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Kinetics of the reaction of $Ca(OH)_2$/fly ash sorbent with SO_2 at low temperatures

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Abstract

A differential fixed-bed reactor was employed to study the reaction between $Ca(OH)_2$/fly ash sorbent and SO_2 under the conditions similar to those in the bag filters of the spray-drying flue gas desulfurization system. The $Ca(OH)_2$/fly ash sorbent was prepared at weight ratio of 70/30, slurrying time of 16 h, and slurrying temperature of 65°C. Foil-like calcium silicate hydrates were found in the sorbent. The $Ca(OH)_2$/fly ash sorbent was highly reactive towards SO_2 and its initial reaction rate and maximum conversion were much higher than pure $Ca(OH)_2$. Increasing the relative humidity of the gas significantly increased the initial reaction rate and the maximum Ca utilization of the sorbent. Temperature and SO_2 concentration had slight effects on the initial reaction rate and negligible effects on the maximum conversion. The reaction kinetics of $Ca(OH)_2$/fly ash sorbent with SO_2 was well described by the surface coverage model which assumes the sulfation rate being controlled by chemical reaction on sorbent grain surface and takes into account the surface coverage by products. The results of this study are useful to the design and operation of the dry or semidry processes using $Ca(OH)_2$/fly ash sorbent to remove SO_2 from flue gas. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Flue gas desulfurization; $Ca(OH)_2$; Kinetics; Mathematical modelling; Multiphase reaction; Pollution

1. Introduction

Reducing SO_2 emission from power plants is a main issue for the environmental protection. Many flue gas desulfurization (FGD) processes are available for the reduction of SO_2 emission. The dry and semi-dry FGD processes have the advantage of lower capital cost than the wet processes commonly adopted in power plants; however, the conversion of the sorbent, which is mostly hydrated lime, in the dry and semi-dry processes is low. How to increase the utilization of hydrated lime has been an important subject for the application of the dry or semi-dry processes.

Many researchers have shown that sorbents prepared from fly ash and hydrated lime have higher SO_2 capture and Ca utilization than hydrated lime (Jozewicz & Rochelle, 1986; Ho, 1987; Jozewicz, Chang, Sedman, & Brna, 1988a; Jozewicz, Jorgensen, Chang, Sedman, & Brna, 1988b; Martinez, Izquierdo, Cunill, Tejero, & Querol, 1991; Ho & Shih, 1992, 1993a; Davini, 1995; Sanders, Keener, & Wang, 1995; Garea et al., 1997a; Garea, Viguri, & Irabein, 1997b; Ishizuka, Tsuchiai, Murayama, Tanaka, & Hattori, 2000). The sorbents were prepared by slurrying hydrated lime and fly ash in water for a certain period of time and drying the slurry subsequently. Fly ash is a pozzolanic material, its main components are SiO_2, Al_2O_3, and Fe_2O_3 (Taylor, 1964). In the presence of water, amorphous silica in fly ash would react with hydrated lime to form calcium silicate hydrates ($x\mathrm{CaO} \cdot \mathrm{SiO_2} \cdot y\mathrm{H_2O}$), which may lead to sorbents having higher reactivities towards SO_2 than hydrated lime.

The literature on the kinetic model of the reaction of the $Ca(OH)_2$/fly ash sorbent with SO_2, however, is scarce. Recently, Garea et al. (1997b) studied the sulfation of fly ash/$Ca(OH)_2$(3/1 wt. ratio) sorbent at low temperatures and proposed a kinetic model based on the nonideal surface adsorption model (Irabien, Cortabitarte, & Ortiz, 1992) to describe the reaction of their sorbent.

In this work, the reaction of $Ca(OH)_2$/fly ash (70/30 wt. ratio) sorbent with SO_2 was studied under the conditions similar to those of the bag filters in a semi-dry scrubbing system by using a differential fixed-bed

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reactor, and a kinetic model describing the reaction of the sorbent was derived.

2. Experimental section

The hydrated lime used was reagent grade $Ca(OH)_2$ (purity > 95%; Hayashi Pure Chemical Industries, Ltd). Fly ash was from Boiler 3 of Shin-Da pulverized-coal power plant of Taiwan Power Company. The chemical compositions of the fly ash are: 59.0% SiO_2, 26.7% Al_2O_3, 5.5% K_2O, 1.6% CaO, 1.3% TiO_2, 1.2% Na_2O, 0.9% MgO, 0.47% SO_3, 0.05% V_2O_5, and 2.7% ignition loss (Ho, 1987). The volume mean particle diameters of $Ca(OH)_2$ and fly ash were 7.4 and 8.1 μm, respectively.

The hydrated lime and fly ash, together with 80 g deionized water, were placed into a 250 ml polypropylene conical beaker at a $Ca(OH)_2$/fly ash weight ratio of 70/30 and a water/solid weight ratio of 10. The beaker was then sealed with a rubber stopper at the mouth and inserted into a water bath at 65°C. The slurry was stirred with a magnetic stirrer for 16 h. After slurrying, the water in the slurry was evaporated in a vacuum oven, the solid phase left was further vacuum-dried at 105°C. The dried cake obtained was crashed into powder and sealed in a bottle before use. The particle size distribution of the sorbent was 98 wt% in the range of 0.6–60.6 μm with a volume mean particle diameter of 10.3 μm. The specific (BET) surface area of the sorbent was 38.0 m^2/g. The specific surface areas of sorbents prepared at different slurrying times were found to increase with slurrying time, as shown in Fig. 1. Except those used for studying the effect of specific surface area, all the samples used were prepared at a slurrying time of 16 h.

Experiments for the reaction of the sorbent with SO_2 were carried out by using a differential fixed-bed reactor. The details of the experimental setup and procedure were described in Ho and Shih (1992). In this study, about 30 mg sample was used for each run. The sorbent powder was dispersed into quartz wool; the wool was then set into the quartz sample pan. The sample pan had dimensions of 10 mm o.d. and 15 mm height and was perforated at the bottom to facilitate the passage of the sweep gas. The sweep gas entered the bottom of the reactor, passed through the 25 mm i.d. and 365 mm length outer tube, and went downward through the sample pan and the 10 mm i.d. and 315 mm length inner tube. The sweep gas was comprised of SO_2, H_2O, and N_2. The SO_2 and N_2 gases were supplied from cylinders and H_2O vapor was provided by a water evaporator. Prior to each run, the sample bed was humidified for 30 min by humid N_2 with a relative humidity at which the experiment was to be performed, which had been proved to be long enough for the sample to equilibrate with the gas stream. After humidification, the reactive gas was admitted into the sweep gas to start the run. The total gas flow rate was 4 l/min (STP).

The differential condition of the reactor with respect to interparticle SO_2 levels at the selected total gas flowrate and sample weight was confirmed by the results of experiment using different sample weights (Liu, 1999). The results showed that no effect of sample weight on the reaction when the weight was smaller than 40 mg.

The utilization or conversion of $Ca(OH)_2$ for a reacted sample was determined from its SO_3^{2-}/Ca^{2+} molar ratio. The SO_3^{2-} content in a sample was determined by iodometric titration, and the Ca^{2+} content by EDTA titration.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of unreacted sorbent and samples reacted with SO_2 for 10 and 60 min are shown in Fig. 2. The main peaks of the unreacted sorbent are those of $Ca(OH)_2$. The presence of $CaCO_3$ in the sample is due to the CO_2 contamination during the sample preparing process. The quartz is contained in the fly ash. The peaks of calcium silicate hydrates (C–S–H) formed during the preparing process are not found in this figure, indicating that the calcium silicate hydrates are amorphous. The reaction product is $CaSO_3 \cdot 0.5H_2O$. The intensities of the characteristic peaks of $CaSO_3 \cdot 0.5H_2O$ increase with reaction time.

3.2. Structure

Fig. 3(a) is the SEM micrograph of a typical $Ca(OH)_2$/fly ash sorbent particle. It was evident that the particle is highly porous and constituted by foil-like substances which are calcium silicate hydrates. The SEM micrograph of a particle of the sorbent which had reacted with SO_2 to a conversion of 0.59, Fig. 3(b), shows that the reacted particle is less porous and the foil-like substances become thicker.

The nitrogen adsorption and desorption isotherms for the sorbent show that the sorbent exhibits a type IV isotherm with a type H3 hysteresis (IUPAC, 1985). Type H3 hysteresis is associated with slit-shaped pores or the space between plate-like particles. Observation by SEM confirms this pore shape (Fig. 3(a)).

The pore volume distributions of sulfated samples are shown in Fig. 4. The volumes of micropore, mesopore, and total pores smaller than 3000 Å at different reaction extent are listed in Table 1. The pores of the sorbent are mainly the mesopores and macropores. Pore volumes of sulfated samples are observed to decrease with reaction extent, indicating that reaction takes place inside the pores and the reaction products formed on the pore walls have larger molar volumes than the solid reactants.

The specific surface areas of unreacted and sulfated samples are listed in Table 1. One can see that the

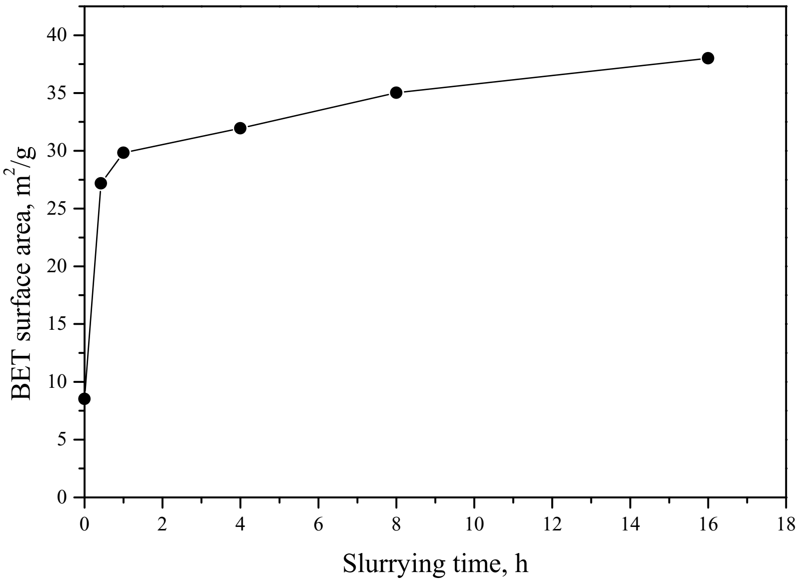


Fig. 1. Effect of slurrying time on the specific surface area of $Ca(OH)_2$/fly ash(70/30 wt. ratio) sorbent. Slurrying conditions: 65°C, $L/S=10/1$.

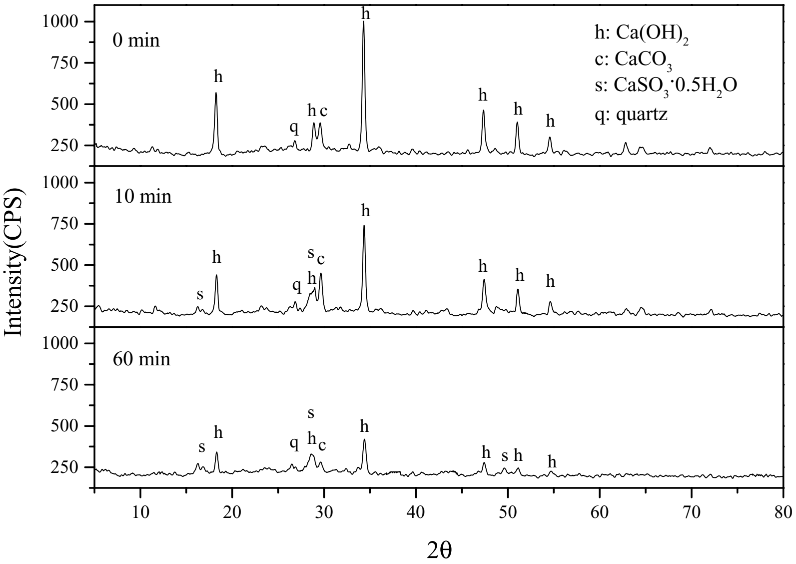
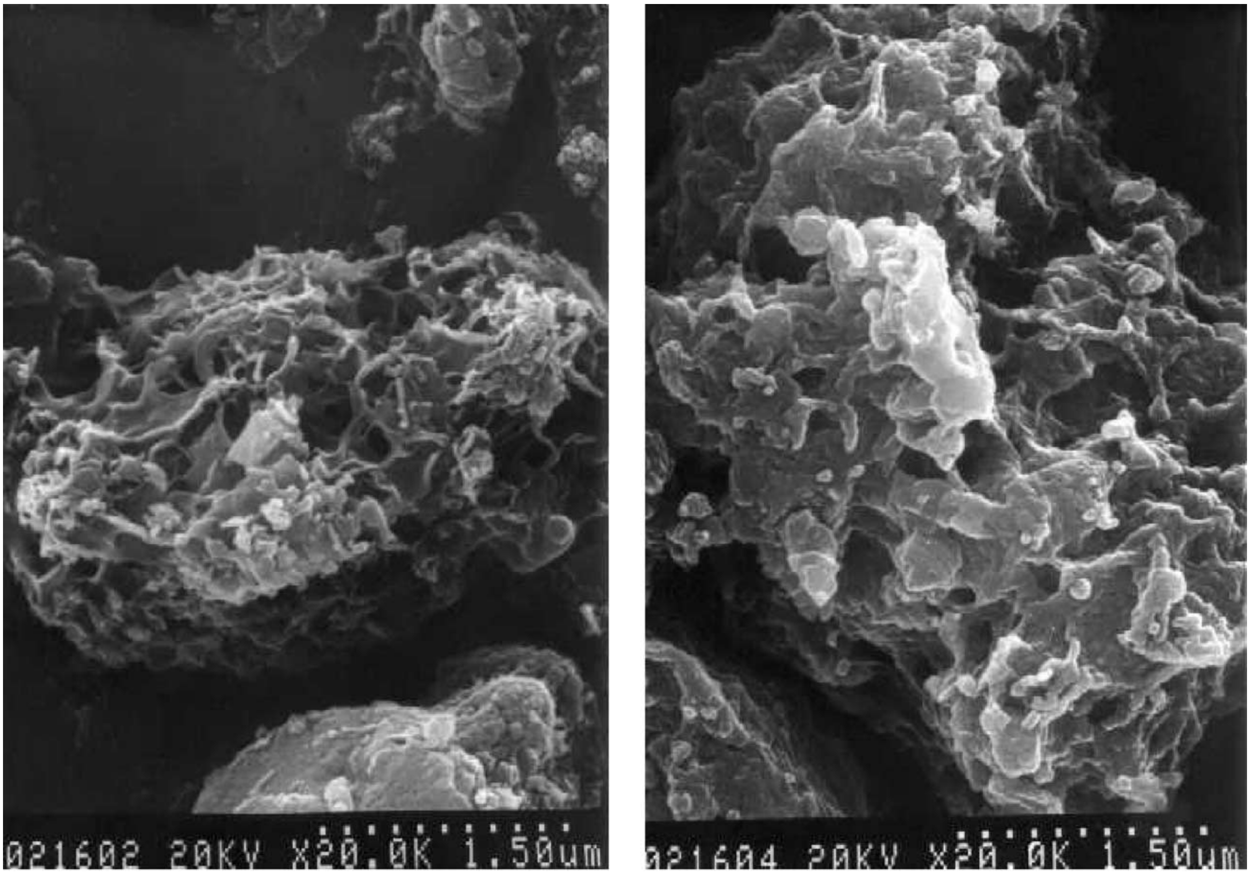


Fig. 2. XRD patterns of $Ca(OH)_2$/fly ash sorbent(70/30 wt. ratio) reacted at 60°C, 70% RH, and 1000 ppm SO_2 for different reaction times.

specific surface areas of samples decrease with reaction extent and the reduction of surface area is much greater in the initial period. This indicates that the formation of product crystals would reduce the pore volume and make the rough reactant surface to become more smooth. This explanation can be confirmed by the SEM observation (Fig. 3(b)).

3.3. *Effects of reaction variables*

The experimental results for the reaction of $Ca(OH)_2$/fly ash sorbent with SO_2 are shown in Fig. 5 in terms of conversion X versus time t. As can be seen from these plots, the reaction is rapid in the initial period, but the conversion levels off after about 10 min, and the sorbent is incompletely converted for a reaction time as long as 1 h. This reaction behavior is similar to that of pure $Ca(OH)_2$ (Ho & Shih, 1993b). However, the initial reaction rate and the maximum conversion (for 1 h) of the $Ca(OH)_2$/fly ash sorbent are remarkably higher than those of pure $Ca(OH)_2$ reacted at the same experimental conditions. For example, at the conditions of 60°C, 70% RH, and 1000 ppmv SO_2, the 1 h conversion of the $Ca(OH)_2$/fly ash sorbent was 0.60, which is much higher than the value of 0.19 for pure $Ca(OH)_2$.



(a) (b)

Fig. 3. SEM micrographs of (a) $Ca(OH)_2$/fly ash(70/30 wt. ratio) sorbent and (b) $Ca(OH)_2$/fly ash sorbent(70/30 wt. ratio) reacted at 60°C, 70% RH, and 1000 ppm SO_2 for 60 min.

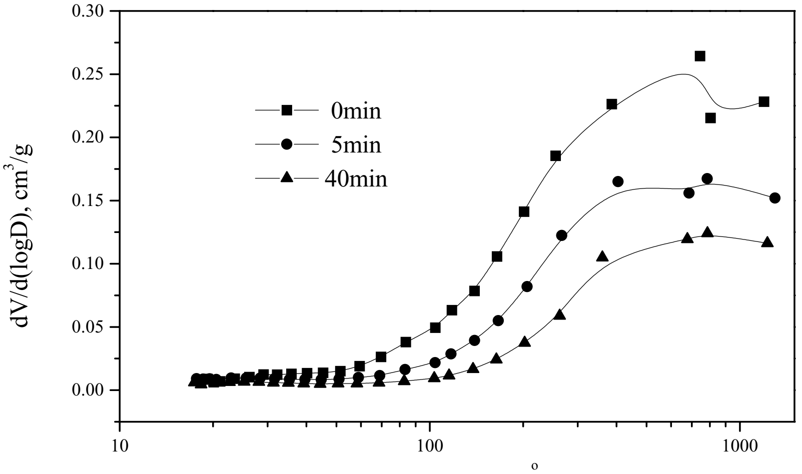


Fig. 4. Pore volume distribution of $Ca(OH)_2$/fly ash(70/30 wt. ratio) sorbent reacted at 60°C, 70% RH, and 1000 ppm SO_2 for different reaction times.

The effect of temperature (60–80°C) on the reaction was weak; after 10 min reaction, the differences between the conversions at 60°C and 80°C were within the experimental error (±0.02). Increasing temperature could raise the chemical reaction rate constant, but reduce the adsorption amounts of water vapor and reaction gas, the

Table 1
BET surface areas (m^2/g) and pore volumes (cm^3/g)[a] of $Ca(OH)_2$/fly ash(70/30 wt. ratio) sorbents reacted at 60°C, 70% RH, and 1000 ppm SO_2

t (min)	X	Surface area	Micropore vol. (< 20 Å)	Mesopore vol. (20–500 Å)	Total pore vol. (17–3000 Å)
0	0	38.0	0.0024	0.1078	0.2318
5	0.39	19.8	0.0026	0.0701	0.1670
		(23.8)	(0.0031)	(0.0843)	(0.2009)
40	0.59	15.1	0.0016	0.0402	0.1026
		(18.9)	(0.0021)	(0.0525)	(0.1341)

[a] The value in parentheses is based on the weight of the unreacted sorbent.

effects caused by the temperature change might offset each other and resulted in the weak overall effect of temperature on the reaction.

The major factor affecting the reaction was the relative humidity of the gas phase. The initial reaction rate and the maximum conversion of the sorbent increased significantly with increasing relative humidity.

The reaction was also affected by SO_2 concentration slightly. The differences between the conversions at 5000 and 1000 ppm SO_2 in initial stage (before 7.5 min) were higher than the experimental error, but the differences after 7.5 min were within the experimental error.

The effect of the specific surface area of sorbent on the reaction was studied by using sorbents prepared at different slurrying times. As can be seen Fig. 6, both the initial reaction rate and the maximum conversion increased with increasing sorbent specific surface area.

3.4. Analysis of reaction kinetics

The reaction rate of $Ca(OH)_2$/fly ash sorbent with SO_2 is fast in the initial stage and decreases abruptly, leaving the sorbent incompletely converted. Relative humidity is the major factor affecting the reaction, whereas the influences of temperature and SO_2 concentration on the reaction are small. This reaction behavior of $Ca(OH)_2$/fly ash sorbent is similar to the reaction behaviors of pure $Ca(OH)_2$ with SO_2 (Ho, 1987; Ho & Shih, 1993b; Ho, Shih, & Lee, 1996) and with CO_2 (Shih, HO, Song, & Lin, 1999). From previous kinetic studies by Ho et al. (1996) and Shih et al. (1999), the surface coverage model was found to be the most suitable model to describe the reaction between $Ca(OH)_2$ and SO_2 or CO_2. The same model was employed in this study to describe the reaction kinetics of $Ca(OH)_2$/fly ash sorbent with SO_2.

The hypothesis of the surface coverage model is that the sorbent is made up of plate grains and that the reaction is controlled by chemical reaction on the surface of a grain and the reacting surface area of the grain decreases with the deposition of solid product. According to this model, the reaction of a sorbent reaches a maximum conversion when its reacting surface is fully covered by the product. Thus the reaction rate of sorbent per unit initial surface area, r_s, can be expressed as

$$r_s = k_s \Phi, \tag{1}$$

where k_s is a function of temperature, concentrations of reacting species, and relative humidity, Φ is the fraction of surface area which is not covered by product. The rate of conversion of the sorbent is

$$\mathrm{d}X/\mathrm{d}t = S_{g0} M r_s = S_{g0} M k_s \Phi, \tag{2}$$

where S_{g0} is the initial specific surface area of the sorbent and M is the sorbent weight per mole Ca.

How Φ changes with reaction time depends on the reaction rate and the way by which the product deposits on the surface; one may assume that

$$-\mathrm{d}\Phi/\mathrm{d}t = k_p r_s = k_p k_s \Phi, \tag{3}$$

where k_p is a proportional constant, which is a function of temperature, concentrations of reacting species, and relative humidity. Eq. (3) can be integrated to get Φ as a function of time

$$\Phi = \exp(-k_1 k_2 t), \tag{4}$$

where

$$k_1 = k_s S_{g0} M, \tag{5}$$

$$k_2 = k_p/(S_{g0} M). \tag{6}$$

By substitution of Eq. (4) into Eq. (2), one can integrate Eq. (2) to obtain the relation between conversion and time

$$X = [1 - \exp(-k_1 k_2 t)]/k_2. \tag{7}$$

From Eqs. (2), (4), and (7), the rate of conversion can be expressed as a function of conversion

$$\mathrm{d}X/\mathrm{d}t = k_1(1 - k_2 X). \tag{8}$$

Equation similar to Eq. (7), named as asymptotic equation, has been used to describe the film growth for the oxidation of metals at low temperatures (Scully, 1975; Evans, 1981). Also similar equation which is obtained by the pore-plugging model has been applied to the sulfation of limestone at high temperatures (Lee & Georgakis, 1981).

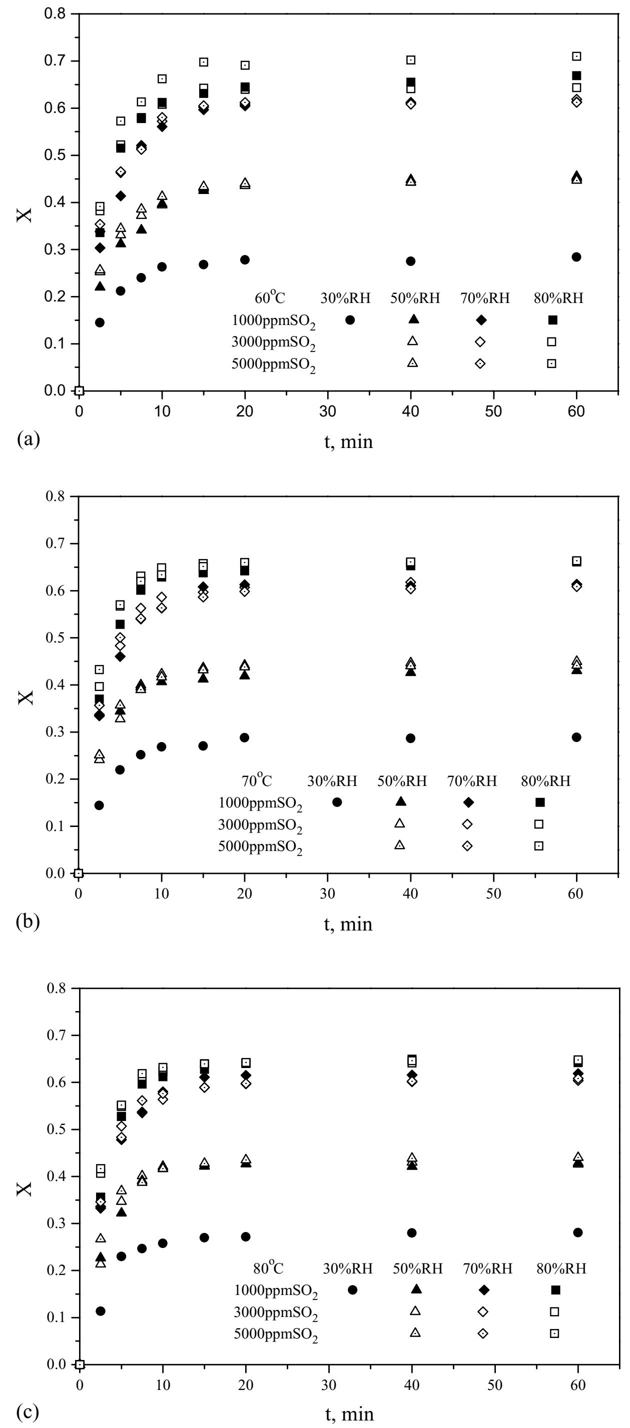


Fig. 5. Plot of conversion versus time for the sulfation of $Ca(OH)_2$/fly ash(70/30 wt. ratio) sorbent: (a) 60°C, (b) 70°C and (c) 80°C.

The two parameters, k_1 and k_2, in Eq. (7) can be obtained by least-squares fitting of Eq. (7) to the experimental data. One can easily see from Eq. (7) that k_2 is the reciprocal of the maximum conversion. Figs. 6 and 7 show that the experimental data are described by Eq. (7) very well. According to the definitions of k_1 and k_2, they are functions of initial specific surface area, temperature, SO_2 concentration, and relative humidity. These functions can be derived by analyzing the values of k_1 and k_2 obtained at different experimental conditions.

The values of k_1 and k_2^{-1} obtained for samples of different initial specific surface areas are plotted in Figs. 8 and 9, respectively. One can see that both k_1 and k_2^{-1} follow the linear relationship with $S_{g0}M$ ($M = 108.8$ g/mol Ca) in accordance with Eqs. (5) and (6), respectively. This indicates that the present model can adequately describe the reaction kinetics and that k_s and k_p for the sorbent did not change with the specific surface area. The values of k_1 and k_2 for pure $Ca(OH)_2$ ($S_{g0} = 9.5\ m^2/g$, $M = 74$ g/mol Ca) reacted under the same conditions were also plotted in the above figures; one can see that k_s of $Ca(OH)_2$ is about the same as that of $Ca(OH)_2$/fly ash sorbent, but k_p of $Ca(OH)_2$ is smaller.

The following analyses were based on the experimental results obtained for samples having a specific surface area of 38.0 m^2/g.

As shown in Fig. 10, plots of $\ln k_1$ versus relative humidity, RH (%), are linear and the fitting lines have nearly the same slopes for the temperatures and SO_2 concentrations considered, indicating that the relationship between k_1 and relative humidity is

$$k_1 = e^{0.0102\mathrm{RH}} f(y, T), \tag{9}$$

where $f(y,T)$ is a function of SO_2 concentration, y (ppm), and temperature, T.

Values of $\ln(k_1 e^{-0.0102\mathrm{RH}})$ were plotted against $\ln y$ in Fig. 11. The slopes of the straight fitting lines seem to decrease as temperature increases; however, the differences between the slopes are within the range of variation estimated from the error of the data. Thus the slope was considered to be independent of temperature. Using the average value of the slopes of the straight lines in Fig. 11, the relationship between $k_1 e^{-0.0102\mathrm{RH}}$ and y can be written as

$$k_1 = e^{0.0102\mathrm{RH}}\, y^{0.17} g(T), \tag{10}$$

where $g(T)$ is a function of temperature.

Values of $g(T)$ for different temperatures were calculated from $k_1 e^{-0.0102\mathrm{RH}}\, y^{-0.17}$ and the average value for each temperature is shown in Fig. 12. The plot shows that $g(T)$ can be expressed by the Arrhenius law. The linear least-squares fitting of the data gives

$$k_1 = 0.83\, e^{0.0102\mathrm{RH}}\, y^{0.17}\, e^{-9977/RT}. \tag{11}$$

The small value of the apparent activation energy, 9.977 kJ/mol, indicates that the effect of temperature on the reaction rate is weak.

As can be seen from Fig. 13, relative humidity is the only variable affecting the value of k_2, and the logarithmic

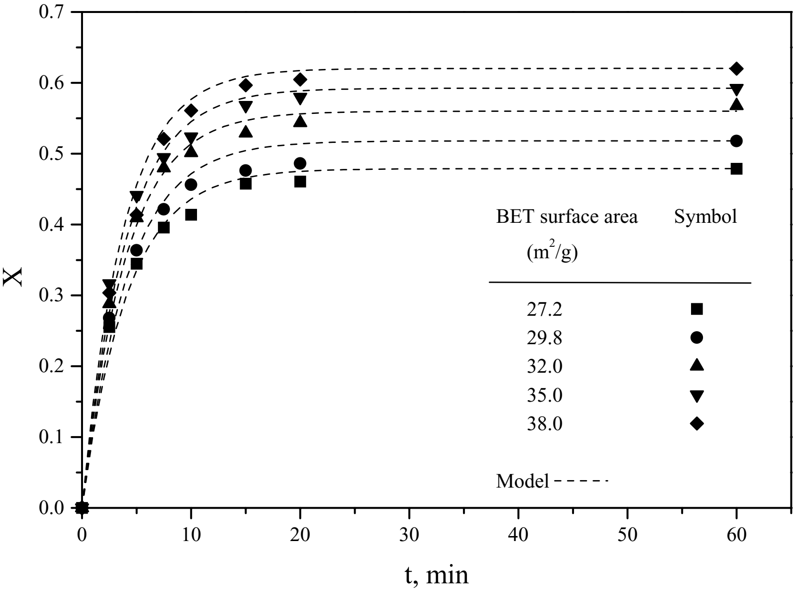


Fig. 6. Effect of S_{g0} on the reaction of $Ca(OH)_2$/fly ash sorbent with SO_2. Reaction conditions: 60°C, 70% RH, and 1000 ppm SO_2.

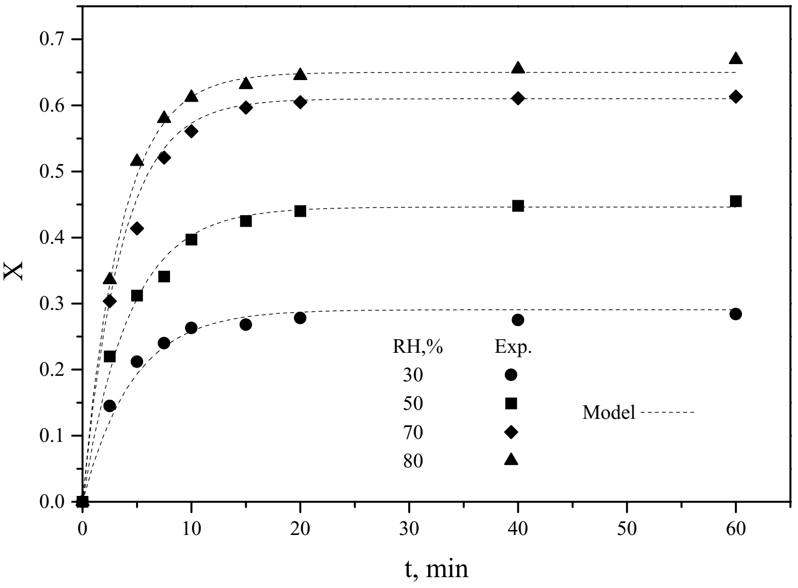


Fig. 7. Comparison of model predictions and experimental data for the reaction of $Ca(OH)_2$/fly ash at 60°C, 1000 ppm SO_2, and various relative humidities.

plot of k_2 versus RH is linear. The relationship between k_2 and relative humidity obtained from Fig. 13 is

$$k_2 = 66.0\,\mathrm{RH}^{-0.864}. \tag{12}$$

Since the constants in Eqs. (11) and (12) contain the initial specific surface area, S_{g0}, of the sample, they are only applicable to the sample which has a S_{g0} value of 38.0 m^2/g. Thus for sorbents with other values of S_{g0}, Eqs. (11) and (12) can be rewritten as

$$k_1 = 0.0218\,S_{g0}\,\mathrm{e}^{0.0102\mathrm{RH}}\,y^{0.17}\,\mathrm{e}^{-9977/\mathrm{RT}}, \tag{13}$$

$$k_2 = 2508.0\,S_{g0}^{-1}\,\mathrm{RH}^{-0.864}. \tag{14}$$

Eq. (7) together with Eqs. (13) and (14) constitutes the kinetic model for the sulfation of $Ca(OH)_2$/fly ash(70/30 wt. ratio) sorbent. Conversions calculated by the kinetic model are compared with the experimental results in Fig. 14, which shows that the calculated results are in good agreement with experimental data with a standard deviation (σ_{N-1}) of 0.02 in conversion.

3.5. Discussion on reaction kinetics

From the above kinetic analysis, one can see that relative humidity is the major factor affecting the reaction.

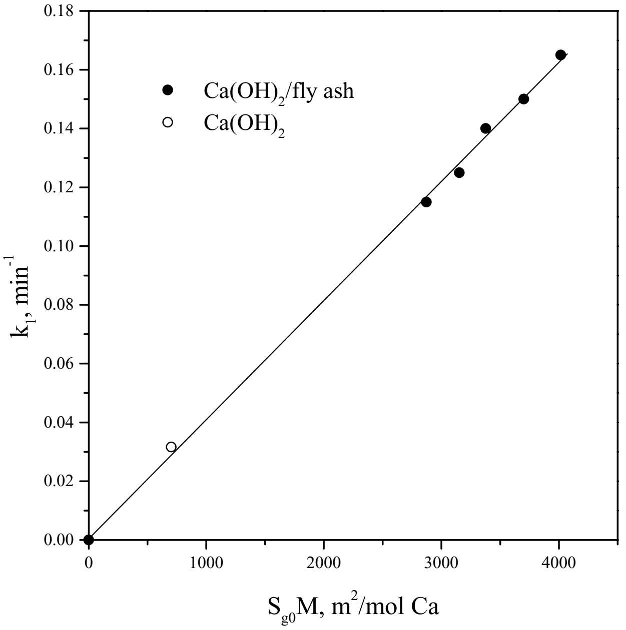


Fig. 8. Plot of k_1 versus $S_{g0}M$. Reaction conditions: 60°C, 70% RH, and 1000 ppm SO_2.

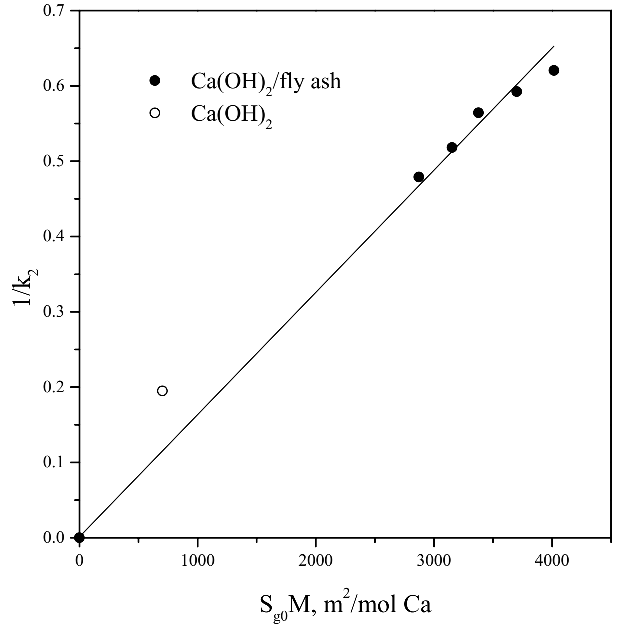


Fig. 9. Plot of k_2^{-1} versus $S_{g0}M$. Reaction conditions: 60°C, 70% RH, and 1000 ppm SO_2.

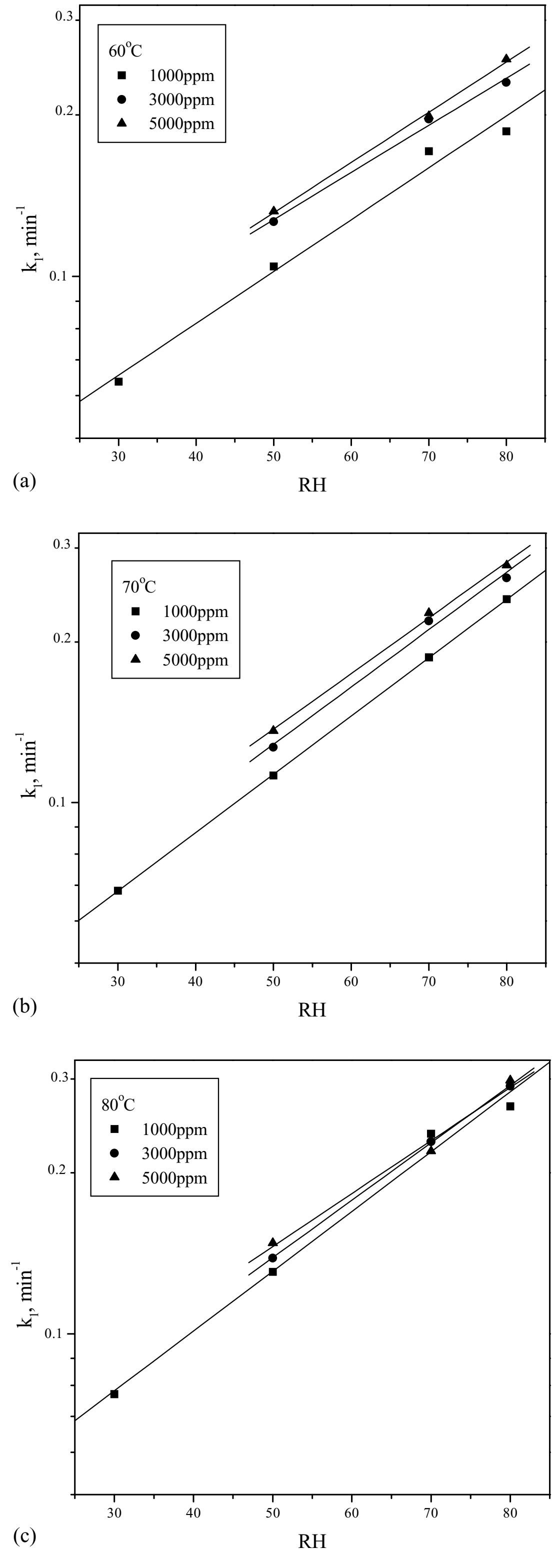


Fig. 10. Relationship between k_1 and relative humidity: (a) 60°C, (b) 70°C and (c) 80°C.

This implies that the water adsorbed on the sorbent surface plays an important role in the reaction. Fig. 15 shows the water adsorption isotherms on the sorbent at 60–80°C; one can see that the amount of water adsorbed increased with increasing relative humidity and decreased with increasing temperature. The monolayer water adsorption capacity at each temperature was estimated by the BET equation, and the water layer thickness equivalent to the amount of water adsorbed on the sorbent surface at each relative humidity was calculated. The thickness is about 1.6 ML thick at 30% RH, and increases to about 3.2 at

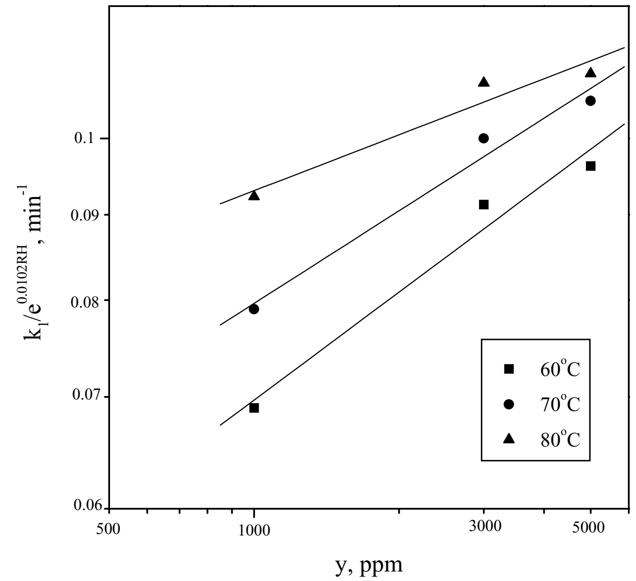


Fig. 11. Relationship between k_1 and SO$_2$ concentration.

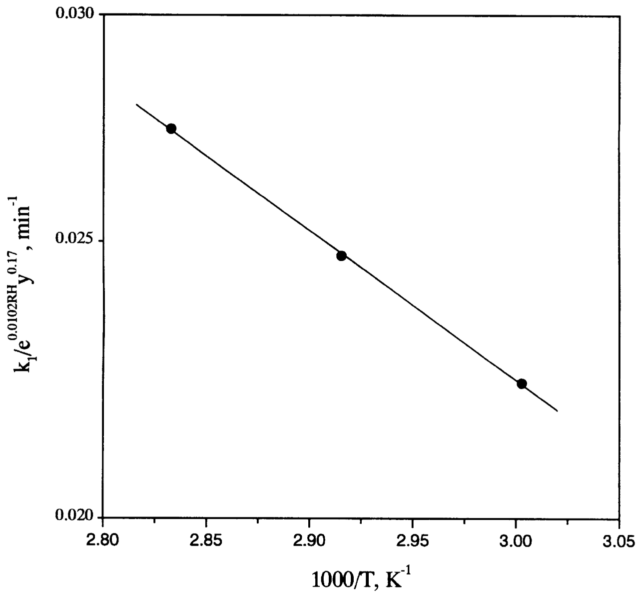


Fig. 12. Arrhenius plot of k_1.

80% RH, being nearly independent of temperature (Liu, 1999).

The fundamental processes taking place at the water adsorbed surface may include: (1) adsorption of SO$_2$ on the outer surface of water layer; (2) hydration of SO$_2$ to form SO$_2\cdot$H$_2$O; (3) diffusion of SO$_2\cdot$H$_2$O inward; (4) dissolution of Ca(OH)$_2$ and C–S–H to form Ca^{2+} and OH$^-$; (5) diffusion of Ca^{2+} and OH$^-$ outward; (6) reaction of OH$^-$ with SO$_2 \cdot$ H$_2$O to form HSO$_3^-$ and SO$_3^{2-}$; (7) reaction of Ca^{2+} with SO$_3^{2-}$ to form calcium sulfite precipitate. These processes have been considered to take place in the absorption of SO$_2$ into a lime slurry. In the present case, the water is only several molecular layers thick, these processes may also take place, but the rates of the processes involving reactions (processes 2, 4, 6, and 7)

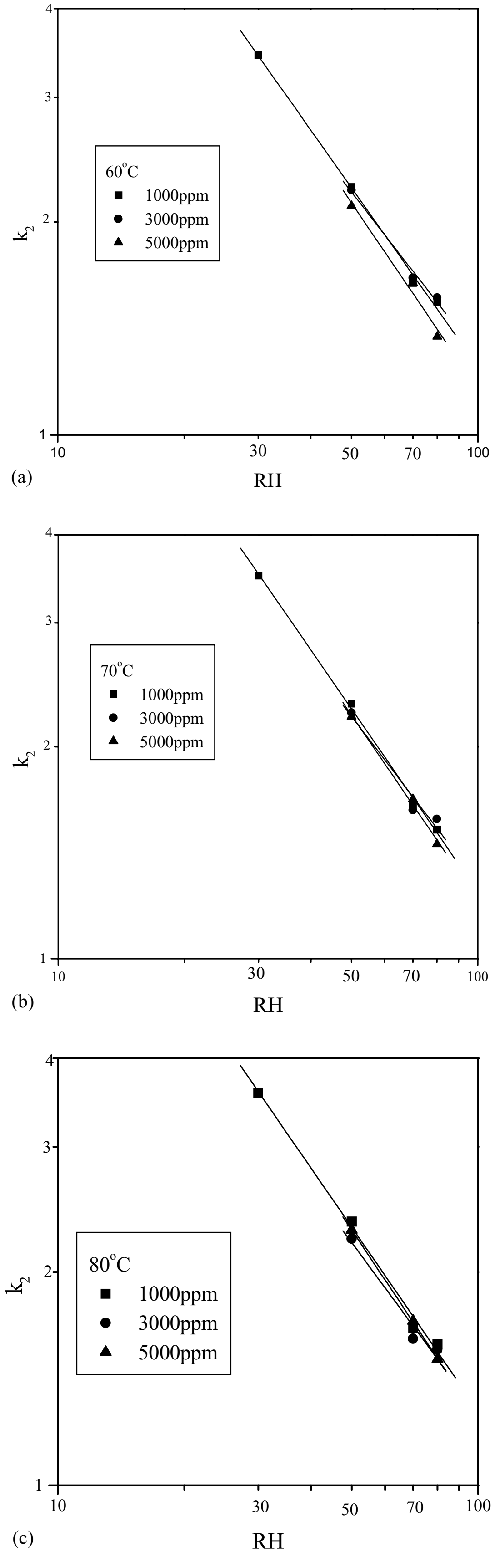


Fig. 13. Relationship between k_2 and relative humidity: (a) 60°C, (b) 70°C and (c) 80°C.

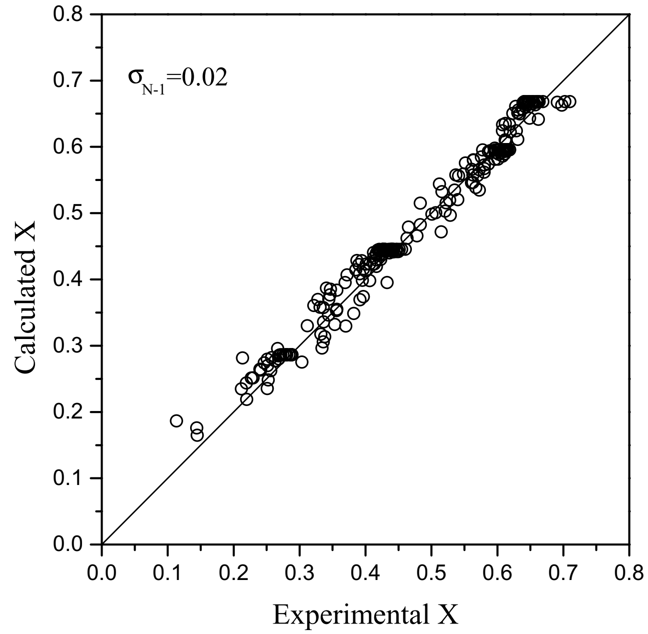


Fig. 14. Comparison of the calculated and the experimental conversion values.

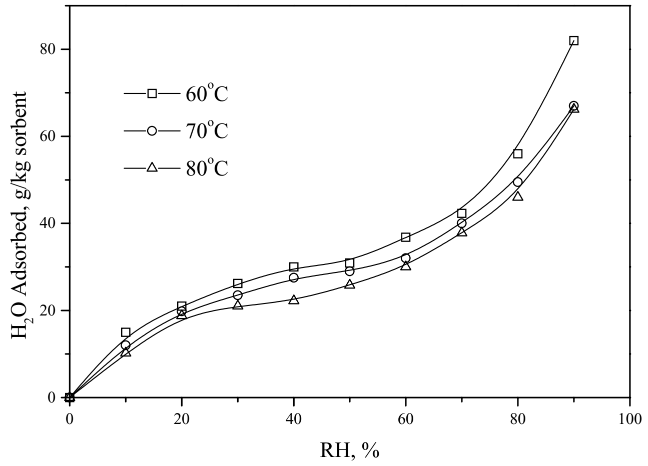


Fig. 15. Water adsorption isotherms on $Ca(OH)_2$/fly ash(70/30 wt. ratio, 38 m^2/g) sorbent.

may be greatly reduced, and the diffusion of species (processes 3 and 5) through such thin layer should be very fast.

Since the overall reaction rate of the sorbent decreases with conversion and is slightly affected by SO_2 concentration in the early period of the reaction, the rate-controlling step for the reaction may be that involving OH^- or Ca^{2+} ions, which are generated by the dissolution of the sorbent surface where the surface is not covered by the product, i.e., process 6 or 7. Process 6 is the reaction of OH^- with $SO_2 \cdot H_2O$ and process 7 is that of Ca^{2+} with SO_3^{2-}.

The slight effect of SO_2 concentration may be due to that the SO_2 molecules adsorbed on the outer surface of water layer is limited to a monolayer capacity, which is insensitive to the SO_2 concentration in the SO_2 concentration range used in this study like the behavior of the Langmuir adsorption isotherm (Smith, 1981). The adsorbed SO_2 molecule then react with water molecules to form $SO_2 \cdot H_2O$. If the reaction between OH^- and $SO_2 \cdot H_2O$ is the slowest step, the concentration of $SO_2 \cdot H_2O$ would be in equilibrium with the amount of SO_2 adsorbed, hence the rate would be a weak function of SO_2 concentration. If the reaction of Ca^{2+} with SO_3^{2-} is the slowest step, the concentration of SO_3^{2-} would also be in equilibrium with the amount of SO_2 adsorbed, and the rate would also be insensitive to the SO_2 concentration.

The rate of either process 6 or 7 will increase with increasing relative humidity because higher amount of adsorbed water can produce higher amounts of reactants to react.

The mild effect of temperature on the overall reaction rate may be due to that as the temperature increases, the chemical reaction rate constants increase, whereas the amounts of water and SO_2 adsorbed decrease.

The value of k_2^{-1} or the maximum conversion increases as the relative humidity increases. This phenomenon may indicate that the thicker water layer provides a wider range for the product molecules to deposit. Thus at lower relative humidity the reaction product covers the sorbent surface more uniformly, and the overall reaction rate diminishes at a lower conversion; whereas at higher relative humidity the product builds up more clusterlike and covers less surface, and the reaction reaches a higher maximum conversion. Similar arguments have been set forth by Krammer, Brunner, Khinast, and Staudinger (1997) and Shih et al. (1999) to explain the effect of relative humidity on the reaction rates of $Ca(OH)_2$ with SO_2 and with CO_2, respectively.

In the actual flue gas, CO_2, O_2, and NO_X are present with SO_2; CO_2 has the ability to react with the $Ca(OH)_2$/fly ash sorbent, and O_2 and NO_X can oxidize calcium sulfite to calcium sulfate. The effects of these components on the reaction of the $Ca(OH)_2$/fly ash sorbent with SO_2 have been studied by the authors, and the results will be reported in the future. The results of the present study can be extended to the more realistic case. Accurate modelling of the sulfation kinetics of $Ca(OH)_2$/fly ash sorbent is important to the design and operation of the dry or semidry processes using this kind of sorbent.

4. Conclusion

The kinetics of the reaction of $Ca(OH)_2$/fly ash (70/30 wt. ratio) sorbent with SO_2 in humid N_2 has been studied at 60–80°C by using a differential fixed-bed reactor.

The utilization of Ca content of $Ca(OH)_2$/fly ash sorbent is incomplete. Both the initial sulfation rate and the maximum conversion of $Ca(OH)_2$/fly ash sorbent are higher than those of pure $Ca(OH)_2$. Relative humidity is the most important factor affecting the reaction and the initial reaction rate and maximum conversion of sorbent increase with increasing relative humidity. Temperature and SO_2 concentration have slight effects on the initial reaction rate and negligible effects on the maximum conversion.

The reaction kinetics of $Ca(OH)_2$/fly ash sorbent with SO_2 can be well described by the surface coverage model proposed by Shih et al. (1999) which assumes the sulfation rate being controlled by chemical reaction on the sorbent grain surface and takes into account the surface coverage by product.

The results of this study are useful to the design and operation of the dry or semi-dry processes using $Ca(OH)_2$/fly ash sorbent to remove SO_2 from flue gas.

Notation

$f(y,T)$	function defined by Eq. (9)
$g(T)$	function defined by Eq. (10)
k_p	constant defined by Eq. (3), m^2/mol
k_s	initial reaction rate of solid, mol/(min m^2)
k_1	$k_s S_{g0} M$, min^{-1}
k_2	$k_p/S_{g0}M$, dimensionless
M	weight of solid per mole Ca, g/mol Ca
R	gas constant, 8.314 J/mol K
RH	relative humidity, %
r_s	reaction rate of solid per unit initial surface area, mol/(min m^2)
S_{g0}	initial specific surface area of solid, m^2/g
t	time, min
T	reaction temperature, K
X	conversion, dimensionless
y	SO_2 concentration, ppm

Greek letters

σ_{N-1}	standard deviation, dimensionless
Φ	fraction of surface area which is not covered by product, dimensionless

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