

# Kinetic Analysis of Iron Blast Furnace Slag/Hydrated Lime Sorbents with SO<sub>2</sub> at Low Temperatures

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**Abstract**— A differential fixed-bed reactor was employed to study the reaction between iron blast furnace slag (BFS)/hydrated lime (HL) sorbent and SO<sub>2</sub> under conditions similar to those in the bag filters of a spray-drying flue gas desulfurization system. The BFS/HL sorbent was prepared at a weight ratio of 30/70 with a slurring time of 16 h and a slurring temperature of 65°C. The sorbent was highly reactive towards SO<sub>2</sub> as compared with hydrated lime alone. Increasing the relative humidity of the gas significantly increased the initial reaction rate and the ultimate Ca utilization of the sorbent. The temperature and SO<sub>2</sub> concentration had slight effects on the initial reaction rate and negligible effects on the ultimate Ca utilization. The reaction kinetics of the sorbent with SO<sub>2</sub> was well described by the surface coverage model, which assumes that the sulfation rate is controlled by the chemical reaction on the sorbent grain surface and takes into account the surface covered by the product. The results of this study are useful for the design and operation of dry or semidry processes that use BFS/HL sorbents to remove SO<sub>2</sub> from flue gas.

**Key Words** : Flue gas desulfurization, Ca(OH)<sub>2</sub>, Iron blast furnace slag, Kinetics, Mathematical modelling, Multiphase reaction, Pollution

## INTRODUCTION

Dry and semidry flue gas desulfurization (FGD) processes have been used in many power plants to reduce SO<sub>2</sub> emissions. These processes have the advantages of low capital cost and easy waste treatment (Miller, 1986; Srivastava and Jozewicz, 2001). However, the utilization of the sorbent, which is mostly hydrated lime (HL), in these processes is low. These processes can be more economical if the sorbent reactivity is raised.

Sorbents prepared from hydrated lime and silica-containing materials, such as fly ash (Garea *et al.*, 1997a, 1997b; Ho, 1987; Ho and Shih, 1992, 1993a; Jozewicz and Rochelle, 1986; Jozewicz *et al.*, 1988a, 1988b; Lin *et al.*, 2003a; Liu, 1999; Liu *et al.*, 2002, 2004a, 2004b), diatomaceous earths (Jozewicz *et al.*, 1988a, 1988b), and silica fume (Chiu, 1989; Kind, 1994; Lin *et al.*, 2003b; Liu, 1999), have been found to be more reactive with SO<sub>2</sub> than hydrated lime. The silica-enhanced lime sorbents were prepared through a hydration process, in which silica reacts with hy-

drated lime to form foil-like calcium silicate hydrates in the presence of water; this reaction is called the "pozzolanic reaction" (Taylor, 1964). It has been confirmed in the previous studies that the pozzolanic reaction, which results in sorbents with large surface areas, is responsible for the enhancement of sorbent reactivities.

Recently, Brodnax and Rochelle (2000) and Liu and Shih (2004a, 2004b, 2004c) reported that iron blast furnace slag (BFS) can also be used to prepare SO<sub>2</sub> reactive sorbents. Iron blast furnace slag, composed mainly of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO, is similar in the constituents to fly ash, but its CaO content is higher. Liu and Shih (2004a, 2004c) confirmed that sorbents prepared from iron blast furnace slag and hydrated lime indeed have greater specific surface areas and higher reactivities than hydrated lime. It was also found that the maximum SO<sub>2</sub> capture for BFS/HL sorbents is higher than that for sorbents prepared with fly ash (Lin *et al.*, 2003a), and that the reaction of the sorbents with SO<sub>2</sub> was well described by a modified surface coverage model.

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Because the sorbent with a BFS/HL ratio of 30/70 was found to have the highest reactivity toward  $\text{SO}_2$  among sorbents with different ratios (Liu and Shih, 2004a, 2004c), we were motivated to undertake a thorough study of the reaction kinetics of this sorbent with  $\text{SO}_2$ . The results of the kinetic study are reported in this work.

## EXPERIMENTAL PROCEDURE

### Preparation of sorbents

The hydrated lime (HL) used in this study was reagent grade  $\text{Ca}(\text{OH})_2$  (purity > 95%, Hayashi Pure Chemical Industries, LTD). The iron blast furnace slag (BFS) was supplied by the China Hi-Ment Corporation, and high fineness slag was used. The chemical composition of the BFS was: 42.00%  $\text{CaO}$ , 33.47%  $\text{SiO}_2$ , 13.78%  $\text{Al}_2\text{O}_3$ , 6.98%  $\text{MgO}$ , 0.39%  $\text{Fe}_2\text{O}_3$ , 0.42%  $\text{SO}_3$ , 1.67% alkalinity, 0.27% sulfite, and 1.67% ignition loss.

HL and BFS, together with 80 g of deionized water, were placed into a 250 mL polypropylene conical flask at a BFS/HL weight ratio of 30/70 and a water/solid weight ratio (L/S) of 10. The flask was then sealed with a rubber stopper at the mouth and inserted into a water bath at 65°C. The slurry was stirred with a magnetic stirrer for 16 h. After slurring ended, the slurry was vacuum dried at 105°C for 8 h. The dry cake was crush into powder and sealed in a bottle before it was used.

### Sulfation test

Experiments on the reaction of the sorbent with  $\text{SO}_2$  were carried out using a differential fixed-bed reactor. The experimental setup and procedure were similar to those employed by Ho and Shih (1992). In this study, an approximately 30 mg sample was used in each run. The gas mixture was comprised of  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$ . The  $\text{SO}_2$  and  $\text{N}_2$  gases were supplied from cylinders, and the  $\text{H}_2\text{O}$  vapor was provided by a water evaporator. Prior to each run, the sample bed was humidified for 30 min with humid  $\text{N}_2$  at a selected relative humidity (*RH*) under which the subsequent sulfation experiment was performed. Following humidification,  $\text{SO}_2$  gas was admitted into the reactor to start the run. The total gas flow rate was 4 L/min (STP). The reaction conditions in this study were 40-80°C, 30-80% *RH*, and 500-5000 ppm  $\text{SO}_2$ .

The utilization of Ca or the conversion,  $X$ , of a reacted sample was defined as its  $\text{SO}_3^{2-}/\text{Ca}^{2+}$  molar ratio. The  $\text{SO}_3^{2-}$  content in a sample was determined by means of iodometric titration, and the  $\text{Ca}^{2+}$  content by means of EDTA titration (Ho and Shih, 1993).

At least two repeated measurements were performed for each set of experimental conditions. The experimental error of conversion was about  $\pm 0.03$ .

In the present study,  $\text{CO}_2$  and  $\text{O}_2$  were not added to make the synthetic flue gas, because our preliminary tests showed that the presence of  $\text{CO}_2$  and  $\text{O}_2$  had a negligible effect on the sulfation of sorbents. Both sulfite and sulfate were formed when  $\text{O}_2$  was present in the gas mixture, but the total conversion of a sorbent in this case was about the same as that in the case without  $\text{O}_2$ .

### Characterization of sorbents

The sorbents were subjected to X-ray diffraction analysis using a Mac Science M03XHF X-ray diffractometer with a Cu target. A Hitachi S-2400 scanning electron microscope was used to observe the sorbent morphology. The sorbent particle size was measured by means of laser diffraction using a Coulter LS-230 analyzer. The BET specific surface area and the pore volume distribution of the sorbent were determined by means of nitrogen adsorption using a Micromeritics ASAP 2010 analyzer.

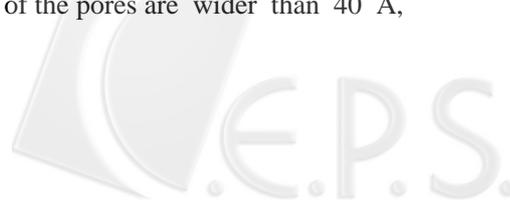
The volume mean particle diameters of  $\text{Ca}(\text{OH})_2$  and BFS were 7.4 and 5.9  $\mu\text{m}$ , respectively. The XRD pattern of the sorbent was illustrated in Liu and Shih (2004c). For the BFS/HL sorbent, the pattern showed characteristic peaks of  $\text{Ca}(\text{OH})_2$  as well as hydration products, calcium silicate hydrates (*e.g.*, ill-crystallized tobermorites), calcium aluminum oxide hydrates ( $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot x\text{H}_2\text{O}$ ), and calcium aluminum silicate hydroxide ( $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$ ). The SEM micrographs of the sorbent can also be found in Liu and Shih (2004c). The particles were composed of foil-like substances and had a highly porous structure.

## RESULTS AND DISCUSSION

### Structural properties

The nitrogen adsorption and desorption isotherms for the BFS/HL sorbent with a ratio of 30/70 are shown in Fig. 1. The sorbent exhibited a type IV isotherm based upon the International Union of Pure and Applied Chemical (IUPAC) classification. The type IV isotherm typically exhibits a hysteresis loop and is characteristic of materials with porosity in the mesopore range. The hysteresis loop for the sorbent has a shape similar to a type H3 loop (IUPAC). The type H3 loop is associated with slit-shaped pores or spaces between plate-like particles.

The pore size distribution of the sorbent was calculated using desorption data. As can be seen from Fig. 2, most of the pores are wider than 40 Å,



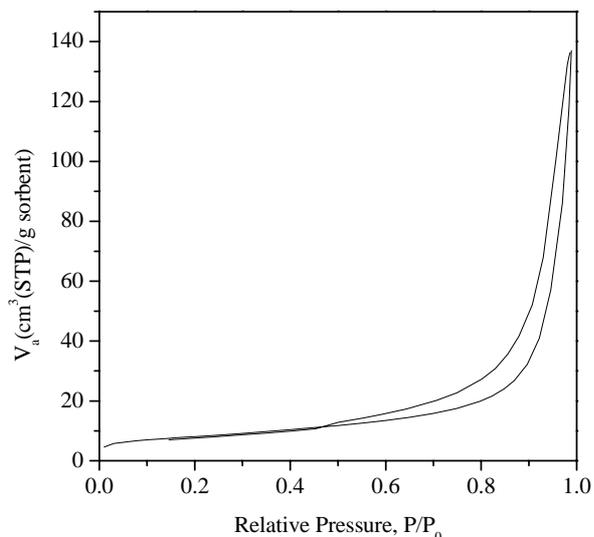


Fig. 1. N<sub>2</sub> adsorption and desorption isotherms for the BFS/HL sorbent with a ratio of 30/70. Slurrying conditions: 65°C, L/S=10/1, and 16 h.

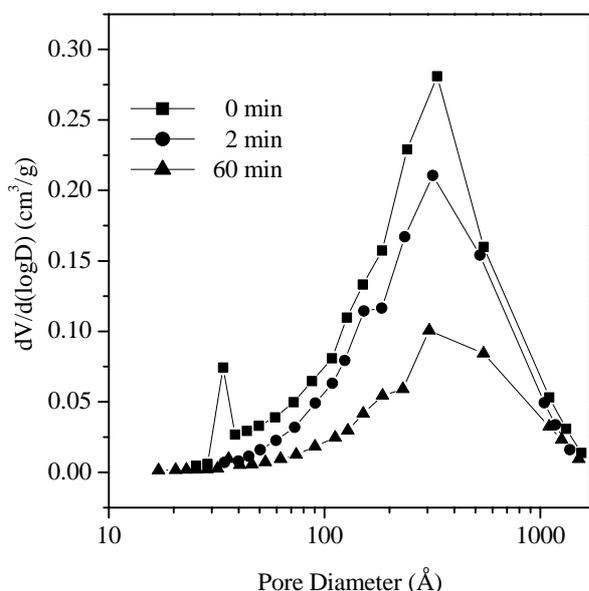


Fig. 2. Pore volume distribution of BFS/HL (30/70 wt. ratio) sorbent reacted at 60°C with 70% RH and 1000 ppm SO<sub>2</sub>; slurrying conditions: 65°C, L/S=10/1, and 16 h.

and the peak pore volume is at a pore diameter of about 300 Å. The volume of the micropores (with a pore width less than 20 Å) was negligible. The pore volume was observed to decrease as the reaction time increased, but the pores had not completely disappeared when the reaction time reached 60 min.

### Effects of the reaction variables

Some typical experimental data for the sulfation of the BFS/HL sorbent are shown in Figs. 3-5 in terms of conversion  $X$  versus time  $t$ . As can be seen from these plots, the reaction was rapid during the initial period, but the conversion leveled off after

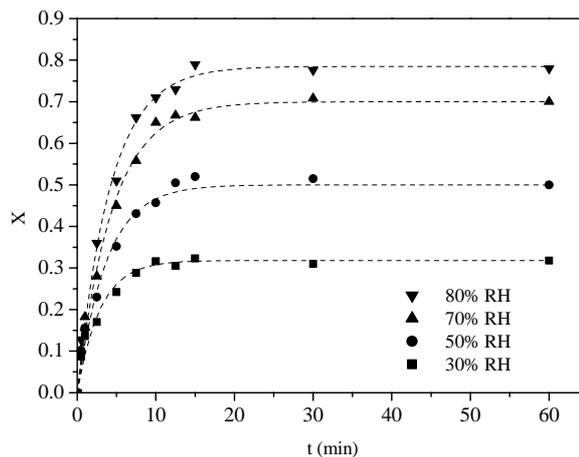


Fig. 3. Effect of the relative humidity on the sulfation of the BFS/HL (30/70 wt. ratio) sorbent. Slurrying conditions: 65°C, L/S=10/1, and 16 h; sulfation conditions: 60°C and 1000 ppm SO<sub>2</sub>.

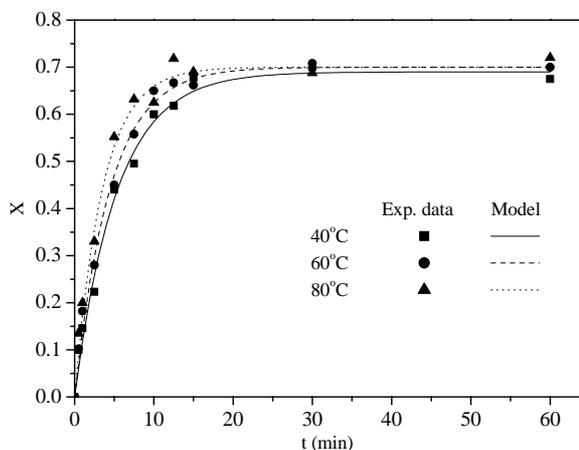
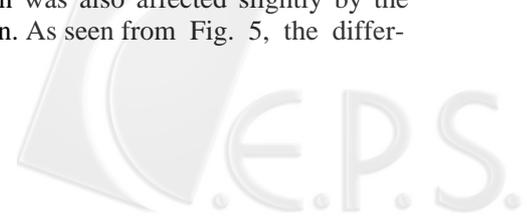


Fig. 4. Effect of the temperature on the sulfation of the BFS/HL (30/70 wt. ratio) sorbent. Slurrying conditions: 65°C, L/S=10/1, and 16 h; sulfation conditions: 70% RH and 1000 ppm SO<sub>2</sub>.

about 15 min, and the sorbent was incompletely converted when the reaction time reached 1 h.

As can be seen from Figs. 3 and 4, the reaction rate during the initial period increased as the reaction temperature or the RH increased, but the effect of the temperature on the overall reaction was mild, and that of the RH became more significant as the reaction proceeded. Increasing the temperature could raise the chemical reaction rate constants but reduce the amounts of water and SO<sub>2</sub> adsorbed. Thus, the effects of the temperature change may have offset each other, resulting in a weak overall effect of the temperature on the reaction. The major factor affecting the reaction was the relative humidity of the gas phase. The initial reaction rate and the ultimate conversion of the sorbent increased significantly as the relative humidity increased.

The reaction was also affected slightly by the SO<sub>2</sub> concentration. As seen from Fig. 5, the differ-



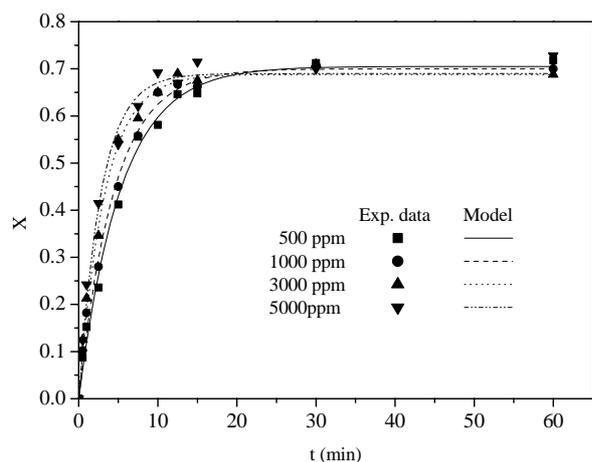


Fig. 5. Effect of the  $\text{SO}_2$  concentration on the sulfation of the BFS/HL (30/70 wt. ratio) sorbent. Slurrying conditions:  $65^\circ\text{C}$ ,  $L/S=10/1$ , and 16 h; sulfation conditions:  $60^\circ\text{C}$  and 70% RH.

ences between the conversions at 500 and 5000 ppm during the initial stage (before 15 min) were higher than the experimental error ( $\pm 0.03$ ), but the differences after 15 min were within the experimental error.

The initial reaction rate and the ultimate conversion (for 1 h) of the BFS/HL sorbent were markedly higher than those of pure  $\text{Ca}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2/\text{fly ash}$  (70/30 wt. ratio) sorbent reacted under the same experimental conditions (Liu *et al.*, 2002). For example, when the conditions were  $60^\circ\text{C}$ , 70% RH, and 1000 ppm  $\text{SO}_2$ , 1 h conversion of the BFS/HL sorbent reached 0.70, which was higher than the values of 0.19 and 0.60 achieved with pure  $\text{Ca}(\text{OH})_2$  and the  $\text{Ca}(\text{OH})_2/\text{fly ash}$  sorbent, respectively.

### Analysis of reaction kinetics

The reaction rate of the BFS/HL sorbent with  $\text{SO}_2$  was fast during the initial stage and then slowed abruptly, leaving the sorbent incompletely converted. The relative humidity was the major factor affecting the reaction, whereas the effects of the temperature and  $\text{SO}_2$  concentration on the reaction were small. This reaction behavior of the BFS/HL sorbent with  $\text{SO}_2$  was similar to those of pure  $\text{Ca}(\text{OH})_2$  with  $\text{SO}_2$  (Ho and Shih, 1993b; Ho *et al.*, 1996, 2002) and with  $\text{CO}_2$  (Shih *et al.*, 1999), and  $\text{Ca}(\text{OH})_2/\text{fly ash}$  sorbent with  $\text{SO}_2$  (Liu *et al.*, 2002). In previous kinetic studies conducted by Ho *et al.* (1996, 2002), Shih *et al.* (1999), Liu and Shih (2002, 2004a), and Liu *et al.* (2002, 2004a, 2004b), the surface coverage model was found to be the most suitable model for describing the reaction between the sorbent and  $\text{SO}_2$  or  $\text{CO}_2$ . The same model was employed in this study to describe the reaction kinetics of the BFS/HL sorbent with  $\text{SO}_2$ .

The hypothesis of the surface coverage model states that the sorbent is made up of plate grains, that the reaction is controlled by the chemical reaction on the surface of a grain, and that the reacting surface area of the grain decreases with the deposition of solid product. According to this model, the reaction of a sorbent reaches ultimate conversion when its reacting surface is fully covered by the product.

The asymptotic equation derived from the surface coverage model by Shih *et al.* (1999) is expressed as

$$X = [1 - \exp(-k_1 k_2 t)] / k_2 \quad (1)$$

The parameters,  $k_1$  and  $k_2$ , are defined as

$$k_1 = k_S S_{g0} M, \quad (2)$$

$$k_2 = k_P / S_{g0} M, \quad (3)$$

where  $k_S$  is the initial reaction rate of the sorbent,  $k_P$  is a proportional constant relating the surface coverage rate to the reaction rate,  $S_{g0}$  is the initial specific surface area, and  $M$  is the initial sorbent weight per mole Ca.

The two parameters  $k_1$  and  $k_2$  in Eq. (1) can be obtained through nonlinear least-squares fitting of that equation to the experimental  $X$  versus  $t$  data. One can easily see from Eq. (1) that  $k_2$  is the reciprocal of the ultimate conversion; thus, the initial guess of  $k_2$  was taken as the inverse of the 1 h conversion. Table 1 summarizes the values of  $k_1$  and  $k_2$  thus obtained, and the standard deviation of  $X$  ( $\sigma$ ) for the fitting for each set of experimental conditions.

According to the definitions of  $k_1$  and  $k_2$  given by Shih *et al.* (1999), these parameters are functions of the initial specific surface area, reaction temperature,  $\text{SO}_2$  concentration, and relative humidity. These functions can be derived by analyzing the values of  $k_1$  and  $k_2$  obtained under different experimental conditions.

In Fig. 6, the plots of  $\ln k_1$  versus RH are linear, and the fitting lines have nearly the same slopes for the  $\text{SO}_2$  concentrations and temperatures considered. Values of  $\ln k_1$  are plotted against the inverse of the reaction temperature ( $T$ ) according to the Arrhenius relationship in Fig. 7. The values corresponding to the same RH can be represented by a straight line, and the slopes of the lines are nearly equal. Values of  $\ln k_1$  are plotted against  $\ln y$  in Fig. 8, where  $y$  is the  $\text{SO}_2$  concentration. A linear relationship can be observed for each RH, and the line slopes are also about the same. As can be seen from Fig. 9, the relative humidity was the only variable affecting the values of  $k_2$ , and the logarithmic plots of  $k_2$  versus RH are linear. The following function forms were found to best represent  $k_1$  and  $k_2$ :

$$k_1 = k_{10} e^{\beta_1 RH} y^{n_1} e^{-E_1/RT}, \quad (4)$$

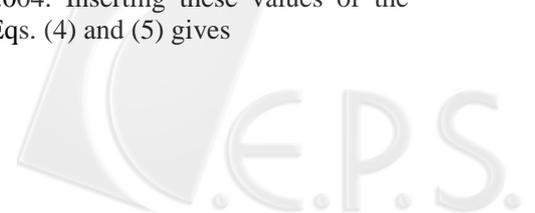
$$k_2 = k_{20} RH^{-\beta_2}. \quad (5)$$

Table 1. Values of  $k_1$  and  $k_2$  obtained by fitting Eq. (1) to the differential fixed-bed reactor data for the sulfation of the BFS/HL(30/70 wt. ratio) sorbent.

$T$ (°C)	$RH$ (%)	$y$ (ppm)	$k_1$ (min <sup>-1</sup> )	$1/k_2$	$\sigma$ (%)
40	30	500	0.0784	0.315	1.99
40	50	500	0.1008	0.505	2.20
40	70	500	0.1158	0.689	2.12
40	80	500	0.1181	0.800	2.08
40	30	1000	0.0909	0.310	2.01
40	50	1000	0.1091	0.505	2.12
40	70	1000	0.1297	0.690	2.59
40	80	1000	0.1465	0.790	2.60
40	30	3000	0.1132	0.312	1.92
40	50	3000	0.1411	0.510	2.21
40	70	3000	0.1716	0.700	0.24
40	80	3000	0.1857	0.791	2.50
40	30	5000	0.1415	0.315	2.21
40	50	5000	0.1532	0.510	2.20
40	70	5000	0.1835	0.705	2.29
40	80	5000	0.2061	0.790	2.74
60	30	500	0.0943	0.308	1.71
60	50	500	0.1153	0.505	2.24
60	70	500	0.1326	0.705	2.07
60	80	500	0.1474	0.805	2.45
60	30	1000	0.1093	0.318	2.22
60	50	1000	0.1349	0.500	2.39
60	70	1000	0.1563	0.700	2.23
60	80	1000	0.1866	0.785	2.24
60	30	3000	0.1519	0.318	1.83
60	50	3000	0.1843	0.510	2.26
60	70	3000	0.2113	0.688	2.04
60	80	3000	0.2263	0.785	2.59
60	30	5000	0.1741	0.307	1.51
60	50	5000	0.2055	0.505	2.17
60	70	5000	0.2472	0.690	2.95
60	80	5000	0.2630	0.786	2.93
80	30	500	0.1113	0.315	2.36
80	50	500	0.1420	0.512	1.93
80	70	500	0.1742	0.695	2.39
80	80	500	0.1818	0.795	2.25
80	30	1000	0.1407	0.310	2.10
80	50	1000	0.1656	0.510	2.48
80	70	1000	0.1998	0.700	2.70
80	80	1000	0.2113	0.810	2.93
80	30	3000	0.1882	0.310	2.25
80	50	3000	0.2198	0.506	2.53
80	70	3000	0.2637	0.695	2.18
80	80	3000	0.2824	0.790	2.68
80	30	5000	0.2100	0.309	2.21
80	50	5000	0.2408	0.505	2.25
80	70	5000	0.2811	0.700	2.29
80	80	5000	0.3160	0.805	2.23

The parameters  $k_{10}$ ,  $\beta_1$ ,  $E_1$ , and  $n_1$ , and  $k_{20}$  and  $\beta_2$  in Eqs. (4) and (5), respectively, were estimated by means of multiple regression. Equations (4) and (5) were transformed into linear equations by taking the logarithm. With a 95% confidence interval, these pa-

rameters were estimated to be  $k_{10}=\exp(-0.6267 \pm 0.0310)$ ,  $\beta_1 = 8.7 \times 10^{-3} \pm 7.29 \times 10^{-5}$ ,  $E_1 = 9596 \pm 78.7$ ,  $n_1 = 0.2410 \pm 0.0156$ ,  $k_{20} = \exp(4.3962 \pm 0.1496)$ , and  $\beta_2=0.950 \pm 0.004$ . Inserting these values of the parameters into Eqs. (4) and (5) gives



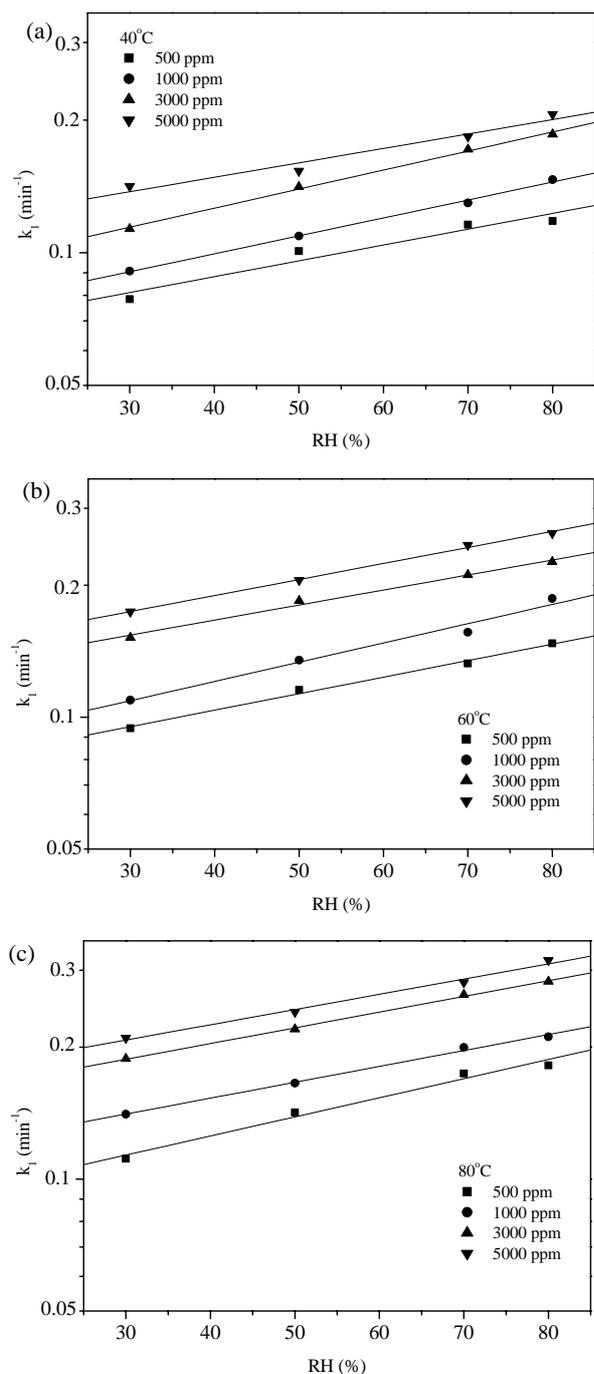


Fig. 6. Relationship between  $k_1$  and the relative humidity: (a) 40°C, (b) 60°C, and (c) 80°C.

$$k_1 = 0.5344e^{0.0087RH} y^{0.241} e^{-9696/RT}, \quad (6)$$

$$k_2^{-1} = 0.0123RH^{0.95}. \quad (7)$$

Equation (1) together with Eqs. (6) and (7) constitutes the kinetic model for the sulfation of the BFS/HL sorbent. Conversions calculated by the kinetic model are compared with the experimental results in Fig. 10, which shows that the calculated results are in good agreement with experimental data with a standard deviation ( $\sigma$ ) of 0.03 in conversion.

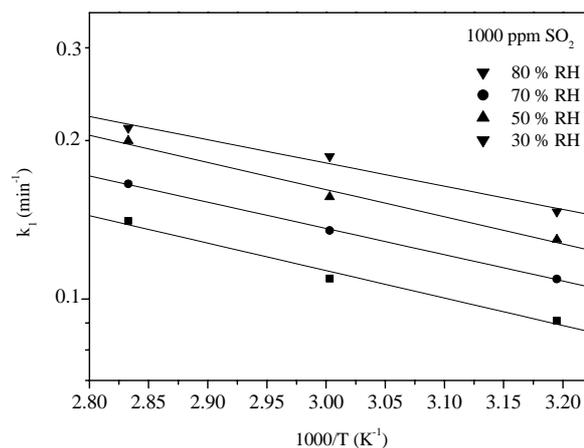


Fig. 7. Arrhenius plot of  $k_1$ .

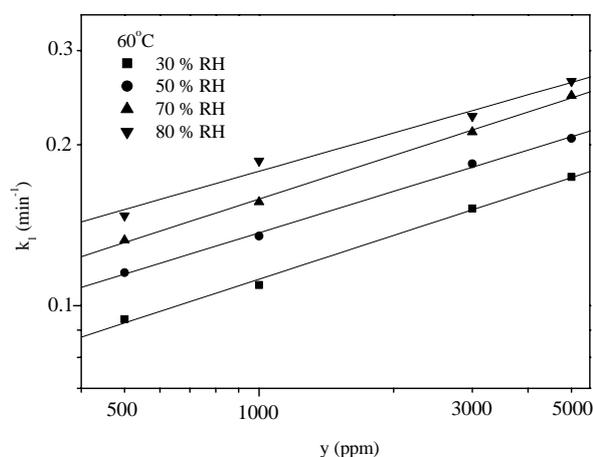


Fig. 8. Relationship between  $k_1$  and the  $\text{SO}_2$  concentration.

### Discussion on reaction kinetics

From the above kinetic analysis, one can see that the relative humidity is the major factor affecting the reaction. This implies that the water adsorbed on the sorbent surface played an important role in the reaction.

The rate-controlling step for the reaction of the sorbents with  $\text{SO}_2$  at low temperatures is thought to be the dissolution of Ca-containing reactants, which proceeds through their reactions with  $\text{SO}_2 \cdot \text{H}_2\text{O}$  or  $\text{H}^+$ . Water is required for  $\text{SO}_2 \cdot \text{H}_2\text{O}$  and its hydrolysis product,  $\text{H}^+$ , to form. Raising the relative humidity increases the amount of water adsorbed and  $\text{SO}_2 \cdot \text{H}_2\text{O}$  and  $\text{H}^+$  formed, therefore resulting in an increase in the dissolution rate.

The amounts of  $\text{SO}_2 \cdot \text{H}_2\text{O}$  and  $\text{H}^+$  are also functions of the gas phase  $\text{SO}_2$  concentration. The mild effect of the gas phase  $\text{SO}_2$  concentration may be due to the limited  $\text{SO}_2$  adsorption on the water layer, which is like the case of Langmuir adsorption isotherm (Smith, 1981).

The mild effect of the temperature on the overall reaction rate may be explained as follows: as the

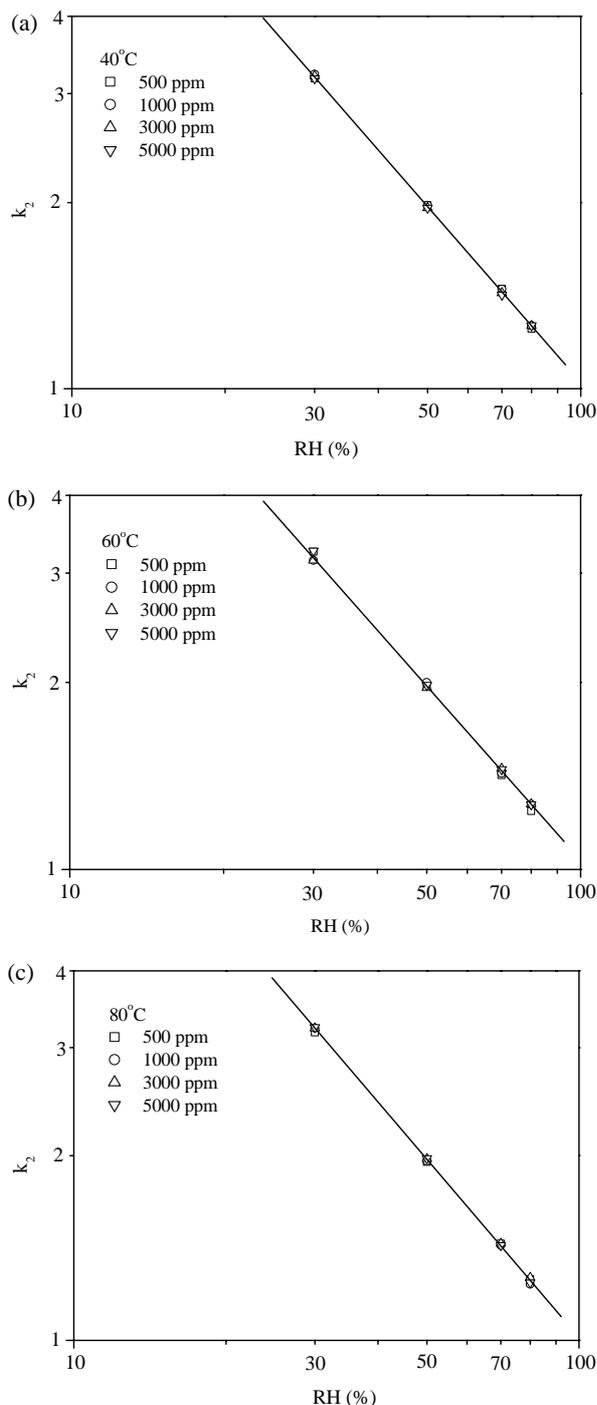


Fig. 9. Relationship between  $k_2$  and the relative humidity: (a) 40°C, (b) 60°C, and (c) 80°C.

temperature increases, the chemical reaction rate constants increase, whereas the amounts of water and SO<sub>2</sub> adsorbed decrease.

The value of  $k_2^{-1}$  or the ultimate conversion increases as the relative humidity increases. This phenomenon may indicate that the thicker water layer provides a wider space for the product molecules to deposit. Thus, at a lower relative humidity, the reaction product covers the sorbent surface more uniformly, and the overall reaction rate diminishes at a

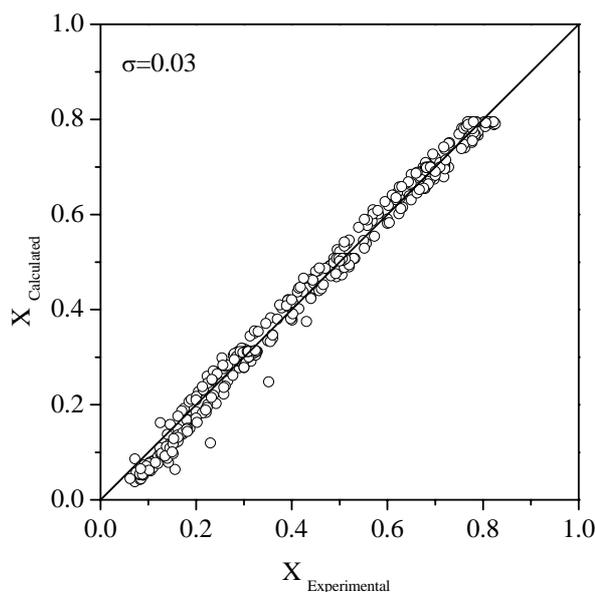


Fig. 10. Comparison of the calculated and the experimental conversion values.

lower conversion; on the other hand, at a higher relative humidity, the product becomes more cluster-like and covers less of the surface, and the reaction achieves higher ultimate conversion. Similar arguments have been set forth by Krammer *et al.* (1997) and Shih *et al.* (1999) to explain the effect of the relative humidity on the reaction of Ca(OH)<sub>2</sub> with SO<sub>2</sub> and with CO<sub>2</sub>, respectively.

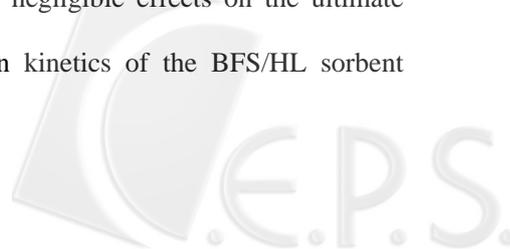
In the actual flue gas, CO<sub>2</sub>, O<sub>2</sub>, and NO<sub>x</sub> are present with SO<sub>2</sub>; CO<sub>2</sub> has the ability to react with the BFS/HL sorbent, and O<sub>2</sub> and NO<sub>x</sub> can oxidize calcium sulfite to form calcium sulfate. The effects of these components on the reaction of BFS/HL sorbent with SO<sub>2</sub> have been studied by the authors, and the results will be reported in the future. The results of the present study can be extended to the more realistic case. Accurate modeling of the sulfation kinetics of the BFS/HL sorbent is important for the design and operation of dry or semidry processes that use this kind of sorbent.

## CONCLUSION

The kinetics of the reaction of the BFS/HL sorbent with a ratio of 30/70 with SO<sub>2</sub> in humid N<sub>2</sub> has been studied using a differential-fixed bed reactor.

The relative humidity was the most important factor affecting the reaction; the initial reaction rate and the ultimate conversion of the sorbent increased as the relative humidity increased. The temperature and SO<sub>2</sub> concentration had slight effects on the initial reaction rate and negligible effects on the ultimate conversion.

The reaction kinetics of the BFS/HL sorbent



with SO<sub>2</sub> could be well described by the surface coverage model proposed by Shih *et al.* (1999), which assumes that the sulfation rate is controlled by the chemical reaction on the sorbent grain surface and takes into account the surface covered by the product. The values of the kinetic parameters pertinent to the sorbent with a BFS/HL ratio of 30/70 were evaluated.

The results of this study are useful for the design and operation of dry or semidry processes that use the BFS/HL sorbent to remove SO<sub>2</sub> from flue gas.

### NOMENCLATURE

$D$	pore diameter, Å
$E_1$	activation energy for $k_1$ , J/mol
$k_1$	$k_S S_{g0} M$ , min <sup>-1</sup>
$k_{10}$	constant defined by Eq. (4), min <sup>-1</sup>
$k_2$	$k_P / (S_{g0} M)$ , dimensionless
$k_{20}$	constant defined by Eq. (5), dimensionless
$k_P$	proportional constant relating the surface coverage rate to the reaction rate, m <sup>2</sup> /mol
$k_S$	initial reaction rate of solid, mol/(min·m <sup>2</sup> )
$M$	initial weight of solid per mol of Ca, g/mol of Ca
$n_1$	index of $y$ in Eq. (4)
$R$	gas constant, 8.314 J/mol·K
$RH$	relative humidity, %
$S_{g0}$	initial specific surface area of solid, m <sup>2</sup> /g
$T$	reaction temperature, K
$t$	time, min
$V$	pore volume, cm <sup>3</sup> /g
$V_a$	volume of N <sub>2</sub> adsorbed, cm <sup>3</sup> (STP)/g sorbent
$X$	conversion, dimensionless
$y$	SO <sub>2</sub> concentration, ppm

### Greek symbols

$\beta_1$	coefficient of $RH$ in Eq. (4)
$\beta_2$	coefficient of $RH^{-1}$ in Eq. (5)
$\sigma$	standard deviation of $X$

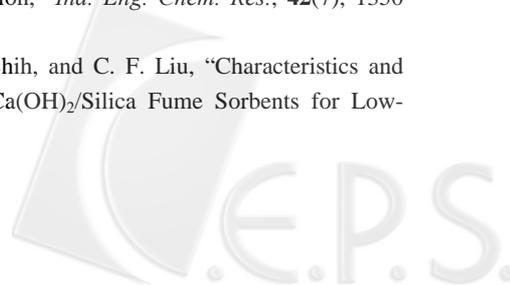
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### REFERENCES

Brodnax, L. F. and G. T. Rochelle, "Preparation of Calcium Silicate Absorbent from iron Blast Furnace Slag," *J. Air Waste Manage.*, **50**, 1655 (2000).  
 Chiu, C. S. "The Reactivity of Ca(OH)<sub>2</sub>/SiO<sub>2</sub> Sorbent with

SO<sub>2</sub>," M.S. Thesis, Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, R.O.C. (1989).  
 Garea, A., J. R. Viguri, J. Fernandez, M. I. Ortiz, M. J. Renedo, and A. Irabien, "Fly Ash/Calcium Hydroxide Mixtures for SO<sub>2</sub> Removal: Structural Properties and Maximum Yield," *Chem. Eng. J.*, **66**, 171 (1997a).  
 Garea, A., J. R. Viguri, and A. Irabien, "Kinetics of the Flue Gas Desulfurization at Low Temperature: Fly Ash/Calcium (3/1) Sorbent Behavior," *Chem. Eng. Sci.*, **52**, 715 (1997b).  
 Ho, C. S. "Reaction of Ca(OH)<sub>2</sub> and fly ash/Ca(OH)<sub>2</sub> slurry with SO<sub>2</sub>," M. S. Thesis, Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, R.O.C. (1987).  
 Ho, C. S. and S. M. Shih, "Ca(OH)<sub>2</sub>/Fly Ash Sorbents for SO<sub>2</sub> Removal," *Ind. Eng. Chem. Res.*, **31**, 1130 (1992).  
 Ho, C. S. and S. M. Shih, "Characteristic and SO<sub>2</sub> Capture Capacities of Sorbents Prepared from Products of Spray-Drying Flue Gas Desulfurization," *Can. J. Chem. Eng.*, **71**, 934 (1993a).  
 Ho, C. S. and S. M. Shih, "Factors Influencing the Reaction of Ca(OH)<sub>2</sub> with SO<sub>2</sub>," *J. Chin. Inst. Chem. Engrs.*, **24**, 187 (1993b).  
 Ho, C. S., S. M. Shih, and C. D. Lee, "Influence of CO<sub>2</sub> and O<sub>2</sub> on the Reaction of Ca(OH)<sub>2</sub> under Spray-Drying Flue Gas Desulfurization Conditions," *Ind. Eng. Chem. Res.*, **35**, 3915 (1996).  
 Ho, C. S., S. M. Shih, C. F. Liu, H. M. Chu, and C. D. Lee, "Kinetics of the Sulfation of Ca(OH)<sub>2</sub> at Low Temperatures," *Ind. Eng. Chem. Res.*, **44**, 3357 (2002).  
 Jozewicz, W. and G. T. Rochelle, "Fly Ash Recycle in Dry Scrubbing," *Environ. Prog.*, **5**, 219 (1986).  
 Jozewicz, W., C. Jorgensen, J. C. S. Chang, C. B. Sedman, and T. Brna, "Development and Pilot Plant Evaluation of Silica-Enhanced Lime Sorbents for Dry Flue Gas Desulfurization," *J. Air Pollut. Control Assoc.*, **38**, 796 (1988a).  
 Jozewicz, W., J. C. S., Chang, C. B. Sedman, and T. Brna, "Silica-Enhanced Sorbents for Dry Injection Removal of SO<sub>2</sub> from Flue Gas," *J. Air Pollut. Control Assoc.*, **38**, 1027 (1988b).  
 Kind, K. K. "Hydrothermal Preparation of High Surface Area Calcium Silicate from Lime and Fly Ash in a Flow Reactor," Ph.D. Dissertation, Department of Chemical Engineering, University of Texas at Austin, U. S. A. (1994).  
 Lin, R. B., S. M. Shih, and C. F. Liu, "Structural Properties and Reactivities of Ca(OH)<sub>2</sub>/Fly Ash Sorbents for Flue Gas Desulfurization," *Ind. Eng. Chem. Res.*, **42**(7), 1350 (2003a).  
 Lin, R. B., S. M. Shih, and C. F. Liu, "Characteristics and Reactivities of Ca(OH)<sub>2</sub>/Silica Fume Sorbents for Low-



- Temperature Flue gas Desulfurization," *Chem. Eng. Sci.*, **58**, 3659 (2003b).
- Liu, C. F. "Kinetics of the Reactions of Ca(OH)<sub>2</sub>/Silica Fume and Ca(OH)<sub>2</sub>/Fly Ash Sorbents with SO<sub>2</sub>," M.S. Thesis, Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, R.O.C. (1999).
- Liu, C. F. and S. M. Shih, "A Surface Coverage Model for the Reaction of Ca(OH)<sub>2</sub> with SO<sub>2</sub> at Low Temperatures," *J. Chin. Inst. Chem. Engrs.*, **33**(4), 407 (2002).
- Liu, C. F., S. M. Shih, and R. B. Lin, "Kinetics of the Reaction of Ca(OH)<sub>2</sub>/Fly Ash Sorbent with SO<sub>2</sub> at Low Temperatures," *Chem. Eng. Sci.*, **57**, 93 (2002).
- Liu, C. F. and S. M. Shih, "Kinetics of the Reaction of Iron Blast Furnace Slag/Hydrated Lime Sorbents with SO<sub>2</sub> at Low Temperatures: Effects of Sorbent Preparation Conditions," *Chem. Eng. Sci.*, **59**, 1001 (2004a).
- Liu, C. F. and S. M. Shih, "Enhancement of the Reactivities of Iron Blast Furnace Slag/Hydrated Lime Sorbents toward SO<sub>2</sub> by NaOH," *J. Chin. Inst. Chem. Engrs.*, **34**(5), 525 (2004b).
- Liu, C. F. and S. M. Shih, "Iron Blast Furnace Slag/Hydrated Lime Sorbents for Flue Gas Desulfurization," *Environ. Sci. Technol.*, **38**, 4451 (2004c).
- Liu, C. F., S. M. Shih, and R. B. Lin, "Effect of Ca(OH)<sub>2</sub>/Fly Ash Weight Ratio on the Kinetic of the Reaction of Ca(OH)<sub>2</sub>/Fly Ash Sorbents with SO<sub>2</sub> at Low Temperatures," *Chem. Eng. Sci.*, **59**, 4653 (2004a).
- Liu, C. F., S. M. Shih, and R. B. Lin, "Kinetic Model for the Reaction of Ca(OH)<sub>2</sub>/Fly Ash Sorbents with SO<sub>2</sub> at Low Temperatures," *Ind. Eng. Chem. Res.*, **43**(15), 4112 (2004b).
- Miller, M. J., "Retrofit SO<sub>2</sub> and NO<sub>x</sub> Control Technologies for Coal-Fired Power Plants," *Environ. Prog.*, **5**, 171 (1986).
- Shih, S. M., C. S. Ho, Y. S. Song, and J. P. Lin, "Kinetics of the Reaction of Ca(OH)<sub>2</sub> with CO<sub>2</sub> at Low Temperature," *Ind. Eng. Chem. Res.*, **38**, 1316(1999).
- Smith, J. M., *Chemical Engineering Kinetics*, 3<sup>rd</sup> Ed., McGraw-Hill, New York, U.S.A. (1981).
- Srivastava, R. K. and W. Jozewicz, "Flue Gas Desulfurization: The State of the Art," *J. Air Waste Manage.*, **51**, 1676 (2001).
- Taylor, H. F. W., *The Chemistry of Cement*, Academic Press, London, U.K. (1964).
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## 爐石/氫氧化鈣吸收劑與二氧化硫低溫下之反應動力學分析

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### 摘要

本研究以微分固定床反應器，在模擬噴霧乾燥除硫系統中的袋式過濾器的條件下，探討爐石/氫氧化鈣吸收劑與二氧化硫於低溫下之反應動力學模式。爐石/氫氧化鈣吸收劑重量配比为 30/70，於 65°C 漿化 16 小時後乾燥後研磨製備而成。該吸收劑對二氧化硫之反應性比氫氧化鈣佳。吸收劑之起始反應速率與鈣最終利用率明顯隨氣相中相對溼度的增加而增加。溫度與二氧化硫濃度對起始速率有些微影響，對鈣最終利用率之影響則可忽略。吸收劑與二氧化硫的反應可用表面覆蓋模式很好地描述；該模式假設吸收劑晶粒表面之化學反應為速率控制步驟，並且考量被產物覆蓋的表面積。本研究的結果有助於使用爐石/氫氧化鈣作為吸收劑的乾式與半乾式除硫系統之設計與操作。

