

Development of kinetic model for the reaction between SO₂/NO and coal fly ash/CaO/CaSO₄ sorbent

Keat-Teong Lee *, Kok-Chong Tan, Irvan Dahlan, Abdul Rahman Mohamed

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

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Abstract

Sorbents for semidry-type flue gas desulfurization (FGD) process can be synthesized by mixing coal fly ash, calcium oxide, and calcium sulfate in a hydration process. As sorbent reactivity is directly correlated with the specific surface area of the sorbent, reacting temperature, concentration of the reacting gas species and relative humidity, two major aim in the development of a kinetic model for the FGD process are to obtain an accurate model and at the same time, incorporating all the parameters above. Thus, the objective of this work is to achieve these two aims. The kinetic model proposed is based on the material balance for the gaseous and solid phase using partial differential equations incorporating a modified surface coverage model which assumes that the reaction is controlled by chemical reaction on sorbent grain surface. The kinetic parameters of the mathematical model were obtained from a series of experimental desulfurization reactions carried out under isothermal conditions at various operating parameters; inlet concentration of SO₂ (500 ppm ≤ C_{0,SO₂} ≤ 2000 ppm), inlet concentration of NO (250 ppm ≤ C_{0,NO} ≤ 750 ppm), reaction temperature (60 °C ≤ T ≤ 80 °C) and relative humidity (50% ≤ RH ≤ 70%). For a variety of initial operating conditions, the mathematical model is shown to give comparable predictive capability when used for interpolation and extrapolation with error less than 7%. The model was found useful to predict the daily operation of flue gas desulfurization processes by using CaO/CaSO₄/coal fly ash sorbent to remove SO₂ from flue gas. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Coal fly ash; Flue gas desulfurization; Finite difference; Kinetic model; Sorbent

1. Introduction

The increasing world population has pushed the global demand of energy to a higher limit. Although there are many sources of energy, both renewable and non-renewable, however, coal still plays an important role as a source of energy in countries with large population like China, India and USA. Nevertheless, increasing environmental awareness has instigated the need to have an effective flue gas desulfurization technology to remove sulfur dioxide (SO₂) from coal-fired power plants. At the same time, the technology should be cheap so that it could be affordable by power plants in developing countries like China and India. Currently, the control of SO₂ emissions is focused

on the post-combustion desulfurization process. Lately, the removal of SO₂ through sorption process using sorbents prepared from Ca(OH)₂/CaO/CaSO₄ and coal fly ash has received considerable attention [1–10]. It was reported that when Ca(OH)₂/CaO/CaSO₄ and coal fly ash were mixed at proper proportion in a hydration process, sorbents with high SO₂ sorption activity could be attained. These sorbents with high surface area are a product of the pozzolanic reaction between silica eluted from the coal fly ash and Ca(OH)₂/CaO/CaSO₄. Upon absorbing SO₂, the sorbents are converted to SO₃²⁻ (sulfite) and/or SO₄²⁻ (sulfate) salts. The use of coal fly ash as the base material in sorbent synthesis is attractive both economically and environmentally, as it is the most voluminous by-product of coal-fired power plants.

The reactivity of sorbent derived from coal fly ash/CaO/Ca(OH)₂/CaSO₄ varies significantly under different

* Corresponding author. Tel.: +60 4 5996467; fax: +60 4 5941013.

E-mail address: chktee@eng.usm.my (K.-T. Lee).

reaction conditions such as structural properties of the sorbent (surface area), different concentration of inlet gas, reaction temperature and relative humidity [11–13]. Apart from that, the kinetics of the reaction between hydrated coal fly ash sorbent with sulfur dioxide (SO_2) is very complicated as it involves a series of reactions in parallel and many species. The changing product layer diffusivity and the porosity in the sorbent further complicates the kinetics [14].

Garea et al. [11] studied the desulfurization of $\text{Ca}(\text{OH})_2$ /coal fly ash sorbent at low temperatures (52–67 °C) in an iso-thermal integral fixed-bed reactor. In their study, a reaction rate expression was developed based on SO_2 absorption on a non-ideal surface as the controlling step, in terms of an exponential influence of the calcium conversion in the reaction rate. The influence of SO_2 concentration in the gas phase has been described by a partial reaction order equal to 1. It was concluded that relative humidity was the most relevant variable that affect the kinetics of the sorbent. Therefore, a non-ideality parameter, in the form of an empirical equation was incorporated into their proposed model to take into account the effect of relative humidity on the sulfation reaction. Based on the proposed model, the error between the simulated and experimental values was found to lie within an error of $\pm 15\%$.

Karatepe et al. [12] studied the kinetics of the sulfation reaction of hydrated silica fume/ $\text{Ca}(\text{OH})_2$ sorbents 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 balance of nitrogen. It was reported that the experimental conversion-time curves obtained in this work have a convex shape indicating that the reaction between the sorbent and sulfur dioxide (SO_2) is controlled by the diffusion through the product layer. The model proposed to represent the sulfation reaction is a shrinking core model with two types of rate limiting mechanism. At the initial period of the reaction, chemical reaction is partly rate limiting and diffusion through the product layer generally controls the rate of reaction at a later period of reaction. In the mathematical model proposed to represent the desulfurization reaction, two parameters, reaction rate constant and effective diffusion coefficient, were determined from least-square fitting of the experimental data.

Liu et al. [13] studied the reaction between $\text{Ca}(\text{OH})_2$ /fly ash sorbent and sulfur dioxide (SO_2) under the conditions similar to those in the bag filter of the spray drying flue gas desulfurization system using a fixed-bed reactor. The reaction rate of $\text{Ca}(\text{OH})_2$ /fly ash sorbent with SO_2 was described as fast in the initial stage and decreases abruptly leaving the sorbent incompletely converted. The reaction kinetics of the sulfation reaction was well described by the surface coverage model. In the surface coverage model, it was assumed that the sorbent is made up of plate grains and 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. When the reaction surface is fully covered by the product, the reac-

tion will reach a maximum conversion. The standard deviation between the calculated results and experimental data were reported to be 0.2 with respect to conversion.

The mathematical models developed so far to represent the kinetics of the reaction between coal fly ash/ CaO/CaSO_4 sorbent and SO_2 were only based on the concentration of SO_2 , reaction temperature, properties of the sorbent structure (surface area and quantity) and relative humidity. However, in recent studies, it was shown that the coexistence of nitrogen oxides (NO_x) in the flue gas can also influence the reactivity of the sorbent. Most of the studies reported that the presence of NO_x can actually enhance the desulfurization ability of calcium-based sorbents [15–18]. In our previous study, the role of NO in enhancing the desulfurization activity was thoroughly reported [15]. Thus the aim of this study is to develop a mathematical model which includes the effect of inlet NO concentration that can be used to predict the performance of the sorbent in flue gas desulfurization processes. The model will be useful for prediction of reactor performance for the desulfurization reaction under different modes of operations and also as a tool for design and optimization of the flue gas desulfurization processes.

2. Experimental

2.1. Preparation of the sorbent

Sorbents used in this study were prepared from coal fly ash, CaO and CaSO_4 . The coal fly ash used in this study 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. Five grams 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 [19]. 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 ($\varepsilon = 0.6$) was packed in the center of the adsorber supported by 0.05 g of borosilicate glass wool. 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 ($500\text{--}2000 \text{ ppm}$, where $1 \text{ ppm} = 2.62 \text{ mg/m}^3$), O_2 (5.2%), CO_2 (13%), NO ($250\text{--}750 \text{ ppm}$) and balance N_2 were passed through the sorbent consisting of particles size ranging from 200 to $250 \mu\text{m}$. 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 mass flow controller. The concentration of the SO_2 in the flue gas was measured using a Portable Flue Gas Analyzer IMR2800P before and after the adsorption process. The concentration of SO_2 was recorded continuously every 1 min until 60 min . The schematic diagram of the experimental equipment 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 $t/\text{inlet } \text{SO}_2$ concentration vs. time, ($C_{\text{SO}_2}/C_{0,\text{SO}_2}$) vs. t).

2.3. Experimental data

The model proposed to predict the desulfurization reaction of the $\text{CaO}/\text{CaSO}_4/\text{coal fly ash}$ sorbent is based on

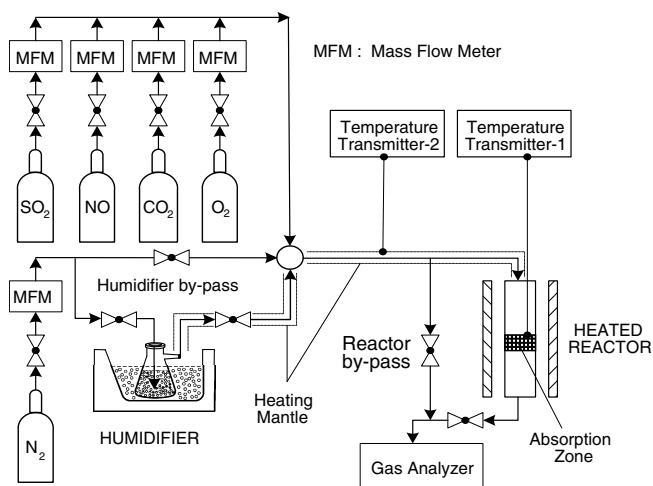


Fig. 1. Schematic diagram of the experimental set-up for fixed-bed desulfurization.

experimental data obtained from a fixed-bed reactor operated under various operating conditions; inlet concentration of SO_2 ($500 \text{ ppm} \leq C_{0,\text{SO}_2} \leq 2000 \text{ ppm}$), inlet concentration of NO ($250 \text{ ppm} \leq C_{0,\text{NO}} \leq 750 \text{ ppm}$), reaction temperature ($60 \text{ }^\circ\text{C} \leq T \leq 80 \text{ }^\circ\text{C}$) and relative humidity ($50\% \leq \text{RH} \leq 70\%$). The range of the variables selected is based on the typical conditions encountered in the industries. A series of experiments have been performed in order to study the influences of these four variables on the desulfurization reaction. Fig. 2a–d shows the breakthrough curves for the experimental desulfurization reaction carried out at various operating conditions. These data were used to develop the mathematical model. The sorption capacity of the sorbent at 90% removal of SO_2 was found to range from 73 to $250.6 \text{ mmol SO}_2/\text{g sorbent}$.

2.4. Software

The partial differential equations employed in this work were solved using finite difference method implemented in Matlab v6.5 and run under the Microsoft Windows NT environment.

2.5. Model development

The model proposed is based on the mass balance of the gas and solid phase representing the sorption of SO_2 on the sorbent of changing composition in a fixed-bed reactor [11]. The following equation represents the gas phase,

$$\frac{n}{LQ} \frac{\partial Y}{\partial z} + \varepsilon \rho C_{0,\text{SO}_2} \frac{\partial Y}{\partial t} + \frac{S_e w}{V_R} r_s = 0 \quad (1)$$

where n is the molar flow rate of SO_2 (mol/s), Y is the concentration of SO_2 flowing through the bed (dimensionless), L is the length of fixed-bed (m), Q is the transversal bed section (m^2), z is the length of the reaction bed (dimensionless), ε is the reaction bed porosity (dimensionless), ρ is the gas molar density (mol/m^3), C_{0,SO_2} is the inlet concentration of SO_2 (ppm), t is the reaction time (s), S_e is the specific surface area of the sorbent (m^2/g), w is the sorbent weight (g), r_s is the reaction rate ($\text{mol/m}^2 \text{ s}$), V_R is the volume of reaction bed (m^3). In many cases, the concentration of SO_2 in the gas phase does not change rapidly with time at a given point. Thus, the time derivative on Y is much smaller than the spatial derivatives of Y , so the term $\partial Y/\partial t$ is negligible in comparison to the term $\partial Y/\partial z$ [11].

For the solid phase equation, it was modified based on surface coverage model. The hypotheses of 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 products. According to this model, the reaction of a sorbent reaches a maximum conversion when its reacting surface is fully covered by the products [13]. Thus, for the solid phase, the equation is expressed in terms of surface coverage rather than conversion as

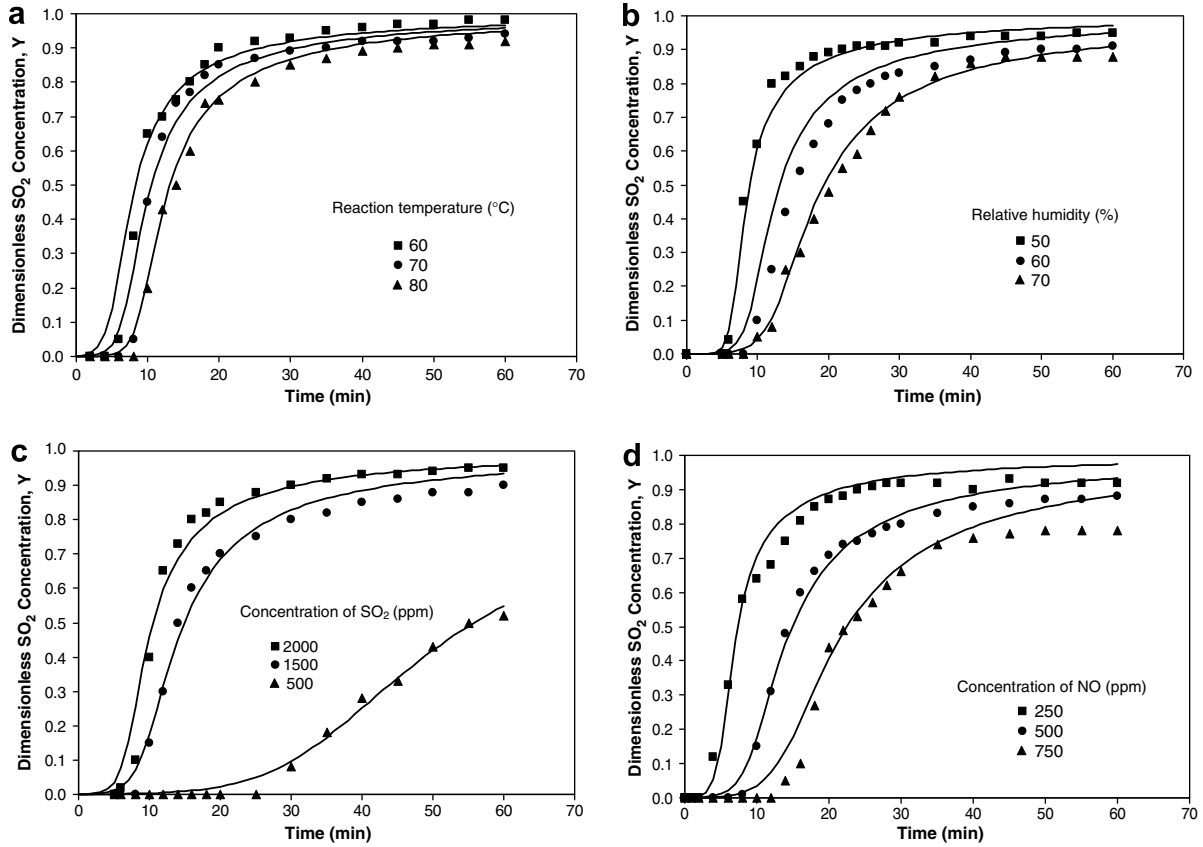


Fig. 2. Experimental and simulated breakthrough curves at various operating conditions showing the effect of (a) reaction temperature at RH = 60%, SO₂ = 2000 ppm, NO = 500 ppm; (b) relative humidity at T = 80 °C, SO₂ = 2000 ppm, NO = 500 ppm; (c) SO₂ at RH = 60%, T = 70 °C, NO = 500 ppm; (d) NO concentration at RH = 60%, T = 70 °C and SO₂ = 1500 ppm. Solid lines indicate simulated results.

$$-\frac{d\theta}{dt} = K_c r_s \quad (2)$$

where θ is the fraction of surface area which is not covered by-product (dimensionless) and K_c is the proportional constant (m²/mol) which take effects of the concentration of the reacting species (SO₂ and NO), sorbent properties (surface area) and relative humidity. There are many ways to express this proportional constant, however the proportional constant expressed by Liu et al. [13] for the reaction between SO₂ and fly ash/hydrated lime sorbent will be used with modification to suite this specific reaction. The following expression was found to best represent the proportional constant

$$K_c = S_m C_{0,SO_2}^\alpha C_{O,NO}^\beta e^{\gamma RH} \quad (3)$$

where S_m is the molar surface area of the sorbent (m²/mol), $C_{O,NO}$ is the inlet concentration of NO (ppm), RH is the relative humidity (dimensionless) and α , β and γ is the order of the reaction with respect to SO₂, NO and relative humidity, respectively (dimensionless).

Based on the surface coverage model, the reaction rate of sorbent per unit inlet surface area, r_s , is express as [13],

$$r_s = K_s W \theta \quad (4)$$

where W is the amount of reactive species (Ca ions) present in the sorbent per unit surface area (mol/m²) and K_s is the reaction rate constant (s⁻¹) in the function of reaction temperature that can be expressed as

$$K_s = A e^{\left(-\frac{E}{RT}\right)} \quad (5)$$

where A is the pre-exponential constant (s⁻¹), E is the activation energy (kJ/mol) and R is the universal gas constant (J/mol K). Replacing Eq. (5) into Eq. (4), the reaction rate per sorbent surface area is express as

$$r_s = A e^{\left(-\frac{E}{RT}\right)} W \theta \quad (6)$$

Replacing Eq. (6) into Eq. (1), the gas phase equation can now be expressed as

$$\frac{\partial Y}{\partial Z} = -\frac{L Q S_\epsilon w A e^{\left(-\frac{E}{RT}\right)} W \theta}{n V_R} \quad (7)$$

Replacing Eq. (3) and (6) into Eq. (2), the solid phase equation can now be expressed as

$$-\frac{\partial \theta}{\partial t} = S_m W \theta A e^{\left(-\frac{E}{RT}\right)} C_{0,SO_2}^\alpha C_{O,NO}^\beta e^{\gamma RH} \quad (8)$$

The two partial differential equations (Eqs. (7) and (8)) were solved numerically by approximation using the forward finite difference method [20]. The values of A , E , α ,

β and γ were then obtained by least-square fitting of the solved partial differential equations to the experimental data. The values of A , E , α , β and γ were found to be 0.7 s^{-1} , 14.67 kJ/mol , 1.05 , 1.2 and 0.8 , respectively. The standard deviations for the five parameters were 3.80%, 5.61%, 6.71%, 5.26% and 3.86%, respectively.

3. Results and discussion

The validity of the proposed mathematical model was verified by comparing the simulated breakthrough curves with experimental data. The simulated data is represented by the solid lines as shown in Fig. 2. It is evident that most of the mathematical model prediction lies very close to the experimental data. The mean absolute error is used here to measure quantitatively the accuracy of the mathematical model:

$$\text{Mean absolute error} = \frac{1}{n} \sum_{j=1}^n |e_j - m_j| \quad (9)$$

where e and m denote experimental and calculated dimensionless SO_2 concentration, respectively, and n is the number of data points. The mean absolute error (calculated from Eq. (9)) between experimental and calculated dimensionless SO_2 concentration values for all the desulfurization experimental runs that were used to develop the model is found to be 6.4%. To assess the ability of the mathematical model to interpolate, a sorbent activity test was conducted within the range of the four variables studied. The experiment was carried out at a reaction temperature of $70 \text{ }^\circ\text{C}$, relative humidity of 55%, inlet SO_2 concentration of 1300 ppm and inlet NO concentration of 600 ppm. Fig. 3 shows the experimental and model-predicted dimensionless concentration of SO_2 . The mean absolute error is 3.5%, indicating excellent agreement between the experimental and predicted data and confirming the model's ability to interpolate the multidimensional initial conditions of the sulfation process with satisfactory accuracy.

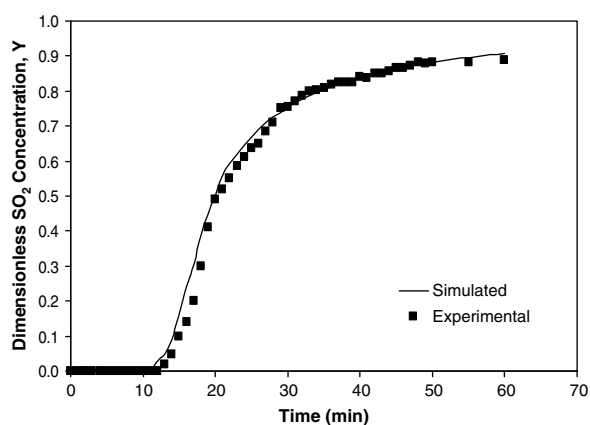


Fig. 3. Experimental and simulated breakthrough curves at $T = 70 \text{ }^\circ\text{C}$, $\text{RH} = 55\%$, SO_2 concentration = 1300 ppm and NO concentration = 600 ppm.

Although the mathematical model possesses excellent interpolation properties, it can give less reliable predictions outside the range of the variables studied due to the empirical nature of obtaining some of the parameters of the model; A , E , α , β and γ . A significant test of the predictive capability of the mathematical model is the extent to which it can predict the breakthrough curves of desulfurization reaction outside the range of the variables studied. Fig. 4 shows the results of plotting the breakthrough curves for predictions vs. experimental for two cases whose inlet conditions were outside the range of the variables studied. For the first case, Fig. 4 shows the breakthrough curves of a sorbent activity test carried out with the relative humidity, inlet concentration of SO_2 and inlet concentration of NO within the range of variables studied (60%, 2000 ppm and 500 ppm, respectively) and reaction temperature outside the range of the variables studied ($100 \text{ }^\circ\text{C}$). For the second case, as shown in Fig. 4, the relative humidity were within the range of the variable studied (60%) while the other three variables; reaction temperature, inlet concentration of SO_2 and inlet concentration of NO were selected outside the range of the variables studied ($100 \text{ }^\circ\text{C}$, 2500 ppm and 1000 ppm, respectively). It is clear that the predictions given by the mathematical model are very close to the actual values, yielding mean absolute errors of 1.3% and 2.7% on cases 1 and 2, respectively. The results indicate that, if a case has some of its initial conditions outside the range of variable used for developing the model, extrapolation is still possible. Nevertheless, it should be noted that under normal circumstance, the model should not be used to predict the desulfurization reactions outside from the range studied as the model does not always guarantee acceptable accurate results. However, the capability of the model in giving accurate predictions for the two cases tested outside the range studied further strengthen the reliability of the model in the prediction of desulfurization reaction within the range studied. The model developed in this study will be very important for the

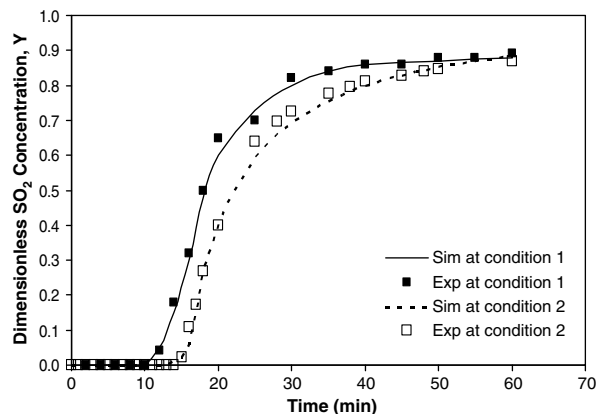


Fig. 4. Experimental and simulated breakthrough curves at condition 1: $T = 100 \text{ }^\circ\text{C}$, $\text{RH} = 60\%$, SO_2 concentration = 2000 ppm and NO concentration = 500 ppm; condition 2: $T = 100 \text{ }^\circ\text{C}$, $\text{RH} = 60\%$, SO_2 concentration = 2500 ppm and NO concentration = 1000 ppm.

prediction of the daily operation of flue gas desulfurization processes by using CaO/CaSO₄/coal fly ash sorbent as different industries operate their FGD unit at different operating conditions.

The activation energy of the sulfation reaction using the sorbent synthesized from coal fly ash/CaO/CaSO₄ was found to be way much lower than the sulfation reaction when CaO (41.8 kJ/mol) and Ca(OH)₂ (133.9 kJ/mol) is used as the sorbent [21]. This result shows that the reaction between SO₂ and the sorbent synthesized from coal fly ash/CaO/CaSO₄ is easier to occur as compared to using CaO or Ca(OH)₂ alone as the sorbent. The effect the four variables (reaction temperature, relative humidity, inlet concentration of SO₂ & NO) on the desulfurization activity will not be discussed in detail here as it has been well reported in the literature. The drop in the activity of the sorbent at higher inlet SO₂ concentration is a direct consequence of exposing a fixed amount of sorbent to increasing amount of SO₂ molecules [22]. On the other hand, the positive effect of relative humidity on the desulfurization activity of the sorbent was in agreement with the results reported in the literature [11–13]. At a higher relative humidity, there will be sufficient water vapor on the surface of the sorbent that could provide a better contact between the SO₂ molecules and the active species of the sorbent for the desulfurization reaction. The weak effect of reaction temperature below 100 °C on the desulfurization activity of fly ash/Ca(OH)₂ sorbent has also been widely reported in the literature [11,13,22]. The increase in desulfurization activity with higher inlet NO concentration is due to its catalytic role in the oxidation of SO₂ to SO₃. SO₃ was believed to be able to react with the reactive species in the sorbent faster than SO₂ [15].

4. Conclusion

In this study, a mathematical model that can predict the desulfurization reaction between SO₂ and sorbent prepared from coal fly ash/CaO/CaSO₄ while incorporating all the significant variables that effect the desulfurization reaction has been developed. The model was found not only capable in predicting the desulfurization reaction within the range of the variables studied but also outside the range of the variables studied with high accuracy. Thus, this model will be very useful in predicting the daily operation of dry flue gas desulfurization processes by using CaO/CaSO₄/coal fly ash sorbent to remove SO₂ from flue gases.

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