Thermochimica Acta 319 (1998) 163–170

thermochimica acta

Modeling of the isothermal sulphation reactions of natural sorbents

Ayşegül Ersoy-Meriçboyu*, Sadriye Küçükbayrak

Istanbul Technical University, Chemical and Metallurgical Engineering Faculty, 80626, Maslak-Istanbul, Turkey

Received 17 February 1998; accepted 2 June 1998

Abstract

The sulphation reaction of the calcines produced from four limestone and one dolomite samples were investigated and modeled. The experiments were conducted in a thermogravimetric analyzer under isothermal conditions and in a gaseous atmosphere consisting of 15 vol% CO_2, 0.35 vol% SO_2 and balance of dry air by volume. The variation of reaction rate with temperature was determined by sulphating of calcines at three different temperatures: 1023, 1173 and 1273 K. Based on the initial sulphation rates, the apparent activation energies were calculated as 51.58, 145.20 and −37.79 kJ/mol for L01, L04 and D01 samples, respectively. The unreacted shrinking core model was chosen to describe this non-catalytic solid/gas (CaO/SO_2) reaction mechanism. The experimental results were found to be correlated successfully by this model and diffusion through the calcium sulphate product layer is rate limiting. © 1998 Elsevier Science B.V.

Keywords: Modeling; Sorbents; Sulphation

1. Introduction

The sulphation reactions of natural sorbents, such as limestone and dolomite, have been widely studied due to their utilization in coal-fired combustion systems for controlling sulphur dioxide emission. The sulphation rates and the total sulphation capacities of sorbents are very important factors which influence the operating costs of combustors. Good correlations between sulphur dioxide sorption capacity and physical properties of calcined sorbents have been reported [1–4].

Generally, thermogravimetric studies on the sulphation of limestone and dolomite are performed to obtain design parameters for fluidized-bed desulphurization systems [5]. Sulphation reactions strongly effected from the operational variables, such as particle size, temperature, pressure, gas composition and sorbent type. Thermogravimetric data can provide an estimate about the effect of these parameters on desulphurization processes.

In the previous paper [6], the conversion–time curves obtained for the sulphation of calcines used in this work were given and discussed. These curves were derived from the experimental thermogravimetric data. The kinetic model which provides the best correlation with these experimental results is being presented in this study.

2. Experimental

The chemical composition of the natural sorbent samples were determined according to ASTM Standards [7]. The total sulphation capacities of these

---

*Corresponding author. Tel.: 0090 212 285 35 40; fax: 0090 212 285 2925.

PII S0040-6031(98)00401-8

Table 1
Chemical composition and total sulphation capacities of the sorbent samples

Sample origin	CaO/ %	MgO/ %	Fe_2O_3/ %	SiO_2/ %	Al_2O_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
Kapakli (D01)	31.52	19.87	0.12	0.64	0.26	0.443

sorbents were also determined at 1173 K in a tube furnace [4]. The results are given in Table 1.

The reaction between calcined sorbent particles and sulphur dioxide was studied, using a Shimadzu 41 thermal analyser. Further details on the experimental conditions were described elsewhere [6].

3. Modeling and discussion

Several model equations have been proposed in the literature to describe the heterogeneous non-catalytic solid–gas reaction mechanism [8–15]. These models can be grouped into three main categories:

1. Grain models;
2. Pore models; and
3. Network models.

The model used, in this study, belongs to the first group and assumes that the solid reactant particle consists of spherical grains. Sulphation of these grains proceeds according to shrinking core process. The shrinking unreacted core model was developed by Szekely et al. [8]. In this model, for spherical particles and a first-order chemical reaction with respect to SO_2 concentration, the relationship between the time and conversion is given depending on the rate-limiting step:

1. If the chemical reaction is the rate-limiting step

$$\frac{t}{\tau} = [1-(1-x)^{1/3}] \quad \tau = \frac{\rho_s d_s}{a M_s k C_g} \tag{1}$$

2. If the diffusion through the product layer is the rate-limiting step

$$\frac{t}{\tau} = [3-3(1-x)^{2/3}-2x] \quad \tau = \frac{\rho_s d_s^2}{6 a M_s D_e C_g} \tag{2}$$

3. If the mass transfer through gas film is the rate-limiting step

$$\frac{t}{\tau} = x \quad \tau = \frac{\rho_s d_s}{3 a M_s \beta C_g} \tag{3}$$

The experimental conversion–time curves obtained, in this work, for CaO–SO_2 reaction have a sharp convex shape [6] as would be expected when the diffusion through the product layer is rate limiting (Eq. (2)). However, the relationship between the time and conversion is linear if the mass transfer through gas film is rate limiting (Eq. (3)). The CaO conversion–time curves of samples were derived from their experimental sulphation TG data. The effects of the experimental variables, such as sulphation temperature, sorbent type and the physical properties of calcines, on the results of sulphation have been discussed in detail elsewhere [6].

As known the molar volume of $CaSO_4$ is three times that of CaO; therefore, a non-porous protective layer forms on the CaO surface soon after the start of reaction which prevents further contact of CaO with reacting gas. Since the diffusional resistance is negligible before the formation of the $CaSO_4$ product layer, the chemical reaction can be rate limiting at the beginning of sulphation (Eq. (1)).

In this study, the modeling of the reaction between CaO particle and sulphur dioxide was achieved using Eq. (2) (Model-1), a combination of Eqs. (1) and (2) (Model-2) and Eq. (1) (Model-3). The kinetic parameters (k and D_e) were determined from the experimental data. The reaction rate constant (k) was calculated from Eq. (1) using the initial rate of reaction which is equal to the slope of the conversion–time curve at t=0 ($|dx/dt|_{t=0}$).

The effective diffusion coefficient of gaseous reactant through product layer was assumed to be conversion dependent and calculated from experimental $x-t$

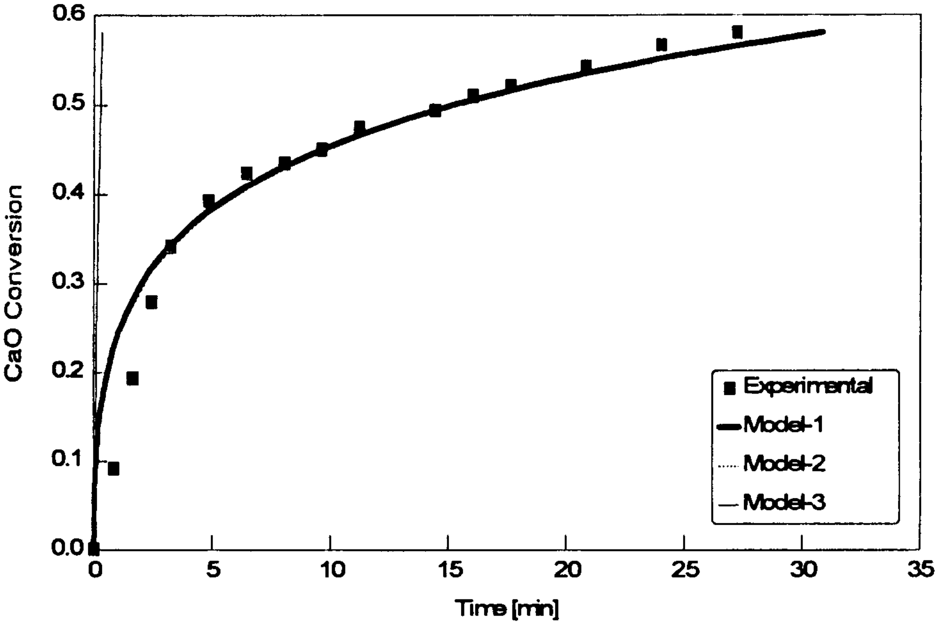

Fig. 1. Comparison of CaO conversions determined experimentally and theoretically (for the sulphation of L01 at 1073 K).

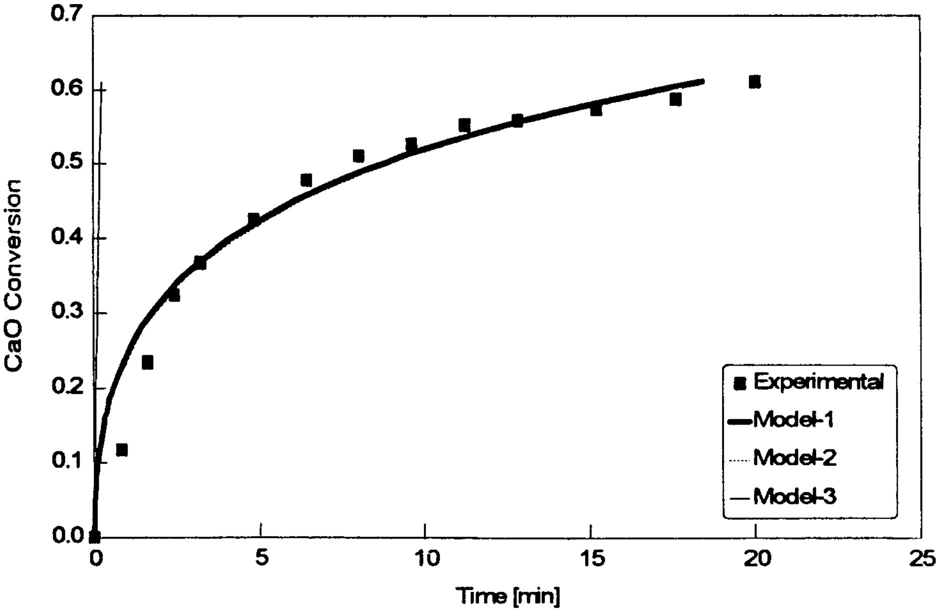

Fig. 2. Comparison of CaO conversions determined experimentally and theoretically (for the sulphation of L01 at 1173 K).

data using the following semi-empirical equation [16]:

$$D_e = D_{e,0} e^{-bx} \quad (4)$$

The conversion–time data, obtained experimentally for the sulphation reactions of sorbents, were compared with the computed

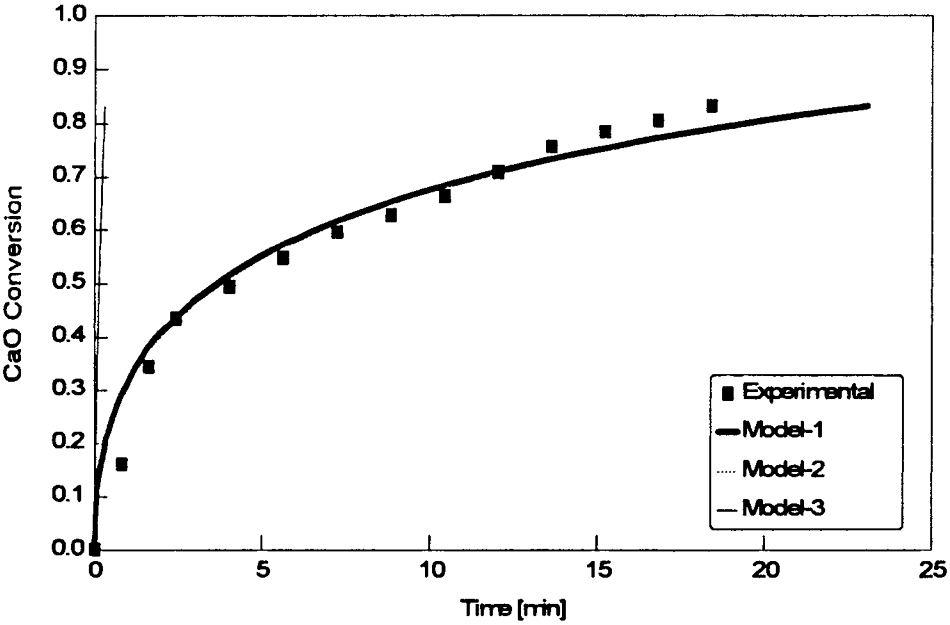

Fig. 3. Comparison of CaO conversions determined experimentally and theoretically (for the sulphation of L01 at 1273 K).

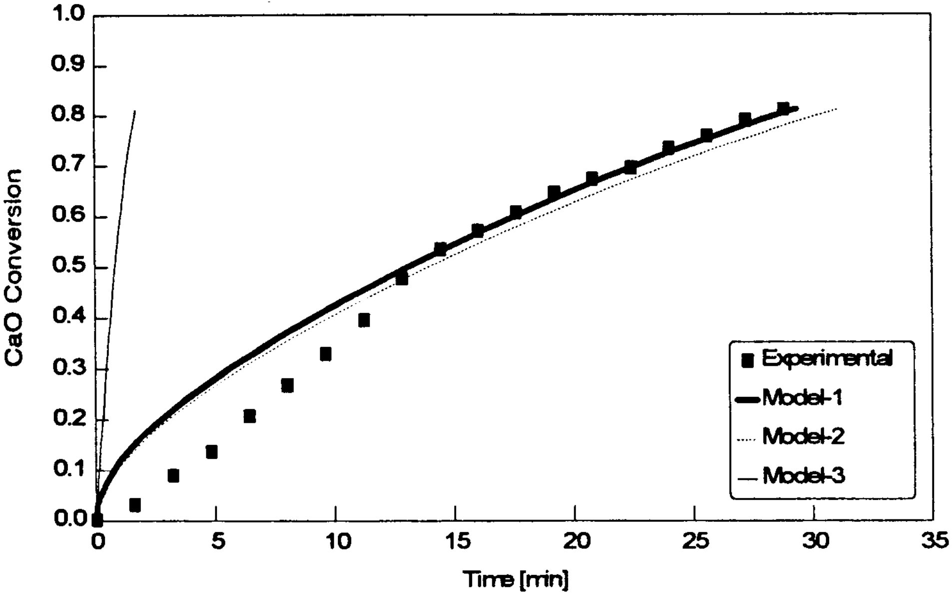

Fig. 4. Comparison of CaO conversions determined experimentally and theoretically (for the sulphation of L04 at 1073 K).

values, using the above mentioned three different model equations; the results are illustrated in Figs. 1–11.

It is clearly seen from the figures that conversion–time curves predicted by Model-3 (Eq. (1)) do not provide any approximation to the experimental data. However, experimental conversion–time data are, generally, well correlated by Model-1 (Eq. (2)) which represents the product layer diffusion as a rate-limiting mechanism.

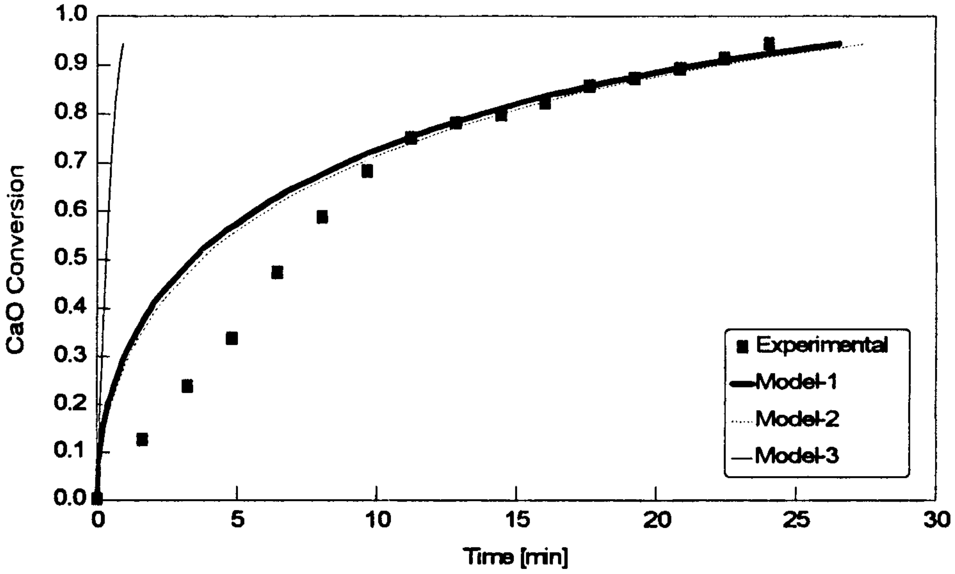

Fig. 5. Comparison of CaO conversions determined experimentally and theoretically (for the sulphation of L04 at 1173 K).

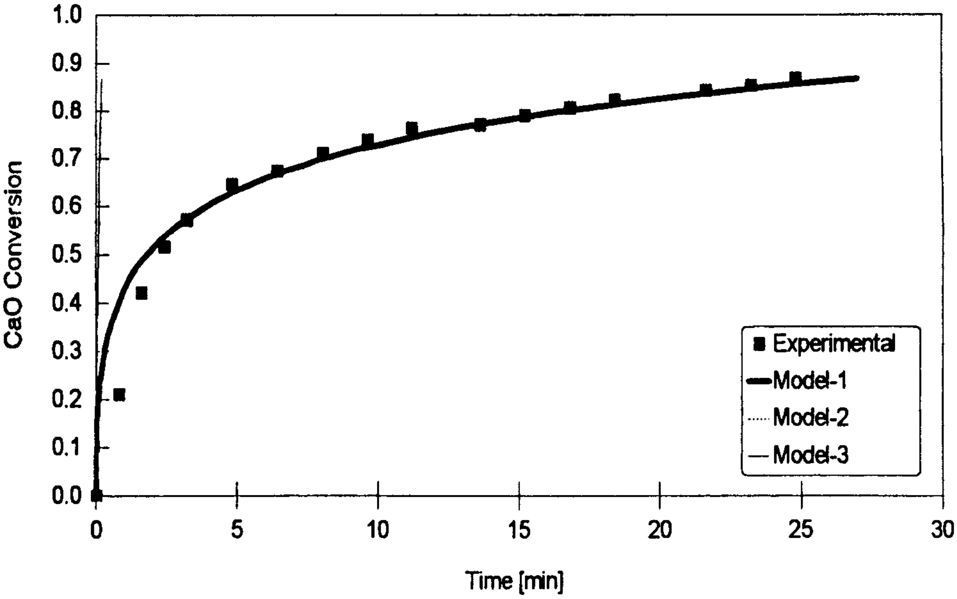

Fig. 6. Comparison of CaO conversions determined experimentally and theoretically (for the sulphation of L04 at 1273 K).

If we compare conversion values given in Figs. 4, 5, 7–10 it can be seen that, at the early stages of the reaction, experimentally determined values are not adequately described by Model-1. These differences might be due to the reaction being limited by the chemical reaction at low conversion degrees; therefore, a combination of Eqs. (1) and (2) (Model-2) was used for computation. But the curves obtained using Model-2 are overlapped on the curves obtained by Model 1. This clearly shows that the chemical reaction may only control the overall rate at very low conversion degrees. Therefore,

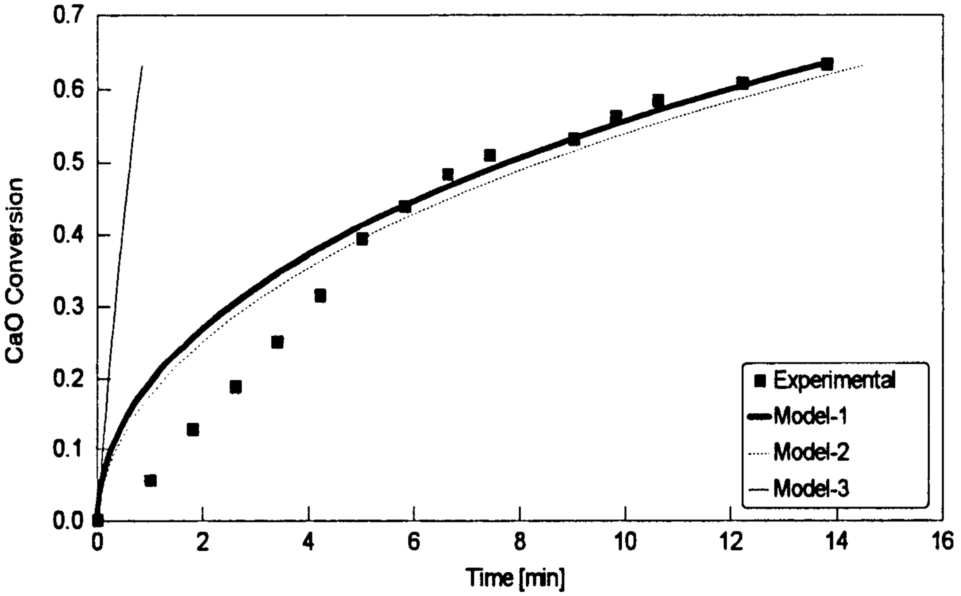

Fig. 7. Comparison of CaO conversions determined experimentally and theoretically (for the sulphation of L02 at 1173 K).

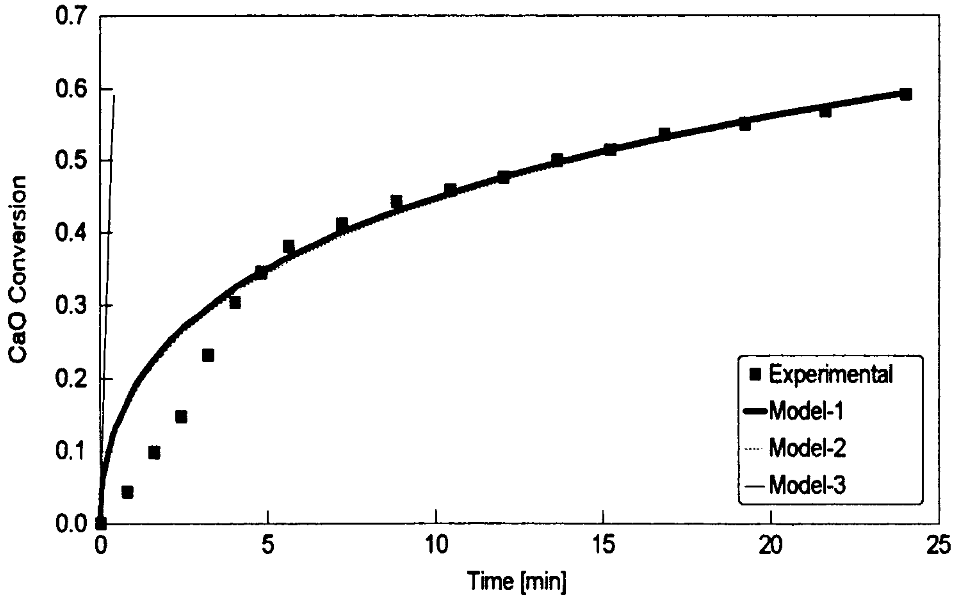

Fig. 8. Comparison of CaO conversions determined experimentally and theoretically (for the sulphation of L03 at 1173 K).

the shape of the curves obtained by Models 1 and 2 are found to be identical. On the other hand, after a certain CaO conversion is obtained, the experimental data have been successfully correlated by Model-1. This point is changed depending on sample properties and working conditions. As a result it is concluded that, among the three possible rate-limiting mechanisms, only product layer

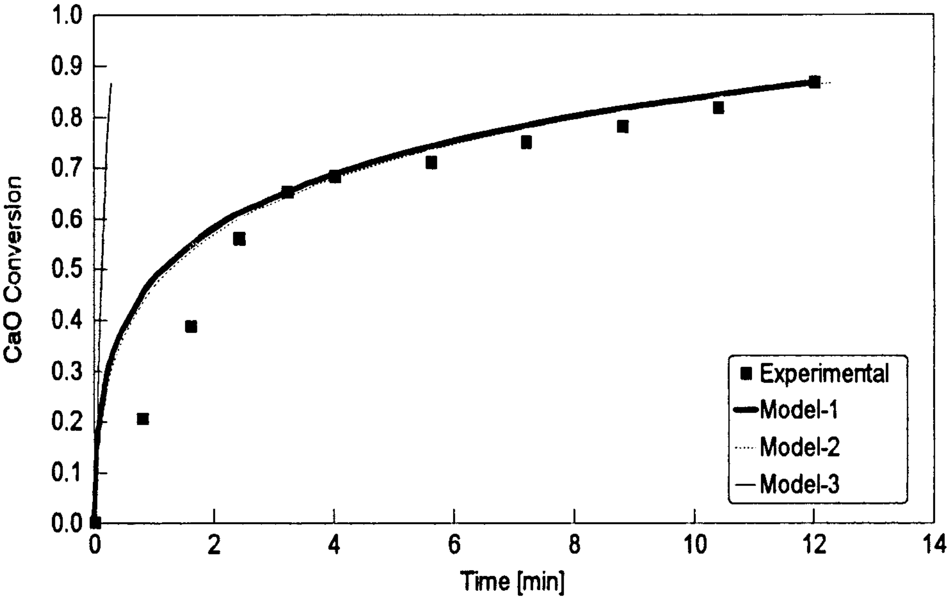

Fig. 9. Comparison of CaO conversions determined experimentally and theoretically (for the sulphation of D01 at 1073 K).

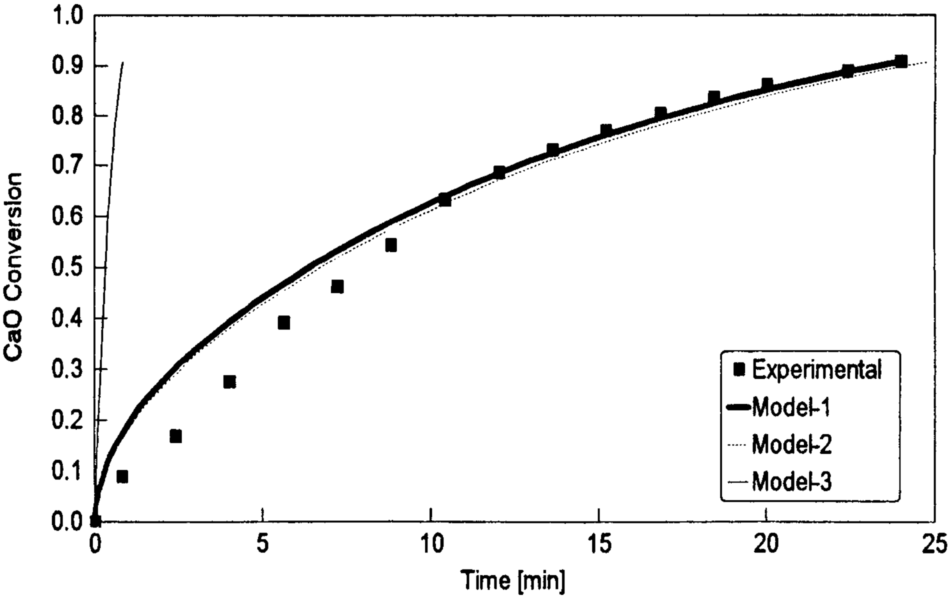

Fig. 10. Comparison of CaO conversions determined experimentally and theoretically (for the sulphation of D01 at 1173 K).

diffusion (Model-1) satisfactorily correlates the experimental data.

The effect of temperature on the overall reaction rates of calcines produced from L01, L04 and D01 was also investigated. The rate constant (*k*) was calculated for each temperature using the initial rate of reaction. The apparent activation energy values were then calculated from $k-1/T$ data using Arrhenius relation-

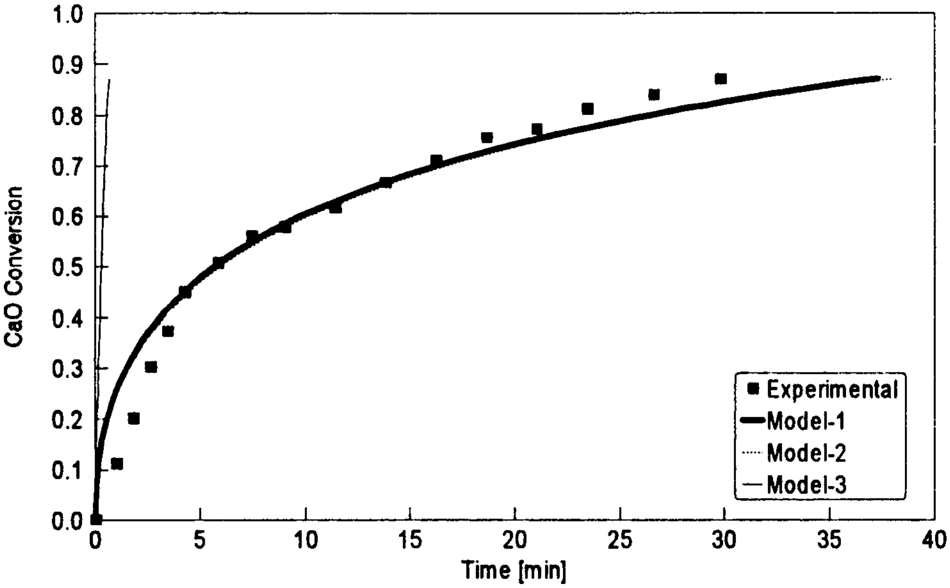

Fig. 11. Comparison of CaO conversions determined experimentally and theoretically (for the sulphation of D01 at 1273 K).

ship. These values were calculated as 51.58, 145.20 and −37.79 kJ/mol for L01, L04 and D01 samples, respectively. Stouffer and Yoon [17] have reported the apparent activation energy values ranged from negative values up to 92 kJ/mol for the sulphation reactions of calcines produced from different dolomites and limestones. They indicated that activation energies below 40 kJ/mol are indicative of rapid premature pore mouth plugging.

4. Nomenclature

ρ_s	Density of solid reactant (g/cc)
d_s	Initial radius of solid reactant (cm)
a	Stoichiometric coefficient of solid reactant
M_s	Molecular weight of solid reactant (g/g mol)
k	Reaction rate constant (cm/s)
C_g	Bulk concentration of gaseous reactant (mol/cc)
x	Conversion of CaO to $CaSO_4$
D_e	Effective diffusion coefficient (cm^2/s)
β	Mass transfer coefficient (cm/s)
$D_{e,0}$	Effective diffusion coefficient at x=0 (cm^2/s)
b	Constant in Eq. (4)

References

[1] R.H. Borgwardt, R.D. Harvey, Environmental Science and Technology 6 (1972) 350.
[2] A.E. Potter, Am. Cram. Soc. Bull. 48 (1969) 855.
[3] M. Hartman, J. Pata, R.W. Coughlin, Ind. Eng. Chem. Process Des. Dev. 17 (1978) 411.
[4] A.E. Meriçboyu, S. Küçükbayrak, S. Yaman, Environ. Technol. 14 (1993) 787.
[5] R. Snyder, W.I. Wilson, I. Johnson, Thermochimica Acta 26 (1978) 257.
[6] A.E. Meriçboyu, S. Küçükbayrak, Thermochimica Acta 260 (1995) 45.
[7] Annual Book of ASTM Standards, Part 13, Method C25-72, American Society for Testing and Materials Easton, 1977.
[8] J. Szekely, J.W. Evans, H.Y. Sohn, Gas Solid Reactions, 1st ed., Academic Press, New York, 1976, Chaps. 3–4.
[9] R.L. Pigford, G. Sliger, Ind. Eng. Chem. Process Des. Dev. 12 (1973) 85.
[10] M. Hartman, R.W. Coughlin, AIChE Journal 22 (1976) 490.
[11] T. Dogu, Chem. Eng. J. 21 (1981) 213.
[12] C. Georgakis, C.W. Chang, J. Szekely, Chem. Eng. Science 34 (1979) 1072.
[13] P.A. Ramachandran, J.M. Smith, AIChE Journal 23 (1977) 353.
[14] S.K. Bhatia, D.D. Perlmutter, AIChE Journal 26 (1980) 379.
[15] S.K. Bhatia, D.D. Perlmutter, AIChE Journal 27 (1981) 247.
[16] A.F. Shaaban, Thermochimica Acta 180 (1991) 9.
[17] M.R. Stouffer, H. Yoon, AIChE Journal 35 (1989) 1253.