Effect of Specific Surface Area on the Reactivity of CaO with SO_2

The rate of reaction of calcined limestone with SO_2 and O_2 was measured at conditions that eliminate all resistances not associated with the CaO grain surface. Reactivity increased with the square of the BET surface area when grain size was varied as an experimental parameter. The observed effects of surface area and temperature account for the SO_2 capture reported for boiler tests of the limestone injection process.

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SCOPE

The increasing complexity of pollution control equipment poses a dilemma for the electric utility industry. The current cost of the flue gas desulfurization system for a new coal-fired power plant is exceeded only by the cost of the boiler itself. Especially for older plants, considerations of economics and retrofit dictate that a simpler system will be needed if all SO_2 emissions are to be reduced for the purpose of controlling acid rain. A process based on injection of pulverized limestone is generally considered the best potential solution of the problem, and a successful process of this type has been the subject of research, virtually worldwide, for two decades (Wickert, 1963; Falkenberry and Slack, 1969; Ishihara et al., 1975b). Interest in this approach is periodically renewed by pilot-scale boiler tests which indicate that SO_2 removals as high as 65% may be possible at acceptable limestone injection rates. Recent development of staged combustion burners to control NO_x has given special impetus to this approach. Favorable tests of these burners with limestone injection suggest that they may achieve adequate SO_2 reduction concurrently with NO_x control. Intensive efforts are now in progress under sponsorship of both private industry and the Environmental Protection Agency to develop the limestone injection multistage burner (LIMB) as a practical method of preventing acid rain (Parkinson and McQueen, 1984).

An impediment to the systematic development of the LIMB process is a lack of fundamental information on the mechanism of sulfur capture. Although it is accepted that CaO is the active solid species, it has long been recognized that existing laboratory measurements of the kinetics of CaO reaction with SO_2 or other gaseous sulfur species are far too slow to account for any significant sulfur capture in the short residence times (ca. 2 s) available in a boiler furnace. This discrepancy has caused some to question the validity of the field results, given the inherent difficulties of sampling and measurement under boiler test conditions. Because of the importance of the SO_2/CaO reaction to the fluidized bed combustion (FBC) process, it has been one of the most intensively investigated gas/solid reactions. Nearly all of the experimental studies, however, have been confined to large particles and constant temperature (850°C) appropriate to FBC.

A recent experimental study of the calcination kinetics and surface area of small (1 to 90 μm), well-dispersed limestone particles has shown that the specific surface area of the CaO immediately after $CaCO_3$ decomposition is as high as 90 m^2/g (Borgwardt, 1985). This value is an order of magnitude greater than those obtained when large particles are calcined at the slower rates corresponding to FBC conditions. If the specific surface of the CaO appreciably affects the kinetics of sulfur capture, then the failure of prior laboratory data to account for the observed results of boiler injection tests can be explained. This hypothesis is supported by recent measurements of the effect of surface area on the reactivity of CaO with H_2S and COS, which was shown to increase with the second power of BET surface area over the range of 5 to 70 m^2/g (Borgwardt et al., 1984a). It is thus apparent that the mechanism of sulfur capture in LIMB, in either of its reducing or oxidizing combustion zones, is probably quite different from that of FBC in the sense that efficiency may be strongly dependent on the high surface areas peculiar to the rapid calcination of smaller particles. Since no prior study of the SO_2/CaO reaction has included surface area as an experimental variable, and because of the importance of such data to an elucidation of the rate controlling mechanism in LIMB, this study was carried out with the objective of quantifying the surface area effect using the experimental techniques recently developed for producing nascent CaO.

CONCLUSIONS AND SIGNIFICANCE

In the temperature range of this study, 760 to 1,125°C, SO_2 reacts with CaO in the presence of 5% O_2 to form $CaSO_4$ as the sole product. The rate of $CaSO_4$ formation increases with temperature over this full range in accordance with the Arrhenius

relationship when pore diffusion resistance is eliminated. The apparent activation energy at these conditions was 36.6 kcal/mol at constant SO_2 partial pressure. The reactivity increased with the square of the BET surface area of the calcine over the range of 2 to 63 m^2/g, a result that is interpreted as manifestation of a dominant diffusion resistance in the product layer. Contrary to prior studies of this reaction, the effect of SO_2 concentration was not first order; in the absence of pore diffusion resistance, the rate of $CaSO_4$ formation increased with the 0.62 ± 0.07 power of SO_2 partial pressure at constant O_2 partial pressure of 5.07 kPa (5%). This result, together with the high sensitivity to temperature, implies that SO_2 is not the diffusing species. The results are best explained if diffusion occurs in the product layer by an ionic process, a conclusion that is consistent with prior investigations of the reaction of CaO with CO_2, H_2S, and COS.

The capture of SO_2 by pulverized limestone injected into boiler furnaces for the purpose of pollution control can be understood in terms of the high specific surface area existing briefly after $CaCO_3$ decomposition. On the basis of available data on the magnitude of the surface areas thus produced, the laboratory kinetic measurements are in satisfactory agreement with furnace tests reported by Ishihara and Hukusawa. The agreement indicates that the temperature/time profile of the furnace and the sintering rate of the CaO will be critical to SO_2 capture.

INTRODUCTION

It was first shown in 1970 that the internal pore structure of CaO participates in the reaction of SO_2 with small particles, not just the exterior surface, as was previously assumed. In one of the earliest applications of the grain model to this reaction, Pigford and Sliger (1973) found that particles as small as 96 μm showed some pore diffusion resistance at 980°C, even for CaO of low specific surface area. After mathematically separating the pore diffusion resistance, they concluded that the ultimate rate-limiting step at the grain surface is diffusion of SO_2 (and, presumably, O_2) through the $CaSO_4$ product layer. From the available data on temperature effect, they estimated an activation energy of 30 kcal/mol for this step, but did not attempt to reconcile that value with the much lower activation energy that would be expected for SO_2 diffusion.

James and Hughes (1976) studied the reaction of 70 μm particles over the temperature range 800 to 1,050°C. They found no pore diffusion resistance in particles of that size having specific surface areas of 5.8 to 10 m^2/g. The reaction rate followed a linear Arrhenius relationship over the full temperature range, showing an activation energy of 31 ± 3 kcal/mol, in agreement with Pigford and Sliger's estimate. They concluded, however, that chemical reaction controls the overall rate in absence of pore diffusion, an inference that is more consistent with the observed temperature sensitivity. The importance of the issue regarding rate controlling mechanism, as it pertains to LIMB, is well illustrated by the data of James and Hughes. At 1,050°C, for example, CaO having 8.5 m^2/g surface area required 22 s to achieve 20% conversion. If their conclusion is correct and chemical reaction is controlling, the rate will increase—at most—in direct proportion to surface area, and nascent CaO of 55 m^2/g surface area would require 3.7 s to achieve that conversion. Under such circumstances, efficient sulfur capture could not be expected for boiler injection. If, on the other hand, product layer diffusion is controlling, the effect of specific surface would be much stronger, and one would predict from the same data that 20% conversion could be attained in 0.6 s, and quite different prospects for this process.

Hartman and Trnka (1980) point out that the main objection to product layer diffusion—the high sensitivity of reaction rate to temperature—is overcome if the diffusion process involves ions in the solid state rather than SO_2 gas. Analysis by Bhatia and Perlmutter (1981a) yielded an estimate of 69×10^{-12} m^2/s for the diffusivity in the $CaSO_4$ product layer at 980°C, a value they indicate is within the range often found for ionic diffusion.

Further evidence of solid-state diffusion control in reactions having high activation energies is reported for the reaction of CaO with CO_2 (Bhatia and Perlmutter, 1983), and with H_2S (Borgwardt et al., 1984a). In the latter case, chemical reaction could be demonstrably eliminated as the controlling step by variation of the CaO grain size. The objective of this study is to apply similar techniques to identify the limiting mechanism for the SO_2 reaction.

EXPERIMENTAL

Reaction rates were measured in a differential reactor by techniques previously described (Borgwardt, 1984a, 1986, 1985) to eliminate interparticle diffusion and intraparticle pore diffusion resistances. An identical reactor was used for calcination of the limestone particles prior to SO_2 exposure. The reasons for using two reactors were: (1) to permit calcination and sintering to be carried out at temperatures different from the reactor temperatures, thus broadening the range of CaO grain size that could be evaluated, and (2) to avoid contamination of the sample during long periods of sintering in a reactor previously exposed to SO_2. (The quartz reactor proved to be not completely inert to $SO_2 + O_2$ at temperatures above 700°C.)

Normal procedure was to load the sample holder with 15 mg of 1 μm limestone particles, dispersed into a quartz wool substrate, and insert it into the calcination reactor at operating temperature. After 2 min heat-up, nitrogen was passed through the sample at a rate of 23 std L/min for 90 s. The resulting CaO was retained in the reactor without gas flow for an additional period to reduce its specific surface area, by sintering, to the desired value. The sintered sample was transferred to the adjacent SO_2 reactor (time required for transfer ca. 5 s) and allowed to equilibrate for 2 min. The reactive gas was then passed through the sample at 23 std L/min, with a normal composition of 3,000 ppm SO_2, 5% O_2 (which was maintained constant in all cases), and balance N_2. Approximately 10 samples were exposed for varied time intervals, following which each was analyzed to determine the conversion vs. time response at the given reaction conditions. To insure reproducibility of these responses, data for each were collected over several cycles of measurement, which required reproduction of temperatures, surface areas, and gas concentrations at least twice for all values of each major variable.

The mol ratio S/Ca, or conversion, was measured by wet chemical analysis. The reacted particles were dissolved by ejecting the contents of the sample holder into 30 mL deionized water containing 2 drops of 30% H_2O_2 and 0.5 mL of 1N HCl. The solution was filtered and made to 100 mL. For Ca^{++} analysis, a 25 mL aliquot was adjusted to pH 12 and titrated with 0.3% EDTA to a murexide endpoint. Sulfate analysis was carried out by ion chromatography with a 10:1 dilution of another aliquot, in a Dionex Mod 2110I analyzer calibrated with calcium sulfate/limestone mixtures carried through the dissolution steps. Confirmatory sulfate analyses were performed on all samples by $Ba(ClO_4)_2$ titration on the remaining solution after removal of Ca^{++} with ion exchange resin.

Specific surface areas were measured by nitrogen adsorption at −195°C using the BET method. Composites of 20 to 40 samples were prepared in the differential reactor for each measurement. Every 15 mg sample was carried through the same calcination, sintering, transfer, and reheat steps that preceded actual SO_2 exposure. Calcines having specific surface areas less than 6 m^2/g, which require larger amounts for

BET analysis, were prepared in 1 g batches in Pt crucibles. Such calcines were stored in sealed vials prior to use, taking 8 mg for each reactor test.

The limestone was the same described previously (Borgwardt et al., 1984a) from Fredonia Quarries, Kentucky, containing 94.6% $CaCO_3$. Particles of nominal 1 μm diameter were fractionated with a Donaldson Accucut Classifier. Particle size analysis by SEM and Coulter counter showed 95 mass % smaller than 2 μm, and 30% smaller than 1 μm.

RESULTS

In the absence of pore diffusion, the principal variables that are expected to determine the rate of SO_2 capture by a given limestone are reaction temperature, specific surface area of the CaO, and the SO_2 partial pressure. The results of experimental evaluation of these variables are shown in Figures 1–5. By using 1 μm particles, small sample size, and high gas velocity, all transport resistances were eliminated other than those associated with the reaction at individual grain surfaces within the particles. The effect of reaction temperature under these conditions is shown in Figure 1, as obtained with CaO having a specific surface area of 3.0 m^2/g. The CaO used for the tests of Figure 1 was sintered at 980°C for 90 min to insure that the surface area remained constant during the subsequent SO_2 exposures. Analysis of the exposed particles showed the sole reaction product at these temperatures was $CaSO_4$.

The effect of specific surface area on the reaction rate was determined at a constant temperature of 800°C with the results shown in Figure 2 (short exposure times) and Figure 3 (long exposures). The highest surface area was obtained by calcination in situ, followed immediately by exposure to SO_2. The lowest surface area was prepared by calcination in Pt crucibles as described previously; all others were calcined and sintered in the second differential reactor, then transferred to the SO_2 reactor. This transfer procedure was also used to obtain the data of Figure 4 for cases in which both temperature and surface area were varied. Measurements of reaction rate as a function of SO_2 partial pressure are shown in Figure 5, again using the transfer procedure. The data shown with open symbols in Figures 2, 4, and 5 denote 15 mg limestone sample size, closed symbols are for 7 mg limestone.

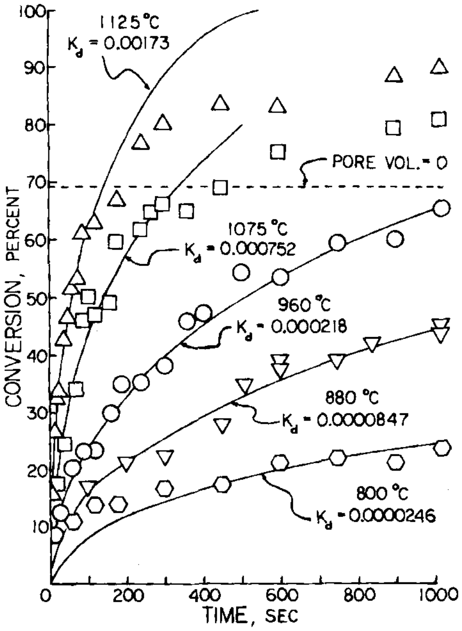

Figure 1. Reactivity of 3.0 m^2/g CaO as a function of temperature at p_{SO_2} = 304 Pa (3,000 ppm). Curves are Eq. 5 with k_d values in s^{-1}.

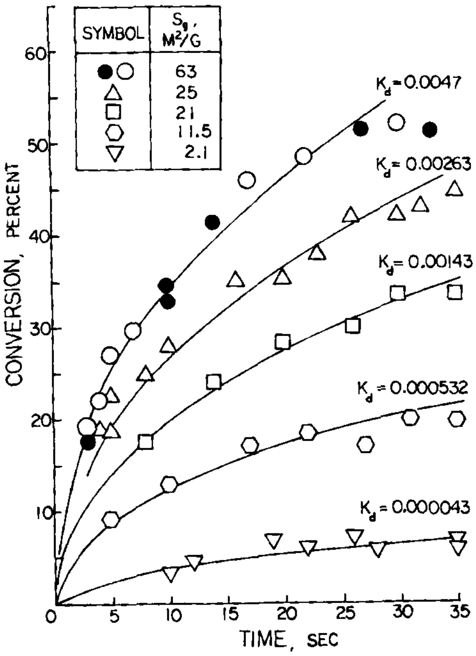

Figure 2. Reactivity of CaO at 800°C as a function of its specific surface area; p_{SO_2} = 304 Pa. Curves are Eq. 5 with k_d values in s^{-1}.

ANALYSIS AND DISCUSSION OF RESULTS

When the SO_2 partial pressure is uniform within the pore structure, which can be assumed to be the case for 1 μm particles of low surface area, the conversion vs. time data will be

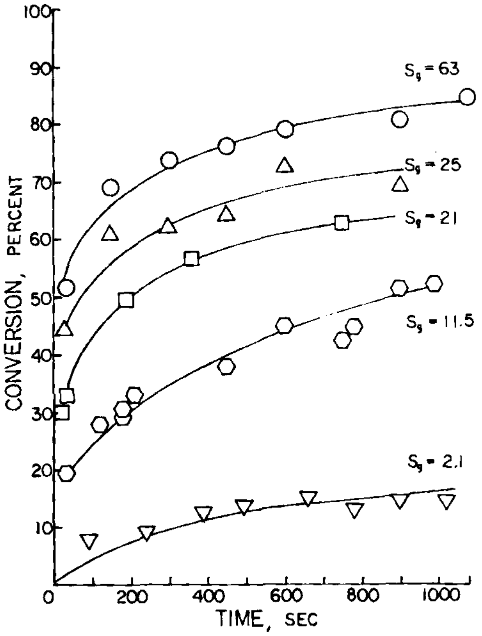

Figure 3. The maximum conversion attained at long SO_2 exposure times also increases with specific surface area (S_g, in m^2/g). T = 800°C, p_{SO_2} = 304 Pa.

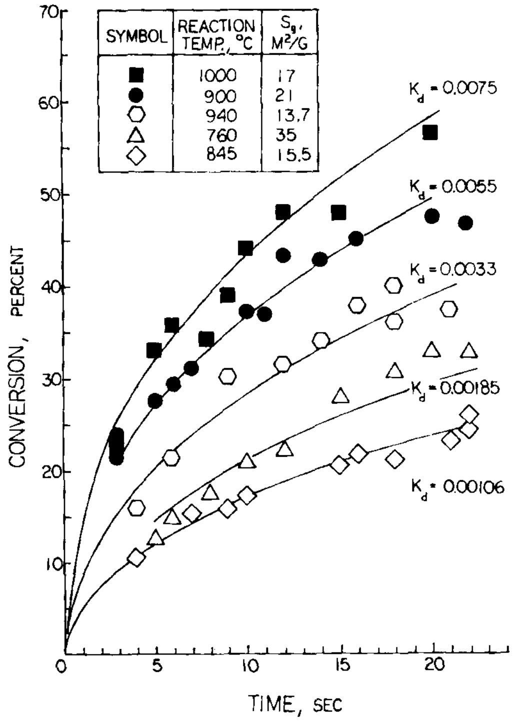

Figure 4. Effect of specific surface area and temperature on CaO reactivity at constant SO_2 partial pressure (304 Pa). Curves are Eq. 5 with k_d values in s^{-1}.

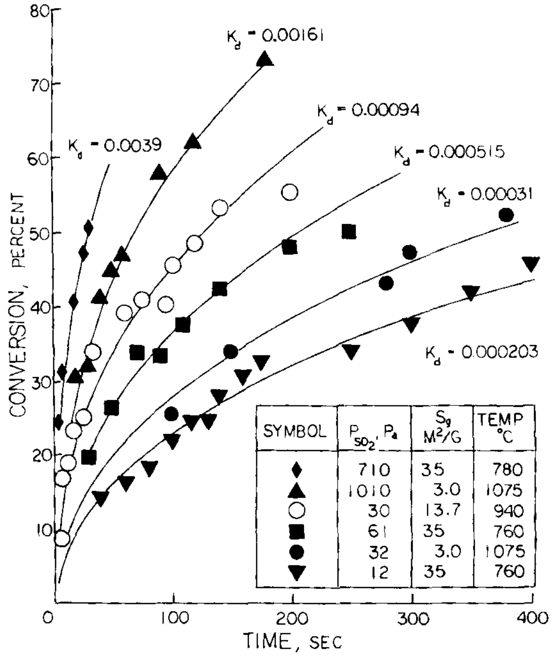

Figure 5. Effect of SO_2 partial pressure on CaO reactivity. Curves are Eq. 5 with k_d values in s^{-1}.

expected to follow one of five possible responses depending on the rate-controlling process at the grain surface. These responses, as described by Sohn and Kim (1980) and by Szekely et al. (1976), can be written for constant temperature and constant grain size as follows:

If chemical reaction controls at the surface of a shrinking core of unreacted CaO within the grains:

$$1-(1-X)^{1/n}=k_c t \quad n=1,2,3 \tag{1}$$

If homogeneous first-order reaction occurs within the grains:

$$-\ln(1-X)=k_h t \tag{2}$$

For power law reaction within the grains:

$$(1-X)^{-n}=k_p t \quad n>0 \tag{3}$$

For product nucleation and growth on grain surfaces:

$$[-\ln(1-X)]^{1/n}=k_g t \quad n=1,2,3,4 \tag{4}$$

For diffusion through the product layer surrounding unreacted cores of (spherical) grains:

$$1-3(1-X)^{2/3}+2(1-X)=k_d t \tag{5}$$

The appropriate rate expression was determined by fitting the data of Figure 1 to each of the above equations, with the results summarized in Table 1. Because Eq. 4 reduces to Eq. 2 at $n = 1$, the next best value of n was used for that case, within the limits defined in its derivation (Avrami, 1940). The comparisons in Table 1 show that the conversion vs. time responses are most accurately correlated by Eq. 5, representing product layer diffusion. The curves shown in Figure 1 are calculated from that equation using the k_d values (also shown in Figure 1) yielding minimum deviation up to $X = 0.7$ for each set of data. Values of $X > 0.7$ were excluded because porosity should be reduced to zero at that conversion and the interior grain surfaces are no longer exposed to SO_2. It is evident from Figure 1 that the overall rate is sharply reduced at $X \approx 0.7$ in accordance with this expectation.

Surface Area

The equilibrium SO_2 partial pressure at the maximum temperature of this study (1,125°C) is 13.7 Pa; therefore, the data can be treated as though the reaction is irreversible. In this case, the value of k_d as derived from Fick's law for diffusion into a spherical grain (assumed nonexpanding) is:

$$k_d=\frac{6MD_e(C_{SO_2})}{\rho_{CaO}(r_g)^2} \tag{6}$$

The specific surface area is related to the initial grain radius by:

$$r_g=\frac{3}{S_g\rho_{CaO}} \tag{7}$$

Of the five possible rate-limiting mechanisms, only product layer diffusion would yield a greater sensitivity to specific surface area than a direct proportionality. The effect of surface area on reactivity should therefore identify most clearly a reaction controlled by this process. Such a test is shown in Figure 6, where the times required to reach 20% conversion, as read

TABLE 1. COMPARISON OF RATE EQUATIONS WITH X VS. t RESPONSES OF FIGURE 1

Eq. No.	Optimum Value of n	Sum of Absolute Deviations of X, Fraction Conversion					
		Reaction Temp., °C					All
		800	880	960	1,075	1,125	Temps.
1	3	0.505	0.600	1.375	1.135	0.978	4.593
2	—	0.489	0.526	1.106	0.922	0.773	3.816
3	2.1	0.400	0.244	0.328	0.376	0.169	1.517
4	2	0.834	1.32	2.75	2.30	1.806	9.01
5	—	0.203	0.173	0.260	0.425	0.287	1.348
No. of data		9	11	16	12	10	58

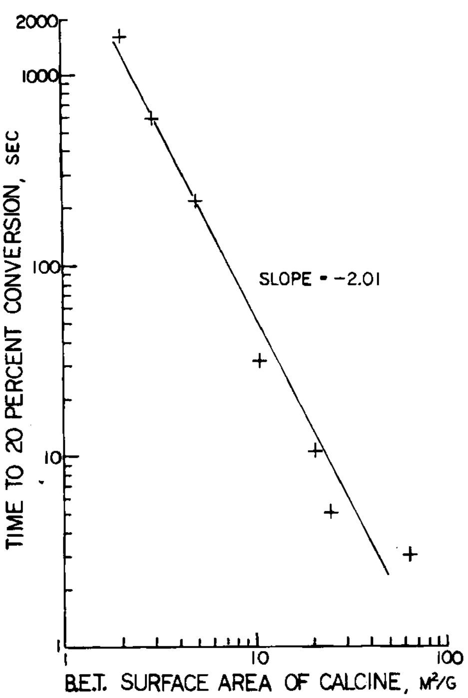

Figure 6. Test for product layer diffusion control according to Eq. 5. $T = 800°C$, $p_{SO_2} = 304$ Pa.

from Figure 1, are plotted logarithmically against the initial BET surface areas of the calcines. The slope of the least-squares line fitted to these data is −2.01, in agreement with Eqs. 5, 6, and 7. The experimental results thus confirm the conclusion of Pigford and Sliger that product layer diffusion controls the ultimate rate of this reaction.

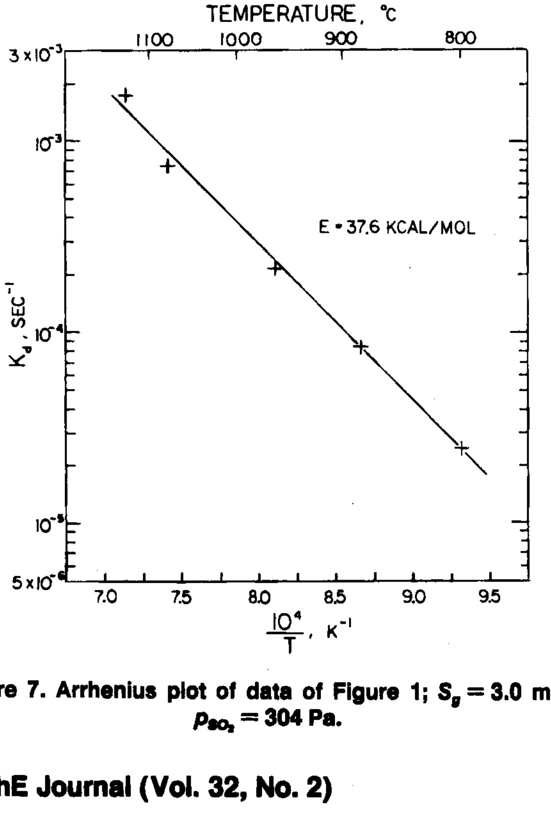

Figure 7. Arrhenius plot of data of Figure 1; $S_g = 3.0$ m²/g, $p_{SO_2} = 304$ Pa.

Reaction Temperature

The k_d values obtained from the data of Figure 1 are plotted according to the Arrhenius relationship in Figure 7. The correlation is linear to the highest temperature examined, 1,125°C, verifying the absence of pore diffusion resistance in the 1 μm, 3 m²/g particles. The apparent activation energy corresponding to the slope of this least-squares line is 37.6 kcal/mol. The effect of temperature is much too great to be reconciled with the diffusion of SO_2 or SO_3 gas through a porous or cracked product layer, which could account for only 5 kcal/mol. It is therefore concluded that the diffusion process controlling the ultimate rate does not involve gaseous species. Under these circumstances, Figure 7 is interpreted in accordance with the solid state migration of ions and vacancies within the product layer. The diffusion coefficient for this process is defined (Jost, 1960) by:

$$D_e = D_o \exp(-E/RT) \qquad (8)$$

The observed activation energy is within the normal range reported for the diffusion of ions due to thermally induced lattice defects (Beniere and Catlow, 1983). To be consistent with prior conclusions regarding the nature of the migrating ions (Bhatia and Perlmutter, 1983), one would expect $O^=$ to diffuse from the CaO to the product layer surface accompanied by the diffusion of a positively charged vacancy (or equivalent counterdiffusion of $SO_4^=$). At the product layer surface the reaction would thus be:

$$SO_3 + O^= \rightarrow SO_4^=$$

SO_2 Partial Pressure

The effect of bulk gas concentration was evaluated by fitting Eq. 5 to the data of Figures 1, 4, and 5 representing different partial pressures. The values of k_d thus obtained for constant T and S_g are plotted in Figure 8 assuming:

$$C_{SO_3} = k_o(p_{SO_2})^m \qquad (9)$$

The average slope of the straight lines fitted to the three sets of data is 0.57, the value of m in Eq. 9. Since a value of $m = 1$ would be expected for the diffusion of SO_2 gas, the result is interpreted as additional evidence of a rate-controlling process that involves ionic diffusion, either alone or in combination with surface oxidation.

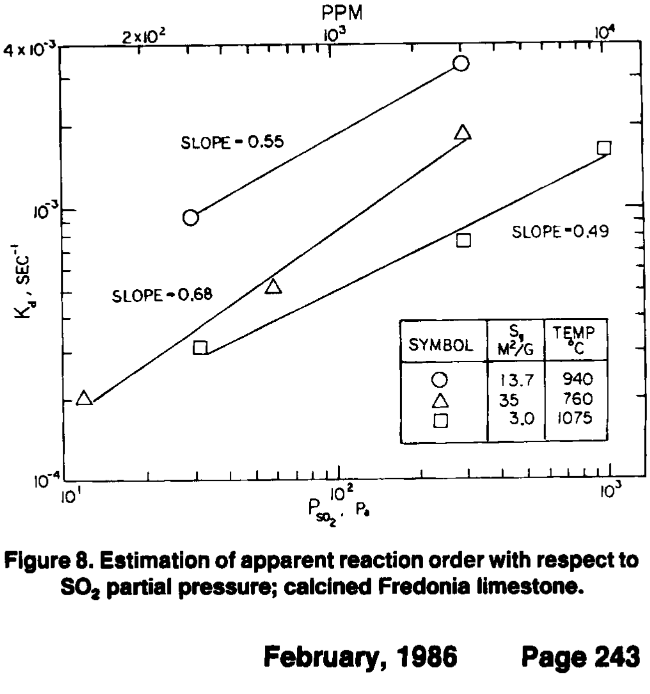

Figure 8. Estimation of apparent reaction order with respect to SO_2 partial pressure; calcined Fredonia limestone.

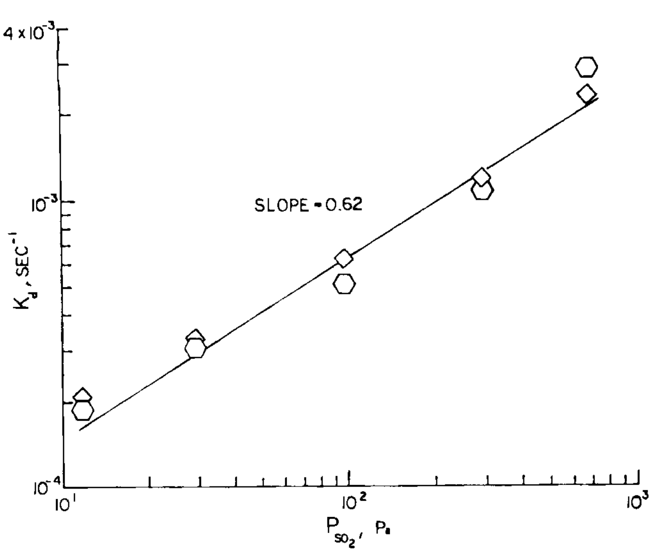

Figure 9. Verification of reaction order using calcined Vicron limestone ⬡ and Georgia marble ◇ at 800°C.

Several prior investigations have reported this reaction to be first order with respect to p_{SO_2}, a result that is contradicted by Figure 8. Of two reported exceptions, Coutant et al. (1971) found that the overall reactivity of 90 μm limestone particles increased with $(p_{SO_2})^{0.48}$ when injected into combustion gases at differential reaction conditions; i.e., constant SO_2 partial pressure. Interpretation of those results was obscured, however, by the simultaneous calcination reaction. The other exception was reported by Yang et al. (1978) who found $m = 0.59$ with reagent grade CaO. The estimate of $m = 1$ made by Borgwardt (1970) at differential conditions with precalcined limestone can be explained by the large particle size (12/16 mesh) used for those measurements, and the resulting dominance of pore diffusion effects. The data of James and Hughes (1976), who also found $m = 1$ for 70 μm particles, were most probably nondifferential at the lowest p_{SO_2} values because of the large sample size (100 mg CaO) and low gas throughput (<3 L/m) used for their study.

The particle size used in the present work is smaller by a factor of 70 than any previously examined. Also, the much larger ratio of gas feed to CaO sample size insures differential operation over the full p_{SO_2} range. These improvements of experimental technique should eliminate any possible misinterpretation of the concentration effect. Because of its importance, additional measurements of m were made with two other types of high purity limestones at constant temperature and constant S_g with the results shown in Figure 9. Comparison of Figures 8 and 9 shows no significant difference between the average m obtained for Fredonia limestone (0.57) and that obtained for Vicron limestone (0.64) or Georgia marble (0.60), and the resulting best estimate is $m = 0.62 \pm 0.07$. The calcination conditions used for the two stones of Figure 9 were the same as those used for the 21 m²/g curve of Figure 2. The agreement between the k_d values for all three calcines [0.00133 ± 0.00013 s⁻¹ at 800°C and $SO_2 = 304$ Pa (3,000 ppm)] indicates that the specific surface areas as well as the intrinsic reactivities are equal within experimental error.

Reaction Model

Like those in Figure 1, the curves shown in Figures 2, 4, and 5 represent Eq. 5 with k_d values which best correlate each set of data. They show that the product layer diffusion response is followed over broad ranges of each experimental variable. In accordance with this fact, Eqs. 6, 7, and 9 yield:

$$D_e = \frac{1.5k_d}{\rho_{CaO} k_o M S_g^2 (p_{SO_2})^{0.62}} \tag{10}$$

which, with Eq. 8, suggests that a plot of $k_d/S_g^2(p_{SO_2})^{0.62}$ vs. $1/T$ should normalize the data for all reaction conditions. Figure 10 shows this correlation; the least-squares straight line fit to the data giving:

$$k_d = 2.65 S_g^2 (p_{SO_2})^{0.62} \exp(-36{,}600/RT) \tag{11}$$

for S_g in m²/g, p_{SO_2} in Pa, and T in K. The apparent activation energy derived from the 19 data of Figure 10 is 36.6 ± 3.8 kcal/mol, which compares favorably with the 34 kcal/mol reported by Hartman and Trnka (1980) and by Bardakci (1984) for the product layer diffusion step of this reaction.

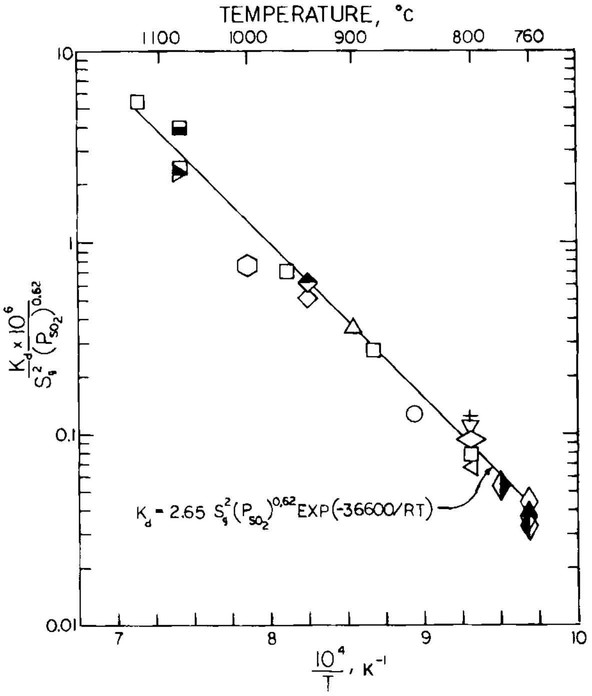

Figure 10. Normalization of CaO reactivity data. See Table 3 for key to symbols. The data of Figure 3 are used for evaluation of k_d at S_g = 2.1 m²/g.

Table 3. Key to Data of Figure 10

Symbol	S_g m²/g	p_{SO_2} Pa
◁	2.1	304
□	3.0	304
⬡	17	304
◇	13.7	304
△	21	304
○	15.5	304
◇	21	304
+	25	304
▽	11.5	304
◇	35	304
▶	3.0	1010
⬒	3.0	32
⬘	13.7	30
⬖	35	61
⬘	35	12
⬗	35	710

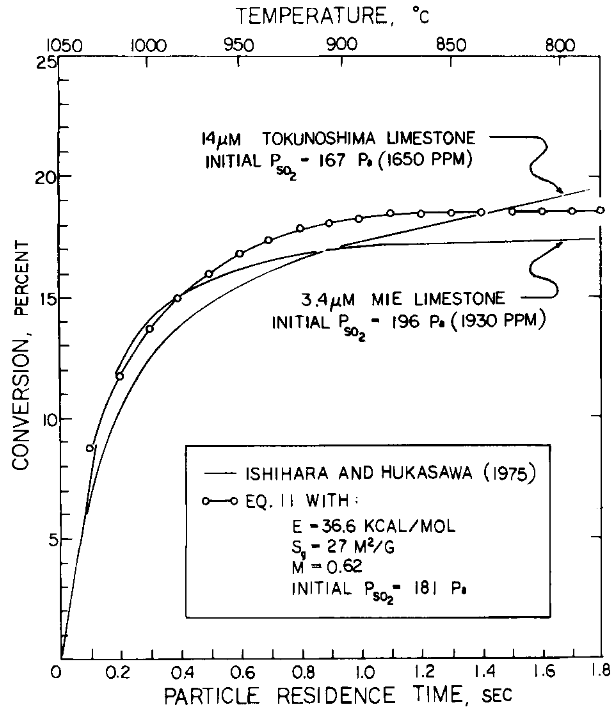

Figure 11. Comparison of SO_2 capture estimated from laboratory data (this paper) with furnace injection test data of Ishihara and Hukusawa (1975).

Ishihara and Hukusawa (1975a) conducted a series of pilot-scale furnace tests injecting limestones of particle size approaching those used in this work. The furnace temperature vs. t and typical X vs. t responses are shown in Figure 11 together with the response predicted by Eq. 11 using a S_g value of 27 m²/g providing best fit. Eight measurements reported by Ishihara and Hukusawa averaged 22.2 ± 3.8 m²/g, but they did not specifically define the conditions of calcination. Table 2 shows surface area measurements of calcines prepared in the EPA entrained-flow reactor (Borgwardt, 1985) at the same injection temperature used in Ishihara's SO_2 reaction tests. These calcinations, made in an entrainment gas of 12% CO_2 in nitrogen, yield surface areas in satisfactory agreement with the expected value. It should be noted that this surface area is significantly lower than the 50–60 m²/g obtained by entrainment in pure N_2. The difference is due to CO_2 catalysis of the sintering process (Borgwardt et al., 1986). Included in Table 2 are data reported by Coutant et al. (1971) for larger particles injected into combustion flue gas. These surface areas are somewhat greater, perhaps due to the retardation of sintering by endothermic cooling in large particles. Six other tests made by Coutant with 50 μm particles of high purity limestones injected at higher temperatures (1,170°C) averaged 17.6 m²/g of CaO. We conclude that the 27 m²/g value of S_g assumed for the furnace injection tests at 1,050°C is in agreement with the available data and is within 10% of the true surface area of the particles used in Ishihara's work.

Figure 11 shows that the salient features of the furnace tests are consistent with the response predicted from the laboratory measurements, including the rapid flagging after the first second and the ultimate value of conversion achieved. This agreement indicates that the mechanism of SO_2 capture in a furnace environment is reproducible under laboratory conditions and that the effects of temperature and specific surface area are correctly accounted for by Eq. 11.

Limits

Rigorous models of structural changes occurring within a CaO particle have been proposed for this reaction (Linder and Simonsson, 1981; Bhatia and Perlmutter, 1981b); they assume constant particle volume as the reacting grains expand. Such models accurately describe the self-limiting effects on ultimate conversion in large particles caused by coalescence of grains, filling of pore space, and pore-mouth closure. The results of this study, however, suggest that the conversion vs. time response of small particles can be described by the simplest version of the grain model that assumes no coalescence. At high temperatures and small grain size the response is adequately described by assuming independent expansion of the grains up to ca. 70% conversion—a result that implies that particle volume is not constant. That particle expansion can occur was previously shown by mercury intrusion measurements on particles as large as 0.025 cm (Borgwardt and Harvey, 1972). Although such measurements are not possible on 1 μm particles, it is clear from the nature of the responses that the internal grain structure of nascent CaO is not fully rigid.

A limit of another sort is evident in the data of Figure 3, which show ultimate conversion also to increase with surface area. The effect is more strongly apparent in the reaction at 700°C (Borgwardt et al., 1986) and suggests that a mechanism more fundamental than pore-mouth plugging is responsible.

NOTATION

C_{SO_3} = concentration of SO_3 on the product layer surface
D_e = effective product layer diffusivity

Table 2. Specific Surface Area of Limestone Particles Calcined in SO_2-free Entrainment Gas

Data Source	Particle Dia., μm	Temp., °C Injection	Temp., °C Collection	Residence Time, s	Calcination, %	Specific Surface Area m²/g Solid	Specific Surface Area m²/g CaO
This work*	10	1,050	1,050	0.39	88.9	27.0	30.4
	10	1,050	1,050	0.39	84.7	26.8	31.6
	10	1,050	970	0.40	89.3	28.3	31.7
	10	1,050	970	0.40	88.4	23.4	26.5
	10	1,050	970	0.60	84.9	27.1	31.9
	10	1,050	970	0.60	82.7	23.2	28.0
	10	1,050	970	0.60	92.4	21.6	23.4
This work, avg.							29.1 ± 3.2
Coutant et al. (1971)**	50	1,050	815	1.35	78	28.5	36.6
	90	1,096	933	1.03	72	24.8	34.4

* Entrainment gas: 12% CO_2 in nitrogen.
** Entrainment gas: combustion flue gas, 10% CO_2.

D_o = Arrhenius pre-exponential factor
E = apparent activation energy at constant SO_2 partial pressure
k_c, k_h, k_p, k_g, k_d = constants defined by Eqs. 1 – 5 for a given temperature, grain size, and SO_2 partial pressure relating conversion and time for grain reactions controlled, respectively, by: c, chemical reaction at surface; h, homogeneous reaction; p, power law reaction; g, product nucleation; d, product layer diffusion
k_o = constant relating C_{SO_3} to bulk gas SO_2 partial pressure by Eq. 9
M = molecular weight of CaO
m = apparent reaction order with respect to p_{SO_2}
p_{SO_2} = partial pressure of SO_2 in the bulk gas
r_g = radius of CaO grain within a calcine particle
S_g = specific surface area of calcine
t = time
T = temperature
X = conversion, atom S per atom Ca
ρ_{CaO} = mass per unit volume of CaO grain

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