

# 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

Chiung-Fang Liu, Shih-Min Shih\*

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

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## Abstract

Sorbents highly reactive towards SO<sub>2</sub> have been prepared from iron blast furnace slag and hydrated lime under different hydration conditions. The reaction of the dry sorbents with SO<sub>2</sub> has been studied under the conditions similar to those in the bag filters in the spray-drying flue gas desulfurization system. The reaction was well described by a modified surface coverage model which assumes the reaction rate being controlled by chemical reaction on sorbent grain surface and takes into account the effect of sorbent Ca molar content and the surface coverage by product. The effects of sorbent preparation conditions on sorbent reactivity were entirely represented by the effects of the initial specific surface area ( $S_{g0}$ ) and the Ca molar content ( $M^{-1}$ ) of sorbent. The initial conversion rate of sorbent increased linearly with increasing  $S_{g0}$ , and the ultimate conversion increased linearly with increasing  $S_{g0}M^{-1}$ . The initial conversion rate and ultimate conversion of sorbent increased significantly with increasing relative humidity of the gas. Temperature and SO<sub>2</sub> concentration had mild effects on the initial conversion rate and negligible effects on the ultimate conversion.

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## 1. Introduction

Reducing SO<sub>2</sub> emission from power plants is a main issue for the environmental protection. Many flue gas desulfurization (FGD) processes are available for the reduction of SO<sub>2</sub> emissions (Miller, 1986; Srivastava and Jozewicz, 2001). Compared with other processes, the semidry and dry flue gas desulfurization processes need less space and are easier to retrofit, and they produce dry solid product, which is easier to treat; however, the sorbent, which is mostly hydrated lime (HL), is not highly converted in the operation of these processes. How to increase the utilization of hydrated lime has been an important subject for the application of the dry or semidry processes.

Sorbents prepared from hydrated lime and silica-containing materials, such as fly ash (Jozewicz and Rochelle, 1986; Ho, 1987; Jozewicz et al., 1988a,b; Ho and Shih, 1992, 1993; Garea et al., 1997; Liu et al., 2002; Lin et al., 2003), diatomaceous earths (Jozewicz et al., 1988a,b), and

silica fume (Chiu, 1989; Kind, 1994; 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 hydrated lime to form foil-like calcium silicate hydrates in the presence of water; this reaction is called “pozzolanic reaction” (Taylor, 1964). It is confirmed 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) reported that iron blast furnace slag (BFS) also can be used to prepare SO<sub>2</sub> reactive sorbents. Iron blast furnace slag, mainly composed of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO, is similar in constituents to fly ash, but its CaO content is higher. Our recent study (Liu and Shih, 2001) 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 the BFS/HL sorbents is higher than that for the sorbents prepared with fly ash (Lin et al., 2003).

In this work, BFS/HL sorbents were prepared at different preparation conditions, and their reaction with SO<sub>2</sub> was studied under the conditions similar to those in the bag

\* Corresponding author. Tel.: +886-2-23633974; fax: +886-2-23623040.

E-mail address: smshih@ntu.edu (S.-M. Shih).

filters in a semidry SO<sub>2</sub> scrubbing system using a differential fixed-bed reactor. A kinetic model describing the reaction of the sorbents was derived.

## 2. Experimental section

### 2.1. Preparation of sorbents

The hydrated lime used was reagent grade Ca(OH)<sub>2</sub> (purity > 95%, Hayashi Pure Chemical Industries, LTD). The iron blast furnace slag was supplied by the China Hi-Ment Corporation in two size ranges, high fineness (HBFS) and general fineness (GBFS). The chemical compositions of HBFS and GBFS are listed in Table 1. The volume mean particle diameters of Ca(OH)<sub>2</sub>, HBFS, and GBFS were 6.0, 5.9, and 7.9 μm, and the specific surface areas were 10.0, 1.5, and 1.4 m<sup>2</sup>/g, respectively.

The hydration of BFS and hydrated lime using deionized water was performed in a 250 ml polypropylene conical flask, keeping the total solid weight at 8 g. The BFS/HL weight ratios tested were 0/100, 10/90, 30/70, 50/50, 70/30, 90/10, and 100/0. The water/solid (*L/S*) weight ratios was 10/1. The flask containing the slurry was sealed with a rubber stopper at the mouth and inserted into a thermostat. The slurry was stirred with a magnetic stirrer for a certain period of time. The slurring temperatures used were 25–85°C, and the slurring times 0.42–32 h. After slurring ended, the slurry was vacuum dried at 105°C for 8 h. The dry cake was crushed into powder and sealed in a bottle before use.

### 2.2. Characterization of sorbents

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

The characterization of the BFS/HL sorbents showed that their compositions and physical properties varied with the preparation conditions. The raw BFS particles were non-porous, but the BFS/HL sorbents were mesoporous due to

the formation of the products of hydration, calcium silicate hydrates and calcium aluminum oxide carbonate hydrate. The mean particle diameter of sorbent was in the range of 7–24 μm. The specific surface area of sorbent (*S*<sub>g0</sub>), as shown in Table 2, was in the range of 11–33 m<sup>2</sup>/g. The molar content of Ca in a sorbent was determined by EDTA titration (Ho and Shih, 1993), and its inverse, the sorbent weight per mole of Ca (*M*), is listed in Table 2.

### 2.3. Reaction experiments

Experiments for the reaction of the sorbents with SO<sub>2</sub> were carried out by using a differential fixed-bed reactor. The details of the experimental setup and procedure were described in Ho and Shih (1992).

In this study, a fresh sample of about 30 mg was used for each reaction time. The sweep gas was comprised of SO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub>. SO<sub>2</sub> and N<sub>2</sub> gases were supplied from cylinders and H<sub>2</sub>O vapor was provided by a water evaporator. Prior to each run, the sample bed was humidified for 30 min by humid N<sub>2</sub> with a relative humidity (RH) at which the experiment was to be performed, which had been proved to be long enough for the sample to equilibrate with the gas stream. After humidification, the reactive gas was admitted into the sweep gas 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 SO<sub>2</sub>.

The differential condition of the reactor with respect to interparticle SO<sub>2</sub> levels at the selected total gas flowrate and sample weight was confirmed by the results of experiments using different sample weights. The results showed no effect of sample weight on the reaction when the weight was smaller than 40 mg.

CaSO<sub>3</sub> · 1/2H<sub>2</sub>O was identified to be the reaction product. The conversion (*X*) for a reacted sample was determined from its SO<sub>3</sub><sup>2-</sup>/Ca<sup>2+</sup> molar ratio. The SO<sub>3</sub><sup>2-</sup> content in a sample was determined by iodometric titration, and the Ca<sup>2+</sup> content by EDTA titration (Ho and Shih, 1993).

At least two repeated measurements were made for each experimental conditions. The experimental error of conversion was about ±0.03.

In the present study, CO<sub>2</sub> and O<sub>2</sub> were not added to make the synthetic flue gas because our aim is to study the relative reactivity of the sorbents. Thus, the kinetic parameters obtained in this study may not directly represent those

Table 1  
Composition of iron blast furnace slag

Iron blast furnace slag	Composition (wt%)								
	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	Alkalinity	<i>S</i>	Ignition loss
High fineness	42.00	33.47	13.78	6.98	0.39	0.42	1.67	0.27	1.67
General fineness	42.32	34.29	14.52	6.77	0.18	0.44	1.83	0.23	0.64

Table 2

Preparation conditions ( $L/S = 10/1$ ), sorbent weights per mole of Ca, BET specific surface areas, and values of  $k_1$  and  $k_2^{-1}$  in Eq. (7) for BFS/HL sorbents

BFS/HL wt. ratio	Slurrying temp. (°C)	Slurrying time (h)	$M$ (g/mol)	$S_{g0}$ ( $m^2/g$ )	$k_1$ ( $\text{min}^{-1}$ )	$k_2^{-1}$
Raw HBFS	—	—	146	1.5	0.016	0.035
HBFS/HL						
100/0	65	16	147	17.1	0.108	0.108
90/10	65	16	139	25.9	0.123	0.429
70/30	65	16	128	31.1	0.150	0.510
50/50	65	16	114	32.6	0.161	0.590
30/70	65	16	96	28.9	0.156	0.700
10/90	65	16	82	23.6	0.120	0.446
0/100	65	16	76	11.8	0.057	0.225
30/70	25	16	97	22.3	0.113	0.385
30/70	45	16	98	28.8	0.143	0.579
30/70	85	16	99	31.1	0.142	0.689
30/70	65	0.42	100	26.8	0.126	0.600
30/70	65	4	98	28.4	0.163	0.622
30/70	65	32	99	30.9	0.179	0.719
Raw GBFS	—	—	149	1.4	0.015	0.020
GBFS/HL						
100/0*	65	16	151	12.4	0.086	0.080
90/10*	65	16	145	28.1	0.152	0.349
70/30*	65	16	125	—	0.155	0.415
50/50*	65	16	114	32.8	0.141	0.524
30/70*	65	16	97	26.0	0.142	0.611
10/90*	65	16	83	—	0.158	0.350

Sulfation conditions: 60°C, 70% RH, and 1000 ppm SO<sub>2</sub>.

\*GBFS.

in the presence of oxygen. Our preliminary tests at 60°C, 70% RH, 1000 ppm SO<sub>2</sub>, and 5% O<sub>2</sub> for sorbents with ratios of 30/70, 50/50, and 70/30 showed that when O<sub>2</sub> was present in the gas mixture, the total conversion of a sorbent to both sulfite and sulfate was slightly higher ( $\leq 0.04$ ) than the conversion to sulfite for the case without O<sub>2</sub>.

### 3. Results and discussion

#### 3.1. Effects of sorbent preparation conditions

The BFS/HL sorbents prepared at different conditions were reacted with SO<sub>2</sub> at 60°C, 70% RH, and 1000 ppm SO<sub>2</sub>. The results are shown in Figs. 1–4 in terms of conversion  $X$  versus time  $t$ .

As can be seen from Figs. 1 and 2, the reaction is rapid in the initial period, but the conversion levels off after about 15 min, and the sorbent is incompletely converted for a reaction time as long as 1 h. The reactivity of sorbent increases with decreasing BFS/HL ratio until a ratio of 30/70 and then decreases. The reactivity of the sorbent prepared from HBFS is higher than that prepared from GBFS at the same BFS/HL ratio.

From Fig. 3, one can see that sorbents prepared with longer times have higher reactivities. As seen from Fig. 4, the sorbent reactivity increases as the slurrying temperature

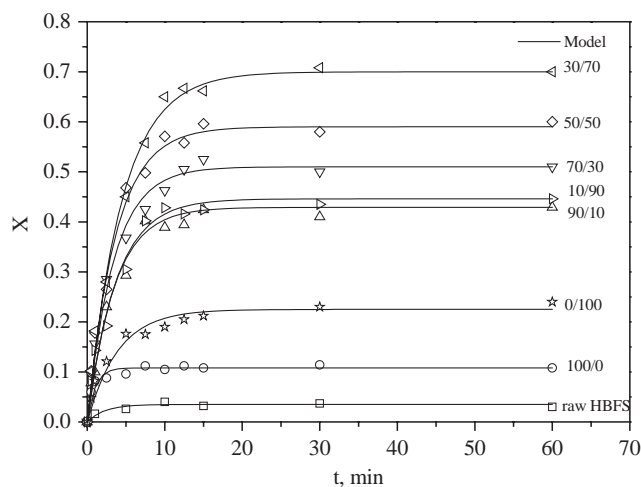


Fig. 1. Effect of BFS/HL weight ratio on the reaction of HBFS/HL sorbents with SO<sub>2</sub>. Slurrying conditions: 65°C,  $L/S = 10/1$ , and 16 h. Reaction conditions: 60°C, 70% RH, and 1000 ppm SO<sub>2</sub>.

increases from 25°C to 65°C and remains about the same as the temperature increases further to 85°C.

The variation of sorbent reactivity with preparation conditions is caused by the variation of sorbent structural properties and composition. The relations between the sorbent reactivity, structural properties, and composition will be analyzed in Section 3.3.

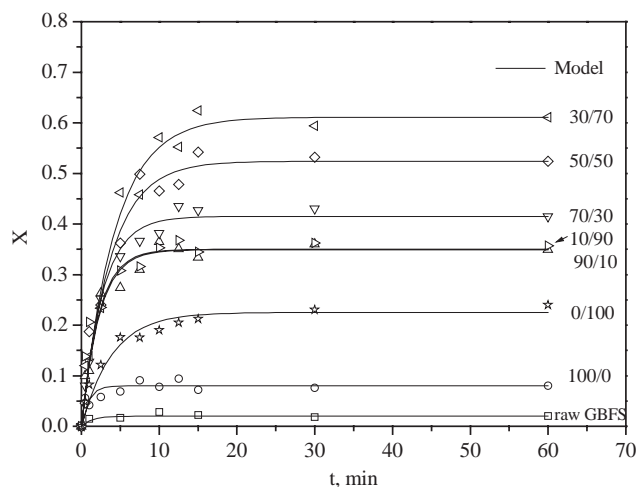


Fig. 2. Effect of BFS/HL weight ratio on the reaction of GBFS/HL sorbents with  $\text{SO}_2$ . Slurrying conditions:  $65^\circ\text{C}$ ,  $L/S = 10/1$ , and 16 h. Reaction conditions:  $60^\circ\text{C}$ , 70% RH, and 1000 ppm  $\text{SO}_2$ .

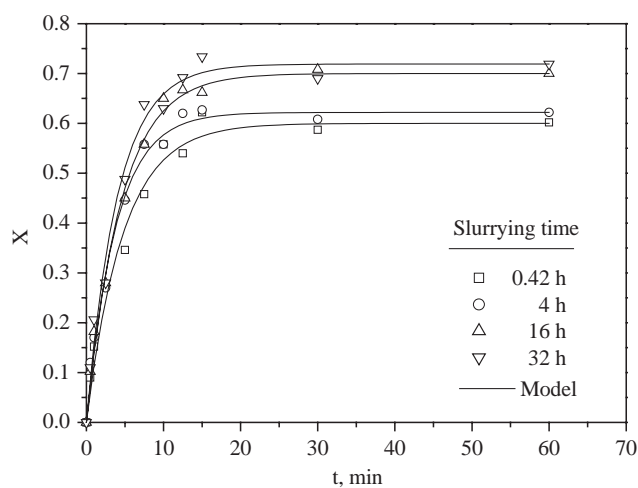


Fig. 3. Effect of slurrying time on the reaction of HBFS/HL (30/70 weight ratio) sorbents with  $\text{SO}_2$ . Slurrying conditions:  $65^\circ\text{C}$  and  $L/S = 10/1$ . Reaction conditions:  $60^\circ\text{C}$ , 70% RH, and 1000 ppm  $\text{SO}_2$ .

### 3.2. Effects of reaction conditions

Some sorbents were subjected to reaction under different reaction conditions; the sorbents and the reaction conditions are summarized in Table 3.

The results for the sorbents with HBFS/HL ratios of 30/70 and 70/30 reacted at various relative humidities (30–80%) are shown in Figs. 5 and 6, respectively. One can see that the initial conversion rate and the ultimate conversion of sorbent increase markedly with increasing relative humidity.

As seen from Figs. 7 and 8, the initial conversion rate increases mildly and the ultimate conversion remains about the same when the reaction temperature increases from  $40^\circ\text{C}$  to  $80^\circ\text{C}$  (Fig. 7) or the  $\text{SO}_2$  concentration from 500 to 5000 ppm (Fig. 8).

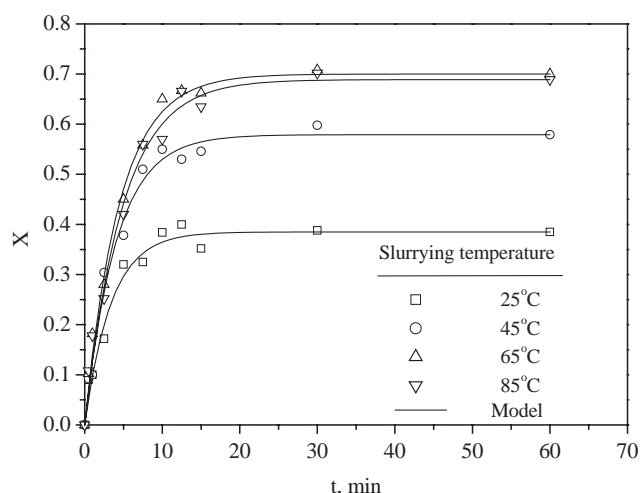


Fig. 4. Effect of slurrying temperature on the reaction of HBFS/HL (30/70 weight ratio) sorbents with  $\text{SO}_2$ . Slurrying conditions:  $L/S = 10/1$  and 16 h. Reaction conditions:  $60^\circ\text{C}$ , 70% RH, and 1000 ppm  $\text{SO}_2$ .

### 3.3. Analysis of reaction kinetics

The foregoing results show that the reaction of a BFS/HL sorbent with  $\text{SO}_2$  is fast in the initial stage and then slows down abruptly, leaving the sorbent incompletely converted. This reaction behavior is similar to those of  $\text{Ca}(\text{OH})_2$  with  $\text{CO}_2$  (Shih et al., 1999),  $\text{Ca}(\text{OH})_2$  with  $\text{SO}_2$  (Ho et al., 2002), and the  $\text{Ca}(\text{OH})_2$ /fly ash sorbent with a ratio of 70/30 with  $\text{SO}_2$  (Liu et al., 2002). The latter reactions have been well described by the surface coverage model proposed by Shih et al. (1999).

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 product. According to this model, the reaction of a sorbent reaches an ultimate conversion when its reacting surface is fully covered by the product.

The surface coverage model proposed by Shih et al. (1999) is for the reaction of  $\text{Ca}(\text{OH})_2$ . The model can be modified to describe the reaction of the sorbents of this study, which are mixtures of several solid reactants and have different Ca molar contents.

The reaction rate of a sorbent per unit initial surface area,  $r_s$ , can be expressed as

$$r_s = k'_s M^{-1} \Phi, \quad (1)$$

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 it represents the effect of Ca dispersion on the sorbent reactivity; and  $\Phi$  is the fraction of the surface area which is not covered by product. The rate of conversion of the sorbent is

$$dX/dt = S_{g0} M r_s = S_{g0} k'_s M^{-1} \Phi, \quad (2)$$

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

Table 3  
Experimental conditions and values of  $k_1$  and  $k_2^{-1}$  in Eq. (7) for HBFS/HL sorbents

HBFS/HL wt. ratio	$S_{g0}$ (m <sup>2</sup> /g)	$M$ (g/mol)	RH (%)	$T$ (K)	$y$ (ppm)	$k_1$ (min <sup>-1</sup> )	$k_2^{-1}$
0/100	11.8	76	30	333	1000	0.033	0.128
	11.8	76	50	333	1000	0.042	0.186
	11.8	76	70	333	1000	0.057	0.225
	11.8	76	80	333	1000	0.053	0.323
10/90	23.6	82	30	333	1000	0.061	0.191
	23.6	82	50	333	1000	0.076	0.357
	23.6	82	70	333	1000	0.120	0.446
	23.6	82	80	333	1000	0.105	0.535
30/70	28.9	96	30	333	1000	0.109	0.318
	28.9	96	50	333	1000	0.135	0.500
	28.9	96	70	333	1000	0.156	0.700
	28.9	96	80	333	1000	0.187	0.785
	28.9	96	70	313	1000	0.130	0.690
	28.9	96	70	353	1000	0.200	0.700
	28.9	96	70	333	500	0.133	0.705
	28.9	96	70	333	5000	0.247	0.690
50/50	32.6	114	30	333	1000	0.100	0.287
	32.6	114	50	333	1000	0.145	0.447
	32.6	114	70	333	1000	0.161	0.590
	32.6	114	80	333	1000	0.160	0.635
70/30	31.1	128	30	333	1000	0.073	0.245
	31.1	128	50	333	1000	0.131	0.352
	31.1	128	70	333	1000	0.150	0.510
	31.1	128	80	333	1000	0.173	0.570

Sorbent preparation conditions: 65°C,  $L/S = 10/1$ , and 16 h.

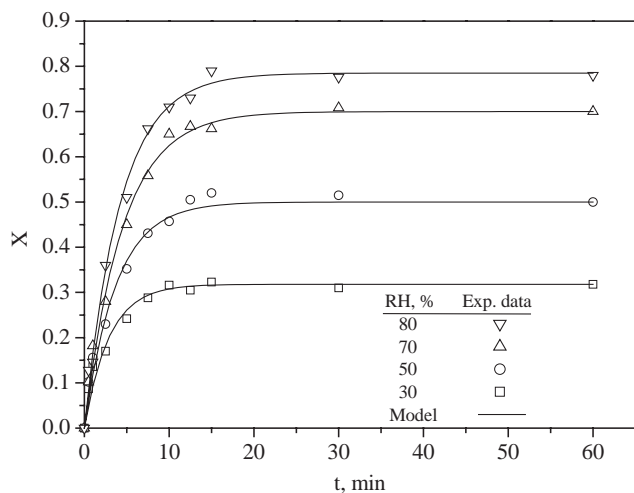


Fig. 5. Conversion versus time for the reaction of HBFS/HL (30/70 wt. ratio) sorbent at 60°C, 1000 ppm SO<sub>2</sub>, and various relative humidities.

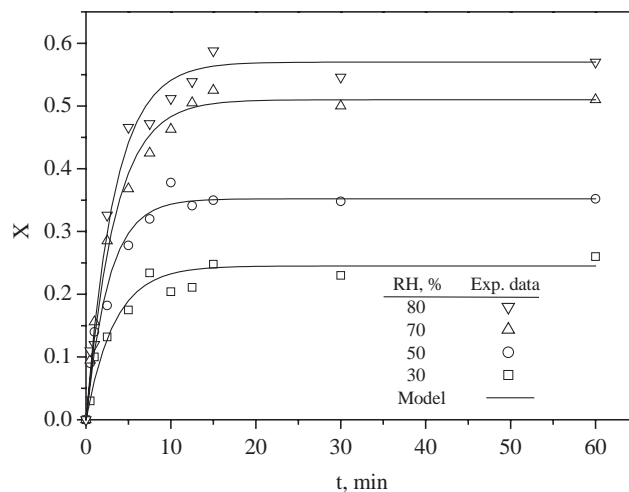


Fig. 6. Conversion versus time for the reaction of HBFS/HL (70/30 wt. ratio) sorbent at 60°C, 1000 ppm SO<sub>2</sub>, and various relative humidities.

The change of  $\Phi$  with reaction time depends on the reaction rate, the dispersion of Ca, and the way by which the product deposits on the surface. The effect of Ca dispersion on  $\Phi$  can be seen from Figs. 1 and 2. The figures show that the sorbent seems to reach the ultimate conversion earlier

when its  $M$  value is larger. This fact indicates that the rate of change of  $\Phi$  increased with increasing  $M$ . Thus, one may assume that

$$-d\Phi/dt = k'_p k'_S M \Phi, \quad (3)$$

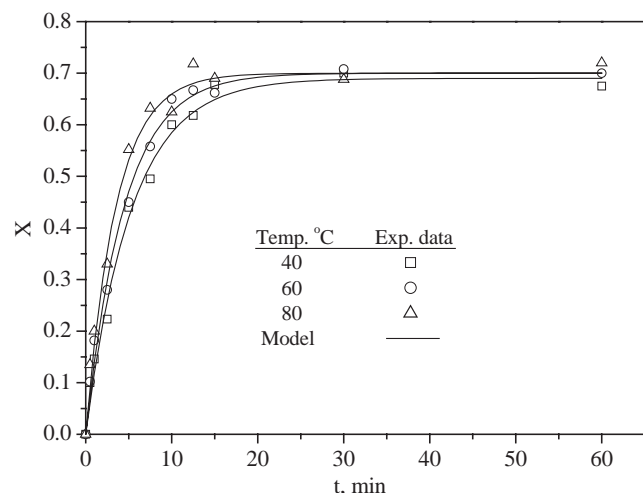


Fig. 7. Conversion versus time for the reaction of HBFS/HL (30/70 wt. ratio) sorbent at 70% RH, 1000 ppm  $\text{SO}_2$ , and various temperatures.

where  $k'_p$  is a proportional constant, which may be also a function of temperature, concentrations of reacting gas species, and relative humidity. Eq. (3) can be integrated to get  $\Phi$  as a function of time

$$\Phi = \exp(-k_1 k_2 t), \quad (4)$$

where

$$k_1 = k'_S S_{g0}, \quad (5)$$

$$k_2 = k'_p M / S_{g0}. \quad (6)$$

By substitution of Eq. (4) into Eq. (2), one can integrate Eq. (2) to obtain the relation between conversion and time:

$$X = [1 - \exp(-k_1 k_2 t)] / k_2. \quad (7)$$

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

$$dX/dt = k_1(1 - k_2 X), \quad (8)$$

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

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. Tables 2 and 3 summarize the values of  $k_1$  and  $k_2^{-1}$  thus obtained. The curves plotted in Figs. 1–8 using Eq. (7) show that the experimental data are well described by Eq. (7).

As seen from Table 2, the values of  $k_1$  and  $k_2^{-1}$  vary from sorbent to sorbent, indicating that they are affected by the sorbent preparation conditions, i.e., BFS fineness, BFS/HL weight ratio, slurring temperature, and slurring time. However, from the following analyses, one can see that the effects of the sorbent preparation conditions on the values of  $k_1$  and  $k_2^{-1}$  were entirely represented by the effects of  $S_{g0}$  and  $M$ .

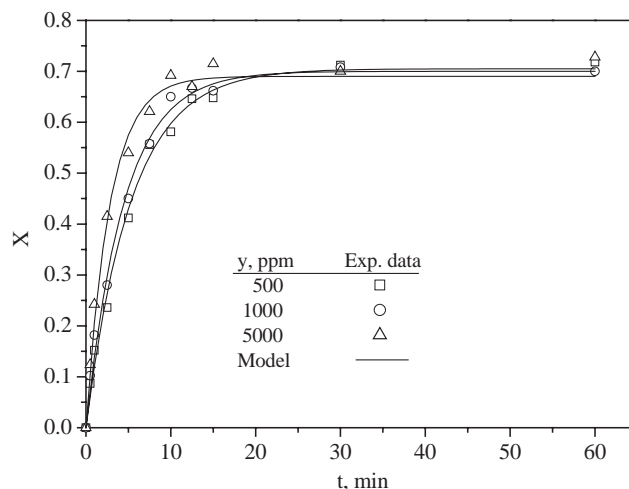


Fig. 8. Conversion versus time for the reaction of HBFS/HL (30/70 wt. ratio) sorbent at 60°C, 70% RH, and various  $\text{SO}_2$  concentrations.

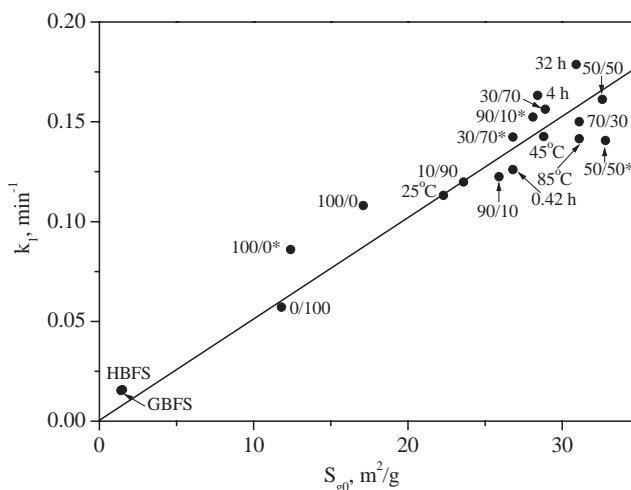


Fig. 9. Plot of  $k_1$  versus  $S_{g0}$ . Sorbent preparation conditions are listed in Table 2. Reaction conditions: 60°C, 70% RH, and 1000 ppm  $\text{SO}_2$ .

The  $k_1$  value for each sorbent is plotted against its  $S_{g0}$  in Fig. 9. As can be seen from the figure,  $k_1$  and  $S_{g0}$  follow a linear relationship; the linear least-squares fitting line has a correlation coefficient of 0.96. This result is in agreement with Eq. (5) and indicates that all sorbents have about the same  $k'_S$  value at the same reaction conditions.

As can be seen from Fig. 10, there is a linear relationship between  $k_2^{-1}$  and  $S_{g0}/M$ ; the linear least-squares fitting line has a correlation coefficient of 0.95. This result is in agreement with Eq. (6) and indicates that all sorbents have about the same  $k'_p$  value at the same reaction conditions.

As seen from Table 3,  $k_1$  is also a function of reaction temperature,  $\text{SO}_2$  concentration, and relative humidity, and  $k_2^{-1}$  is also a function of relative humidity. These functions can be derived by analyzing the values of  $k_1$  and  $k_2^{-1}$  obtained at different reaction conditions.

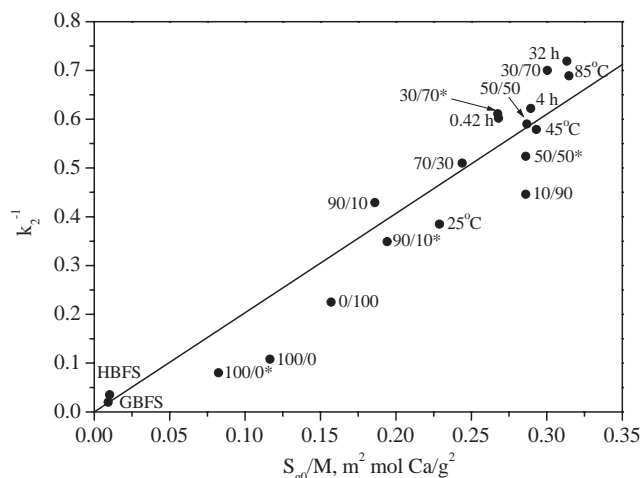


Fig. 10. Plot of  $k_2^{-1}$  versus  $S_{g0}/M$ . Sorbent preparation conditions are listed in Table 2. Reaction conditions: 60°C, 70% RH, and 1000 ppm  $\text{SO}_2$ .

The following function forms were found to best represent  $k_1$  and  $k_2^{-1}$ :

$$k_1 = \alpha_1 S_{g0} e^{\beta_1 \text{RH}} e^{-E_1/RT} y^{n_1}, \quad (9)$$

$$k_2^{-1} = \alpha_2 S_{g0} M^{-1} \text{RH}^{\beta_2}, \quad (10)$$

where RH is the relative humidity (%),  $R$  is the gas constant, and  $y$  is the  $\text{SO}_2$  concentration (ppm). The parameters  $\alpha_1$ ,  $\beta_1$ ,  $E_1$ ,  $n_1$ ,  $\alpha_2$ , and  $\beta_2$  in Eqs. (9) and (10) were estimated by multiple regression. With a 95% confidence interval, these parameters were estimated to be  $\alpha_1 = 0.00779 e^{\pm 0.85} \text{ min}^{-1}$ ,  $\beta_1 = 0.0124 \pm 0.0007$ ,  $E_1 = 9.5 \pm 2.2 \text{ kJ/mol}$ ,  $n_1 = 0.31 \pm 0.04$ ,  $\alpha_2 = 0.0344 e^{\pm 0.36}$ , and  $\beta_2 = 0.96 \pm 0.09$ . Inserting these values of parameters into Eqs. (9) and (10) gives

$$k_1 = 0.00779 S_{g0} e^{0.0124 \text{RH}} e^{-9500/RT} y^{0.31}, \quad (11)$$

$$k_2^{-1} = 0.0344 S_{g0} M^{-1} \text{RH}^{0.96}. \quad (12)$$

Eq. (7) together with Eqs. (11) and (12) constitutes the kinetic model for the sulfation of BFS/HL sorbents.

In Fig. 11, conversions calculated by the kinetic model are compared with the experimental results. The comparison shows that the calculated values are in good agreement with the experimental data with a standard deviation of 0.055 in conversion.

From the above analyses, one can see that although sorbents prepared at different conditions have different compositions and structural properties and hence have different reactivities, their reaction with  $\text{SO}_2$  can be described by the same model and the sorbent reactivity is well correlated with  $S_{g0}$  and  $M$  through the kinetic parameters  $k_1$  and  $k_2$ .

Eqs. (11) and (12) indicate that relative humidity significantly affects both  $k_1$  and  $k_2^{-1}$ , but reaction temperature and  $\text{SO}_2$  concentration mildly affect  $k_1$  only, in accordance to that observed for the initial rate of conversion and the ultimate conversion in Section 3.2.

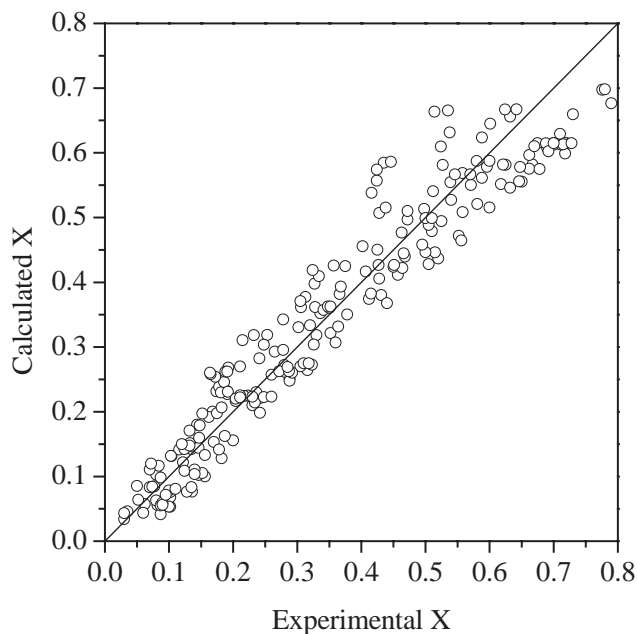


Fig. 11. Comparison of the calculated and experimental conversion values.

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 amounts of water adsorbed and  $\text{SO}_2 \cdot \text{H}_2\text{O}$  and  $\text{H}^+$  formed, and therefore results 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 like the type of Langmuir adsorption (Smith, 1981).

The mild effect of the reaction temperature may be due to the fact that as the temperature increases, the chemical reaction rate constants increase, whereas the amounts of water and  $\text{SO}_2$  adsorbed decrease.

The dissolution reaction of a Ca-containing reactant takes place only at the surface which is not occupied by the products of sulfation. The area of unoccupied surface reduces as the conversion increases. Therefore, the overall reaction rate diminishes with reaction time, and the conversion reaches an ultimate value eventually. The ultimate conversion increases as the relative humidity increases, because a thicker water layer provides a wider range for the product molecules to deposit and leads to a lower rate of surface coverage (Ho et al., 2002).

#### 4. Conclusion

The kinetics of the reaction of BFS/HL sorbents with  $\text{SO}_2$  in humid  $\text{N}_2$  at low temperatures has been studied. The

reaction can be well described by a modified surface coverage model which assumes that the reaction rate is controlled by chemical reaction on sorbent grain surface and takes into account the effect of sorbent Ca molar content and the surface coverage by product. The effects of sorbent preparation conditions, such as BFS fineness, BFS/HL weight ratio, slurring temperature, and slurring time, on sorbent reactivity were entirely represented by the effects of the initial specific surface area ( $S_{g0}$ ) and the Ca molar content ( $M^{-1}$ ) of sorbent. The initial conversion rate of sorbent increased linearly with increasing  $S_{g0}$ , and the ultimate conversion increased linearly with increasing  $S_{g0}M^{-1}$ . The initial conversion rate and ultimate conversion of sorbent increased significantly with increasing relative humidity of the gas. Temperature and  $\text{SO}_2$  concentration had mild effects on the initial conversion rate and negligible effects on the ultimate conversion.

### Notation

$E_1$	activation energy for $k_1$ , J/mol
$k'_p$	constant defined by Eq. (3), $\text{m}^2 \text{mol/g}^2$
$k'_S$	constant defined by Eq. (1), $\text{g/min m}^2$
$k_1$	$k'_s S_{g0}$ , $\text{min}^{-1}$
$k_2$	$k'_p M/S_{g0}$
$M$	initial weight of solid per mol of Ca, g/mol Ca
$n_1$	reaction order of $\text{SO}_2$ , dimensionless
$R$	gas constant, 8.314 J/mol K
RH	relative humidity
$r_s$	reaction rate of solid per unit initial surface area, $\text{mol/min m}^2$
$S_{g0}$	initial specific surface area of solid, $\text{m}^2/\text{g}$
$T$	reaction temperature, K
$t$	time, min
$X$	conversion, dimensionless
$y$	$\text{SO}_2$ concentration, ppm

### Greek letters

$\alpha_1$	constant in Eq. (9), $\text{min}^{-1}$
$\alpha_2$	constant in Eq. (10), dimensionless
$\beta_1$	coefficient of RH in Eq. (9), dimensionless
$\beta_2$	index of $\text{RH}^{-1}$ in Eq. (10), dimensionless
$\Phi$	fraction of surface area which is not covered by product

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