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SOLID-GAS REACTIONS: STUDY OF SULPHATION OF LIMESTONE USING THERMOGRAVIMETRY

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Comparative data are presented on the absorption rate and capacity for SO_2 capture by a natural Polish limestone with and without sodium chloride additive. Two sets of experiments were carried out, under dry and wet conditions during limestone calcination and sulphation.

The presence of water vapour brought about a higher reactivity of the sorbent, probably as a result of an effect on the sintering of lime and through the influence of the $CaSO_4$ layer. Further morphological investigations could provide confirmation of the present hypothesis.

Because of the importance of the SO_2/CaO reaction in the fluidized bed coal combustion process, it has been one of the most intensively studied gas/solid reactions.

From a technological point of view, the chief problem is that it is impossible to achieve stoichiometric utilization of the Ca in the sorbent.

The present paper describes results obtained from a study of this reaction by using thermogravimetry.

The overall reaction whereby the Ca in the limestone sorbent is converted into $CaSO_4$ is influenced by many factors [1]. In any systematic investigation of the influence of additives, e.g. NaCl, or the presence/absence of water vapour, it is necessary to differentiate their effects on limestone calcination and the sulphation of CaO. Moreover, it is also necessary to take into account the possibility of mutual interactions between the gaseous reactants. Exploratory investigations have shown that under both dry and wet conditions, the formation of SO_3 is very rapid and the concentration of SO_3 is sufficient for sulphation [2]. The presence of additives can then exert an influence by causing changes in the physical properties of the solid phase. Accordingly the additives do not influence the chemical kinetics directly.

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Experimental

Equipment and methods of measurement

Study of the calcination and sulphation of samples was carried out by using a Mettler TA-2 thermoanalyzer equipped with a corrosive gas atmosphere accessory.

The flow of gases through the system is shown schematically in Fig. 1. Argon as carrier gas was passed through the balance compartment to prevent the diffusion of corrosive gases (SO_2). The SO_2 or argon was introduced through the auxiliary gas inlet. Gas flow rates were monitored individually by rotameters.

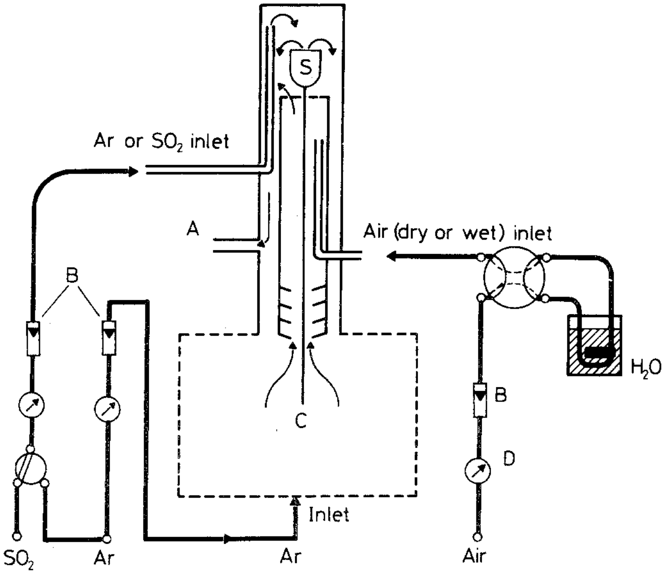

Fig. 1 Scheme of gas flow through the thermoanalyzer.
S: sample, A: gas outlet, B: flowmeters, C: balance, D: flow regulator

The air was passed over molecular sieves 5A to remove any traces of water or was saturated with water vapour at 293 K.

The samples for calcination were heated up to 1200 K at a rate of 25 deg min^{-1} in a flow of dry or wet 1–2 vol.% H_2O air and after about 10 min they were sulphated isothermally at 1100 K in a flow of a mixture of ca. 15 vol.% SO_2, ca. 38 vol.% air, and ca. 47 vol.% Ar.

Hemispherical Pt crucibles were used in all experiments.

The reaction conditions were kept strictly constant for all runs, except for the factor investigated.

Materials

The material was natural limestone quarried in Zabierzów near Cracow. It has previously been studied as a potential SO_2 sorbent during the fluidized bed combustion of coal [3]. Samples were crushed and sieved to the desired size range (0.5–0.6 mm). 300 mg samples were used. The limestone contained about 96% of $CaCO_3$; chemical analysis and X-ray diffraction indicated that the principal impurity was α-quartz.

For the admixture of 2% of NaCl to a sample of limestone, the required amount of NaCl was dissolved in the smallest possible amount of deionized water. The solution was mixed with the sample, and the mixture was dried in an oven at ca. 420 K.

Results and discussion

Experiments were carried out in two series: A – limestone (L), and B – limestone + NaCl (L, Cl). In each of these two series, the following experiments were performed:

L–D and L–W	— the limestone was calcined under dry or wet conditions;
L–DD and L–DW	— the limestone previously calcined under dry conditions was sulphated under dry or wet conditions;
L–WD and L–WW	— the limestone previously calcined under wet conditions was sulphated under dry or wet conditions.

From the TG/DTG curves it can be seen that the sulphation takes place in three stages: I – dm/dt increases up to a maximum, II – dm/dt decreases fairly rapidly, III – dm/dt decreases slowly over an extended period of time.

Behaviour of L

In the presence of water vapour the calcination temperature is lower, i.e. water vapour accelerates limestone decomposition (confirming the results of [4]).

Calcination under wet conditions leads to a slight increase in Ca utilization during sulphation.

In the presence of water vapour during sulphation, independently of the calcination conditions, the reaction rate appears to rise practically instantaneously at first, but the maximum rate is lower. The final degree of Ca utilization (close to 50%) is increased, however.*

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* Some of these results were presented at the J.C.A.T., Ferrara, 1986.

Behaviour of L, Cl

Water vapour brings about a slight decrease in the calcination temperature. The influence of the calcination conditions on the sulphation, and the effect of water vapour on the sulphation, are similar to those in the previous case.

Effect of NaCl

The presence of NaCl brings about an appreciable lowering of the temperature at which calcination begins (in comparison with the effect of water vapour, according to the general opinion, e.g. [5]).

In these presence of NaCl, the degree of Ca utilization at the end of stage II is reduced. This effect is independent of the presence/absence of water vapour during calcination and sulphation.

The third stage of sulphation deserves particular attention. The presence of NaCl under either dry or wet conditions of calcination and/or sulphation leads to an increase in the slow reaction rate and increases the ultimate Ca utilization.

The effect of NaCl on slow sulphation suggests that its presence leads to the opening of a new reaction path.

During stage III, the presence of water vapour enhances the effect of NaCl, but by itself it slightly inhibits sulphation.

The work is continuing, and it is hoped that morphological studies of the limestone particles at various stages of the reaction may help in the elucidation of the mechanisms responsible for the phenomena observed.

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Zusammenfassung — Absorptionsgeschwindigkeit und -kapazität für SO_2 an einem polnischen Kalkstein mit oder ohne NaCl-Zusatz werden verglichen. Zwei Reihen von Experimenten wurden in trockener bzw. wasserdampfhaltiger Atmosphäre bei der Calcination und Sulfatbildung durchgeführt. In Gegenwart von Wasserdampf wird die Reaktivität des Absorbens infolge Sinterung des Kalks und trotz des Einflusses der $CaSO_4$-Schicht erhöht. Künftige morphologische Untersuchungen sollen diese Hypothese eventuel bestätigen.

Резюме — Представлены сравнительные данные о скорости и количестве поглощения двуокиси серы природным польским известняком в присутствии добавки хлориастого натрия и без него. Обжиг и поглощение двуокиси серы были проведены в сухой и влажной атмосферах. Присутствие паров воды вызывает более высокую реакционную способность сорбента, вероятно, вследствии спекания извести и влияния образующегося слоя сульфата кальция. Дальнейшие морфологические исследования могут дать подтверждение выдвинутой гипотезе.