

Kinetics of the Reaction of Sulfur Dioxide with Calcium Oxide Powder

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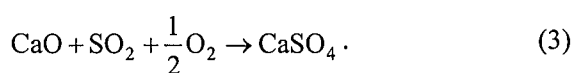
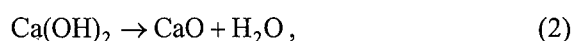
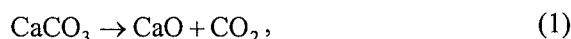
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Abstract—The kinetics of the reaction of CaO powder with SO₂ was studied in a differential packed-bed reactor. The reaction rate was controlled by product layer diffusion, except in the initial stage. The intrinsic chemical reaction rate constant was insensitive to the precursor and the calcination history of CaO, but the product layer diffusivity was affected by these two factors in the initial stage and decreased to a constant value with increasing conversion of CaO. The variation of product layer diffusivity with these factors was explained by its dependence on the concentrations of defects in CaO and CaSO₄ crystals.

Key Words : CaO, SO₂, Desulfurization, Reaction kinetics

INTRODUCTION

Limestone (CaCO₃) or hydrated lime (Ca(OH)₂) has been used as a sorbent to reduce the emission of sulfur dioxide from the combustion of coal. In the high temperature environment of combustion, limestone or hydrated lime decomposes into lime (CaO), and the lime reacts with SO₂ and O₂ in the gas to form CaSO₄:



Because of its importance, the kinetics of the reaction of sulfur dioxide with lime has been studied by many investigators (Bardakci, 1984; Bhatia and Perlmutter, 1981; Borgwardt, 1970; Borgwardt and Harvey, 1972; Borgwardt *et al.*, 1987; Christman and Edgar, 1983; Georgakis *et al.*, 1979; Hartman and Coughlin, 1976; Hung, 1985; Marsh and Ulrichson, 1985; Ramachandran and Smith, 1977; Wen and Ishda, 1973). But the results obtained vary considerably among the investigators. As can be seen from Tables 1 and 2, the values reported for the intrinsic chemical reaction rate constant *k* and the product layer diffusivity *D_s*, respectively, vary over two orders of magnitude. In fact, the reaction kinetics is complicated by many factors, such as the precursor

of CaO, the mass transfer processes, including gas phase and solid-state diffusions, and the structural change caused by sintering and reaction (Mahuli *et al.*, 1999). The values of kinetic parameters are affected by these factors as well as the model used. However, by properly selecting the reaction conditions, some factors affecting the reaction can be neglected.

The first purpose of this study is to evaluate the intrinsic chemical reaction rate constant and the product layer diffusivity for the sulfation of CaO at the conditions where the effects of external mass transfer and intraparticle diffusion are negligible.

Table 1. Values of *k* for CaO sulfation reported in the literature.

Investigators	Temperature (°C)	<i>k</i> (cm/s)
Borgwardt and Harvey (1972)	980	0.22±0.05
Wen and Ishida (1973)	750	0.026
	850	0.053
	950	0.106
Hartman and Coughlin (1976)	850	6.6
Ramachandran and Smith (1977)	850	0.102
Bhatia and Perlmutter (1981)	760	0.151
	870	0.280
	980	0.493
Christman and Edgar (1983)	815	0.19
Bardakci (1984)	840	2.75
Marsh and Ulrichson (1985)	835	0.076
Mahuli <i>et al.</i> (1999)	980	0.22

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Table 2. Values of D_s for CaO sulfation reported in the literature.

Investigators	Model	T ($^{\circ}\text{C}$)	$D_s \times 10^8$ (cm^2/s)
Hartman and Coughlin (1976)	grain	850	0.6
Ramachandran and Smith (1977)	single pore	850	75
Georgakis <i>et al.</i> (1979)	changing grain size	850	0.8
		980	250
Bhatia and Perlmutter (1981)	random pore	650	1.3
		760	6
		870	19
		980	69
		850	0.86
Chrisman and Edgar (1983)	distributed pore size	815	4
Bardakci (1984)	changing grain size	840	0.08
Marsh and Ulrichson (1985)	changing grain size	841	18
		932	63
Borgwardt <i>et al.</i> (1987)	random pore	800	1.25-3.22 (limestones) 0.30-0.74 (pure CaCO_3)

The second purpose is to elucidate the effects of the precursor and the calcination history of CaO on the reaction kinetics.

EXPERIMENTAL

The calcium oxide samples, Calcines I, II, and III, were obtained by calcining reagent grade calcium carbonate powder. The powder has 99.5% purity and 4 μm average particle diameter.

Calcine I was prepared by first calcining the calcium carbonate powder in nitrogen for two hours at 950 $^{\circ}\text{C}$ and then keeping the calcine in storage for several days; samples taken from this batch of calcine were heated directly to the reaction temperature before the reaction was started. Calcine II was obtained by calcining the calcium carbonate powder in the reactor for about 18 min at 950 $^{\circ}\text{C}$ and then cooling it to the reaction temperature. Calcine III was obtained by using the same batch of calcine as Calcine I, but instead of heating the sample directly to the reaction temperature, it was heated to 900 $^{\circ}\text{C}$, staying there for 3 min, and then cooled to the reaction temperature.

X-ray diffraction analysis showed that the calcine obtained at 950 $^{\circ}\text{C}$ was completely converted to $\text{Ca}(\text{OH})_2$ after several days of storage due to its reaction with the moisture in air. Thus, the precursor of Calcines I and III was $\text{Ca}(\text{OH})_2$.

The reaction of a sample with SO_2 was started at about 3 min after the sample temperature reached the desired reaction temperature (750-950 $^{\circ}\text{C}$). The BET surface area (S_g) measured and the grain radius (r_g) calculated, assuming spherical grains, for each sample at this moment is listed in Table 3.

The calcination and the sulfation of samples were performed in a differential packed-bed reactor as shown in Fig. 1. The packed-bed reactor consisted

Table 3. BET surface areas and grain radii of calcines.

Calcine	Temperature ($^{\circ}\text{C}$)	S_g (m^2/g)	r_g (10^{-6}cm)
I	950	8.6	10.6
	850	10.0	9.1
	750	18.4	4.9
II	950	11.7	7.7
	850	12.6	7.2
	750	19.3	4.7
III	850	8.1	11.2
	750	9.5	9.5

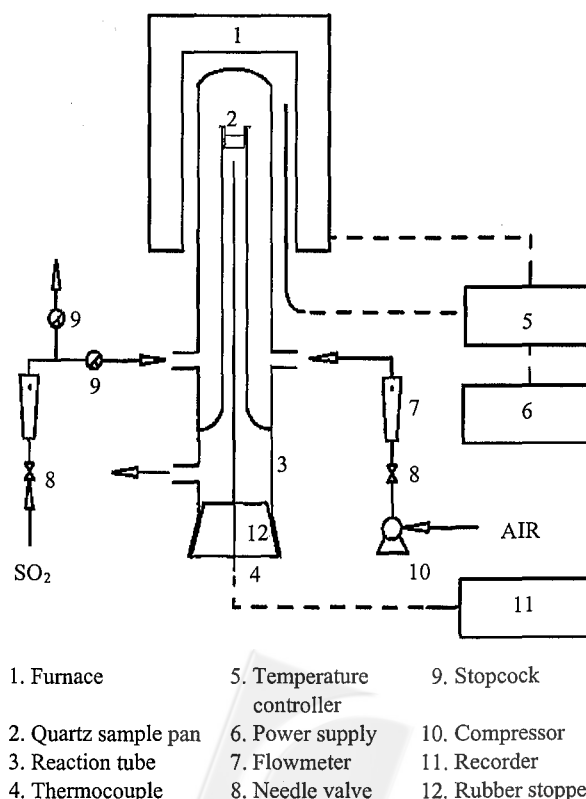


Fig. 1. Schematic diagram of the experimental apparatus.

of a quartz sample pan and two quartz tubes. The pan, 1 cm diameter and 1.5 cm height, was perforated at the bottom and inserted in the upper end of the inner tube. Before the run, the pan was filled with quartz wool and into which the sample was dispersed. The sample weight after calcination was about 15 mg. Air and SO₂ mixture at a rate of 4 L/min (room temperature) and a SO₂ concentration of 3000 ppm was passed through the reactor during the sulfation test.

Fresh samples were used for different sulfation times. At least two repeated runs were performed for each set of reaction conditions. The conversion of CaO was calculated from the weight increase due to reaction according to Eq. (3). The weight measurement was accurate to 0.01 mg. The absolute error in conversion was about 0.02.

The detailed experimental procedures have been described elsewhere (Hung, 1985).

RESULTS AND DISCUSSION

Results of sulfation test

Figures 2 and 3 show the conversion x and reaction time t data for calcines. From Fig. 2, one can see

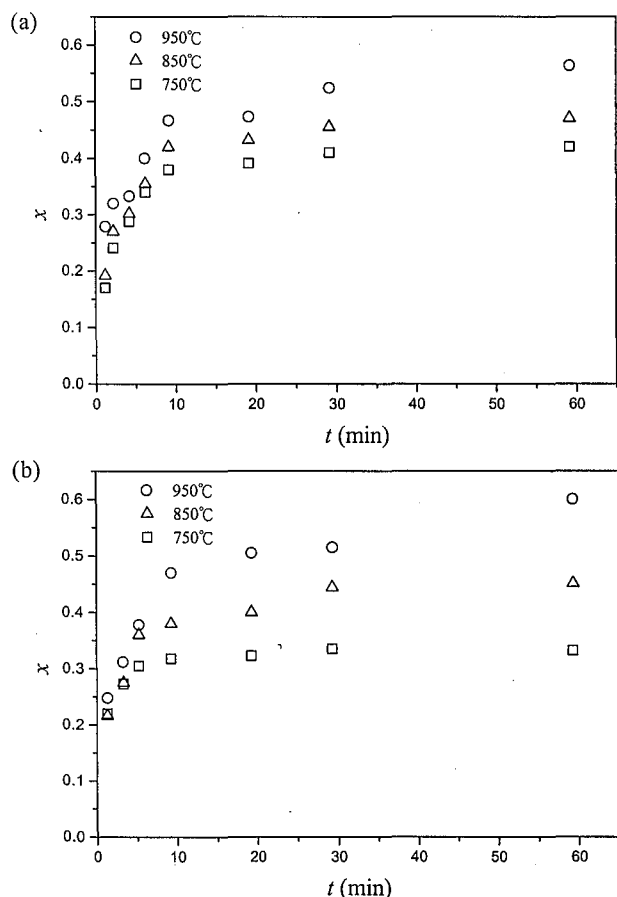


Fig. 2. Conversion vs. time for the sulfation of (a) Calcine I; (b) Calcine II.

that the reaction is rapid in the initial period (< 1.5 min) but slows down drastically at about 10 min, and the CaO is incompletely converted for a reaction time as long as 1 h.

The reaction was faster at a higher temperature. But, the reaction of a sample was also affected by the specific surface area of the sample. As can be seen from Figs. 3(a) and 3(b), the data at 750°C and 850°C are quite close to each other in the initial period for both Calcines I and II. This is because the samples reacted at 750°C have much greater initial specific surface areas than those reacted at 850°C

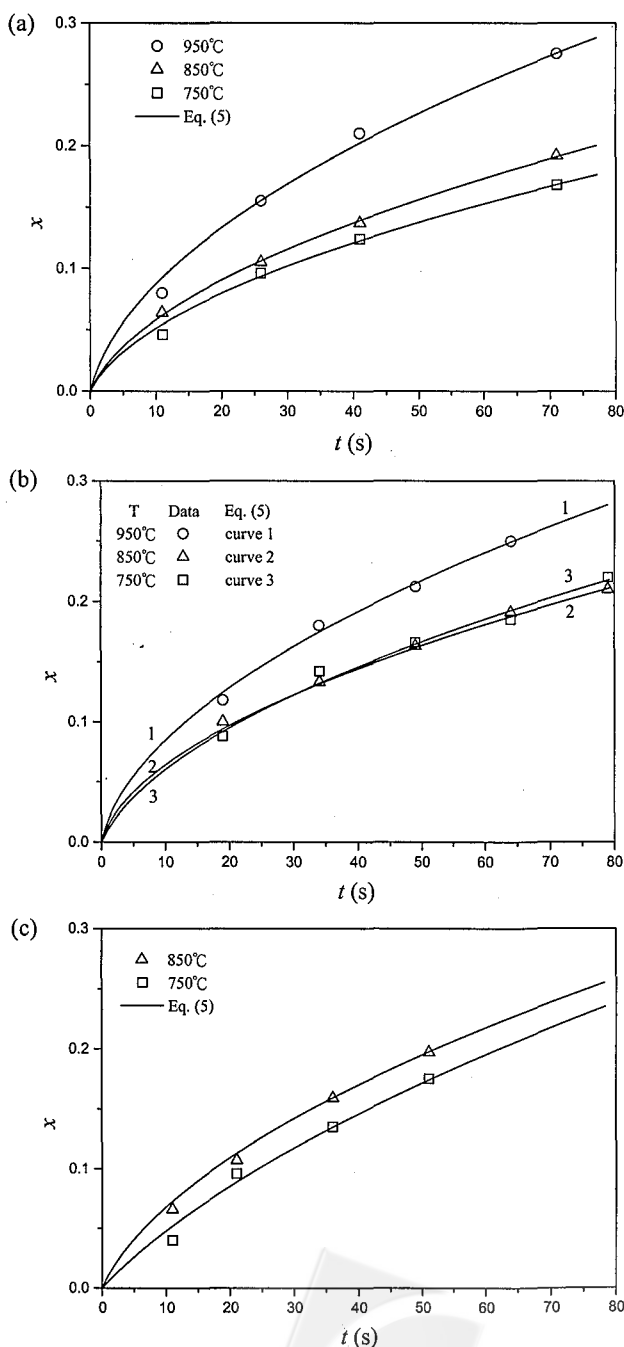


Fig. 3. Conversion vs. time for the initial period of sulfation of (a) Calcine I; (b) Calcine II; (c) Calcine III.

and 950°C (Table 3). However, Fig. 3(c) shows that Calcine III is more reactive than Calcine I at 750°C and 850°C (Fig. 3(a)), although the specific surface areas of the samples of Calcine III are smaller. This result indicates that there were factors other than the specific surface area affecting the reactivity of CaO.

Maximum conversion

The decrease in the sulfation rate of CaO was resulted from the formation of CaSO₄. CaSO₄ has a molar volume larger than that of CaO; their molar volume ratio, z , is 3.09. Thus, CaSO₄ would form a dense product layer surrounding the unreacted CaO, and the layer would give rise to a significant diffusion resistance for the reaction. Moreover, the formation of CaSO₄ would reduce the pore volume and pore size of a particle, and even cause the blockage of pores.

The change of the porosity ε of a particle with reaction can be expressed as (Szekely *et al.*, 1976)

$$\varepsilon = \varepsilon_0 - x(z-1)(1-\varepsilon_0), \quad (4)$$

where ε_0 is the initial porosity. The reaction proceeds extremely slowly after ε equals zero because of the loss of the entire interior reaction sites. Thus, the conversion attained when ε equals zero is the maximum conversion, if the reaction time is not excessively long. The maximum conversion of the present CaO can be estimated using the above equation. Since the particles of the CaCO₃ reagent are nonporous, the initial porosity ε_0 of a CaO particle was calculated to be 0.542, assuming no particle volume change due to calcination. The maximum conversion thus obtained is 0.562, which is very close to the one hour values measured at 950°C for Calcines I and II, 0.57 and 0.60, respectively.

Kinetic model

Many kinetic models have been proposed to simulate the sulfation of CaO (Bhatia and Perlmutter, 1981; Christman and Edgar, 1983; Georgakis *et al.*, 1979; Hartman and Coughlin, 1976; Ramachandran and Smith, 1977; Wen and Ishida, 1973). Here the changing grain size model (Georgakis *et al.*, 1979) was used because the SEM micrograph showed that the CaO particles are composed of sphere-like grains (Hung, 1985). When the CaO particle is small and the gas flow rate is very high, the intraparticle diffusion and external mass transfer resistances for the reaction are negligible, and only the intrinsic chemical reaction and the product layer diffusion have to be considered (Borgwardt and Bruce, 1986; Hung, 1985). For this case, the changing grain size model can be expressed as (Szekely *et al.*, 1976)

$$t = \frac{\rho_S r_g}{k C_{A0}} g(x) + \frac{\rho_S r_g^2}{6 D_S C_{A0}} p(x), \quad (5)$$

where

$$g(x) = 1 - (1-x)^{1/3}, \quad (6)$$

$$p(x) = 3 \left\{ \frac{z - [z + (1-z)(1-x)]^{2/3}}{z-1} - (1-x)^{2/3} \right\}. \quad (7)$$

Two of the assumptions made for the present model are that SO₂ diffuses inward through the product-layer and reacts with CaO at the CaSO₄-CaO interface and that the reaction is first order with respect to SO₂ concentration. These assumptions are adopted by most models reported in the literature. However, some investigators have pointed out that the product layer diffusion is a solid-state diffusion and the diffusing species is not SO₂ (Bhatia and Perlmutter, 1981; Borgwardt and Bruce, 1986; Mahuli *et al.*, 1999). It has been proved experimentally that during CaO sulfation, Ca²⁺ and O²⁻ ions diffuse outward in a coupled manner through the product layer and react with SO₂ at the outer surface of CaSO₄ (Hsia *et al.*, 1993, 1995). Moreover, the sulfation rate has been found to increase with SO₂ concentration or partial pressure with a power less than unity (Borgwardt and Bruce, 1986; Borgwardt *et al.*, 1987; Lai and Shih, 1989). Therefore, the present model may only represent the "apparent" behavior of the sulfation of CaO. Nevertheless, the present model was used to evaluate the kinetic parameters in order to compare them with those reported in the literature, which were evaluated with the same assumptions mentioned above.

Kinetic analysis for the initial period of reaction

A plot of $p(x)-t$ for the data in the initial period (< 1.5 min) gives a straight line for each calcine at each temperature, as shown in Fig. 4 for Calcine I. This result indicates that the product layer diffusion dominated the reaction process. These straight lines do not go through the origin because at the very beginning the reaction was controlled by the intrinsic surface chemical reaction with a finite rate (Szekely *et al.*, 1976). By least-squares fitting of Eq. (5) to the $x-t$ data for the calcines, the values of k and D_S were obtained. These values are shown in Table 4. As shown in Fig. 3, the curves plotted using Eq. (5) agree well with the data. The average deviation of the data from the fitting curves was about 2 s in t .

As can be seen in Table 4, the values of k for different calcines at the same reaction temperature are essentially the same, since their differences are

Table 4. Values of k , D_S , and D'_S measured for the sulfation of CaO powder (3000 ppm SO₂).

Calcine	Temperature (°C)	k (cm/s)	$D_S \times 10^8$ (cm ² /s)	$D'_S \times 10^8$ (cm ² /s)
I	950	0.16	4.6	1.0
	850	0.07	1.6	0.58
	750	0.03	0.33	0.14
II	950	0.12	2.2	0.60
	850	0.08	1.0	0.51
	750	0.03	0.47	0.12
III	850	0.08	4.3	—
	750	0.03	3.9	—

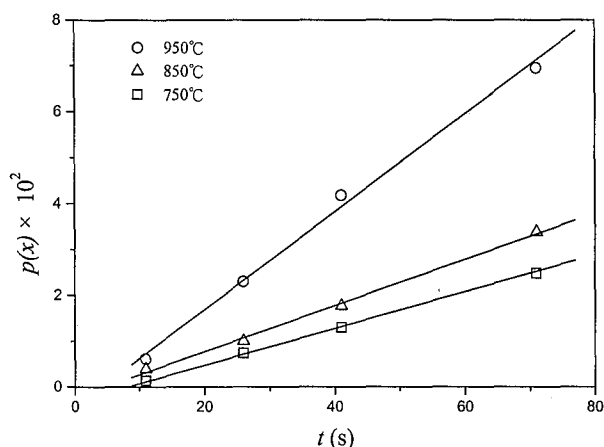
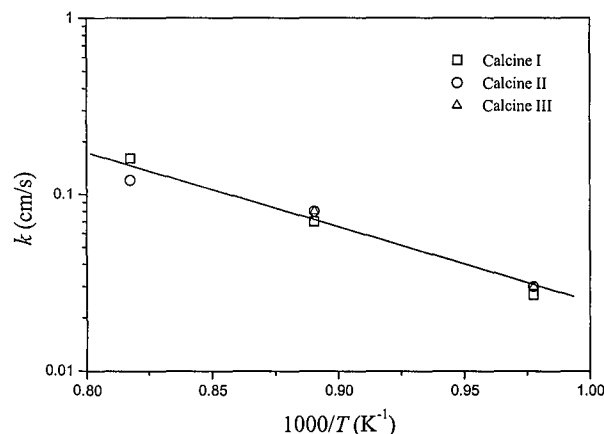

 Fig. 4. $p(x)$ vs. t for the sulfation of Calcine I. — initial period.


Fig. 5. Arrhenius plot for the intrinsic reaction rate constant.

within the experimental error. The relative standard error for the k value was about $\pm 43\%$. These values of k can be compared with those reported in the literature. As shown in Table 1, the values of k at 850°C are from 0.053 (Wen and Ishida, 1973) to 6.6 cm/s (Hartman and Coughlin, 1976) in the literature. The values of this study at 850°C, 0.07-0.08 cm/s, fall in the lower end of this range. Also one can see that the values reported by Wen and Ishida (1973) are in good agreement with the present results.

The activation energy of k of this study was determined to be 82 kJ/mol in average (Fig. 5), which agrees well with that reported by Marsh and Ulrichson (1985), 80 kJ/mol.

As shown in Table 4, the values of D_S at each temperature vary markedly with the calcine, in contrast to the values of k . The relative standard error for the D_S value was about $\pm 13\%$, which is much smaller than that for the k value. The range of D_S values reported in the literature is also wider than that of k values. As shown in Table 2, the values of D_S reported in the literature are from 8.0×10^{-10} (Bardakci, 1984) to 7.5×10^{-7} cm²/s (Ramachandran and Smith, 1977) at 840-850°C. The values of this study at 850°C, 1.0×10^{-8} - 4.3×10^{-8} cm²/s, fall in this range.

The activation energies of D_S for Calcines I and II were determined to be 137 and 80 kJ/mol, respectively (Fig. 6), the average value of which, 109 kJ/mol, is almost the same as that given by Bhatia and Perlmutter (1983), 108 kJ/mol.

The small D_S value and the large activation energy of D_S indicate that the product layer diffusion is a solid-state diffusion (Shih and Stark, 1978). This conclusion agrees with that set forth by other researchers, such as Bhatia and Perlmutter (1981), Borgwardt and Bruce (1986), and Mahuli *et al.* (1999).

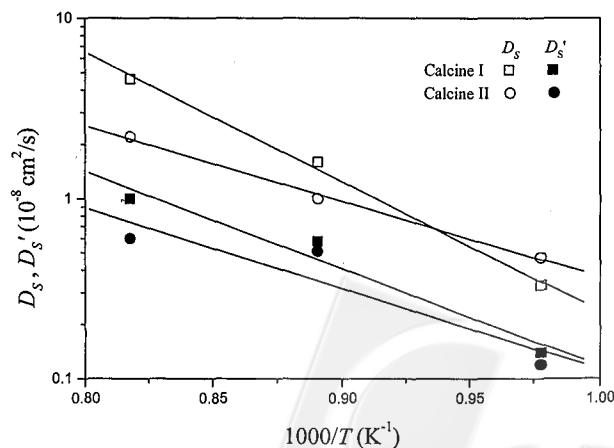


Fig. 6. Arrhenius plot for the product layer diffusivity.

Solid-state diffusion proceeds mainly through the crystal defects, such as vacancy, dislocation, and grain boundary (Shewmon, 1989). The CaO crystals of the samples prepared from different precursors and through different calcination histories may have different concentrations of crystal defects, due to different extents of lattice transformation and crystal growth. The CaSO₄ product layer formed from the CaO crystals in the initial period may be ill-crystallized and have lots of defects which are closely related to original defects of the CaO crystals. As the reaction proceeds, the crystallinity of the product layer will increase due to the continuing arrangement of the ions into the lattice sites, and the D_S value will decrease. Thus, the D_S value determined is an average value in the initial period. Therefore, the great variation of the D_S value with the calcine in this period is thought to be due to the concentrations of crystal defects in the CaO crystals being different for different calcines.

Kinetic analysis for the long period of reaction

A plot of $p(x)$ - t for the 30 min sulfation of each calcine at each temperature indicates that the reaction can be divided into three stages and that the data in the second and the third stages can be represented by straight lines with different slopes, as shown in Fig. 7 for Calcine I. This result indicates that the product layer diffusion controlled the sulfation rate in the latter two stages, and the product layer diffusivities were almost constant in these two stages. The linear relationship in the $p(x)$ - t plot can be explained by the mechanism of solid-state diffusion, and the abrupt decrease in the line slope by the coherence and coalescence of grains.

As discussed above, the D_S value will decrease as the concentration of defects in the CaSO₄ product layer decreases. As the reaction proceeds, the CaSO₄ product layer continues to thicken. The Ca²⁺ and

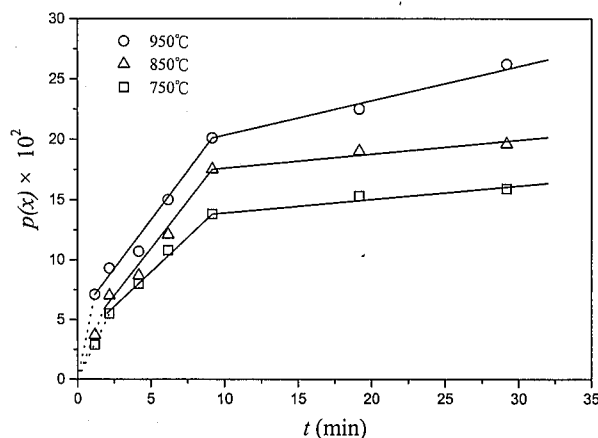


Fig. 7. $p(x)$ vs. t for the sulfation of Calcine I — long period.

SO₄²⁻ ions would arrange to give a more perfect crystal structure. Accordingly the crystal defects would decrease in amount and eventually reach an equilibrium value, which is a function of temperature. Thus the D_S value would become constant thereafter. The time when the D_S value became constant is thought to be the starting time of the second stage of reaction (about 1.5 to 9 min for Calcine I).

The value of D_S for the second stage, D'_S , can not be evaluated using Eq. (5). The pertinent equation for this stage was derived and is written as

$$t = t_1 + \frac{\rho_S r_g^2}{6D'_S C_{A0}} [p(x) - p(x_1)], \quad (8)$$

where x_1 and t_1 are the starting x and t of the second stage of reaction; x_1 was in the range from 0.21 to 0.27 and t_1 from 71 to 131 s for Calcines I and II. The D'_S values obtained using Eq. (8) are smaller than the D_S values for the first stage by about three times, as can be seen in Table 4; but they are still within the range of values reported in the literature (Table 2). The differences between the D'_S values for the calcines are also much smaller, especially for the temperatures of 750°C and 850°C. This result is in accordance with the foregoing postulate on the D'_S value, and indicates that the product layer was well-crystallized and the D'_S value is mainly determined by the temperature instead of the calcine. The activation energies of D'_S for Calcines I and II were determined to be 103 and 84 kJ/mol, respectively (Fig. 6), which are in the range determined for the first stage.

As the reaction proceeds further, the grains in a CaO particle continue to expand in volume, and at some extent of reaction they start to contact each other and cohere together. When this happens, the surface area available for the reaction to take place decreases greatly and the reaction rate diminishes drastically. The reaction therefore proceeds very slowly afterward. This is thought to be the case for the third stage of reaction.

The starting x and t of the third stage of reaction depend on the characteristic of the pores in the calcine. Because the calcine reacted at a lower temperature had smaller pores, the size of which is proportional to the inverse of S_g (Table 3), its starting x was lower. The corresponding values of t at 750°C, 850°C, and 950°C were coincidentally to be about 9 min for Calcine I (Fig. 7); but they were about 5, 6, and 9 min, respectively, for Calcine II. The coherence or coalescence of grains was confirmed by SEM observations on the samples reacted for more than 9 min (Hung, 1985). Furthermore, the period of the third stage can be defined to include t at 1 h. If this is the case, the slopes of the lines in Fig. 7 would be slightly smaller.

Evaluation of the D_S value for the third stage was not attempted in this study, because of the difficulty in estimating the reaction surface area and the product layer thickness; but it should be about the same as D'_S . However, if the effect of grain coherence was neglected and the changing grain size model was used to analyze the data, the D_S value obtained for the third stage would be much lower than the true value.

Discussion

From the above analyses, it is evident that D_S depends not only on the precursor and the calcination history of CaO, but also on the conversion of CaO. This fact may be the reason that there is a broad range of D_S values reported in the literature. Although the D_S values reported in the literature are also model-dependent and subjected to experimental errors, our results, obtained using the same model, do show that the variation of the D_S values reported can not be totally attributed to the model used and the errors in measurements.

Our results show that the k value is insensitive to the type of calcine but has a greater standard error than D_S . Therefore, the variation of the k values reported in the literature may be mainly due to the model used and the experimental errors. Because the k value can be determined only in the initial period and this period is short (< 1.5 min), the error in the measurement of reaction time would be great. Another important error is that of S_g . The S_g of a CaO sample is sensitive not only to the calcination temperature and time (Table 3), but also to the way of sample handling. The S_g of a CaO sample would change significantly before it is subjected to surface area measurement or sulfation test, if its reaction with the moisture in air is not properly prevented.

Our results also show that when the product layer is well-crystallized, the D_S value is nearly independent of the type of calcine and the conversion of CaO. However, in the process of furnace dry injection, the residence time of sorbent particles in the furnace is much shorter than the time required for a well-crystallized product layer to form. Thus a D_S value pertinent to the sorbent and process characteristics should be used when modeling the sulfation of CaO in the furnace dry injection process.

The results of this study have been well explained by the mechanism of solid-state diffusion. More evidences, however, are required to further substantiate the explanation.

CONCLUSION

Changing grain size model was used to analyze

the kinetics of the sulfation of CaO powder. At the conditions of high gas flow rate and small particle size, the sulfation rate of CaO was controlled by product layer diffusion except in the initial period where chemical reaction was also important.

The intrinsic reaction rate constant was insensitive to the precursor and the calcination history of CaO, but the product layer diffusivity was affected by these two factors in the initial period and decreased to a constant value with increasing conversion of CaO. The variation of product layer diffusivity with these factors can be explained by its dependence on the concentrations of defects in CaO and CaSO₄ crystals; however, more evidences are needed to further substantiate the explanation.

NOMENCLATURE

C_{A0}	bulk concentration of gaseous reactant, mol/cm ³
D_S	product layer diffusivity, or that for the first stage of reaction, cm ² /s
D'_S	product layer diffusivity for the second stage of reaction, cm ² /s
$g(x)$	conversion function defined by Eq. (6)
k	intrinsic chemical reaction rate constant, cm/s
$p(x)$	conversion function defined by Eq. (7)
r_g	initial radius of the grain of solid reactant, cm
S_g	initial BET specific surface area of solid, m ² /g
t	time, s
t_1	starting t for the second stage of reaction, s
x	conversion
x_1	starting x for the second stage of reaction
z	ratio of the molar volume of solid product to that of solid reactant, 3.09 for CaSO ₄ /CaO system

Greek symbols

ε	porosity of solid
ε_0	initial porosity of solid
ρ_S	molar density of solid reactant, 5.917×10^{-2} mol/cm ³ for CaO

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氧化鈣粉粒與二氧化硫反應的動力學

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摘 要

本研究以一微分填充床反應器探討氧化鈣粉粒與二氧化硫反應的動力學。除了初始階段外，反應速率是由產物層擴散所控制。化學反應速率常數不受氧化鈣的先驅物與其鍛燒程序所影響，但產物層擴散係數在初始階段則受到上述兩因素的影響，並隨著氧化鈣的轉化而減少至一定值。產物層擴散係數的變化可以其受氧化鈣及硫酸鈣結晶缺陷的濃度的影響來解釋。

