The Kinetic Rate of SO_2 Sorption by CaO

The intrinsic rate constant for the rate of reaction of SO_2 with porous CaO in an excess of O_2 to form $CaSO_4$ has been determined from SO_2 sorption data on a wide range of particle diameters (1 μm-1mm), SO_2 partial pressures (60 Pa to 5 kPa), and temperatures (973-1,478 K). An intrinsic SO_2 reaction order of unity has been validated through current fixed-bed experiments in the 60 to 300 Pa SO_2 partial pressure range, while fluidized-bed data were used to validate the reaction order from 500 Pa to 5 kPa SO_2 partial pressure. The absolute value of the rate constant and the activation energy was derived from data on small (1 μm) particles, which approach the limit of kinetic control. While analysis of this data base does minimize the role of intraparticle diffusion through the porous sorbent particle, the filling of the small pores by the product deposits and the associated loss of internal surface area is critical to the data reduction. It is believed that the intrinsic rate constant is known to the accuracy to which the reactivity and the BET surface area may be measured.

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Introduction

Limestone is a well-known and commonly used sorbent for SO_2 removal from combustion gases. The limestone ($CaCO_3$) is calcined (heated to decompose into CO_2 and highly porous CaO), then sulfated. The sulfation step represents the complex coupling of chemical reactions with the mass transport through a time-varying porous structure. To understand this process, the effects of the reaction kinetics and intraparticle diffusion and the role of the evolving sulfur product layer must be isolated and examined. Numerous studies have been directed toward this goal. Borgwardt and Harvey (1972) studied the rate of reaction of CaO with SO_2 in an oxygen-rich (with respect to SO_2) environment to form $CaSO_4$. Particle sizes were decreased until the measured rates were particle-size independent, thus indicating kinetic control. The intrinsic reaction rate was determined by extrapolating data to zero utilization (no sulfur deposition). The rate constant at 1,250 K and 300 Pa SO_2 partial pressure was determined to be 0.22 cm/s or, in present units, 0.014 kg SO_2 adsorbed/s/m^2 of CaO internal surface per MPa SO_2 partial pressure. These units reflect the fact that the intrinsic rate constant is first order in SO_2 partial pressure and first order in surface area.

The intrinsic rate constant, k_s, has been integrated into a pore-structure/pore-transport model (Simons and Rawlins, 1980) to describe sulfur sorption in the limit of zero utilization for arbitrary particle size, porosity, internal surface area, and SO_2 partial pressure. The intrinsic rate constant and the model were confirmed only over a narrow range of particle size, 100 μm-1 mm, and at one SO_2 partial pressure, 300 Pa. The analysis is valid only for CaO utilization less than 20% above which the SO_2 sorption rates decrease dramatically due to the buildup of the $CaSO_4$ deposit layer.

The role of the $CaSO_4$ deposits on the sulfation process has been the subject of several investigations. The molar volume of $CaSO_4$ is sufficiently large that the pores of the CaO may either plug (at one end) or fill prior to complete CaO utilization. Pore plugging and the loss of porosity at the outer edge of the particle is the dominant cause of the deactivation of large sorbent particles in fluidized-bed combustors. Models describing this process (Georgakis et al., 1979; Lee and Georgakis, 1981) are semi-empirical in nature. More fundamental mechanistic models have been proposed by Hartman and Coughlin (1974, 1976, 1978), Bhatia and Perlmutter (1981a,b), Christman and Edgar (1983), Bardakci (1984), Marsh and Ulrichson (1982), and Ramachandran and Smith (1977). These models are very similar in that they treat the diffusion of the SO_2 through the porous structure, the development of the product layer, and the ultimate plugging of the porous structure. They also include an important intermediate rate-limiting step: the activated diffusion of the SO_2 through the product layer. The values of the product layer diffusion coefficient, D_p, are obtained by fitting the model predictions to the sorption data.

In an alternative approach, Simons and Garman (1986) have

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shown that the activated diffusion of SO_2 through the product layer need not be rate-limiting. It is possible for product deposits to fill the smallest pores and reduce the internal surface area on which the intrinsic kinetics are reacting. The intrinsic rate constant is obtained by fitting the model predictions to the sorption data. The rate constant they obtained is approximately the same as that quoted by Bhatia and Perlmutter (1981a):

$$k_s = A \exp(-6{,}750/T)$$

where

$$A = 7 \frac{\text{kg SO}_2}{\text{s} \cdot \text{m}^2 \cdot \text{MPa SO}_2}$$

which is a factor of two greater than the rate measured by Borgwardt and Harvey (1972).

These modeling approaches suggest that there are basically two ways to interpret sulfation data:

1. In the limit of infinite kinetics ($k_s \rightarrow \infty$), D_p is inferred from data
2. In the limit of infinitely fast diffusion ($D_p \rightarrow \infty$), k_s is inferred from data

Both approaches yield seemingly self-consistent results over narrow ranges of data, and the valid approach may be identified only through extensive comparisons with a large data base. Below, a wide range of sulfation data is examined in the limit of infinitely fast diffusion through the product layer. By proper reduction of existing data, and through the generation and reduction of additional data, the intrinsic SO_2 reaction order and the transport model (Simons and Rawlins, 1980; Simons and Garman, 1986) are verified over a wide range of temperature (973 to 1,478 K), particle size (1 μm to 1 mm), and SO_2 partial pressure (60 Pa to 5 kPa). The intrinsic rate constant is found to possess a higher activation energy (17,000 ± 1,000 K) than quoted above, and the absolute value of the rate constant is confirmed to within a factor of two. Attempts to reduce the same data base in the limit of infinite kinetics are not reported here but did fail to yield a correlation for the value of the product layer diffusion coefficient.

Physical Description of Model

There are three basic components to the sulfation model of Simons and Garman (1986):

1. The intrinsic rate constant of the global reaction $SO_2 + CaO + \frac{1}{2} O_2 \rightarrow CaSO_4$
2. The pore-structure/pore-transport model
3. The role of the product deposits

The intrinsic rate constant is derived from available data and specifies the kg of SO_2 reacted per second per m^2 surface area per unit pressure of SO_2 above the surface. The major problem becomes that of determining the SO_2 partial pressure distribution over the internal surface area of the sorbent. This requires a pore-structure/pore-transport model.

The pore structure model utilized here is known as the pore tree (Simons, 1982). A single element, or tree, of the model is illustrated in Figure 1. The essence of the pore tree model is a description of the sorbent pore structure as a set of trees of various sizes whose trunks are located at the particle surface. The branches of a tree and its leaves describe a progression of pores from maximum to minimum radius. The distribution of pores of radius r_p is proportional to $(1/r_p)^3$. The transport equations include the effects of bulk diffusion to the particle exterior surface, continuum diffusion within the large pores, and Knudsen diffusion within the small pores. The model calculates the proportion of sulfur removal that is controlled by each of these processes and by chemical kinetics at the pore walls. The intrinsic rate constant k_s, the particle radius a, porosity θ, internal surface area S_p, and the mass fraction c_∞ of gas in the ambient stream are the required inputs to the model; there are no free parameters. This pore-structure/pore-transport model yields the reactivity as a function of temperature and time and has been extended to include the effects of the product deposits.

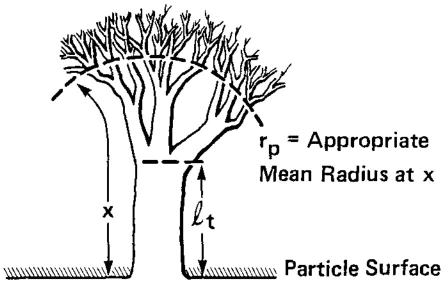

Figure 1. Pore tree model of pore structure.

As the sulfation process proceeds, the product ($CaSO_4$) forms a layer on the walls of the pores. Since the molar volume of $CaSO_4$ is greater than that of the initial reactant CaO, the pores will eventually either plug or fill. Prior to the plugging or filling of an individual pore, the activated diffusion of SO_2 through the $CaSO_4$ may become rate-limiting. The pore tree model is capable of simultaneously describing all of these processes and allowing the rate-controlling mechanism to be identified as a consequence of the model. The mathematical details are given by Simons and Garman (1986) and the essence of the model is illustrated in Figure 2. Consider a branch point in the pore tree where a single large pore branches into two smaller ones. Figure 2a illustrates the case where the smaller trees (or smaller particles) tend to be under kinetic control wherein the SO_2 concentration will be uniform in the pore structure. The thickness $\delta(x, t)$ of the $CaSO_4$ layer will be uniform in pore space and will tend to fill the smallest pores first. This small-pore filling will deactivate the particle via loss in internal surface area. Alternatively, the larger trees (or larger particles) tend to be controlled by diffusion through the pores, Figure 2b. The SO_2 concentra-

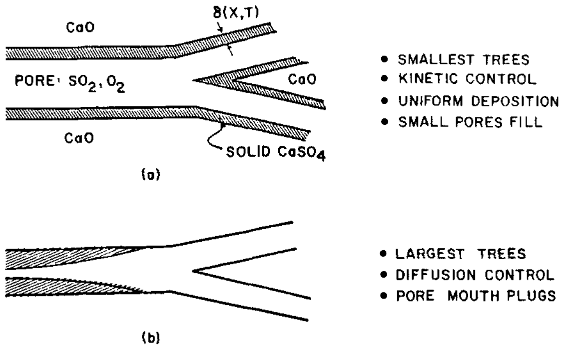

Figure 2. Sulfation modes.
a. Small-pore filling
b. Pore mouth plugging

tion decreases with depth and the $CaSO_4$ deposits build up at the mouth of the pore. The mouth of the pore can completely plug and prevent SO_2 from utilizing the CaO on the walls of the rest of the pore tree. Small-pore filling is dominant for 1 to 10 μm dia. particles, while pore mouth plugging is dominant for 100 μm to 1 mm dia. particles. Rate limitations due to product layer diffusion (prior to plugging or filling) are more pronounced for the thicker product layers occurring within the larger particles.

Range of Validation

To validate the rate constant and the transport model it is first necessary to exercise the model over a wide range of parameter space in order to indicate the various scaling regimes. Figure 3 illustrates the predicted SO_2 sorption rates for a 50% porous particle with 10 m^2/g internal surface area subjected to SO_2 partial pressures of 60, 300, and 500 Pa and 5 kPa at a temperature of 1,250 K. The reactivity decreases with increasing particle radius from 1 μm to 1 mm. Small particles are kinetically controlled and the reactivity scales in direct proportion to the SO_2 partial pressure, while larger particles are influenced by intraparticle diffusion and the reactivity scales as the pressure to some power between 0.5 and 1.0 (Simons, 1983a). Borgwardt and Bruce (1986) demonstrate a 0.62 pressure dependence in the late time (400 s) limit of product layer diffusion control. Clearly, in order to test both the model and the rate constant, sulfur sorption data must be obtained for both large (100 μm) and small (1 μm) particles over a wide range of SO_2 partial pressures. The shaded regions of Figure 3 illustrate the regimes where the present rate constant has been validated with data.

A large data base exists for 50 to 500 μm radius particles at 100 kPa pressure and 3,000 ppm SO_2 (Borgwardt and Harvey, 1972; Hartman and Coughlin, 1976, 1978; Bhatia and Perlmutter, 1981a). Modeling and data analysis by Bhatia and Perlmutter (1981a), Simons and Rawlins (1980), and Simons and Garman (1986), confirm the value of the intrinsic rate constant for these data. Modeling efforts of Hartman and Coughlin (1976) yielded a value of k_s that is a factor of 20 faster. However, this difference has been attributed to an erroneous value of the intraparticle diffusion coefficient (Simons and Rawlins, 1980).

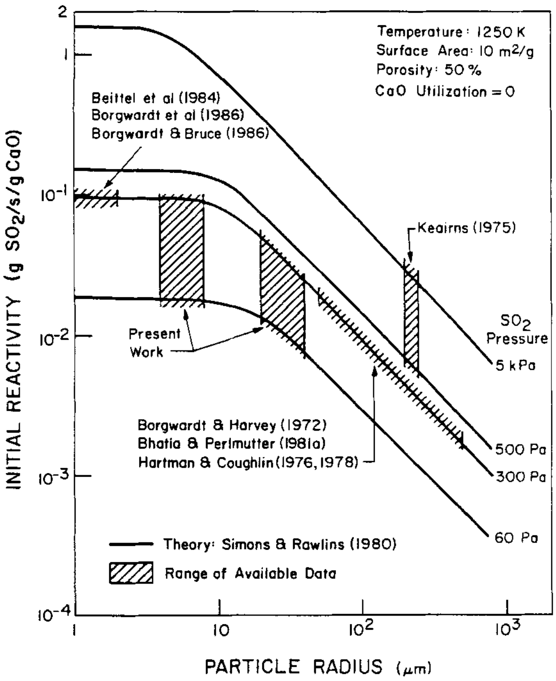

Figure 3. Initial SO_2 sorption rate and regimes of validation.

Experimental data taken at high pressure are scarce. The only data available for this comparison derive from fluidized-bed experiments at Westinghouse (Keairns et al., 1975), illustrated in Figure 4. The data, obtained at a temperature of 1,144 K and total pressures of 100 kPa and 1 MPa with 5,000 ppm SO_2, are restricted to large (500 μm) dolomite sorbent particles. These sorbent particles were not characterized with respect to their porosity and internal surface area. Since the sulfation model (Simons and Garman, 1986) is extremely sensitive to these parameters, a comparison of theory with the data for the actual reaction rate at fixed pressure is not possible. Instead, we compare the ratio of the sulfation rate at 1 MPa to that at 100 kPa. For this purpose, the porosity and internal surface area are adequately assumed to be 50% and 10 m^2/g, respectively. The excellent agreement between the theory and the data suggests that the intrinsic reaction rate is indeed first order in SO_2 partial pressure. Note that the peak in Figure 4 is not indicative of an increase in the reaction rate at high pressure; rather, it is due to a faster decay in the low-pressure rate with utilization. This effect has not yet been explained adequately, but it has important implications for gas turbine applications for it suggests that greater calcium utilization is possible at higher pressures.

Additional pressure-dependent data have been obtained by the present authors for the purpose of validating the first-order SO_2 partial pressure dependence of the intrinsic rate constant for gas turbine applications. Data were taken at 1,000 K and 300 ppm SO_2 in a fixed-bed reactor using sorbent masses sufficiently small that entrained flow conditions were simulated. Two different limestones were tested, El Dorado limestone (EDL) and Pfizer dolomite (PD), at two pressures, 210 kPa and 0.95 MPa. The EDL was nominally less than 15 μm dia. and the PD was 42 to 78 μm dia. The two sorbents were calcined *in situ* and yielded dramatically different internal surface areas at the two pressures. The ratio of the sulfation rate at 0.95 MPa to that at 210 kPa agrees with theory for each sorbent tested and demonstrates the validity of the first-order SO_2 partial-pressure dependence of the intrinsic rate constant. Details of the reactor,

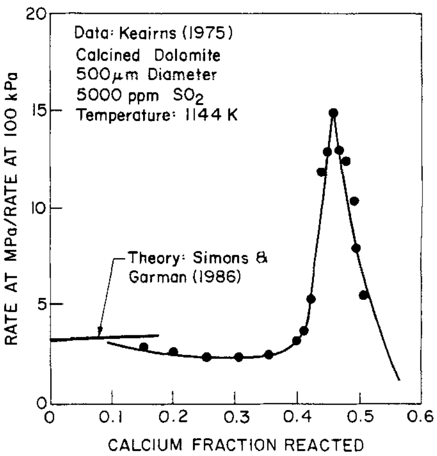

Figure 4. Effect of pressure on sulfation of calcined dolomite.

the calcination process, the sulfation measurements, and the data reduction are given in the next section.

The data comparisons described above have been made for particle sizes sufficiently large that intraparticle diffusion and pore structure can influence the reactivity. Indeed, such effects have been studied for char oxidation (Simons 1983a,b) and it has been shown that the distribution of porosity alone can change the reactivity by a factor or two. Variations in the total porosity will have similar effects on the sulfation rate (Simons and Garman, 1986). Hence, reactivity data that is influenced by intraparticle diffusion is useful for verifying scaling laws, but highly accurate absolute measurements of the intrinsic rate constant require data obtained in the absence of these effects. Such data are available from particles that are sufficiently small that the reactivity is kinetically controlled. The data of Beittel et al. (1984), Borgwardt et al. (1986), and the early-time (30 s) data of Borgwardt and Bruce (1986) taken on 1 μm dia. particles at 300 Pa SO_2 partial pressure are adequate for this purpose. The data analysis is described in the later section on the kinetically controlled limit. The intrinsic rate constant is obtained to a higher degree of accuracy from these data but the SO_2 partial-pressure dependence has been validated only through the present work (60 to 300 Pa SO_2) and that of Keairns (1975) (500 Pa to 5 kPa SO_2).

Fixed-Bed Reactivity Tests

High-pressure sulfur sorption experiments have been conducted in the high-temperature, fixed-bed test facility illustrated in Figure 5. Simulated combustion gases are available from up to five compressed gas cylinders at delivery pressures up to 1.1 MPa. The mass flow rates of four of the gas streams are monitored by Teledyne-Hastings Raydist (THR) ST series mass flowmeters with operating ranges between 0 to 50 sccm or 0 to 1,000 sccm with less than 1% absolute error. Flow control is provided by high-precision Matheson regulating needle valves. The fifth gas stream is controlled electronically by a model CST-100 mass flow controller. The five streams are combined into two, the first containing $SO_2/CO_2/N_2$ and the second containing the appropriate mixture of O_2/H_2 for the required simulation. The latter stream passes through a heated platinum catalyst honeycomb. The catalyst induces reaction between H_2 and O_2 to produce accurately known flows of steam and excess oxygen.

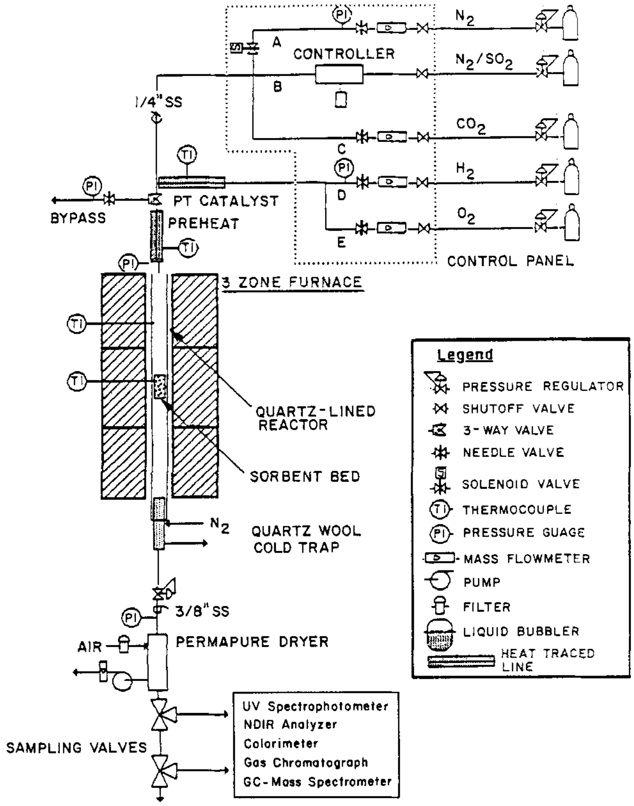

Figure 5. High-temperature, fixed-bed reactor.

The cylindrical shell furnace, manufactured by BTU Engineering Corp., Waltham, MA, has three independent heating elements in series. The temperature in each zone is regulated to within 5 K accuracy by SCR controllers up to a maximum temperature of 1,500 K. The gas stream passes through the sorbent bed via a quartz-lined reaction tube that inhibits the possibility of heterogeneous reactions at the wall. The quartz insert can readily be removed from the furnace at temperature to change sorbent beds with rapid turnaround time. A ceramic-shielded chromel-alumel thermocouple penetrates the reaction tube from above to monitor the sorbent bed temperature.

The gas stream exits the reactor, is cooled, and the pressure dropped across a regulating valve when necessary. Water is removed from the mixture prior to gas analysis by a Permapure model 750 permeation tube dryer pumped by a Teflon-coated Thomas model 727 diaphragm vacuum pump. Sampling valves are available for continuous monitoring of trace species with a CEA Instruments TGM colorimetric monitor. Up to 5,000 ppm SO_2 may be detected with a Teledyne UV photometric analyzer, and up to 20% CO_2 by a Beckman model 805 NDIR analyzer. Batch samples can be taken and analyzed by a Hewlett-Packard model 5990 gas chromatograph/mass spectrometer system, and other major nonsulfur combustion species can be measured quantitatively with a Carle analytical gas chromatograph.

All experiments were conducted in a gas mixture typical of the effluent of a gas turbine combustor fired on an Eastern bituminous coal-water slurry with 500% overall excess air: 77.9%

Table 1. Test Conditions

	Sorbent			
	EDL*	EDL	PD*	PD
Particle dia. μm	1–15	1–15	42–78	42–78
Bed wt. mg	52.1	56.0	98.7	98.0
Pressure, kPa	950	210	950	210
Temperature, K	1,023	1,028	1,018	1,023
Gas flow, scm^3/s	85.4	86.6	86.5	85.4
Inlet SO_2, ppm	315	317	297	315
Surface area after calcination, m^2/g	0.81	2.74	2.46	16.6
Porosity after calcination, %	0(35)	0(35)	0(39)	0(39)
Sulfation rate, g SO_2/g CaO · s	2.5×10^{-3}	1.8×10^{-3}	8.6×10^{-4}	5.7×10^{-4}
Normalized	1.4	1	1.5	1
Theory	1.34	1	1.58	1

*EDL, El Dorado Limestone
PD, Pfizer Dolomite

N_2, 16.1% O_2, 4.1% CO_2, 2.9% H_2O, and 300 ppm SO_2. The tests were carried out using El Dorado limestone (EDL) and Pfizer dolomite (PD) at each of two reactor absolute pressures, 210 kPa and 0.95 MPa, in order to investigate the scaling of particle reactivity with pressure. Test conditions are summarized in Table 1.

The calcination of the EDL and the PD was conducted at pressure. High background pressure can impede the development of high internal surface. The internal gas pressure required to drive the CO_2 from the calcining sorbent increases with decreasing pore size (increasing transport resistance). As the CO_2 pressure increases to the equilibrium CO_2 vapor pressure, the calcination process will proceed only in the larger pores. The smaller pores, which account for the majority of the internal surface area, do not form at the higher background pressure. This is demonstrated by the surface area data in Table 1.

A sulfation experiment consists of passing the known gas stream through a heated bed of sorbent particles and continuously monitoring the SO_2 at the exit of the bed. The average bed utilization and instaneous rate of conversion are obtained from the measured rate of depletion of the SO_2 stream. The mass of the bed was chosen to yield a 50% reduction in the SO_2 flowing through the bed, thereby simultaneously producing a measurable signal and nearly simulating entrained flow conditions. The measured rates of sulfation are illustrated in Figure 6. Comparison of the absolute value of the bulk SO_2 sorption rate to the theoretical prediction is not possible because the bulk reactivity reflects the collective effects of all particle sizes at various levels of calcium utilization in the bed. However, since the SO_2 partial pressure was relatively uniform throughout the bed, the scaling of the reactivity with the pressure is valid in the limit of zero utilization. The ratio of the reactivity at 950 kPa to that at 210 kPa is compared to theory in Table 1. In each case the reactivity at 950 kPa pressure is only about 50% higher than that at 210 kPa. This is due to the reduction in the surface area with the higher calcination pressure. The theory accounts for these differences and the data comparisons demonstrate that the intrinsic rate constant is first order in SO_2 partial pressure.

Kinetically Controlled Limit

While it is the data at the various SO_2 partial pressures that confirm the first-order pressure dependence of the intrinsic rate constant, it is the data taken on small (1 μm) particles in the limit of kinetic control and in the absence of intraparticle diffusive effects that are the most appropriate for determining the absolute value of the intrinsic rate constant. The model of Simons and Garman (1986), which accurately accounts for small-pore filling and the loss of internal surface area with utilization, is used to analyze the data base on small particles at 100 kPa total pressure and 3,000 ppm SO_2.

Sulfation data on small particles (1 μm) has been obtained at various temperatures by Borgwardt and Bruce (1986). Figure 7 illustrates SO_2 sorption data at 1,073 K on five limestone samples, all presintered (by preheating) to different internal surface areas and porosities. The porosity is inferred from the measured value of the surface area as described by Simons and Garman (1986). Decreasing the rate constant by a factor of 0.6 to 1.0 at 1,073 K yields the indicated agreement between the model and the data.

Additional data of Borgwardt and Bruce (1986) taken at 1,033, 1,118, 1,173, 1,213, and 1,273 K is illustrated in Figure 8. Each sample was presintered to a different porosity and internal surface area and then sulfated at the designated temperature, 4 kPa O_2 partial pressure, and 300 Pa SO_2 partial pressure. The agreement between the model and the data was obtained by adjusting the rate constant to achieve the best fit at each temperature. The empirically derived values of the rate constant at these temperatures, together with those derived for 1,073 K are illustrated in Figure 9. The data demonstrate that the intrinsic rate constant possesses an activation energy of the order of 17,000 K, and the absolute value of k_s is known to well within a factor of 2. Note that the data point at 973 K, derived by Simons and Garman (1986) from the data of Borgwardt et al. (1986), has been omitted from this correlation due to the large percent-

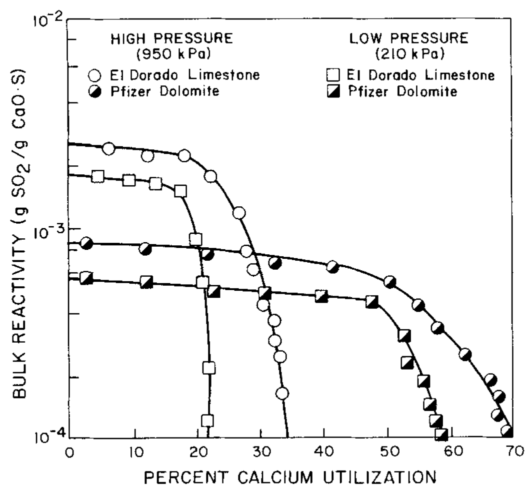

Figure 6. Bulk reactivity of a fixed bed of EDL and PD.

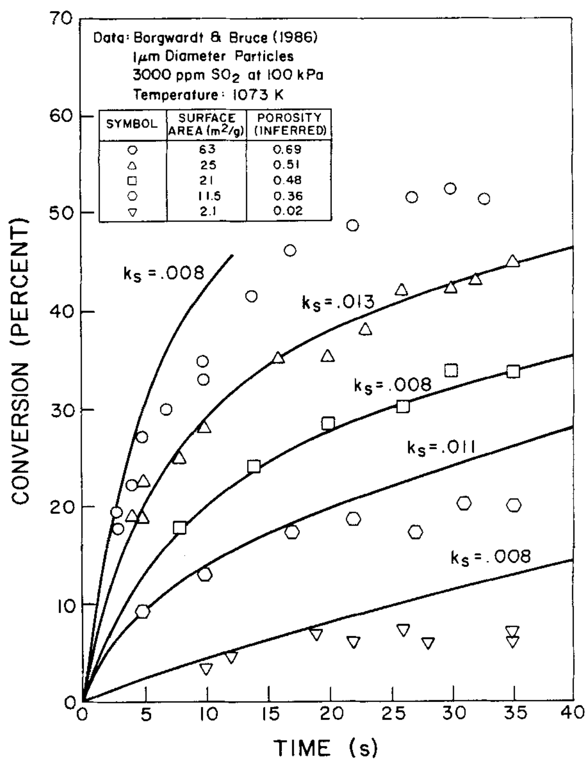

Figure 7. Reactivity of small particles at 1,073 K.

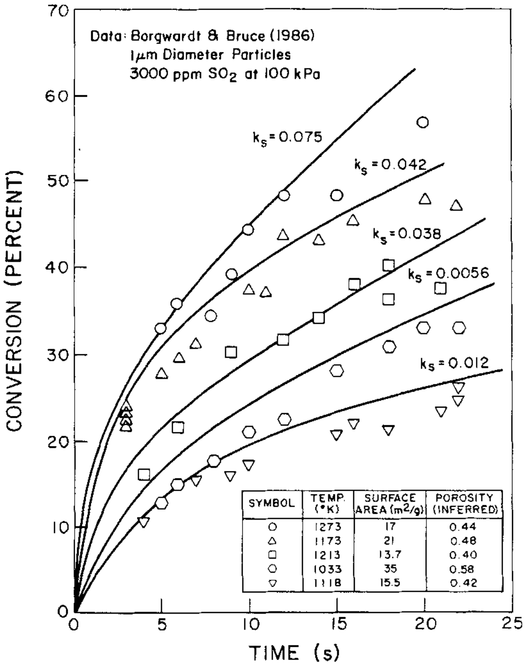

Figure 8. Small-particle reactivity at intermediate temperatures.

age of $CaSO_3$ observed to form below 1,033 K. Borgwardt and Bruce (1986) also eliminate this low-temperature data from their correlations.

The validity of the model and the rate constant has been extended to higher temperatures through proper treatment of the stability of the $CaSO_4$. There is a decrease in the net SO_2 sorption rate when the equilibrium vapor pressure, p_v, of the SO_2 approaches the partial pressure of the SO_2, $p_G c_o \xi$. This decrease in the net conversion rate is accounted for by adjusting the intrinsic rate constant according to

$$k_s' = k_s[1 - p_v/(p_G c_o \xi)]$$

where

$$p_v \simeq [10^{12}/(p_{O_2})^{1/2}] \exp(-52{,}000/T)\,\mathrm{MPa}$$

and p_{O_2} is the oxygen partial pressure in kPa. For a p_{O_2} of 4 kPa and a SO_2 partial pressure of 300 Pa, $CaSO_4$ is unstable above 1,484 K.

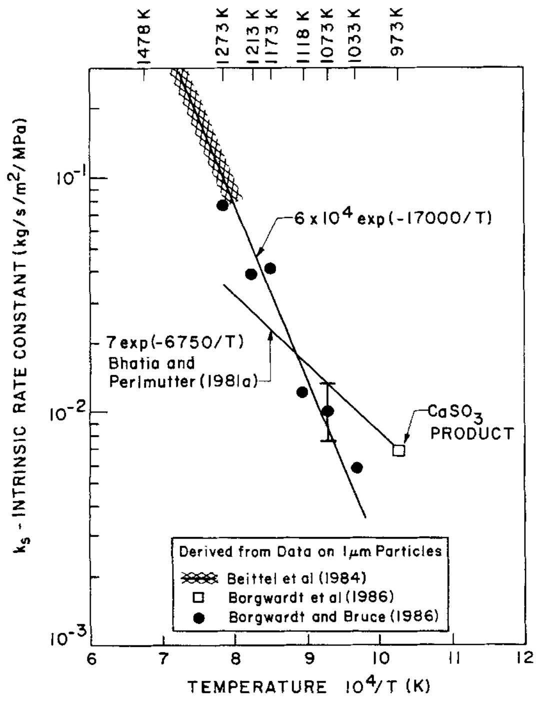

Figure 9. Intrinsic rate constant at 4 kPa O_2 partial pressure.

High-temperature sulfur sorption data from a coal-fired, pilot-scale furnace operated at 1.0 MBtu/h (293 kW/h) has been obtained by Beittel et al., (1984). Tests were performed using a pressure-hydrated dolomite (Genstar), a hydrated limestone (Longview), and a uncalcined limestone (Marianna). The temperature decreased linearly from 1,478 K at the injection point to 1,225 K at a location 1.3 s downstream of the injection port. Measurements of surface area development from coincident tests with the combustor fired on natural gas and with no sulfur present showed that the sintering of internal surface area is insignificant over these temperatures and time scales. The initial surface area was 33, 15, and 8 m^2/g for the Genstar, Longview, and Marianna, respectively. The particle diameters were 1.2, 2.3, and 13 μm, respectively, and the porosity of each of the sorbent particle types was roughly the same, between 71 and 79% (Dismukes, 1984).

Figure 10 illustrates the observed SO_2 reduction as a function of sorbent loading, expressed as a molar Ca:S ratio. The theoretical predictions were obtained by integrating the model of Simons and Garman (1986) through the specified temperature history and simultaneously calculating the decreasing background SO_2 pressure. The agreement with the pilot-scale data demonstrates the validity of the intrinsic rate constant to within

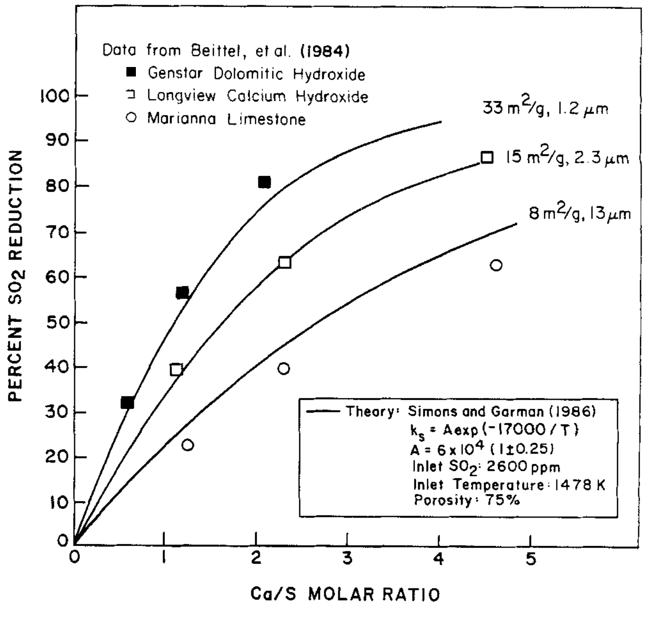

Figure 10. Coal-fired pilot-scale furnace data.

±25% in this temperature range. Furthermore, the agreement of the model with the data indicates that the enhanced reactivity of the pressure-hydrated sorbents depends predominantly on the greater particle surface area, not on the sorbent chemical composition.

This data analysis demonstrates that the sorption rate, measured in the limit of kinetic control on particles whose internal surface area is known, represents the most accurate method for obtaining k_s. While the filling of the smallest pores does reduce the internal surface area with utilization (Bhatia, 1985; Simons and Garman, 1986), this aspect of the theory has been validated (Simons and Garman, 1986) from the data of Roman et al. (1984). Hence, the intrinsic rate constant derived above from the data on 1 μm particles is probably as accurate as the SO_2 sorption data and/or the BET surface area measurements themselves.

It is emphasized that the absolute value of the intrinsic rate constant derived above is valid only for oxygen partial pressures of order 4 kPa. While the global reaction discussed in the physical description of the model suggests a half-order oxygen pressure dependence, the determination of the oxygen reaction order is beyond the scope of this work. It is further emphasized that the reaction order of unity with respect to SO_2 reflects a global reaction. It is not known if the rate-limiting step is the adsorption of SO_2 onto the $CaSO_4$, the formation of an intermediate species S*, or the reaction of either S* or SO_2 with the CaO. This work demonstrates only that the sulfation process is controlled by a heterogeneous chemical reaction that is first order in SO_2.

Summary

A wide data base on SO_2 sorption by calcined limestone has been examined to determine the intrinsic rate constant k_s for the reaction of SO_2 with CaO. The rate constant has been shown to be first order in SO_2 partial pressure over the range of 60 Pa to 5 kPa SO_2 and to possess an activation energy of 17,000 K over the temperature range 973 to 1,478 K.

Variations in the determination of k_s arise primarily due to the intraparticle diffusion effects. The reactivity of large particles scales as $\theta(k_s D)^{1/2}$ where D is the intraparticle diffusion coefficient and θ is the porosity (Simons, 1983a). Hence a 100% error in k_s may result from a 40% error in reactivity, a 40% error in θ, a 100% error in D, or from the inability to accurately specify the pore size distribution (Simons, 1983b). Sorption data on the larger particles in both fixed- and fluidized-bed experiments were used only to verify the first-order dependence of the intrinsic reaction rate with SO_2 partial pressure. To minimize the intraparticle diffusion as a source of error in determining the absolute value of the intrinsic rate constant, this analysis concentrated on small, kinetically controlled particles wherein the internal surface area had been measured. Available data indicate that the intrinsic rate constant has been obtained to within a factor of two and that the rate constant applies to CaO derived from both hydrates and carbonates sulfated in 4 kPa oxygen.

Acknowledgment

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