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Reaction of Sulfur Dioxide with Limestone and the Grain Model

Experimental measurements of the reaction of sulfur dioxide and oxygen with limestones have demonstrated substantial influence of the geologic origin of the stone, its porosity and particle size, gaseous concentration of sulfur dioxide, and temperature on the course of reaction and the conversion (that is, the degree of utilization of the limestone content of the particles as a sorbent for sulfur dioxide). A mathematical model including intraparticle transport and chemical reaction within the particles (grain theory) has been developed to simulate this sulfur dioxide sorption reaction.

MILOSLAV HARTMAN
and
ROBERT W. COUGHLIN

Institute of Chemical Process Fundamentals
Czechoslovak Academy of Science,
165 02 Prague, Czechoslovakia

SCOPE

One of the more promising techniques of sulfur dioxide removal from flue gas is sorption using a fluidized bed of limestone. A major drawback in such processes, however, is the fact that the limestone reacts only partially. Although an extensive pore structure develops during calcination of the limestone, the sulfation reaction causes large decreases in porosity of the reacting particles (Borgwardt and Harvey, 1972; Hartman and Coughlin, 1974).

The purpose of the present study was to develop a better understanding of the intricacies of reaction involving limestone particles, sulfur dioxide, and oxygen, and to quantitatively describe the effects of particle size, gaseous sulfur dioxide concentration, and reaction time on the course of the chemical reaction.

Whereas previous investigations appear to have been largely confined to calcined limestone, the use of uncalcined limestone is a more practical expedient for fluidized-bed combustion. In the present work, uncalcined samples of reactive, high-grade limestone were exposed to flue gas in a differential, packed-bed reactor. The amount of sulfate formed in the samples was determined by titration with 0.005 N $Ba(ClO_4)_2$ and electron microprobe, and x-ray diffraction analyses were employed to study the spatial distribution of reaction within the particles. The effects of such variables as temperature, time of exposure to the gas, particle size, and gaseous concentration of sulfur dioxide were also determined.

The reaction model developed herein for this gas-solid reaction system takes into account the reduction in porosity caused by the sulfation reaction and the resulting effect on the rate of transport of sulfur dioxide through the pores. The development includes a quantitative description of the diffusion of sulfur dioxide through an accumulating shell of reaction product at the periphery of a limestone particle as well as the chemical reaction taking place at the active surface of the grains within the particle.

Correspondence concerning this paper should be addressed to Robert W. Coughlin, Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015.

CONCLUSIONS AND SIGNIFICANCE

The optimum temperature for the reaction of raw limestone with sulfur dioxide and oxygen is near 850°-900°C. Both the diameter and porosity of the limestone particles, and the concentration of sulfur dioxide in the flue gas, have a considerable effect on the conversion at any time of exposure.

During the first minutes of exposure, the sulfation occurs almost entirely in the outer parts of the particle but, as time continues, this reaction zone gradually spreads throughout the whole particle interior. However, as the model itself predicts and as the substantial dependence of the sorption capacities of limestone particles on their size suggests, a concentration gradient of sulfate persists within the particles even after long exposure times. In the advanced stage of the reaction, a dense shell of the reaction product exists at the outer surface of the particles, and the overall process is then governed by transport of sulfur dioxide through the remaining pores. As the findings herein indicate, carbonate rocks and their calcines having large pore volumes and small grains are best suited as sorbents for removal of sulfur dioxide from the flue gases.

Although there are a number of promising processes for sulfur dioxide removal from flue gas, the problem of sulfur dioxide pollution abatement still awaits fully operational solutions. There has been considerable interest in a dry process using a fluidized bed of inexpensive limestone or dolomite. The fluidized bed, with its excellent mass and heat transfer characteristics, offers attractive possibilities for efficient contact between gas and solid and complete combustion of fuel. Two most attractive schemes would be passing combustion gases through the fluidized bed of limestone or actually burning fuel within such a bed (Zielke et al., 1970). The latter alternative seems to be more attractive. Not only would such a fluidized-bed combustor be able to burn low-grade coal, but it also holds the potential of smaller size as compared to conventional boilers.

At high temperature, the limestone or dolomite rock is usually calcined immediately, and, in the presence of excess oxygen, sulfur dioxide combines with calcium oxide to form calcium sulfate. The design of a reactor and preliminary evaluation of a corresponding process require data on kinetics of the sulfation reaction. The main factors affecting the rate of this reaction are the mineral type and geological origin of the carbonate rock, its particle size, the concentration of sulfur dioxide, temperature, pressure, and time of exposure of the solid to the gas.

The reaction of sulfur dioxide and oxygen within porous particles of lime is of a complex nature, and its mechanism has not been yet fully elucidated. Working with precalcined limestones and dolomites, Borgwardt (1970) found that the reaction was of first order with respect to sulfur dioxide, and the rate of reaction decreased rapidly as the sulfation continued. The primary importance of physical properties such as porosity, pore size distribution, surface area, and grain size of limestones and their calcines for the course of reaction was suggested by Potter (1969) and by Borgwardt and Harvey (1972). In our previous paper (1974) we showed that both the porosity of the reacting particles and the sulfation reaction rate decreased rapidly with increasing conversion. The reaction also affected the pore size distribution within the solid.

The concept of grain theory, dealt with by many previous authors (Szekely and Evans, 1970, 71; Papanastassiou and Bitsianes, 1973; Sohn and Szekely, 1974) is useful for an analysis of the reaction. According to this theory, a porous particle is comprised of spherical grains of uniform size separated by pores through which the reacting gases diffuse. As the reaction proceeds, a shell of the reaction product is formed on the surface of the grains. In their approach, Pigford and Sliger (1973) assumed that the reaction rate was governed either by the diffusion of sulfur dioxide through the pores or by its diffusion through the developing shells of the reaction product. This model was tested on the data of Coutant et al. (1971) and Borgwardt. Their times of exposure of solids were very short and varied from a fraction of a second to tens of seconds. In contrast to the assumptions of Pigford and Sliger, experimental findings of Wen and Ishida (1973) showed that at low temperatures (590° to 680°C) the overall rate was controlled by the chemical reaction taking place on the grains of calcium oxide. Borgwardt concluded that the diffusional resistance developed in the interior of the particles becomes limiting only after the conversion reaches the value of 20% or higher.

The present study is a continuation in our effort to develop better understanding of the intricate reaction between limestone particles and sulfur dioxide. In light of the experimental findings, we believe that a feature of the reaction of major importance is the rapid decrease in porosity of the reacting particles and that this observation should be reflected in an analysis of the reaction system. By considering the behavior of this kind of system under a broader range of experimental conditions, the effect of the chemical reaction step should also be included in its modeling or simulation as suggested by Shen and Smith (1965). In this paper we present a version of the grain model that has been expanded in these respects. Agreement is also explored between the predictions of this model and experimental results obtained under conditions similar to those in fluidized beds of practical interest.

THEORY

Based on experimental findings to be described below, the calcination reaction is essentially instantaneous compared to the sulfation reaction. Accordingly, it is assumed that the porous structure is fully developed at $t = 0$, and unsteady state diffusion and reaction of sulfur dioxide within a porous spherical particle of lime made up of a large number of uniform grains are treated here by using the following assumptions.

1. Mass transfer to the external surface of the particle does not affect the rate of reaction.
2. The temperature is uniform throughout the stone.
3. The constituent grains are sufficiently small that variations in gas concentration on their surface is negligible.
4. The reaction between the gas and the grains is of first order with respect to sulfur dioxide and proceeds by the unreacted shrinking core mechanism (McClellan et al., 1970).
5. The reaction takes place in the presence of an excess

of oxygen and is irreversible.

6. The pseudo steady state approximation is sufficiently accurate for application in this reaction system (Wen, 1968).

Transport of sulfur dioxide within a spherical particle of lime can be described by the diffusion equation for the present case:

$$\frac{\partial^2 C}{\partial R^2} + \frac{2}{R}\frac{\partial C}{\partial R} - \frac{N}{D_{ef}} = 0 \qquad (1)$$

Implicit in this equation is the assumption that the radial gradient of D_{ef} is negligible; such an assumption is based on more rigorous calculations which gave overall conversions ranging from less than 1% lower than Equation (1) at exposure time of 21 s to about 6% lower at exposure time of about 45 min. Because the effect on the final calculated results is so small, the simpler Equation (1) was used for computing all results presented herein as described in the following.

The reaction interfacial area per unit volume of a limestone grain F is

$$F = 3(1 - e_C)\frac{r^2}{r_g^3} \qquad (2)$$

and the rate N at which gas reacts with the solid is

$$N = K \cdot F \cdot C_C \qquad (3)$$

where K is the chemical reaction rate constant per unit area of reaction interface, and C_C is the concentration at the reaction interface. As follows from the unreacted shrinking core model as applied to a grain, the concentration profile of sulfur dioxide in the outer spherical layer of the grain (that is, the product layer in which there is no further chemical reaction), the concentration C_1 at position r_1 within this layer is given by

$$\frac{\partial^2 C_1}{\partial r_1} + \frac{2}{r_1}\frac{\partial C_1}{\partial r_1} = 0 \qquad (4)$$

with boundary conditions

$$C_1 = C(R) \quad \text{at} \quad r_1 = r_g \qquad (5)$$

$$D_s(dC_1/dr_1)_{r_1=r} = K\,C_c \qquad (6)$$

which, upon integration, gives

$$C_C = \frac{D_S C}{D_S + Kr(1 - r/r_g)} \qquad (7)$$

In our previous paper (1974) we deduced a general relation between the porosity of the reacting particle and the progress of the sulfation reaction which was verified by experiments. For complete thermal decomposition of calcium carbonate, this relation becomes

$$e_X = 1 - (1 - e_{LS}) \cdot \left\{ \rho_{LS}\frac{y}{M_{CC}}[V_{CO} + X(V_{CS} - V_{CO})] - (1 - y)\,\rho_{CC} \right\} \qquad (8)$$

where X is conversion of calcium oxide to sulfate. The following values were used to evaluate the coefficients in Equation (8): $y = 0.982$, $e_{LS} = 0$, $\rho_{LS} = \rho_{CC} = 2.71$ g/cm^3, $V_{CO} = 16.9$ cm^3/mole, and $V_{CS} = 52.2$ cm^3/mole; these densities and molar volumes are from Weast (1968). The porosity of calcined limestone e_C appearing in Equation (2) was determined experimentally as 0.52.

According to Equation (8), an extensive pore structure develops during calcination of limestone, but these pores are reduced in volume by the sulfation reaction. On a molar basis, the pore volume consumed as calcium sulfate is formed is greater than the pore volume developed by the decomposition of calcium carbonate ($V_{CC} = 36.9$ cm^3/mole). Consequently, the porosity of the reacting particle falls rapidly as the sulfation proceeds.

Campbell et al. (1970) measured the diffusion coefficients of carbon dioxide in porous lime and concluded that Knudsen diffusion predominates with a tortuosity factor of 1.5. Adjusting Campbell's values for differences in molecular weight and temperature results in an estimation of the diffusion coefficient D at about 0.075 cm^2/s. Focusing only on the influence of porosity and neglecting explicit differences in porosity, we write

$$D_{ef} = D\,e_X \qquad (9)$$

With respect to the diffusional resistance of the sulfate layer on the surface of a grain, the rate at which the reaction interface moves inward may be expressed by

$$\frac{\partial r}{\partial t} = -\frac{K}{\rho}\frac{D_S C}{D_S + Kr(1 - r/rg)} \quad \text{for } r > 0 \qquad (10)$$

The boundary and initial conditions are

$$\left.\begin{array}{llll} \text{for Equation (1):} & \left\{\begin{array}{l} C = C_O \\ \dfrac{\partial C}{\partial R} = 0 \end{array}\right. & \begin{array}{l} \text{at} \\ \text{at} \end{array} & \begin{array}{l} R = R_p \\ R = 0 \end{array} \\ & \text{and} & & \\ \text{for Equation (10):} & r = r_g & \text{at} & t = 0 \\ & \dfrac{\partial r}{\partial t} = 0 & \text{at} & r = 0 \end{array}\right\} \qquad (11)$$

The set of foregoing equations describes the concentration profile of sulfur dioxide within a spherical limestone particle and position of the reaction fronts within the individual grains of the limestone particle during the course of reaction.

The local (in a grain) and overall (in the stone) conversion may be expressed in terms of the position of the reaction interface by the following equations:

$$X_L = 1 - r^3/r_g^3 \qquad (12)$$

$$X_O = \frac{3}{R_p^3}\int_O^{R_p} R^2\left(1 - \frac{r^3}{r_g^3}\right) dR \qquad (13)$$

The local extent of reaction defined by Equation (12) was used in evaluating the porosity of the sulfated interior of the particle by using Equation (8).

The coupled Equations (1) and (10) were approximated by finite difference formulation and solved as a boundary value problem. An implicit form of the finite difference approximation of Equation (1) was used in numerical integration by using the Tesla 200 digital computer. Preliminary calculations showed that a net with thirty grid points on the particle radius and a time step as large as 1 s provide a numerical solution of sufficient accuracy.

Of the several parameters or coefficients in the equations of the model describing the process of diffusion and reaction within the particle, the only adjustable parameters are D_S and the limiting porosity. The effective diffusivity D_{ef} varies with the progress of reaction as determined by Equations (8) and (9). The solid diffusion coefficient D_S is difficult to measure, and the value of 6×10^{-9} cm^2/s was found to fit the kinetic data by a trial-and-error procedure. The reaction rate constant K per unit area of reaction interface evaluated at a conversion of 0.04 was 6.6 cm/s. The reacting particles were assumed to be spherical with a diameter equal to the arithmetical average of size of the two sieves between which the fraction was retained. Microphotographs of different natural limestones show that only a small portion of the particles possess spherical shape. Most of them are sharp edged and irregular in shape, and small, smooth crystals, oriented in random directions, can be often seen on the surface of the particles.

Because of the simplifications and assumptions inherent in the theoretical development (for example, treating particles and grains as uniform spheres), any extrapolation beyond the range of the experimental data should be made with caution. The major aim here is to show that the model is a suitable means for correlating data obtained by relatively simple experiments with a view toward employing this information in design of fluidized-bed contactors for removing sulfur dioxide.

The broadening of x-ray diffraction lines was used to determine the mean grain size of the calcined samples. Such values were about 2×10^{-5} cm.

EXPERIMENTAL SECTION

For the kinetic studies, a differential reactor containing limestone was fed with flue gas generated by combustion of propane. Sulfur dioxide was added from a cylinder to the gases leaving the combustor. The composition of the gas entering the reactor was 12.6% water, 10.1% carbon dioxide, 3 5% oxygen, 0.05 to 0.29% sulfur dioxide by volume, with the remainder consisting of nitrogen. The flue gas passed through a thin layer (about 50 mg) of dried, uncalcined limestone at a superficial velocity of 2.5 m/s. The limestone particles were dispersed on quartz gauze in a removable cup, the bottom of which was uniformly perforated.

The amount of sulfate in the reacted limestone was determined by titration with 0.005 N $Ba(ClO_4)_2$ solution in isopropyl alcohol by using a mixture of thorin and methylene blue as indicator. Further details on the reactor design, experiments, and the analyses of solid and gas samples can be found elsewhere (Hartman and Coughlin, 1974; Hartman, 1974).

The reactivity of ten different commercial limestones from various quarries was measured in preliminary experiments. The present study was conducted with the most reactive limestone VI, a crystalline, coarse-grained, high-grade mineral of the following chemical composition: 55.0% calcium oxide, 0.21% magnesium oxide, 0.29% silica, 0.10% aluminum oxide, and 0.08% ferric oxide by weight. The hand-picked stones, which contained no visible inclusions or impurities, were crushed and sieved; the fractions investigated in this study comprised three size ranges: 0.50 to 0.63 mm ($\overline{D}_p = 0.565$ mm), 0.80 to 1.00 ($\overline{D}_p = 0.900$ mm), and 1.00 to 1.25 mm ($\overline{D}_p = 1.12$ mm). Since the use of precalcined limestone in commercial fluidized beds does not appear practical, dried but uncalcined samples of the limestone were used in all the experiments.

RESULTS AND DISCUSSION

At first, an effort was made to investigate the effect of temperature on the reaction rate of the particles of mean size $\overline{D} = 0.565$ mm. The samples were exposed to the flue gas containing 0.29% sulfur dioxide by volume for 2 to 20 min at temperatures in the range 750° to 1 000°C. From smoothed graphs of conversion vs. time of exposure, the times required to attain a conversion of 17% were obtained and plotted in Figure 1. The x-ray analyses revealed the presence of unreacted calcium carbonate in the samples sulfated at 750°C. After 16 min of exposure to the gas, about 60% of the original limestone was decomposed at this temperature. The sulfation reaction proceeds most rapidly at temperatures near 900°C; at higher temperatures the rate of the reaction is lower.

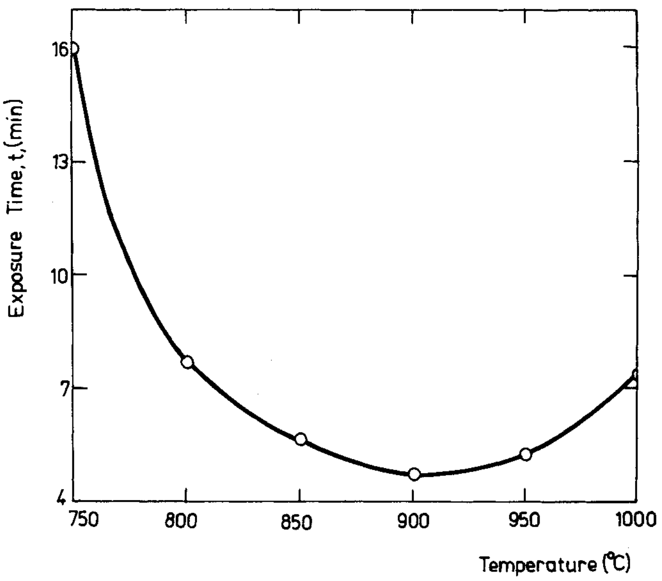

Fig. 1. Effect of temperature on the reaction rate: exposure time to reach 17% conversion plotted vs. temperature. Concentration of sulfur dioxide 0.29% by volume; particle size, 0.565 mm; fractional conversion of calcium oxide, 0.17.

Working with precalcined particles, Borgwardt (1970) found that the rate of sulfation increased up to 980°C which is higher than the optimum shown in Figure 1. There is some question as to what extent pore structure is influenced by temperature after calcination to 1 000°C. Little influence would be expected if the calcination temperature is higher than the subsequent sulfation temperature as shown by Borgwardt (1972). If the temperature of sulfation is higher than the previous calcination temperature, however, then the pore structure of unsulfated lime can be altered by higher temperatures of sulfation. This is strongly suggested by the work of McClellan et al. (1970) who amassed much data as to the temperature sensitivity of surface area and pore size of lime between 750° and 1 100°C; the lower the calcination temperature, the larger the surface area and the higher the reactivity. The rate of the sulfation reaction itself increases with temperature until equilibrium constraints become evident at about 1 150°C. When both sulfation and calcination occur simultaneously, an optimum temperature can be expected to result from the two opposing tendencies. Such an optimum has also been noted by Jonke et al. (1972) at about 800°C.

Aside from the origin and nature of the limestone itself, the reactivity of calcium oxide formed by thermal decomposition of carbonate rock greatly varies with the operating conditions of calcination. Raising the temperature of calcination causes a decrease in surface area, an increase in grain size, and adversely affects the pore size distribution and void fraction in the solid (McClellan and Eades, 1970). It is such changes in physical properties which obviously result in lowered reaction rates at higher temperature since the chemical equilibrium remains favorable over a wide range of temperatures (Reid, 1970). In general, the optimum temperature may be expected to be different for different types of limestones, and its value should be always found for each rock by experiment. All the results reported below were obtained at 850°C at which temperature the lime formed is "soft burned" and remains reactive even after long exposure times.

The reactivity of limestone VI used in this study was compared with that of the precalcined dolomite 1351 of Borgwardt who investigated several types of stone and

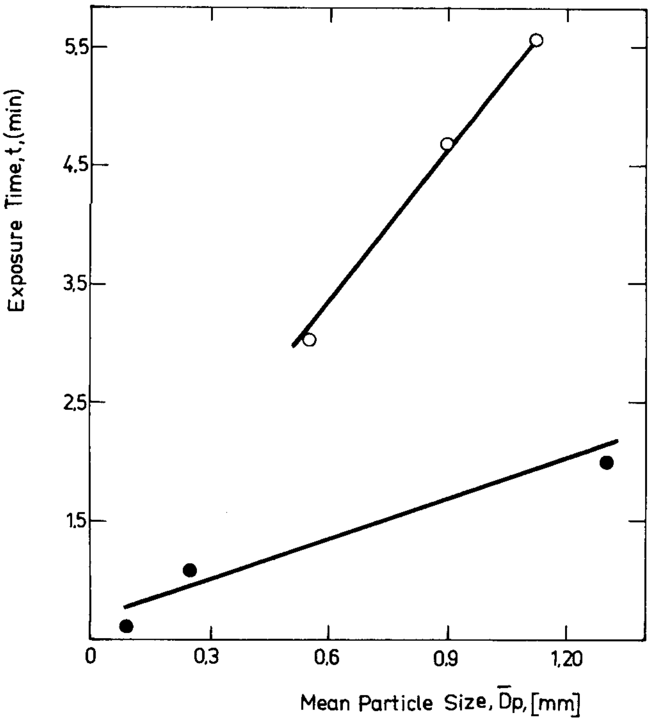

Fig. 2. Comparison of the reaction rates of different carbonate rocks at a sulfate loading of 0.17 g sulfur trioxide/g of calcine: ● data of Borgwardt (1970); temperature, 870°C; concentration of sulfur dioxide, 0.30% by volume; precalcined dolomite 1 351; fractional conversion of calcium oxide, 0.22; ○ this work; temperature, 850°C; concentration of sulfur dioxide, 0.29% by volume; high-grade limestone VI; fractional conversion of calcium oxide 0.13.

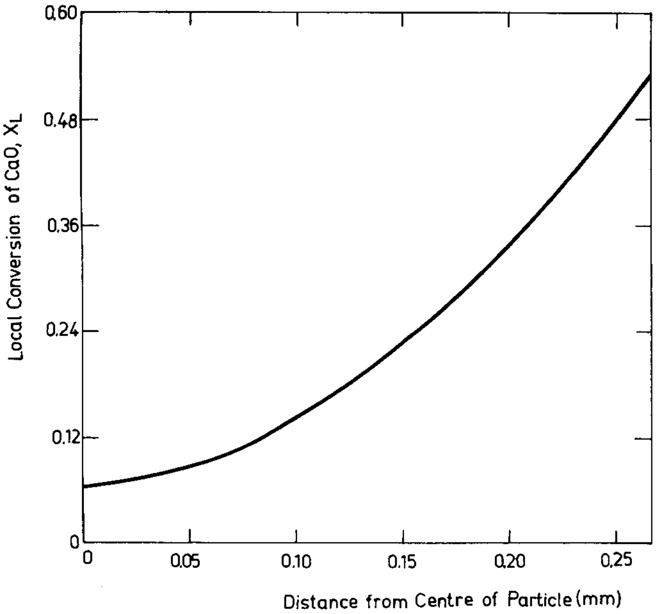

Fig. 4. Computed local extent of the sulfation reaction throughout the particle interior: $R_p = 0.282$ mm, $C_o = 1.43 \times 10^{-8}$ mole/cm^3, $K = 6.6$ cm/s, $r_g = 1 \times 10^{-5}$ cm, $D = 7.5 \times 10^{-2}$ cm^2/s, $D_s = 6 \times 10^{-9}$ cm^2/s, and $t = 60$ min.

found that this dolomite showed the highest reactivity for sorption of sulfur dioxide. The times of exposure of the limestone VI required for sorption of 0.17 g sulfur trioxide per grain of calcine are plotted in Figure 2 for particles of several different sizes. Under similar conditions, the dolomite 1 351 was more reactive than our limestone VI by a factor of about 2.

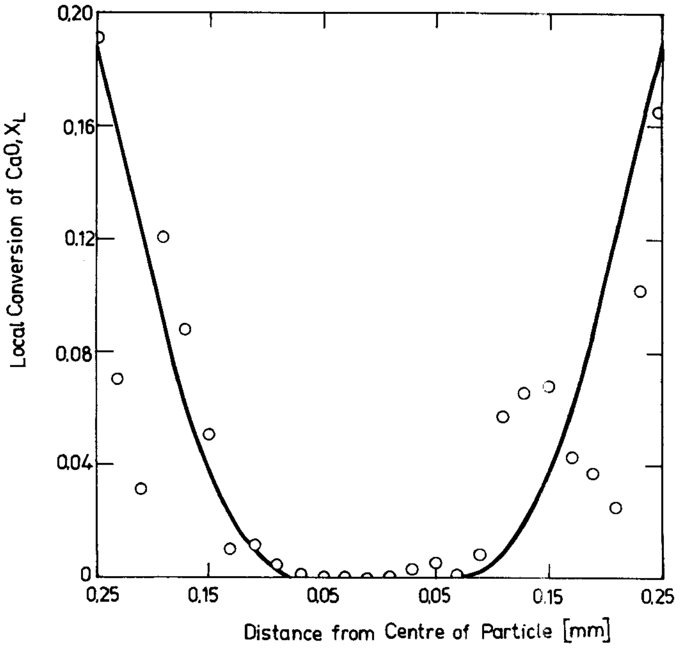

Fig. 3. Local extent of the sulfation reaction throughout the particle interior: ○ experimental values determined by electron microprobe. Particle size, 0.565 mm; temperature, 850°C; concentration of sulfur dioxide, 0.132% by volume, time of exposure, 8 min. The solid curve shows the values predicted by the present grain model for $R_p = 2.82 \times 10^{-2}$ cm, $c_o = 1.43 \times 10^{-8}$ mole/cm^3, $K = 6.6$ cm/s, $r_g = 1 \times 10^{-5}$ cm, $D = 7.5 \times 10^{-2}$ cm^2/s, $D_s = 6 \times 10^{-9}$ cm^2/s, and $t = 8$ min.

DISTRIBUTION OF SULFATE WITHIN REACTED PARTICLES

Electron microprobe analysis was employed to investigate the manner in which the sulfation reaction proceeds within the interior of the particles. Particles exposed for various times to the flue gas were split, and their cross sections were examined by using the electron microprobe JX A-5. Distribution of sulfur within the selected sphere-like particles was obtained at discrete sites across the cross section. The distance between two scanned sites was 0.02 mm, and the local content of sulfur was expressed as the local conversion to sulfate by assuming a uniform distribution of calcium oxide.

In Figure 3 are plotted the local conversions in the interior of a particle ($\bar{D}_p = 0.565$ mm) which was exposed for 8 min to the flue gas containing 0.13% sulfur dioxide. Although the data points are scattered, higher conversions are apparent in the outer zone of the reacted particle. But even at the outermost surface of the particle, the conversion is lower than 20%. The inner core, which remains completely unreacted, is separated from the outer layer by a rather distinct reaction interface. This distinct boundary between the reacted and unreacted calcium oxide was also visible on photographs taken by a scanning electron microscope. After the particles had been in contact with the flue gas for longer periods of time, calcium sulfate was present throughout the particle interior. It is of interest that after exposure to the flue gas for as long as 2 hr, a considerable amount of calcium oxide still remained unreacted even on the outer edge of the particles.

It is seen that during the early stages the sulfation reaction takes place preferentially in the outer zone of the particles. As the time of exposure continues, the reaction zone expands inward, and after longer elapsed time the sulfation reaction occurs throughout the internal structure of the particle. The solid curve in Figure 3 shows the local conversions throughout the particle interior as computed from the mathematical model. The computed results are in general agreement with the data provided by experiment.

The values of the local extent of reaction within a particle computed for an exposure time of 1 hr are plotted in Figure 4. Analysis by the electron microprobe confirmed that the sulfation reaction also takes place in the very center of the particle as the model predictions suggest. Unfortunately, because of the scatter inherent in the microprobe data, no conclusive comparison of the theoretical and experimental concentration profiles of calcium sulfate can be made. As we found in a separate study, the conversions of lime particles to calcium sulfate attained after 2 hr of exposure to the flue gas increased with decreasing particle size, although the reaction occurred throughout their interior. This fact suggests that the outer zone of the particles is somewhat enriched in sulfate. Some gradient of sulfate concentration is very likely to exist, therefore, even in the particles exposed to the flue gas for long times and in which sulfation has occurred to some extent throughout the interior.

EFFECT OF EXPOSURE TIME, PARTICLE SIZE, AND GAS CONCENTRATION OF SULFUR DIOXIDE ON CONVERSION OF CALCIUM OXIDE

By the use of limestone particles of three diameters (0.565, 0.900, and 1.12 mm), the dependence of their total conversion to sulfate on the time of exposure ranging from a few minutes to 1 h was determined. The experimental results are plotted as the data points in Figure 5. The solid lines in this figure represent the results obtained by solving the equations of the model for the experimental operating conditions. The value of the solid diffusion coefficient used in the computations was 6×10^{-9} cm^2/s. As follows from Equation (8), the porosity is zero when the conversion reaches about 55% if uniform conditions are assumed throughout the particle. In our earlier work we found that the radii of pores in the calcined and sulfated samples are distributed over the wide range 75 to 75 000Å.

Microscopic examinations revealed that the external surfaces of the sulfated samples were very smooth. While most of the pores were filled with the reaction product, some open pore mouths could be always found even on the particles sulfated for long periods of time. This residual porosity e_r, the origin of which may be ascribed to local nonuniformities, is difficult if not impossible to determine by experiment. The value $e_r = 0.002$ used in the present computations was found by trial and error when the experimental data were fitted by the model. This value can be understood as the lowest limiting value of porosity that can be attained during the course of the reaction and which then is not further affected by additional progress of the reaction.

As seen in Figure 5, very good agreement between theory and experiment was achieved for the larger particles. The conversions of 0.565 mm diameter particles predicted by the model for exposure times longer than 13 min are only a few percent higher than the experimentally measured values. The sulfation reaction proceeds rapidly in its early stages but slows down as the time of exposure continues, and the major portion of sulfur dioxide is sorbed by the particles during about the first 15 min of their exposure to the flue gas. It should be noted that this predicted evolution in time would be qualitatively different if the model did not account for changes of D_{ef} with time; in fact, the model would predict 100% conversion within 10 min if changes in D_{ef} were ignored.

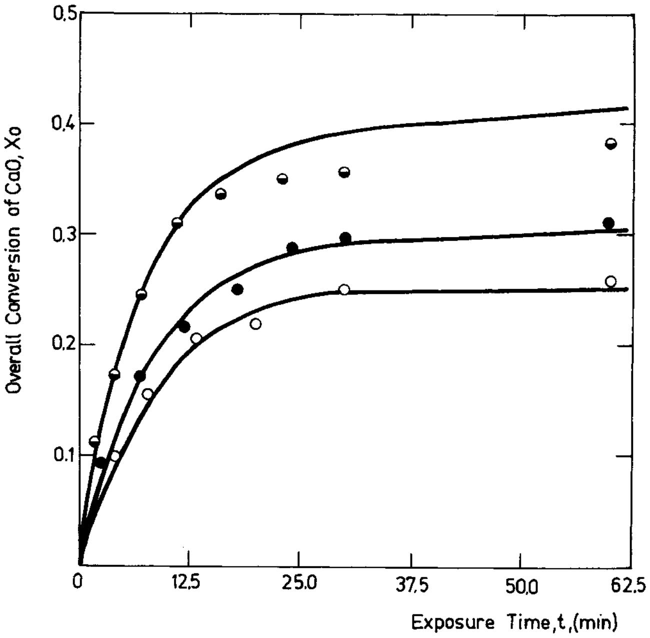

Fig. 5. Dependence of the conversion to sulfate on the exposure time and particle size: temperature, 850°C; concentration of sulfur dioxide, 0.3% by volume; ◓, particle size, 0.565 mm; ●, particle size, 0.900 mm; ○, particle size, 1.12 mm. The solid lines show the values of overall conversion predicted by the model for $C_o = 3.2 \times 10^{-8}$ mole/cm^3, $K = 6.6$ cm/s, $r_g = 1 \times 10^{-5}$ cm, $D = 7.5 \times 10^{-2}$ cm^2/s, $D_S = 6 \times 10^{-9}$ cm^2/s.

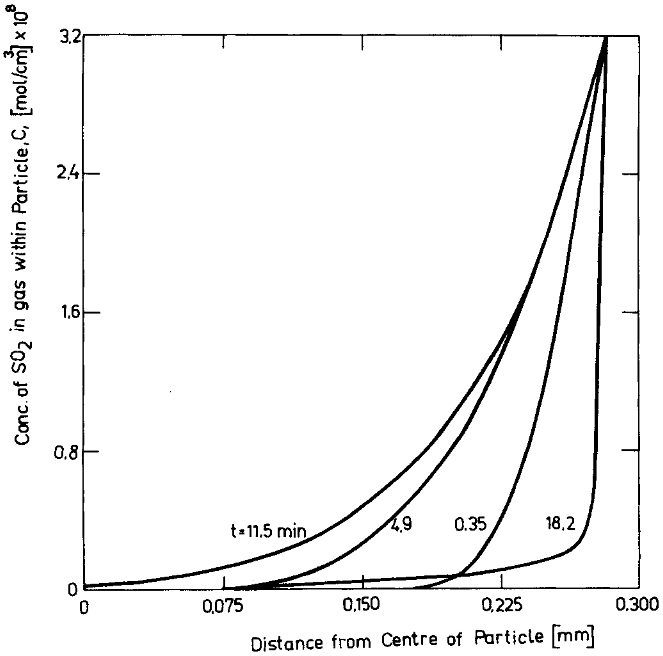

Fig. 6. Computed gaseous concentration profiles of sulfur dioxide in gas within the particle for various times of exposure: $R_p = 2.82 \times 10^{-2}$ cm, $C_o = 3.2 \times 10^{-8}$ mole/cm^3, $K = 6.6$ cm/s, $r_g = 1 \times 10^{-5}$ cm, $D = 7.5 \times 10^{-2}$ cm^2/s, $D_S = 6 \times 10^{-9}$ cm^2/s.

In Figure 6 are shown the computed concentration profiles of the gaseous sulfur dioxide reactant within the interior of the particles at different times of exposure. After sulfur dioxide starts penetrating into the particle, its concentration profile gradually develops a decreased curvature in the early stages, but, regardless of the exposure time, the concentration in the center of the particle remains very low. This fact suggests the importance of the diffusional transport of sulfur dioxide through the pores for the continued progress of the reaction. It is

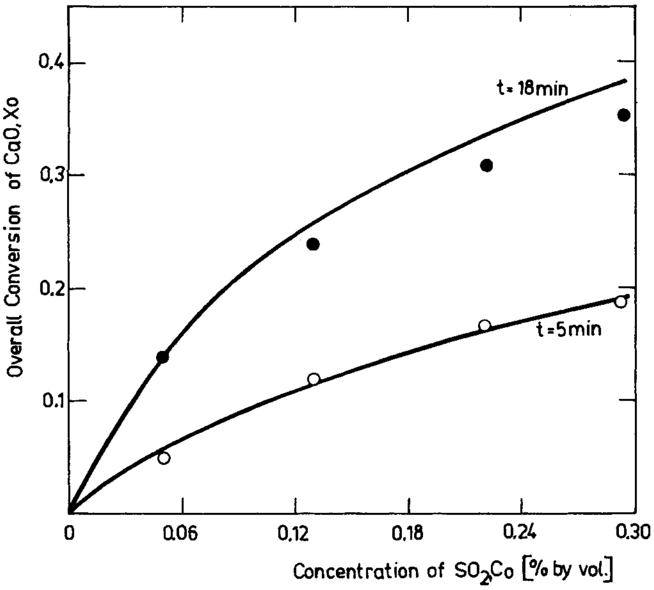

Fig. 7. Dependence of the conversion to sulfate on the concentration of sulfur dioxide in the flue gas and on the exposure time: temperature, 850°C; particle size, 0.565 mm; ○ exposure time, 5 min; ● exposure time 18 min. The solid lines show the values predicted by the model for $K = 6.6$ cm/s, $r_g = 1 \times 10^{-5}$ cm, $D = 7.5 \times 10^{-2}$ cm²/s, $D_S = 6 \times 10^{-9}$ cm²/s, $t = 5$, and 18 min.

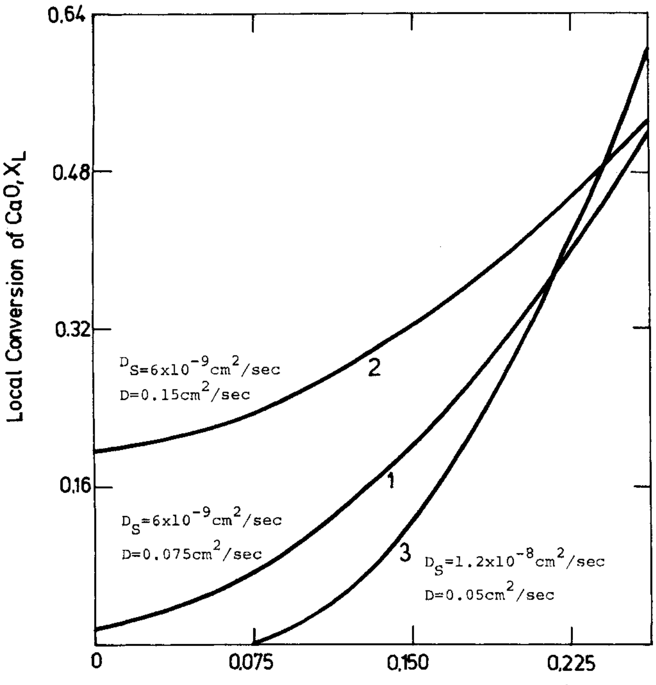

Fig. 9. Sensitivity of the local extent of reaction within the particle to the diffusion coefficient of sulfur dioxide in the pores and to the diffusivity of sulfur dioxide through the product shell. The values of the model parameters and labeling of the curves are the same as in Figure 8. The curves were computed for an exposure time of 11.5 min.

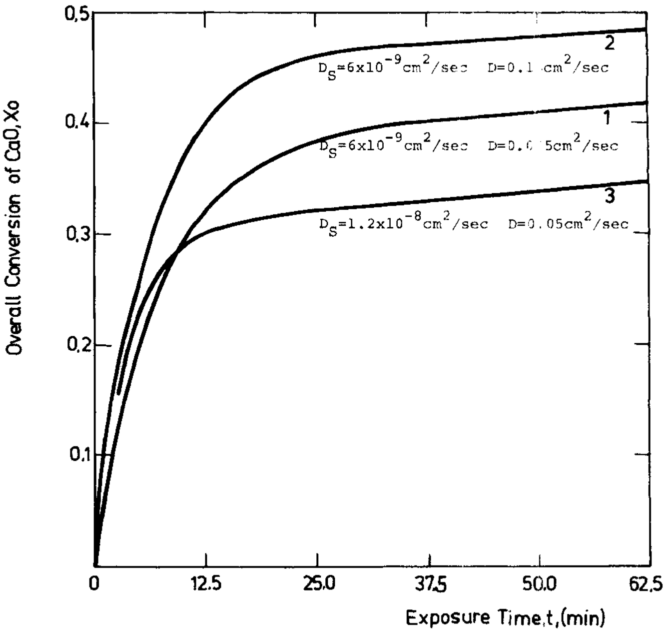

Fig. 8. Sensitivity of the overall conversion of calcium oxide to the diffusion coefficient of sulfur dioxide in the pores and to the diffusivity of sulfur dioxide through the sulfate shell: $R_p = 2.82 \times 10^{-2}$ cm; $r_g = 1 \times 10^{-5}$ cm; $C_o = 3.2 \times 10^{-8}$ mole/cm³; $K = 6.6$ cm/s. Curve 1: $D = 7.5 \times 10^{-2}$ cm²/s, $D_S = 6 \times 10^{-9}$ cm²/s. Curve 2: $D = 1.5 \times 10^{-1}$ cm²/s; $D_S = 6 \times 10^{-9}$ cm²/s. Curve 3: $D = 5 \times 10^{-2}$ cm²/s; $D_S = 1.2 \times 10^{-8}$ cm²/s.

also of special interest that after longer elapsed times, the amount of sulfur dioxide present in the pore volume begins to decrease owing to the decreasing porosity of the outer sulfated shell. It should be emphasized that the model would fail to predict such a decrease in sulfur dioxide concentration were it not for the influence of decreasing porosity on diffusivity. This turning point is reached when conversion at the outer edge of the particle is about 55%, at which stage a dense shell of the reaction product encapsulates the limestone particle. Resistance of the shell to the transport of the reacting gas is determined by its residual or limiting porosity e_r which was discussed above.

By using particles of mean size 0.565 mm measurements were made at four concentrations of sulfur dioxide in the flue gas: 0.048, 0.132, 0.221, and 0.295% sulfur dioxide by volume, for various times of exposure. The data points obtained from the smoothed experimental curves of conversion vs. exposure time are plotted and compared with the theoretical predictions of the model in Figure 7. It can be seen that the computed conversions for an exposure time of 5 min are in very good agreement with the experimental data. For exposure time of 18 min, the computed values are only slightly higher than the experimental results.

As has been shown, the cumulative fraction of calcium oxide reacted can be determined by means of the model with good accuracy. Moreover, the model also provides valuable information, which is rather semiquantitative in nature, on the approximate distribution of sulfate within the particles. Using the model, we explored how the progress of the overall reaction is governed by the three individual processes: diffusion through the pores of particles, diffusion through a shell of sulfate formed on the grains, and chemical reaction occurring at the active interface of the grains. To this end, the equations of the model were solved by using individual values of D, D_S, or K two times greater than the value deduced by comparison with the experimental data. The remaining parameters were maintained unchanged. Computations made with the higher value of the chemical reaction constant K predicted overall conversions only slightly higher than those obtained with the smaller normal value of K and are not discussed further. The results of the other computations shown in Figure 8 indicate that a larger diffusion coefficient in the pores results in higher overall conversion regardless of time of exposure (curve 2). But the case of a lowered diffusional resistance D_S in the product shell (curve 3) encapsulating the grains is markedly different; of course, there does not appear to be any practical way to measure or control D_S. While during the first minutes of exposure the reaction proceeds more rapidly in this case (high D_S), it is soon strongly retarded by the increased resistance of the extensive dense shell of product developed at the particle surface. Because of this, the final overall conversion attained after an hour of exposure is even lower than the corresponding conversion when the solid diffusivity was of its lower, normal value as for curves 1 and 2. The sulfate distribution throughout the particle interior is sensitive to the values of the diffusion parameters as shown in Figure 9. When the solid diffusion coefficient was higher, the sulfation reaction was confined to the outer portions of the particles (curve 3). The structure of calcium oxide, originally porous, was filled with reaction product before sulfur dioxide could reach the center of the particle which remained totally unreacted. These gradual changes in the pore structure of the lime particles during the course of sulfation constitute a specific feature of the reaction that contributes greatly to its complexity.

It has been shown in Figure 6 that only very little of the gaseous reactant can be expected in the particle interior, even at longer exposure times. Since the resistance offered by chemical reaction is low, the pore diffusion appears to be the predominant rate controlling step during the more advanced stages of reaction. Although only minor resistance of chemical reaction was found in these experiments, its effect cannot be neglected a priori. It is not the absolute but rather the relative magnitudes of a number of parameters such as reaction rate constant and diffusivities which determine the overall course of reaction.

During practical industrial use of fluidized beds of limestone, every effort should be made to attain high conversions of the sorbent. Aside from the operating conditions, the particle size and type of carbonate rock appear to be the main factors in this respect. As our results suggest, carbonate rocks and their calcines with large pore volumes and small grain sizes should be better suited for the sulfur dioxide sorption reaction than dense, coarse grained limestones. Marls and chalks described by Harvey et al. (1973) in their extensive survey of carbonate materials show such physical characteristics. The porosities of natural marls amount to about 60% on average, and they are further increased by calcination. Borgwardt and Harvey found that a marl was the most reactive of eleven various rocks tested. Even the particles of marl as large as 1.3 mm were completely converted to sulfate, and the application of Equation (8) suggests that this material remains porous even when completely converted to sulfate.

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NOTATION

C = concentration of reactant gas within pores, mole/cm^3
C_C = concentration of reactant gas at reaction interface at surface of a grain, mole/cm^3
C_O = concentration of reactant gas outside spherical particle, mole/cm^3
C_1 = concentration of reactant gas within product shell of a grain, mole/cm^3
D = diffusion coefficient of reactant gas in pores, cm^2, s
D_S = diffusivity of reactant gas through product shell of grain, cm^2/s
D_{ef} = effective diffusivity in pores of pellet, defined by Equation (9), cm^2/s
e_C = porosity of calcined limestone
e_{LS} = porosity of natural limestone
e_X = porosity of sulfate loaded particle expressed by Equation (8)
F = specific reaction interfacial area, defined by Equation (2), 1/cm
K = chemical reaction rate constant, cm/s
K_1,K_2 = integration constants in Equation (4)
M_o = molecular weight, g/mole
N = rate of disappearance of gas reactant, defined by Equation (3), mole/cm^3 s
R = radial coordinate within spherical particle, cm
R_p = radius of porous particle, cm
r = radius of reaction interface within spherical grain, cm
r_g = radius of grain, cm
r_1 = radial coordinate within product shell, cm
t = time of exposure of solid to gas, s
V_i = molar volume of pure component, cm^3/mol
X_L = local conversion of calcium oxide to sulfate, defined by Equation (12)
X_O = overall conversion of calcium oxide to sulfate, defined by Equation (13)
y = content of calcium carbonate in limestone, weight fraction
ρ = true (helium) density of solid reactant, mole/cm^3
ρ_i = true (helium) density, g/cm^3

Subscripts

CC = calcium carbonate
CO = calcium oxide
CS = calcium sulfate
LS = limestone

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Application of *h*-Transformation for the Solution of Multicomponent Adsorption in Fixed Bed

CHI TIEN
J. S. C. HSIEH
and
R. M. TURIAN

Department of Chemical Engineering and Materials Science
Syracuse University
Syracuse, New York 13210

A procedure for the application of the so-called *h*-transformation in solving fixed-bed multicomponent adsorption problems is developed. In order to apply this procedure, it is necessary to select an appropriate value for the transition-motion factor ξ, and the criteria for making this selection are established in this work.

SCOPE

In studying sorptive processes in fixed beds, the assumption of local equilibrium between the fluid and sorbent phases is often invoked. With the use of this assumption, the mass transfer effect is eliminated. The concentration profile throughout the fixed bed can be predicted on the basis of stoichiometry and equilibrium relationship, which in most cases would be of sufficient accuracy for preliminary design and feasibility studies. Thus, important information about column behavior can be obtained without excessive calculation. The appeal of this approach is particularly strong when the fluid stream contains a number of species which interact and compete in the sorption process.

Although a number of investigators have considered the fixed-bed adsorption under equilibrium conditions (Wilson, 1940; DeVault, 1943; Walter, 1945; Glueckauf, 1946), the applicability of these results is rather restricted. In the present paper we demonstrate that the *h*-transformation proposed by Helfferich and Klein (1970) can be adapted to the nonstoichiometric system. The procedure established is different from that suggested by previous investigators (Klein et al., 1965, 1967; Vermeulen et al., 1973; Helfferich and Klein, 1970; Tondeur et al., 1965, 1967), and its use is demonstrated through an example problem.

CONCLUSIONS AND SIGNIFICANCE

Through an example problem and an examination of the mathematical expressions, a consistent procedure for applying the *h*-transformation to obtain the equilibrium solution of adsorption in fixed bed is developed. By extending the definition of the column capacity parameters T of the single component theory to multicomponent systems, the concentration profiles (or histories) can be obtained in the form of dimensionless concentration vs. $1/T$, provided a properly selected value of the transformation factor ξ is used in the H-function of the *h*-transformation. The results of the present work indicate that there is a unique correspondence between the adsorption and its equivalent stoichiometric system corresponding to this particular value of the transformation factor ξ. A criterion was established empirically for the selection of the transformation factor for cases where the adsorbents are initially free of any adsorbates. In more general cases, it is suggested that the correct solution can be obtained by using arbitrary values of ξ with the transition bounds modified by material balance considerations.