Research Article

Flue Gas Desulphurization at Low Temperatures Using Coal Fly Ash/Ca-Based Sorbent: Determination of Rate Limiting Step

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Abstract A kinetic model for flue gas desulphurization (FGD) using siliceous sorbent was carried out using various different potential/exponential expressions for the rate equation and structural/volumetric expressions for the solid phase equation. The kinetic parameters of the mathematical model were obtained from a series of desulphurization experimental reactions conducted under isothermal conditions at various operating parameters. MATLAB software was utilized to solve the partial differential equations using the finite difference method. It was found that the rate limiting step is a combination of reaction and ash diffusion, in which the former dominates initially and the latter dominates at the later reaction stage. Pre-exponential factor of rate constant, k_o, and activation energy, E_a, have been determined as $0.15\,\mathrm{s}^{-1}$ and $15{,}052\,\mathrm{J/mol}^{-1}$, respectively. As a result, a modified shrinking core model with reaction control coupled with exponential expression of the rate equation was found to best describe the experimental data with an error of 4.8%.

Keywords air pollution; gas-solid reaction; kinetic model; modified shrinking un-reacted core model; process modeling; sorption

1 Introduction

Lately, international legislation has imposed the need for installing a flue gas desulphurization (FGD) unit in power plants, especially coal-fired power plants, to control sulphur dioxide (SO_2) emissions. There are currently many technologies available for FGD, but the most common commercial technology adopted is the wet-process method using limestone derivatives as an absorbent. However, this technology requires a high investment cost that might not be economically viable for small-scale power plants. In contrast, recent studies have shown that calcium-based sorbent prepared from various siliceous materials, such as coal fly ash, rice husk ash and oil palm ash, can be used effectively to remove SO_2, especially for small-scale application. This dry-process is significantly cheaper and simpler than the current wet-process with a decreased space requirement, and it is easier to retrofit and produce dry solid product, which is easier to handle [17]. However, the lower efficiency for SO_2 removal using these siliceous sorbents in the dry-process still hinders this technology from being completely commercialized. Therefore, current studies are focusing on how to further understand the process by developing a proper reaction model that can represent this process.

The general theory for catalytic gas-solid reaction processes has been well developed and documented in many publications since the mid-1950s. However, non-catalytic gas-solid reactions for FGD using siliceous sorbents represent an important class of heterogenous reactions that has not been explored thoroughly. Embarking on this kind of theoretical modeling is not easy due to the complex process involving a large number of sub-processes. Different from their catalytic counterparts, the solids (siliceous sorbent) in non-catalytic gas-solid reactions for FGD are involved as reactants and the consumption of the solid reactants leads to inevitable structural changes during the reaction, and the system as a whole is always in a transient state. This phenomenon also implies that the controlling regime might even continuously change with time for the same particle. Since the pioneering experimental research on synthesizing fly ash/calcium sorbent for FGD by Garea et al. [6] in 1997, many researchers have postulated various models and techniques for the process. In a broad sense, these models for solid conversion can be classified into two categories: structural-type and volumetric models. The structural-type models explicitly consider structural changes during the reaction performed by modeling the variations of the internal pore structure during conversion, allowing for changes in the structure as the reaction proceeds. In the volumetric-type approach, in contrast, changes in porous structure during conversion are considered using experimental correlations [7].

It was well acknowledged that in FGD using sorbents, the diffusion of reactants through the product layer is a crucial factor that must be considered because this might be the main limiting step in the later part of the reaction. Therefore, in 1993, based on an FGD experimental study using limestone, Krishman and Sotirchos [11] were the first to postulate the desulphurization reaction based on the shrinking core model. However, the results obtained indicated that the rate of the reaction decreases much faster than the model can predict, especially during the latter part of the reaction. Subsequently, a modified variable effective diffusivity, D, was introduced to the model as a function of the distance from the external surface of the particles in an exponential form. Only then was the model successful in explaining the sudden increase in average resistance for mass transport in the product shell as the reaction proceeds. In a more recent study by Liu and Shih [15], the modified surface coverage model was proposed for the desulphurization reaction between $Ca(OH)_2$/fly ash sorbent and SO_2. The hypothesis of this model was that the sorbent was made up of plate grains and the reaction rate was controlled by the chemical reaction on the surface of the grain. The reacting surface area of the grain decreased as the reaction progressed further. Based on the proposed model, the reaction reached an ultimate conversion when the entire reacting surface was covered by the product. Additionally, it was assumed that the change of sorbent surface coverage with reaction time depends on reaction rate, dispersion of Ca and the way by which the product deposits on the surface.

In another study, Bausach et al. [3] investigated kinetics of non-catalytic solid-gas FGD reaction between $Ca(OH)_2$ and SO_2 at a low temperature. In their study, they reported a modified deactivation model (DM) to improve the fit of the desulphurization experimental data. The deactivation model assumed that the reaction between gas molecules and solid sorbent depends mainly on the concentration of the gas on the solid surface. As the reaction progressed, solid products deposited on the un-reacted surface reduced the surface area, leading to lower sorbent reactivity. Han et al. [8] proposed a modified grain reaction model for sulphation kinetics between solid sorbents and SO_2. The sulphation process and kinetics were analyzed using the thermogravimetric method using three types of shells and two types of limestone. The microstructure and pore structure of the limestone and shell during the sulphation reaction were investigated using Scanning Electron Microscopy and a Porosimeter, respectively. It was concluded that the rate of sulphation is principally controlled by particle pore diffusion and product layer diffusion.

More recently, the application of the shrinking core model has been used extensively for fitting desulphurization data, but generally, it still fails to explain the decrease in reaction rate as the solid conversion increases, especially at high relative humidity. The development of a kinetic model for the FGD reaction between siliceous calcium-based sorbent and SO_2 has not been conclusive. Nevertheless, it was well accepted that the whole sulphation reaction may be divided into two steps that cannot be separated precisely. Initially, before the formation of reaction products around the solid sorbent particle, the chemical reaction or pore diffusion is the reaction rate-limiting step. However, when a significant amount of products cover the surface of the solid sorbent particle, that is, the pores at the external layer of the particle are then plugged with solid products, the rate-limiting step will change to the product layer diffusion [17]. One possible way to overcome the changing rate-limiting step is to develop a global desulphurization reaction rate model that incorporates both the reaction and the diffusion controlling step, as reported in our previous study [4]. However, this method of global process modeling (volumetric approach) provides little valuable information on the actual physicochemical process that occurs during the desulphurization reaction.

To further complicate this process, the presence of NO in the flue gas may also react with the sorbent and interact with SO_2 directly. According to O'Dowd et al. [16], oxidation of NO to NO_2 has been proven as the reaction step that enhances NO_x removal in conventional FGD processes. Additionally, the presence of significant quantities of NO_2 can increase SO_2 removal. At a later stage, Bausach et al. [2] proposed a reaction mechanism for interaction in the SO_2–NO_2 system in an aqueous solution using a set of reactions divided into a few stages: SO_2 adsorption, NO_2 adsorption, NO_2/SO_3^{2-} interaction and reactions due to O_2. As a result of this study, it was confirmed that the reaction between SO_2 and NO_2 is strongly interrelated, and thus, the kinetics of the desulphurization reaction becomes very complicated.

Therefore, the aim of this study is to thoroughly investigate the complex non-catalytic FGD process using siliceous sorbents by proposing and validating different kinetic models. The kinetic model covered in this study incorporates a combination of structural/volumetric types for the solid phase equation and potential/exponential types for the rate reaction equation. Although similar modeling techniques (the modified shrinking core model) have been reported in our previous study [12] and were shown to have good agreement with experimental data, comments received from experts in this field noted that its high reaction order (potential expression) of 12 does not reveal any comprehension of physicochemical properties. Hence, the ultimate aim of this study is to develop a kinetic model that can truly represent the FGD reaction and determine the rate limiting step. The model must also be able to give insight into the physicochemical properties that occur during the reaction, with special emphasis in explaining the strong decrease in reaction rate due to the gradual increase

of ash layer diffusion resistance in the latter stage of the reaction. The model will be useful for the prediction of reactor performance for the desulphurization reaction under different modes of operation as well as a tool for design and optimization of the process because obtaining the accurate rate constant, k, is crucial in designing the FGD process.

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 the Kapar Power Plant, Malaysia, of Tenaga Nasional Berhad with the following composition: SiO$_2$, 60%; Al$_2$O$_3$, 20%; Fe$_2$O$_3$, 4.7%; CaO, 3.0%; K$_2$O, 1.1%; MgO, 1.0%; C, 7.5%; others, 2.4% and ignition loss, 0.3%. The CaSO$_4$ used was reagent-grade calcium sulphate hemihydrates while the CaO used was of laboratory grade. Both of these chemicals were supplied from BDH Laboratory Supplies, England. The sorbents were prepared using the water hydration method. CaO (5 g) was added into 100 mL of water at 70 °C. Coal fly ash (13.7 g) and 7.4 g of CaSO$_4$ were then added simultaneously into the slurry. The slurry was 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 material, were selected according to an optimization study reported elsewhere. The resulting sorbent had a specific BET surface area of 64.5 m^2/g (Autosorb 1C Quantachrome).

2.2 Desulphurization activity study

The desulphurization activity of the sorbent is based on previous work reported by Lee et al. [13] and was performed in a fixed-bed stainless steel adsorber with 2.2 cm in length (L) of adsorption zone and a transversal bed section of 0.5 cm^2 (A) under isothermal conditions. Sorbent (0.7 g) 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 to a desired temperature using a furnace heater and the bed temperature was continuously measured and monitored by a thermocouple. A stream of a 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$_2$ was passed through the sorbent. Prior, the N$_2$ gas stream was humidified using a humidification system in which the gas was saturated with water vapor. This process was performed by passing N$_2$ gas through two 250-mL conical flasks immersed in a water bath held 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 both before and after the sorption process. The concentration of SO$_2$ was recorded continuously every 1 min for 60 min. A schematic diagram of the experimental set-up used in this activity study is shown in Figure 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 repetitions was less than 10%. This procedure also diminished the impact of variation in the composition or shape of the sorbents in each run. For clarity, only the averages are presented in this paper. The desulphurization activity of the sorbent reported in this work is presented as the breakthrough curves of the desulphurization reaction (SO$_2$ concentration at time t/initial SO$_2$ concentration vs. time (C/C$_o$) vs. t).

2.3 Experimental data

The proposed model for the desulphurization 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; the initial concentration of SO$_2$ was 500 ppm $\leq$ C$_{SO}$ $\leq$ 2000 ppm, the initial concentration of NO was 250 ppm $\leq$ C$_{SO}$ $\leq$ 750 ppm, the reaction temperature was 60 °C $\leq$ T $\leq$ 80 °C and the relative humidity was 50% $\leq$ RH $\leq$ 70%. A series of experiments have been performed to study the influences of these four variables on the desulphurization reaction and are presented in Figures 1, 2, 3, 4 and 5.

2.4 Software

The partial differential equations employed in this work were solved using a spatial and temporal discretization through the finite difference method implemented in MATLAB v7.0 and run under Microsoft Windows NT environment. Separately, the least-square nonlinear optimization method, based on the Levenberg-Marquardt algorithm, was used to adjust the kinetic parameters of F, γ_o, α, k_o, c, g and E_a by comparison of the predicted and the experimental breakthrough curves at the outlet of the reactor. The confidence interval of the fitted kinetic parameters was calculated by means of a standard method for nonlinear models [10].

3 Model development

To evaluate the FGD reaction at low temperatures in a packed-bed system, there are two prevailing variables that must be solved simultaneously. These two variables are the dimensionless SO$_2$ concentration Y, and the conversion of sorbent X. Sorbent conversion X is calculated by subtracting the ratio of calcium oxide at time t (weight)
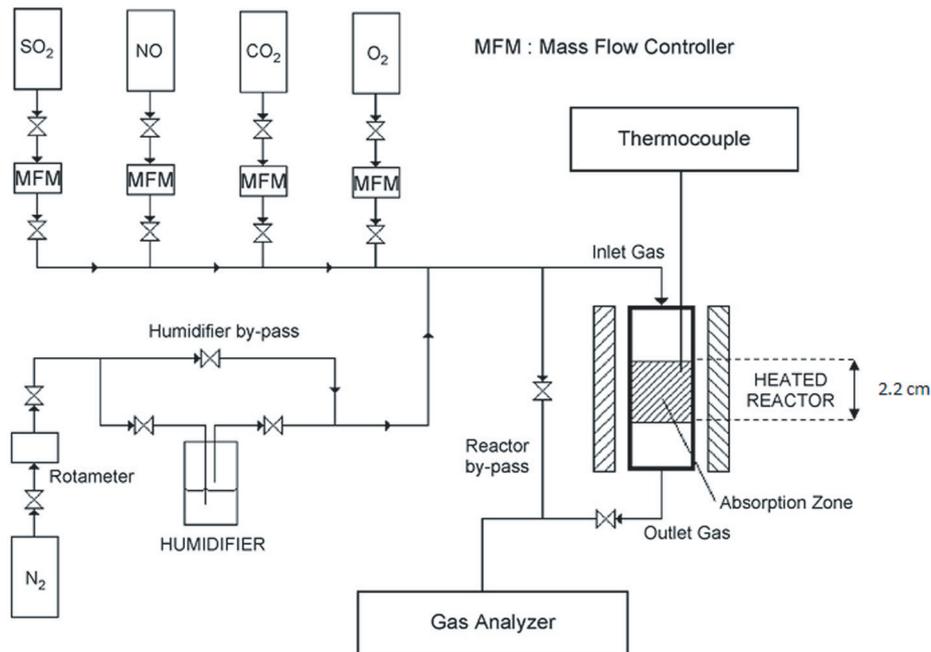
Figure 1: Schematic diagram of the experimental set-up.
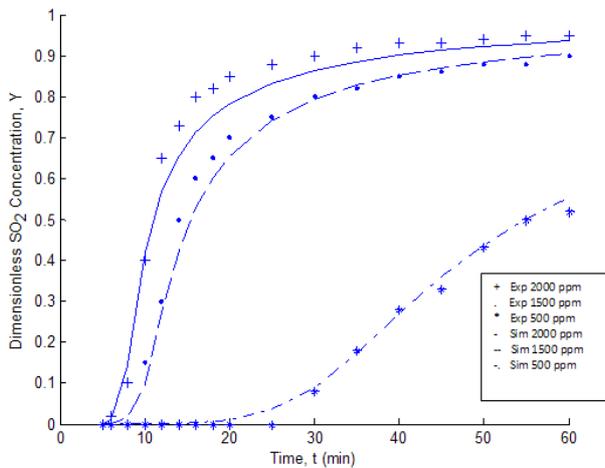
Figure 2: Experimental and simulated desulphurization breakthrough curves for various SO_2 initial concentrations (ppm). Reaction temperature $=$ 70 °C, relative humidity $= 60\%$ and NO concentration $= 500$ ppm.
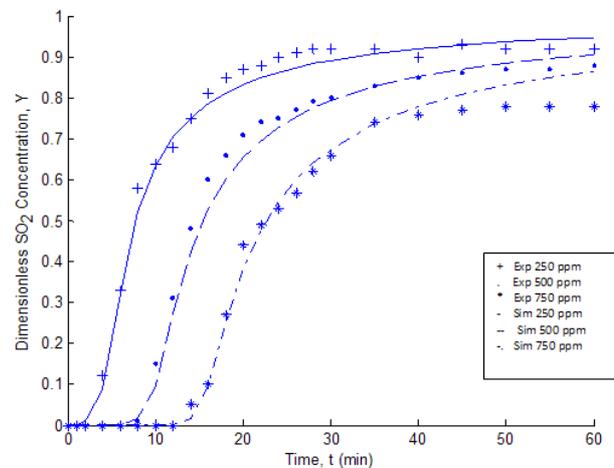
Figure 3: Experimental and simulated desulphurization breakthrough curves for various NO initial concentrations (ppm). Reaction temperature $=$ 70 °C, relative humidity $= 60\%$ and SO_2 concentration $= 2000$ ppm.

to initial weight of calcium oxide by one. Both these variables change progressively as the reaction proceeds. By providing a full simulation result for the values of X and Y for a fixed duration, the developed model could then be verified by comparing to the experimental data. Generally, the easiest method for finding two partial differential equations to describe the changing composition of X and Y could begin with basic mass balances for the gas and solid phases. Both partial differential equations are then

correlated by the rate equation. Due to the complexity of the FGD process utilizing siliceous sorbent, two types of differential equations are proposed herein for the solid phase and rate equation, respectively. However, for the gas phase differential equation, only one single type will be used. For the rate equation, exponential and potential expressions will be proposed. For the solid phase, volumetric or structural expressions will be used. For structural expression, it will be further expanded to study the physicochemical properties
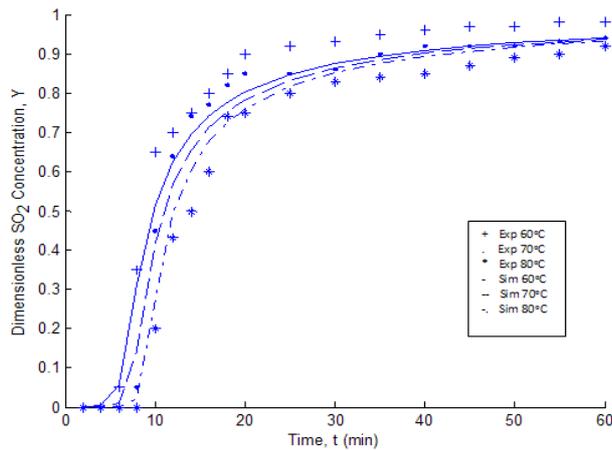
Figure 4: Experimental and simulated desulphurization breakthrough curves for various reaction temperatures (°C). SO$_2$ initial concentration = 2000 ppm, NO initial concentration = 500 ppm and relative humidity = 60%.

Figure 5: Experimental and simulated desulphurization breakthrough curves for various relative humidity (%). Reaction temperature = 80 °C, SO$_2$ initial concentration = 2000 ppm, and NO initial concentration = 500 ppm.

of the reactions by identifying the rate limiting step. The criteria used to identify which model (combinations of differential partial equations) best fits the FGD process are those that give the lowest root mean square error (RMSE) between the experimental and predicted data.

Before deriving both mass balance equations for the gas and solid phases, there are some qualitative aspects of the FGD reaction that must be considered to predict the kinetic behavior of the reaction accurately, which were evaluated through the experimental results presented in Figures 2 to 5:

– for gas-phase composition, the concentrations of SO$_2$ and NO were found to affect the removal efficiency of the sorbent. Therefore, both these variables must be included in the rate reaction. The significant effect of NO concentration on the desulphurization capacity of the sorbents was also reported by Dahlan et al. [5];
– concerning the desulphurization behavior of fly ash/CaO/CaSO$_4$ sorbent, high calcium utilizations can be attained depending on reaction variables such as temperature, concentrations of SO$_2$ and NO and relative humidity; the latter influence being the most significant;
– referring to the rate of reaction, a drastic decrease in the desulphurization rate as the reaction progresses was observed. This phenomenon could be due to the surface coverage of the un-reacted outer layer of sorbents by products of the desulphurization reaction. Therefore, the solid conversion might be one of the crucial influencing factors that causes the sharp decrease in reaction rate and is to be included in the solid phase equation;
– to avoid complicated mathematical procedures, the following assumptions were made:
 (1) the FGD reaction is operating at isothermal conditions;
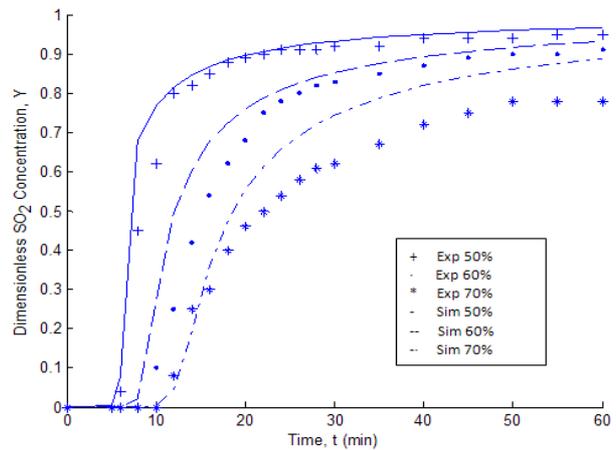
 (2) constant values are used for the gas velocity and void fraction in the fixed-bed;
 (3) the plug flow condition is used for the gas phase without axial dispersion (one-dimensional model along the z-axis).

Equations developed in the following section must therefore be able to take into consideration all the points mentioned above to develop an accurate FGD kinetic model.

3.1 Gas phase

Assuming a small dispersion modulus, the mass balance for gas phase composition in the fixed-bed reactor can be simply represented using (1):

$$\frac{n}{L_o A_s}\frac{\partial Y}{\partial z} + \varepsilon_b \rho C_S \frac{\partial Y}{\partial t} + \frac{S_e w}{V_R} r_s = 0 \qquad (1)$$

where n is 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, z is the dimensionless length position (dimensionless), ε_b is the reaction bed porosity (dimensionless), ρ is the gas molar density (mol/m^3), C_s is the initial SO$_2$ concentration (ppm), 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^{2}s). However, for most non-catalytic solid gas reactions, the concentration of SO$_2$ in the gas phase does not change rapidly with time at any given point. Thus, the time derivative on Y is much smaller than the spatial derivatives of Y, and the time derivative can be removed from (1), resulting in (2). To complete (2), a full expression of the

rate of reaction must be proposed and will be presented in Section 3.3:

$$\frac{\partial Y}{\partial z} = -\frac{L_o A_s S_e w}{n V_R} r_s. \tag{2}$$

3.2 Solid phase

For the solid phase reaction, two different approaches were investigated, volumetric and structural.

3.2.1 Volumetric expression of solid phase

For the volumetric approach, experimental correlations are normally used to represent the changes in solid porous structures as the reaction progresses. Most studies reported in the literature applied the continuous correlation between conversion (X) and time (t) to describe the mass balance in solid phase as shown below:

$$\frac{\partial X}{\partial t} = b r_s S_e M. \tag{3}$$

3.2.2 Structural expression of solid phase

For the structural approach, the un-reacted shrinking core model (SCM) was selected for this study. Un-reacted SCM is generally applied to cases involving a solid reactant that is converted to another solid material leaving behind the un-reacted solid. The converted material, which is sometimes called "ash", is regarded as a porous and inert substance, so that the gas reactants can diffuse from external surface of the particle to the surface of the un-reacted core. Thus, the un-reacted core shrinks as the reaction progresses, but the overall particle size remains constant. Although un-reacted SCM does not precisely represent the whole mechanism of gas-solid reactions, it is accepted as the best simple model for the majority of reacting gas-solid systems. At the microscopic level, un-reacted SCM is applied to each of the siliceous sorbent grains to model the gas-solid reaction. For spherical particles, the model normally assumes a first-order chemical reaction with respect to SO_2 concentration while the correlation between reaction time and solid conversion is dependent on the rate-limiting step as in the following.

(1) If the chemical reaction is the rate-limiting step:

$$\frac{t}{\tau} = 1 - (1 - X)^{1/3}, \tag{4}$$

$$\tau = \frac{\rho_B r}{b k C_{SO} Y}, \tag{5}$$

$$\frac{\partial X}{\partial t} = \frac{3 b k C_{SO} Y}{\rho_B r} (1 - X)^{2/3}, \tag{6}$$

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right). \tag{7}$$

(2) If diffusion through the product layer is the rate-limiting step:

$$\frac{t}{\tau} = 1 - 3(1 - X)^{2/3} + 2(1 - X), \tag{8}$$

$$\tau = \frac{\rho_B r^2}{6 b D_e C_{SO} Y}, \tag{9}$$

$$\frac{\partial X}{\partial t} = \frac{3 b D_e C_{SO} Y}{\rho_B r^2} \left[\frac{1}{(1 - X)^{-1/3} - 1}\right], \tag{10}$$

$$D_e = D_{eo} \exp\left(-\frac{E_{\text{diff}}}{RT}\right). \tag{11}$$

(3) If diffusion through gas reactant is the rate-limiting step:

$$\frac{t}{\tau} = X, \tag{12}$$

$$\tau = \frac{\rho_B r}{3 b k_g C_{SO} Y}, \tag{13}$$

$$\frac{\partial X}{\partial t} = \frac{3 b k_g C_{SO} Y}{\rho_B r}, \tag{14}$$

$$k_g = k_{go} \exp\left(\frac{-E_{\text{gas}}}{RT}\right). \tag{15}$$

In most cases, reactions do not specifically follow a one single rate limiting step. Therefore, an attempt is made in this study to consider a combination of rate limiting steps to model the FGD reaction. According to Levenspiel [14], a combination of resistances can be straightforward and performed by accounting for the simultaneous action of these resistances because they act in series and are all linear in concentration. Thus, by combining (4), (8) and (12) with their individual driving forces and eliminating the intermediate concentrations, it can be shown that the time to reach any stage of conversion is the sum of the times needed if each resistance acted alone, or

$$t_{\text{total}} = t_{\text{film alone}} + t_{\text{ash alone}} + t_{\text{reaction alone}}. \tag{16}$$

Similarly, for complete conversion:

$$\tau_{\text{total}} = \tau_{\text{film alone}} + \tau_{\text{ash alone}} + \tau_{\text{reaction alone}}. \tag{17}$$

3.3 Rate of reaction

To solve both (2) and (3), an expression for the rate of reaction has to be proposed. Various rate expressions have been proposed in the literature to study the complex reaction between SO_2 and siliceous sorbent. In fact, an overview of the gas-solid kinetic reactions has been reported by Garea et al. [6], whereby it was found that the main characteristic of these reactions at low-temperature range is the strong decrease in reaction rate as the reaction progresses (or with sorbent conversion). Besides, a recent study by Qi et al. [17] also claimed that a strong decrease in reaction

rate was observed from the breakthrough curves obtained in his study at medium temperature. Accounting for this behavior, two types of kinetic models with a strong decrease in reaction rate will be selected: the empirical potential model and exponential model.

3.3.1 Potential kinetic model

The following empirical rate equation was reported by Hartman and Trnka [9] for sulphation of CaO at low and medium temperatures:

$$r_s = kY^p(1-X)^q, \tag{18}$$

where k has an Arrhenius dependence with temperature and the solid order (q) sharply deceases with temperature. According to Hartman and Trnka [9], a high value of q was found where the solid order is equal to 24.7 at 300 °C and 16.6 at 400 °C. Because the value of the solid order is very high, this may not have any physicochemical meaning. Therefore, exponential models will also be considered in this study.

3.3.2 Exponential kinetic models

Kinetic models with an exponential dependence of conversion have been developed in recent years to fit gas-solid reaction data. The models can be lumped in the following general exponential rate equation:

$$r_s = f(Y, X, T, \text{RH}, C_{\text{NO}}). \tag{19}$$

Assuming that the terms in (19) are separable,

$$r_s = F_1(T)F_2(Y)F_3(X, T, \text{RH})F_4(C_{\text{NO}}), \tag{20}$$

where

$$F_1(T) = k(T) = k_o \exp\left(-E_a/RT\right), \tag{21}$$

$$F_2(C) = C_{\text{SO}}Y^m, \tag{22}$$

$$F_3(X, T, \text{RH}) = (1-X)\exp\left(-\frac{\gamma X}{RT}\right), \tag{23}$$

$$F_4(C_{\text{NO}}) = (C_{\text{NO}})^g. \tag{24}$$

Equations (21) to (24) proposed for the separable terms in (20) were based on the following assumptions through observing the experimental data trend from Figures 2 to 5. For the temperature-dependent term (see (21)), the kinetic constant based on the Arrhenius law (with activation energy) best describes reactions that are dependent on temperature. For the SO_2 and NO concentration-dependent terms (see (22) and (24)), a potential expression using the fitting parameter of m and with g order, respectively, can describe the sharp increase in SO_2 and NO concentration with time. For the relative humidity-dependent term (see (23)),

an exponential expression with the surface heterogeneity parameter γ was used to explain the influence of relative humidity on the sorption kinetics. The surface heterogeneity parameter was previously reported by Garea et al. [6], whereby it was used to describe the effect of relative humidity on the FGD process at low temperatures using calcium hydroxide as solid sorbent, using the following equation:

$$\gamma = \gamma_o \exp\left(\frac{F}{\text{RH}}\right). \tag{25}$$

Replacing (21) to (24) into (20), the exponential kinetic rate equation then becomes

$$r_s = k(C_{\text{NO}})^g C_{\text{SO}}Y(1-X)\exp\left(-\frac{\gamma_o \exp\left(\frac{F}{\text{RH}}\right)X}{RT}\right). \tag{26}$$

Note that k is supposed to follow the Arrhenius equation as shown in (21). However, in a recent study on the development of a kinetic model for CaO/fly ash sorbent for flue gas desulphurization at moderate temperatures by Qi et al. [17], it was reported that k_o, the pre-exponential factor of Arrhenius equation, was not a constant. In fact, the value of k_o was found to change with temperature and, subsequently, the model developed can only then give a very good agreement between simulated and experimental data. Therefore, on the same basis, the Arrhenius equation will be modified to incorporate SO_2 concentration and the conversion-dependent term as shown in (27). Similar findings were also reported by other researchers working with Ca-based/siliceous-based sorbents, whereby it was reported that the reaction rate constant is more dependent on other parameters such as conversion instead of just temperature [1, 18],

$$k = k_o(C_s)^c(1-X)\exp\left(\frac{-E_a}{RT}\right). \tag{27}$$

4 Results and discussion

Table 1 shows eight different combinations of solid phase and rate equations representing eight models developed for the FGD reaction with the corresponding root mean square error (RMSE). Kinetic parameters used in each model, obtained using the least square fitting method, are also presented in Table 1. For instance, in Combination I, (2), (3) and (26) are used to model the desulphurization reaction and the RMSE obtained between simulated and experimental results (data presented in Figures 2 to 5) is 7.77%. Comparing Combination I and II, both using the volumetric approach for the solid phase equation, it was found that when exponential rate equation is used, the RMSE obtained is well below 10%. This phenomenon

Combination	Solid phase	Rate of reaction	F (—)	γ_o (Jmol^{-1})	α (—)	k_o (s^{-1})	D_{eo} (m^{2}s^{-1})	p (—)	q (—)	c (—)	g (—)	E_{gas} (Jmol^{-1})	E_{diff} (Jmol^{-1})	E_a (Jmol^{-1})	RMSE (%)
I	Volumetric	Exponential	2.58	7,500	—	0.3	—	—	—	—	1	—	—	14,250	7.77
II	Volumetric	Potential	—	—	—	0.15	—	300	2	—	1.38	—	—	12,500	26.8
III	Structural (reaction control)	Potential	—		—	0.1	—	1.1	97.8	—	1.25	—	—	17,500	16.1
IV	Structural (reaction control)	Exponential	2.58	9,026	—	0.02	—	—	—	—	0.78	—	—	15,052	11.3
V	Structural (ash layer diffusion)	Exponential	0.15	17,500	—	—	12.5	—	—	—	0.08	—	45,000	—	52.4
VI	Structural (gas film diffusion)	Exponential	2.58	8,889	—	0.46	—	—	—	—	0.78	24,200	—	—	11.3
VII	Structural (combination of ash and reaction control)	Exponential	2.58	12,500	—	1	0.33	—	—	—	1	—	45,000	15,052	11.6
VIII	Structural (modified SCM)	Exponential	1.85	3,750	150	0.15	—	—	—	0.2	0.73	—	—	15,052	4.77

Table 1: RMSE for models with various combinations and its corresponding kinetic parameters.

shows that the model obtained using Combination I can represent the FGD model relatively well. In contrast, when the potential rate equation (Combination II) is used, the RMSE obtained is very high at 26.76%, indicating that the model developed cannot be accepted. This result most likely occurred because the potential expression of the rate equation cannot describe the drastic drop in the rate of reaction as the desulphurization reaction progresses. Similar results were also obtained when comparing Combinations III and IV; this time, the structural approach was used for the solid phase equation. Again, the exponential expression for the rate equation gave a lower RMSE. Consequently, the exponential expression for the rate of reaction was concluded to best describe the phenomenon for flue gas desulphurization and it will be used for the rest of this study.

At this point, although the model using Combination I (volumetric and exponential expression for solid and rate equation, resp.) gives a low RMSE value, indicating that it can be used to represent the FGD reaction, it provides very little information regarding the physicochemical reaction between the siliceous sorbent and SO_2, including the rate-limiting step for the reaction. Subsequently, using the exponential expression for the rate equation, the structural equation for solid phase was then expanded with another controlling step to identify the rate limiting step for the FGD reaction. The models using Combinations IV, V and VI represent reaction, ash diffusion and gas diffusion

control, respectively. The activation energies obtained for the reaction control, ash layer diffusion and gas film diffusion control models agree very well with the values reported in the literature: 12500–16000 J/mol, 45000 J/mol and 24500 J/mol, respectively [17]. The results show that the reaction and gas diffusion can illustrate the FGD phenomenon between siliceous sorbent and SO_2 relatively well. However, for the ash diffusion control, the RMSE was extremely high at 52.4%. This result probably occurs because, especially at the beginning of reaction, there is no formation of the ash layer (representing the product of the desulphurization reaction). Therefore, the use of the ash control expression as the limiting step resulted in a very large error between simulated and experimental data. Between the reaction control and gas diffusion, in which both give almost similar RMSE, the former rate-limiting step seems to be more appropriate because the sorption of SO_2 onto siliceous material has been proven to be a chemical reaction phenomenon. This phenomenon is further supported by the strong chemical bonding required to form solid product ($CaSO_3$). Furthermore, the amount of SO_2 used in the experimental study is always in excess and continuously fed to the sorbent; therefore, the rate limiting step due to gas diffusion might not be very appropriate. Nevertheless, as shown in Table 1, using the reaction control expression as the rate limiting-step (Combination IV), the RMSE obtained for the model is still not satisfactory

(above 5%). This result is probably due to the fact that the reaction control step cannot describe the sudden decrease in reaction rate at the latter stage (after twenty minutes) of the reaction, resulting in a relatively high RMSE at 11.3%. One possible way to overcome this limitation is to incorporate the ash diffusion control step to account for the formation of product layer at the later stage of the reaction. Therefore, in Combination VII, the combination of ash diffusion and reaction control was selected for the structural solid phase expression. However, this combination failed to improve the accuracy of the model as the RMSE is still above 10%. Nevertheless, two significant findings can be obtained from this exercise. One, combination of the reaction and ash diffusion control can successfully reduce the RMSE for the model instead of using solely the ash diffusion control. Secondly, the reaction control has a greater influence on the FGD reaction compared to the ash diffusion whereby the value for kinetic constant k_o is higher than the effective diffusivity D_{eo} (Table 1).

At this point, it is clear that the reaction is the main rate-limiting step for the desulphurization reaction, and as the reaction progresses, the formation of products will subsequently shift the rate-limiting step toward ash diffusion. On the other hand, it is also clear that the SCM with a combination of reaction and ash diffusion rate-limiting step cannot model the FGD reaction accurately. Thus, in the following section, an attempt will be made to modify the equation for the SCM with reaction control. This modification was performed by developing an additional term for equation (6), named the surface coverage factor, θ, as shown in (28):

$$\frac{\partial X}{\partial t} = f(\theta)\frac{3bkC_{SO}Y}{\rho_B r}(1 - X)^{2/3}. \tag{28}$$

The surface coverage factor was developed to account for the ash diffusion controlling step at the later period in the reaction. Because the formation of the product of the desulphurization reaction that contributes to the ash diffusion rate-limiting step is influenced by solid conversion, the concentration of SO_2, reaction temperature and relative humidity [3], the surface coverage factor can be expressed as shown in (29):

$$f(\theta) = \alpha (C_s)^c (1 - X) \exp\left(-\frac{\gamma X}{RT}\right) \tag{29}$$

with

$$\gamma = \gamma_o \exp\left(\frac{F}{RH}\right) \tag{30}$$

where α is the pre-exponential constant (dimensionless), γ_o is the pre-exponential constant (dimensionless), F is the fitting parameter (dimensionless), RH is the relative humidity and c is the order for the effect of the respective parameter on the surface coverage effect. After substituting (29) and
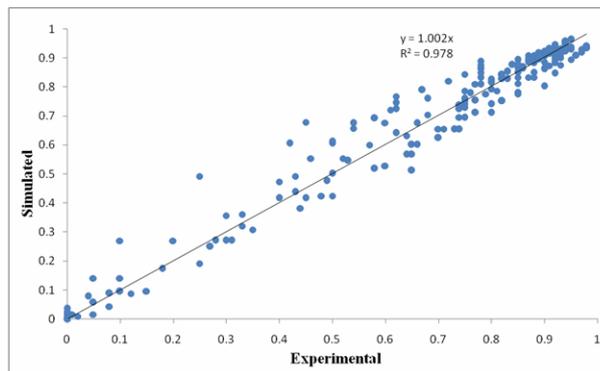
Figure 6: Parity plot for experimental versus simulated data points.

(30) into (28), the mathematical expression for the modified SCM with the reaction control step for solid phase is represented by (31):

$$\frac{\partial X}{\partial t} = \alpha (C_s)^c (1 - X) \exp\left(\frac{-\gamma_o \exp\left(\frac{F}{RH}\right) X}{RT}\right)$$
$$\times \frac{3bkC_{SO}Y}{\rho_B r}(1 - X)^{2/3}. \tag{31}$$

Table 1 shows that using the newly developed modified SCM (Combination VIII), the RMSE between simulated and experimental data was further reduced to less than 5%, indicating that the model now gives a very good prediction of the experimental data. In addition, Figures 2 to 5 show the comparison between simulated data to the experimental data for the desulphurization reaction at various process conditions. Again, the results show very good agreement between simulated and experimental data. To further validate the model, a parity plot between all experimental versus simulated points was given in Figure 6. This plot shows that a small amount of predicted data deviates far from the experimental data. This result could be due to experimental error or due to fixing the coefficient of diffusion D_{eo} as a constant value. As the formation of solid product gradually increases and changes with time, D_{eo} may not be a constant. However, apart from the few points, most of the points were found to fall within an error of 5%.

5 Conclusion

In this present work, kinetic modeling of flue gas desulphurization using CaO/CaSO$_4$/coal fly ash sorbent at a low reaction temperature was reported. In the development of the mathematical model, the original equation for shrinking un-reacted-core model with chemical reaction as the rate limiting step was coupled with surface coverage factor to take into account the diffusion controlling step at the later period of reaction. On the other hand, this study has

proven that the FGD reaction is initially controlled by reaction rate and became ash-diffusion limiting due to the gradual increase in solid product production. Moreover, the activation energy for diffusion was found to be higher than that of the reaction, indicating that physically, the chemical pathway is more feasible and occurs more easily. In contrast, the orders of reaction for SO_2 (g) and NO (g) were found to be 1 and 0.73, respectively. This method was found successful in predicting the whole duration of the desulphurization reaction, yielding an error between simulated and experimental data of less than 5%.

Nomenclature

FGD	Flue Gas Desulphurization
SCM	Shrinking Core Model
BET	Brunauer-Emmett-Teller analysis
A_s	Transversal bed section, m^2
b	Stoichiometric number
C_{SO}	Concentration of SO_2, mol m^{-3}
C_S	Concentration of SO_2, ppm
C_{NO}	Concentration of NO, ppm
D_e	Effective diffusivity, $m^2 s^{-1}$
E_a	Chemical reaction activation energy, J mol^{-1}
E_{diff}	Activation energy for product layer diffusion, J mol^{-1}
E_{gas}	Activation energy for gas film diffusion, J mol^{-1}
F	Fitting parameter defined in (25)
k	Chemical kinetic constant, m s^{-1}
k_g	Gaseous kinetic constant, m s^{-1}
L	Total fixed-bed length, m
M	Molecular weight of SO_2, g
n	Initial molar flow rate of SO_2, mol s^{-1}
R	Gas constant, J mol^{-1} K^{-1}
r	Radius of unreacted core, m
r_s	Reaction rate, mol $m^{-2} s^{-1}$
RH	Relative humidity
Se	Specific surface area of sorbent, m^2 g^{-1}
t	Reaction time, s
V_R	Volume of reaction bed, m^3
w	Sorbent weight in bed, g
X	Dimensionless sorbent conversion
Y	Dimensionless SO_2 concentration
z	Dimensionless length position

Greek Letters

ε_b	Reaction bed porosity
ρ_B	Sorbent density, mol m^{-3}
τ	Tort, s
θ	Surface coverage factor
α	Pre-exponential constant
γ	Pre-exponential constant

Subscript

o	Initial condition

Superscript

c, g, m, p, q	Order for the effect of the respective parameters

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