

# Characterization of Limestone Reactivity for Absorption of SO<sub>2</sub> from Fume Gases

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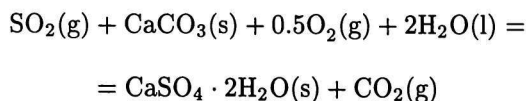
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Methods for estimation of limestone reactivity for absorption of SO<sub>2</sub> from fume gases are described. Eight samples of limestone were tested. Chemical methods are based on the reaction of suspension of limestone powder in water with 0.5 M-H<sub>2</sub>SO<sub>3</sub> and 0.5 M-H<sub>2</sub>SO<sub>4</sub>. It is shown that both procedures give equivalent results. A correlation between the reactivity of limestone and apparent porosity of limestone powder was found. A model describing the rate of the reaction of limestone with aqueous solution of SO<sub>2</sub> is discussed.

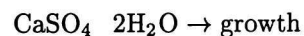
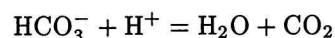
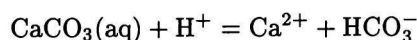
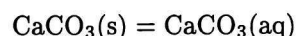
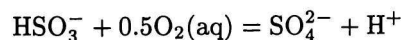
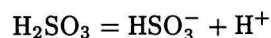
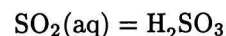
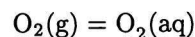
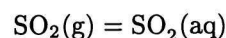
The main product of the combustion of sulfur and sulfur-containing compounds in coal is sulfur dioxide. Only a small amount of sulfur trioxide is formed. The removal of sulfur dioxide which may be harmful for environment is commonly performed using combustion modification [1] or secondary methods. In secondary methods flue gases are treated after combustion and the end product depends on the method and chemicals used in the removal process. The classification of flue gas desulfurization methods can be done according to the end product formed in the process. The methods are divided into regenerable and nonregenerable processes where in the former case the removed sulfur dioxide is recovered as sulfur, sulfur dioxide or sulfuric acid. In the latter case the end product is mainly a waste material which has to be dumped. There is a remarkable effort to minimize wastes by their exploitation in the production of composite building materials.

Most of the nonregenerable methods utilize calcium-based chemicals (limestone or lime) because they produce relatively safe and stable end product, *viz.* calcium sulfate. These processes can further be divided into subgroups depending on the reactive phase where sulfur dioxide is removed – dry, semi-dry or wet processes.

In this paper we will discuss kinetics of desulfurization in the wet process. The total chemical reaction can be described by the following scheme [2]



The major reactions in the reaction zone can be written



The rate-controlling steps depend on the technology used and on the construction of the scrubber. For example, gas-phase mass transfer of SO<sub>2</sub>, liquid-phase mass transfer of O<sub>2</sub>, dissolution of CaCO<sub>3</sub>, and crystal growth of gypsum are considered as the controlling steps [2]. It follows that the quality of limestone influences the process by its dissolution.

For evaluation of suitability of limestone for its sulfation several methods have been developed. They are based on the reaction of limestone with SO<sub>2</sub>, aqueous solution of SO<sub>2</sub>, *i.e.* H<sub>2</sub>SO<sub>3</sub>, or with H<sub>2</sub>SO<sub>4</sub> [3]. The main problem is that the methods using SO<sub>2</sub> are experimentally demanding and take long time. In this work we will compare different methods for evaluation

Table 1. Characterization of Limestone Powder Samples

Number of sample	Content of CaCO <sub>3</sub> mass %	Content of MgCO <sub>3</sub> mass %	Insoluble residue mass %	Apparent porosity %	Half-time of reaction min
1	95.7	0.5	1.50	48.9	11.8
2	95.1	3.2	0.50	44.3	31.4
3	96.4	1.6	0.76	48.7	10.0
4	95.2	2.1	1.19	50.8	3.2
5	96.4	0.5	1.97	52.1	2.8
6	96.0	2.1	0.53	50.4	16.3
7	96.0	2.1	0.53	9.0	75.0
8	99.0		—	58.9	8.9

of limestone reactivity and we will show that the reactivity is related to the porosity of limestone grains.

### EXPERIMENTAL

Eight samples of limestone were investigated. If not stated otherwise the samples were sieved and the size of limestone particles was lower than 0.04 mm. The X-ray phase analysis proved that all samples consisted of calcite. Chemical composition (classical analytical methods were used) of investigated samples is summarized in Table 1.

For investigation of reactivity of limestone the following procedure was used. Limestone powder with chosen particle size distribution was mixed with distilled water (1.5 g of limestone + 200 cm<sup>3</sup> of distilled water). 0.5 M-H<sub>2</sub>SO<sub>3</sub> or 0.5 M-H<sub>2</sub>SO<sub>4</sub> was added to the suspension in such a way that pH of the mixture was kept constant at the value pH = 5. The temperature of the mixture was kept at 55°C. This is the temperature which is close to the temperature in industrial reactor used for desulfurization of fume gas. The suspension was stirred. The pH value of the suspension was measured by a combined glass electrode and it was recorded by a PC computer. The computer controlled a peristaltic pump (PC 100, Villa Labeco, Ltd., Spišská Nová Ves) which dosed the acid in the amount necessary for keeping pH of the mixture at constant pH value. In the beginning of the measurement the mixture was basic and pH was in the range 9–10. Because of that the flow of acid of 6 cm<sup>3</sup> min<sup>-1</sup> (maximum flow which could have been attained) was used until pH reached the desired value. The shortest time of the addition of acid was 1 s which corresponded approximately to the addition of 0.1 cm<sup>3</sup> of acid.

Pore size distribution of powder samples of limestone was determined by a porosimeter C. Erba 1500. This is a standard procedure based on mercury penetration into capillaries of investigated material by external pressure. More details on this method and calculation of the distribution of pore diameters and specific surface of the pores can be found in Ref. [4].

### RESULTS AND DISCUSSION

Porosity data of tested powder limestone samples are summarized in Table 1. Three examples of porosity measurement are shown in Fig. 1 where total volume of pores *vs.* pore radius is plotted. The samples denoted by numbers 6 and 7 are made of the same kind of limestone but they have a different particle size. The porosity used for characterization of powder samples in this work equals the volume of pores and part of the space between particles. In this work we consider that macropores which are not taken into porosity of samples have radius larger than 6500 nm.

In Fig. 2 the degree of conversion of limestone as a function of reaction time is plotted for the reaction of limestone suspension with 0.5 M-H<sub>2</sub>SO<sub>4</sub>. Half-time of the reactions for examined samples is presented in Table 1. Similar reaction curves were obtained with 0.5 M-H<sub>2</sub>SO<sub>3</sub>. Reproducibility of determination of half-time of the reaction is better than ± 5%. For illustration reaction curve for one sample is plotted in Fig. 2. In the process of desulfurization of fume gas it is actually the sulfurous acid which is formed. However, because of high pressure over solutions of 0.5 M-H<sub>2</sub>SO<sub>3</sub> it is more convenient to use sulfuric acid in the test of limestone reactivity. In Fig. 3 the reaction times required for achievement of the given degree of conversion (*viz.* 0.5; 0.6; 0.7; 0.8; 0.9) are compared for both acids used. As at zero time no limestone is consumed by the chemical reaction with sulfuric or sulfurous acid the regression line in Fig. 3 has to go through the origin of coordinates. It follows that there is a linear dependence between both sets of data. Therefore the tests carried out with sulfuric acid are equivalent to those realized with sulfurous acid.

It was found that the degree of conversion of limestone obtained by these tests can be described by the relationship

$$t = a_0 + a_1(1 - x)^{1/3} + a_2(1 - x)^{2/3} + a_3(1 - x) \quad (1)$$

where  $t$  is the time of the reaction and  $x$  is the degree

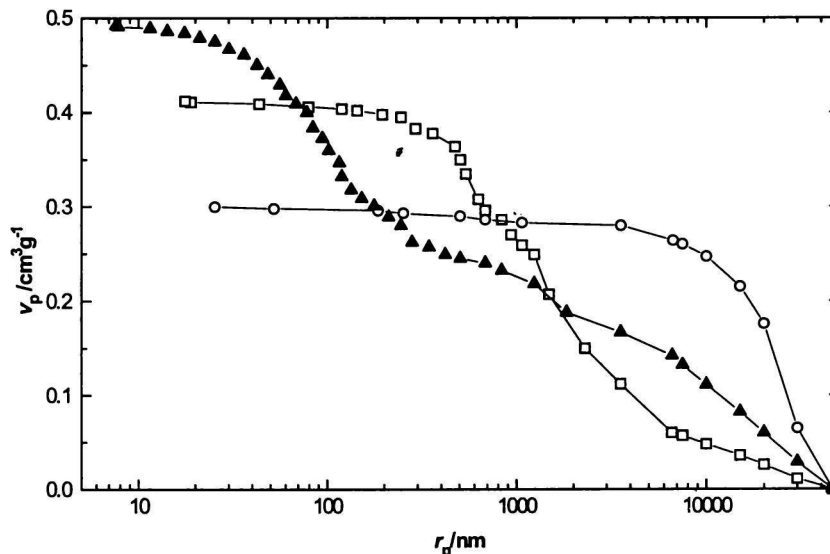


Fig. 1. Specific volume of pores as a function of pore radius.  $\blacktriangle$  Sample No. 5,  $\square$  Sample No. 6 ( $d/\text{mm} < 0.04$ ),  $\circ$  Sample No. 7 ( $d/\text{mm} = 0.08\text{--}0.09$ ).

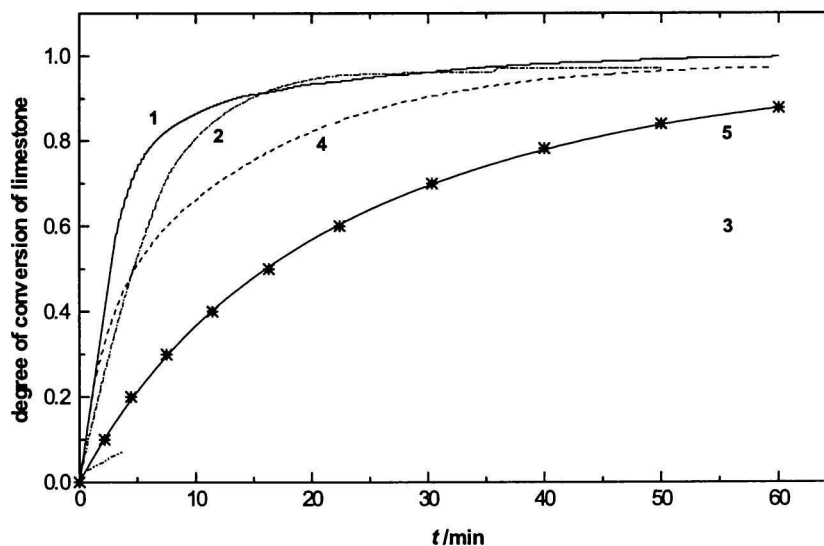


Fig. 2. Degree of conversion of limestone with  $\text{H}_2\text{SO}_4$  or  $\text{H}_2\text{SO}_3$  as a function of reaction time. Stars denote the experimental data for sample No. 6 obtained with sulfurous acid and full line 5 corresponds to the description of these data by eqn (1). Curves 1—4 were obtained with 0.5 M- $\text{H}_2\text{SO}_4$ . 1. Sample No. 5, 2. sample No. 8, 3. sample No. 7, 4. sample No. 6.

of conversion. In Fig. 2 an example of fit of kinetic data with the model is shown. The regression coefficients were high,  $r = 0.999$ . This equation follows from the model of reaction kinetics [5]. The model is based on the assumption of formation of the layer of nonsoluble product formed on a sphere surface of reacting substrate. In the case of limestone reacting with sulfuric acid the X-ray microanalysis proved the existence of calcium sulfate on the surface of limestone grains. However, the sulfate layer is not compact. Therefore one has to admit that eqn (1) is only empirical and that it does not necessarily reflect the mechanism of the reaction between limestone particles and  $\text{SO}_2$  dis-

solved in water. The parameter  $a_0$  corresponds to the time needed for total reaction of limestone.

From the discussion it follows that the reactivity of limestone powder depends remarkably on the reaction surface of samples. This reaction surface is related to the apparent porosity of powder samples as was defined in this work. In Fig. 4 there is a plot of half-time of the reaction of limestone samples with 0.5 M- $\text{H}_2\text{SO}_4$  vs. apparent porosity of powders. It can be seen that there is a correlation between the apparent porosity and kinetics of the reaction. Unfortunately no samples of limestone with apparent porosity between 10—40 % were available. Thus the observed relation-

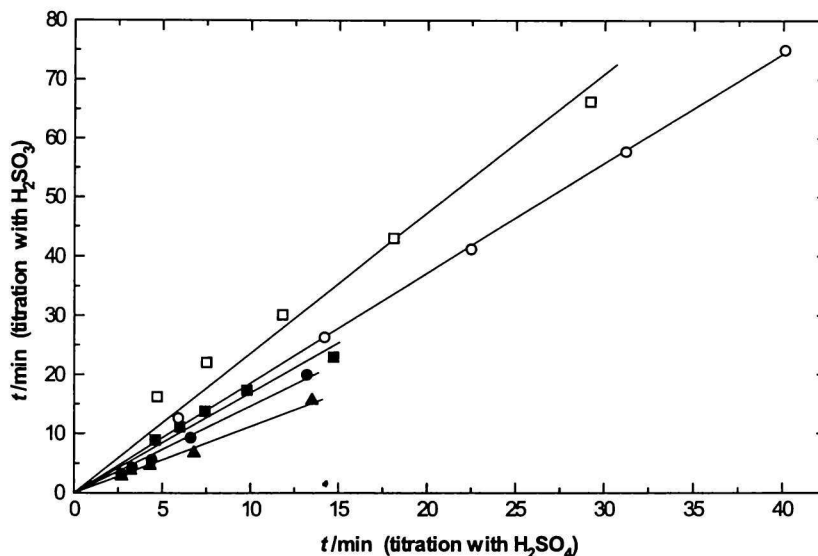


Fig. 3. Correlation between the reaction times obtained with  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_3$ . ● Sample No. 4, ▲ sample No. 5, □ sample No. 6, ○ sample No. 7, ■ sample No. 8.

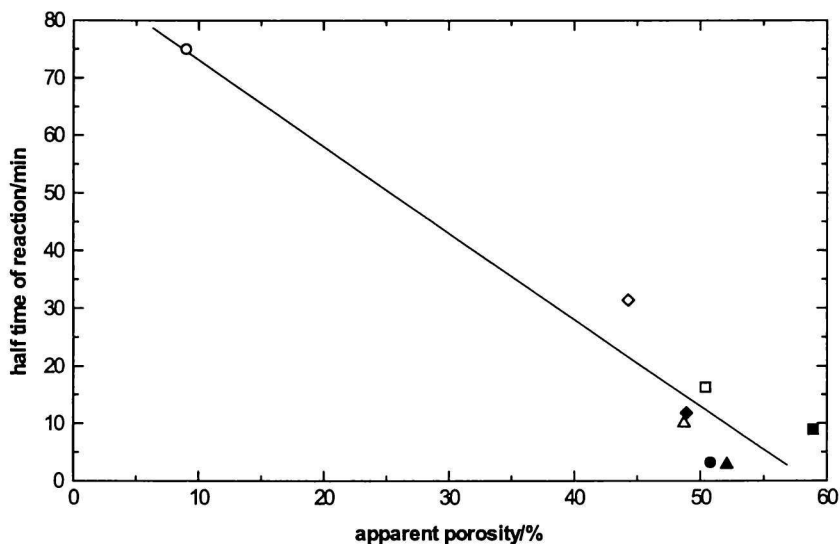


Fig. 4. Relation between the half-time of reaction of limestone powder with  $\text{H}_2\text{SO}_3$  and apparent porosity of limestone samples. ◆ Sample No. 1, ◇ sample No. 2, △ sample No. 3, ● sample No. 4, ▲ sample No. 5, □ sample No. 6, ○ sample No. 7, ■ sample No. 8.

ship between the porosity and kinetics of the reaction can be considered only as a topic for further study.

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