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The isothermal sulphation reactions of natural sorbents

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Abstract

The chemical reaction between sulphur dioxide and calcined limestone and dolomite particles was investigated using a thermogravimetric analyser. The samples used in this study originated from different parts of Turkey. Sulphation reactions were conducted under isothermal conditions in a gaseous mixture consisting of 15 vol% CO₂, 0.35 vol% SO₂ and a balance of dry air by volume. Before sulphation all samples were completely calcined in a gaseous atmosphere of 15 vol% CO₂ and 85 vol% dry air. It was observed that the sulphation reactions of samples are very rapid in their initial stage but after some reaction time, which varies depending on sample properties and temperature, the reaction rates quickly slow down. Also, the conversion–time results of sulphation experiments showed variations depending on the sulphation temperature, sorbent type and the physical properties of calcines.

Keywords: Dolomite; Limestone; Sulphation

1. Introduction

The reaction between sulphur oxides and natural calcium-containing sorbents, such as limestone and dolomite, has been studied extensively due to their potential in the desulphurization of flue gases resulting from the combustion of fossil fuels [1–7]. When coal burns in a fluidized bed of limestone or dolomite, this bed has a dual purpose; it acts as a fluidized medium for heat transfer and it reacts with sulphur dioxide produced by oxidation of sulphur species present in coal. The total sulphation capacities of limestone or dolomite sorbents are an important factor which influence operating costs of fluidized bed combustors. In addition, the rate of the sulphation reaction and its relation to the sorbent utilization is a critical process variable.

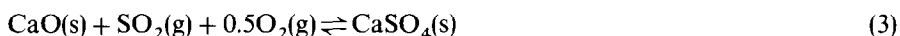
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The sulphation reaction of limestone and dolomite sorbents is assumed to occur in two steps. First, limestone and dolomite particles in the combustor undergo calcination due to the high temperature of the environment and then the calcined product reacts with sulphur dioxide.

1. Calcination steps



2. Sulphation steps



Generally, sulphation extents and rates for calcines produced from different rocks show large differences depending on their properties. Many researchers have reported very good correlations between sulphation capacity and physical properties of calcined rocks [2, 3, 8–10].

In this investigation the sulphation reactions of four limestones and one dolomite were studied by means of the thermogravimetric technique through the direct recording of the weight increase during the reaction. The conversion–time curves for the CaO/SO₂ reaction were derived from the experimental TG data. The effect of sample properties and temperature on the reaction rates was also determined.

2. Experimental

The natural sorbent samples used in this work were initially ground and sieved into a powder with a particle size of < 250 μm. Their chemical compositions were determined according to ASTM Standards [11]. The physical properties of their calcines, such as total pore volume and pore radius, were also determined using a mercury porosimeter (Autoscan-33).

The reaction between sorbent particles and SO₂ was studied using a Shimadzu 41 thermal analyser. The samples with an initial weight of 10 mg were fully calcined in the TG apparatus before sulphation. Calcination experiments were carried out from room temperature to 1173 K using a constant heating rate of 30 K min⁻¹. During calcination, a gaseous mixture consisting of 15 vol% CO₂ and 85 vol% dry air was fed continuously with a constant flow rate of 40 ml min⁻¹. At the end of calcination the calcined sorbents were brought to the selected sulphation temperature and reacted with a synthetic gaseous mixture containing 15 vol% CO₂, 0.35 vol% SO₂ and a balance of dry air by volume, under isothermal conditions.

During each run the SO₂ concentration in the gaseous stream was continuously measured with an SO₂ analyser. In order to protect the weighing unit from corrosion, pure nitrogen was fed through this part at a flow rate of 40 ml min⁻¹. Both calcination and sulphation TG curves were traced using a chart speed of 2.5 mm min⁻¹.

3. Results and discussion

The natural sorbents (four limestones and one dolomite) used in this work were selected from 36 limestone and 6 dolomite samples according to their total sulphation capacities determined at 1173 K in a tube furnace [10]. Table 1 gives the chemical composition and the total sulphation capacity values of the samples.

It is obvious from Table 1 that each rock has a different chemical composition and total sulphation capacity value. The total sulphation capacity values of samples ranged from 0.381 to 0.642 (mg SO₃ per mg sorbent) depending on sample properties. For limestones, these values correspond to CaO conversions ranging from 51.13 to 90.02 (wt%).

The CaO conversion–time curves of all samples were derived from their experimental sulphation TG data and are illustrated in Figs. 1–3. Since the weight of calcined particles increases as CaO is converted to CaSO₄ (Eqs. (3) and (4)), the conversion values can be easily determined by recording the sample weight during sulphation. Thus the relation between CaO conversion and time can be given by the equation

$$x(t) = \Delta m(t)/\Delta M \quad (5)$$

where x is the conversion of CaO to CaSO₄, t time (min), Δm weight gain of the sample until time t (mg), ΔM the maximum possible weight increase of the sample at the end of sulphation which can be predicted from the stoichiometry of the reaction (mg).

The conversion–time curves obtained for the sulphation reactions of sorbents at 1173 K are shown in Fig. 1. From this figure it is clear that the initial reaction rates of four samples (L02, L03, L04 and D01) are almost equal; however, under the same conditions the initial reaction rate of sample L01 is much higher than those of the others. In general, the higher initial reaction rates lead to rapid product layer formation and pore plugging at the external surface of particles and consequently to lower overall conversions. Also, the conversion–time curves of sorbents gradually flatten after some exposure time (Fig. 1). These time intervals were approximately determined as 3 min for L01, 6 min for L02, 5 min for L03, 11 min for L04, and 12 min for D01.

Table 1
Chemical composition and total sulphation capacities of sorbent samples

Sample origin	CaO %	MgO %	Fe ₂ O ₃ %	SiO ₂ %	Al ₂ O ₃ %	Sulphation (mg SO ₃ per mg sorbent)
Sarpdere (L01)	52.17	1.05	0.08	0.61	0.21	0.381
Kartal (L02)	37.45	4.65	3.54	12.64	6.70	0.384
Niğde (L03)	54.48	0.26	0.02	0.22	0.54	0.459
Adiyaman (L04)	49.91	2.70	0.46	3.66	2.04	0.642
Kapaklı (D01)	31.52	19.87	0.12	0.64	0.26	0.443

L: limestone, D: dolomite.

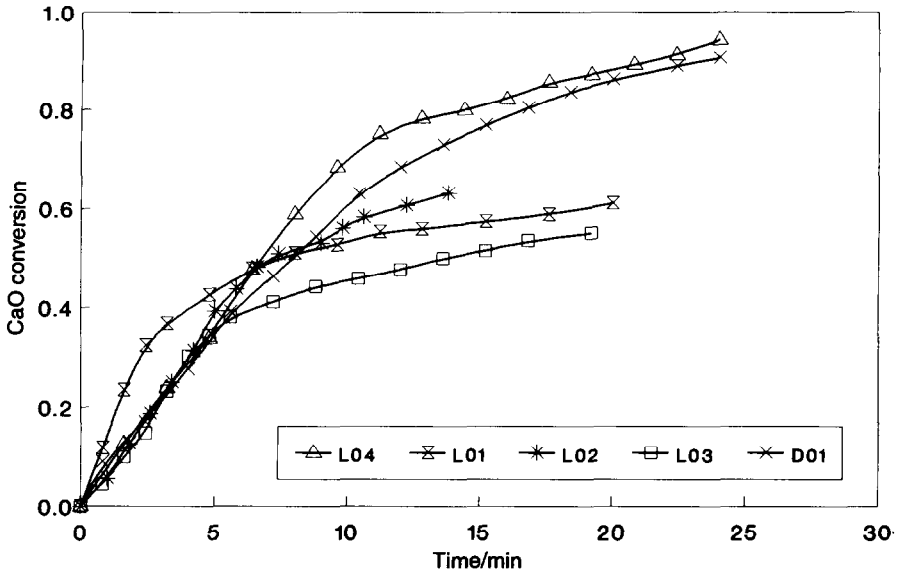


Fig. 1. Conversion–time data for the sulphation reactions of sorbents at 1173 K.

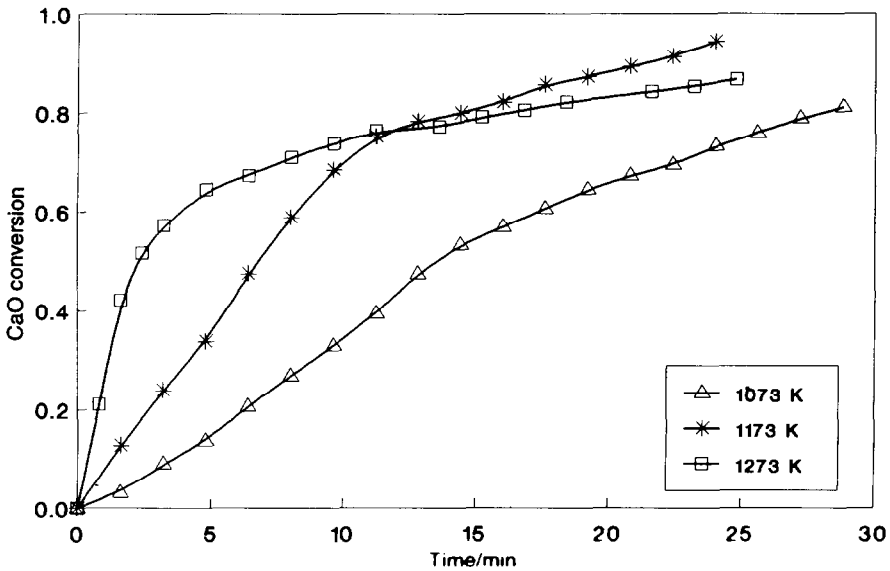


Fig. 2. Effect of temperature on the sulphation reaction of L04 sample.

A series of experiments has been conducted at different temperatures using the L01 and L04 sorbents to investigate the effect of temperature on the extent and rate of sulphation (Figs. 2 and 3). As Fig. 2 illustrates, increasing the sulphation temperature leads to higher initial rate values for sample L04. The time

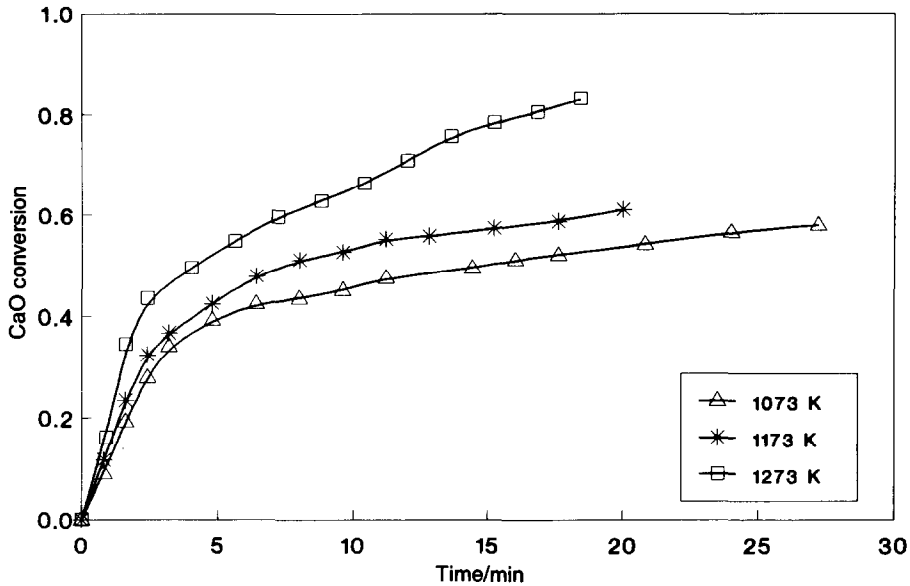


Fig. 3. Effect of temperature on the sulphation reaction of L01 sample.

intervals required to attain a CaO conversion of 50 wt% where the reaction rates start to decrease changed depending on temperature, namely 14 min at 1073 K, 7 min at 1173 K, and 2.5 min at 1273 K. As expected for diffusion-controlled reactions, the shape of the conversion–time curves became sharply convex with the temperature increase. This is probably due to the acceleration of the diffusion resistance by plugging of the external surface of the particles by solid product [12].

In contrast to the sample L04, the initial rate values of sample L01 were only slightly effected by the sulphation temperature. This difference can be attributed to the pore structure variations of calcines produced from these two samples. It is a well-documented fact that the sulphation reaction of limestone particles is strongly influenced by the pore structures of their unsulphated calcines [2, 5, 10, 13]. The mean pore radius values of calcines produced from L01 at 1173 and 1273 K were determined as 0.0462 and 0.0774 μm , and those produced from L04, 0.1370 and 0.3370 μm , respectively. It is obvious from these values that the pore structures of the calcines produced from sample L04 are characterized by larger pore sizes. Therefore, in the initial stage the overall rate of sulphation reaction of this sample is probably limited by the chemical reaction at the interface which makes the temperature effect more apparent. However, the sulphation reaction rate of calcines with small pore sizes can probably be limited by diffusion through the product layer which forms very quickly at the external surface of the particles. In this case the effect of temperature on the reaction rate is not strong [12, 13].

References

- [1] B. Bonn and H. Münzner, Sulphur capture with limestones in fluidized bed combustion, Fluidized Combustion Systems and Applications, in Proc. of the Institute of Energy's Int. Conf., London, Nov. 1980, pp. 1–7.
- [2] R.H. Borgwardt and R.D. Harvey, Properties of carbonate rocks related to SO₂ reactivity, Environ. Sci. Technol., 6(4) (1972), 350–360.
- [3] I. Johnson, J. Shearer, R. Synder and G.J. Vogel, Factors limiting limestone utilisation efficiency in fluidized bed combustors, 13th Energy Conv. Eng. Conf., Vol. 1, 1978, pp. 523–528.
- [4] A. Lallai, G. Mura, A. Viola, F. Giogia, Removal of sulfur during the combustion of coal by adding limestone, Int. Chem. Eng., 19(3) (1979) 445–453.
- [5] N.A. Burdett, The inhibition of the limestone sulphation process during fluidized bed combustion – a theoretical approach, J. Inst. Energy, (1983), 198–208.
- [6] S. Küçükbayrak, D. Boersma, P.J. van den Berg, Freeboard sulfur capture in a fluidized bed combustor, Proc. Engineering Foundation Conf. on Fluidization, Elsinore, Denmark, May 18–23, 1986.
- [7] S. Küçükbayrak, D. Boersma, P.J. van den Berg, Sorbent particle entrainment and sulfur dioxide capture in the freeboard of a fluidized bed combustor, VDI-Gesellschaft Energietechnik, Verbrennung and Feuerungen, VDI-Berichte, 574 (1985), 23–37.
- [8] A. E. Potter, Sulfur oxide capacity of limestones, Am. Ceram. Soc. Bull., 48 (1969) 855–858.
- [9] M. Hartman, J. Pata and R.W. Coughlin, Influence of porosity of calcium carbonates of their reactivity with sulfur dioxide, Ind. Eng. Chem. Process Des. Dev., 17(4) (1978) 411–419.
- [10] A. Ersoy-Meriçboyu, S. Küçükbayrak and S. Yaman, Sulphation capacities of natural turkish limestones and dolomites, Environ. Technol., 14 (1993) 787–794.
- [11] Annual Book of ASTM Standards, Part 13, Method C-25-72, Am. Soc. Test. Mater., Easton, 1977.
- [12] A.F. Shaaban, Determination of the kinetic parameters of the reaction between SO₂ and CaO using the thermogravimetric technique, Thermochim. Acta, 180 (1991) 9–21.
- [13] S. Zarkanitis and S.V. Sotirchos, Pore structure and particle size effect on limestone capacity for SO₂ removal, AIChE J., 35 (1989) 821–830.