Kinetic model for desulphurization at low temperatures using hydrated sorbent

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Abstract

The sulphation reaction of hydrated silica fume–$Ca(OH)_2$ sorbents were investigated and modelled. These experiments were conducted in a thermogravimetric analyzer under isothermal conditions and in a humidified gaseous atmosphere consisting of 5 vol% O_2, 10 vol% CO_2, 0.5 vol% SO_2 and the balance of nitrogen. The effect of the relative humidity on the reaction rate was determined by sulfating of hydrated sorbents in the gaseous atmospheres which have three different relative humidities: 25%, 55% and 90%. The unreacted shrinking core model was chosen to describe this non-catalytic solid/gas (hydrated sorbent/SO_2) reaction mechanism. The experimental results were found to be correlated successfully by this model. It was determined that chemical reaction is partly rate limiting especially at the beginning of sulphation, diffusion through the calcium sulphite hemihydrate product layer generally controls the reaction rate. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydrated sorbents; Sulphation; Modelling

1. Introduction

The humidified duct injection processes for controlling SO_2 emissions at low temperatures from combustion systems have been developed over recent years and today they become a feasible alternative to the established lime or limestone wet scrubbing processes [1].

The humidified duct injection process involves injection of a dry sorbent, in conjunction with flue gas conditioned by water sprying in the ductwork downstream of the air preheater but ahead of the particular collection system. Then the total SO_2 removal achieved is the sum of both capture places, in the duct section and the particulate control device.

This process is very attractive for many reasons relating to the nonrequirement needed for wet processes which are commonly adopted in commercial plants. New silica-enhanced lime sorbents have been developed on the basis of using silica fume or fly ash as a reagent material for humidified duct injection process. This is both economically and environmentally attractive because the sorbent reactivity toward SO_2 increases as a consequence of the pozzolanic reaction between silica fume or fly ash and $Ca(OH)_2$ in the presence of water [2,3].

The kinetics of the reaction between SO_2 and hydrated sorbents at low temperatures has been attended as it is of practical relevance in the design and optimization of desulphurization processes. Several works [1–4] have appeared in the last decade, including the reaction mechanism as well as studies of the kinetics of the reaction. Concerning the reaction

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mechanism, two different phenomena have been suggested:

1. a gas–solid reaction between the adsorbed SO_2 and the solid sorbent and,
2. a liquid-phase reaction between the ions SO_3^{-2} Ca^{+2} to give $CaSO_3 \cdot 1/2H_2O$.

Studies on the kinetics of the reaction between SO_2 and $Ca(OH)_2$ at low temperatures have been conducted using two different systems namely; sand-bed reactors [2,3,5] and differential reactors [6–8]. For the sulphation reactions performed in fixed-bed reactors operating both integral and differential regimes, the application of the shrinking core models has been used for data fitting, leading to various model limitations in order to explain the experimental behaviour of the reaction rate decrease with the solid conversion, especially at high relative humidity.

The objective of this work is to investigate the sulphation reaction of hydrated silica fume/$Ca(OH)_2$ sorbents and to establish the desulphurization kinetic model. Thermogravimetric data have been used to estimate the effect of the experimental parameters on desulphurization processes. The kinetic model which provides the best correlation with these experimental results is being presented.

2. Experimental

The chemical composition of the silica fume which used as siliceous material in this study was determined according to ASTM Standards [9]. Silica fume was hydrated with a natural hydrated lime. The natural hydrated lime was produced from limestone which has a CaO content of 49.9% by weight. Hydration experiments were conducted at two different conditions, keeping the silica fume/$Ca(OH)_2$ weight ratio (R) constant as 1/1. Hydration conditions (temperature (T), pressure (P) and time (t)) were selected as

363 K, 0.101 MPa, 8 h (atmospheric hydration) and 398 K, 0.232 MPa, 2 h (pressure hydration).

Physical properties of the hydrated sorbents, such as total pore volume, surface area and pore size distribution were measured using an Autoscan-33 mercury porosimeter. Desulphurization tests were performed at a temperature of 338 K. A thermobalance was used to record the weight increase of the sorbent during reaction with SO_2. To distinguish between the weight gain by water adsorption and the weight gain by sulphation, the samples were first exposed to a humidified gaseous mixture consisting of 5% O_2, 10% CO_2 and the balance of nitrogen. After this preconditioning, SO_2 was added to the gaseous mixture for sulphation with a concentration of 5000 ppm.

3. Result and discussion

Chemical composition of the silica fume used in this study is given in Table 1. Total surface areas of the hydrated sorbents prepared from silica fume/$Ca(OH)_2$ mixtures at different conditions are listed in Table 2. The reactivity of the hydrated sorbents toward SO_2 is expressed here as $Ca(OH)_2$ conversion and calculated by using Eq. (1). The $Ca(OH)_2$ conversions of the hydrated sorbents were also listed in Table 2.

$$Ca(OH)_2 \text{ conversion } (\%) = \frac{\Delta W/(M_1 - M_2)}{(W_s/M_2) \cdot R} \times 100. \qquad (1)$$

The $Ca(OH)_2$ conversion–time curves of sorbents were derived from their experimental sulphation TG data and are illustrated in Figs. 1–3. As seen from Table 2 and Figs. 1–3, silica fume–$Ca(OH)_2$ sorbents show a better reactivity towards SO_2 than the calcium hydroxide itself This behaviour is closely related to the nature of the products formed during hydration and to the greater surface area. The surface area of a solid sorbent is a very important parameter in the solid gas

Table 1
Chemical composition of the silica fume sample

Sample	SiO_2 (%)	CaO (%)	MgO (%)	Fe_2O_3 (%)	Al_2O_3 (%)	SO_3 (%)	Ignition loss (%)
Silica fume	90.80	2.55	0.94	1.93	1.02	0.49	1.57

Table 2
Total surface area and Ca(OH)$_2$ conversion values of the sorbent samples

Sample	Hydration conditions $T/P/t/R$	Surface area (m^2/g)	Ca(OH)$_2$ conversion	RH (%)
Ca(OH)$_2$	–	9.80	0.03	25
			0.16	55
			0.35	90
Ca(OH)$_2$–silica fume	363/0.101/8/1 : 1	124.93	0.27	25
			0.54	55
			0.83	90
Ca(OH)$_2$–silica fume	398/0.232/2/1 : 1	172.74	0.48	25
			0.96	55
			0.99	90
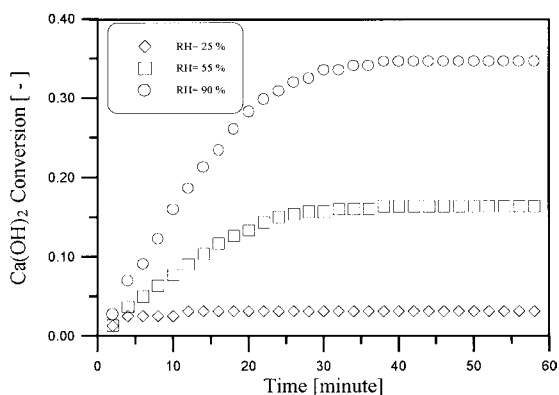
Fig. 1. Influence of relative humidity for the sulphation of Ca(OH)$_2$ at 338 K.

Fig. 2. Influence of relative humidity for the sulphation of Ca(OH)$_2$-silica fume sorbent at 338 K ($T = 363$ K, $P = 0.101$ MPa, $t = 8$ h, $R = 1 : 1$).
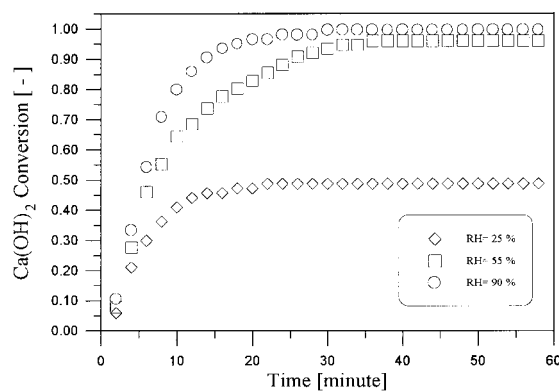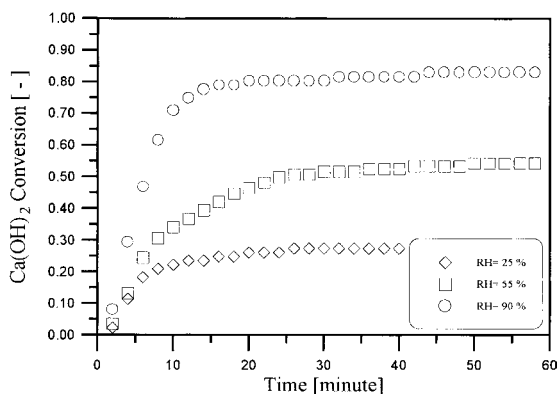

Fig. 3. Influence of relative humidity for the sulphation of Ca(OH)$_2$–silica fume sorbent at 338 K ($T = 398$ K, $P = 0.232$ MPa, $t = 2$ h, $R = 1 : 1$).

adsorption process and may be on the principal factors determining overall reactivity [1,3,10].

As shown in Figs. 1–3 and Table 2, the relative humidity of the sulphation gaseous mixture was changed within the range 25–90% and its influence on the conversion was investigated. It was determined that Ca(OH)$_2$ conversions are increased by increasing the relative humidity of the sulphation gaseous mixture. As reported by several researchers [1,3,4] the relative humidity (RH) of the reaction gaseous mixture is considered to be a key parameter for the sulphation reaction. The adsorption of water vapour on the free surface of the sorbent and the number of water monolayers is considered to be critical for the reaction yield. Thus, at low relative humidities, no reaction occurs because insufficient water molecules are available.

However, at high relative humidities, the number of water monolayers formed is large enough which provide a symmetrical configuration of H_2O ligations around an SO_2 molecule and therefore the reaction rate increases with the increasing relative humidity and becomes independent of the partial pressure of SO_2. Although Klingspor et al. [1] reported that a minimum relative humidity of 20% is required to obtain an appreciable conversion rate; Rice and Bond [11] found considerable conversion at a relative humidity range of 5–10%; Khinast et al. [12] and Irabien et al. [3] report that an increasing water vapour content in the sulphation gaseous mixture improves the SO_2 removal reaction considerably, and they described the effect of relative humidity on the reaction rate of $Ca(OH)_2$ with SO_2 at low temperature by an exponential function. They reported that the reaction is governed by a "non-ideal" surface adsorption process.

It is also clearly seen from the Figs. 1–3 that the conversion–time curves of sorbents gradually flatten after some conversion values depending on the surface area of sorbent used and relative humidity of the sulphation gaseous mixture. These conversion values were determined as 0.02, 0.14 and 0.29 for $Ca(OH)_2$, 0.22, 0.35 and 0.75 for silica fume–$Ca(OH)_2$ sorbent prepared by atmospheric hydration, 0.44, 0.80 and 0.95 for silica fume–$Ca(OH)_2$ sorbent prepared by pressure hydration for the relative humidities of 25%, 55% and 90% respectively.

As expected for $Ca(OH)_2$ sorbent which has low surface area, the shape of the conversion–time curves are flatten at very low conversion values (Fig. 1). This is probably due to the acceleration of the diffusion resistance by plugging of the external surface of the particles by solid product. The conversion–time curves of the hydrated silica fume–$Ca(OH)_2$ sorbents are flatten at high conversion values as compared with $Ca(OH)_2$. These differences can be attributed to the surface area variations of the sorbents used for desulphurization. It is well documented fact that the production of reactive SO_2 sorbents can be achieved by hydration of a siliceous material with $Ca(OH)_2$ slurry. The reaction between the siliceous material and $Ca(OH)_2$ is called a pozzolanic reaction and it gives a reactive product with a large surface area.

The SO_2 concentration of the reaction gas is not considered to be an important parameter for the sulphation reaction. Klingspor et al. [1] found that the bulk concentration of SO_2 becomes significant only when the relative humidity is beyond 70% since SO_2 becomes absorbed in the liquid film on the particle rather than adsorbed. Ruiz-Alsop [13] found that the SO_2 concentration shows a small influence on the reaction rate but only at a small relative humidity and at low SO_2 concentrations. Therefore, in this study SO_2 concentration was kept constant in the sulphation gaseous mixture as 5000 ppm.

3.1. Modelling of the reaction

Several model equations have been proposed in the literature to describe the heterogeneous non-catalytic solid–gas reaction mechanism [14–16]. 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. [14]. 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

$$\frac{t}{\tau} = [1 - (1-x)^{1/3}], \ \ \tau = \frac{\rho_s d_s}{a M_s k C_g}. \qquad (2)$$

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

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

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

$$\frac{t}{\tau} = x, \ \ \ \ \tau = \frac{\rho_s d_s}{3 a M_s \beta C_g}. \qquad (4)$$

As illustrated in Figs. 1–3, the experimental conversion–time curves obtained in this work for the reaction between sorbents ($Ca(OH)_2$, silica fume–$Ca(OH)_2$) and SO_2 have a convex shape as would be expected when the diffusion through the product layer is rate limiting (Eq. (3)).

As known the molar volume of reaction product ($CaSO_3 \cdot 1/2\ H_2O$) has a larger molar volume than $Ca(OH)_2$ or hydrated silica fume–$Ca(OH)_2$ sorbent; therefore, a non-porous protective layer forms on the sorbent surface soon after the start of reaction which prevents further contact of sorbent with reacting gas. Since the diffusional resistance is negligible before the formation of the $CaSO_3 \cdot 1/2\ H_2O$ product layer, the chemical reaction can be rate limiting at the beginning of sulphation (Eq. (2)).

In this study, the modeling of the reaction between $Ca(OH)_2$ or hydrated sorbent particle and sulphur dioxide was achieved using Eq. (2) (Model-1) and Eq. (3) (Model-2). The kinetic parameters (k and D_e) were determined from the experimental data. The reaction rate constant (k) was calculated from Eq. (3) using the initial rate of reaction which is equal to the slope of the conversion–time curve at $t = t_0$ ($|dx/dt|_{t=t_0}$).

The effective diffusion coefficient of gaseous reactant through product layer was assumed to be conversion dependent and calculated from experimental x–t data using the following semi-empirical equation [17,18].

$$D_e = D_{e,0} \cdot e^{-bx}. \qquad (5)$$

The conversion–time data, obtained experimentally for the sulphation reactions of sorbents, were compared with the computed values, using the above mentioned two different model equations; the results are illustrated in Figs. 4–11. Since the relationship between the time and conversion is linear if the mass transfer through gas film is rate limiting, Eq. (4) was not used for modelling. It is clearly seen from the figures that experimentally determined conversion–time data can be partly described by Model-1 (Eq. (2)) which assumed that the chemical reaction is the rate-limiting step. However, experimental conversion–time data are generally well correlated by Model-2 (Eq. (3)) which represents the product layer diffusion as a rate-limiting mechanism.
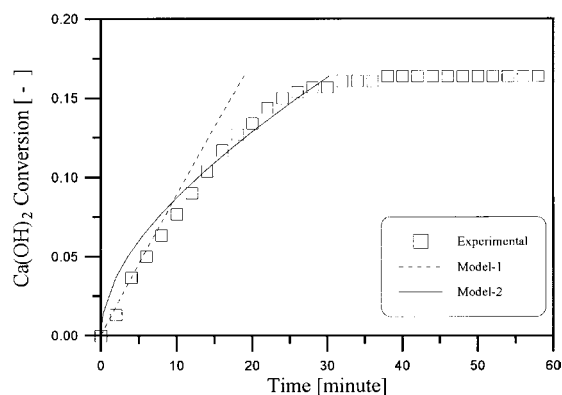

Fig. 4. Comparison of $Ca(OH)_2$ conversions determined experimentally and theoretically (for the sulphation of $Ca(OH)_2$ at 338 K and 55% RH).
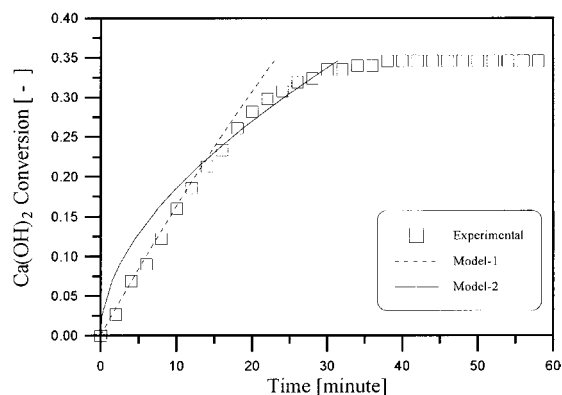

Fig. 5. Comparison of $Ca(OH)_2$ conversions determined experimentally and theoretically (for the sulphation of $Ca(OH)_2$ at 338 K and 90% RH).
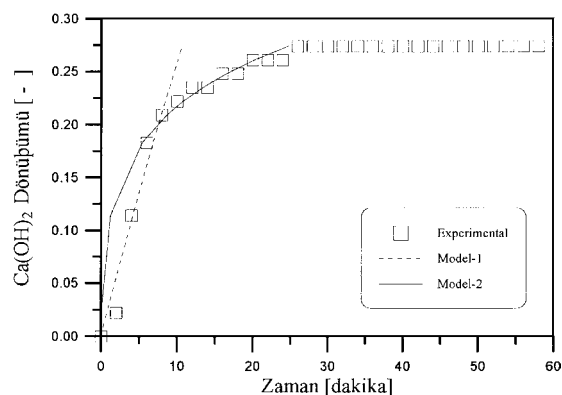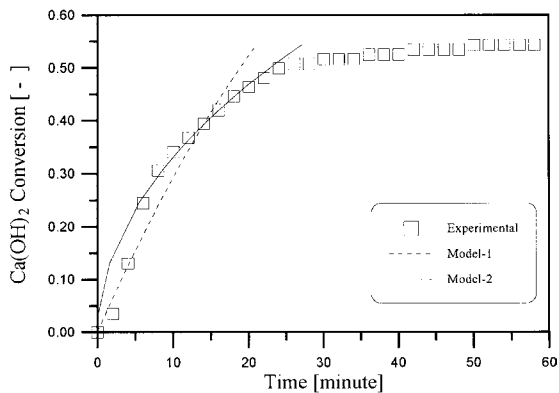

Fig. 6. Comparison of $Ca(OH)_2$ conversions determined experimentally and theoretically (for the sulphation of $Ca(OH)_2$–silica fume sorbent at 338 K and 25% RH) ($T = 363$ K, $P = 0.101$ MPa, $t = 8$ h, $R = 1:1$).

Fig. 7. Comparison of Ca(OH)$_2$ conversions determined experimentally and theoretically (for the sulphation of Ca(OH)$_2$–silica fume sorbent at 338 K and 55% RH) ($T = 363$ K, $P = 0.101$ MPa, $t = 8$ h, $R = 1 : 1$).
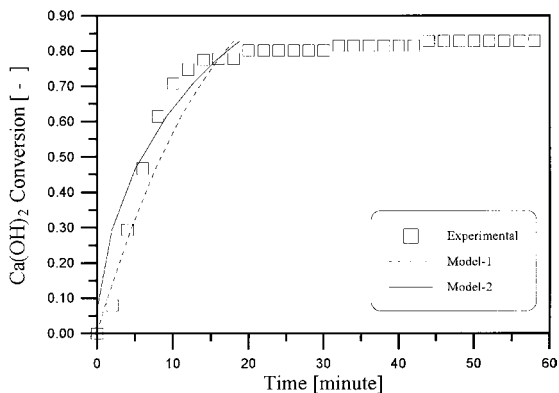

Fig. 9. Comparison of Ca(OH)$_2$ conversions determined experimentally and theoretically (for the sulphation of Ca(OH)$_2$–silica fume sorbent at 338 K and 25% RH) ($T = 398$ K, $P = 0.232$ MPa, $t = 2$ h, $R = 1 : 1$).

If we compare experimental and computed conversion values given in Figs. 4–11, it can be seen that, the chemical reaction may only control the overall rate at low conversion degrees except for sorbents prepared by pressure hydration of silica fume–Ca(OH)$_2$ mixtures (Figs. 9–11).

The uptake on mass at the initial stage can be attributed to the formation of a monolayer of product. Sulphur dioxide molecules are adsorbed and they react with Ca(OH)$_2$ or hydrated sorbent in the presence of adsorbed water molecules to form a monolayer of CaSO$_3$·1/2 H$_2$O. During this stage both the relative

humidity and the SO$_2$ concentration have an influence on the reaction. Calcium ions are already available from the very beginning and therefore the formation of calcium ions is not regarded as the rate-determining step during this stage of the reaction. It is more likely that a chemisorption process of the SO$_2$ on the particle surface seems to be important, but it is still unclear how SO$_2$ is chemisorbed. This chemisorption process is enhanced with the increasing amount of water molecules.

The reduction of the reaction rate can be due to the increasing coverage of the surface with a monolayer of

Fig. 8. Comparison of Ca(OH)$_2$ conversions determined experimentally and theoretically (for the sulphation of Ca(OH)$_2$–silica fume sorbent at 338 K and 90% RH) ($T = 363$ K, $P = 0.101$ MPa, $t = 8$ h, $R = 1 : 1$).
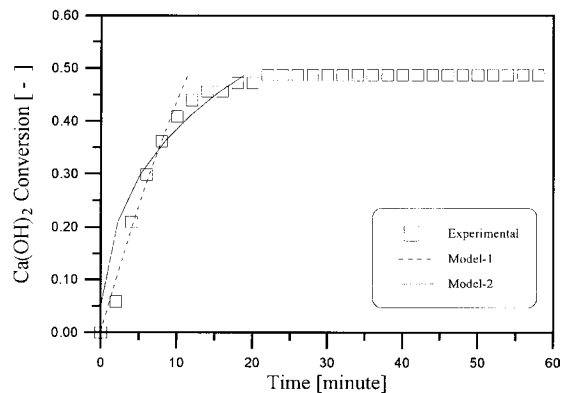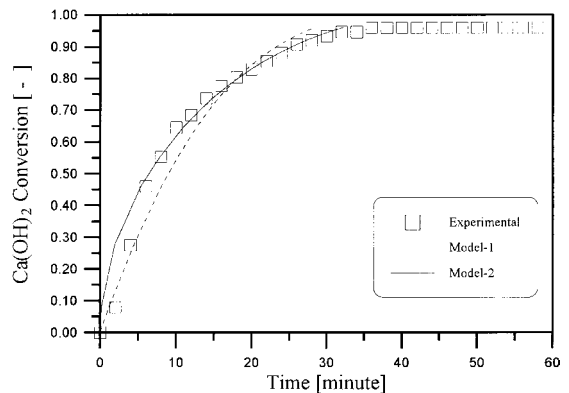

Fig. 10. Comparison of Ca(OH)$_2$ conversions determined experimentally and theoretically (for the sulphation of Ca(OH)$_2$–silica fume sorbent at 338 K and 55% RH) ($T = 398$ K, $P = 0.232$ MPa, $t = 2$ h, $R = 1 : 1$).

Fig. 11. Comparison of $Ca(OH)_2$ conversions determined experimentally and theoretically (for the sulphation of $Ca(OH)_2$–silica fume sorbent at 338 K and 90% RH) ($T = 398$ K, $P = 0.232$ MPa, $t = 2$ h, $R = 1 : 1$).
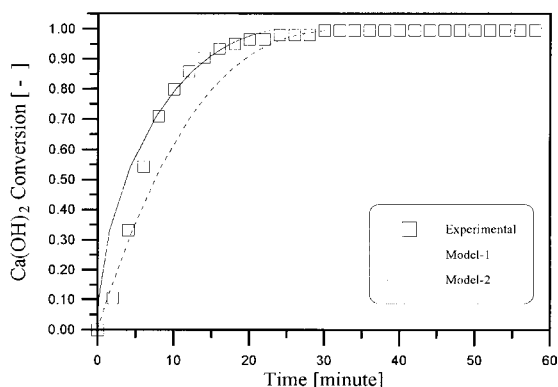
Table 3
The rate constant values obtained for different relative humidities

Sample	Hydration conditions $T/P/t/R$	k (cm min^{-1})	RH (%)
$Ca(OH)_2$	–	1.25	55
		2.35	90
$Ca(OH)_2$–silica fume	363/0.101/8/1 : 1	1.85	25
		2.13	55
		4.77	90
$Ca(OH)_2$–silica fume	398/0.232/2/1 : 1	3.41	25
		4.48	55
		5.38	90

product. While the formation of the first product layer proceeds, the formation of the consecutive product layers occur. Simultaneously another reaction rate that is based on the already formed product of the monolayer increases and it finally exceeds the rate of reaction of the formation of the monolayer until a maximum is achieved which depends mostly on the relative humidity. This step seems to be governed by a nucleation process of the product crystals. Product layer diffusion becomes increasingly rate limiting. Only the relative humidity has an impact effect on the conversion. It was reported that at high relative humidities the reaction product builds up more "cluster-like", whereas at low humidity the product layer covers the surface more uniformly [19]. Therefore product layer diffusion resistance is lower though conversion is higher at higher relative humidity (Figs. 5, 8 and 11); thus, the $Ca(OH)_2$ conversion value of silica fume–$Ca(OH)_2$ sorbent which has the greatest surface area and sulphated at relative humidity of 90% reached nearly to 100% (Fig. 11).

Pore closure and a reduction in reaction surface area contribute to a further decrease of the reaction rate. Available solid reactant ($Ca(OH)_2$) and the reaction surface area can possibly be reduced significantly with increasing conversion. The open pore volume is certainly reduced since the reaction product has a larger molar volume than $Ca(OH)_2$ or hydrated sorbent.

Experimental data obtained in this work show that the relative humidity has a major impact on the conversion throughout the entire reaction which is concurringly reported in the literature. The rate constant values (k) were calculated for each relative humidity using the initial rate of reaction (Table 3). It is clearly seen from the Table 3 that the rate constant of the different sorbents significantly increases with increasing relative humidity.

It was concluded that conversion–time data predicted by computation using (Model-2) (Eq. (3)) are closer to experimental data than the values predicted by the Model-1 (Eq. (2)).

Nomenclature

W_s	the initial sorbent weight (mg)
ΔW	the weight change due to sulphation (mg)
M_1	the molecular weight of $CaSO_3 \cdot 1/2\ H_2O$ (mg/mmol)
M_2	the molecular weight of $Ca(OH)_2$ (mg/mmol)
R	the weight fraction of $Ca(OH)_2$ in the sorbent (−)
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 $Ca(OH)_2$
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. (5)

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