%, MgO 0.4%, SiO_2 0.5% and Al_2O_3 0.1%.

Limestone samples with NaCl (2 wt.%) were obtained by adding an aqueous solution of the required amount of NaCl to the prepared limestone particles, mixing the resultant slurry and drying it at about 420 K.

The calcination of samples was carried out under controlled conditions in a thermogravimetric analysis system.

Two sets of samples were utilized in the studies:

- limestone, (LS)
- limestone+NaCl, (LSCl)

In each of these two sets, the influence of thermal treatment on the surface characteristic and porosity was investigated for:

- limestone calcined up to 1100 K, (L and LCl)
- limestone calcined up to 1200 K and after, isothermally during 60 min, (Lt and LClt).

Methods and procedure

1. Mercury penetration measurements

Hg penetration curves were obtained with the use of an AUTOPORE II 9220 VI.07 porosimeter with computer data handling capabilities. 500 mg of the sample was placed in the penetrometer and was evacuated to remove adsorbed gases from the pores of the sample.

The Washburn equation was used (assuming cylindrical pores):

$$R_p = -(1/p)2\gamma\cos\theta$$

where R is the pore radius in μm, p is the intrusion pressure, γ is the mercury surface tension taken to be 485.0 dynes/cm and θ is wetting angle for mercury which is taken to be 141.3°. The radius from 0.008 to 40 μm were used for calculation of the intrusion data. Smaller pores are not reliably detected because the high pressure may break the particle pore structure.

2. N_2-adsorption

Nitrogen adsorption–desorption isotherms were obtained for the samples in amount of 500 mg outgassed for five hours while heated at 380 K with a Carlo Erba Instruments Sorptomatic 1900. The points in the 0.05 to 0.2 relative pressure range were used for calculation of the BET nitrogen surface area.

3. Morphological observations on uncalcined and calcined samples of limestone were carried out using a scanning electron microscope, model JEOL JSM-35. For the measurements a few particles out of each sample investigated were positioned on a strip of double sticky tape and transferred into carbon stubs for subsequent SEM analysis.

Results and discussion

The calcination of limestone particles at temperature below 1200 K generally takes place without any significant change of particle dimensions. The similar observations were made earlier, e.g. [6]. Thus, the surface area development during calcination occurs through pore formation. Quantitative characterization of the pore structure of chosen calcines is made by mercury intrusion and BET surface area measurements which are summarized in Table 1.

Table 1 Summary of physical properties of uncalcined and calcined limestone without and with NaCl

Sample	Average pore radius/μm	Surface area/$m^2 \cdot g^{-1}$		Pore volume/$cm^3 \cdot g^{-1}$	
	(a)	(a)	(b)	(a)	(b)
LS	0.26	0.57	0.54	0.07	0.011
LSCl	0.28	0.42	0.74	0.06	0.016
L	0.12	5.36	7.09	0.34	0.042
LCl	1.59	0.37	0.93	0.29	0.046
Lt	0.37	1.90	6.53	0.35	0.051
LClt	1.61	0.43	1.30	0.35	0.010

(a) By mercury intrusion
(b) By BET method

For the uncalcined limestones. (LS, LSCl), the nitrogen BET area and the area calculated from mercury penetration are similar, but they are less than one $m^2 \cdot g^{-1}$, so that there is a considerable uncertainty in the absolute value of these

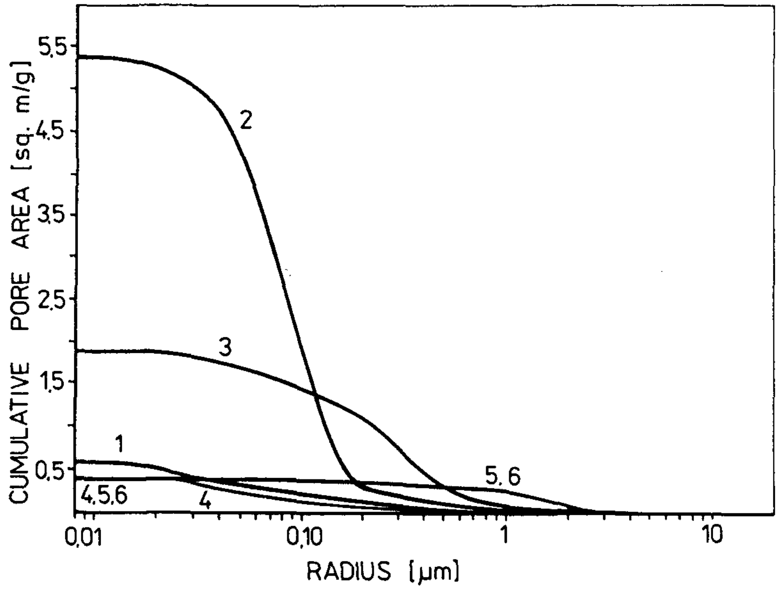

Fig. 1 Effect of the temperature and time calcination of limestone (curves 1–3) and limestone with NaCl (curves 4–6) on the cumulative pore area: 1-sample LS, 2-L, 3-Lt, 4-LSCl, 5-LCl, 6-LClt

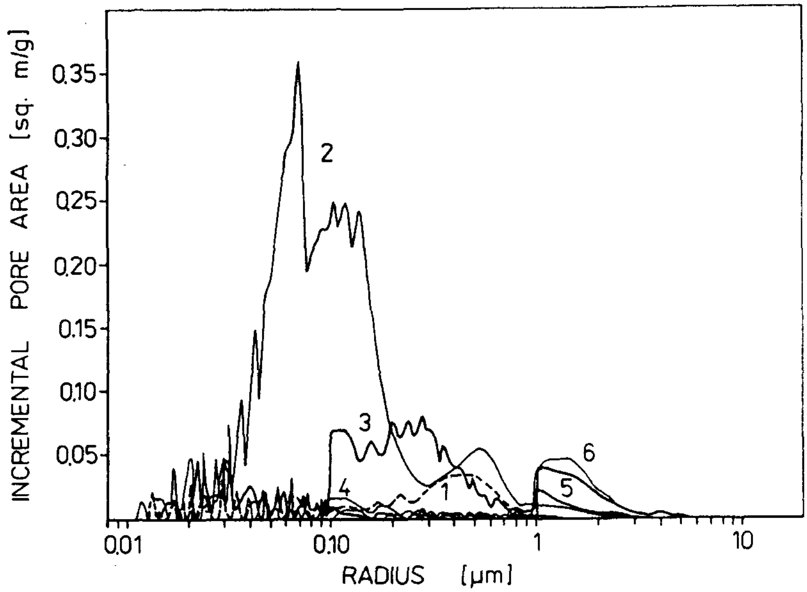

Fig. 2 Effect of the temperature and time calcination of limestone (curves 1–3) and limestone with NaCl (curves 4–6) on the incremental pore area: 1-sample LS, 2-L, 3-Lt, 4-LSCl, 5-LCl, 6-LClt

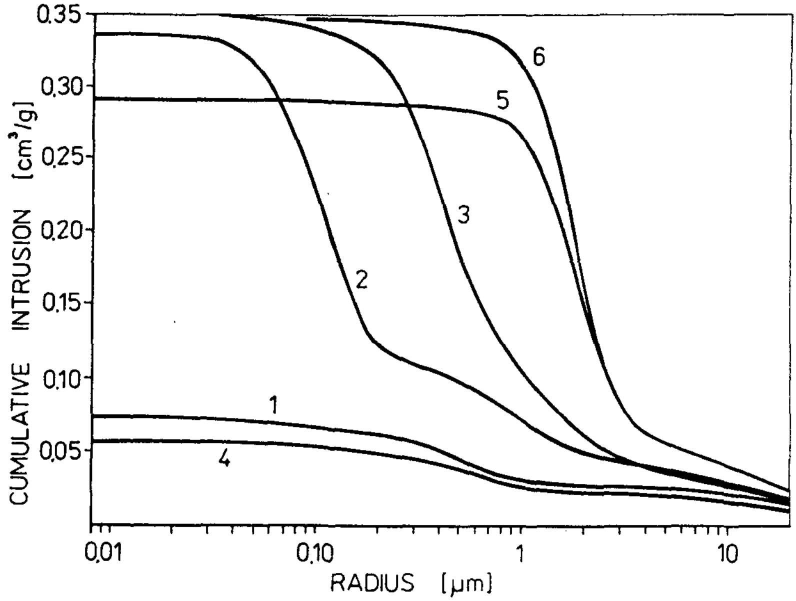

Fig. 3 Effect of the temperature and time calcination of limestone (curves 1–3) and limestone with NaCl (curves 4–6) on the pore volume: 1-sample LS, 2-L, 3-Lt, 4-LSCl, 5-LCl, 6-LClt

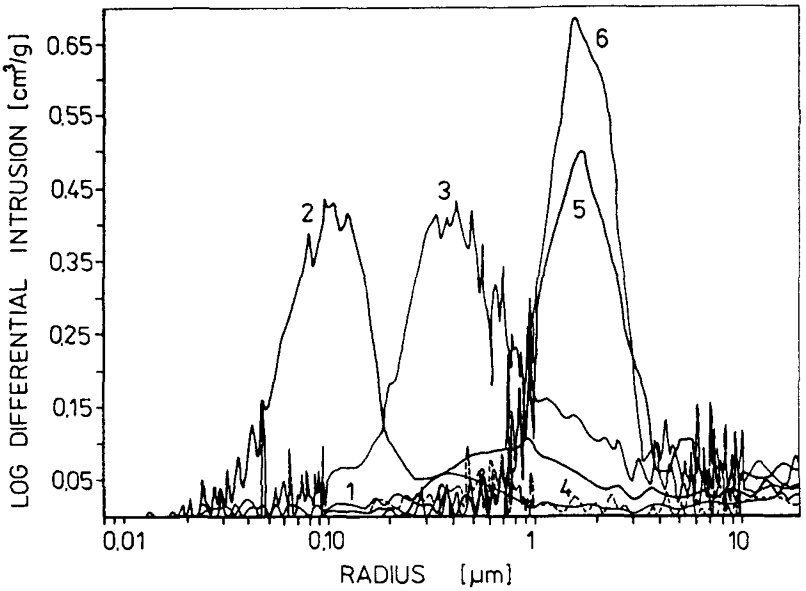

Fig. 4 Effect of the temperature and time calcination of limestone (curves 1–3) and limestone with NaCl (curves 4–6) on the log differential instrusion: 1-sample LS, 2-L, 3-Lt, 4-LSCl, 5-LCl, 6-LClt

areas. For all the other cases listed in Table 1 the nitrogen surface area exceeds the mercury area but no regularity can be observed.

The nitrogen adsorption isotherms at 77 K for all the samples belonged to the type-II isotherm of BDDT classification [14]. There was hardly any histeresis between the adsorption and desorption branches which implied that most of pores were largely in agreement with independent measurements of the most probable pore radius by a mercury intrusion porosimeter (~0.1 µm).

The curves of cumulative pore area, incremental pore area, cumulative intrusion and log differential intrusion versus radius for six samples (as mentioned above) are presented on Figs 1–4, respectively. Curves 2 and 3 show the effect of temperature and time of calcination on the pore volume and pore size distribution, respectively. Calcination at 1100 K (as in the atmospheric fluidized bed combustor) produced calcine (L) with pores of smaller radius (0.05–0.20 µm) than that of calcine (0.20–1 µm) prepared at higher temperature during longer time (Lt). In both cases the same values of cumulation intrusion (the pore volume) equal to ~0.35 cm^3/g are observed.

The pore volume–pore size distribution for limestone with NaCl shows a shift to pores of radius between 1–4 µm (curves 5 and 6). It should be noted that the cumulative pore area of the calcine with NaCl (LCl) is much smaller than that of L (Figs 1 and 2). This leads to the conclusions that at a higher cal-

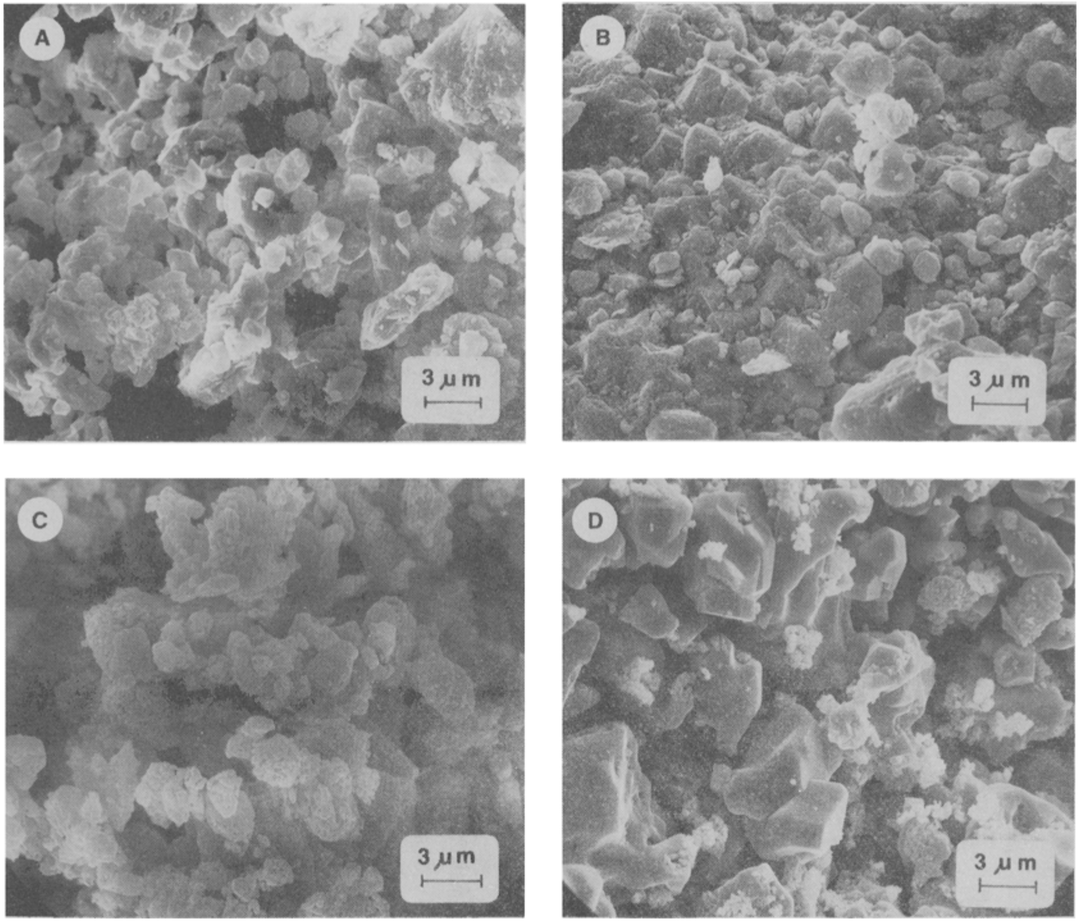

Fig. 5 SEM micrograph with 3000× of magnification of: A) raw limestone, B) raw limestone with NaCl, C) limestone calcined at 1000 K, D) limestone with NaCl calcined at 1100 K

cination temperature and during a longer time, sintering becomes significant and the obtained calcine (Lt) has a smaller internal surface area and thereby the average pore radius increases (Table 1). The additives such as NaCl in the limestone also accelerate sintering, increasing the pore size.

The measurements of porosity using BET method and Hg penetration were supplemented by visual analysis obtained with SEM which were used for qualitative descriptions of pore structure properties. Scanning electron micrographs of (A)-uncalcined limestone particles, LS, (B)-uncalcined limestone particles with NaCl, LSCl, (C)-calcined limestone particles, L and (D)-particles of calcined limestone with NaCl, LCl, used in sulphation studies are shown in Fig. 5.

Particles of both limestones before calcination (A) and (B) are characterized by a sharp-edged structure with rough external surfaces. The existence of relatively large agglomerates are also seen in all micrographs. The micrograph (C) shows clearly that the CaO particles contain a larger fraction of small pores (0.12 μm) than those existing in calcine with NaCl (D) characterized by walled up external surfaces with the much bigger average pore radius (1.59 μm). This is the known sintering effect which reduces the surface area of sample (D). To go for a deep and more detailed analysis, a quantitative treatment should be of great importance. This deserves careful interpretation of data drawn by SEM using digital image analysis techniques concerning the porosity of cross-sectioned calcines [15].

Conclusions

The findings drawn from the present work could be presented as follows:

– calcination of limestone at 1200 K, i.e. at higher temperature than about 1100 K, could cause sintering effects which result in the extension of average pore radius and consequently in reduction the specific pore surface area,

– the above observation could explain the fact of much lower sulphation reactivity and ultimate conversion of calcined limestone at 1200 K than is obtainable for calcines below this temperature,

– there is an upper temperature limit for maintenance of high sulphation reactivity in fluidized bed combustors, when Ca-based sorbents are used. This is evident in surface texture together with other chemical factors.

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References

1 E. M. Bulewicz, K. Wieczorek-Ciurowa, J. Klimek, E. Janicka, S. Kandefer and Cz. Juryś, Selection of Calcium-Based Sorbent for Fossil Fuel Desulphurization in the Fluidized Bed

Combustor. Phase I, Technical University of Cracow, Report to Institute of Power, Warsaw, Poland, December 1978 (in English).
2 J. A. Shearer, I. Johnson and C. B. Turner, Environ. Sci. Technol., 13 (1979) 1113.
3 T. Bardakci, Thermochim. Acta, 106 (1986) 35.
4 K. Wieczorek-Ciurowa, F. Paulik and J. Paulik, Thermochim. Acta, 46 (1981) 1.
5 K. Wieczorek-Ciurowa, L. H. J. Lajunen and P. Kokkonen, J. Thermal Anal., 35 (1989) 361.
6 D. Beruto, I. Barco, A. W. Searcy and G. Spinolo, J. Amer. Ceram. Soc., 63 (1980) 439.
7 N. H. Ulerich, E. P. O'Neill and D. L. Keairns, Thermochim. Acta, 26 (1978) 269.
8 R. H. Borgwardt and R. D. Harvey, Environ. Sci. Technol., 6 (1972) 350.
9 R. K. Chan, K. S. Murthi and D. Harrison, Can. J. Chem., 48 (1970) 2972.
10 M. Hartman and R. W. Coughlin, Ind. Eng. Chem. Process Des. Dev., 13 (1974) 248.
11 I. Bjerle and Z. Ye, Chem. Eng. Technol. 14 (1991) 357.
12 E. M. Bulewicz, E. Janicka, K. Wieczorek-Ciurowa, S. Kandefer and Cz. Juryś, Arch. Comb., 1 (1991) 121.
13 K. Wieczorek-Ciurowa, J. Thermal Anal., 33 (1988) 407.
14 S. J. Gregg and K. S. Sing, Adsorption, Surface Area and Porosity, 2nd Ed., Acad. Press, London 1980.
15 K. Wieczorek-Ciurowa, to be published.

Zusammenfassung — Es werden die Eigenschaften von Kalkstein im Hinblick auf die SO_2/SO_3-Aktivität untersucht. Unter verschiedenen Bedingungen kalzinierter Kalkstein (Temperatur, Zeit und mit und ohne Additiven) ergibt Kalzinationsprodukte mit vollkommen verschiedenen physikalischen Strukturen. Dabei sind von Wichtigkeit die Menge von Poren und die Größe der Poren, die bei der Kalzination gebildet werden.

Hauptziel vorliegender Arbeit war das Erzielen eines besseren Verständnisses und einer besseren Erklärung der Temperatur-Betriebsbedingungen für die Gasentschwefelung unter Einsatz von Sorbentien auf Ca-Basis in atmosphärischen Fluidbett-Verbrennungsanlagen.

Porengröße, Oberflächengröße und Porenvolumen jedes Kalzinationsproduktes wurde mittels Quecksilberporosimetrie und BET-Methoden ermittelt. Bei höheren Kalzinationstemperaturen und während längerer Zeiten tritt Sintern in den Vordergrund und das erhaltene Kalzinationsprodukt besitzt eine kleinere interne Oberflächengröße und somit ist der durchschnittliche Porenradius erhöht. Additive wie NaCl beschleunigen das Sintern und somit die Zunahme der Porengröße ebenfalls. Für eine qualitative Beschreibung der Porenstruktur wurden die Messungen der Porösität noch durch scanning-elektronenmikroskopische Beobachtungen ergänzt. SEM Mikroaufnahmen werden ebenfalls präsentiert.