Chemical Engineering Journal 146 (2009) 57–62

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Modified shrinking unreacted-core model for the reaction between sulfur dioxide and coal fly ash/CaO/$CaSO_4$ sorbent

Keat Teong Lee*, Ooi Wan Koon

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal,
Seberang Perai Selatan, Pulau Pinang, Malaysia

ARTICLE INFO

Article history:
Received 17 July 2007
Received in revised form 5 May 2008
Accepted 13 May 2008

Keywords:
Flue gas desulfurization
Coal fly ash
Kinetics
Shrinking unreacted-core model

ABSTRACT

The kinetics for non-catalytic solid gas reaction between SO_2 and sorbent prepared from coal fly ash, CaO and $CaSO_4$ in a fixed-bed reactor at low temperature were modeled and simulated. A modified shrinking unreacted-core model (SCM) with chemical reaction coupled with diffusion as the rate limiting step were developed to predict the breakthrough curves of the desulfurization reaction. The kinetic parameters of the mathematical model were obtained from a series of experimental desulfurization reactions conducted under isothermal conditions at various operating parameters; SO_2 initial concentration ($500\,\text{ppm} \le C_{SO} \le 2000\,\text{ppm}$), NO initial concentration ($250\,\text{ppm} \le C_{NO} \le 750\,\text{ppm}$), reaction temperature ($60\,^\circ\text{C} \le T \le 90\,^\circ\text{C}$) and relative humidity ($50\% \le \text{RH} \le 80\%$). MATLAB software was used to solve the partial differential equations using finite difference method. The SCM model was found to give a good description of the experimental data with error less than 5%. The validated model was then used to simulate the desulfurization reaction under a wide range of operating conditions. It was found that higher initial concentration of SO_2 reduces the desulfurization activity. In contrast, the presence of higher concentration of NO, reaction temperature and relative humidity in the system enhanced the desulfurization activity of the sorbent.

1. Introduction

Lately, the negative impact of sulfur dioxide (SO_2) released from power plants to the environment has led to national and international legislation to limit the emissions of SO_2. Since the requirement to limit sulfur emissions are being implemented in more and more countries throughout the world, many coal-fired plants are currently under pressure to install flue gas desulfurization (FGD) unit. The commercial technology currently available for FGD is using the wet-process method with lime stone derivatives as the absorbent. However, this technology requires high investment cost that might not be economically viable for small scale power plants. Recently, it was reported that sorbent prepared from various siliceous material such as coal fly ash, rice husk ash and oil palm ash can be used to remove SO_2 from flue gases using the dry-process. This dry-process is significantly cheaper and simpler than the current wet-process, making it a viable option for small scale power plants. The preparation, characterization and activity study of sorbent made from various siliceous material had been thoroughly reported in the literature [1–4], however, reports on kinetic modeling of the sulfation reaction between the sorbent and SO_2 has not been conclusive.

In a study by Liu and Shih [5], modified surface coverage model was proposed for the desulfurization reaction between $Ca(OH)_2$/fly ash sorbent and SO_2. The reaction between the dry sorbents with SO_2 was studied under the conditions similar to those in the bag filters in the spray-drying flue gas desulfurization system. The hypothesis of this model was that the sorbent was made up of plate grains and that the reaction rate was controlled by chemical reaction on the surface of the grain. The reacting surface area of the grain decreases as the reaction progresses further. Based on the proposed model, the reaction reached an ultimate conversion when the entire reacting surface was covered by the product. Besides that, it was assumed that the change of sorbent surface coverage with reaction time depends on the reaction rate, the dispersion of Ca and the way by which the product deposits on the surface. In another study, Bausach et al. [6] investigated the kinetics of the non-catalytic solid gas desulfurization reaction between $Ca(OH)_2$ and SO_2 at low temperature. In their study, they reported a modified deactivation model (DM) to improve the fitting of the desulfurization experimental data. The deactivation model assumed that the reaction between the gas molecules and the solid sorbent depends mainly on the concentration of the gas on the solid surface, which was referred to as active surface and the ratio of active surface of

---

* Corresponding author. Tel.: +60 4 594 1012; fax: +60 4 594 1013.
E-mail address: chktlee@eng.usm.my (K.T. Lee).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.05.012

un-reacted solid to the initial solid surface. As the reaction progressed, the solid activity reduces as solid product deposited on the surface reducing the un-reacted surface area. Han et al. [7] proposed a modified grain reaction model for the sulfation kinetics between solid sorbents and SO_2. The sulfation process and kinetics were analyzed using thermogravimetric method using three types of shells and two types of limestone. The microstructure and pore structure of the limestone and shell during the sulfation reaction were investigated using scanning electron microscope and porosimeter, respectively. It was concluded that the rate of the sulfation reaction is principally controlled by particle pore diffusion and product layer diffusion.

Based on the previous study, it can be concluded that the non-catalytic reaction between SO_2 and solid sorbent is either reaction or diffusion rate limiting. In our previous study, a global reaction rate was proposed for the desulfurization reaction with the aim to incorporate both the reaction and diffusion controlling step [8]. However, this method of global process modeling provides little valuable information on the actual physical and chemical process that is occurring during the desulfurization reaction. Therefore, the aim of this study is to develop an alternative model that can describe the desulfurization reaction in the fixed-bed reactor more accurately. The model will be useful for prediction of reactor performance for the desulfurization reaction under different mode of operation and also as a tool for design and optimization of the flue gas desulfurization processes.

2. Experimental

2.1. Sorbent preparation

Sorbents used in this study were prepared from coal fly ash, CaO and $CaSO_4$. The coal fly ash was supplied by Kapar Power Plant, Malaysia of Tenaga Nasional Berhad with the following composition: SiO_2, 60%; Al_2O_3, 20%; Fe_2O_3, 4.7%; CaO, 3.0%; K_2O, 1.1%; MgO, 1.0%; C, 7.5%; others, 2.4% and ignition loss, 0.3%. The $CaSO_4$ used was reagent grade, calcium sulfate hemihydrate while the CaO used was of laboratory grade. Both of these chemicals were supplied from BDH Laboratory Supplies, England. The sorbents were prepared using water hydration method. 5 g of CaO was added into 100 ml of water at 70 °C. After that, 13.7 g of coal fly ash and 7.4 g of $CaSO_4$ were added simultaneously into the slurry. The slurry was then heated under reflux at 98 °C for 10 h of hydration time. Upon completion of the hydration period, the slurry was then filtered and dried using a vacuum pump. The sorbent in powder form was then palletized and subsequently crushed and sieved into the required particle size range of 200–250 μm. The preparation parameters of the sorbent such as the amount of each starting materials were selected according to an optimization study reported elsewhere [9]. The resulting sorbent had a specific BET surface area of 64.5 m^2/g (Autosorb 1C Quantachrome).

2.2. Desulfurization activity study

The desulfurization activity of the sorbent was carried out in a fixed-bed stainless steel adsorber (2.2 cm in length (L) and transversal bed section of 0.5 cm^2 (A)) under isothermal conditions. 0.7 g of sorbent was packed in the center of the adsorber supported by 0.05 g of borosilicate glass wool. The reaction bed porosity, ε, is taken as the average value reported in the literature, 0.6. The fixed-bed adsorber was heated up to desired temperature by a furnace heater and the bed temperature is continuously measured and monitored by a thermocouple. A stream of gaseous mixture containing SO_2 (500–2000 ppm where 1 ppm = 2.62 mg/m^3), O_2 (5.2%), CO_2 (13%), NO (250–750 ppm) and balance N_2 were passed through the sorbent. Prior to that, the N_2 gas stream was humidified using a humidification system where the gas was saturated with water vapor. This was carried out by passing the N_2 gas through two 250 ml conical flask immersed in a water bath at constant temperature. The total flow rate of the gas stream was controlled at 150 ml/min using a series of mass flow controllers. The concentration of SO_2 in the flue gas was measured using a Portable Flue Gas Analyzer IMR2800P before and after the sorption process. The concentration of SO_2 was recorded continuously every 1 min until 60 min. The schematic diagram of the experimental set-up used in this activity study is shown in Fig. 1. Every experimental run was repeated two to three times to increase the precision of the results. The relative error for the data obtained between the repetitions was less than 10%. This procedure also diminished the impact of the variation in composition or shape of the sorbents in each run. For clarity, only the averages are presented in this paper. The desulfurization activity of the sorbent reported in this work is presented as the breakthrough curves of the desulfurization reaction (SO_2 concentration at time t/initial SO_2 concentration vs. time (C/C_0) vs. t) or is reported as the duration of time the sorbent can maintain 80% removal of SO_2 from the initial feed gas [2].

2.3. Experimental data

The proposed model for the desulfurization reaction of the $CaO/CaSO_4$/coal fly ash sorbent is based on experimental data obtained from a fixed-bed reactor operated under various operating conditions; initial concentration of SO_2 ($500\,\text{ppm} \le C_{SO} \le 2000\,\text{ppm}$), initial concentration of NO ($250\,\text{ppm} \le C_{NO} \le 750\,\text{ppm}$), reaction temperature ($60\,^\circ\text{C} \le T \le 80\,^\circ\text{C}$) and relative humidity ($50\% \le \text{RH} \le 70\%$). A series of experiments have been performed in order to study the influences of these four variables on the desulfurization reaction and is presented in Figs. 2–5.

2.4. Software

The partial differential equations employed in this work were solved using finite difference method implemented in MATLAB v7.0 and run under the Microsoft Windows NT environment.

3. Model development

3.1. Gas phase

The gas phase composition in the fixed-bed reactor is represented using Eq. (1):

$$\frac{n}{L_o A_s}\frac{\partial Y}{\partial z} + \varepsilon \rho C_{SO}\frac{\partial Y}{\partial t} + \frac{S_e w}{V_R} r_s = 0 \tag{1}$$

where n it the initial molar flow rate of SO_2 (mol/s), L_o is the total fixed-bed length (m), A_s is the transversal bed section (m^2), Y is the dimensionless SO_2 concentration (dimensionless), z is the dimensionless length position (dimensionless), ε is the reaction bed porosity (dimensionless), ρ is the gas molar density (mol/m^3), C_{SO} is the initial SO_2 concentration (mol/m^3), t is the reaction time (s), S_e is the specific surface area of sorbent (m^2/g), w is the sorbent weight in bed (g), V_R is the volume of reaction bed (m^3), and r_s is the reaction rate (mol/m^2s). However, for most non-catalytic solid gas reaction, the concentration of SO_2 in the gas phase does not change rapidly with time at a given point [10]. Thus, the time derivative

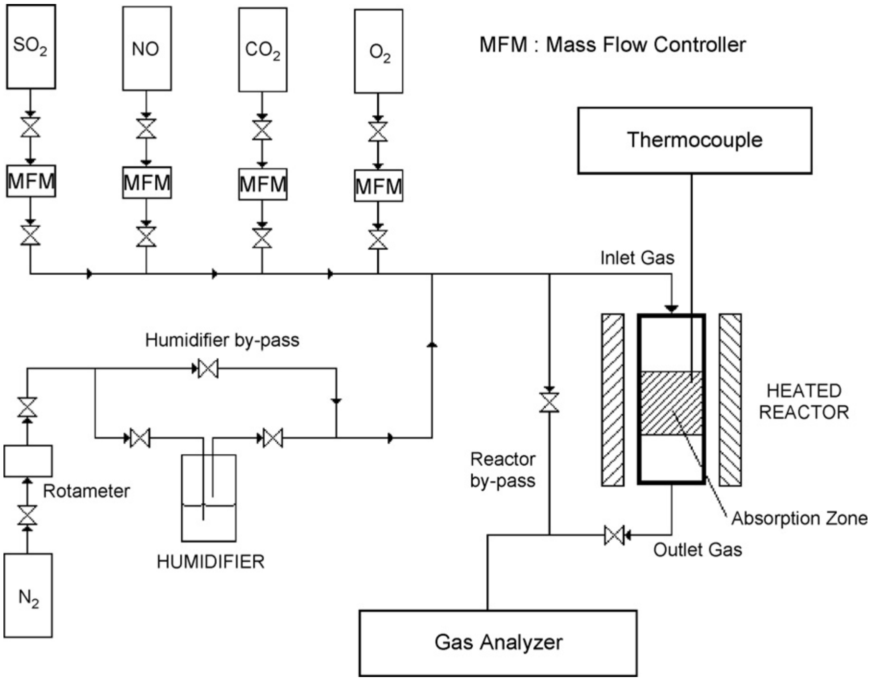

Fig. 1. Schematic diagram of the experimental set-up.

on Y is much smaller than the spatial derivatives of Y, so the time derivative can be taken off from Eq. (1) resulting in Eq. (2):

$$\frac{\partial Y}{\partial z} = -\frac{LA_sS_ew}{nV_R}r_s \tag{2}$$

3.2. *Solid phase*

It was reported in the literature that for the reaction between SO_2 and solid sorbent, chemical reaction is rate limiting, especially at the beginning of the reaction [11]. Thus, shrinking unreacted-core model (SCM) with chemical reaction as the rate limiting step has been selected to model the solid phase reaction. The increase in fractional conversion for the solid particle is expressed in Eq. (3) [11]:

$$\frac{t}{\tau} = 1-(1-X)^{1/3} \tag{3}$$

where

$$\tau = \frac{\rho_p r}{bkC_S} \tag{4}$$

where b is the molar ratio of solid reactant to gas reactant (ratio of stoichiometric coefficient) (dimensionless), k is the first-order rate constant for the surface reaction (m/s), ρ_p is the sorbent density (mol/m^3), r is the radius of unreacted core (m), and X is the sorbent utilization (dimensionless). By differentiating Eq. (4), the change of fractional conversion in the solid phase with time is expressed in Eq. (5):

$$\frac{\partial X}{\partial t} = \frac{3bkC_{SO}Y}{\rho_p r}(1-X)^{2/3} \tag{5}$$

However, using the original equation for shrinking unreacted-core model with chemical reaction as the rate limiting step was found not to be able to represent the whole desulfurization reaction. This is because once the product of the reaction forms at the

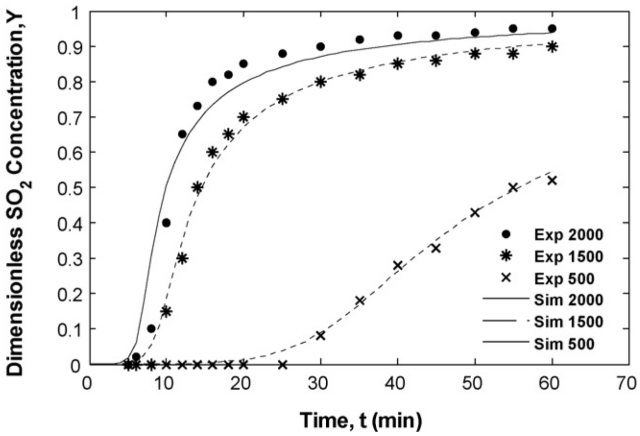

Fig. 2. Experimental and simulated desulfurization breakthrough curves for various SO_2 initial concentration (ppm). Reaction temperature = 70 °C, relative humidity = 60% and NO initial concentration = 500 ppm.

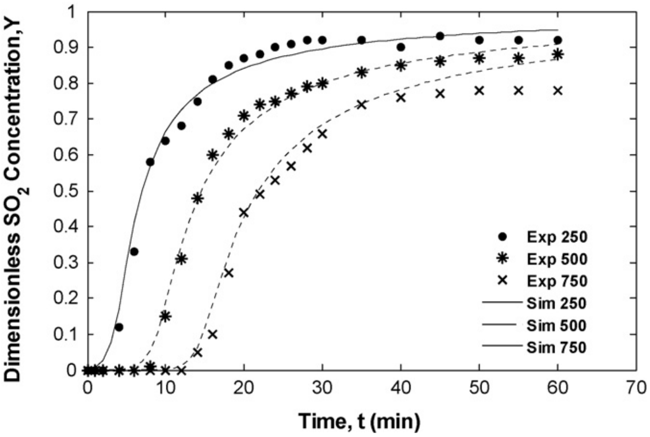

Fig. 3. Experimental and simulated desulfurization breakthrough curves for various NO initial concentration (ppm). Reaction temperature = 70 °C, relative humidity = 60% and SO_2 initial concentration = 1500 ppm.

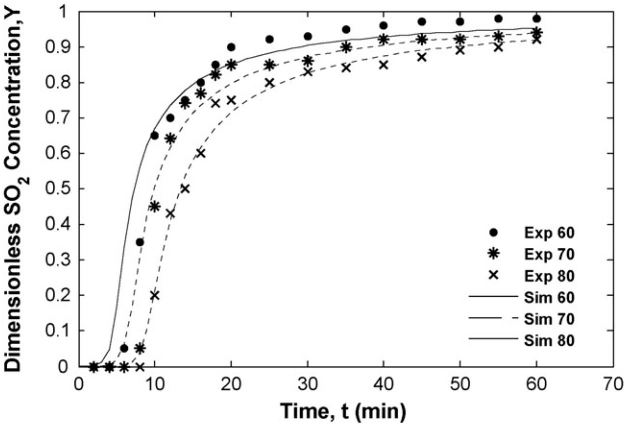

Fig. 4. Experimental and simulated desulfurization breakthrough curves for various reaction temperature (°C). SO_2 initial concentration = 2000 ppm, NO initial concentration = 500 ppm and relative humidity = 60%.

outer surface of the sorbent, the rate limiting step shifted to diffusion as reported by Karatepe et al. [11]. Thus in this work, instead of using the original SCM with chemical reaction as the rate limiting step, it was modified as shown in Eq. (6).

$$\frac{\partial X}{\partial t} = f(\theta) \cdot \frac{3bkC_{SO}Y}{\rho_p r}(1-X)^{2/3} \tag{6}$$

where $f(\theta)$ is the surface coverage effect to take into account the diffusion controlling step at the later period of the reaction. For non-catalytic heterogeneous reaction, the formation of products will cover the original/reactive surface of the sorbent. Thus, the effect of surface coverage is believed to be a function of conversion and concentration of SO_2. Besides that, Bausach et al. [12] reported that relative humidity affect the desulfurization process significantly. Other than that, temperature may also influence the sorption of product formed on the sorbent. Thus, the surface coverage effect in Eq. (6) is expressed as in Eq. (7):

$$f(\theta) = \alpha\, e^{aT}(C_{SO})^c(\mathrm{RH})^d(1-bX)^e \tag{7}$$

where α is the pre-exponential constant (dimensionless), T is the reaction temperature (K), RH is the relative humidity (%), and a, c, d and e are the order for the effect of the respective parameters on the surface coverage effect. Replacing Eq. (7) into Eq. (6), the mathematical expression for solid phase reaction is represented by Eq. (8):

$$\frac{\partial X}{\partial t} = \alpha\, e^{aT}(C_{SO})^c(\mathrm{RH})^d(1-bX)^e \cdot \frac{3bkC_{SO}Y}{\rho_p r}(1-X)^{2/3} \tag{8}$$

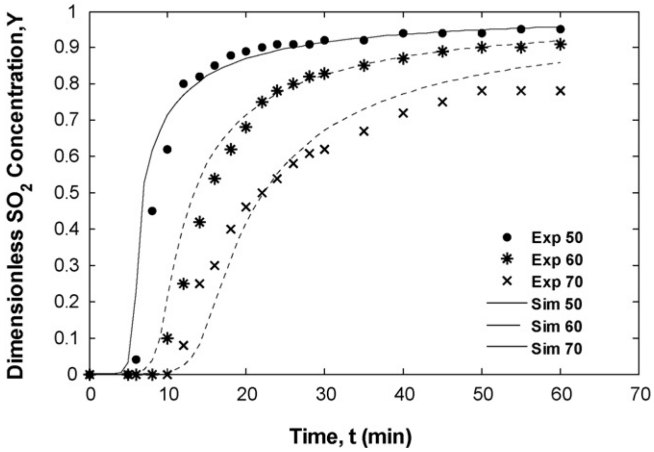

Fig. 5. Experimental and simulated desulfurization breakthrough curves for various relative humidity (%). Reaction temperature = 80 °C, SO_2 initial concentration = 2000 ppm, and NO initial concentration = 500 ppm.

3.3. Rate of reaction

In order to solve both Eqs. (2) and (8), an expression for the rate of the reaction has to be proposed. Various rate expressions have been proposed in the literature to study the complex reaction between SO_2 and the sorbent [5,8,13,14]. In this present work, a new rate of reaction, r_s is expressed as a function of temperature, conversion, SO_2 initial concentration and NO initial concentration, as shown in Eq. (9):

$$r_s = f(T) \cdot f(C_{NO}) \cdot f(C_S, X) \tag{9}$$

where

$$f(T) = k = A\,\exp\left(-\frac{E_a}{RT}\right) \quad \text{; Arrhenius Equation} \tag{10}$$

$$f(C_{NO}) = C_{NO}^g \tag{11}$$

$$f(C_S, X) = C_S(1-bX)^h = C_{SO}Y(1-bX)^h \tag{12}$$

where k is the reaction rate constant (m/s), A is the frequency factor (m/s), E_a is the activation energy (J/mol), R is the universal gas constant (J/mol K), T is the reaction temperature (K), C_{NO} is the initial concentration of NO (ppm), g is the order or reaction with respect to NO (dimensionless), $C_S = C_{SO}\,Y$ is the concentration of SO_2 (mol/m^3) and h is the reaction order (dimensionless). In this study, the frequency factor in Arrhenius equation is proposed as a function of SO_2 concentration, which can be expressed as in Eq. (13).

$$A = \beta C_{SO}^f \tag{13}$$

where β is the non-ideality factor (m/s) and f is the fitting parameter (dimensionless). Thus, Eq. (10) can be written as in Eq. (14):

$$f(T) = k = \beta C_{SO}^f \exp\left(-\frac{E_a}{RT}\right) \tag{14}$$

Replacing Eqs. (11), (12) and (14) into Eq. (9), the overall rate of reaction can be expressed as in Eq. (15):

$$r_s = \beta(C_{SO})^f\,(C_{NO})^g \cdot C_{SO}Y(1-bX)^h \cdot \exp\left(-\frac{E_a}{RT}\right) \tag{15}$$

With the proposed rate of reaction in Eq. (15), the mathematical expressions for the desulfurization reaction in a fixed-bed reactor for the gas and solid phase (Eqs. (2) and (8), respectively) can be finalized as shown in Eqs. (16) and (17).

Gas phase,

$$\frac{\partial Y}{\partial z} = -\frac{LA_sS_ew\beta(C_{SO})^f\,(C_{NO})^g \cdot C_{SO}Y_{i,j}(1-bX_{i,j})^h}{nV_R}\exp\left(-\frac{E_a}{RT}\right) \tag{16}$$

Solid phase,

$$\frac{\partial X}{\partial t} = \alpha\, e^{aT}(C_{SO})^c(\mathrm{RH})^d(1-bX_{i,j})^e\beta C_{SO}^f \exp\left(-\frac{E_a}{RT}\right)$$

$$\frac{3bC_{SO}Y_{i,j}}{\rho_p r}(1-X_{i,j})^{2/3} \tag{17}$$

Both the partial differential equations (Eqs. (16) and (17)) can be solved simultaneously using forward finite differential method by applying boundary condition, $Y = 1$ at $z = 0$ (for all time, t) and $X = 0$ at $t = 0$ (for all position, z). The values of α, β, E_a, a, b, c, d, e, f, g and h were obtained by least-square fitting of the solved partial differential equations to the experimental data. These values were found to be 1309.5 and 0.121 m/s, 16,200 J/mol, −0.02 K^{-1}, 12, 0.2, −3, 5, 0.1, 0.75, and 4, respectively.

4. Results and discussion

4.1. Model validity

The validation of the model was carried out by comparing the simulated results with the experimental data. Figs. 2–5 show the comparison between simulated results with experimental data for various initial conditions. The simulated breakthrough curves show good agreement with the experimental data. Most of the curves simulated were very close to the experimental data except for one of the curves in Fig. 5 that is for 70% relative humidity. The discrepancy could be due to experimental error. Excluding that particular curve, the average absolute percentage error between experimental and simulated data was found to be less than 5%.

4.2. Effect of process variables

The model was then used to simulate the performance of the desulfurization reaction at various operating conditions. Fig. 6 shows the desulfurization reactivity of the sorbent at various SO_2 initial concentration ranging from 500 to 2000 ppm and NO initial concentration ranging from 250 to 750 ppm. The rest of the process variables were fixed at a constant value. The reactivity was reported as the duration the sorbent could maintain 80% removal of the SO_2 initial concentration. From the figure, it was found that the reaction bed get saturated faster at a higher SO_2 initial concentration. At higher SO_2 concentration, there will be more SO_2 molecules that come into contact with the reaction bed at any particular time. This contributes to the increase in the frequency of collision between gaseous reactant with sorbent leading to the occurrence of reaction. With a higher probability of the occurrence of reaction, the reaction bed will be saturated at a shorter period of time. Apart from that, lower initial concentration of SO_2 also indicates lower SO_2 feed rate to the reaction bed. For porous solid reactant, as in this case, more SO_2 molecules will be able to diffuse into the pores of the sorbent and eventually enhance the reaction at the internal surface of the solid reactant. This will lead to an increase in sorbent reactivity because reaction is happening at both internal and external surface of the sorbent. In contrast, at higher feed rate, most of the SO_2 molecules will react only with the sorbent at the external surface of the sorbent and thus blocking excess to the internal surface area of the sorbent leading to lower sorbent reactivity. The effect of SO_2 initial concentration was captured in the model using the rate of reaction with two parameters, frequency factor and order of reaction. As shown in Eq. (13), an increase in SO_2 initial concentration will increase the frequency factor. Besides that, the order of the desulfurization reaction with respect to SO_2 initial concentration was found to be 4 ($h = 4$) as indicated by Eq. (12). Apart from that, the extend of reaction (conversion) will also influence the surface coverage effect. At higher conversion, more products will cover the surface of the sorbent leading to a more significant surface coverage effect. This effect was captured in the model by Eq. (7) where by the values of c and e were found to be 0.2 and 5, respectively.

Besides SO_2 concentration, researchers have also reported that the presence of NO will also influence the kinetic of the desulfurization process [15,16]. The effect of this parameter is also shown in Fig. 6 whereby the NO initial concentration was varied. From the figure, it was observed that the reactivity of the sorbent increases linearly with the increase in NO initial concentration. In our previous experimental study [16], it was reported that NO will be oxidized by O_2, which is also present in flue gas to form NO_2. With the presence of NO_2 in the feed gas, SO_2 will be oxidized to SO_3, and the SO_3 formed will then reacted with the sorbent to form sulfate salts ($SO_4{}^{2-}$). SO_3 is reported to be able to react with the sorbent faster than SO_2. Therefore, the presence of greater amount of NO in the flue gas will accelerate the oxidation of SO_2 to SO_3 leading to sorbent higher reactivity. Thus, the duration of time the sorbent could maintain 80% removal of SO_2 increases linearly with increasing of NO initial concentration in the flue gas. However, in our previous modeling work [8], we were unable to include the effect of NO initial concentration into the model. However, in this study, this effect was captured in the model. Since the presence of NO was reported to increase the rate of SO_2 sorption, thus its effect was included in the rate of the reaction as shown in Eq. (15).

Relative humidity is the most important factor affecting the desulfurization reaction [17]. According to Karatepe et al. [11] and Liu et al. [17], they reported that the reaction products tend to cover the surface of the sorbent more uniformly at lower relative humidity. Consequently, the free surface area for reaction is thus limited and eventually leads to a lower activity in SO_2 removal. Whereas, at higher relative humidity, clusterlike structure products formed, covering less surface area. Hence, the sorbent reactivity increases resulting in a better SO_2 removal activity. Based on this information, the relative humidity factor was included in the surface coverage effect as shown in Eq. (7). Based on the model, an increase in relative humidity reduces the surface coverage effect ($d = -3$). The effect of relative humidity is shown in Fig. 7 whereby higher relative humidity increases the reactivity of the sorbent exponentially. This result

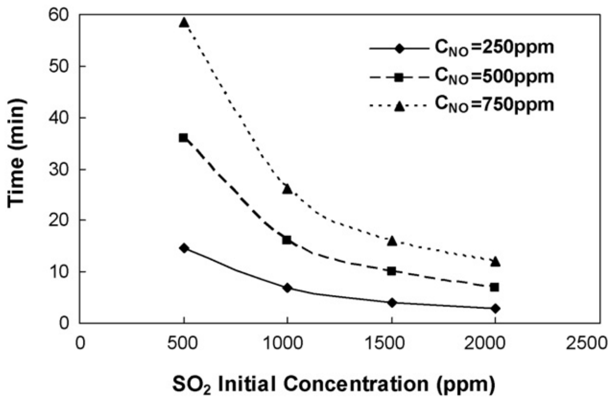

Fig. 6. The duration of time the sorbent could maintain 80% removal of initial SO_2 concentration at various SO_2 initial concentration and various NO initial concentration. Reaction temperature = 70 °C and relative humidity = 60%.

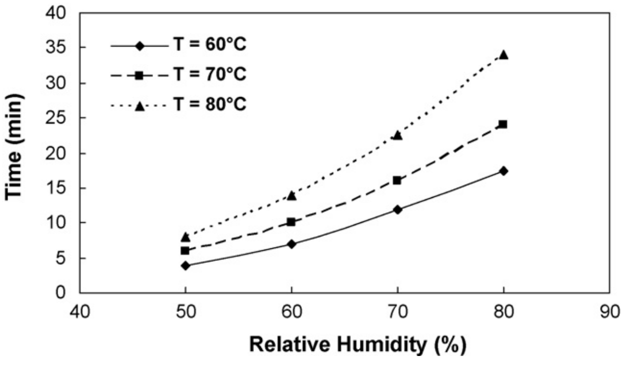

Fig. 7. The duration of time the sorbent could maintain 80% removal of the initial SO_2 concentration at various relative humidity and various reaction temperature. SO_2 initial concentration = 1500 ppm and NO initial concentration = 500 ppm.

is in agreement with those reported by other researcher mentioned earlier [11,17].

Temperature is another essential parameters that influence the kinetic characteristic of the desulfurization reaction. Fig. 7 shows that an increase in reaction temperature increases the reactivity of the sorbent exponentially. These results are again in agreement with those reported by Yan et al. [15] where by it was reported that the final conversion rate of the desulfurization reaction increased with increasing reaction temperature. The increase in desulfurization activity with temperature can be explained by the dependency of reaction rate constant with temperature as shown in Eq. (10). Higher reaction temperature will increase the reaction rate constant, thus increasing the rate of the desulfurization reaction. However, it must be noted that higher reaction rate will cause the surface of the sorbent to be covered by the products faster, thus increasing the surface coverage effect. This was also captured by the model as shown in Eq. (7).

5. Conclusion

In this present work, the kinetic modeling of flue gas desulfurization using $CaO/Ca(SO)_4$/coal fly ash sorbent at low reaction temperature was reported. In the development of the mathematical model, original equation for shrinking unreacted-core model with chemical reaction as the rate limiting step was coupled with surface coverage effect to take into account the diffusion controlling step at the later period of the reaction. This method was found successful in predicting the whole duration of the desulfurization reaction yielding an error between simulated and experimental data to be less than 5%.

Acknowledgement

The authors would like to thank JSPS-VCC (Program on Environmental Science, Engineering and Ethics), Ministry of Science, Technology and Environment Malaysia (Project No. 08-02-05-2040EA001) and Universiti Sains Malaysia (USM Short Term Grant and Research University Grant) for the funding and support on this project.

References

[1] N. Karatepe, A. Ersoy-Mericboyu, S. Kucukbayrak, Activation of $Ca(OH)_2$ using different siliceous materials, Environ. Technol. 20 (1999) 377–385.

[2] T. Ishizuka, H. Tsuchiai, T. Murayama, T. Tanaka, H. Hattori, Preparation of active absorbent for dry-type flue gas desulfurization from calcium oxide, coal fly ash and gypsum, Ind. Eng. Chem. Res. 39 (2000) 1390–1396.

[3] M.J. Renedo, J. Fernandez, Preparation, characterization and calcium utilization of fly ash/$Ca(OH)_2$ sorbents for dry desulfurization at low temperature, Ind. Eng. Chem. Res. 41 (2002) 2412–2417.

[4] K.T. Lee, A.R. Mohamed, S. Bhatia, K.H. Chu, Removal of sulfur dioxide by fly ash/CaO/$CaSO_4$ sorbents, Chem. Eng. J. 114 (2005) 171–177.

[5] C.-F. Liu, S.-M. Shih, Kinetics of the reaction of iron blast furnace slag/hydrated lime sorbents with SO_2 at low temperatures: Effects of sorbent preparation conditions, Chem. Eng. Sci. 59 (2004) 1001–1008.

[6] M. Bausach, M. Pera-Titus, C. Fite, F. Cunill, J.F. Izquierdo, J. Tejero, M. Iborra, Kinetic modeling of the reaction between hydrated lime and SO_2 at low temperature, AICHE J. 51 (2005) 1455–1466.

[7] K. Han, C. Lu, S. Cheng, G. Zhao, Y. Wang, J. Zhao, Effect of characteristics of calcium-based sorbents on the sulfation kinetics, Fuel 84 (2005) 1933–1939.

[8] K.C. Chia, K.T. Lee, W.J.N. Fernando, S. Bhatia, A.R. Mohamed, Modeling and simulation of flue gas desulfurization using $CaO/CaSO_4$/coal fly ash sorbent, J. Chem. Eng. Jpn. 38 (2005) 391–396.

[9] K.T. Lee, S. Bhatia, A.R. Mohamed, Optimization of process parameters for the preparation of $CaO/CaSO_4$/coal fly ash sorbent for sulfur dioxide (SO_2) removal: Part II, Energy Sources 28 (2006) 1251–1258.

[10] A. Garea, J.R. Viguri, A. Irabien, Kinetics of flue gas desulphurization at low temperatures: fly ash/calcium (3/1) sorbent behaviour, Chem. Eng. Sci. 52 (1997) 715–722.

[11] N. Karatepe, A.E. Meriçboyu, R. Yavuz, S. Küçükbayrak, Kinetic model for desulphurization at low temperatures using hydrated sorbent, Thermochim. Acta 335 (1999) 127–134.

[12] M. Bausach, M. Pera-Titus, C. Fite, F. Cunill, J.F. Izquierdo, J. Tejero, M. Iborra, Enhancement of gas desulfurization with hydrated lime at low temperature by the presence of NO_2, Ind. Eng. Chem. Res. 44 (2005) 9040–9049.

[13] A. Garea, J.L. Herrera, J.A. Marques, A. Irabien, Kinetics of dry gas desulfurization at low temperatures using $Ca(OH)_2$: competitive reactions of sulfation and carbonation, Chem. Eng. Sci. 56 (2001) 1387–1393.

[14] M.J. Renedo, J. Fernandez, Kinetic modeling of the hydrothermal reaction of fly ash, $Ca(OH)_2$ and $CaSO_4$ in the preparation of desulfurant sorbents, Fuel 83 (2004) 525–532.

[15] Y. Yan, X.F. Peng, D.J. Lee, Transport and reaction characteristics in flue gas desulfurization, Int. J. Thermal Sci. 42 (2003) 943–949.

[16] K.T. Lee, S. Bhatia, A.R. Mohamed, Removal of sulfur dioxide using absorbent synthesized from coal fly ash: role of oxygen and nitrogen oxide in the desulfurization reaction, Chem. Eng. Sci. 60 (2005) 3419–3423.

[17] C.-F. Liu, S.-M. Shih, R.-B. Lin, Kinetics of the reaction of $Ca(OH)_2$/fly ash sorbent with SO_2 at low temperatures, Chem. Eng. Sci. 57 (2002) 93–104.