

Article

Subscriber access provided by NATIONAL TAIWAN UNIV

## Kinetic Model for the Reaction of Ca(OH)/Fly Ash Sorbents with SO at Low Temperatures

Chiung-Fang Liu, Shin-Min Shih, and Ren-Bin Lin

Ind. Eng. Chem. Res., 2004, 43 (15), 4112-4117 • DOI: 10.1021/ie030840x

Downloaded from http://pubs.acs.org on November 24, 2008

### More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 2 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML



# Kinetic Model for the Reaction of Ca(OH)<sub>2</sub>/Fly Ash Sorbents with SO<sub>2</sub> at Low Temperatures

#### Chiung-Fang Liu, Shin-Min Shih,\* and Ren-Bin Lin

Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

Sorbents prepared with different Ca(OH)<sub>2</sub>/fly ash weight ratios were reacted with SO<sub>2</sub> under conditions similar to those in the bag filters in the spray-drying flue gas desulfurization system. The reaction kinetics was well described by a generalized surface coverage model developed in this study. The model assumes that the sorbent was made up of plate grains and the rate was controlled by the chemical reaction on the grain surface and takes into account the variation in sorbent Ca molar content ( $M^{-1}$ ) and the surface coverage byproducts. The effect of Ca(OH)<sub>2</sub>/fly ash weight ratio on the reaction was represented by the effects of the initial specific surface area ( $S_{g0}$ ) and  $M^{-1}$  of the sorbent on the kinetic parameters. Under the same reaction conditions, the sorbents with weight ratios  $\geq 30/70$  had about the same initial reaction rate per unit surface area of the sorbent; their ultimate conversions increased linearly with increasing  $S_{g0}$ , being independent of  $M^{-1}$ . The effects of relative humidity, SO<sub>2</sub> concentration, and temperature on the reaction were unaffected by the Ca(OH)<sub>2</sub>/fly ash ratio. The results of this study are useful to the design and operation of the dry and semidry processes using Ca(OH)<sub>2</sub>/fly ash sorbents to remove SO<sub>2</sub> from the flue gas.

#### Introduction

Abatement of  $SO_2$  emission from power plants is important for environmental protection. Many flue gas desulfurization (FGD) processes are available for the reduction of  $SO_2$  emission. The dry and semidry FGD processes have the advantages of lower capital cost and easier waste treatment in comparison with the wet processes commonly adopted in power plants; however, the conversion of the sorbent, which is mostly hydrated lime [Ca(OH)<sub>2</sub>], in the dry and semidry processes is low.

Many researchers have shown that sorbents prepared from hydrated lime and fly ash have higher SO<sub>2</sub> captures and Ca utilizations than hydrated lime alone has.<sup>1–14</sup> The sorbents were prepared by slurrying hydrated lime and fly ash in water for a certain period of time and drying the slurry subsequently. Fly ash is the solid waste generated by coal-fired power plants. Thus, the successful use of this kind of sorbent can reduce not only the cost of sorbent but also the cost of waste treatment for coal-fired power plants. The structural properties and the reactivities toward SO<sub>2</sub> for Ca(OH)<sub>2</sub>/fly ash sorbents have been reported to be affected by sorbent preparation conditions, such as the type of fly ash, Ca-(OH)<sub>2</sub>/fly ash weight ratio, water/solid ratio, the type of additive, hydration temperature, and hydration time.

The literature on the kinetic model for the reaction of  $Ca(OH)_2$ /fly ash sorbents with  $SO_2$ , however, is scarce. Garea et al.<sup>11</sup> studied the sulfation of such sorbents (1/3 weight ratio) and proposed a kinetic model based on the nonideal surface adsorption model.<sup>15</sup> Recently, we reported a surface coverage model for sorbents prepared with a weight ratio of 70/30.<sup>13</sup>

In this work, the effect of  $Ca(OH)_2/fly$  ash weight ratio on the kinetics of the reaction of  $Ca(OH)_2/fly$  ash sorbents with SO<sub>2</sub> was investigated, with the aim to develop a kinetic model for sorbents prepared with different weight ratios.

Table 1. Ca(OH)<sub>2</sub>/Fly Ash Weight Ratios, Sorbent Weights per Mole of Ca, True Densities, BET Specific Surface Areas, and Values of  $k_1$  and  $k_2^{-1}$  in eq 1 for Ca(OH)<sub>2</sub>/Fly Ash Sorbents<sup>*a*</sup>

| Ca(OH)2/fly ash<br>wt ratio  | M<br>(g sorbent/<br>mol Ca)         | ρ <sub>g</sub><br>(g/mL)                     | S <sub>g0</sub><br>(m²/g)                   | $k_1$ (min <sup>-1</sup> )  | $k_{2}^{-1}$   |
|--|-------------------------------------|--|---|---|--|
| raw Ca(OH) <sub>2</sub><br>100/0<br>90/10<br>70/30<br>50/50<br>30/70 | 75<br>76<br>86<br>110<br>163<br>252 | 2.29<br>2.31<br>2.36<br>2.43<br>2.41<br>2.38 | 9.6<br>11.8<br>19.8<br>38.0<br>38.7<br>27.5 | $\begin{array}{c} 0.032 \\ 0.049 \\ 0.115 \\ 0.165 \\ 0.329 \\ 0.354 \end{array}$ | $\begin{array}{c} 0.195\\ 0.241\\ 0.413\\ 0.620\\ 0.752\\ 0.694\\ \end{array}$ |

 $^a$  Slurrying conditions: 65 °C, L/S = 10/1, and 16 h. Reaction conditions: 60 °C, 70% RH, and 1000 ppm SO<sub>2</sub>.

#### **Experimental Section**

The Ca(OH)<sub>2</sub> reagent, fly ash, sorbent preparation procedure, and experimental setup and procedure for sulfation experiments used in this work were the same as those described in Liu et al.<sup>13</sup> and Lin et al.<sup>14</sup> Sorbents with different Ca(OH)<sub>2</sub>/fly ash weight ratios, as those listed in Table 1, were prepared at a water/ solid weight ratio of 10/1, a slurrying temperature of 65 °C, and a slurrying time of 16 h. The sorbents were reacted with SO<sub>2</sub> mainly under the conditions of 60 °C, 70% relative humidity (RH), and 1000 ppm SO<sub>2</sub>.

The conversion, *X*, of a reacted sample was defined as its  $SO_3^{2-}/Ca^{2+}$  molar ratio. The  $SO_3^{2-}$  content in a sample was determined by iodometric titration, and the  $Ca^{2+}$  content by EDTA titration. For each Ca(OH)<sub>2</sub>/fly ash weight ratio, the Ca<sup>2+</sup> molar content in the sorbent was determined by EDTA titration, and its reciprocal, *M*, the initial sorbent weight per mole of Ca, is listed in Table 1. The *M* value increases as the Ca(OH)<sub>2</sub>/fly ash weight ratio decreases.

The characterization of the Ca(OH)<sub>2</sub>/fly ash sorbents has been reported in our recent work.<sup>14</sup> The sorbents contained calcium silicate hydrates, which were formed during the sample preparation period. The amounts of

<sup>\*</sup> To whom correspondence should be addressed. Tel: 886-2-23633974. Fax: 886-2-23623040. E-mail: smshih@ ccms.ntu.edu.tw.



**Figure 1.** Effect of Ca(OH)<sub>2</sub>/fly ash weight ratio on the reaction of Ca(OH)<sub>2</sub>/fly ash sorbents with SO<sub>2</sub>. Slurrying conditions: 65 °C, L/S = 10/1, and 16 h. Reaction conditions: 60 °C, 70% RH, and 1000 ppm SO<sub>2</sub>.

calcium silicate hydrates in sorbents with 70/30 to 30/ 70 ratios were more than those in sorbents with 90/10 and 10/90 ratios. The mean particle diameters of the sorbents with 70/30 to 10/90 ratios were in the range of  $9-35 \,\mu$ m, and those of raw Ca(OH)<sub>2</sub>, slurried Ca(OH)<sub>2</sub>, and the sorbents with a 90/10 ratio were in the range of  $4-7 \,\mu$ m. All the Ca(OH)<sub>2</sub>/fly ash sorbents were mesoporous materials; their specific surface areas and pore volumes were larger than those of Ca(OH)<sub>2</sub> or fly ash alone. The BET specific surface area,  $S_{g0}$ , of each sorbent is listed in Table 1.

#### **Results and Discussion**

Effect of Sorbent Ca(OH)<sub>2</sub>/Fly Ash Ratio on the Reaction. The experimental results for the reaction of the sorbents with SO<sub>2</sub> are shown in Figure 1 in terms of conversion X versus time t. As shown in Figure 1, the sorbent reactivity increases with decreasing Ca-(OH)<sub>2</sub>/fly ash ratio except the sorbents with ratios of 50/ 50 and 30/70; the latter sorbent is slightly less reactive than the former. The reaction of each sorbent is seen to stop at an ultimate conversion after about a 20 min reaction time. The ultimate conversion of the sorbent with a ratio of 10/90 exceeds unity; this is because the contribution of the reactive compounds of Na, K, and Mg other than Ca present in the fly ash particles was also included in the calculation of conversion.

**Kinetic Model.** The foregoing results show that all the sorbents have similar reaction behavior that the reaction is fast in the initial stage and then levels off abruptly. Among the sorbents,  $Ca(OH)_2^{16,17}$  and the Ca- $(OH)_2$ /fly ash sorbent with a ratio of 70/30<sup>13</sup> have been subjected to extensive kinetic studies, and their reaction kinetics have been found to be well described by the surface coverage model proposed by Shih et al.<sup>18</sup>

The hypotheses of the surface coverage model are that the sorbent is made up of plate grains and that the reaction rate 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 an ultimate conversion when its reacting surface is fully covered by the products.

The surface coverage model proposed in the previous studies <sup>13,16–18</sup> is for the sorbents which have the same

Ca molar content. The model can be generalized to describe the reaction of the sorbents which have different Ca molar contents.

The reaction rate of a sorbent per unit initial surface area,  $r_{S}$ , can be expressed as

$$r_{\rm s} = k_{\rm S} M^{-a} \Phi \tag{1}$$

where  $k_s$  is a function of temperature, concentrations of reacting gas species, and relative humidity;  $M^{-1}$  is the Ca molar content in the sorbent and the index *a* represents the effect of Ca content on the sorbent reactivity; and  $\Phi$  is the fraction of the surface area which is not covered byproducts. The rate of conversion of the sorbent is

$$dX/dt = S_{g0}Mr_{S} = S_{g0}k_{s}M^{1-a}\Phi$$
 (2)

where  $S_{\rm g0}$  is the initial specific surface area of the sorbent.

The change of  $\Phi$  with reaction time depends on the reaction rate, the content of Ca, and the way by which the products deposit on the surface. The effect of Ca content on  $\Phi$  can be seen from Figure 1. Figure 1 shows that the sorbent has a higher initial rate of conversion when its Ca(OH)<sub>2</sub>/fly ash ratio is lower (that is, its *M* value is larger), but it reaches the ultimate conversion no later. This fact indicates that the rate of change of  $\Phi$  increased with increasing *M*. Thus, one may assume that

$$-\mathrm{d}\Phi/\mathrm{d}t = k_{\mathrm{P}}k_{\mathrm{s}}M^{0}\Phi \tag{3}$$

where  $k_{\rm P}$  is a proportional constant, which may be also a function of temperature, concentrations of reacting gas species, and relative humidity, and *b* is an index representing the effect of *M*. If  $k_{\rm s}$  and  $k_{\rm p}$  do not vary with time, eq 3 can be integrated to get

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

where

$$k_1 = k_{\rm S} S_{\rm g0} M^{1-a} \tag{5}$$

$$k_2 = k_{\rm P} M^{a+b-1} / S_{\rm g0} \tag{6}$$

By substitution of eq 4 into eq 2, one can integrate eq 2 to obtain the relation between conversion and time

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

From eq 7 one can see that the ultimate conversion is equal to  $k_2^{-1}$ . From the differential form of eq 7

$$dX/dt = k_1(1 - k_2X)$$
(8)

it is obvious that the initial rate of conversion is equal to  $k_1$ .

In the previous studies, <sup>13,16–18</sup> the same equation as eq 7 was obtained for X as a function of t, but the  $k_1$  and  $k_2$  equations were defined as the case that a and b in eqs 5 and 6 equal zero.

The two parameters,  $k_1$  and  $k_2$ , in eq 7 can be obtained by nonlinear least-squares fitting of the equation to the experimental *X* versus *t* data. Table 1 summarizes the



**Figure 2.** Plot of  $k_1$  versus  $S_{g0}M$ . Slurrying conditions: 65 °C, L/S = 10/1, 16 h. Reaction conditions: 60 °C, 70% RH, and 1000 ppm SO<sub>2</sub>.

Table 2. Values of  $k_1$  and  $k_2^{-1}$  for Ca(OH)<sub>2</sub> (M = 74 g/mol Ca,  $S_{g0} = 10.3$  m<sup>2</sup>/g) and the Sorbent with a Ca(OH)<sub>2</sub>/Fly Ash Weight Ratio of 30/70 (M = 248 g/mol Ca,  $S_{g0} = 25.6$  m<sup>2</sup>/g) Reacted with SO<sub>2</sub>

| sorbent                      | T (K) | RH (%) | <i>y</i> (ppm) | $k_1 \ (min^{-1})$ | $k_{2}^{-1}$ |
|------------------------------|-------|--------|----------------|--------------------|--------------|
| Ca(OH) <sub>2</sub>          | 333   | 50     | 1000           | 0.033              | 0.140        |
|                              | 333   | 70     | 1000           | 0.040              | 0.186        |
|                              | 333   | 80     | 1000           | 0.049              | 0.255        |
| Ca(OH) <sub>2</sub> /fly ash | 333   | 30     | 1000           | 0.163              | 0.330        |
| C C                          | 333   | 50     | 1000           | 0.220              | 0.527        |
|                              | 333   | 70     | 1000           | 0.314              | 0.672        |
|                              | 333   | 80     | 1000           | 0.355              | 0.787        |
|                              | 333   | 70     | 5000           | 0.435              | 0.694        |
|                              | 353   | 70     | 1000           | 0.466              | 0.694        |

values of  $k_1$  and  $k_2^{-1}$  thus obtained. The curves plotted in Figure 1 using eq 7 show that the experimental data are well described by eq 7.

Effect of Ca(OH)<sub>2</sub>/Fly Ash Ratio on  $k_1$  and  $k_2$ . From Table 1, one can see that the values of  $k_1$  and  $k_2^{-1}$  vary from sorbent to sorbent, indicating that they are affected by the Ca(OH)<sub>2</sub>/fly ash weight ratio. However, eqs 5 and 6 predict that the effect of the Ca(OH)<sub>2</sub>/fly ash weight ratio on the values of  $k_1$  and  $k_2^{-1}$  is entirely represented by the effects of  $S_{g0}$  and M. These correlations can be confirmed and the parameters a and b in the equations can be determined using the data of  $k_1$ ,  $k_2$ ,  $S_{g0}$ , and M. In the following analysis, the data listed in Table 1 and those listed in Table 2 for another batch of Ca(OH)<sub>2</sub> and another batch of the sorbent with a Ca-(OH)<sub>2</sub>/fly ash ratio of 30/70 are taken into consideration. The data given by Ho et al.<sup>16</sup> for Ca(OH)<sub>2</sub> (M = 74 g/mol,  $S_{g0} = 10.0$  m<sup>2</sup>/g) are also included.

The  $k_1$  value for each sorbent is plotted against its  $S_{g0}M$  in Figure 2. Except the data for the sorbent with a 10/90 ratio,  $k_1$  and  $S_{g0}M$  follow the linear relationship given by eq 5 when a = 0. The linear least-squares fitting line in Figure 2 gave

$$k_1 \,({\rm min}^{-1}) = [(5.00 \pm 0.23) \times 10^{-5}]S_{\rm g0}M$$
 (9)

with a correlation coefficient of 0.992. The standard error of the slope of the line is also indicated in eq 9. This result indicates that under the same reaction conditions all the sorbents except the one with a 10/90 ratio have about the same  $k_{\rm S}$  value or the same initial rate per unit surface area of the sorbent according to eq 1. Moreover, according to eqs 8 and 9, the initial



**Figure 3.** Plot of  $k_2^{-1}$  versus  $S_{g0}$ . Slurrying conditions: 65 °C, L/S = 10/1, 16 h. Reaction conditions: 60 °C, 70% RH, and 1000 ppm SO<sub>2</sub>.

rate of conversion for a sorbent is proportional to its  $S_{\rm g0}$  and M.

As shown in Figure 3, there is a linear relationship between  $k_2^{-1}$  and  $S_{\rm g0}$ , except the data for the sorbent with 10/90 ratio. The linear least-squares fitting line in Figure 3 gave

$$k_2^{-1} = [(2.04 \pm 0.12) \times 10^{-2}]S_{g0}$$
 (10)

with a correlation coefficient of 0.946. This result indicates that  $k_2$  is independent of M. Thus, b in eq 6 must be unity because a in eq 5 has been found to be zero.

According to eq 7,  $k_2^{-1}$  equals the ultimate conversion. Therefore, eq 10 implies that the ultimate conversion of a sorbent is proportional to its  $S_{g0}$  and independent of its M.

The reason that the  $k_1$  or  $k_2^{-1}$  value for the sorbent with a 10/90 ratio could not be predicted by eq 9 or 10 is thought to be due to the excess of the fly ash content; this sorbent contained much more reactive constituents other than Ca(OH)<sub>2</sub> and calcium silicate hydrates than the sorbents with ratios  $\geq 30/70$ .

**Discussion on Ultimate Conversion.** For a sorbent made up of plate grains, the conversion of the sorbent can be expressed as<sup>19</sup>

$$X = \frac{\Delta r}{r_0} \tag{11}$$

where  $r_0$  is the initial half-thickness of the plate and  $\Delta r$  is the thickness of the outer layer of the original grain that has been reacted.  $r_0$  can be estimated by

$$r_0 = \frac{1}{\rho_{\rm g} S_{\rm g0}} \tag{12}$$

where  $\rho_g$  is the true density of the sorbent. Combining eqs 11 and 12 gives

$$X = \rho_{\rm g} S_{\rm g0} \Delta r \tag{13}$$

When the reaction stops due to the complete coverage of the reactive surface, X and  $\Delta r$  reach the maximum values,  $X_{\rm m}$  and  $\Delta r_{\rm m}$ , and

$$X_{\rm m} = \rho_{\rm g} S_{\rm g0} \Delta r_{\rm m} \tag{14}$$



**Figure 4.** Effect of the RH on the reaction of Ca(OH)<sub>2</sub>/fly ash (30/70 wt ratio, M = 248 g/mol Ca) sorbent. Slurrying conditions: 65 °C, L/S = 10/1, and 16 h. Reaction conditions: 60 °C and 1000 ppm SO<sub>2</sub>.

Comparing eqs 6 and 14 gives

$$(k_{\rm p}M^{a+b-1})^{-1} = \rho_{\rm g}\Delta r_{\rm m}$$
(15)

Thus, the inverse of  $k_p M^{a+b-1}$  can be interpreted as the maximum weight reacted per unit surface area of the sorbent.

According to eq 14,  $X_{\rm m}$  is proportional to  $S_{\rm g0}$  alone only when  $\rho_{\rm g}\Delta r_{\rm m}$  is constant. Thus, the linear relationship between  $X_{\rm m}$  and  $S_{\rm g0}$  represented by eq 10 implies that  $\rho_{\rm g}\Delta r_{\rm m}$  for each sorbent must be about the same. Furthermore, the  $\rho_{\rm g}$ 's of the sorbents, as shown in Table 1, are about the same, being in the range of 2.29 to 2.43 g/cm<sup>3</sup>. Therefore,  $\Delta r_{\rm m}$ , the maximum thickness of the reacted layer, must be about the same for each sorbent also.

**Effects of Reaction Conditions on**  $k_1$  **and**  $k_2$ . Equations 9 and 10 were obtained under the reactions of 60 °C, 70% RH, and 1000 ppm SO<sub>2</sub>. According to Ho et al.<sup>16</sup> and Liu et al.,<sup>13</sup>  $k_1$  and  $k_2$  are also functions of RH, temperature, and SO<sub>2</sub> concentration, but only RH affects  $k_1$  and  $k_2$  significantly.

To know whether the relationship between  $k_1$  or  $k_2$ and  $S_{g0}$  and M is affected by the RH and whether the relationship between  $k_1$  or  $k_2$  and RH is affected by the Ca(OH)<sub>2</sub>/fly ash weight ratio, samples of Ca(OH)<sub>2</sub> (M= 74 g/mol Ca,  $S_{g0}$ =10.3 m<sup>2</sup>/g) and the sorbent with a ratio of 30/70 (M = 248 g/mol Ca,  $S_{g0}$  = 25.6 m<sup>2</sup>/g) were reacted with 1000 ppm of SO<sub>2</sub> at 60 °C and different RHs (30–80% RH). The results for the latter sorbent are shown in Figure 4, indicating that the RH indeed enhances the reaction significantly. The latter sorbent was also reacted at a higher SO<sub>2</sub> concentration(5000 ppm) and a higher temperature(80 °C). The X vs tresults, not shown here, indicated that the increase in SO<sub>2</sub> concentration or temperature increased only mildly the initial rate of conversion, having a negligible effect on the ultimate conversion.

The  $k_1$  and  $k_2$  values obtained for the foregoing reactions, as shown in Table 2, are compared with those already reported for Ca(OH)<sub>2</sub><sup>16</sup> and the Ca(OH)<sub>2</sub>/fly ash sorbent with a 70/30 ratio<sup>13</sup> in terms of  $\ln[k_1/(S_{g0}M)]$ versus RH in Figure 5 and  $\ln[k_2^{-1}/S_{g0}]$  versus ln RH in Figure 6 . According to the correlations given by Liu et al.,<sup>13</sup> these plots are linear for the sorbent with a 70/30 ratio. As can be seen in Figures 5 and 6, the data for each sorbent seem to exhibit a linear trend in general.



**Figure 5.** Relationship between  $k_1$  and relative humidity for sorbents. Other reaction conditions: 60 °C and 1000 ppm SO<sub>2</sub>.



**Figure 6.** Relationship between  $k_2$  and relative humidity for sorbents. Other reaction conditions: 60 °C and 1000 ppm SO<sub>2</sub>.

For  $k_1/(S_{g0}M)$  (Figure 5), the range of the data at each RH is smaller than that for the data considered in Figure 2 (70% RH); however, for  $k_2^{-1}/S_{g0}$  (Figure 6), the range of the data at 80% RH is greater than that for the data considered in Figure 3 (70% RH). These results indicate that the linear relationship between  $k_1$  and  $S_{g0}M$  or between  $k_2^{-1}$  and  $S_{g0}$  is as good as that at 70% RH for RH  $\leq$  70% and that the relationship between  $k_1$  or  $k_2$  and RH is nearly unaffected by the Ca(OH)<sub>2</sub>/fly ash ratio.

The equations representing the effects of RH (30–70% RH), temperature (T, 333–353 K), and SO<sub>2</sub> concentration (y, 1000–5000 ppm) on  $k_1$  and  $k_2$  for the sorbents with weight ratios  $\geq$  30/70 were further derived and the parameters in the equations were determined by multiple regression,<sup>16</sup> using the data shown in Tables 1 and 2, Figures 5 and 6, and those at 70% RH, 70 and 80 °C, and 3000 and 5000 ppm SO<sub>2</sub> given in the article by Liu et al. <sup>13</sup> The resulting  $k_1$  and  $k_2^{-1}$  equations are

$$k_1 \text{ (min}^{-1}) = (2.15 \times 10^{-4}) S_{g0} M e^{0.022 \text{RH}} y^{0.10} e^{-10000/RT}$$
(16)

$$k_2^{-1} = (2.33 \times 10^{-4}) S_{g0} \text{RH}^{1.05}$$
 (17)

The 95% confidence intervals for the parameters in the above equations are (2.15  $\times$   $10^{-4})e^{\pm5.76}$  min^{-1},



Figure 7. Comparison of the calculated and experimental conversion values.

 $0.022 \pm 0.007, 0.10 \pm 0.20, \text{ and } -10000 \pm 16000 \text{ J/mol},$ respectively, for eq 16, and  $(2.33 \times 10^{-4})e^{\pm 3.19}$  and 1.05  $\pm$  0.78 for eq 17. The standard deviations of  $k_1$  and  $k_2^{-1}$ from the values calculated by eqs 16 and 17 are 0.04  $min^{-1}$  and 0.12, respectively. The lines plotted in Figures 5 and 6 show the agreement of eqs 16 and 17 with the data.

In Figure 7, conversions calculated by eq 7 together with eqs 16 and 17 are compared with the experimental results obtained for the sorbents and reaction conditions mentioned in the above paragraph. The comparison shows that both conversions are in agreement with a standard deviation of 0.09. This agreement is considered to be satisfactory for the Ca(OH)<sub>2</sub>/fly ash sorbents, which have complex sorbent compositions and reaction behaviors.

The rate-controlling step for the reaction of sorbents is thought to be the dissolution of the Ca-containing solid reactants proceeding through the reaction with the acid formed by the SO<sub>2</sub> and H<sub>2</sub>O molecules adsorbed on the sorbent surface. Raising the RH increases the amount of water adsorbed and hence the amount of acid formed and the amount of solid reactants dissolved. A greater amount of adsorbed water also provides a wider range for the product molecules to deposit and thus would result in a lower rate of covering the reaction surface.<sup>13,16,17</sup> Therefore, the RH showed a significant effect on the reaction rate and the ultimate conversion. The amount of SO<sub>2</sub> molecules dissolved in the water layer may be limited by the amount of the adsorbed water; thus, the reaction would be insensitive to the gasphase SO<sub>2</sub> concentration. The mild effect of temperature on the reaction rate may be due to the fact that as the temperature increases, the chemical reaction rate constants increase, whereas the amounts of water and SO<sub>2</sub> adsorbed decrease. Although the amount of water adsorbed decreased with increasing temperature, the thickness of the water layer was mainly function of RH and nearly independent of temperature, according to the measurements by Liu et al.<sup>13</sup> This may be the reason that the ultimate conversion was mainly affected by the RH

When the reaction conditions vary with time, like the case encountered in industrial FGD processes, the differential form of the model can be used. Substituting eqs 5 and 6 into eqs 2 and 3 gives

$$dX/dt = k_1 \Phi \tag{18}$$

$$\mathrm{d}\Phi/\mathrm{d}t = -k_1 k_2 \Phi \tag{19}$$

Substituting eqs 16 and 17 into eqs 18 and 19, the latter two equations can be integrated to obtain X if the variations of reaction conditions with time are known.

#### Conclusion

From the above analyses, we can conclude that for a Ca(OH)<sub>2</sub>/fly ash sorbent prepared with a weight ratio  $\geq$  30/70, its reaction with SO<sub>2</sub> at low temperatures can well be described by the generalized surface coverage model developed in this study. The model assumes that the sorbent was made up of plate grains and the rate was controlled by the chemical reaction on the grain surface and takes into account the variation in sorbent Ca molar content  $(M^{-1})$  and the surface coverage byproducts. The effect of Ca(OH)<sub>2</sub>/fly ash weight ratio on the reaction kinetics was represented by the effects of the  $S_{g0}$  and M of the sorbent on the kinetic parameters. Under the same reaction conditions, the sorbents with weight ratios  $\geq$  30/70, including Ca(OH)<sub>2</sub> alone, had about the same initial rate per unit surface area of the sorbent and their ultimate conversions, being independent of the *M* value, increased linearly with increasing  $S_{g0}$ . The effects of relative humidity, SO<sub>2</sub> concentration, and temperature on the reaction were unaffected by the Ca(OH)<sub>2</sub>/fly ash ratio. The initial conversion rate and ultimate conversion of a sorbent increased significantly with increasing relative humidity. Temperature and SO<sub>2</sub> concentration had mild effects on the initial conversion rate and negligible effects on the ultimate conversion. The results of this study are useful to the design and operation of the dry and semidry processes using  $Ca(OH)_2/fly$  ash sorbents to remove  $SO_2$  from the flue gas.

#### Acknowledgment

This research was supported by the National Science Council of Republic of China, Taiwan.

#### Nomenclature

- a = index of M<sup>-1</sup> in eq 1, dimensionless
- b = index of M in eq 3, dimensionless
- $k_{\rm P}$  = constant defined by eq 3, m<sup>2</sup>mol<sup>*a*+*b*-1</sup>/g<sup>*a*+*b*</sup>
- $k_{\rm S}$  = constant defined by eq 1, g<sup>a</sup>mol<sup>1-a</sup>/(min m<sup>2</sup>)
- $k_1 = k_S S_{g0} M^{1-a}$ , min<sup>-1</sup>  $k_2 = k_P M^{a+b-1}/S_{g0}$ , dimensionless
- M = initial weight of solid per mol of Ca, g/mol
- R = gas constant, 8.314 J/mol K
- RH = relative humidity, %
- $r_0$  = initial half-thickness of a plate grain, m
- $r_{\rm S}$  = reaction rate of solid, mol/(min m<sup>2</sup>)
- $\Delta r$  = thickness of reacted layer of a grain, m
- $\Delta r_{\rm m}$  = the maximum value of  $\Delta r$ , m
- $S_{g0}$  = initial specific surface area of solid, m<sup>2</sup>/g T = reaction temperature, K
- t = time, min
- X = conversion, dimensionless
- $X_{\rm m}$  = the maximum value of X, dimensionless
- $y = SO_2$  concentration, ppm

 $\rho_{\rm g}$  = true density of sorbent, g/mL

#### **Literature Cited**

(1) Jozewicz, W.; Rochelle, G. T. Fly ash recycle in dry scrubbing. *Environ. Prog.* **1986**, *5*, 219–224.

(2) Ho, C. S. Reaction of  $Ca(OH)_2$  and fly  $ash/Ca(OH)_2$  slurry with SO<sub>2</sub>. MS. Engr. Thesis, Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, R. O. C., 1987.

(3) Jozewicz, W.; Jorgensen, C.; Chang, J. C. S.; Sedman, C. B.; Brna, T. Development and pilot plant evaluation of silicaenhanced lime sorbents for dry flue gas desulfurization. *J. Air Pollut. Control Assoc.* **1988**, *38*, 796–805.

(4) Jozewicz, W.; Chang, J. C. S.; Sedman, C. B.; Brna, T. Silicaenhanced sorbents for dry injection removal of SO<sub>2</sub> from flue gas. *J. Air Pollut. Control Assoc.* **1988**, *38*, 1027–1034.

(5) Martinez, J. C.; Izquierdo, J. F.; Cunill, F.; Tejero, J.; Querol, J. Reactivation of fly ash and  $Ca(OH)_2$  mixtures for  $SO_2$  removal

of flue gas. *Ind. Eng. Chem. Res.* **1991**, *30*, 2143–2147. (6) Ho, C. S.; Shih, S. M. Ca(OH)<sub>2</sub>/fly ash sorbents for SO<sub>2</sub>

removal. *Ind. Eng. Chem. Res.* **1992**, *31*, 1130–1135. (7) Ho, C. S.; Shih, S. M. Characteristic and SO<sub>2</sub> capture

capacities of sorbents prepared from products of spray-drying flue gas desulfurization. *Can. J. Chem. Eng.* **1993**, *71*, 934–939.

(8) Davini, P. Investigation of flue gas desulfurization by fly ash and calcium hydroxide mixtures. *Resour. Conserv. Recycl.* **1995**, *15*, 193–202.

(9) Sanders, J. R.; Keener, T. C.; Wang, J. Heated fly ash/hydrated lime slurries for  $SO_2$  removal in spray dryer absorbers. *Ind. Eng. Chem. Res.* **1995**, *34*, 302–307.

(10) Garea, A.; Fernandez, J.; Viguri, J. R.; Ortiz, M. I., Renedo; M. J.; Irabien, A. Fly ash/calcium hydroxide mixtures for  $SO_2$  removal: structural properties and maximum Yield. *Chem. Eng. J.* **1997**, *66*, 171–179.

(11) Garea, A.; Viguri, J. R.; Irabien, A. Kinetics of the flue gas desulfurization at low temperature: fly ash/calcium (3/1) sorbent behavior. *Chem. Eng. Sci.* **1997**, *52*, 715–732.

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

(13) Liu, C. F.; Shih, S. M.; Lin, R. B. Kinetics of the reaction of Ca(OH)<sub>2</sub>/fly ash sorbent with SO<sub>2</sub> at low temperatures. *Chem. Eng. Sci.* **2002**, *57*, 93–104.

(14) Lin, R. B.; Shih, S. M.; Liu, C. F. Structural properties and reactivities of  $Ca(OH)_2/fly$  ash sorbents for flue gas desulfurization. *Ind. Eng. Chem. Res.* **2003**, *42*, 1350–1356.

(15) Irabien, A.; Cortabitarte, F.; Ortiz, M. I. Kinetics of flue gas desulfurization at low temperature: nonideal surface adsorption model. *Chem. Eng. Sci.* **1992**, *47*, 1533–1543.

(16) Ho, C. S.; Shih, S. M.; Liu, C. F.; Chu. H. M.; Lee, C. D. Kinetics of the sulfation of Ca(OH)<sub>2</sub> at low temperatures. *Ind. Eng. Chem. Res.* **2002**, *41*, 3357–3364.

(17) Liu, C. F.; Shih, S. M. A surface coverage model for the reaction of  $Ca(OH)_2$  with  $SO_2$  at low temperatures. *J. Chin. Inst. Chem. Engrs.* **2002**, *33*, 407–413.

(18) Shih, S. M.; Ho, C. S.; Song, Y. S.; Lin, J. P. Kinetics of the reaction of  $Ca(OH)_2$  with  $CO_2$  at low temperature. *Ind. Eng. Chem. Res.* **1999**, *38*, 8, 1316–1322.

(19) Szekely, J.; Evans, J. W.; Sohn, H. Y. *Gas-solid reactions*; Academic Press: New York, 1976.

Received for review November 21, 2003 Revised manuscript received May 17, 2004

Accepted May 20, 2004

IE030840X