**Comparative Study of the Reactions of Metal Oxides
and Carbonates with H_2S and SO_2**

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EXECUTIVE SUMMARY

The primary objective of this project had been the investigation of the effects of pore structure on the capacity of porous metal oxides for removal of gaseous pollutants from flue gases of power plants (SO_2) and hot coal gas (primarily H_2S). Porous calcines obtained from natural precursors (limestones and dolomites) and sorbents based on zinc oxide were used as model systems in our experimental studies, which included reactivity evolution experiments and pore structure characterization using a variety of methods. The key idea behind this project was to appropriately exploit the differences of the sulfidation and sulfation reactions (for instance, different molar volumes of solid products) to elucidate the dependence of the sorptive capacity of a porous sorbent on its physical microstructure.

In order to be able to proceed faster and more productively on the analysis of the above defined problem, it was decided to employ in our studies solids whose reaction with SO_2 (limestone calcines) or H_2S (sorbents based on zinc oxide) had been investigated in detail in past studies by our research group. Calcines derived from limestones of high (> 95%) calcium carbonate content and commercially available desulfurization sorbents (e.g., zinc oxide) of qualitatively (or quantitatively) different pore size distributions were used in our experiments. Reactivity vs. time or conversion vs. time studies were conducted using thermogravimetry and fixed-bed and fluidized-bed reactors. The pore structure of partially reacted samples collected at selected time instants or conversion levels was analyzed by gas adsorption and mercury porosimetry. For better characterization of the pore structure of the solid samples, we also carried out intraparticle diffusivity measurements by the peak-broadening (chromatographic) method, using a system developed for this purpose in our laboratory. In the context of this part of the project, we also conducted a detailed theoretical investigation of the measurement of effective diffusivities in porous solids using the diffusion-cell method.

Our experiments on the reaction of ZnO -based sorbents with SO_2 showed that it proceeded with extremely low rate. As a result, conclusions on the effects of pore struc-

ture on the sulfidation and sulfation reactions were mainly reached from the comparative analysis of the $CaO-SO_2$ and $CaO-H_2S$ reactions. The comparison of model predictions and experimental data showed that the key factor influencing the behavior of a sorbent during sulfidation and sulfation was the connectivity of its pore space. In both cases, the reactivity of the sorbent and the connectivity of its pore structure were found to, in general, increase with increasing average grain in the precursor stone, and the same behavior was also exhibited by the calcination rates of the precursors. Detailed models for transport, reaction, and structure evolution in porous media undergoing gas-solid reactions were used to analyze the experimental data. Among these mathematical models was a novel structural model developed under this project, which uses an assemblage of partially overlapping grains to represent the solid phase of the porous medium. Very good agreement between model and experiment was obtained using in almost all cases the same pore connectivity parameter for sulfidation as for sulfation. The particle models were used as basis to develop a predictive design model for desulfurization in beds, and experimental data obtained for the $ZnO-H_2S$ reaction in a fixed-bed reactor were used for its testing and validation.

Results and conclusions on the reaction of CaO with H_2S and SO_2 at atmospheric pressure cannot be applied to flue gas and coal gas desulfurization by limestone addition in units (combustors and gasifiers) operating at high pressures since calcination is, in general, not favored in such units. For this reason, we decided to comparatively investigate the direct reaction with H_2S and SO_2 of the limestones we used as CaO precursors. Reactivity evolution experiments were thus carried out in a thermogravimetric analysis system under simulated high pressure conditions, that is, in the presence of enough CO_2 to prevent decomposition of $CaCO_3$. The direct sulfidation reaction of limestones was found to be much faster than their direct sulfation, but both direct reactions were much slower than the corresponding reactions of the calcined solids. In agreement with the behavior seen in the study of the indirect reactions, the direct reactivity of limestone with H_2S and SO_2

was found to increase with decreasing grain size.

The preliminary analysis of the experimental data using a shrinking core model suggested that the effective diffusivity in the product layer depended on the distance from the external surface of the reacting particles. A variable diffusivity, shrinking core model was thus developed and then employed to extract from the experimental conversion vs. time profiles the effective diffusivity in the product layer as a function of distance from the external surface. Several interesting conclusions about the resistance for diffusion in the product during the direct and indirect reactions were reached from the estimated values of effective diffusivities. For instance, it was concluded that the product layer formed during direct sulfation presented much less resistance to diffusion than that formed during the indirect process. On the other hand, the diffusional resistance of the product formed during direct sulfidation was found to be much larger than what should be expected for a 30% porous solid – as it should be the case if the particle did not change size during reaction. In agreement with this result, pore structure characterization of fully sulfided particles revealed that the product layer formed during sulfidation underwent extensive sintering.

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1. BACKGROUND STATEMENT

The reactions of metal oxides with sulfur-containing compounds, such as SO_2 and H_2S , find extensive use in controlling emissions of gaseous pollutants from coal utilization systems. Limestone and dolomite, for instance, are used in the control of emissions of sulfur dioxide from coal-fired power plants. In the high temperature environment of a combustor, the limestone or dolomite particles undergo calcination, and the calcined product (CaO or MgO) reacts with the sulfur dioxide produced during coal combustion forming, mainly, calcium or magnesium sulfate. Calcium oxide and other metal oxide sorbents (iron oxide, zinc oxide, zinc ferrite, zinc titanate, etc.), on the other hand, are used to remove sulfur-containing compounds (predominantly H_2S) from hot coal gas.

The reaction of metal oxides with SO_2 and H_2S are typical examples of noncatalytic gas solid reactions with solid product formation and pore closure behavior. Such gas-solid reactions with solid product are encountered in a number of chemical process industries with applications ranging from ceramic material manufacture to gas scrubbing for pollution control. The calcination and sulfation reactions of limestone and dolomite have been the subject of extensive experimental investigation, but unambiguous experimental evidence that leads to a clear understanding of the effects of pore size distribution of calcined stones on their capacity for SO_2 removal is still lacking. Most investigators tend to focus on the global kinetics of the sulfation or sulfidation reactions while paying little attention to the pore structure of the calcined solid. A review of the experimental evidence of the literature reveals an anomalous dependence of the reactivity and SO_2 uptake of calcined limestones on the initial values of average properties of their pore structure, such as porosity and surface area, indicating strong effects of the pore size distribution on the overall reactivity of the calcined solids (Borgwardt and Harvey, 1972; Wen and Ishida, 1973; Hartman and Coughlin, 1974, 1976; Simons and Garman, 1986; Yu, 1987; Gullett and Bruce, 1987).

Analogous observations apply to the reaction of metal oxides (calcium oxide, zinc oxide, zinc ferrite, zinc titanate, etc.) with H_2S . A good deal of experimental effort has been put in the area of hot gas desulfurization into the investigation the reactivity and capacity of various metal/metal oxide sorbents for sulfur compound removal from coal

gas (e.g., see studies by Gibson and Harrison (1980), Tamhankar et al., (1981 and 1985), Ranade and Harrison (1981), Jalan (1983), Sick and Schwerdtfeger (1987), and Sa et al. (1989)). However, limited work has been done on the characterization of these sorbents in terms of their pore size distribution and resistance for intraparticle diffusion. Simplistic models of structure evolution are usually employed for data treatment and interpretation, while few studies have looked into the variation of the properties of the pore structure, such as the internal surface area (Caillet and Harrison, 1982; Sa et al., 1989), with the progress of the reaction.

A systematic investigation of the dependence of the transient behavior of large limestone particles reacting with SO_2 in the presence of oxygen on pore structure and particle size related factors has been carried out by my research group (Zarkanitis and Sotirchos, 1989; Yu, 1987). Our results have shown strong dependence of the transient behavior of reacting particles of calcined limestone and, consequently, of their sorptive capacity for SO_2 removal on their initial pore size distribution, but this dependence seems to follow an anomalous pattern when the sulfation capacities of calcines obtained from different precursors (stones) are compared. Specifically, calcines of similar composition and pore structure properties have been found to exhibit considerably different capacities for removal of SO_2 from flue gases. Comparison of the experimental data with the predictions of a generalized pore model for gas-solid reactions with solid product (Yu and Sotirchos, 1987) showed that these differences could be due to the formation of inaccessible pore space in the course of the reaction, which takes place when the small feeder pores of finite clusters of large pores or large cavities, in aperture-cavity pore structures, are filled with solid product.

Similar conclusions have been reached by analyzing reactivity data for zinc oxide sulfidation obtained in our laboratory (Efthimiadis and Sotirchos, 1989). However, an important difference exists between the reaction of metal oxides with H_2S and their reaction with SO_2 . The sulfide produced during reaction with H_2S occupies less space than the solid product produced during sulfation (sulfate (mainly) or sulfite), and as a result, complete pore closure in the case of sulfidation can happen only for low initial porosities. This difference suggests that a comparative study of the reactions of porous metal oxides with SO_2 and H_2S can lead to a better assessment of the effects of pore structure on sorptive

capacity than studies of the effects of the parameters of a single reaction only.

On the basis of the above observations, a research program has been formulated for the comparative investigation of the reactions of metal oxides with SO_2 and H_2S . Initially, it was planned to work with CaO , limestone-derived, and ZnO solids and specifically with solids whose reactions with SO_2 (limestone calcines) and H_2S (zinc oxide sorbents) had been studied in detail in the past with our research group. However, in order to make our results and conclusions useful to those interested in SO_2 or H_2S removal from high pressure units (combustors or gasifiers), it was decided to extend our work to the case in which sulfidation or sulfation occurs under noncalcining conditions. Reactivity evolution experiments for limestone sulfation and sulfidation were thus carried out in a thermogravimetric analysis system under simulated high pressure conditions, that is, in the presence of enough CO_2 to prevent decomposition of $CaCO_3$ to CaO .

In this technical report, we present some of the most important results that we obtained on the study of the above problems using various experimental and theoretical methods. Each section of the report is developed in a self-contained manner, and as a result, it can be read and followed independently of the others. Section 2 presents experimental and theoretical results on the reaction of calcined limestones with H_2S and compares them with those obtained for the sulfation of the same solids in our past studies. Section 3 deals with the investigation of the direct (i.e., under noncalcining conditions) sulfation of limestones, while Section 4 discusses the development of a variable diffusivity shrinking core model and its application to the analysis of the direct limestone sulfation data. Section 5 examines the effective diffusivity changes that occur during calcination, carbonation, recalcination, and sulfation of limestones – studied using pulse chromatographic experiments on reacted samples – and discusses these changes in conjunction with the behavior seen in sulfation and sulfidation experiments. The study of the direct sulfidation of limestones and the comparison of the obtained results with those for direct sulfation and indirect sulfidation is the subject of Section 6. The subject of Section 7 is the validation of a predictive model for desulfurization in fixed beds using thermogravimetric single particle reactivity data and breakthrough curves from fixed-bed experiments for zinc oxide particles. Section 8 presents a new grain model for gas-solid reactions, which allows for

partial overlapping of the constituent grains and, as a result, can cover the whole range between the nonoverlapping and randomly overlapping models. Finally, in Section 9, we present a detailed theoretical analysis of the problem of effective diffusivity measurement in porous solids using the diffusion-cell method. The motivation behind this study was to elucidate the effects of the connectivity of the pore structure on the interpretation of mass transport data and the estimation of effective diffusion coefficients.

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2. SULFIDATION OF LIMESTONE-DERIVED CALCINES

2.1. Introduction

The sulfidation of CaO particles is of importance in the control of toxic emissions from Limestone Injection Multistage Burners (LIMB) (Borgwardt et al., 1984). The same reaction is also encountered in the desulfurization unit of an Integrated Gasification Combined Cycle (IGCC) (Jalan (1983)). Limestones and dolomites are the most common sources of calcium oxide used in these applications. The thermal decomposition of the calcium carbonate and the sulfidation of the produced calcium oxide can be described by the overall reactions:

The kinetics of reaction (2.2) were investigated in a number of past studies in thermogravimetric analysis systems (TGA) and other types of reactors, using fully calcined limestones or reagent grade CaO as the solid reactant. In most studies, the carbonates were calcined under an inert atmosphere (usually nitrogen) at temperatures in the range 700-900 °C, and they were subsequently sulfided at the calcination or at a lower temperature. Mixtures of H_2S , a reducing gas (H_2 or CO), and nitrogen were used as the reactive gas in most cases. Experiments performed in TGA reactors showed in most cases a weak influence of the reaction temperature on the initial sulfidation rates and, as a result, gave low activation energies for Arrhenius-type dependence of the sulfidation rate on temperature (e.g., 5.16 kcal/mol (Westmoreland et al., 1977) and 3.6 kcal/mol (Kamath and Petrie, 1981). Low activation energies were also determined for the reaction of COS with CaO , which is similar to reaction (2.2), in the same temperature range as that of the previous studies (e.g., 3.9 kcal/mol (Kamath and Petrie, 1981) and 4.3 kcal/mol (Yang and Chen, 1979)). The reactivity experiments in these studies were carried out isothermally in the temperature range of 300-900°C using solid material in particle form from 1 to about 400 μm in size. Much larger in size dolomite-derived pellets (spheres of about 7 mm in diameter) were sulfided by Squires et al. (1971) in a thermogravimetric analysis system. Reaction rates were measured at different temperatures and gave an activation energy of 30 kcal/mol for

sulfidation in the temperature range 475-700°C. However, the reaction rate measured at 800°C was found to deviate significantly from the value estimated from the Arrhenius plot for reaction at temperatures between 475 and 700°C. Control of the overall reaction by pore diffusion at high temperatures was postulated by Squires et al. (1971) to explain this behavior. The sulfidation experiments of Westmoreland et al. (1977) gave a linear relation between the initial reaction rate of reagent grade CaO and the H_2S concentration in the reactive mixture at temperatures in the range of 300-800°C, and this led these investigators to conclude that reaction (2.2) is of first order with respect to H_2S .

The reaction of calcined limestones in a differential fixed-bed reactor was studied by Borgwardt et al. (1984). Small amounts of solid sorbent (particles of 1-9.4 μm size) and large reactive gas flow rate were used to ensure differential operation of the reactor. Preparation of calcines under different conditions gave solid reactants covering a broad range of initial internal surface areas. The sulfur uptake was determined by chemical analysis of the solid product at different sulfidation times, and an activation energy of 31 $kcal/mol$ was computed from the reaction rates at 50% conversion. Experiments in a fixed-bed reactor were carried out by Freund (1984) who impregnated amorphous carbon particles with CaO and sulfided them at high temperatures (1120-1425 °C), where significant H_2S dissociation takes place. The rate of CaO consumption was determined from the analysis of the outlet stream of the reactor after correction for the loss of H_2S by dissociation. By assuming intraparticle mass transport control – the effectiveness factor of 115 μm particles was estimated to be about 0.002 – and first-order reaction, an estimate of 45.5 $kcal/mol$ was obtained for the activation energy. Attar and Dupuis (1979) reacted minerals found in coal (calcite, dolomite, and siderite) with H_2S in a pulsed differential reactor. The reaction rate was determined from the analysis of the outlet gaseous stream, and an activation energy of 37 $kcal/mol$ was estimated in the temperature range 560-670 °C for the calcite- H_2S reaction. A much lower activation energy (4 $kcal/mol$) was observed at higher temperatures, and this was attributed to mass transfer limitations in their apparatus.

In most of the above experimental studies, the experimental data were interpreted by considering that the rate of reaction was controlled by intrinsic kinetics or one of the transport mechanisms of the gaseous reactant and by assuming that negligible structural

changes occurred in the solid during the reaction. Variants of the shrinking-core and grain models (Szekely et al., 1976) were used in most cases to analyze the experimental data (e.g., Yang and Chen (1979), Borgwardt et al. (1984), and Squires et al. (1971)) for the extreme cases of local reactivity (intrinsic kinetics and (or) product layer diffusion) and intraparticle mass transport control, respectively. However, highly porous sorbent particles result from limestone or dolomite calcination, and as a result, the overall rate of sulfidation reaction is in general influenced by both the transport and reaction details in the intraparticle space. Moreover, since the solid product (CaS) in reaction (2.2) has larger molar volume than the solid reactant (CaO), various phenomena associated with pore structure evolution (such as pore plugging and formation of inaccessible pore space) may play an important role in determining the evolution of the reactivity of the solid with the progress of its sulfidation.

Gas-solid reactions with solid product were modelled by Yu and Sotirchos (1987) in the so-called generalized random pore model. This model represents the void volume in the solid using pore segments randomly distributed in space around the bonds of a three-dimensional lattice and predicts the evolution of the reactivity of the solid as well as of its pore structure with the progress of the reaction. The generalized random pore model was applied by Zarkanitis et al. (1990) and Sotirchos and Zarkanitis (1992) to the sulfation of calcined limestones, where it was found to provide satisfactory approximations to the experimentally determined conversion vs. time curves over a rather broad range of operating conditions. It was also used successfully for the interpretation of reactivity evolution data for the reaction of porous zinc oxide sorbents with H_2S (Efthimiadis and Sotirchos, 1993). In both cases, it was found that depending on particle size, reaction temperature, and extent of the reaction (average solid conversion), the overall reaction rate could be controlled by intraparticle diffusion, reaction at the unreacted-reacted solid interface, diffusion in the product layer, or by a combination of these three processes.

The reaction of limestone-derived calcines with H_2S - N_2 mixtures was investigated experimentally in this study. Reactivity evolution experiments were carried out in a thermogravimetric analysis system, and the structure of the unreacted solid was characterized using gas adsorption and mercury porosimetry. Calcines prepared from the calcination of precursors of high (>95%) calcium carbonate content were used in our experiments.

Calcination was carried out at 750 or 850°C, while the produced material was sulfided at 650 or 750°C. We chose to work with these precursors and the above calcination temperatures because the behavior of these calcines during sulfation was investigated in detail by Zarkanitis and Sotirchos (1989), Zarkanitis (1991), and Sotirchos and Zarkanitis (1992). The sulfidation and sulfation of CaO solids are gas-solid reactions with solid product formation involving the same solid reactant but different solid products. Their most important difference is that the solid formed during sulfation ($CaSO_4$) occupies considerably more volume than that formed during sulfidation (CaS). The solid product to solid reactant volume ratio is the parameter that has the strongest effect on the predictions of the mathematical models for gas-solid reactions with solid product. Therefore, comparison of the reactivity evolution results of the same sorbents during sulfation and sulfidation can provide information on the effects of pore structure than cannot be obtained by changing any of the other parameters of the process.

2.2. Materials and Procedures

The solid sorbents used for sulfidation were obtained through the decomposition of two high purity calcitic limestones, a limestone supplied by Greer Limestone Co. and a marble supplied by Georgia Marble Co., and calcitic single crystals (Iceland spar) supplied by Wards Inc. The Greer limestone (GL) and the Georgia marble (GM) samples were provided in the form of about 5 mm fragments, while the Iceland spar (IS) came in the form of large crystals of a few cm in size. The precursors were crushed into particles and sieved to isolate the following ranges of particle sizes: 53-62, 88-105, 210-250, and 297-350 μm . The carbonate content of the stones (magnesium and calcium) is summarized in Table 2.1, while a detailed compositional analysis of the three samples is given elsewhere (Zarkanitis, 1991). It is seen from Table 2.1 that all samples contain more than 95% $CaCO_3$, with the Iceland spar consisting almost entirely of $CaCO_3$ and the Georgia marble exhibiting the highest $MgCO_3$ content. Mineralogical analysis of the solids showed that Greer limestone consisted mainly of fine calcitic grains, while the structure of Georgia marble was spanned by much larger calcitic grains (Zarkanitis, 1991).

Precursor	GL	GM	IS
% $CaCO_3$	97.84	95.19	99.14
% $MgCO_3$	0.95	3.04	0.35

Table 2.1: Carbonate content of the precursors. GL=Greer limestone, GM=Georgia marble, and IS=Iceland spar.

The pore structure of the solids was characterized by mercury porosimetry using a Micromeritics porosimeter and gas adsorption (N_2 in 77 K) using a flow-type apparatus. The mercury porosimetry results for the precursors showed little mercury penetration, and this only at very high pressures. Since mercury penetration is plagued by several uncertainties at high pressures, mainly because of mercury and sample compressibility, we did not think that it was possible to reach reliable quantitative conclusions about the porosity of the precursors from the mercury intrusion data. The BET analysis of the nitrogen adsorption data showed that all samples had significantly larger surface area than that corresponding to nonporous spheres of diameter equal to the arithmetic mean of the two limits of the particle size range. Moreover, application of the capillary condensation theory to the isotherm data revealed that the precursors possessed some natural porosity, which increased in the direction Greer limestone $\rightarrow$ Georgia marble $\rightarrow$ Iceland spar, that is, in the direction of increasing grain size. Almost the same average pore radius was computed from the surface area and the pore volume data of the three precursor solids. More results on the characterization of the precursor are given by Efthimiadis (1991).

Mercury porosimetry and gas adsorption measurements were also carried out for the calcined samples. The relatively large samples needed for the structural analysis were prepared in a fluidized-bed reactor under reaction conditions identical to those employed to study reactivity evolution. About 4 g of each sample (710-850 μm particles) was placed in a 1.5 cm I.D. quartz reactor. The reactor was brought to the calcination temperature under CO_2 to prevent decomposition of the solid. Decomposition was started by replacing the CO_2 with N_2 flowing at 2 l/min (at standard conditions). The BET surface area of the calcined sorbents ranged from 30 to 80 m^2/g and increased in the direction

Greer limestone $\rightarrow$ Georgia marble $\rightarrow$ Iceland spar, with the calcines produced at 850°C exhibiting lower surface areas. In general, the results obtained from our pore structure characterization experiments were similar, both qualitatively and quantitatively, to those obtained by Zarkanitis (1991) even though he used samples prepared in small batches in a fixed-bed reactor and smaller particles ($88\text{--}105\ \mu\text{m}$ in size). Nevertheless, in order to make our sulfidation results directly comparable with those of Zarkanitis (1991) for the sulfation of the same sorbents, it was decided to use the pore size distributions reported in his study for the analysis of our sulfidation data using the mathematical model of Yu and Sotirchos (1987).

The porosity distribution curves that were determined for the six samples (three precursors at two calcination temperatures) from the mercury porosimetry results, by assuming a perfectly interconnected network of cylindrical pores, are shown in Fig. 2.1 (750°C) and Fig. 2.2 (850°C). If no change in the particle dimensions takes place during calcination, the porosity of the resulting calcines should be about 54%, without accounting for the natural porosity of the precursors. As the curves of Figs. 2.1 and 2.2 show, the measured total porosities were indeed around this value. For both calcination temperatures, the most probable pore radius of the Greer limestone calcine – the point where there is a sharp rise in the intrusion volume – is larger than those of the other two samples. The porosity distribution curves of Figs. 2.1 and 2.2 were estimated from the mercury porosimetry data using the skeletal density based on the chemical analysis of the oxides. This value was found to agree with that measured experimentally by N_2 pycnometry.

Particles of $53\text{--}62$, $88\text{--}105$, $210\text{--}250$, and $297\text{--}350\ \mu\text{m}$ were calcined, and subsequently sulfided in a thermogravimetric analysis system. The samples ($3\text{--}5\ \text{mg}$) of the precursor solids were placed on a circular quartz pan, hang from the sample arm of the microbalance, and were outgassed under CO_2 during the heating period to prevent thermal dissociation of the carbonates. Calcination was carried out isothermally at 750 or 850°C by sending N_2 through the system. The reactor was then brought to the sulfidation temperature (same as the calcination or lower) and the calcined samples were sulfided using a mixture of H_2S and N_2 flowing at $200\ \text{ml/min}$ (standard conditions). The percentage of H_2S consumed during the initial stages of the reaction was estimated by performing a mass balance on the

Figure 2.1: Pore size distributions of calcines produced at 750°C .

Figure 2.2: Pore size distributions of calcines produced at 850°C.

H_2S entering and leaving the reactor, and it was found to be less than 10% for all cases studied. In view of this result, the operation of the reactor was assumed to be differential, and the measured weight gain vs. time data were converted to conversion vs. time curves by attributing the observed weight change to transformation of CaO to CaS .

2.3. Calcination Experiments

The decomposition of calcium carbonate produces a porous oxide whose physical properties depend on the calcination conditions and the morphology of the precursor stone. Experimental studies have shown that parameters influencing the final product of the calcination reaction are the sample size, the calcination temperature, the heating rate (for nonisothermal calcination), and the sweep gas flow rate and composition. For instance, experiments in TGA reactors showed that the decomposition rate of particles of 20-44 μm depended on the sample size (Gallagher and Johnson, 1973) and the composition of the reactive mixture (Caldwell et al., 1977). Caldwell et al. (1977) calcined 4 mg of 20-44 μm particles under flow of gases of different thermal conductivity. Higher reaction rates were measured when the thermal conductivity of the reactive gas increased, implying effects of heat transfer limitations. No effects of sample size and of the thermal conductivity of the sweep gas were observed by Borgwardt (1985), who had samples of 7-50 mg dispersed in a differential packed-bed reactor and calcined under flow of inert gases with velocities of the order of 9 m/s (24-44 l/min). Calcination conditions like the above cannot be applied in TGA systems, and thus it is possible that mass and heat transfer limitations may compete with the intrinsic kinetics of the $CaCO_3$ decomposition in such reactors.

The calcination conditions of this study were similar to those used in the preparation of the solids for the sulfation experiments of Zarkanitis and Sotirchos (1989) and Sotirchos and Zarkanitis (1992). The particle size effect on the experimental results is shown in Fig. 2.3 for the Iceland spar sample calcined at 750°C. Qualitatively similar results were obtained for the other two solids. The calcination rates of the three solids are compared in Fig. 2.4 for calcination of three particle sizes at 750°C and Fig. 2.5 for calcination of two particles sizes at 850°C. The calcination data are presented in Figs. 2.3-2.5 as the evolution with time of the ratio of the weight of the calcined material to the initial sample weight.

The horizontal line in Figs. 2.3-2.5 corresponds to the ratio of the molecular weight of CaO to that of $CaCO_3$. At the completion of calcination, the weight ratio vs. time curves should coincide with this line if the precursor rocks consisted of 100% $CaCO_3$. It can be easily verified that the final weight ratios reached by the various samples of Figs. 2.3-2.5 are in good agreement with the values expected on the basis of the carbonate content of the precursor stones (see Table 2.1).

The results of Figs. 2.3-2.5, and especially those shown in Fig. 2.3, clearly show that there is strong particle size effect on the calcination rate in all cases, implying strong mass, and possibly heat, transfer limitations in the interior of the calcining particles. Significant differences exist among the calcination rates of same size particles of different sorbents. The calcination rate of Iceland spar is influenced more strongly by the particle size than the rates of the other two samples. As a result, even though there are not very large differences in the calcination rates of small (53-62 μm) particles, much larger reaction times are required for complete calcination of Iceland spar samples of large particle size (Figs. 2.4 and 2.5). The Greer limestone sample was found to exhibit higher calcination rate for all particle sizes but the largest one, while exactly the opposite behavior was demonstrated by the Georgia marble sample. If we assume that the calcination rates of the three sorbents are mostly controlled by intraparticle mass transport, the obtained results for the 53-62, 210-250, and 297-350 μm particles (see Fig. 2.4) point to the conclusion that the intraparticle mass transport resistance increases in the direction of increasing grain size in the precursors, that is, in the order Greer limestone $\rightarrow$ Georgia marble $\rightarrow$ Iceland spar. Zarkanitis (1991) explained this phenomenon by arguing that pores formed during calcination at the periphery of the grains are larger and better interconnected than those formed in the interior of the crystallites. This, however, does not offer an explanation as to why the large (297-350 μm) Georgia marble particles present higher calcination rates than the other samples.

Georgia marble samples of large particle size (larger than 200 μm) behaved differently during heating under 1 atm of CO_2 to the reaction temperature. Unless very low rates of heating (temperature rise) were employed, the large Georgia marble particles tended to explode, thus leading to loss of solid material from the pan and, as a result, abortion

Figure 2.3: Particle size effect on rate of calcination of Iceland spar at 750°C.

Figure 2.4: Comparison of the calcination rates of the three solids at 750°C.

Figure 2.5: Comparison of the calcination rates of the three solids at 850°C.

of the experiment. This phenomenon occurs at temperatures above $500\text{--}600^\circ\text{C}$ and is most probably caused by the decomposition of the magnesium carbonate contained in the Georgia marble sample and the resulting pressure build-up in the interior of the particles as the released CO_2 is trying to escape through the low porosity matrix. Such behavior was also observed by Hasler et al. (1984) for some of the samples they studied, and the term 'popcorn' effect was used to describe it. We thus believe that the apparently weak effect of particle size on the calcination of Georgia marble samples is caused by the existence of cracks in the interior of the larger particles, formed during heating of the precursor particles under CO_2 . It should be pointed out even when explosion of the heated particles is avoided by using low heating rates – as it was done in our experiments – it is still possible the pressure build-up in the interior of the particles to lead to formation of cracks in uncalcined particles. We will discuss the behavior of the large Georgia marble particles in more detail in the next two sections.

2.4. Sulfidation Experiments

It is usually assumed in sulfidation studies that reaction (2.2) is irreversible. We examined the validity of this assumption by estimating the equilibrium constant of reaction (2.2) at the sulfidation temperatures employed in our study (650 and 750°C) using thermodynamic data from Barin and Knacke (1973). The equilibrium H_2S concentrations at the reaction conditions of this study ($10,500$ ppm H_2S in nitrogen) was found to be 2.5 and 5.6 ppm at 650 and 750°C , respectively, thus indicating that the above assumption can be considered valid for all practical purposes. Comparative thermodynamic calculations for the sulfidation of twelve metal oxides were performed by Furimsky and Yumura (1986), who found that CaO had the second largest equilibrium constant (after ZnO) in a wide temperature range. Moreover, they concluded that in a reducing atmosphere CaO is the most resistant to reduction among the twelve metal oxides examined. It can thus be argued that efficient and satisfactory removal of hydrogen sulfide from a hot coal gas stream can be achieved using CaO -based sorbents.

All results presented and discussed in this study were obtained using a reaction mixture of 1.05% H_2S in nitrogen. We examined the concentration dependence of the

sulfidation rates of the solids used in our study by carrying out experiments with lower concentrations of H_2S . A linear relationship was found to exist between the initial rate of sulfidation and the concentration of H_2S . Moreover, the reactivity evolution curves for different concentrations but with all the other conditions being the same were found to practically coincide with each other when plotted as conversion vs. normalized time, with the latter defined as (real time) $\times$ (H_2S percentage in the reactive mixture). On the basis of these two findings it was concluded that the reaction of CaO with H_2S is of first order with respect to the concentration of H_2S . A similar conclusion was reached from our reactivity evolution studies during sulfidation of ZnO -based sorbents (Efthimiadis and Sotirchos, 1993).

Figs. 2.6, 2.7, and 2.8 present reactivity evolution data, in the form of conversion vs. time curves, for the sulfidation at $750^\circ C$ of calcines produced at the same temperature for Greer limestone, Georgia marble, and Iceland spar, respectively, for four particle sizes. Shown in the figures are also the conversion vs. time curves measured for the sulfation of the same sorbents at $750^\circ C$ by Sotirchos and Zarkanitis (1992) using a mixture of 3,000 ppm SO_2 and 12% O_2 in N_2 . A general observation from the experimental sulfidation data of Figs. 2.6-2.8 is that there is a strong influence of particle size on the overall rate of the CaO - H_2S reaction, indicating that the process occurs under strong intraparticle diffusional limitations. Consequently, it is necessary to use a model for mass transport and reaction in the interior of the porous particles to analyze the obtained conversion vs. time data.

Comparison of the sulfidation data of Figs. 2.6-2.8 with the corresponding sulfation results shows that while the sulfidation reaction always reaches complete conversion, the sulfation reaction stops before complete conversion is reached. Moreover, the maximum conversion reached during sulfation decreases drastically with increasing particle size. This difference in the behavior of the two reactions is caused by the fact that the molar volume of the solid product formed during sulfidation (CaS) is smaller (by a factor of two) than that of $CaSO_4$ produced during sulfation of CaO . Assuming that the physical dimensions of a particle do not change during reaction, a mass balance on the volume of the solid phase gives the following relation between the maximum conversion that can be attained

Figure 2.6: Effect of particle size on the conversion vs. time results during sulfidation at 750°C of Greer limestone calcines produced at the same temperature. The sulfation data shown were obtained by Zarkanitis (1990) at the same temperature with 0.3% SO_2 and 12% O_2 in N_2 .

Figure 2.7: Effect of particle size on the conversion vs. time results during sulfidation at 750°C of Georgia marble calcines produced at the same temperature. The sulfation data shown were obtained by Zarkanitis (1990) at the same temperature with 0.3% SO_2 and 12% O_2 in N_2 .

Figure 2.8: Effect of particle size on the conversion vs. time results during sulfidation at 750°C of Iceland spar calcines produced at the same temperature. The sulfation data shown were obtained by Zarkanitis (1990) at the same temperature with 0.3% SO_2 and 12% O_2 in N_2 .

before the interior of the porous sorbent is completely filled with the solid product, ξ_{max} , and the initial porosity of the solid, ε_0 :

$$\xi_{max} = \frac{\varepsilon_0}{(1 - \varepsilon_0)(Z - 1)} \quad (2.3)$$

Z is the stoichiometric volume ratio of the gas-solid reaction, defined as volume of reacted solid phase per unit volume of a stoichiometrically equivalent amount of unreacted solid phase. For a pure sorbent (100% CaO), Z is equal to the ratio of the molar volume of CaS or $CaSO_4$ to that of CaO . In the presence of impurities, Z may be estimated using the equation:

$$Z = \psi \frac{v_{CaS \text{ or } CaSO_4}}{v_{CaO}} + (1 - \psi) \quad (2.4)$$

ψ is the volume fraction of CaO in the unreacted calcine, and v_i is the molar volume of solid i . The stoichiometric volume ratios for the calcines used in our experiments are shown in Table 2.2 which also lists the volume of the solid phase of the unreacted calcines per mole of CaO ('molar' volume, $v_s = v_{CaO}/\psi$). Introducing the Z values of Table 2.2 in eq. (2.3), we find that porosities lower than about 0.67 lead to incomplete conversion during sulfation, while the corresponding porosity limit for sulfidation is about 0.33. On the other hand, for an initial porosity of 0.5, as it is approximately the case with all the solids used in this study (see Figs. 2.1 and 2.2), eq. (2.3) predicts complete conversion for sulfidation with 0.25 final porosity ($\xi = (\varepsilon_0 - \varepsilon)/[(1 - \varepsilon_0)(Z - 1)]$) but about 50% maximum conversion for sulfation. The sulfation conversions reached in Figs. 2.6-2.8 are much lower than 50% since the presence of intraparticle mass transport limitations causes the pore openings at the external surface of the particles to be plugged first. The maximum conversion may also be limited by inaccessible pore volume formation, a situation occurring when small feeder pores of a cluster of large pores are filled with solid product.

The conversion vs. time results of Figs. 2.6-2.8 reveal that the sulfation reactivity of the CaO sorbents and the maximum conversion they reach decrease significantly in the order Greer limestone $\rightarrow$ Georgia marble $\rightarrow$ Iceland spar, that is, with increasing grain size in the precursors. Since there are no significant qualitative differences in the pore size distributions of the calcines (see Fig. 2.1) to justify the differences seen in the sulfation reactivities, Sotirchos and Zarkanitis (1992) concluded that decreasing grain size in the

precursor leads to a better interconnected pore structure in the calcine and, hence, lower intraparticle diffusion resistance and smaller inaccessible pore space. This explanation is in agreement with the observed sulfidation behavior of the Greer limestone and Iceland spar samples, as it can be seen from the results of Figs. 2.9-2.11 which compare the sulfidation results of the three sorbents at the various combinations of calcination and sulfidation temperature employed in our experiments. It also applies to the small particles of the Georgia marble calcines (53-62 and 88-105 μm), which in general exhibited reactivity intermediate to that of the other two sorbents, but it is in obvious contradiction with the behavior of the large particles (210-250 and 297-350 μm), which showed much larger reactivities than same particle sizes of the other sorbents.

Precursor	GL	GM	IS
Z for sulfidation	1.508	1.492	1.522
Z for sulfation (MgO treated as inert)	3.015	2.952	3.070
v_s of the unreacted solid phase, $cm^3/gmol$	18.1	17.5	17.1

Table 2.2: Stoichiometric volume ratio (Z) and 'molar' volume (v_s) of the unreacted solids used in the application of the generalized random pore model. GL=Greer limestone, GM=Georgia marble, and IS=Iceland spar.

The behavior of the Georgia marble samples during sulfidation in relation to the behavior of the other sorbents, is strikingly similar to their behavior during calcination (Fig. 2.4 and 2.5), where it was seen that the Georgia marble sample exhibited higher overall reactivity for the large particle size (297-350 μm) even though its reactivity for smaller particles was lower than or between those of the other solids. This observation points out to the conclusion that the apparently weak effect of particle size on the sulfidation of Georgia marble samples is caused by the existence of large pores in the interior of the larger particles, formed from the cracks in the heat-treated precursors. These pores facilitate transport of the reactive gas (H_2S) in the interior of the calcine, thus reducing the effective size of the particle. The presence of cracks (large pores) in the interior of the Georgia marble calcines does not have an effect of the same magnitude on their sulfation

behavior since sulfation leads to complete pore plugging, and as a result, even these large pores are eventually filled with solid product. The peculiar behavior of the Georgia marble calcines will be discussed in some more detail in the next section of our paper.

Comparison of the conversion vs. time curves of Fig. 2.9 with the respective results shown in Fig. 2.11 suggests that calcination at higher temperatures yields sorbents of higher overall reactivity. Similar conclusions were reached by Zarkanitis and Sotirchos (1989) and Sotirchos and Zarkanitis (1992) from the study of the sulfation of the same sorbents. The theoretical analysis of the sulfation data of Zarkanitis and Sotirchos (1989) using the generalized random pore model of Yu and Sotirchos (1987) showed that the sulfation reactivity of the calcines improves with increasing calcination temperature because the connectivity (degree of interaction) of their pores increases as the calcination temperature is raised. We will reach a similar conclusion in this study from the analysis of the sulfidation data that we will carry out in the next section.

The effects of sulfidation temperature on the sulfidation reactivity of the CaO sorbent can be determined by comparing the conversion vs. time results of Fig. 2.9 with those of Fig. 2.10. It is seen that sulfidation at a lower temperature slows down the overall reaction rate, but not significantly. The initial slopes of the conversion vs. time curves in Fig. 2.10 are slightly smaller than the slopes of the corresponding curves of Fig. 2.9, indicating weak dependence of the reaction rate constants on temperature and, hence, small activation energies. The temperature effect is in general stronger for the small particles, and only the behavior of the large particles of the Iceland spar calcines is significantly influenced by the temperature. This is not unexpected since the overall reaction rate of the small particles is usually controlled by intrinsic reaction (low conversions) and diffusion in the product layer (high conversions), whose rates increase exponentially with the temperature. On the other hand, the reaction of large particles is more influenced by the rate for intraparticle diffusion, which for Knudsen diffusion – as it is most probably the case in this study – varies proportionally to the square root of the temperature. In order to be able to derive any quantitative conclusions on the effects of the above processes on the sulfidation of the sorbents, it is necessary that a mathematical model be used to analyze the experimental data. This is done in the following section.

Figure 2.9: Comparison of the sulfidation rates at 750°C of calcines produced at the same temperature for two particle sizes.

Figure 2.10: Comparison of the sulfidation rates at 650°C of calcines produced at 750°C for two particle sizes.

Figure 2.11: Comparison of the sulfidation rates at 750°C of calcines produced at 850°C for two particle sizes.

2.5. Experimental Results and Model Predictions

Past studies on *CaO* sulfidation, employed particles of a few μm in size (Yang and Chen, 1979; Borgwardt et al., 1984) or large pellets (Squires et al., 1971) in order to eliminate the effects of intraparticle diffusional limitations or make the diffusion the controlling step of the process. However, the need for a controlling step in the interpretation of the experimental data can be avoided by analyzing the experimental data using a mathematical model developed by Yu and Sotirchos (1987), which accounts not only for reaction and diffusion of the reactive gaseous species but also for the evolution of the internal pore structure of the solid with the progress of the reaction. The model represents the void space using a network of cylindrical capillaries arranged around the bonds (with the bonds serving as axes) of a three-dimensional lattice. The reactive gas diffuses through the product layer and reacts with the solid at a sharp interface between reacted and unreacted solid. The effective diffusivity in the porous medium is computed using the effective medium theory-smooth field approximation approach developed by Burganos and Sotirchos (1987), which is consistent with the network structure assumed in the structural model. Readers interested in the equations and the details of the model are advised to consult the papers of Yu and Sotirchos (1987) and Zarkanitis et al. (1990).

For the application of the generalized random pore model to our sulfidation data, the only parameters are the diffusion coefficient in the product layer, D_P , and the topology of the network. The topology of the network is determined by a three-dimensional lattice formed by the axes of the pore segments. Like in past applications of the generalized random pore model, the topology of the lattice will be assumed to be that of a Bethe lattice (Fisher and Essam, 1961). Bethe lattices are tree-like structures, whose characteristics are completely defined by their coordination number, z , that is, the number of bonds (pore segments) per node. D_P and z are determined by fitting the experimental data to the model predictions under the conditions that D_P depend only on sorbent and sulfidation temperature and z depend only on sorbent. Obviously, since the topology of the initial structure of the solid is independent of the reaction that the solid undergoes, z should, in principle, be the same both for sulfidation and sulfation reactions. All other parameters are estimated using the experimental data.

The mass transfer coefficient was estimated from correlations for mass transfer during flow past spherical objects (Bird et al., 1960). Using these correlations, it was found that the Sherwood number was equal to 2 (based on diameter) and practically independent of particle size. The reaction rate constant was estimated from the initial reaction rates of 53-62 μm particles after correcting them for the effects of intraparticle diffusion using the expression for the effectiveness factor of a first-order reaction (Smith, 1981). Negligible H_2S dissociation was assumed to occur at the temperatures used for sulfidation. Thermodynamic calculations showed that even if the reaction reached equilibrium in the reactor, less than 5.2% of H_2S would dissociate at 750°C.

The coordination numbers, product layer diffusivities, and reaction rate constants that had to be used in the mathematical model to reproduce the reactivity evolution data are shown in Table 2.3. The reaction rate constants of Table 2.3 were obtained using the initial reaction rates of 53-62 μm particles. At least four independent measurements of the initial reaction rate were used to arrive at an average value for the initial reaction rate for each set of operating conditions. Since the calcination temperature affects only the physical structure of the resulting product, calcines produced from the same sorbent at different temperatures were assumed to have the same reaction rate constant. Notice that for the Georgia marble sample, parameter values are shown for two coordination numbers at each temperature. We will explain the use of two coordination numbers later during the discussion of the model predictions for sulfidation of this solid.

It is seen from the results of Table 2.3 that the differences among the intrinsic reaction rate constants of the three sorbents are very small. This is not an unexpected result since the initial reaction rates of the three sorbents are comparable (see Figs. 2.9-2.11) and their pore size distributions are not much different from each other (see Figs. 2.1 and 2.2). Relatively small differences were also found to exist between the diffusivities in the product layer. The largest product layer diffusivities was estimated for the Greer limestone calcines and the smallest for the Iceland spar samples. The activation energies that are determined from the results of Table 2.3 if k_s and D_P are assumed to obey an Arrhenius-type equation are given in Table 2.4. The activation energies of Table 2.4 should be used with some caution since only two temperatures were used for their estimation. Similar

values of reaction rate constant, solid product layer diffusivity, and activation energy were determined by Sotirchos and Zarkanitis (1992) for sulfation of these sorbents. For example, the intrinsic reaction rate constant for sulfidation at 750°C was found to have an average value of $1.5 \times 10^{-3} \text{ cm/s}$, which is about 2 times smaller than the value estimated here for sulfidation.

Precursor	GL	GM	GM	IS
Coordination number, z for calcination at 750°C	6	3	1000	3
k_s at 750°C , cm/s	3.6×10^{-3}	3.7×10^{-3}	3.3×10^{-3}	3.8×10^{-3}
D_P at 750°C , cm^2/s	7×10^{-8}	1×10^{-8}	1×10^{-8}	2×10^{-9}
k_s at 650°C , cm/s	2.5×10^{-3}	2.6×10^{-3}	2.3×10^{-3}	2.7×10^{-3}
D_P at 650°C , cm^2/s	3×10^{-8}	5×10^{-9}	5×10^{-9}	1×10^{-9}
Coordination number, z for calcination at 850°C	12	4	4000	6.5
k_s at 750°C , cm/s	3.6×10^{-3}	3.8×10^{-3}	3.4×10^{-3}	3.7×10^{-3}

Table 2.3: Reaction rate constants (k_s) estimated from the initial sulfidation rates of particles of $53\text{-}62 \mu\text{m}$ and diffusion coefficients in the product layer (D_P) used in the application of the generalized random pore model. GL=Greer limestone, GM=Georgia marble, and IS=Iceland spar.

Figs. 2.12 and 2.13 compare the predictions of the generalized random pore model with the experimental data for sulfidation at 750°C of Greer limestone calcines produced at 750 and 850°C , respectively. Very good agreement is seen to exist between model and experiment in both figures and for all particle sizes. The model was also successful in reproducing the experimental data at 650°C . Only the product layer diffusivity was used as free parameter to fit the model predictions to the experimental data since the coordination number was set equal to the value estimated for each calcination temperature by Sotirchos and Zarkanitis (1992) in their sulfation study. The successful use of the generalized random pore model to describe the behavior of the sulfidation reaction of the

Greer limestone calcines using parameters determined independently from the study of their sulfation behavior underscores its capacity to function as a predictive model for gas-solid reactions with solid product. The comparison of the predictions of the mathematical model with the experimental data for the Georgia marble calcines led to the conclusion that a particle size dependent coordination number had to be used to successfully reproduce the experimental data. Fig. 2.14 compares the experimental data for sulfidation at 750°C of Georgia marble calcines produced at the same temperature with the model predictions for two values of coordination number. A coordination number equal to 3, the value used by Sotirchos and Zarkanitis (1992) for the sulfation of the same calcines, was found to provide very good approximation to the conversion vs. time results of the 53-62 and 88-105 μm particles, but a much larger coordination number ($z = 1,000$) had to be used to reproduce the behavior displayed by the largest (297-350 μm) particles. For the calcines prepared at 850°C , the corresponding values of coordination number were 4 and 4,000 (see Table 2.3). This result indicates that there is much smaller resistance for mass transport in the interior of the large particles since larger coordination numbers imply increased interaction of pores of different size. Indeed, as it can be seen in Table 2.5 which lists initial and final effective diffusivities predicted by the model for the Georgia marble sample, the initial effective diffusivity for $z = 1,000$ is about two times larger than the diffusivity for $z = 3$, but smaller by about the same factor than that for perfectly interconnected pores ($z = \infty$). This rather peculiar dependence of the effective diffusivity on the coordination number will be discussed in detail later.

Precursor	GL	GM	IS
Activation energy for k_s , kcal/gmol	6.8	6.9	6.2
Activation energy for D_P , kcal/gmol	16	13	13

Table 2.4: Activation energies estimated from the reaction rate constants and the diffusion coefficients of Table 2.3. GL=Greer limestone, GM=Georgia marble, and IS=Iceland spar.

Coordination number, z	3	1,000	∞
Initial diffusivity, cm^2/s	6.14×10^{-3}	13.5×10^{-3}	28.32×10^{-3}
Diffusivity ratio at $\xi = 0$, $D_e^z/D_e^{z=\infty}$	0.217	0.477	1
Final diffusivity, cm^2/s	0.57×10^{-3}	6.19×10^{-3}	21.87×10^{-3}
Diffusivity ratio at $\xi = 1$, $D_e^z/D_e^{z=\infty}$	0.026	0.283	1

Table 2.5: Initial effective diffusivities computed from the generalized random pore model for the Georgia marble for different coordination numbers. Calcination temperature= 750°C ; Sulfidation temperature= 750°C .

The need to use very large coordination numbers to reproduce the results for Georgia marble sulfidation suggests that a pore network model, with all pores participating in the network in the same way, is not appropriate for describing the pore structure of this solid. It was argued during the presentation of the calcination and sulfidation results that the apparently lower resistance of the large Georgia marble particles for mass transport in their interior is caused by formation of cracks and possibly fragmentation into smaller pieces during heating under CO_2 . We tested this explanation by carrying out the following experiment: A sample of 297-350 μm Georgia marble particles was treated under CO_2 for about 30 min. It was then cooled down to room temperature, resieved to remove the fragmented material, and used for calcination and sulfidation experiments in exactly the same manner as the fresh samples. Since decomposition of MgCO_3 had already taken place, no explosions were observed during heating of the treated material under CO_2 . Typical results of those test experiments are shown in Fig. 2.15. The overall reactivities of calcines obtained from the treated samples were found to be systematically lower than those of calcines prepared from fresh material, indicating that particle disintegration indeed took place during treatment of the Georgia marble under CO_2 . Comparison of the results of Figs. 2.14 and 2.15 reveals that the reactivity of the treated samples is still higher than that predicted by the mathematical model using the coordination number of the sulfation study (e.g., $z = 3$ for calcination at 750°C). This is not unexpected since sieving removes the fragments but does not have any effect on cracks formed in the interior of the heated particles.

Figure 2.12: Comparison of experimental data and model predictions for sulfidation at 750°C of Greer limestone calcines produced at 750°C.

Figure 2.13: Comparison of experimental data and model predictions for sulfidation at 750°C of Greer limestone calcines produced at 850°C.

Figure 2.14: Comparison of experimental data and model predictions for sulfidation at 750°C of Georgia marble calcines produced at 750°C.

Figure 2.15: Dependence of the sulfidation rate of Georgia marble calcines produced at 750°C on the pretreatment of the precursor (—: fresh sorbent particles; - - -: particles heat-treated under 1 atm of CO_2 at the calcination temperature and resieved).

Good agreement between model and experiment was also observed for the Iceland spar experimental data when the coordination numbers estimated by Sotirchos and Zarkanitis (1992) for sulfation were used in the mathematical model. The experimental and theoretical results for sulfidation at 750°C of sorbents calcined at the same temperature are shown in Fig. 2.16. The mathematical model successfully reproduced the effect of particle size on the evolution of the reactivity of the Iceland spar, but it tended – as it can be seen in Fig. 2.16 – to overestimate the reaction rate at the initial stages of the reaction and underestimate it at high conversions. The pore structure of the calcined Iceland spar sample was examined by Michail et al. (1980). Crystals of 1-2 mm in thickness and 1 cm in length were calcined under vacuum in the temperature range of $580\text{--}750^{\circ}\text{C}$. The physical structure of fresh and calcined samples was analyzed using nitrogen adsorption and scanning electron microscopy. The obtained results showed that the pore structure of the calcined materials consisted primarily of slit-shaped (parallel plate) mesopores. The development of this pore structure was attributed to the decomposition of initial plate-like carbonate layers. The slow variation of the reaction rate of Iceland spar calcines with time after the initial stages of the reaction is in qualitative agreement with the findings of Michail et al. (1980) since such behavior is typical – as those with some experience in the analysis of gas-solid reaction data using pore or grain-based model know – of plate-like pores or grains.

As the results of Table 2.3 show, higher coordination numbers had to be used to reproduce the experimental data for calcines produced at 850°C . Since the pore size distributions are shifted toward larger pores with increasing calcination temperature (compare Figs. 2.1 and 2.2), this indicates that calcination at higher temperatures leads to better interconnected pore structures. For the same calcination temperature, higher coordination numbers had to be used for the Greer limestone calcines than for the Iceland spar samples, and therefore, it can be argued that the higher reactivities of the former sample are primarily due to the higher connectivity of their pore structure. For the coordination numbers needed to reproduce the sulfidation results for the small particles and the sulfation results for all particle sizes (Sotirchos and Zarkanitis, 1992), the Georgia marble calcines exhibit pore space connectivity intermediate to that of the other two solids. This is not obvious

Figure 2.16: Comparison of experimental data and model predictions for sulfidation at 750°C of Iceland spar calcines produced at 750°C .

from the coordination numbers of Table 2.3, since the coordination number of Iceland spar and Georgia marble are the same at 750°C , while the latter is larger at 850°C . However, the coordination number gives only the number-based percolation threshold ($= 1/(z - 1)$), that is, the number fraction of pores that must be eliminated (blocked) in order to get an inaccessible pore structure. Thus, a better measure of the accessibility and connectivity characteristics of the pore space of a porous medium is offered by its porosity-based percolation threshold, namely the porosity of small pores that must be removed to obtain an inaccessible pore structure. The porosity threshold depends on the coordination number and the pore size distribution of the solid. A rough estimate for the number distribution density can be obtained by dividing the porosity distribution density by the volume of a pore segment $\pi R^2 \bar{l}$, with R being the pore radius and $\bar{l}$ the pore length. Therefore, shifting a small fraction of porosity toward the small pores can make a big difference in the location of the coordination number for a given coordination number. Using the pore size distributions of Fig. 2.1 for calcination at 750°C , we find that the internal pore structure of Greer limestone ($z = 6$) becomes inaccessible when pores accounting for 0.23 initial porosity are plugged ($<140 \text{ \AA}$ in radius), that of Georgia marble ($z = 3$) when pores accounting for 0.12 initial porosity ($<94 \text{ \AA}$ in radius) are plugged, and that of Iceland spar when pores accounting for 0.085 initial porosity ($<94 \text{ \AA}$ in radius) are plugged. Clearly, the initial porosity that must be removed to obtain an inaccessible pore structure (starting from the lower limit of the pore size range) increases from Greer limestone, to Georgia marble, to Iceland spar, that is, in the order decreasing overall reactivity during sulfidation (for the small particles of Georgia marble) and sulfation.

In the case of sulfation, the location of the percolation threshold affects both the amount of inaccessible pore volume and the effective diffusion coefficient. In the case of sulfidation, it only affects the intraparticle diffusion coefficient variation since the final porosity is far from being zero (about 0.25). The conversion dependence of the effective diffusion coefficients that are predicted by the mathematical model for the calcines produced at 750°C for sulfidation at the same temperature is shown in Fig. 2.17. We see that the effective diffusivity coefficient varies among the samples in the same order as the accessibility (or pore connectivity) of the pore structure, as it is quantified by the porosity-based

percolation threshold. Fig. 2.17 also gives the variation of the effective diffusivity that is predicted by the model for the larger coordination number that is needed to reproduce the sulfidation results for large Georgia marble particles. As it can also be seen from Table 2.5 which gives the initial and final diffusivities predicted by the mathematical model for the Georgia marble calcines at 750°C , much larger diffusivities are needed for these particles. It is interesting to point out that despite having very large coordination numbers ($z = 1,000$ for calcination at 750°C), the predicted diffusivity for the large Georgia marble particles is still two times lower than that predicted for a thoroughly interconnected structure of pores ($z = \infty$) or equivalently for a structure of parallel, infinitely long pores. This is a direct consequence of the broad form of the pore size distribution of the Georgia marble samples. The number-based percolation threshold ($1/(z-1)$) is equal to 0.9989, that is almost unity, but the corresponding initial pore radius is $385 \text{ \AA}$ and the corresponding porosity-based percolation threshold is 0.42. As a result, the large pores that are mainly responsible for the large diffusion coefficient for $z = \infty$ are still governed by transport in smaller size pores.

2.6. Summary and Conclusions

A detailed investigation of the sulfidation of calcines prepared from three limestones of high ($>95\%$) calcium carbonate content was carried out in this study. Reactivity experiments were carried out in a thermogravimetric analysis system, the solids were characterized by mercury porosimetry and gas adsorption, and the obtained sulfidation data were analyzed using the generalized random pore model of Yu and Sotirchos (1987), a model describing reaction, transport, and structure evolution in gas-solid reactions with solid product.

Our results showed very strong dependence of the overall reaction rate of each sorbent and of its evolution with the progress of the reaction on particle size. The overall reactivity of the solids increased with the calcination temperature, but the sulfidation temperature was found to influence weakly the conversion vs. time behavior of all sorbents, with its effect diminishing with increasing particle size. The results and conclusions of our sulfidation study were in relative agreement with those reached by Sotirchos and Zarkanitis (1992)

Figure 2.17: Variation of the effective diffusivities with the conversion for calcines produced and sulfided at 750°C.

from the study of the sulfation of the same solids. In both cases, the reactivity of the sorbent was found to increase with increasing average grain in the precursor stone, and the same behavior was also exhibited by the calcination rates of the precursors. The only exception was observed for large ($> 200 \mu\text{m}$) particles of one of the sorbents, a calcitic marble (Georgia marble), which had larger calcination and sulfidation rates than same size particles of the other sorbents even though smaller size particles exhibited intermediate reactivity. Since large particles of Georgia marble tended to explode during heating under CO_2 at high heating rates, it is believed that the apparently aberrant behavior of these particles during calcination and sulfidation is due to development of cracks in their interior, which lower the resistance for mass transport in their pore space.

With the exception of the data for large Georgia marble particles, very good agreement was obtained between model and experiment using parameter values consistent with those needed to describe the sulfation of the same solids (Sotirchos and Zarkanitis, 1992). In general, the comparison of model predictions and experimental data showed that the key factor influencing the behavior of a sorbent during sulfidation and sulfation is the connectivity of its pore space.

2.7 Notation

D_e	effective diffusivity, cm^2/s
D_P	diffusivity in the product layer, cm^2/s
R	pore radius, cm
v_s	volume of unreacted solid phase per mole of CaO , cm^3/gmol
v_i	molar volume of unreacted solid i , cm^3/gmol
z	coordination number
Z	volume of reacted solid phase per unit volume of unreacted phase (see Eq. (2.4))

Other Symbols

GR	Greer limestone
GM	Georgia marble

IS Iceland spar

Greek

ε	porosity
ε_0	initial porosity
ξ	conversion
ξ_{max}	maximum conversion for complete pore plugging
ψ	volume fraction of CaO in the sorbent

2.8. Literature References

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3. SULFATION OF HIGH PURITY LIMESTONES UNDER SIMULATED PFBC CONDITIONS

3.1. Introduction

Fluidized-bed combustion (FBC) possesses a number of environmental and operational advantages over conventional combustion systems, with the former becoming increasingly attractive as stricter limits are imposed on the concentration of gaseous pollutants (primarily, NO_x and SO_2) in the flue gases of coal combustion facilities. Fluidized-bed combustion exhibits high flexibility with respect to the sulfur and ash content of the coal feed and does not require a separate flue gas desulfurization unit. Moreover, because of lower combustion temperatures, it presents smaller concentrations of NO_x in the flue gases than combustion in other units (METC, 1984). When combustion of the coal matter in the fluidized bed is carried out under pressure, several additional advantages are encountered in comparison to having the process occurring under atmospheric pressure. These include smaller fluidized beds and smaller equipment size for comparable power - which make possible modular fabrication of the units - larger volumetric rates of heat release, lower combustion temperatures and, hence, smaller NO_x concentrations in the flue gas, and increased thermal efficiencies for combined cycle systems (METC, 1984). All these interesting features make pressurized fluidized-bed combustion (PFBC) very attractive as a high-efficiency alternative to the better developed atmospheric fluidized-bed combustion (AFBC), although the latter is still favored in the industry, especially by boiler manufacturers (Fox et al., 1986).

In a fluidized-bed combustor, a bed of combustible (coal) and noncombustible material is fluidized using air blown upward. Using dolomite or limestone as the noncombustible material, it is possible to have fuel combustion and flue gas desulfurization taking place simultaneously in the combustion vessel. If operation occurs under atmospheric pressure, the average partial pressure of carbon dioxide in the combustor (typically, 10-15% of the total pressure) is considerably lower than the equilibrium CO_2 pressure for decomposition of limestone ($CaCO_3$) or dolomite ($CaCO_3 \cdot MgCO_3$) at the temperatures usually encountered in FBC units (800- 950°C). In the high temperature environment of the AFBC unit,

the limestone or dolomite particles undergo calcination, yielding a highly porous product (CaO or MgO), which reacts with the sulfur dioxide produced during coal combustion forming, mainly, calcium or magnesium sulfate. The sulfates occupy more space than the oxides they replace, and as a result, the pores of the calcine are completely plugged with solid product before complete conversion takes place. (The conversion for complete pore plugging is about 50% for the calcine of a stone consisting of CaCO_3 only.) Pores of different size are plugged at different conversion levels, and it is thus possible to have formation of inaccessible pore space in the interior of the particles when the small feeder pores of clusters of large pore are filled with solid product (Zarkanitis and Sotirchos, 1989). Moreover, under conditions of strong internal diffusional limitations, complete pore closure may first take place at the external surface of the particles while there is still open pore space left in the interior. In reactors operating at higher temperatures, porosity loss may also occur through CO_2 -activated sintering (Newton et al., 1989). For these reasons, ultimate conversions much lower than those predicted by the stoichiometry of the reaction for complete plugging of the internal pore space (less than 30-40%) are seen in AFBC units.

The reaction of calcined limestones (primarily) and dolomites with SO_2 has been the subject of extensive investigation. The experimental evidence gathered in most of the past studies indicates strong effects of the pore size distribution on the overall reactivity of the calcined solids (Borgwardt and Harvey, 1972; Wen and Ishida, 1973; Hartman and Coughlin, 1974, 1976; Ulerich et al., 1977; Simons and Garman, 1986; Yu, 1987; Gullett and Bruce, 1987; Zarkanitis and Sotirchos, 1989; Sotirchos and Zarkanitis, 1992). Unfortunately, the immense volume of information that has accumulated over the years on the reaction of calcined limestones and dolomites with SO_2 is not applicable to SO_2 emissions control by limestones and dolomites under PFBC conditions. PFBC units normally operate under a pressure of 1600 kPa, which for an average CO_2 content of 15% gives a partial pressure of CO_2 in the reactor of about 240 kPa. Thermodynamic calculations show that the temperature for CaCO_3 calcination in the presence of 240 kPa of CO_2 must be larger than 980°C , that is, well above the temperature range ($750\text{--}950^\circ\text{C}$) encountered in a PFBC unit. Nevertheless, despite that formation of a highly porous material with a high specific surface area cannot take place under PFBC conditions, favorable desulfurization is known

to occur in PFBC units (Bulewicz et al., 1986; Hoy et al., 1982; Murthy et al., 1979). For dolomites, the situation is somewhat different since half-calcination (formation of a $MgO - CaCO_3$ product) is possible under 240 kPa of CO_2 . Even in this case, however, if sorption of SO_2 occurred only in the pore space of the half-calcined solid, the utilization of the calcium content of dolomites should be much smaller than what is seen in practice under PFBC conditions.

The reaction of $CaCO_3$ with SO_2 may involve various reaction steps (Van Houte et al., 1981):

$CaSO_3$ decomposes at temperatures higher than $650^\circ C$, and therefore, under typical operating conditions in a PFBC unit, the overall reaction may be written as:

For dolomites, one should also address the question of the reaction of MgO with SO_2 .

Spatial variation of the partial pressure of CO_2 within the bed will obviously lead to calcination of $CaCO_3$ in the regions where CO_2 pressures lower than the equilibrium are prevailing. Calcination of $CaCO_3$ will yield a partially calcined product, the extent of calcination depending on the residence time of the solid in the low CO_2 concentration region. The CaO formed in the solid will then react with the SO_2 present in the bed in the same fashion as in the case of AFBC units:

When the partially calcined solid moves into regions rich in CO_2 , where reaction (3.5) is favored to proceed from right to left, carbonation, i.e., recovery of $CaCO_3$, will take place, and reaction (3.4) will be competing with reaction (3.5) for CaO . Decomposition of

CaCO_3 may take place even if there is no variation of the CO_2 pressure in the reactor. Large variations in the temperature profile (100-140°C) within the combustor unit have been reported by Smith et al. (1982). Therefore, if the solid particles move into regions where the temperature of the reactor is above the temperature at which CaCO_3 is stable at the average partial pressure of CO_2 in the reactor, decomposition of CaCO_3 may occur. However, only small amounts of CaO have been found in the reactor by Ljungstrom and Lindqvist (1982), suggesting that direct sulfation of limestones (equation (3.4)) is the main reaction occurring in the combustor. Similarly, PFBC data from Exxon (Hoke et al., 1977) with uncalcined Grove limestone showed that most of the unreacted Ca in the bed for CO_2 partial pressures above the equilibrium value existed in the form of CaCO_3 .

Studies of SO_2 removal at high pressures have been carried out both with carbonates and precalcined solids. However, because of the aforementioned complexities, with the exception of the general conclusion that favorable desulfurization is possible under PFBC conditions, there is not much agreement in the literature on the effects of the various parameters on the process. Dennis and Hayhurst (1984, 1987) found that the reaction rate of precalcined limestones in a fluidized-bed reactor decreases with an increase in the operating pressure, both in the absence and presence of CO_2 . On the basis of the experience gained from the study of the $\text{CaO} - \text{SO}_2$ reaction at atmospheric pressure, these results are reasonable since an increase in the pressure also leads to a smaller effective diffusion coefficient, but the change would be relatively small in view of the fact that diffusion takes place close to the knudsen diffusion regime. Also, the presence of CO_2 favors sintering of the porous solid, and if the carbonation reaction is favored, it may compete with reaction (3.4) for CaO. Working with a laboratory-size PFBC, Bulewicz et al. (1986) observed an increase in the sorption capacity of Ca-based sorbents (chalk, limestones and dolomites) with an increase in pressure up to 200 kPa, but further increase in pressure caused a reduction in the sorption capacity of all samples. Although there is no obvious explanation for the observed increase of the sulfation capacity of the sorbents for low pressures, the second observation of Bulewicz et al. can be explained from a thermodynamic standpoint. At an operating temperature of 835°C, calcination of CaCO_3 takes place for pressures less than 200 kPa yielding a highly porous structure, while for pressures above 200 kPa, direct

sulfation of limestones would be the alternate route, where the absence of a developed porous matrix would result in lower sorption capacities. Such a behavior has also been observed by Jansson et al. (1982).

PFBC studies at Exxon (Hoke et al., 1977) showed better sulfur retention for precalcined limestones, but Stantan et al. (1982) observed no improvement in sorbent utilization by precalcination. Stantan et al. also reported that under weakly noncalcining conditions, a feed of uncalcined limestone gave better sulfur retention than that observed from thermogravimetric experiments. They postulated that no improvement was observed for precalcined solids because of the existence of a calcining zone near the base of the PFBC unit, which helps the uncalcined material achieve reactivity levels similar to those of the precalcined solid. Detailed tests done at the Illinois State Geological Survey (Chen, 1990) on several limestones and dolomites showed that some of the raw stones captured more SO_2 under noncalcining conditions than precalcined samples derived from these precursors. Moreover, an increase in pressure tended to increase sorbent utilization in the case of dolomites, but it had the opposite effect for solids with significant calcitic content.

It is possible to study the direct sulfation of calcium carbonate-containing sorbents under atmospheric pressure, provided that there is enough CO_2 in the reactor to prevent decomposition of the carbonate (simulated PFBC conditions). Tullin and Ljungstrom (1989), performed sulfation experiments in a thermogravimetric analyzer (TGA) under conditions inhibiting calcination of $CaCO_3$. They observed that the sulfation rate of uncalcined $CaCO_3$ was comparable with the sulfation rate of calcined material and concluded that desulfurization in PFBC units may proceed by direct sulfation of limestone. However, large amounts of sample and small particles (around 150 mg and 10-90 μm) were employed in the above study, and as a result, because of potentially strong interparticle diffusional limitations, extracting any quantitative information from the reported data is practically impossible. A similar procedure was employed by Snow et al. (1988) and Hajaligol et al. (1988), who also observed that the direct sulfation of $CaCO_3$ can reach, for some precursors, higher conversions than the sulfation of the calcines (CaO). They argued that the counter-diffusion of the CO_2 that is generated during the direct sulfation reaction (equation (3.4)) forms a porous product layer that offers less diffusion resistance than

the essentially nonporous layer formed during the $\text{CaO} - \text{SO}_2$ reaction. A shrinking core model was used by the above authors to analyze the experimental data, and the effective diffusivities they obtained were two to three orders of magnitude higher than the product layer diffusivity estimated from calcined limestone sulfation data.

A detailed experimental investigation of the direct sulfation of limestones with SO_2 is presented in this study. Reactivity evolution experiments were carried out in a thermogravimetric analysis system under simulated PFBC conditions, that is, in the presence of enough CO_2 to prevent decomposition of CaCO_3 , as it was done in the studies of Snow et al. (1988) and Tullin and Ljungstrom (1989). The structure of precursor rocks and partially reacted samples was analyzed by gas sorption and mercury porosimetry. In order to examine the influence of the various experimental conditions and parameters on the overall rate of the limestone- SO_2 reaction, experiments were conducted using a broad range of particle size (53-350 μm), two temperatures (750 and 850°C) and two SO_2 concentrations (1,500 and 6,000 mL/m^3). Three solids of high (> 95%) calcium carbonate content and different petrographic structure were employed in our experiments. The reaction of the calcined forms of these solids with SO_2 had been investigated in detail in a previous study (Zarkanitis and Sotirchos, 1989; Sotirchos and Zarkanitis, 1992), and as a result, a comparison of the rates of direct and indirect reaction of the same CaCO_3 solids with SO_2 is also presented in our study.

3.2. Materials and Procedures

Experiments were carried out using the following limestone specimens: a limestone of very high CaCO_3 content distributed by Greer Limestone Co. (Greer limestone), a calcitic marble (Tate White Aggregate) distributed by Georgia Marble Co. (Georgia marble), and a calcite (Iceland spar) distributed by Wards Inc. Chemical analysis of the solids showed that the calcium carbonate content was the highest in the Iceland spar (99.19 %), followed by those of the Greer limestone (97.89 %) and of the Georgia marble (95.19 %). Detailed chemical analyses of the three solids are given elsewhere (Krishnan, 1993). Mineralogical analysis of the stones revealed that the calcium carbonate was present in the form of calcite. Examination under a petrographic microscope showed that the Greer limestone

mainly consisted of calcitic, microgranular mud with inclusions of aggregates of small calcitic grains and that the Georgia marble consisted of coarse calcitic grains. The Iceland spar was found to be translucent and to consist of single crystals. More details on these materials are given by Zarkanitis (1991), who carried out a detailed investigation of the reaction of their calcined products with SO_2 .

Direct sulfation experiments were carried out in a thermogravimetric analysis (TGA) system. A Cahn 2000 electrobalance capable of handling weights up to 2.5 g and sensing weight changes as small as $0.1 \mu\text{g}$ constitutes the main part of the TGA system. In order to avoid having significant interparticle diffusional limitations, a small amount of solid (3-10 mg) was used for reactivity experiments. The effects of particle size on conversion vs. time results were studied by carrying out experiments with particles in three size ranges (53-62, 88-105, and 297-350 μm) for each of the three solids. Two inlet concentrations of 1,500 and 6,000 mL/m^3 of SO_2 were employed to estimate the order of the reaction with respect to SO_2 , which in past studies was assumed to be unity. The temperature effect was also studied by performing experiments at two different temperatures, 750 and 850°C. The inlet gases were composed of a mixture of 70% CO_2 (99.99% purity), and 30% air (containing 0.5% SO_2 or 2% SO_2). The sample was heated to the desired reaction temperature of 750°C or 850°C in an environment of pure CO_2 to ensure that calcination would not take place. After temperature stabilization, the CO_2 stream was substituted with a mixture of 70% CO_2 and 30% N_2 to verify that calcination was inhibited under these conditions. The $CO_2 - N_2$ stream was then replaced by the reactive mixture, and the transient weight gain of the sample was recorded. A flow rate of 200 mL/min at standard conditions was employed in all experiments discussed in this study.

3.3. Reactivity Evolution Results

Figs. 3.1-3.3 present conversion vs. time data for the direct sulfation at 850°C of 53-62, 88-105, and 297-350 μm particles of Greer limestone, Georgia marble, and Iceland spar, respectively, using 1,500 and 6,000 mL/m^3 SO_2 with 70% CO_2 (by volume) in air. Reactivity evolution results for the direct sulfation of the three solids (for the same particle sizes and SO_2 concentrations as in Figs. 3.1-3.3) at 750°C are shown in Figs. 3.4-3.6. It is

obvious from the results of Figs. 3.1-3.6 that the particle size strongly influences the overall reactivity of limestone with SO_2 , an indication that the reaction occurs under strong mass transport limitations. The existence of heat transport limitations is not an issue under the reaction conditions used in our study. Because of the small concentrations of gaseous reactant, the amount of heat involved in the chemical reaction is too low to cause significant temperature gradients in the interior of the particles or in the surrounding gas phase.

The effect of particle size on the overall reaction rate of small Greer limestone particles appears to be considerably stronger, on a relative basis, than in all other cases. Increasing the particle size from 53-62 to 88-105 μm (that is, by a factor of 1.8) decreases the conversion level reached at large reaction times by more than 50%, while the corresponding decrease in the cases of Georgia marble and Iceland spar is less than 30%. This observation suggests that the overall mechanism of reaction of small Greer limestone particles may be qualitatively different from that of the other solids and of large particles of the same solid. For the 88-105 and 297-350 μm particles, the effects of particle size on the conversion evolution curves are in quantitative agreement, on a relative basis, for all three sorbents.

The reaction temperature has a strong influence on the overall rate of the $CaCO_3 - SO_2$ reaction, similar in extent to that of particle size. As a comparison of the results of Figs. 3.1-3.3 with the corresponding curves of Figs. 3.4-3.6 show, a $100^\circ C$ reduction in the reaction temperature causes a large drop in the sulfur uptake of the sorbents for a given reaction time. The sulfation temperature appears to influence both the kinetic and mass transport characteristics of the process. The initial slopes of the conversion evolution curves show that the overall reaction rate at the start of the process, where presumably there are no diffusional limitations, decreases significantly as the temperature goes from 850 to $750^\circ C$, implying that a proportionate decrease is experienced by the intrinsic reaction rate. The variation of the slopes of the conversion vs. time curves with time indicates that the overall rates of reaction at the two temperatures are much different even at high conversion levels. Since the process is expected to be controlled at high conversion levels by diffusion through the product layer, one concludes that the mass transport resistance in the product layer must also be affected by temperature.

Figure 3.1: Conversion vs. time results during direct sulfation at 850°C of Greer limestone particles in an atmosphere of 30% air and 70% CO_2 (mole %).

Figure 3.2: Conversion vs. time results during direct sulfation at 850°C of Georgia marble particles in an atmosphere of 30% air and 70% CO₂ (mole %).

Figure 3.3: Conversion vs. time results during direct sulfation at 850°C of Iceland spar particles in an atmosphere of 30% air and 70% CO₂ (mole %).

Figure 3.4: Conversion vs. time results during direct sulfation at 750°C of Greer limestone particles in an atmosphere of 30% air and 70% CO₂ (mole %).

Figure 3.5.: Conversion vs. time results during direct sulfation at 750°C of Georgia marble particles in an atmosphere of 30% air and 70% CO₂ (mole %).

Figure 3.6: Conversion vs. time results during direct sulfation at 750°C of Iceland spar particles in an atmosphere of 30% air and 70% CO_2 (mole %).

Increasing the concentration of SO_2 leads to higher reaction rates and conversions, but the increase is for all combinations of limestone, particle size, and temperature much smaller than what should be expected for a four-fold increase in the concentration under conditions controlled by the intrinsic kinetics of the reaction for a first order (with respect to SO_2) reaction or by mass transport in the intraparticle space with the mass transport (diffusion) resistance being independent of the concentration. This result leads us to conclude that the order of reaction with respect to SO_2 is different from unity and that the diffusion coefficient in the product layer is a function of the SO_2 concentration.

Figs. 3.7 and 3.8 compare at 850 and 750°C, respectively, the conversion vs. time curves that we measured in this study for the direct reaction of 53-62 μm particles with 1500 mL/m^3 SO_2 with the corresponding curves that were obtained by Zarkanitis (1991) for the sulfation of the calcines of the three sorbents (same size particles). In the experiments of Zarkanitis (1991), the calcines were produced and sulfated at the same temperature. Sulfation was carried out using a mixture of 3000 mL/m^3 SO_2 and 12% (by volume) O_2 in N_2 . Experiments for different SO_2 concentrations showed that the overall rate of reaction was of first order with respect to the concentration of SO_2 at all conversions. Thus, in order to make the results of Zarkanitis comparable with those obtained in our study for 1500 mL/m^3 of SO_2 , the reaction time of his experiments was multiplied by 2.

It is seen in Figs. 3.7 and 3.8 that the overall reaction rate is much higher at low conversions for the sulfation of the calcines ($CaO - SO_2$ reaction) than for the sulfation of the precursors under conditions that prohibit decomposition to CaO ($CaCO_3 - SO_2$ reaction). However, the reaction rate of the calcines drops sharply after some conversion level (after about 10 min of exposure to the reactive environment), beyond which insignificant sorption of SO_2 takes place, whereas sulfation is seen to occur with significant rate for the uncalcined limestones throughout the 150 min window shown in Fig. 3.1. It is interesting to observe that in the case of the Greer limestone particles, the conversion of the uncalcined sorbent surpasses that of the calcine after about 30 min of reaction time.

The results of Figs. 3.7 and 3.8 cannot be used to determine the effect of temperature on the reaction of calcined limestones since the calcines of each figure were produced at different temperatures, and as a result, they have different pore structures. Zarkanitis and

Figure 3.7: Comparison of the conversion evolution curves during direct sulfation of 53-62 μm particles at 850°C with those obtained during sulfation of same size particles of the calcined solids (Zarkanitis, 1991) at the same temperature. The calcines were prepared by calcination at 850°C.

Figure 3.8: Comparison of the conversion evolution curves during direct sulfation of 53-62 μm particles at 750°C with those obtained during sulfation of same size particles of the calcined solids (Zarkanitis, 1991) at the same temperature. The calcines were prepared by calcination at 750°C.

Sotirchos (1989) found that lowering of temperature does result in a decrease in the overall reaction rate for the sulfation of limestone calcines (Zarkanitis and Sotirchos, 1989), but of much smaller extent than for direct sulfation of limestones. The fact that temperature affects the two reactions differently lends further support to the conclusion that the overall mechanisms of the two processes are radically different.

Particle Size (μm)	Temp. ($^{\circ}\text{C}$)	GL			GM			IS		
		(% Conv.)			(% Conv.)			(% Conv.)		
		A	B	C	A	B	C	A	B	C
53-62	850	75	79	54	25	28	34	19	21	20
88-105	850	26	32	38	15	19	25	13	16	16
297-350	850	09	10	17	06	07	12	04	05	07
53-62	750	32	36	35	09	11	28	07	08	25
88-105	750	14	17	28	07	09	13	04	05	18
297-350	750	03	04	15	02	03	11	02	02	10

Table 3.1: Comparison of conversion levels obtained by direct sulfation or sulfation of calcined samples after 2 hours. GL=Greer Limestone, GM=Georgia Marble, and IS=Iceland Spar. A=Direct sulfation using 70% CO_2 , 30% air (containing 0.5% SO_2), B=Direct sulfation using 70% CO_2 , 30% air (containing 2% SO_2), and C=Sulfation of calcine using a mixture of 3000 ppm SO_2 and 12% O_2 (by volume) in N_2 .

A quantity of much importance is the conversion level attained by the sorbent particles for reaction times comparable to the average residence time of the particles in a fluidized-bed combustor. Table 3.1 summarizes the comparison between conversion levels obtained through the two different routes of sulfation (direct and through calcination) after 2 hr of reaction time. The conversion level reached by the 53-62 μm particles of Greer limestone during direct sulfation at 850 $^{\circ}\text{C}$ for large exposure times (see Fig. 3.1 and Table 3.1) far exceeds the maximum allowable conversion for complete plugging of the pore space of its calcine with calcium sulfate (about 55%). For the other two sorbents, the conversions reached by the small (53-62 μm) particles during direct sulfation are comparable to those

attained by their uncalcined counterparts. However, because of the very strong effect of particle size on the rate of direct sulfation, which is much stronger than that on the calcined sorbent reaction, the conversion levels attained by larger particles are much lower for the direct sulfation reaction.

3.4. Pore Structure Results

Mercury penetration experiments using a Micromeritics 9220 II mercury porosimeter showed that the stones were nearly nonporous in their natural state as only minute quantities (typically, 0.01-0.02 mL/g) of mercury penetrated the void space of the samples. Mercury porosimetry was used by Hajaligol et al. (1988) to characterize the pore structure of the solids that were used in their studies. Since very small penetration volumes were observed in our experiments and mercury intrusion mainly occurred at high pressures, where sample and mercury compressibility introduce significant errors in the interpreted data for small intrusion volumes, it was decided to base the analysis of the pore structure of the samples of unreacted and partially reacted solids on gas sorption data instead. Gas sorption isotherms (N_2 at 77 K) were measured using a volumetric sorption instrument (Autosorb-1 by Quantachrome). The relatively large quantities of partially reacted samples needed for the porosimetry and sorption experiments were prepared in a fixed-bed reactor under differential operation at the same conditions used in the TGA experiments. The differential operation of the reactor was verified using a gas chromatograph (Varian 3300) equipped with a flame photometric detector to analyze the effluent stream.

Fig. 3.9 presents cumulative pore volume vs. pore radius results for the three limestones obtained through gas N_2 sorption at 77 K. The porosities for pores of radius smaller than 100 nm and the surface areas determined from BET analysis of the results of Fig. 3.9 are given in Table 3.2. Greer limestone is seen to have the highest natural porosity followed by Georgia marble and Iceland spar. The surface areas show the same trend as the porosities, with Greer limestone having about three times larger surface area than Georgia marble and four times than Iceland spar. Interestingly enough, the reaction rates and the sulfation efficiencies, both for direct and indirect (after calcination) sulfation (see Figs. 3.7 and 3.8), of the three solids increase in the same order as their porosities and

surface areas, while, on the contrary, their average grain size, as revealed by petrographic analysis, decreases. This observation indicates that the petrographic texture of a limestone plays an important role in determining its performance as a sorbent for SO_2 removal under both calcining and noncalcining conditions (AFBC and PFBC). In the case of sulfation of calcined stones, analysis of the reactivity evolution data using detailed models for transport, reaction, and structure change in porous solids (Sotirchos and Zarkanitis, 1992) suggested that the petrographic texture of the precursor affects the connectivity of the pores, which appears to increase with decreasing grain size. For the case in which direct sulfation takes place, the limestone characteristics influence the structure of the resulting product layer and, hence, the effective diffusion coefficient through it. Hajaligol et al. (1988) also attributed the differences among the various limestones they considered to the natural porosity of the samples.

Limestone	Particle size (μm)	Surface Area (m^2/g)	Porosity (pores of radius < 100 nm)
Greer Limestone	53-62	0.91	0.015
Georgia Marble	53-62	0.31	0.007
Iceland Spar	53-62	0.23	0.004

Table 3.2: Surface Areas and Porosities of Georgia Marble, Greer Limestone, and Iceland Spar Precursors.

The analysis of the sorption isotherm of a Greer limestone sample exposed to the reactive mixture for 1 min only showed (Fig. 3.10) that its cumulative porosity was much smaller than that of the unreacted precursor. Since the direct sulfation of calcium carbonate involves formation of a bulkier solid product (calcium sulfate), it may be argued that the apparent porosity of the solid decreases immediately upon reaction because some of the pores of the precursor are plugged with solid product. However, gas sorption experiments on Greer limestone precursors that were heat-treated under N_2 revealed a similar decrease in cumulative porosity (Fig. 3.10). The pore size distribution of the heat-treated precursor

Figure 3.9: Cumulative pore volume vs. pore radius curves for the precursors obtained from N_2 sorption data.

was restored to its initial form after washing the sample in water and drying it in an oven at 150°C . The last finding suggests that the main reason for the immediate decrease that the apparent cumulative porosity of Greer limestone undergoes during sulfation may be due to the exposure of the sample to high temperatures and not the formation of the solid product. Greer limestone contains 0.163% of P_2O_5 on a mass basis which has a melting point of $580\text{--}585^{\circ}\text{C}$ (Weast, 1987). During heat treatment at 850°C , molten phosphorous pentaoxide may probably fill the interstitial space, blocking some of the pores and causing a reduction in apparent porosity. Washing with water dissolves the oxide and unplugs the pores, restoring the initial pore size distribution. A similar scenario was postulated by Huang and Daugherty (1988) in their attempt to explain the role of P_2O_5 in some of their results concerning the calcination of calcium carbonate solids. Heat treatment also affected the porosity of the Georgia marble sample, but it had practically no effect on Iceland spar. This behavior is in agreement with the postulated role of P_2O_5 , since Georgia marble also contains P_2O_5 , while Iceland spar contains very little.

Fig. 3.11 shows how the cumulative pore size distribution of Greer limestone changes with the conversion during sulfation at 850°C and 1500 mL/m^3 of SO_2 under noncalcining (70% CO_2) conditions. Partially reacted samples are seen to have smaller porosities than the original material at all conversions. The overall porosity tends to increase with increasing conversion, but the rate of increase appears to fall as the conversion increases. If it is assumed that the apparent pore size distribution of the unreacted material is the same as that of the heat treated sample of Fig. 3.10, the above result indicates that the average porosity of the reacted solid phase decreases with increasing conversion. The effect of conversion on the pore size distribution of the other two solids was qualitatively similar to that shown in Fig. 3.11 for Greer limestone. However, since the pore size distribution of these solids did not decrease as much at the outset of the process, the cumulative porosity varied less with the conversion. This behaviour may be seen in Fig. 3.12 which compares the original pore size distribution of Iceland spar with that of a 20% converted sample.

The CaSO_4 product of the 8% converted sample of Fig. 3.11 was removed by washing with water, and the remaining solid was dried in an oven at 150°C . The weight of the washed solid was found to be in good agreement with that expected from the conversion

Figure 3.10: Effects of heat treatment and sulfation on the pore size distribution of Greer limestone. The sulfation was carried out in an atmosphere of 30% air (2% SO_2) and 70% CO_2 (mole %) at 850°C. The samples were heat treated in an atmosphere of 30% N_2 and 70% CO_2 (mole %).

Figure 3.11: Effects of conversion on the pore size distribution of Greer limestone particles (53-62 μm). The sulfation was carried out in an atmosphere of 30% air (2% SO_2) and 70% CO_2 (mole %) at 850°C.

Figure 3.12: Effects of conversion on the pore size distribution of Iceland spar particles (53-62 μm). The sulfation was carried out in an atmosphere of 30% air (2% SO_2) and 70% CO_2 (mole %) at 850°C.

level, while gas sorption analysis (see Fig. 3.11) showed its pore size distribution to be almost the same as that of the original solid. This result offers a strong indication that the direct sulfation process proceeds in a shrinking-core fashion, in agreement with the scanning electron microscopy results of Hajaligol et al. (1988).

3.5. Discussion

Let the intrinsic reaction rate, expressed as $\text{mol}/\text{cm}^2\cdot\text{s}$, be of the form $R_s = k_s c^n$, with c being the concentration of SO_2 at the reaction interface. The initial reaction rate data may be used to estimate the constant, k_s , and the order with respect to SO_2 , n , of the intrinsic rate of the $\text{CaCO}_3 - \text{SO}_2$ reaction. Let a_0 be the initial particle size, c_s the concentration of SO_2 at the surface of the particle, and $\bar{R}_{obs}$ the observed overall reaction rate (mol/s). Because of the low porosity of the precursors, reaction at $t = 0$ will mainly take place on the external surface of the particle. Therefore, the initial rate observed experimentally, $\bar{R}_{obs}$, is directly proportional to the external surface area of the reacting particles and hence we can write:

$$\bar{R}_{obs} = 4\pi a_0^2 k_s c_s^n \quad (3.7)$$

The mass balance on SO_2 at the external surface of the particles requires that the following relationship be valid at all times:

$$\bar{R}_{obs} = 4\pi a^2 k_g (c_b - c_s) \quad (3.8)$$

with k_g being the mass transfer coefficient at the external surface of the particles, and c_b the concentration of SO_2 in the bulk. Equation (3.8) may be used to find the concentration of SO_2 at the surface of the particles at $t = 0$ needed for the estimation of k_s and n from equation (3.7). Use of standard correlations for flow past freely suspended spheres (Bird et al., 1960) gives for all particle sizes used in our study a Sherwood number (Sh) of about 2 (based on diameter), that is, the value obtained for diffusion without flow around spherical particles. Since the particles are placed on the pan and are not uniformly exposed to the reactive mixture, this number should only be interpreted as an upper bound on the actual Sherwood number of the particles. However, when the mass transfer coefficient

for $Sh = 2$ is used in equation (3.8), it is found that even at the initial stages of the reaction – where the highest reaction rates are encountered – the concentration at the surface of the particles is practically identical to that in the bulk of the gas phase. At the conditions of our experiments, therefore, mass transfer from the bulk of the gas phase to the particles plays a minor role in the overall reaction process, and as a result, the exact value of Sherwood number – provided that is not much smaller than 2 – is immaterial for data analysis.

k_s and n can be obtained by linear regression on the logarithmic form of equation (3.7) with $c_s = c_b$. However, since for fixed particle size and reaction temperature, the initial rate of reaction is influenced only by the concentration of SO_2 (that is, by the order of reaction), a two-step procedure was employed to estimate n and k_s . It follows from equation (3.7) that for a given combination of particle size and temperature, the ratio of the initial reaction rates at the two concentrations used in our study must satisfy the equation:

$$\bar{R}_{obs}|_{1500 \text{ mL/m}^3} / \bar{R}_{obs}|_{6000 \text{ mL/m}^3} = (0.25)^n \quad (3.9)$$

The order of the reaction was estimated as the arithmetic mean of the six n values that are determined from equation (3.9) for each sorbent (three particle sizes and two temperatures). The n values that were estimated by this procedure for the three sorbents were very close to each other, and it was thus decided to use the same reaction order for all solids ($n = 0.4$), determined as the arithmetic mean of all n estimates. This value of n was then used to find k_s for each sorbent at each temperature as the arithmetic mean of the six values obtained from equation (3.7) (three particles and two concentrations).

The intrinsic reaction rate constants at the two temperatures of our experiments are given in Table 3.3. At least three independent measurements of the initial reaction rate for each combination of particle size, temperature, and concentration were employed to obtain each initial reaction rate value used to get the order of the reaction and the rate constants of Table 3.3. The rate constant decreases in the direction Greer limestone → Georgia marble → Iceland spar, that is, in the direction of decreasing overall reactivity, but the decrease is not enough to justify the observed overall reactivity differences. Hajaligol

et al. (1988) reported kinetic constants dependent on particle size, but such a trend was not evident in our results. The intrinsic reaction rate constant shows strong dependence on the temperature of the reaction, reflecting the strong influence of temperature on the conversion vs. time curves. Assuming Arrhenius-type dependence of the rate constants on temperature, the results of Table 3.3 yield 138.44 kJ/mol activation energy for Greer limestone, 109.73 kJ/mol for Georgia marble, and 113.57 kJ/mol for Iceland spar. In his study of sulfation of calcined samples of the same precursors, Zarkanitis (1991) determined activation energies of about 17.14 kJ/mol for all three solids. The higher values of activation energies of the direct sulfation reaction reflect the greater sensitivity of the kinetics of reaction (3.4) with respect to the reaction temperature than that observed for the reaction of CaO with SO_2 (reaction (3.6)).

Temp. ($^{\circ}C$)	Greer Limestone	Georgia Marble	Iceland Spar
750	9.06×10^{-6}	3.04×10^{-6}	2.28×10^{-6}
850	3.83×10^{-5}	9.53×10^{-6}	7.77×10^{-6}

Table 3.3: Reaction Rate Constant Values ($\text{moles}^{0.6}/\text{cm}^{0.8}\cdot\text{s}$) at 750 and 850 $^{\circ}C$, $n = 0.4$.

Our pore structure characterization data (Fig. 3.11) suggested that the direct sulfation of limestones proceeds in a shrinking-core fashion. An attempt was thus made to analyze our conversion vs. time data using the shrinking-core model (Levenspiel, 1972; Szekely et al., 1976). However, the solid product formed during direct sulfation of limestones ($CaSO_4$) occupies more space than the solid it results from ($CaCO_3$). As a result, the particle size increases with increasing conversion, and it is necessary that this variation be accounted for in the shrinking-core model. Following the change of the particle size with the conversion requires knowledge of the volume of fully reacted solid per unit volume of unreacted solid, which in turn needs for its determination the porosities of the unreacted and fully reacted solids – and possibly their variation with the radial distance in the particle – and the volume of reacted dense solid phase per unit volume of unreacted dense solid phase (stoichiometric volume ratio, Z). Since the porosities of the three solids we used in

our study are very low in both unreacted and fully reacted form (see Figs. 3.9-3.12) and all solids have CaCO_3 as their main constituent, the volume of reacted solid per unit volume of unreacted solid in all cases can be approximated using the ratio of the molar volume of CaSO_4 to that of CaCO_3 (about 1.24).

With the intrinsic kinetics of the reaction and the mass transfer coefficient from the gas phase to the particles known, only the effective diffusion coefficient of SO_2 in the product layer is needed to apply the shrinking-core model to the experimental data. The predictions of the shrinking-core model are compared in Fig. 3.13 for three values of the effective diffusion coefficient of SO_2 in the reacted layer with the experimental data for 88-105 μm Greer limestone particles reacted at 850°C . The results of Fig. 3.13 indicate that there is no effective diffusivity value that can bring the predictions of the shrinking-core model into agreement with the experimental data. The overall reaction rate decreases much faster with the extent of the reaction than what the shrinking-core model predicts. If the effective diffusive coefficient is chosen so that the experimental conversion matches the theoretical one at some reaction time, the model would give lower conversions below that time and overpredict the conversion past it. Results similar to those shown in Fig. 3.13 were obtained by applying the shrinking-core model to other precursors, particle sizes, and reaction temperatures.

The behavior seen in Fig. 3.13 suggests that the average resistance for mass transport in the product shell increases with the progress of the reaction. Therefore, the diffusion coefficient in the product shell must be varied with the progress of the reaction (that is, be decreased) in order to be able to reproduce the results using the shrinking-core model. The formation of a solid product that occupies more space than the solid reactant it replaces is most probably the main reason for the occurrence of this situation. Nascent solid product formed at the reaction interface at conversions different from zero has to push against a progressively thicker product layer to accommodate itself within the product shell. This in turn causes the density of the product layer to increase away from the external surface of the particles and the effective diffusion coefficient to decrease. This explanation is in qualitative agreement with the pore structure data, which, as we pointed out when we discussed the results of Fig. 3.11, suggest that the average porosity of the reacted solid

Figure 3.13: Comparison of the experimental data for 88-105 μm Greer limestone particles at 850°C with the predictions of a shrinking core model for various effective diffusivities.

phase decreases with increasing conversion. It also agrees with the observed increase of the overall reactivity of the solids in the direction of increasing precursor porosity, in view of the fact that the average product layer porosity varies among the three precursors in the same way as their initial porosity (see Figs 3.11 and 3.12).

Hajaligol et al. (1988) reached a similar conclusion when they attempted to analyze their direct sulfation data using the shrinking-core model. They treated the average diffusion coefficient in the product layer as function of time (or, equivalently, of conversion) and determined its value at selected conversion levels by fitting the shrinking-core model predictions to the experimental data. The results they obtained showed some scattering but suggested the existence of a correlation between average effective diffusivity in the product layer and conversion. The experimental data that we obtained here are analyzed using a variable diffusivity shrinking-core model in another study (Krishnan and Sotirchos, 1993). Since the effective diffusivity is treated as a function of distance from the external surface of the particles, its functional form is determined through a parameter estimation procedure under the constraint that the diffusivity expression be the same for all particles of the same solid at the same reaction conditions.

3.6. Conclusions

The reaction between $CaCO_3$ and SO_2 , which is of immense importance in a PFBC unit, was studied in depth in this work. Three types of limestones, each consisting of more than 95% $CaCO_3$ on a mass basis, were directly sulfated for this purpose. The sulfation of these stones were carried out in a TGA system in an atmosphere of 70% CO_2 to prevent the decomposition of $CaCO_3$ at the reaction temperatures of 750 and 850°C. A broad range of particle size (53-350 μm) and two concentrations of SO_2 (1500 and 6000 mL/m³) were employed in this investigation.

The particle size was found to have a strong influence on the conversion-time profile for all limestones under all reaction conditions indicating that the reaction was controlled by mass transport in the intraparticle space. Small Greer limestone particles tended to show a stronger influence of particle size on the conversion profile, but the larger size ranges were in agreement, quantitatively on a relative basis, with the profiles seen for the other

stones. Temperature was also found to strongly influence the conversion-time profiles for all stones, and the strong dependence of the conversion trajectory on the reaction temperature was noticeable throughout the duration of the experiment. This indicated that temperature had a strong impact on both the kinetics (the controlling factor during the initial stages of the reaction) and mass transport (the controlling factor during the later stages). The concentration of SO_2 had rather small effects on the conversion-time profile. The lack of a proportionate change in the reaction rate with the concentration of SO_2 in the bulk at either the earlier or the later stages of the reaction led us to conclude that the order with respect to SO_2 was different from unity and that the mass transport coefficient was a function of reactant concentration.

The conversion-time profiles for the $CaCO_3 - SO_2$ reaction that we obtained in this study were found to be markedly different from those for the $CaO - SO_2$ reaction obtained with the same limestones in an earlier investigation (Sotirchos and Zarkanitis, 1992). The $CaO - SO_2$ reaction proceeded much faster initially on account of a developed porous structure, but leveled off beyond certain exposure time or, equivalently, conversion, because of pore closure. On the contrary, the $CaCO_3 - SO_2$ reaction proceeded at a relatively lower rate during the initial stages of the process, but even after prolonged exposure times reacted at a significant rate. This rather striking difference between the two reactions has been attributed to a lower mass transport resistance offered by the product shell of the $CaCO_3 - SO_2$ reaction compared to that of the $CaO - SO_2$ reaction. A strong correlation between desulfurization capacity and initial porosity of the solids was observed, in agreement with a similar observation made by Hajaligol et al. (1988). Interestingly, the limestones showed the same order of performance as in the $CaO - SO_2$ reaction. The fact that the reactivity increased with decreasing grain size in the solid led us to conclude that the petrographic texture of limestones plays an important role in determining their capacity for SO_2 removal.

The structure of unreacted and partially reacted solids was analyzed using N_2 sorption and the results were used to study the changing morphology of the product layer. The measurements showed that both the fresh and partially reacted solids possessed very little porosity, and that the average porosity of the fully reacted part of the solid decreased with

increasing conversion or equivalently product layer thickness. Therefore, based on the ratio of molar volume of the solid product to that of the solid reactant, the change of $CaCO_3$ (the main reactant) to $CaSO_4$ (the main product) caused approximately a 25% change in volume. Furthermore, the pore structure results of unreacted solid and a solid washed with water after sulfation indicated that the direct sulfation of limestones proceeded in a shrinking-core fashion.

The initial reaction rates were used to determine the intrinsic reaction rate constant and the order of the reaction with respect to SO_2 . The order of the reaction was found to be similar for the three different stones and an average value of 0.4 was estimated. The intrinsic reaction rate constant was found to decrease among the three solids in the same order as the overall reactivity but not enough to justify the drop in overall reactivity. The kinetic data were used in a shrinking-core model with constant effective diffusivity in the product shell, but this simple model failed to bring any agreement between theory and experiment. It was observed that an increasing mass transport resistance through the product layer was needed to yield agreement between model predictions and experimental results. Therefore, a variable diffusivity shrinking-core model must be employed to describe the direct sulfation of limestones. The increase in the average resistance for mass transport in the product layer with increasing conversion is most probably caused by the formation of denser product layer away from the external surface of the particles.

3.7. Notation

a	outer radius of the particle, cm
a_0	initial radius of the particle, cm
c_b	concentration of SO_2 in the bulk, mol/mL
c_s	concentration of SO_2 at the surface of the particle, mol/mL
D_m	molecular diffusivity of SO_2 -gas mixture, cm^2/s
D_e	effective diffusivity of SO_2 in the product layer, cm^2/s
k_g	external mass transfer coefficient, cm/s
k_s	intrinsic reaction rate constant, $mol^{0.6}/cm^{0.8} \cdot s$
n	order of reaction with respect to SO_2

$\bar{R}_{obs}$	observed overall reaction rate, mol/s
R_s	intrinsic reaction rate, $mol/cm^2 \cdot s$
Sh	Sherwood number, $2k_g a/D_m$
t	real time, s
Z	volume of dense reacted solid phase per unit volume of dense unreacted solid phase

3.8. Literature References

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4. A VARIABLE DIFFUSIVITY SHRINKING-CORE MODEL AND ITS APPLICATION TO THE DIRECT SULFATION OF LIMESTONES

4.1. Introduction

In an earlier investigation (Krishnan and Sotirchos, 1993), we carried out an extensive study of the direct reaction of high purity limestones with SO_2 under various reaction conditions in a thermogravimetric analyzer (TGA). Reactivity experiments were performed at atmospheric pressure in the presence of CO_2 in order to inhibit the decomposition of $CaCO_3$ and, thereby, simulate conditions met in pressurized fluidized-bed combustion (PFBC) units. Various interesting results concerning the influence of particle size, temperature, and concentration were obtained in that study. Analysis of the initial reactivity data yielded a value of 0.4 for the order of the reaction with respect to SO_2 and enabled us to obtain values for the intrinsic rate constant of the $CaCO_3 - SO_2$ reaction for two temperatures and three limestone precursors.

One of the most interesting observations from our earlier study was that the rate of the direct sulfation of limestones (limestone- SO_2 reaction) could be larger at high conversion levels than that of the sulfation of the corresponding calcines ($CaO - SO_2$ reaction), in qualitative agreement with similar observations made by Snow et al. (1988) and Tullin and Ljungstrom (1988). Since at high conversion levels, the reaction rate is primarily controlled in both cases by diffusion of SO_2 through the product layer (mainly $CaSO_4$), a major conclusion arrived at on the basis of the above finding was that the product layer exhibits lower diffusional resistance in the case of direct sulfation.

In order to gain better insight into the overall mechanism of the direct sulfation of limestones, mercury penetration porosimetry and gas sorption were used to characterize the pore structure of precursors and partially reacted samples. Because of very small mercury penetration volumes and, consequently, large relative errors in the interpretation of mercury penetration data, only the gas sorption data (N_2 at 77 K) were used to extract quantitative information on the pore structure of the solids (for pores smaller than about 200 nm in diameter). Our measurements showed that both the fresh (unreacted) and partially reacted solids possessed very small porosity (smaller than 1.5%) and that the

average porosity of the fully reacted part of the solid decreased with increasing conversion or, equivalently, product layer thickness. Moreover, characterization of the pore structure of samples in which the reacted solid had been removed by washing in water suggested that the reaction proceeded in a shrinking-core fashion. Qualitatively similar conclusions were reached by Hajaligol et al. (1988) from mercury porosimetry and scanning electron microscopy measurements on partially reacted solids.

An attempt was made to reproduce the experimentally observed behavior using a shrinking-core model with constant diffusivity in the product layer, but it failed. Specifically, a comparison of model predictions and experimental data showed that the overall reaction rate in the experimental data fell more rapidly with the reaction time (or, equivalently, the conversion of the solid), especially during the initial stages of the reaction, than what the shrinking-core model predicted, indicating that the average resistance for mass transport in the product shell increased with the progress of the reaction. This result and the results from our pore structure characterization experiments led us to conclude that because of the formation of a solid product ($CaSO_4$) that occupies more space than the solid reactant ($CaCO_3$) – about 25% more – and the presence of the product shell around the unreacted core, progressively denser layers of solid product are formed during reaction away from the external surface of the particles. Therefore, an effective diffusion coefficient that decreases with the distance from the external surface of the particles should be used in the shrinking-core to reproduce the behavior seen in the experimental data. A similar conclusion led Hajaligol et al. (1988) to use a conversion dependent diffusivity in the shrinking-core model in order to reproduce their experimental data. Good agreement between model predictions and experimental data was observed by these investigators. However, aside from assuming uniform effective diffusivity in the product layer, their assumption that the variation of the effective diffusivity with conversion was independent of the particle size is difficult to justify on physical grounds inasmuch as the same conversion level corresponds to significantly different product layer thicknesses for different size particles.

A variable diffusivity shrinking-core model is developed and used in this study to analyze the experimental data obtained by Krishnan and Sotirchos (1993) for the reaction

of SO_2 with limestones under simulated PFBC conditions. The effective diffusivity in the product layer is assumed to vary with the distance from the external surface of the particles, and a parameter estimation procedure is developed to handle the ill-posed numerical problem that arises when one tries to extract the effective diffusivity as a distributed parameter from the experimental data.

4.2. Model Equations and Parametric Sensitivity

The physical picture that needs to be mathematically modeled for the direct sulfation of limestones involves a shrinking core of unreacted material surrounded by an expanding shell of reacted solid. At the interface, gas A and solid S react to produce solid P according to the reaction

where $\dots$ stands for other gaseous species that may participate in the reaction but do not have to be considered to describe the process. In the case of limestone sulfation, the overall chemical reaction has the form

Several sources of the literature (e.g., Szekely et al. (1976) and Levenspiel (1972)) describe models involving the above general features, and thus, we will provide details only for the most important aspects of the model that is developed here.

Assuming isothermal conditions and pseudosteady-state for the concentration profile of the gaseous reactant (SO_2 in the case of limestone sulfation), a mass balance on the gaseous reactant yields

$$(1/r^s) \frac{\partial}{\partial r} (r^s D_e(r) \frac{\partial c}{\partial r}) = 0 \quad (4.3)$$

s is the particle shape factor (0: slab; 1: cylinder; 2: sphere), c is the concentration of the reactive species in the product layer, and $D_e(t, r)$ is the effective diffusivity in the product layer varying in time, t , and locally along the radial direction, r . At the external surface of the particles, we have the boundary condition

$$D_e(r, t) (\partial c / \partial r)|_{r=a} = k_g (c_b - c_s) \quad (4.4)$$

k_g is the external mass transfer coefficient, c_b the bulk concentration of SO_2 , c_s the concentration of SO_2 at the external surface of the particle, and a the size of the particle. In our previous study, it was found that even for the highest reaction rates measured in our experiments, c_s was practically equal to c_b even when the Sherwood number (Sh) was given values much lower than 2, the value corresponding to spherical particles exposed to a stagnant environment. Therefore, for all practical purposes Eq. (4.4) can be replaced by

$$c|_{r=a} \equiv c_s = c_b \quad (4.5)$$

At the reaction front ($r = a_c$), a mass balance on the gas gives

$$D_e(r, t)(\partial c / \partial r)|_{r=a_c} = R_s(c_c) \quad (4.6)$$

whereas a mass balance on the solid leads to

$$da_c/dt = -v_s R_s(c_c) \quad (4.7)$$

v_s is the volume of unreacted core per mole of solid reactant, c_c is the concentration at the reaction front, and $R_s(c)$ is the reaction rate per unit surface area, which is assumed to be related to the concentration at the reaction front by the equation

$$R_s(c) = k_s c^n \quad (4.8)$$

k_s is the intrinsic reaction rate constant, and n the order of the reaction with respect to reactant A (SO_2). Before reaction starts (i.e., at time zero), we obviously have

$$a = a_c = a_0 \quad (4.9)$$

with a_0 being the initial size of the particle.

The conversion of the solid is related to the core size by the obvious equation

$$X = 1 - (a_c/a_0)^{s+1} \quad (4.10)$$

An equation relating a , a_c , and a_0 is obtained from an overall balance on the solid reactant. Let ϵ_0 be the porosity of the unreacted solid and $\epsilon(r, t)$ the porosity of the product shell at position r and time t . Then we have

$$Z(a_0^{s+1} - a_c^{s+1}) = (1/1 - \epsilon_0) \int_{a_c}^a (1 - \epsilon(r, t)) dr^{s+1} \quad (4.11)$$

Z is the stoichiometric volume ratio of the solid product-solid reactant system, that is, the volume of reacted solid phase per unit volume of unreacted solid phase. If the unreacted solid phase consists of solid reactant only, then Z is equal to the ratio of the molar volume of solid product to the molar volume of solid reactant. This value can also be used for solids that contain very small amounts of inert solids, like the three limestones used to obtain the results reported in our previous study. For the direct sulfation of $CaCO_3$, Z is equal to 1.24 (based on densities for $CaSO_4$ and $CaCO_3$ given in Perry et al. (1984)). For very small values of ϵ_0 and $\epsilon(r, t)$ – as it was found to be the case for the limestones used in our direct sulfation experiments – Eq. (4.11) can be simplified to

$$a^{s+1} = Z a_0^{s+1} + (1 - Z) a_c^{s+1} \quad (4.12)$$

Integration of Eq. (4.3), using Eqs. (4.5) and (4.6) as boundary conditions, yields

$$\int_{a_c}^a (1/D_e(r, t) r^s) dr = (c_b - c_c)/a_c^s R_s(c_c) \quad (4.13)$$

With the kinetics of the reaction (i.e., the form of $R_s(c)$) and $D_e(r, t)$ known, Eqs. (4.7), (4.10), (4.12) (or (4.11) given ϵ_0 and $\epsilon(r, t)$), and Eq. (4.13) can be solved numerically to determine the evolution of the conversion with time. In the application of the mathematical model to the direct sulfation of limestones, it will be assumed that D_e is determined only by the distance from the external surface of the particles, x , i.e.,

$$D_e(r, t) = D_e(a(t) - r) \equiv D_e(x); \quad x = a - r \quad (4.14a, b)$$

Some results regarding the dependence of the model predictions on the model parameters are shown in Fig. 4.1 for $D_e(x) = \alpha \exp(-\beta x)$. The results shown in the figure are for sulfation of 53-62 μm limestone particles of spherical shape ($s = 2$) at 850°C with 1500 $mL/m^3 SO_2$. The reaction rate was assumed to be given by Eq. (4.8), and the various combinations of n and k_s were chosen so that the initial reaction rate ($k_s c_b^n$) was the same for all cases and similar in value to the rate measured by Krishnan and Sotirchos (1993) for Iceland spar at 850°C and 1500 $mL/m^3 SO_2$. Therefore, differences among the various curves of Fig. 4.1 are solely due to the existence of diffusional limitations in the product shell.

Figure 4.1: Conversion-time trajectories predicted by the variable diffusivity shrinking-core model for several forms of effective diffusivity varying exponentially along the product layer for identical kinetics. Results shown are for sulfation of spherical ($s = 2$) particles ($53\text{--}62 \mu\text{m}$) at 850°C and $1500 \text{ mL}/\text{m}^3$ of SO_2 . The units of k_s are $\text{mol}^{0.6}/\text{cm}^{0.8} \cdot \text{s}$.

As expected, lowering the value of α (i.e., the effective diffusivity at the external surface of the particles) causes a proportionate change to the value of effective diffusivity at all depths and slows the overall reaction. For higher values of α (in other words, lower diffusional resistance), the kinetics of the reaction controls the process until the shell thickness becomes large enough to effect significant diffusional limitations. Thus, notice that there is confluence of all curves (for different combinations of n and k_s) for $\alpha = 10^{-3} \text{ cm}^2/\text{s}$ up to nearly 20% conversion, whereas the four curves diverge from each other much earlier for $\alpha = 10^{-5} \text{ cm}^2/\text{s}$.

Parameter β dictates how the effective diffusivity falls with distance in the product shell, and therefore, how the average resistance for diffusion in the product layer increases with the product layer thickness. A value of $\beta = 0$ was employed in our previous study, but, as we have already mentioned, it failed to bring any agreement between theory and experiment. Nonzero values of β cause the overall rate of reaction to decrease faster with time, and our computations revealed that this effect can be intensified by increasing β . Therefore, the variable diffusivity shrinking-core is capable of describing, at least qualitatively, the behavior seen in our experimental data.

It can be shown using the model equations that for a diffusion coefficient varying according to Eq. (4.14), the variation of the product layer with time for slab geometry particles ($s=0$) is independent of the particle size. This is also approximately valid for other geometries (spherical or cylindrical particles) for relatively small product layer thickness, that is, before the curvature of the particles (see Eqs. (4.11), (4.12), and (4.13)) starts to influence significantly the predictions of the mathematical model. Product layer thickness, d , vs. time curves can be constructed from experimentally measured conversion vs. time profiles by using Eqs. (4.10) and (4.12) to compute a and a_c (and hence $d = a - a_c$) at each conversion level. This procedure was applied to our experimental data, and Fig. 4.2 presents the variation of the product layer thickness with time for three sizes of Iceland spar particles reacted at 850°C under $1500 \text{ mL}/\text{m}^3$ of SO_2 . In order to get the results of Fig. 4.2, the particles were assumed to be of spherical geometry, in which case $d = a_0[(Z + (1 - Z)(1 - X))^{1/3} - (1 - X)^{1/3}]$. This geometry was also employed for all other results we will present in this study.

Figure 4.2: Development of product layer thickness for Iceland spar sulfated directly at 850°C and 1500 mL/m³ of SO₂ in an atmosphere of 70% CO₂(mol%).

The results of Fig. 4.2 show that the product layer has the same thickness at a given time for all particle sizes during the initial stages of the reaction, thus supporting our assumption that the variation of the diffusivity is given by Eq. (4.14). Significant differences among the three d vs. t curves appear only as the product layer thickness increases, and curvature starts to influence significantly the behavior of small particles. Qualitatively similar results to those shown in Fig. 4.2 were obtained from the experimental data for all other cases involving Iceland spar and Georgia marble particles. The product layer also developed at the same rate during the initial stages of the reaction of the 88-105 and 297-350 μm particle size ranges of Greer limestone samples, but 53-62 μm particles of this solid tended to react much faster. This behavior can be seen in Fig. 4.3 which presents product layer thickness vs. time curves for Greer limestone particles reacted at 850°C under 1500 mL/m^3 of SO_2 . Lack of confluence between the smallest particle size range and the other two size ranges was seen at all reaction conditions for the Greer limestone sample. A similar behavior was observed in sulfation data of calcined samples of the same solid (Sotirchos and Zarkanitis, 1992).

All these results indicate that the small Greer limestone particles react differently from all other samples used in our experiments. The origins of this difference in behavior most probably lie in the different petrographic texture of the three solids. As it was pointed out in previous studies (Zarkanitis and Sotirchos, 1992; Krishnan and Sotirchos, 1993), petrographic characterization revealed that whereas Georgia marble and Iceland spar exist in the form of coarse, mm-size calcitic grains and large single crystals, respectively, the structure of Greer limestone is spanned by small calcitic grains, a few μm in size. For the particle sizes used in our experiments, therefore, each Georgia marble or Iceland spar particle is essentially part of a single grain, while each Greer limestone particle is an aggregate of small grains. Since the small Greer limestone particles are only a few grains thick, the mechanical stresses that are developed in their interior by the formation of a bulkier solid product could cause movement of the individual grains relative to each other and particle expansion. This in turn would reduce the average resistance for diffusion in the intraparticle space and lead to larger conversions than those expected from the behavior of larger particles.

Figure 4.3: Development of product layer thickness for Greer limestone sulfated directly at 850°C and 1500 mL/m³ of SO₂ in an atmosphere of 70% CO₂(mol%).

It follows from Eq. (4.7) that a similar growth rate for the product layer implies similar reactant concentrations at the reaction front. Fig. 4.4 gives reactant concentration at the interface (c_c) vs. time curves obtained from the experimental conversion vs. time data for Greer limestone particles reacted at 750°C and $6000\text{ mL}/\text{m}^3\text{SO}_2$. The conversion values were converted to concentration by using Eq. (4.10) to compute a_c , differentiating the $a_c(t)$ function to get (da_c/dt) , and solving Eq. (4.7) to find c_c . IMSL routines CSAKM and CSDER, based on a method by Akima (1970), were used to compute the derivative from the values of a_c at the sampling time instants. The k_s and n values for each solid were those obtained from the initial reaction rate data in our previous study and are listed in Table 4.1. In agreement with the results of Fig. 4.3, it is seen that the concentration of SO_2 at the reaction front has similar values for the two larger sizes. However, the concentration for the $53\text{--}62\text{ }\mu\text{m}$ particles is much higher than that of the other two size ranges, implying the existence of a much smaller resistance for diffusion in the product layer of the small particles. The different behavior of the small Greer limestone particles will be discussed in more detail during the analysis of our experimental data using the variable diffusivity shrinking-core model.

Rate Constant ($\text{mol}^{0.6}/\text{cm}^{0.8} \cdot \text{s}$)			
Temp. ($^\circ\text{C}$)	GL	GM	IS
750	9.06×10^{-6}	3.04×10^{-6}	2.28×10^{-6}
850	3.83×10^{-5}	9.53×10^{-6}	7.77×10^{-6}

Table 4.1: Reaction Kinetics at 750 and 850°C , $n = 0.4$. GL=Greer limestone, GM=Georgia Marble, and IS=Iceland Spar.

4.3. Parameter Estimation Procedure

The order of the reaction with respect to SO_2 , n , and the intrinsic reaction rates, k_s , have been estimated by Krishnan and Sotirchos (1993), and the procedure used for their estimation is described in detail there. The stoichiometric volume ratio, Z , can be estimated from the composition of the precursor, but for high purity stones – as it is the case here – it can be approximated by the ratio of the molar volumes of CaSO_4 to CaCO_3

Figure 4.4: Concentration of SO₂ at the reaction interface for Greer limestone sulfated directly at 750°C and 6000 mL/m³ of SO₂ in an atmosphere of 70% CO₂(mol%).

(=1.24). The porosities of the unreacted and reacted solid are very low, and as a result, we can use Eq. (4.12) instead of Eq. (4.11) to relate a , a_0 , and a_c . Therefore, the sole parameter that needs to be determined is the effective diffusivity through the product shell.

Using the procedure that we used to obtain the results shown in Figs. 4.2-4.4, all the experimental conversion vs. time data obtained from our thermogravimetric analysis experiments can be converted to equivalent d vs. time, c_c vs. time, and a_c vs. time curves. Once the experimental data are available in these forms, Eq. (4.13) can be used to determine the effective diffusivity as a function of x . Using Eq. (4.8) and (4.14) and changing the integration variable from r to x , Eq. (4.13) is written

$$\int_0^d [1/(D_e(x)(a-x)^s)] dx = (c_b - c_c)/a_c^s k_s c_c^n \quad (4.15)$$

Eq. (15) can be written in the general form of Fredholm integral equations of the first kind as

$$\int_{p_1}^{p_2} F_1(t, x) F_2(x) dx = g(t) \quad (4.16)$$

by defining, $F_1(t, x) = 1/(a-x)^2$, $F_2(x) = 1/D_e(x)$, and $g(t) = (c_b - c_c)/a_c^2 k_s c_c^n$. $g(t)$ and $F_1(t, x)$ are known from the experimental data, and the objective is to find $F_2(x)$.

$F_2(x)$ can be expressed as a linear expansion of a set of known functions,

$$F_2(x) = \sum_{i=1}^N A_i \phi_i(x) \quad (4.17)$$

Eq. (4.17) is introduced in Eq. (4.16) to give

$$\sum_{i=1}^N A_i \int_{p_1}^{p_2} F_1(t, x) \phi_i(x) dx = g(t) \quad (4.18)$$

Application of Eq. (4.18) to M data points ($M > N$), using some quadrature formula to compute the integral appearing in it, yields an overdetermined set of linear equations

$$\mathbf{BA} = \mathbf{g} \quad (4.19)$$

which may be solved by using the least-squares method for A_i and, therefore, the form of $D_e(x)$. $\mathbf{B}$ is an $M \times N$ matrix, $\mathbf{A}$ is the N -dimensional vector of coefficients in the

expansion of $F_2(g)$, and g is an M -dimensional vector consisting of the right-hand side of Eq. (4.13) at the data points.

Unfortunately, the inversion of Eq. (4.16) is a well known ill-posed problem, and as a result, the above described procedure yields oscillatory solutions (Allison, 1979). This difficulty may be avoided by using a regularization method (Tikhonov and Arsenin, 1977). Such a method has been used, among others, by Brown and Travis (1983) to extract pore size distributions of porous media from effective diffusivity measurements. However, the application of the regularization method requires the values of $F_2(x)$ at the limits of integration (p_i), whereas such information is not available for the problem at hand. For this reason, we will use a method based on the concept of singular value decomposition of matrices (Golub and Van Loan, 1983), which can yield smooth solutions from the overdetermined set of equations (Eq. (4.19)) that result from discretization of Eq. (4.16) at the data points, but it does not require knowledge of $F_2(x)$ at p_i for its application.

Singular value decomposition decomposes an $M \times N$ matrix B into a product of three matrices, an $M \times N$ column-orthogonal matrix U , an $N \times N$ diagonal matrix with positive or zero elements W , and the transpose of an $N \times N$ orthogonal matrix V :

$$B = UWV^T; W = \text{diag}(w_1, w_2, \dots, w_m) \quad (4.20)$$

In terms of the elements of these three matrices, the least squares solution of Eq. (4.19) is given by

$$A = \sum_{i=1}^N (u_i \cdot g/w_i) v_i \quad (4.21)$$

where u_i and v_i are the i th columns of matrices U and V , respectively. When A is computed from Eq. (4.21), oscillating solutions arise because some of the singular values of the matrix B are very small, tending to amplify the experimental errors present in the data used to form B and g . Therefore getting smooth solutions from Eq. (4.21) amounts to filtering out the small singular values, that is, omitting from the summation the terms that correspond to small singular values. An algorithm described by Press et al. (1986) was employed to compute the singular value decomposition of matrix B and A from Eq. (4.21).

4.4. Results and Discussion

Monomials were used as basis functions ($\phi_i(x)$) in the expansion of $1/D_e(x)$ in order to obtain the results that we present and discuss in this section, that is, $1/D_e(x)$ was expressed as

$$1/D_e(x) = \sum_{i=0}^N A_i x^i \quad (4.22)$$

Preliminary calculations showed that for $N \geq 2$ the obtained estimates of $D_e(x)$ were close to each other, and thus, it was decided to employ $N = 2$ (in other words, use a quadratic approximation for $1/D_e(x)$) in all cases. Of the three singular values obtained for each case, the term corresponding to the smallest singular value in Eq. (4.21) was set equal to zero to get the solution. Typically, the smallest singular value was from 6 times to an order smaller than the middle singular value. For example, the three singular values used for Greer limestone at 850°C and 1500 mL/m^3 using the results for the larger two size ranges were 9.89×10^{-2} , 1.45×10^{-2} , and 1.64×10^{-3} . On the other hand, Iceland spar reacted at 850°C and 6000 mL/m^3 had singular values of 4.11×10^{-3} , 1.33×10^{-3} , and 2.61×10^{-4} . The solution obtained by omitting the contribution of the smallest singular value proved to be smoother and better, from a physical standpoint, than that resulting from SVD with all three singular values since it exhibited neither irregular (nonmonotonic) variation of $D_e(x)$ with depth nor negative values of effective diffusivity. It should be pointed out that both effective diffusivity functions (that is, obtained with three or two singular values) gave, both qualitatively and quantitatively, similar conversion vs. time curves when they were used in the mathematical model, indicating that our decision to work only with two singular values was justified. Unless mentioned otherwise, the effective diffusivity results and functions we will present and discuss hereafter were obtained using conversion vs. time data for three particle size ranges (53-62, 88-105, and 297-350 μm) and with the right-hand side of each equation in Eq. (4.19) normalized to 1.

Diffusivity Results

Figs. 4.5 and 4.6 show the variation of effective diffusivity of SO_2 along the distance from the external surface for Greer limestone, Georgia marble, and Iceland spar for the two

temperatures used in the experiments (750 and 850°C) for a bulk concentration of 1500 and 6000 mL/m³ of SO₂, respectively. The variation of $D_e(x)$ is terminated at the largest product thickness obtained for each case experimentally. For example, after sulfation for 150 min at 750°C, the Iceland spar samples had a product layer thickness of only 1 μm, and thus, $D_e(x)$ values are shown only within this window of product layer thickness. On the other hand, Greer limestone particles reacted at 850°C and 1500 mL/m³ developed a product layer thickness of approximately 6 μm during 150 min sulfation.

The results of Figs. 4.5 and 4.6 show that the effective diffusivity decreases very fast with the distance from the external surface of the particles, but its rate of decrease varies widely among the three stones. The value of effective diffusivity at the maximum depth (6 μm) for Greer limestone at 850 °C and 1500 mL/m³ is about an order in magnitude lower than the value at the external surface of the particles. A similar drop in the value of effective diffusivity is seen for Iceland spar reacted at 750°C and 1500 mL/m³ along a product layer only 1 μm thick. For most cases shown in Figs. 4.5 and 4.6, the effective diffusivity at the maximum depth was 3 to 5 times smaller than the value at the external surface. The fall in the value of effective diffusivity toward the unreacted core leads to increasing resistance for diffusion in the product shell with increasing conversion, and this in turn makes possible to obtain an agreement between theory and experiment.

Despite the sharp decrease that the effective diffusivity experiences with the distance from the surface, the value seen at the maximum depth for each case is generally two to three orders of magnitude higher than the value of effective diffusivity through the product layer for the reaction of the calcines of the same solids (Sotirchos and Zarkanitis, 1992), which had a value of 10⁻¹² m²/s on the average. The higher diffusivity of SO₂ through the product layer formed during direct sulfation must obviously be the reason for which this reaction proceeds with rate comparable to that of the reaction of calcined limestones with SO₂ even though it involves essentially nonporous solids.

Our experimental results (Krishnan and Sotirchos, 1993) showed that calcium utilization was the highest for Greer limestone, followed by Georgia marble and Iceland spar. Pore structure characterization and petrographic examination of the three solids revealed that their porosity decreased and their average grain size increased in the same order.

Figure 4.5: Form of effective diffusivity obtained for the three stones reacted under 1500 mL/m^3 of SO_2 in an atmosphere of 70% CO_2 (mol%) and the two temperatures of 750 and 850°C from the parameter estimation procedure.

Figure 4.6: Form of effective diffusivity obtained for the three stones reacted under 6000 mL/m^3 of SO_2 in an atmosphere of 70% CO_2 (mol%) and the two temperatures of 750 and 850°C from the parameter estimation procedure.

It was thus postulated that the structure of the precursor influences the structure of the product layer that is formed during direct sulfation, yielding a more open structure and, hence, lower diffusional resistance in the direction Iceland spar $\rightarrow$ Georgia marble $\rightarrow$ Greer limestone. The relative values of effective diffusivities that were extracted from our parameter estimation scheme corroborate this hypothesis. It is seen in Figs. 4.5 and 4.6 that under identical reaction conditions, Greer limestone always has the highest value of effective diffusivity at a given depth from the surface. The diffusivity values for Georgia marble and Iceland spar are much lower than that of Greer limestone with the product layer of Georgia marble offering lesser mass transport resistance than Iceland spar at a certain thickness. It is interesting to point out that the very same order was found to be generally followed by the solid product diffusivities that were extracted from the analysis of reactivity data for the sulfation of the calcines of the same solids by Sotirchos and Zarkanitis (1992).

Model predictions obtained using the estimated form of $D_e(x)$ in Fig. 4.5 are shown in Fig. 4.7 for Iceland spar particles directly sulfated at 850°C under 1500 mL/m^3 of SO_2 . Very good agreement between the model and experimental results is seen for the two larger size ranges over the entire time period and also for the smallest size range up to a conversion level of about 10%. At higher conversion levels, the model tends to overpredict the conversion for the smallest size range, and therefore, the value of effective diffusivity that would be obtained from our parametric estimation procedure using the conversion vs. time results for the $53\text{-}62\text{ }\mu\text{m}$ particles only would be smaller than that obtained for all three size ranges, i.e., the one shown in Fig. 4.5 and used to get the results of Fig. 4.7. This point will be discussed in more detail in the following figures.

Fig. 4.8 shows the comparison between model predictions and experimental results for Georgia marble particles reacted at 750°C and 6000 mL/m^3 of SO_2 . It is seen from Fig. 4.8 that model and experiment agree very well at lower conversion levels, where presumably the reaction is under kinetic control. At higher conversion levels, though, where diffusion through the product layer starts to dominate, the model results tend to underpredict the conversion profile for the larger two size ranges but overpredict it for the $53\text{-}62\text{ }\mu\text{m}$ size range. The reason for this behavior can be seen in Fig. 4.9 which gives the estimated form

Figure 4.7: Comparison of model predictions with experimental results for Iceland spar directly sulfated at 850°C and 1500 mL/m³ of SO₂ in an atmosphere of 70% CO₂(mol%).

of $D_e(x)$ when all three particle size ranges are employed and when each size is treated individually. We see in Fig. 4.9 that the value of $D_e(x)$ obtained for all three particle size ranges (solid line) is always higher at a given depth than the value obtained by employing only the 53-62 μm size range. Thus, using the functional form of effective diffusivity based on all three size ranges leads to higher mass transport rates for the smallest size range and causes the model to overpredict the conversion-time profile. Similarly, the underprediction of the conversion for the 88-105 and the 297-350 μm sized particles can be explained on the basis of the difference between the diffusivity for all sizes and the diffusivities for each of the larger sizes individually.

Since we had observed that the 53-62 μm size range for the Greer limestone sample behaved differently from the other size ranges under a given set of reaction conditions (temperature and concentration), the experimental conversion vs. time data for the smallest size range were excluded in obtaining the functional form of effective diffusivity; that is, only the larger two size ranges were employed in our parameter estimation procedure for Greer limestone samples. Figs. 4.10 and 4.11 show the comparison between model predictions and experimental results for Greer limestone reacted at 850°C and under a concentration of SO_2 of 1500 and 6000 mL/m^3 , respectively. Very good agreement is obtained between theory and experiment for the larger two particle size ranges, but the model underpredicts badly the results for the smallest size range. This behavior lends further support to our conclusion that the smallest Greer limestone particles form a more open product layer structure, reacting almost as unconsolidated structures, than the larger two size ranges.

The results shown in Figs. 4.10 and 4.11 can be better understood and explained with the aid of Fig. 4.12, which shows the comparison between the form of effective diffusivity obtained by employing the larger two size ranges and that obtained by treating the size ranges individually. The individual results for the larger two particle size ranges follow closely the result obtained by combining the two size ranges, and thus, there is insignificant disparity between model and experiment when the form of $D_e(x)$ for the larger two size ranges is employed in the model. On the other hand, the value of effective diffusivity at a given radial depth in the product of the 53-62 μm particle is much higher than the value of effective diffusivity obtained by combining the larger two size ranges. The higher mass

Figure 4.8: Comparison of model predictions with experimental results for Georgia marble directly sulfated at 750°C and 6000 mL/m³ of SO₂ in an atmosphere of 70% CO₂(mol%).

Figure 4.9: Comparison of the effective diffusivity profiles obtained for Georgia marble reacted at 750°C and $6000 \text{ mL}/\text{m}^3$ of SO_2 in an atmosphere of 70% CO_2 (mol%) between employing all three size ranges together and treating each size range individually.

Figure 4.10: Comparison of model predictions with experimental results for Greer limestone directly sulfated at 850°C and 1500 mL/m³ of SO₂ in an atmosphere of 70% CO₂(mol%).

Figure 4.11: Comparison of model predictions with experimental results for Greer limestone directly sulfated at 850°C and 6000 mL/m³ of SO₂ in an atmosphere of 70% CO₂(mol%).

transport resistance used in the model is the reason for having much lower conversions predicted by the model for the smallest size range in Figs. 4.10 and 4.11. Similar behavior to that seen in Figs. 4.10 and 4.11 was observed for all cases concerning Greer limestone. It should be pointed out, however, that the estimated form of $D_e(x)$ for the case of Greer limestone with all three sizes taken into account was not much different from that obtained for the 88-105 and 297-350 μm sizes only. The parameter estimation scheme tended to favor the results for the larger two sizes since they were in most cases consistent with each other. This behavior can be seen in Fig. 4.7 where, although all results were used to determine the form of $D_e(x)$, the model predictions overpredict the results for the smallest size range only.

A different way of verifying the model results is shown in Fig. 4.13 which shows the comparison between the growth of the product layer obtained from the experimental conversion-time results and that given by the model using the effective diffusivity obtained from the parameter estimation scheme. The results presented are for the three solids (88-105 μm particles) reacted at 850°C under 1500 mL/m³ of SO₂ and 70% CO₂. Excellent agreement is found for all three solid samples between model predictions and experimental results.

Effect of Temperature and Concentration on Diffusivity

The experimental conversion vs. time revealed that temperature had a strong influence on the overall reaction rate not only in the earlier stages of the reaction but also at larger reaction times. Since the overall process is initially under kinetic control, the temperature of reaction was found to have a strong effect on the reaction rate constant (see Table 4.1). However, at the later stages of the reaction, the process is chiefly controlled by diffusion in the product layer, and consequently, the influence of temperature on the reaction trajectories is almost exclusively due to variations in the value of effective diffusivity with temperature. Indeed, as it can be seen in Figs. 4.5 and 4.6, a fall of nearly an order in magnitude takes place in the value of effective diffusivity at a given depth from the external surface for all reaction conditions with a decrease in temperature from 850 to 750°C.

Figure 4.12: Comparison of the effective diffusivity profiles obtained for Greer limestone reacted at 850°C and 6000 mL/m³ of SO₂ in an atmosphere of 70% CO₂(mol%) between employing the larger two size ranges together and treating each size range individually.

Figure 4.13: Comparison of the growth of the product layer predicted by the model and that obtained from experiments for the three samples (88–105 μm) reacted at 850°C and 1500 mL/m³ of SO₂ in an atmosphere of 70% CO₂(mol%).

The diffusivities calculated for the solids under identical reaction conditions but at different concentrations of SO_2 in the bulk (1500 and 6000 mL/m^3) differ significantly for a given distance from the external surface (compare the results of Figs. 4.5 and 4.6). The effective diffusivity of SO_2 through the product layer at a certain depth from the surface for reaction under 6000 $mL/m^3 SO_2$ is in most cases about two to three times smaller than the value estimated at 1500 mL/m^3 of SO_2 at the same reaction temperature and for the same solid. There are two possible explanations, not necessarily mutually exclusive, for this occurrence: 1) The concentration of the gaseous reactant (SO_2) in the bulk may be influencing the structure of the product layer formed during direct sulfation, with the higher concentrations leading to denser layers of solid product; 2) the effective diffusivity in the product layer may be a function of the concentration. In our opinion, the first of these two explanations is the most plausible one since the effective diffusivities that are shown in Figs. 4.5 and 4.6 are comparable to those that one would expect for Knudsen diffusion on the basis of the pore structure characterization data that we presented in the previous study, whereas the coefficient for Knudsen diffusion is independent of the concentration of the diffusing species.

If the effective diffusivity in the product layer is a function of the concentration, it is obvious that for a rigorous application of the variable diffusivity shrinking-core model, the diffusivity would have to vary with both the concentration and the distance in the product layer. It is relatively straightforward to extend the mathematical model so that it allows for a concentration and distance dependent diffusivity and to devise a parameter estimation scheme that would extract D_e as a bidistributed parameter from the experimental data. However, examination of the concentration profile in the product layer and of its evolution in time revealed that the concentration at a given depth from the external surface varied, with the exception of a relatively small time interval after the reactant reached this depth, within a relatively narrow range. Therefore, even if D_e were allowed to vary with both distance and concentration, the obtained results would not be much different, qualitatively and quantitatively, from those shown in Figs. 4.5 and 4.6. Fig. 4.14 shows the concentration profile at 0.5, 1.0, and 2.0 μm from the external surface of the particles, as it is given by the mathematical model, for Greer limestone (53-62 μm) reacted at 750°C at the two

concentrations of 1500 and 6000 mL/m^3 of SO_2 . In agreement with the general remarks made above, it is seen that after the reactant reaches a certain depth within the particles, the concentration there rises very fast reaching a 'plateau' value within a very small, on a relative basis, interval of time for both values of bulk concentration.

The product layer diffusivity was assumed to follow an Arrhenius-type dependence on temperature, and the activation energy was estimated as a function of distance from the external surface of the particles for the various cases of Fig. 4.5. The obtained results are shown in Fig. 4.15. Results are shown only for the range of product layer thickness covered experimentally at 750°C where the lower rates of reaction were observed. It is seen from Fig. 4.15 that at a given depth, Iceland spar has the highest activation energy and Greer limestone the smallest. Therefore, temperature plays a stronger role in influencing the diffusion of SO_2 and, hence, the reaction rate for Iceland spar than for Georgia marble, with Greer limestone being the least affected of the three solids. From experimental data for the sulfation of the calcines of the same solid in the same temperature range, the activation energy for the product layer diffusivities for the $CaO - SO_2$ reaction was found to be 83, 188, and 125 kJ/mol for Greer limestone, Georgia marble, and Iceland spar, respectively (Sotirchos and Zarkanitis, 1992). Comparison of these values with the results of Fig. 4.15 shows that the effect of temperature on the product layer diffusivity during direct sulfation is qualitatively similar to that for the sulfation of the calcines for the Greer limestone and the Georgia marble solids, but it is much stronger in the case of Iceland spar. (Similar values of activation energy of product layer diffusivity were reported by several investigators for other calcined limestones: e.g., 142 kJ/mol by Hartman and Trnka (1980) and 146 kJ/mol by Marsh and Ulrichson (1985)).

It is seen in Fig. 4.15 that for Georgia marble and Iceland spar, there occurs an increase in activation energy with increasing distance from the external surface of the particles. Greer limestone, on the other hand, manifests decreasing activation energy towards the reaction interface. As we mentioned during discussion of the concentration effects on the effective diffusivity values, the mechanism of mass transport in the product layer is most probably Knudsen diffusion. Therefore, the temperature effects on the effective diffusivity seen in Fig. 4.15 in terms of the activation energy should be viewed as indicative

Figure 4.14: Concentration profiles obtained at fixed depths from the external surface of Greer limestone ($53\text{--}62 \mu\text{m}$) particles reacting under different bulk concentrations of SO_2 (1500 and 6000 mL/m^3) at 750°C in an atmosphere of $70\% \text{ CO}_2(\text{mol}\%)$.

Figure 4.15: Variation of activation energy of product layer diffusivity with product thickness for the three samples reacting under a bulk concentration of SO_2 of 1500 mL/m^3 in an atmosphere of 70% CO_2 (mol%).

not of the effect of temperature on the diffusion process but rather of the effects of temperature on the structure of the product layer. Examination of sulfated (directly) limestone samples by scanning electron microscopy by Hajaligol et al. (1988) suggested that the structure of the product layer became coarser and more open with increasing temperature, in agreement with the results of Figs. 4.5 and 4.6. Hajaligol et al. postulated that since an increase in the temperature increases the rate of reaction, it is the higher rate of CO_2 evolution at higher temperature that is responsible for the development of a more open structure. However, this explanation does not account for other gaseous species involved in the reaction since, as Eq. (4.2) that describes the overall reaction during direct limestone sulfation shows, there is net gas flow toward the unreacted core and not away from it – there is a loss of $1/2$ mole of gas per each mole of SO_2 consumed.

In order to be able to obtain a better explanation for the effect of temperature and concentration on the structure of the product layer and, therefore, on the resistance for diffusion of SO_2 through it, one must consider the processes involved in the formation of the $CaSO_4$ layer during direct sulfation. Since the solid product occupies more space than the solid reactant, the solid product formed at the reaction interface must always push against a progressively thicker shell to accommodate itself at the interface. This scenario was used to explain the decreasing diffusivity with increasing distance from the external surface, but it can also be used to explain the effect of concentration at a given temperature and of temperature at a given concentration. A higher concentration leads to a much higher rate of reaction and, therefore, of production of $CaSO_4$ at the interface. The higher rate of $CaSO_4$ formation in turn leads to more compact layers of solid product at a given depth since it gives less time to the grains that comprise the product shell to rearrange themselves to accommodate the added solid volume at the interface. Higher rates of formation of $CaSO_4$ are also encountered at higher temperatures, but temperature is also expected to increase the 'mobility' of the grains in the product layer, thereby making it easier for them to move to accommodate the newly formed solid.

4.5. Summary and Concluding Remarks

A detailed analysis of the process of mass transport within the product shell formed

during the limestone- SO_2 reaction was presented in this study. Experimental results obtained in an earlier investigation (Krishnan and Sotirchos, 1993) for the direct sulfation of three stones of high ($> 95\%$) calcium carbonate content (Greer limestone, Georgia marble, and Iceland spar) were used in the analysis. Characterization of the pore structure of the partially reacted solid in our previous study by N_2 sorption experiments revealed a shrinking-core behavior for the limestone- SO_2 reaction, but analysis of the data with a constant diffusivity shrinking-core model failed to bring theory and experiment into agreement. It was observed that a model incorporating an increasing mass transport resistance in the product shell with time or, equivalently, conversion was needed to make the model predictions agree with the experimental results. Further analysis of the experimental data, performed in the present study, indicated uniform growth rate of the product layer for different particle size ranges, for small values of product layer thickness, at a given set of reaction conditions. Moreover, the calculated concentration of SO_2 at the reaction core had similar values for the different particle size ranges at a given reaction time. These two observations taken together indicated that the average mass transport resistance through the product shell was a function of the thickness of the shell only (without accounting for particle curvature effects).

On the basis of the above results, the direct sulfation of limestone was modelled by a shrinking unreacted core with a diffusion coefficient varying locally with the distance from the external surface of the particles. The functional dependence of the effective diffusivity on the distance in the product layer was determined by fitting the model predictions to the experimental data for three particle sizes for each solid and each set of reaction conditions (temperature and concentration). The parameter estimation scheme gave rise to an ill-posed problem – it was equivalent to the inversion of a Fredholm equation of the first kind – and a procedure based on singular value decomposition was formulated to circumvent this difficulty. Very good agreement between experimental results and model predictions was generally observed when the estimated functional form of effective diffusivity was introduced in the variable diffusivity shrinking-core model. The only exception was seen for the 53-62 μm size particles of Greer limestone at all reaction conditions, which appeared to exhibit much lower resistance for diffusion than the other two other two size ranges (88-

105 and 297-350 μm) of the same solid.

The value of effective diffusivity in the product layer for the limestone- SO_2 reaction fell by an order in magnitude for some cases and by two to three times for all others from the external surface to the maximum depth seen in the experiments. Despite this significant drop, the value of effective diffusivity at the maximum depth was at least two to three orders of magnitude higher than the value of product layer diffusivity for the $\text{CaO} - \text{SO}_2$ reaction. It is thus believed that the formation of a more open product layer is the main reason for having significant reaction rates in the limestone- SO_2 reaction despite having an essentially nonporous reactant. The effective diffusivity at a certain depth was always the highest for Greer limestone, with Iceland spar displaying the lowest value. Not surprisingly, the overall reaction rates for the three solids followed the same order. It is believed that the differences in the value of effective diffusivity for the three solids are due to the influence of the natural porosity and petrographic texture of the limestones on the structure of the product shell.

The effective diffusivity was found to be a strong function of the temperature and of the concentration of SO_2 in the bulk of the gas phase. Specifically, it increased with increasing temperature but decreased with increasing concentration. The results were in agreement with the observed sensitivity of the experimental conversion vs. time results on temperature and concentration in our earlier investigation. Since the estimated effective diffusivities were comparable to those expected for Knudsen diffusion from the pore structure data, we believe that the main reason for the strong influence of concentration and temperature on the effective diffusivity is their effects on the structure of the product layer.

4.6. Notation

a	outer radius of the particle, cm
a_0	initial radius of the particle, cm
A	N -dimensional vector of coefficients in the expansion of $F_2(l)$
A_i	coefficients of polynomial describing the functional form of effective diffusivity in the product layer

a_c	radius of the unreacted core, cm
B	matrix of dimension $M \times J$ (see Eq. 4.19)
c	concentration of SO_2 in the product layer, mol/mL
c_b	concentration of SO_2 in the bulk, mol/mL
c_c	concentration of SO_2 at the reaction interface, mol/mL
c_s	concentration of SO_2 at the surface of the particle, mol/mL
d	thickness of the product layer ($a - a_c$), cm
$D_e(x)$	effective diffusivity (local) of SO_2 in the product layer, cm^2/s
D_m	molecular diffusivity of SO_2 -gas mixture, cm^2/s
$F_1(t, x)$	equal to $1/(a - x)^2$ by definition
$F_2(x)$	equal to $1/D_e(x)$ by definition
g	M -dimensional vector consisting of the right-hand side of Eq. (4.13)
$g(t)$	equal to $(c_b - c_c)/a_c^2 k_s c_c^n$ by definition
k_g	external mass transfer coefficient, cm/s
k_s	intrinsic reaction rate constant, $mol^{0.6}/cm^{0.8} \cdot s$
M	number of data points at which Eq. (4.18) is applied
N	number of terms in the linear expansion of $F_2(l)$
n	order of reaction with respect to SO_2
r	radial distance along the product layer, cm
R_s	reaction rate per unit surface area, $mol/s/cm^2$
s	shape factor - 0: slab; 1: cylinder; 2: sphere
Sh	Sherwood number defined as $2k_g a/D_m$
t	real time, s
v_s	molar volume of unreacted core, mL/mol
x	distance in the product layer from the external surface, cm
X	conversion of the reacting solid
Z	volume of dense reacted solid phase per unit volume of dense unreacted solid phase
Greek	
α	value of diffusivity at external surface of particle, $x = 0$ in Fig. 4.1, cm^2/s

- β parameter describing variation of diffusivity along product depth in Fig. 4.1, cm^{-1}
- ϵ_0 porosity of the unreacted solid
- $\epsilon(r, t)$ porosity of the product shell at position r and time t

4.7. Literature References

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5. EFFECTIVE DIFFUSIVITY CHANGES DURING CALCINATION, CARBONATION RECALCINATION, AND SULFATION OF LIMESTONES

5.1. Introduction

Sulfation of limestones is an important gas-solid reaction used for controlling sulfur dioxide emissions from fluidized-bed coal combustors. The limestone precursors used for reducing emissions undergo several changes in their structure depending on the operating conditions of the combustor. In atmospheric fluidized-bed combustors (AFBC), limestone (primarily $CaCO_3$) decomposes almost instantaneously (reaction (5.1)) to yield its calcined form (primarily CaO):

The calcine then reacts with SO_2 leading to desulfurization of the flue gas (reaction (5.2)):

A different situation occurs in a pressurized fluidized-bed combustor (PFBC) where on account of the high partial pressures of CO_2 , decomposition of $CaCO_3$ (reaction (5.1)) is inhibited, and direct reaction of $CaCO_3$ with SO_2 takes place instead. Since the temperature and CO_2 partial pressure are not uniform in a PFBC unit, decomposition of $CaCO_3$ (reaction (5.1)) may occur in certain regions of the reactor, while the decomposed limestone may in turn react with SO_2 like in the AFBC units (reaction (5.2)) or undergo recarbonation in regions of high CO_2 concentration or low temperature according to the reaction (reverse of reaction (5.1)):

The above reactions are typical examples of noncatalytic gas-solid reactions, involving a porous structure which evolves both temporally and spatially. Limestone precursors are essentially nonporous with very small surface areas. The decomposition reaction (reaction (5.1)) leads to formation of well developed pore structure, with high values of porosity and internal surface area. The sulfation of the calcine (reaction (5.2)) is a very complex reaction characterized by pore closure and formation of inaccessible pore space, both being

a consequence of the fact that CaSO_4 (the primary solid product) occupies considerable more space than CaO (the primary solid reactant). The ratio of the volume occupied by the solid product to that of the solid reactant, according to the stoichiometry of the reaction, is approximately 2.7 (using data from Perry et al. (1984)). The additional solid volume formed during sulfation reduces the pore space of the calcine, eventually leading to pore closure. If the reaction occurs under internal diffusion control, sulfation mainly occurs at the periphery of the porous particles, causing pore blockage at the outer surface while there is much open pore space left in the interior. However, even under kinetic control, it is possible small pores that act as feeder pores to clusters of large pores to get plugged, leading to formation of locally inaccessible pore space (Sotirchos and Zarkanitis (19920, (1993)). This situation may also be encountered in reaction (5.33) though not to the same extent as in the sulfation of calcines.

Pore closure and formation of inaccessible pore space cause incomplete utilization of the calcine to levels well below what is stoichiometrically possible. For improved sulfur capture and combustor operation, reaction conditions must be optimized to maximize the utilization of the sorbent. Limestone precursors in the size range of 50-500 μm are typically used for the purpose of desulfurization in fluidized-bed combustors. Sulfation of particles of this size usually occurs in the regime where the diffusion resistance of the reactants through the pore space is one of the important controlling parameters of the reaction (Sotirchos and Zarkanitis (1992)). Therefore, modeling of the sulfation and of the other sorbent reactions for combustor design with the aim of enhancing sorbent efficiency almost always requires knowledge of the intraparticle mass transport resistance in the solid.

Theoretical estimates of effective diffusivities of gases through porous medium have been known to significantly differ from the experimentally measured values, at times by more than an order in magnitude (Haynes (1988)), necessitating the development of reliable experimental techniques to obtain information on the intraparticle mass transport process. Experimental values of effective diffusivity of CO_2 through porous CaO have been obtained by various approaches. Hills (1968) studied the mass transport of CO_2 through the porous CaO formed during the thermal decomposition of calcium carbonate (reaction (5.1)) in a thermobalance. Assuming a sharp interface at the reaction front, the diffusivity

of CO_2 through the calcined layer was obtained at various temperatures by measuring the transient weight change. However, despite the simplicity of the calcination reaction, there are conflicting views in the literature on its controlling mechanism (Narsimhan (1961); Hills (1968); Borgwardt (1985)). Therefore, the results obtained by Hills (1968) strongly depend on the validity of the model proposed for the calcination step. Campbell et al. (1970) measured the diffusion coefficient of CO_2 through hollow lime spheres prepared from spherical compacts of calcium carbonate with the porosity of the original compact ranging up to 0.66. Diffusion coefficients were measured directly in both the original compact and its calcined form in a manner similar to that of the Wicke-Kallenbach experiment (Wicke and Kallenbach, 1941). The diffusion coefficients measured by Campbell et al. cannot be used to obtain information about diffusion of gases in calcines of limestones or dolomites since it is difficult to isolate the individual mass transfer resistances, that is, through the pores of the original compact and through the pores formed during calcination.

Bardakci (1984) measured the effective diffusivity of argon through a calcined pellet in a Wicke-Kallenbach diffusion cell in the course of sulfation. The data were used to obtain the diffusivity of SO_2 through the porous layer by using the fact that under isobaric conditions the ratio of the fluxes of the two gases is equal to the inverse square root of the ratio of their molecular weights (Evans et al., 1961). The product layer diffusivity as a function of conversion was subsequently estimated from an expanding grain model based on the effective diffusivity of SO_2 through the reacting shell. Using the same experimental setup, effective diffusivities of Ar and N_2 were measured as a function of time during calcination (Bardakci and Gasner, 1984). Limestone pellets of large size were used in the study of Bardakci (1984) to measure diffusivities during the sequence of calcination and sulfation carried out in the Wicke-Kallenbach apparatus. As a result, only a relatively thin layer of the solid was reacted during sulfation, and thus, the measured transport resistance accounted for the resistances of both the reacted and unreacted sections of the pellet. To extract the value of the average effective diffusivity in the reacted section, additivity of the diffusion resistances in the reacted and unreacted sections was assumed, and the thickness of the reacted layer was determined from the average conversion of the pellet, the latter estimated with the aid of the grain model.

In view of the importance of intraparticle mass transport in the control of sulfur emissions from coal-fired power plants using limestones as the desulfurizing agent, an investigation of the diffusion resistance in calcined limestones is carried out in this study. Pulse chromatographic experiments are performed for this purpose by employing two different types of limestones. Different calcination temperatures are used to study the effect of calcination temperature on the internal pore structure and effective diffusivity of the calcine formed. Effective diffusivities through the carbonated and recalcined forms of the calcines are also measured to investigate changes in intraparticle mass transfer resistance. One of the limestone calcines is sulfated, and the effective diffusivity is measured at several conversion levels. The pore size distributions of all the solids used in this study are determined from mercury intrusion (using a Micromeritics, Autopore II 9220 system) and gas sorption experiments (using a Quantachrome Autosorb-1 unit). Employing the pore size distribution and the measured values of effective diffusivities, information about the connectivity of the pores is obtained using the effective medium theory-smooth field approximation approach of Burganos and Sotirchos (1987).

5.2. Materials and Sample Preparation

Two types of limestone were used as precursors to carry out diffusivity measurements in calcines, carbonated calcines, and sulfated calcines. The two limestones, each with a very high CaCO_3 content ($> 95\%$ by weight), were distributed by Greer Limestone Co. and Georgia Marble Co., and will be for brevity denoted as GL and GM respectively. From mercury porosimetry and gas sorption experiments, the limestones were found to be essentially nonporous in their natural states. Petrographic examination of the two stones showed differences in their grain structure, and details are given by Sotirchos and Zarkanitis (1992). Particles in the size range of 20-24 mesh (710 - 850 μm) were used to measure the diffusivities reported in this study.

The relatively large amounts of solid sample needed to pack the chromatographic column were prepared in a fluidized-bed reactor. A brief description of the preparation procedure is given in the following paragraphs. Details on the experimental set up and the procedure used for the preparation of the samples are presented by Krishnan (1993).

About 35 g of calcined limestone was needed to fill the chromatographic column chosen in our study. To obtain this amount, approximately 120 g of the uncalcined limestone precursor was calcined in the fluidized-bed reactor for 1 hr in six batches (for each limestone and reaction temperature) to produce the required amount of the calcined material. The sample was brought to the calcination temperature under CO_2 to prevent its decomposition during heating, and calcination was started by switching the CO_2 stream to a N_2 stream. The same procedure was used for the calcination of carbonated calcines. To verify that complete calcination had taken place, the reacted material and the fines trapped in a cyclone located at the outlet of the fluidized-bed reactor were weighed at the end of each experiment. The reacted material was resieved to isolate the size range (710-850 μm) that we used to pack the chromatographic column.

Carbonation of the calcines was carried out by reversing the procedure used for calcination of the precursors. Specifically, N_2 was passed through the reactor until the desired reaction temperature was attained, whereupon the N_2 stream was substituted with a CO_2 stream. Carbonation for each batch of material was carried out for 1 hr. Approximately 50 g of the calcined material was carbonated in four batches for each case investigated. The carbonated material in the reactor and the fines in the cyclone were weighed to estimate the conversion level attained upon carbonation. Again, the carbonated material was resieved to isolate the 710-850 μm size range.

To study mass transport in calcines undergoing sulfation, fresh samples of Georgia marble calcine were prepared at 850°C in batches of approximately 7.5 g of the precursor. The calcines were subsequently sulfated in batches of approximately 5 g at the same temperature using a mixture of 1500 ppm of SO_2 in air. The extent of sulfation was determined by measuring the concentration of SO_2 in the exit stream with the aid of a chromatograph (Varian 3300) equipped with an flame photometric detector. The calcines were sulfated for periods of 5, 15, 30, and 45 min which resulted in conversion levels of approximately 1, 2, 5, and 8 %, respectively. The conversion levels were also verified by weighing the reacted samples and the fines collected in the cyclone. The sulfated samples from the reactor were resieved after every stage to obtain the 710-850 μm size range.

A summary of the physical properties of the solids (calcined, carbonated, and recal-

cined) prepared in the ways described above is given in Table 5.1. The reported skeletal densities were determined from He pycnometry experiments. The skeletal densities so obtained were found to be in close agreement with those estimated from the composition of the solids using values for the pure compounds from Perry et al. (1984). The surface areas of the solids were estimated from multipoint BET analysis of the adsorption isotherm. All calcines are found to have similar surface areas, with the Greer limestone calcined at $750^{\circ}C$ exhibiting the highest and that calcined at $850^{\circ}C$ the lowest. Very small surface areas were estimated for the carbonated samples (both Georgia marble and Greer limestone). Recalcination increased the surface areas of the solid samples, but the measured values were much lower than those of the one-time calcined samples. The variations seen in the surface areas are discussed in more detail later using pore size distributions of the solids and other experimental data.

Solid	State	React. Temp. ($^{\circ}C$)	Conv. (%)	Porosity merc. int. (cc/cc)	Porosity N_2 sorpt. (cc/cc)	Porosity Eq. (5.4) (cc/cc)	Porosity moment (cc/cc)	Surface Area (m^2/g)	Skeletal Density (g/cc)
GL	calcined	850	100	0.51	0.48	0.54	0.52	45.09	3.29
GL	carbonated	850	74	0.07	0.02	0.14	0.14	0.66	2.78
GM	calcined	850	100	0.46	0.47	0.53	0.51	52.48	3.31
GM	carbonated	850	56	0.03	0.01	0.23	0.22	0.34	2.95
GM	recalcined	850	100	0.36	0.43	0.53	0.51	33.96	3.25
GL	calcined	750	100	0.51	0.49	0.54	0.52	56.19	3.24
GL	recalcined	750	100	0.34	0.44	0.54	0.52	27.36	3.27

Table 5.1: Data for Calcined, Carbonated, and Recalcined Limestones. GL=Greer limestone, GM=Georgia marble, and IS=Iceland spar.

The porosities reported in Table 5.1 were obtained employing three different approaches. Mercury porosimetry porosities were determined on the basis of intrusion volumes above an applied pressure of 80 psi (that is, for pores smaller than about $1 \mu m$).

Sorption isotherm porosities were obtained for pores of radius up to 1000 Å. It is well known that these experimental techniques suffer from drawbacks. Mercury porosimetry is known to be unreliable in the region of small sized pores (radius less than 20 Å) because of mercury and sample compressibility effects. Nitrogen sorption, on the other hand, is unreliable for larger sized pores (pores greater than 1000 Å), and therefore, it furnishes only partial information about the internal void space. On account of the above limitations, these two experimental techniques did not yield the same porosity values for the solid samples (see Table 5.1). Moreover, for the reacted solids both gave results different from those predicted from volume changes accompanying the reaction. The predicted porosities were calculated using the expression

$$\xi = \frac{\epsilon_0 - \epsilon}{(Z - 1)(1 - \epsilon_0)} \quad (5.4)$$

where ξ is the conversion level of the solid, ϵ_0 and ϵ are the initial (theoretically determined) and final porosities of the solid, respectively, and Z is the ratio of the molar volume of the solid product to that of the solid reactant for each gas-solid reaction.

Conversion (%)	Porosity merc. int. (cc/cc)	Porosity Eq. (5.4) (cc/cc)	Porosity moment (cc/cc)	Surface Area (m ² /g)
0	0.46	0.53	0.51	52.48
1	0.44	0.52	0.49	33.20
2	0.43	0.51	0.47	30.80
5	0.40	0.49	0.46	31.2
8	0.38	0.47	0.43	27.5

Table 5.2: Data for Georgia Marble Calcines Sulfated at 850°C.

Table 5.2 provides the surface areas and porosities of the sulfated samples of Georgia marble at the conversion levels studied. The surface areas were obtained from BET analysis of the nitrogen sorption data and the particle porosities from mercury intrusion data. Similarly

to the results seen in Table 5.1, the experimentally measured porosities do not agree with the theoretically estimated values (from Eq. (5.4)). The discrepancies in the estimated voidage of the porous solids by different methods are explained later on the basis of the pulse chromatographic response curves.

5.3. Pulse Chromatographic Experiments and Data Analysis

A chromatographic setup equipped with a high speed and high resolution data acquisition system was used for pulse chromatographic experiments. Details about the system are given by Krishnan (1993). Two different column lengths (50 and 150 cm) were used in our study. The chromatographic column was filled with the solid and a dilute pulse of He in N_2 (less than 15% He on a molar basis) was injected in the column with N_2 as the carrier gas. Chromatographic response curves were obtained at the same flow rate for both the 50 and the 150 cm columns packed in the same way and with the same solid. Six to seven sets of responses were used to cover the operating range of flow rates used in this study.

High flow rates and large size particles increase the sensitivity of the response to the particle effective diffusivity. The maximum flow rate is limited by the need to have insignificant pressure drop along the chromatographic column, whereas the particle size can be as large as the internal diameter of the column (single pellet string reactor). However, since our aim was to obtain uniformly calcined particles within a reasonable amount of time – very large particles require extremely long times for complete calcination – a size range of 710–850 μm was chosen for our experiments. The flow rate of the carrier gas, on the other hand, ranged from 70 to 110 ml/min. In general, these conditions led to chromatographic column responses that were highly sensitive with respect to the particle effective diffusivity.

The reproducibility of the tracer response is among the factors that have the strongest influence on the accuracy of the estimated effective diffusivity. Irreproducible response curves are most frequently caused by differences in column packing. To avoid this problem, the two columns (50 and 150 cm) were packed with particles of the same size range and with sample amounts that would result in identical bed voidage (about 0.44) for each case

(Krishnan, 1983). Test experiments were carried out using packed and repacked columns to verify the reproducibility of the response curves. Identical response curves were obtained in all cases for the same solid and bed length.

It is well known that end effects, such as those resulting from the dynamics of the response of the detector and the presence of dead space in the fittings and the injection valve, also contribute to the spread of the injected pulse. These effects can be minimized by proper design of the experimental setup but can never be eliminated. In addition to the above factors, the method of analysis plays a crucial role in determining the accuracy of the estimated value of effective diffusivities (Aust et al., 1987). In order to remove the uncertainty resulting from the presence of end effects and inaccuracies in the data at the tail section of the response, a time domain procedure (Krishnan, 1993) was employed for data analysis and effective diffusivity estimation. The method is based on the assumption that the end effects are at a given set of operating conditions the same in both the 50 and 150 *cm* columns and that the transfer function that represents them is arranged in series with the transfer function yielding the response of an ideal column.

It follows from this assumption that if the response of the real 50 *cm* column is convoluted with the response of an ideal 100 *cm* column, the result should be the response of the real 150 *cm* column. Therefore, our method of analysis rests in convoluting the response 50 *cm* column with the theoretically predicting response of an ideal (without end effects) 100 *cm* column and matching the result with the measured response of the 150 *cm* column. The method is illustrated in Fig. 5.1. In estimating the effective diffusivities of a certain sample, all chromatographic responses measured for it (that is for all flow rates) were employed. The parameter estimation scheme rests in the minimization of the integral square error between the theoretical (convoluted) and the experimental response curves of the 150 *cm* column, that is, in the minimization of the quantity

$$ISE = \sum_{k=1}^M \sum_{i=1}^{N^k} (c_{th}^k(t_i) - c_{ex}^k(t_i))^2 \quad (5.5)$$

where M is the number of flow rates at which the responses for both the 50 and 150 *cm* columns were recorded, and N^k is the number of data points for the k^{th} flow rate, and $c_{th}^k(t)$ and $c_{ex}^k(t)$ are the convoluted and the experimental 150 *cm* column responses,

respectively, for the k^{th} flow rate.

The Kubin-Kucera model (Kubin, 1965; Kucera, 1965) was used to describe the response of the ideal column. For the first two moments (first absolute and second central), it yields the expressions (Suzuki and Smith, 1975)

$$\mu_1 = \frac{L}{u} \left(1 + \frac{(1-\beta)}{\beta} \epsilon (1+K) \right) \quad (5.6)$$

$$\sigma^2 = \frac{2L}{u} \left[\left(1 + \frac{(1-\beta)}{\beta} \epsilon (1+K) \right)^2 \frac{D_b}{u^2} + \frac{(1-\beta)}{\beta} \left(\frac{b\epsilon^2(1+K)^2}{3k_g} + \frac{b^2\epsilon^2(1+K)^2}{15D_e} \right) \right] \quad (5.7)$$

It is seen from these equations that in addition to several known quantities (the particle porosity, ϵ , the bed porosity β , the bed length, L , the particle size, b , and the interstitial velocity, u), three more parameters appear in the model in addition to the effective diffusivity, D_e : the axial dispersion coefficient, D_b , the mass transfer coefficient at the external surface of the particles, k_g , and the volumetric equilibrium adsorption constant, K . Some information on the estimation of these parameters is given in the following paragraphs.

Noise and inaccuracies in the measured response, especially at its tail, have a dramatic effect on the value of the second central moment (σ^2), but influence insignificantly the first moment (μ_1) (Krishnan, 1993). The first moment of the response curves was thus used to find the value of K . It can be shown that the first moment of an ideal 100 cm column can be determined by subtracting the value of μ_1 of the 50 cm column from that of the 150 cm column. K can then be determined from Eq. (5.6) provided that the particle porosity is known. Preliminary calculations using the response curves for the calcines of Greer limestone – for which the porosities found from pore structure characterization are comparable to that expected theoretically (see Table 5.1) – suggested insignificant adsorption on the solid. It was thus decided to proceed assuming nonadsorbing behavior for all cases ($K = 0$). This is a reasonable assumption considering that the diffusing species is He . The particle porosities that were determined for the once calcined solids were in rather good agreement with those predicted from Eq. (5.4) (see Table 5.1).

The external mass transfer coefficient plays a minor role in influencing the shape of the response curve under the experimental conditions used in this study. This was verified

Figure 5.1: Illustration of the time domain parameter estimation procedure employed in this study showing the comparison of the 150 cm experimental response curve with the 150 cm theoretical response curve. The theoretical curve is obtained by convoluting the 50 cm experimental response with the simulated 100 cm column response.

by carrying out simulation studies in the time domain (Krishnan, 1993) using Sherwood numbers (based on particle radius) ranging from 1 (the value for a stagnant film in spherical geometry) to ∞ . The response curves were thus analyzed assuming that there was no mass transfer resistance between the particles and the bulk of the gas phase.

Despite experimenting under conditions that yield high sensitivity of the chromatographic response curves with respect to the particle effective diffusivity, the axial dispersion in the column contributes a significant fraction to the total spread of the curve. For a tortuosity factor of two for the bed packing ($D_b = 0.35 \text{ cm}^2/\text{s}$) and nonadsorbing molecules, the contribution of axial dispersion for the calcines to the overall spread of the curve turns out to be approximately 40% for an effective diffusivity of $10^{-2} \text{ cm}^2/\text{s}$ at the higher flow rates. Of course, for smaller effective diffusivities – as it is probably the case for the carbonated samples – the contribution of axial dispersion to the total spread of the response is much smaller. D_b can be determined together with the effective diffusivity by minimizing the integral square error (Eq. (5.5)) with respect to both these parameters. However, since the only transport parameter that causes dispersion of the injected pulse in columns packed with nonporous solids is the axial dispersion in the bed, it was decided to determine D_b independently of D_e by using the response curves for the precursors.

Analysis of the chromatographic response curves was performed in the time domain for columns packed with Greer limestone and Georgia marble precursors. The method of analysis was again based on minimization of the quantity given by Eq. (5.4) for all flow rates used in the experiments (70–110 ml/min). Analysis of the response curves for the precursors gave a value of $D_b = 0.4 \text{ cm}^2/\text{s}$ for Greer limestone and $0.35 \text{ cm}^2/\text{s}$ for Georgia marble. Excellent agreement was found to exist between theoretical predictions and experimental results (Krishnan, 1993). Based on a value of $0.69 \text{ cm}^2/\text{s}$ for the molecular diffusion coefficient for the He-N_2 pair, calculated from the Chapman-Enskog equation (Bird et al., 1960) under the experimental conditions of our studies, the values of D_b estimated for Greer limestone and Georgia marble predict a tortuosity factor of 1.73 and 1.97, respectively, for diffusion in the space between particles.

5.4. Effective Diffusivities and Pore Structure Properties

The effective diffusivities that were estimated from the analysis of the experimental data for all the samples we employed in this study are given in Table 5.3. The relative differences that are observed among the diffusivities of the various samples are discussed in the following sections in conjunction with the mercury and gas adsorption pore size distributions and the porosity values that are extracted from the chromatographic response curves.

Fig. 5.2 shows experimental response curves obtained for the 150 cm long column packed with Greer limestone particles calcined at 750 or 850°C and Georgia marble particles calcined at 850°C at a flow rate of 107 ml/min. Because of their highly symmetric shape and the occurrence of their peaks at about the same time, the three response curves have first moments that are similar in value. Parameters L , u , and β have the same values for all cases of Fig. 5.2, and thus, the same porosity is determined from Eq. (5.6) for all solids (see Table 5.1). (Recall that the adsorption equilibrium constant is set equal to zero to obtain the results reported here.) The spread of the response curve decreases in the order Greer limestone calcined at 750°C $\rightarrow$ Georgia marble calcined at 850°C $\rightarrow$ Greer limestone calcined at 850°C, while, as the results of Table 5.3, show the effective diffusivity increases in the same order. This result is agreement with the predictions of the equation for the second moment of the response which suggests increasing second moment with decreasing intraparticle effective diffusivity.

Fig. 5.3 shows the pore size distributions of the calcines obtained from mercury intrusion and nitrogen desorption. Pore size distributions obtained through these methods generally shift the actual pore size distribution towards smaller pore sizes (Efthimiadis and Sotirchos, 1993). Provided that all pores are filled with adsorbate before desorption starts and that nucleation effects are absent during desorption (that is, a pore empties only if it can reach the external surface of the particles through a path of empty pores), the theory predicts that mercury intrusion and gas desorption should produce the same pore size distribution curve. If there are empty pores when desorption starts – this is usually the case since most solids have some porosity residing in the above 1000 Å size range – the nitrogen desorption pore size distribution should be shifted toward larger pore

Figure 5.2: Chromatographic response curves of the 150 cm column packed with either Greer limestone calcined at 850°C, Georgia marble calcined at 850°C, or Greer limestone calcined at 750°C. The response curves were obtained at a flow rate of 107 ml/min.

Figure 5.3: Pore size distributions of the calcines obtained from mercury intrusion (solid lines) and nitrogen desorption (dashed lines).

sizes relative to that resulting from mercury intrusion (Efthimiadis and Sotirchos, 1993). However, the opposite behavior is observed in Fig. 5.3, that is, the mercury intrusion pore size distributions are shifted towards larger pores in comparison to those obtained from nitrogen desorption. This is probably due to the destructive nature of mercury porosimetry, which can cause crushing of small pores at pressures corresponding to larger pore sizes and thus shift the measured pore size distribution toward larger pores.

Solid	State	Reaction Temp. (°C)	D_e (cm^2/s)
GL	calcined	850	1.9×10^{-2}
GL	carbonated	850	6.0×10^{-4}
GM	calcined	850	1.2×10^{-2}
GM	carbonated	850	6.4×10^{-4}
GM	recalcined	850	1.9×10^{-2}
GL	calcined	750	5.0×10^{-3}
GL	recalcined	750	7.0×10^{-3}
GM	sulfated (0 %)	850	1.2×10^{-2}
GM	sulfated (1 %)	850	9.5×10^{-3}
GM	sulfated (2 %)	850	8.0×10^{-3}
GM	sulfated (5 %)	850	7.0×10^{-3}
GM	sulfated (8 %)	850	6.5×10^{-3}

Table 5.3: Effective Diffusivities of He (in N_2) in Calcined, Carbonated, Recalcined, and Sulfated Samples. GL=Greer limestone, GM=Georgia marble, and IS=Iceland spar.

Nitrogen adsorption does not suffer from the above drawbacks, and therefore a more meaningful comparison of the pore size distributions of different solids for pores smaller than about $1000 \text{ \AA}$ can be carried out by employing the pore size distributions obtained through it. According to the results of Fig. 5.3, Greer limestone calcined at 850°C displays the largest most probable pore radius among the three samples, and – provided that the

pore connectivities of the three porous solids are comparable – is therefore expected to offer the least mass transport resistance, in agreement with the results obtained from the pulse chromatographic experiments (Fig. 5.2 and Table 5.3). Because of the similar pore size distributions of the other two calcines, no conclusions can be reached on their mass transport resistance from their pore size distributions. It should be noted that the pore size distributions of the three calcines that are determined from nitrogen adsorption are shifted towards larger pores, as expected because of hysteresis effects, but follow the same pattern as those obtained from nitrogen desorption (Krishnan, 1993).

The changes occurring in the intraparticle mass transport resistance during calcination and carbonation of Greer limestone at 850°C , calcination, carbonation, and recalcination of Georgia marble at 850°C , and calcination and recalcination of Greer limestone at 750°C can be qualitatively followed from the chromatographic response curves shown in Figs. 5.4, 5.5, and 5.6, respectively. The physical changes that the precursor undergoes upon reaction (that is, the development of internal pore space during calcination or the reduction of the size of existing pores during carbonation) can be the only cause of the differences seen in the response curves. The particle voidage and the intraparticle effective diffusivity are in turn (see eqs. (5) and (6)) the only parameters of the chromatographic response model that are affected by the internal structure of the particles. In all three cases, the unreacted precursors yield the response with the least spread and the smallest first moment, while the curve for the calcined sample appears in each case much later than that of the precursor.

The response of the column packed with the carbonated sample appears immediately after that of the column packed with the nonporous precursors, and this is a consequence of the fact that carbonation leads to a drastic decrease in the particle voidage (see Table 5.1). Despite the low porosity of the carbonated sample, the spread of its response is larger than that of the response of the precursor and similar to that of the response of the calcined sample. This result is indicative of a much lower value of effective diffusivity for the carbonated sample than for the calcined sample, and this is exactly what the results of Table 5.3 show. The peak of the response of the recalcined sample appears at the same time instant as that of the calcined sample (see Figs. 5.5 and 5.6), reflecting the fact that

Figure 5.4: Chromatographic response curves of the 150 cm column for calcined and carbonated Greer limestone samples. The calcination and carbonation reactions were carried out in the fluidized-bed reactor at 850°C under pure N_2 and CO_2 , respectively. The response curves shown in the figure were obtained at a flow rate of 107 ml/min.

Figure 5.5: Chromatographic response curves of the 150 cm column for calcined, carbonated, and recalcined Georgia marble samples. The reactions were carried out in the fluidized-bed reactor at 850°C. The response curves shown in the figure were obtained at a flow rate of 107 ml/min.

Figure 5.6: Chromatographic response curves of the 150 cm column for calcined and recalcined Greer limestone samples. The calcination and recalcination reactions were carried out in the fluidized-bed reactor at 750°C. The response curves shown in the figure were obtained at a flow rate of 107 ml/min.

recalcination restores the porosity to its original value (see Table 5.1). The spread of the response of the recalcined sample is smaller than that of the calcined sample, and this result is in agreement (see Table 5.3) with having a smaller diffusivity in the void space of the former.

The changes that the internal void space of the three samples undergoes during the reaction sequences considered in Figs. 5.4, 5.5, and 5.6 may be seen in Figs. 5.7, 5.8, and 5.9, respectively, which give the pore size distributions obtained from nitrogen desorption and mercury intrusion. Nitrogen desorption, which in general gives reliable information for pores with radius less than 1000 Å, shows very little particle voidage for the carbonated sample, whereas mercury porosimetry indicates much higher porosity, even for pores smaller than 1000 Å. For example, for the Greer limestone sample reacted at 850°C, a theoretical porosity of 0.14 is predicted for the carbonated sample based on the conversion level attained (see Table 5.1). This value is identical to that predicted from the first moment but much higher than the value given in Fig. 5.7 by either of the pore structure characterization methods. BET analysis of the desorption data yields a very small surface area for the carbonated sample (Table 5.1). All these observations point to the conclusion that carbonation causes closure of most pores, and that the major part of the void space of the particles resides in pores larger than 1000 Å that are accessed from the outside through very small micropores. Mercury penetration gives much larger porosities for the carbonated sample probably because of crushing of closed pores at high pressures.

Even though the first moments of the response curves of Figs. 5.5 and 5.6 predict (see Table 5.1) that calcined and recalcined samples have the same porosity, the pore size distribution data of Fig. 5.8 and 5.9 reveal that both mercury porosimetry and nitrogen adsorption account only for part of the total porosity of the recalcined samples. The inability of the mercury intrusion and nitrogen desorption methods to account for the total porosity of the recalcined solid can be due to large pores that are filled by mercury below 80 *psi* pressure or, as in the case of the carbonated solid, pores larger than 1000 Å which are accessed through very small micropores. Two observations lead us to believe that the latter explanation is more probable. First, the mercury intrusion vs. pressure curves

Figure 5.7: Pore size distributions of the calcined and carbonated Greer limestone samples (reacted at 850°C). The pore size distributions were obtained from mercury intrusion (solid lines) and nitrogen desorption (dashed lines).

Figure 5.8: Pore size distributions of the calcined, carbonated, and recalcined Georgia marble samples (850°C). The pore size distributions were obtained from mercury intrusion (solid lines) and nitrogen desorption (dashed lines).

Figure 5.9: Pore size distributions of the calcined and recalcined Greer limestone samples (750°C). The pore size distributions were obtained from mercury intrusion (solid lines) and nitrogen desorption (dashed lines).

of the recalcined samples were not much different from those of the precursors and the calcines for intrusion pressures below 80 psi. Second, the mercury intrusion volume of the recalcined, as well as of the carbonated, sample tended to increase sharply with the applied pressure as the operating pressure limit (about 60,000 psi) of the porosimeter was approached. The existence of larger effective diffusivities in the recalcined samples was probably due to the fact that the part of their porosity that was uncovered by mercury porosimetry or gas sorption belonged to much larger pores than those seen in the calcined samples (see Figs. 5.8 and 5.9).

Pulse chromatographic response curves for partially sulfated Georgia marble calcines are shown in Fig. 5.10. These results were obtained for the Georgia marble calcines sulfated to 1, 2, 5, and 8% conversion levels. It is seen that the response curves for the sulfated calcines spread more with increasing conversion levels and their peaks appear earlier in time in the same order. The decrease in particle porosity during sulfation (see Table 5.2) is most probably the reason for the shifting of the peak of the response (see Eq. (5.6)). On the other hand, the increase in the spread of the response curves is due to increasing average diffusion resistance in the intraparticle space (see Eq. (5.7) and Table 5.3) caused by closure of the pores in the sulfated layer next to the external surface of the particles.

The experiments of Zarkanitis and Sotirchos (1989) and Sotirchos and Zarkanitis (1992) showed that the sulfation of Georgia marble calcines is a relatively fast reaction, and as a result, the maximum conversion that can be reached is a strong function of the particle size. Even particles with size in the 53-62 μm range were found to reach conversions below the value expected from the stoichiometry of the sulfation reaction for complete pore plugging with CaSO_4 . Sotirchos and Zarkanitis (1992) showed that significant concentration gradients were present in 53-62 μm Georgia marble particles at all conversion levels, and therefore, even for particles in this size range, closure of pores at the external surface occurred while there was significant open space in the interior. For particles in the size range used in our experiments (710-850 μm), fluidized-bed and thermogravimetric analysis experiments showed that about 8% was the maximum conversion that could be achieved, and this is the reason for which bed response curves are shown only for this conversion range. The converted solid is located only in a very thin shell very close to the

external surface of the particles, and therefore, the response curves of Fig. 5.10 and the diffusivities of Table 5.3 should be viewed as being indicative only of the average transport resistance in the interior of the nonuniformly reacted particles. However, this does not mean that the reported diffusivity values are useless for model testing and validation. Given a mathematical model for the sulfation of calcined limestone particles, one can use the predicted porosity and effective diffusivity profiles in the interior of the particles in a pulse chromatographic model that allows for radial variation of the porosity and effective diffusivity and compare the predicted response curves with those found from the average effective diffusivities of Table 5.3.

Fig. 5.11 shows the pore size distributions of the sulfated samples whose chromatographic response curves are shown in Fig. 5.10. Mercury porosimetry was employed to obtain the curves shown in Fig. 5.11. The porosities of Fig. 5.11, though not in agreement with those predicted theoretically (see Table 5.2), follow the same variation pattern with the conversion as them (Fig. 5.10). Because of the nonuniformity of the structure of the reactive particles in the radial direction, the pore size distributions of Fig. 5.12 are of qualitative value only. Since the pores in the sulfated layer, which is next to the external surface of the particles, are much smaller than those in the interior, the pore size distribution of the sulfated samples from mercury intrusion data should be shifted towards smaller pore sizes had the sulfated layer maintained its integrity during mercury porosimetry. In particular, the 8% converted sample, whose conversion level corresponds to the maximum conversion that could be achieved in the experiment, should show no porosity at all outside the micropore range. The fact that the pore size distributions of the sulfated samples in Fig. 5.12 are not much different, qualitatively, from that of the unreacted solid and exhibit a larger fraction of macropores suggests, in view of the above observations, that the thin sulfated layer is destroyed by the high pressures applied during mercury porosimetry.

Fig. 5.12 is given to demonstrate that the extracted values of effective diffusivity for the various samples yield bed responses that match closely the experimental ones. The comparison is carried out between the 150 *cm* column experimental response (solid curve) and the curve obtained by convoluting the 50 *cm* column experimental response with an ideal 100 *cm* column (theoretically generated) response using the effective diffusivity of

Figure 5.10: Chromatographic response curves of the 150 cm column for sulfated Georgia marble calcines at 0, 1, 2, 5, or 8% overall conversion levels. The sulfation of the calcine was carried out in the fluidized-bed reactor at 850°C under 1500 ppm of SO_2 . The response curves shown in the figure were obtained at a flow rate of 107 ml/min.

Figure 5.11: Pore size distributions of the sulfated Georgia marble calcines reacted in the fluidized-bed reactor at 850°C and 1500 ppm of SO_2 . The curves are for calcines reacted to 0, 1, 2, 5, or 8% overall conversion levels. The pore size distributions were obtained from mercury intrusion.

Figure 5.12: Comparison of the 150 cm experimental response with the 150 cm theoretical response for the column packed with Greer limestone calcine (850°C).

Table 5.4 (dashed curve). Very good agreement is seen to exist between the experimental and theoretical results for all flow rates. Results that are qualitatively identical to those of Fig. 5.12 are obtained for all other solids (Krishnan, 1993).

5.5. Measured vs. Theoretically Predicted Diffusivities

The magnitudes of the effective diffusivities of the three calcines show a direct correlation with the conversion levels attained by these solids during sulfation or sulfidation. For instance, in the study of Sotirchos and Zarkanitis (1992) Greer limestone calcined at 850°C was found to reach much higher conversion than Greer limestone calcined at 750°C . Similarly, Efthimiadis and Sotirchos (1992) found that the sample calcined at 750°C was again sulfided more slowly than the sample prepared at 850°C , although in this case complete conversion was reached for both samples on account of the lower molar volume (than CaSO_4) of CaS . By matching the experimental conversion vs. time results with the predictions of a mathematical model for diffusion, reaction, and structure evolution, an estimate for the connectivity of the pores was obtained in the above studies in terms of the coordination number of the pore network, z , that is, the average number of pores per node in the pore network. The effective medium theory-smooth field approximation (EMT-SFA) approach of Burganos and Sotirchos (1987) was used to calculate the effective diffusivity from the pore size distribution of the porous solid by Sotirchos and Zarkanitis (1992) and Efthimiadis and Sotirchos (1992). A brief description of this approach and of the smooth field approximation is given in the following paragraphs.

The smooth field approximation (SFA) amounts to assuming that the microscopic concentration field in each pore in the pore network coincides with the macroscopic one (Jackson, 1977). This approximation leads to an expression for the effective diffusivity in terms of the pore size distribution which is simply the average over the pore size distribution of the diffusion coefficient in a single pore, that is, the same expression as that obtained for a bundle of randomly oriented noninteracting pores (Johnson and Stewart, 1965). Specifically, for a discrete pore size distribution, like that extracted from pore structure

characterization data, we have

$$D_e^{SFA} = \frac{1}{3} \sum_{i=1}^N D(R_i) \epsilon_i \quad (5.8)$$

with N being the number of pore sizes, and ϵ_i and $D(R_i)$ the porosity and diffusion coefficient of pores of size R_i . $D(R_i)$ is computed from the reciprocal additivity (Bosanquet formula), viz.

$$\frac{1}{D(R_i)} = \frac{1}{\mathcal{D}} + \frac{1}{D_K(R_i)} \quad (5.9)$$

with $\mathcal{D}$ being the molecular diffusivity and $D_K(R_i)$ the Knudsen diffusivity in a pore of radius R_i .

The smooth field approximation violates the mass balance equations at the nodes of a network, and Eq. (5.10) turns out to be an upper bound on the actual diffusivity of the porous medium for a given pore size distribution. Burganos and Sotirchos (1987) suggested to use the effective medium theory approach (Kirkpatrick, 1973) to obtain an equivalent, with respect to the overall diffusion resistance network, of uniform pore conductance ($\pi \times (\text{pore radius})^2 \times \text{pore diffusivity} / (\text{pore length})$) and then apply the smooth field approximation to this network to determine the effective diffusivity. The result turns out to be

$$D_e^{EMT-SFA} = \frac{\epsilon}{3} \frac{\langle D(R)R^2 \rangle_e}{\langle R^2 \rangle_a} \quad (5.10)$$

where $\langle D(R)R^2 \rangle_e$ is the effective medium theory average of $\langle D(R_i)R_i^2 \rangle$ with weight factor the length per unit volume of pores of size R_i , l_i and $\langle R^2 \rangle_a$ is the arithmetic average of R^2 with the same weight factor. For a discrete pore size distribution, we have

$$\sum_{i=1}^N l_i \frac{D(R_i)R_i^2 - \langle D(R)R^2 \rangle_e}{D(R_i)R_i^2 + (\frac{1}{p_c} - 1) \langle D(R)R^2 \rangle_e} = 0 \quad (5.11)$$

$$\langle R^2 \rangle_a = \frac{\sum_{i=1}^N l_i R_i^2}{\sum_{i=1}^N l_i} \quad (5.12)$$

p_c is the percolation threshold of the structure, that is, the number fraction of open pores below which all pores in the network exist in the form of finite clusters and transport through the solid cannot take place (equal to $z/2$ for a network having a regular lattice

structure and $1/(z - 1)$ for a Bethe lattice). For infinitely large coordination number, the percolation threshold becomes zero, and the EMT-SFA diffusivity becomes almost identical to the SFA value (Eq. (5.8)).

If pore overlapping is ignored, l_i is simply given by $\epsilon_i/\pi R_i^2$, while in the case of a network of randomly overlapping pore segments, it may be obtained from the equation (Sotirchos and Zarkanitis, 1993)

$$l_i = \frac{1}{\pi R_i^2} \ln \left(\frac{1 - \sum_{j=i+1}^N \epsilon_j}{1 - \sum_{j=i}^N \epsilon_j} \right) \quad (5.13)$$

In writing Eq. (5.13), it is assumed that the index of the pores increases in the direction of increasing pore size.

Employing the EMT-SFA model to predict effective diffusivities during simulation of the sulfation and sulfidation processes of the calcines, Sotirchos and Zarkanitis (1992) and Efthimiadis and Sotirchos (1992) determined the coordination numbers (z) shown in Table 5.4 for the three calcines employed in this study. These z values were obtained assuming the topology of the porous network to be that of a Bethe lattice (Fisher and Essam, 1961). In the case of Greer limestone, it was found that the same z value could be used to describe both the sulfidation and sulfation behavior of the calcines, for the same pore size distribution. For the Georgia marble sample, however, Efthimiadis and Sotirchos (1992) found that the z values determined from sulfation data (by Sotirchos and Zarkanitis (1992)) were satisfactory for the sulfidation data of 53-62 and 88-105 μm particles only and that a much larger value had to be used to reproduce the sulfidation behavior of 210-250 and 297-350 μm particles ($z = 4$ vs. $z = 4000$ for the sample calcined at $850^\circ C$). Since they had observed that large Georgia marble particles tended to explode during heating under CO_2 (probably because of decomposition of the small amount of $MgCO_3$ they contained), they attributed the above discrepancy to the existence of large pores in the interior of the larger calcine particles, formed from the cracks in the heat-treated precursors.

The effective diffusivities obtained from the EMT-SFA model employing the pore size distributions of the calcines shown earlier and the coordination numbers determined in the above studies are shown in Table 5.4. Values have been determined using the

pore size distributions obtained from all three procedures, that is, mercury intrusion, nitrogen desorption, and nitrogen adsorption. The use of a finite value for z has a much stronger effect on the effective diffusivities from mercury penetration data because of the practically unimodal and very narrow form of the nitrogen desorption or adsorption pore size distribution. (Obviously, for a solid with uniform size pores, the EMT-SFA approach produces the same estimate as the smooth field approximation irrespective of the value of z used.) Before a comparison of the predicted diffusivities with the experimental values reported in Table 5.3 is made, one should again be reminded that the pore size distributions obtained through these methods do not reflect the true morphology of the solids. This is because a pore is emptied during desorption (or filled during mercury intrusion) at the pressure corresponding to its own radius only if it is connected to the external surface through a path involving larger pores. Otherwise it gets emptied (or filled) at the pressure that corresponds to the radius of the smallest pore that must be emptied (or filled) to establish a continuous path of emptied (or filled) pores leading to the external surface. These effects are absent during nitrogen adsorption. However, nitrogen adsorption like the desorption process fails to provide reliable information for pores larger than about 1000 Å.

Very good agreement is seen between the predicted effective diffusivity for the Greer limestone calcine prepared at 850°C employing a coordination number of 12 and that obtained from our experimental studies (see Tables 5.3 and 5.4). All three pore size distributions yield values that are very close to the experimental effective diffusivity and to each other. The SFA effective diffusivity based on the pore size distribution obtained from mercury porosimetry overpredicts the experimentally measured value. On the other hand, the SFA effective diffusivities that are based on the pore size distributions obtained from nitrogen sorption data are very close to the experimental value. This agreement is coincidental and probably due to the fact that pores larger than 1000 Å are not included in the pore size distributions from sorption data. Despite their small contribution to the total porosity, when the smooth field approximation is employed, these pores contribute significantly to the total flux because they are assumed to work in parallel with the smaller pores.

Solid	Calc.	Z	D_e	D_e	D_e	D_e	D_e	D_e
	Temp.		SFA	SFA	SFA	EMT-SFA	EMT-SFA	EMT-SFA
			merc. int.	N_2 Des.	N_2 Ads.	merc. int.	N_2 Des.	N_2 Ads.
	(°C)		(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)
GL	850	12	2.98×10^{-2}	1.84×10^{-2}	1.98×10^{-2}	1.60×10^{-2}	1.45×10^{-2}	1.50×10^{-2}
G	750	6	2.41×10^{-2}	1.52×10^{-2}	2.0×10^{-2}	1.06×10^{-2}	1.13×10^{-2}	1.16×10^{-2}
GM	850	4	2.36×10^{-2}	1.35×10^{-2}	1.77×10^{-2}	7.93×10^{-3}	9.15×10^{-3}	8.87×10^{-3}
IS	850	4000	2.36×10^{-2}	1.35×10^{-2}	1.77×10^{-2}	1.45×10^{-2}	1.33×10^{-2}	1.66×10^{-2}

Table 5.4: Effective Diffusivities of He (in N_2) in the Calcines Predicted Using the EMT-SFA Model and Coordination Number Values Obtained in Previous Studies (Sotirchos and Zarkanitis (1992); Efthimiadis and Sotirchos (1992)). GL=Greer limestone, GM=Georgia marble, and IS=Iceland spar.

Reasonable estimates of the effective diffusivity are also obtained for the Greer limestone sample calcined at $750^\circ C$ from the EMT-SFA model employing any of the three pore size distributions. The predicted EMT-SFA values differ by a factor of two from the measured value of effective diffusivity (Tables 5.3 and 5.4). Differences between predicted and measured values are not uncommon, and discrepancies up to an order of magnitude have been known to occur (Haynes, 1988). However, much greater deviations occur between the SFA predicted values and the measured values.

Since, two different values of coordination number were obtained by Efthimiadis and Sotirchos (1992) for the Georgia marble calcine prepared at $850^\circ C$, Table 5.4 reports the predicted values of effective diffusivities for both values of z and the three different pore size distributions. As for the other two solids, the SFA estimate based on the mercury intrusion data overpredicts the measured value by a wide margin (see Table 5.3 for the measured value), while the SFA effective diffusivities for the pore size distributions obtained from nitrogen sorption show very good agreement with the measured value. This again is coincidental and due to the absence of large pores from the pore size distribution obtained from sorption data. Interestingly enough, the experimentally measured value for the Georgia marble sample turns out to be between the EMT-SFA values predicted for the two coordination numbers. It should be pointed out that the need to use unreasonably large

coordination numbers to describe the sulfidation of large Georgia marble particles is an indication that the pore network assumed in the EMT-SFA approach is not appropriate for these particles (Efthimiadis and Sotirchos, 1992). All pore sizes are treated in the same way in the EMT-SFA model, and therefore, if pervasive large pores are present in a porous medium – as it is probably the case for large Georgia marble particles – very large coordination numbers must be employed in order not to underestimate the contribution of the large pores in the mass transport process.

It should be noted that the mercury intrusion pore size distributions that were used in the studies of Sotirchos and Zarkanitis (1992) and Efthimiadis and Sotirchos (1992) were slightly different from those used in this study because a different arrangement (viz., a fixed-bed reactor) was employed for the preparation of the samples. Using those pore size distributions yields slightly different (actually larger) effective diffusivities both for finite (EMT-SFA) and infinite (SFA) coordination number, but the relative differences among the various diffusivities and between the EMT-SFA and SFA results are similar to seen in the results of Tables 5.3 and 5.4.

5.6. Summary and Concluding Remarks

Pulse chromatographic experiments were performed in this study to investigate evolution of the intraparticle diffusional limitations during calcination, carbonation, recalcination, and sulfation of limestones. Two types of limestones differing in their petrographic structure, one with small grains (Greer limestone) and another coarsely grained (Georgia marble), were used for this purpose. The measured chromatographic response curves were analyzed in the time domain by employing a procedure that uses the responses of two different length columns to eliminate uncertainties associated with end effects and the form of the input to the chromatographic column.

The intraparticle effective diffusivity of the once calcined samples was found to increase in the order Greer limestone calcined at 850°C $\rightarrow$ Georgia marble calcined at 850°C $\rightarrow$ Greer limestone calcined at 750°C . The effective diffusivities of the three calcines differed by as much as a factor of 4 despite the fact that the pore size distributions of the solids were similar and gave similar values of effective diffusivity assuming a network of

randomly arranged noninteracting pores (parallel pore bundle model). The carbonated samples showed much higher resistance to intraparticle mass transport than the calcined samples. Based on several experimental observations, such as the form of pore size distributions obtained from mercury intrusion and nitrogen sorption, the low surface areas measured from BET analysis of their sorption isotherms, and the fact that the theoretical porosities of the carbonated samples were in agreement with those estimated from the first moments of the response curves but much higher than those found from mercury intrusion or N_2 sorption data, it was concluded that a significant fraction of the porosity of carbonated samples was due to large pores with feeder pores of micropore size.

The porosities estimated from first moments of the chromatographic response curves of recalcined samples indicated that recalcination restored the porosity to its original (before carbonation) value. Only part of the porosity of recalcined samples could be revealed by mercury penetration or gas adsorption experiments, and this indicated that, like in the case of the carbonated sample, some large pores were accessed through micropores only. However, the part of the pore size distribution of the recalcined samples that could be traced by mercury penetration or gas adsorption showed much larger pores than those found in one-time calcined samples, and thus, the effective diffusivities of the recalcined samples were found, for the two cases of Georgia marble reacted at 850°C and Greer limestone reacted at 750°C that we studied, to be higher than those of the unreacted calcines. Sulfation of the calcines resulted in a rapid decline in the value of the average effective diffusivity. Because of closure of the pores at the external surface of the particles, only conversions less than 8% could be achieved for the 710-850 μm particles we used in the experiments. Because of the small thickness of the sulfated layer and the strong effect of conversion on the average effective diffusivity in the particles it was concluded that the pore space of the sulfated layer presented very high resistance to the transport of SO_2 .

The observed variation of effective diffusivity among the three calcines we studied (Georgia marble and Greer limestone calcined at 850°C and Greer limestone calcined at 750°C) was in relative agreement with the reported behavior of the solids during sulfation and sulfidation experiments by Sotirchos and Zarkanitis (1992) and Efthimiadis and Sotirchos (1992), respectively. We used estimates that were made in the above studies for

the connectivity of the pores in the calcines, in terms of the coordination number of the pore network, to predict the effective diffusion coefficient from the mercury intrusion pore size distributions using the effective medium theory- smooth field approximation approach of Burganos and Sotirchos (1987). Fairly good, and in some cases very good, agreement was observed between the predicted and experimental values. On the other hand, the effective diffusivities that were estimated by assuming a perfectly interconnected network of pores or equivalently a network of noninteracting pores (smooth field approximation) were much larger than the experimentally measured values. This result lends further support to the conclusion reached by Sotirchos and Zarkanitis (1992) and Efthimiadis and Sotirchos (1992) in their sulfation and sulfidation, respectively, studies that the connectivity of the pores is among the most important factors that determine the performance of a limestone-derived calcine as a sorbent for SO_2 removal.

5.7. Notation

Symbols that do not appear here are defined in the text.

b	Radius of the porous particle, cm
$\mathcal{D}$	Binary diffusivity, cm^2/s
$D(R)$	Diffusivity in a pore of radius R_i , cm^2/s
D_b	Axial dispersion coefficient, cm^2/s
D_e	Effective diffusivity of the gas in the particle, cm^2/s
$D_K(R)$	Knudsen diffusivity in a pore of radius R , cm^2/s
K	Lumped adsorption equilibrium constant
k_g	External mass transfer coefficient, cm/s
l_i	Length per unit volume of pores with radius R_i , cm/cm^3
L	Length of bed, cm
N	Number of pore sizes
p_c	Number-based percolation threshold of pore network
R_i	Radius of i th group of pores ($R_i < R_{i+1}$), cm
u	Interstitial velocity, cm/s
z	Coordination number of the pore network

Greek

β	Porosity of the bed
ϵ	Porosity of the solid
ϵ_0	Initial porosity of the solid
ϵ_i	Porosity due to pores of size R_i
μ_1	First absolute moment (Eq. (5.6)), s
σ^2	Second central moment (Eq. (5.7)), s^2
ξ	Conversion of the solid

5.8. Literature References

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6. EXPERIMENTAL AND THEORETICAL INVESTIGATION OF FACTORS AFFECTING THE DIRECT LIMESTONE- H_2S REACTION

6.1. Introduction

The gasification of coal is a versatile method of coal utilization where the generated coal gas can subsequently be used to synthesize other fuels or produce energy by combustion or in fuel cells. The sulfur contained in coal reacts in the reducing atmosphere of a gasifier forming H_2S and COS . Because of their corrosive nature and potentially negative environmental impact, H_2S and COS must be removed from the coal gas before it is further processed. Coal gas desulfurization can be carried out at low ($< 120^\circ C$) or high temperatures ($> 500^\circ C$) (Jalan, 1983). Hot coal gas desulfurization, which uses solid sorbents, such as oxides of metals (e.g., of iron, manganese, zinc, and vanadium) and limestones, possesses several distinct technical and economic advantages over low temperature processes, which make it an attractive desulfurization technique.

Typical fixed-bed and fluidized-bed gasifiers operate around $850^\circ C$ with a temperature at the exit between 500 and $800^\circ C$. Entrained-flow gasifiers operate at higher temperatures, about $1200^\circ C$. Most gasifiers operate at 200-300 psi pressures. Among the objectives of a successful desulfurization process is to carry out the removal of sulfur compounds at the temperature and pressure of the coal gas in the gasifier. This can be achieved by employing sorbents that can be used to desulfurize the coal gas within the gasifier itself.

Several reactions take place within a gasifier that employs limestones ($CaCO_3$) and dolomites ($CaCO_3 \cdot MgCO_3$) or their pre-calcined forms (CaO and $CaO \cdot MgO$) for the removal of H_2S from coal gas. The typical composition of CO_2 in an oxygen blown gasifier is 26% and for an air blown gasifier is 11% on a molar basis (Grindley, 1985). Under an operating pressure of 250 psi in the gasifier, the average partial pressure of CO_2 in the coal gas is about 1.8 and 4.3 atm for the air blown and oxygen blown gasifiers, respectively. Thermodynamic calculations for the decomposition of $CaCO_3$ to CaO show that temperatures higher than $950^\circ C$ are required for decomposition at a partial CO_2 pressure of 1.8 atm. At a CO_2 partial pressure of 4.3 atm, $CaCO_3$ decomposition can only take place at temperatures much higher than those encountered in any gasifier. The

CaCO_3 contained in limestones and dolomites must therefore react directly with H_2S in the gasifier to effect coal gas desulfurization according to either of the reactions:

(MgCO_3 contained in dolomite is shown as MgO in reaction R6.1b because the conditions prevailing in a gasifier favor its decomposition.)

There may be regions in the gasifier of higher, than the average, reaction temperature or lower partial pressures of CO_2 (than the average values) where decomposition of CaCO_3 to CaO may occur:

CaO formed from the decomposition of CaCO_3 or present in precalcined limestones and dolomites may then react with CO_2 to form CaCO_3 in regions of the reactor where the carbonation reaction is favored:

It can therefore be argued that in such regions reaction R6.3 might be competing for CaO with the indirect sulfidation reaction, i.e., the reaction

On the other hand, in regions that favor the decomposition of CaCO_3 , only the latter may take place. An analogous situation occurs in pressurized fluidized-bed combustors that employ limestones for SO_2 removal, where CaCO_3 is believed to react directly with SO_2 (Tullin and Ljungström, (1989); Snow et al. (1988); Jansson et al. (19820; Krishnan and Sotirchos, (1993a)).

A fundamental difference between the reaction of H_2S with limestone-derived calcines (CaO) (reaction R6.4) and that with limestone (CaCO_3) (reaction R6.1a) is the lack of a highly developed pore structure in the reacting solid taking part in the latter. The reaction between limestone-derived calcines and H_2S proceeds through diffusion of the reactive gas

in the pore space of the calcine and the reacted solid layer at the pore walls (CaS) and its subsequent reaction with CaO at the reacted-unreacted solid interface. Similarly, the reaction of H_2S with half-calcined dolomites (reaction R6.1b) involves diffusion of the reactive gases in the pore space formed through decomposition of $MgCO_3$. However, in the case of nonporous, uncalcined limestones, H_2S initially reacts only at the external surface of the reacting particles, leading to formation of a solid product layer at their periphery. Further reaction between limestone and H_2S takes place only after the reactive gas diffuses through this product layer. Because of this difference, the information that is presently available on the sulfidation of limestone-derived calcines and of other porous oxides (e.g., see Westmoreland et al. (1977), Borgwardt et al. (1984), and Efthimiadis and Sotirchos (1992)) and sulfidation of half-calcined dolomites (e.g., see Ruth et al. (1972) and Yen et al. (1981)) from studies in thermogravimetric analysis (TGA) systems and other types of reactors is inapplicable to the direct reaction of low porosity limestones with H_2S .

Fundamental knowledge on the interplay between transport and reaction in the limestone- H_2S reaction is required for design and operation of gasifiers capable of achieving efficient removal of H_2S through limestone addition. Unfortunately, the number of fundamental studies on the direct sulfidation reaction is rather small in comparison to that for the indirect process. Moreover, most of those studies have been carried using limestones of special petrographic structure or in narrow ranges of operating conditions. As a result, it is difficult or even impossible to use the results and conclusions reported in them to predict the behavior of other limestone- H_2S systems.

Attar and Dupuis (1979) studied the reaction of $CaCO_3$ (calcite) with H_2S and found that at temperatures below $640^\circ C$ diffusion of the gases through the product layer controls calcite consumption. However, no reliable information on the mechanism of the $CaCO_3$ - H_2S reaction can be extracted from their results at higher temperatures since the occurrence reactions R6.2 and R6.4 becomes possible in their reaction environment. Borgwardt and Roache (1984) investigated the reaction of limestone particles with H_2S (reaction R6.1a) at atmospheric pressure in an environment of 70% CO_2 by volume to prevent the decomposition of $CaCO_3$ to CaO . The limestone samples were periodically removed from the reactor to determine the conversion level. Since Borgwardt and Roache

used a limestone precursor (Fredonia limestone) with 8% natural porosity, they were able to explain the behavior of the conversion-time trajectories for large particles (diameter greater than $15\ \mu\text{m}$) along the lines of the overall mechanism for the sulfidation of limestone-derived calcines (reaction R6.4). However, as a survey of the pertinent literature shows, most limestones are nearly nonporous in their natural state. For example, porosities of 1.5% and 0.7% were measured by Krishnan and Sotirchos (1993a) for Greer limestone and Georgia marble, respectively, 0.4-1% by Krishnan and Sotirchos (1993a) and Hajaligol et al. (1988) for Iceland spar, and 2-3% for Rigsby and Fredonia limestones by Hajaligol et al. (1988).

A detailed investigation of the reaction between limestones and H_2S is presented in this study. The limestones were directly sulfided in a thermogravimetric analysis (TGA) system at atmospheric pressure under 70% CO_2 (on a molar basis) to prevent the decomposition of CaCO_3 to CaO . The effect of reaction conditions on the limestone- H_2S reaction were examined by employing different bulk phase concentrations of H_2S (3000 and 6000 ppm) and two temperatures (650 and 750°C). The particle size effect on the conversion-time profile was investigated by employing a broad range of particle size (53-62, 88-105, and 297-350 μm). The influence of the above conditions (particle size, temperature and concentration) on the conversion-time history was examined for three limestones having high CaCO_3 content ($> 95\%$) but differing in petrographic texture. A shrinking-core model was employed to obtain information, both quantitative and qualitative, on the kinetics of the reaction and the mass transport process in the sulfided layer. Finally, by using results obtained by our research group in past studies for the same limestones, a comparison of the direct sulfidation and direct sulfation of limestones (the $\text{CaCO}_3\text{-SO}_2$ reaction) and of the sulfation and sulfidation of the limestone-derived calcines (the CaO-SO_2 and the $\text{CaO-H}_2\text{S}$ reactions, respectively) was carried out.

6.2. Materials and Experimental Procedures

Three high purity limestones, which will be referred to as Greer limestone, Georgia marble, and Iceland spar, were used to study the limestone- H_2S reaction. Each has CaCO_3 content higher than 95% (on a mass basis), with Georgia marble having the highest MgCO_3

content (approximately 3% on a mass basis) of the three. The CaCO_3 present in the limestones was found from petrographic studies to be calcitic, with the grain size increasing in the order Greer limestone $\rightarrow$ Georgia marble $\rightarrow$ Iceland spar. The limestones supplied as fragments in the 1/4-1/2" size range were crushed into smaller particles and screened using mechanical sieving to filter out the fine and coarse sizes and obtain three particle size ranges: 53-62, 88-105, and 297-350 μm . The porosities and surface areas of the three samples were determined from N_2 sorption data using a volumetric adsorption unit (Autosorb 1, Quantachrome, Inc.). They are listed in Table 6.1, where they are seen to increase in the order Iceland spar $\rightarrow$ Georgia marble $\rightarrow$ Greer limestone, that is, in the order of decreasing grain size.

Limestone	Particle Size (μm)	Surface Area (m^2/g)	Porosity (pores of radius $< 1000\text{\AA}$)
<i>GL</i>	53 – 62	0.91	0.015
<i>GM</i>	53 – 62	0.31	0.007
<i>IS</i>	53 – 62	0.23	0.004

Table 6.1: Surface areas and porosities of Georgia marble, Greer limestone, and Iceland spar precursors. GL=Greer limestone, GM=Georgia marble, and IS=Iceland spar.

A TGA system based on a Cahn 2000 electrobalance was used to obtain conversion vs. time data. Very small amounts of solid (2-5 mg) were placed in a gold pan hang with platinum wire inside a quartz reactor. The samples were heated to the reaction temperature (650 or 750°C) in an atmosphere of 100% CO_2 flowing at 200 ml/min (standard conditions). All direct sulfidation experiments were performed in an atmosphere of 70% CO_2 , and thus, the pure CO_2 stream was substituted with a 70% CO_2 -30% N_2 stream to ensure the existence of noncalcining conditions for CaCO_3 at the conditions of our experiments. Of course, the small amounts of MgCO_3 present in the limestones decomposed at the temperature used to form MgO even under 100% CO_2 . Once the desired reaction temperature was attained, a stream consisting of CO_2 (70% on a molar basis) and a 1%

or 2% H_2S in N_2 (molar basis) mixture was sent through the reactor, and the transient weight change was recorded.

The large quantities of reacted samples needed for pore structure characterization through N_2 sorption were prepared in a fixed-bed reactor. Approximately 0.5-0.75 g of limestone were directly sulfided under a total flow of 2000 ml/min (standard conditions) at $750^\circ C$ and 6000 ppm H_2S . The procedures followed to start desulfurization in the fixed-bed reactor were the same as in the thermogravimetric experiments. The conversions of the solids were determined from the concentration of H_2S at the exit, measured using a chromatograph (Varian 3300) equipped with a flame photometric detector, as well as from the observed weight change.

6.3. Reactivity results

CO_2 and H_2S can react under the experimental conditions employed in our study and form COS according to the overall reaction

Borgwardt and Roache (1984) reported a 12% conversion of H_2S in their experimental system (10% of H_2S to COS and 2% to S) at a reaction temperature of $700^\circ C$. Thermodynamic calculations for the reactive gas mixture used in our experiments revealed that significant conversion of H_2S to other species could take place at equilibrium. The variation of the thermodynamic equilibrium concentrations of the various species with the reaction temperature is given in Fig. 6.1. These results were computed using the STAN-JAN code (Reynolds, 1986) with thermodynamic data from the JANAF Tables (Chase et al., 1985). Fig. 6.1 shows that nearly 85% of H_2S is converted to other sulfur-containing species at equilibrium at $750^\circ C$. However, the chromatographic analysis of the exit stream of our TGA system showed a H_2S depletion of less than 9% at $750^\circ C$. Since the reaction mixture of H_2S - CO_2 - N_2 encounters the limestone sample at residence times much smaller than those at the reactor's exit, considerably lower depletion levels were measured for gas samples collected by sampling at the vicinity of the pan (less than 3% at $750^\circ C$). In view of these results, we concluded that the concentration of H_2S in the bulk of the gas phase

around the sample could safely be assumed to be the same as the inlet concentration.

Conversion vs. time profiles for the three solids directly sulfided under 3000 ppm of H_2S and at a reaction temperature of $750^\circ C$ are shown in Figs. 6.2-6.4. The conversion-time trajectories of these figures reveal strong effects of particle size on the direct sulfidation of all limestones, which suggest that the reactive gas encounters significant resistance in its transport through the intraparticle space. Similar effect of particle size on the overall reaction profile was seen for the three solids sulfided at $650^\circ C$ under 3000 ppm of H_2S .

Typical effects of temperature on the conversion-time profile for the direct sulfidation of the limestones is shown in Fig. 6.5 for Georgia marble reacted under 3000 ppm of H_2S . The reaction trajectory is seen to be very sensitive to the reaction temperature throughout the duration of the experiment. The conversion levels for Georgia marble attained at the two temperatures after two hours of direct sulfidation differ by about a factor of two for all particle size ranges. Much smaller differences are obtained at smaller reaction times, suggesting that the intrinsic kinetics of the reaction, the controlling step during the early stages of the reaction, is less influenced by the reaction temperature than the diffusion of H_2S through the product layer, the controlling step at larger reaction times. Similar effects of temperature on the conversion vs. time curves were observed for the other limestones. The influence of reaction temperature on the conversion-time profile was weaker in the sulfidation of calcines derived from the same limestones (Efthimiadis and Sotirchos, 1992). This observation suggests that the mechanisms of the direct and indirect reaction of limestones with H_2S are different.

Studies were conducted at two concentrations of 3000 and 6000 ppm of H_2S in the bulk phase to investigate the effect of concentration on the conversion-time history of the limestones. Fig. 6.6 shows the comparison between the conversion-time curves for Georgia marble directly sulfided at $750^\circ C$ under the two concentrations over a 1 hr period for the smallest size range ($53\text{--}62\ \mu m$). Strong dependence of conversion level attained by the reacting solid on the bulk phase concentration of H_2S is seen throughout this period. A better understanding of the effect of concentration on the limestone- H_2S reaction can be obtained by comparing the conversion vs. time curve for the reaction carried out under 3000 ppm of H_2S (solid curve) and the normalized curve (dotted curve) obtained by scaling

Figure 6.1: Theoretical equilibrium concentrations of species formed from a mixture of 70% CO_2 , 0.6% H_2S , and 29.4% N_2 (molar basis) as a function of temperature.

Figure 6.2: Experimental (—) and theoretical (- - -) conversion vs. time profiles for Georgia marble sulfided at 750°C and 3000 ppm H_2S under an atmosphere of 70% CO_2 (molar basis) and N_2 .

Figure 6.3: Experimental (—) and theoretical (---) conversion vs. time profiles for Greer limestone sulfided at 750°C and 3000 ppm H_2S under an atmosphere of 70% CO_2 (molar basis) and N_2 .

Figure 6.4: Experimental (—) and theoretical (- - -) conversion vs. time profiles for Iceland spar sulfided at 750°C and 3000 ppm H_2S under an atmosphere of 70% CO_2 (molar basis) and N_2 .

Figure 6.5: Effect of temperature on the conversion-time curves for the direct sulfidation of Georgia marble with 3000 ppm H_2S .

the time axis by a factor of 2 (that is, the ratio of the two concentrations) for the reaction carried out under 6000 ppm of H_2S (dashed curve). Nearly overlapping conversion-time profiles are seen from the comparison of the solid line with the dotted line over the whole reaction. This indicates that the overall diffusion-reaction mechanism of the limestone- H_2S reaction is affected linearly by changes in the concentration of the reactive gas. A similar observation was made by Yen et al. (1981) for the initial reaction rates of half-calcined dolomites with H_2S . However, the concentration of SO_2 in the bulk phase had highly nonlinear effects on the diffusion-reaction mechanism for the direct sulfation of the limestones used in our present study (Krishnan and Sotirchos, 1993a).

6.4. Estimation of kinetic parameters

The intrinsic reaction rate, R_s , was assumed to be related to the concentration at the reaction interface, c , by the equation

$$R_s = k_s c^n \quad (6.1)$$

The initial reaction rate data were used to determine the values of the reaction rate constant, k_s , and order of reaction, n . Because of the low porosity of the precursors – pore structure data will be presented and discussed later – very strong intraparticle diffusional limitations exist in the intraparticle pore space. We therefore assumed that the reaction initially occurs on the external surface of the particles only and that subsequently the process proceeds in a shrinking core fashion. The initial (time zero) reaction rate, $\bar{R}_{obs}$, is thus given by

$$\bar{R}_{obs} = 4\pi a_0^2 k_s c_s^n \quad (6.2)$$

with a_0 being the initial size of the particle and c_s the concentration of H_2S at the external surface of the particles.

A mass balance on H_2S gives

$$\bar{R}_{obs} = 4\pi a^2 k_g (c_b - c_s) \quad (6.3)$$

k_g is the external mass transfer coefficient, c_b the concentration of H_2S in the bulk phase, and a the overall size of the reacting particle. Eq. (6.3), which is valid at any time and

Figure 6.6: Comparison of the conversion vs. time results for Georgia marble (53-62 μm particles) for two concentrations at 750°C. The normalized curve (dotted line) is the conversion-time curve of the 6000 ppm case scaled in time by a factor of 2, the ratio of the two concentrations.

not only initially, can be used to find the value of H_2S concentration at the surface of the particle, needed to determine the kinetic parameters from Eq. (6.2). k_g can be found from the Sherwood number, $Sh = k_g a/D$, where D is the bulk diffusion coefficient of H_2S in the H_2S -gas mixture. Employing a value of $Sh = 1$, the value for a stagnant atmosphere around the solid particles, it was found that, even for the largest reaction rates that we measured, the concentration of H_2S at the surface was practically equal to the concentration of H_2S in the bulk phase, viz., $c_s = c_b$.

Limestone	Temp. (°C)	k_s (cm/s)	E (kcal/mol)
GL	750	0.2101	4.304
	650	0.1673	4.304
GM	750	0.1359	5.214
	650	0.1031	5.214
IS	750	0.1019	3.285
	650	0.0856	3.285

Table 6.2: Intrinsic reaction rate constants and activation energies for the direct sulfidation of the limestones. GL=Greer limestone, GM=Georgia marble, and IS=Iceland spar.

In agreement with the results of Fig. 6.6, the initial reaction rates were found to be proportional to the bulk concentration of H_2S for all combinations of limestone, temperature, and particle size, and thus, the order of reaction was estimated to be 1 for all solids. With the value of n known, Eq. (6.2) was used to find k_s for each particle size, temperature, and concentration combinations, and the average of all values determined at a given temperature was adopted as the corresponding intrinsic rate constant at this temperature. The obtained results are reported in Table 6.2, where it is seen that the magnitude of intrinsic kinetic rate decreases in the order Greer limestone $\rightarrow$ Georgia marble $\rightarrow$ Iceland spar. Table 6.2 also lists the activation energies that were computed from the intrinsic reaction rate constants by assuming Arrhenius-type dependence on temperature.

Temperature appears to affect similarly the intrinsic kinetics of all three stones, but its influence is rather weak. Much higher activation energies, of the order of 30 kcal/mole, were obtained for the direct reaction of the same stones with SO_2 (Krishnan and Sotirchos, 1993a). On the other hand, studies on the sulfidation of their calcines gave an activation energy for k_s of the order of 6 kcal/mole (Efthimiadis and Sotirchos, 1992).

6.5. Effects and structure of product layer

Fig. 6.7 compares the conversion-time profiles of the three limestones for direct sulfidation at $750^\circ C$ and under 3000 ppm of H_2S for the two smaller size ranges used in this study. The initial overall reactivities of the three stones vary in the same way as their intrinsic reactivities (see Table 6.2) for both particle sizes because the process is controlled at its initial stages by the intrinsic sulfidation kinetics. As the conversion increases and the product layer becomes thicker, the resistance for diffusion of H_2S through the latter becomes higher, and the transport of H_2S may eventually become the controlling step of the overall process. In the light of this observation, the results of Fig. 6.7 suggest that diffusion through the product layer plays a crucial role in determining the conversion vs. time trajectories of the samples. The relative differences between the conversion levels reached by the Iceland spar samples and those for the other two samples increase with increasing conversion, indicating higher resistance for diffusion through the Iceland spar product layer. Despite their smaller intrinsic reactivity, the Georgia marble particles reach higher conversion than their Greer limestone counterparts after some reaction time increases with decreasing particle size. This behavior indicates that the product layer formed during the direct sulfidation of Georgia marble presents less resistance to H_2S transport than that of Greer limestone.

The last result was corroborated by the pore size distributions that were obtained from nitrogen sorption for fully sulfided samples of Greer limestone and Georgia marble (Fig. 6.8). The samples were sulfided at $750^\circ C$ under 6000 ppm of H_2S . Although the pore size distribution of the sulfided Greer limestone is shifted towards larger pores when compared with that of Georgia marble, the overall pore volume it represents is definitely smaller (0.027 cc/g for Georgia marble vs. 0.02 cc/g for Greer limestone). It appears like the

Figure 6.7: Comparison of the conversion vs. time results during direct sulfidation at 750°C of the three limestones under 3000 ppm H_2S for two particle size ranges.

higher porosity of the fully sulfided Georgia marble sample (approximately 7% compared to 5% for the fully sulfided Greer limestone sample), and hence its more open structure, leads to lower resistance for mass transport of H_2S in its product layer, enabling it to perform better than Greer limestone at high conversions. The observed increase with decreasing particle size in the time needed for the Georgia marble conversion to surpass that of Greer limestone agrees with this explanation. In addition to N_2 sorption, mercury intrusion porosimetry using a Micromeritics Autopore II 9220 unit was employed to characterize the sulfided samples. Intrusion of mercury was seen to occur mainly in the pore size range covered by the N_2 sorption experiments. Because of the very small intrusion volumes, the pore size distributions that could be extracted from the mercury intrusion data were thought not to be as reliable as those determined from adsorption measurements.

A comparison of the direct sulfidation and direct sulfation reactions of the limestones used in our study also reveals variations in the mass transport rates of the reactive gases caused by differences in the structure of the product layer. Fig. 6.9 compares conversion evolution curves for direct sulfidation with direct sulfation results (Krishnan and Sotirchos, 1993a) for Georgia marble at $750^\circ C$ and 1500 ppm of gaseous reactant (H_2S or SO_2). Results analogous to those of Fig. 6.9 were obtained for all size ranges and solids, that is, in all cases the direct sulfidation process proceeded at a much faster rate than direct sulfation. The smaller overall rate of the limestone- SO_2 reaction at small reaction times is a reflection of its lower intrinsic rate. On the other hand, the tendency of the relative difference between the sulfidation and sulfation conversions to increase with the reaction time is an indication of stronger diffusional limitations in the sulfated layer. The higher intraparticle mass transport rate for the limestone- H_2S reaction could be caused by both the more open structure of the sulfid layer and its smaller thickness for the same conversion level.

Some comparative results on the structure of the product shell are shown in Fig. 6.10 which shows pore size distributions, obtained from N_2 sorption data, for different treatments of Greer limestone. The heat treated sample was prepared under 70% CO_2 and 30% N_2 . Its pore size distribution is used as reference in the discussion of the results since the samples were exposed to the same high temperature environment before the start of the reaction. The effects of heat treatment under a noncalcining environment on the pore

Figure 6.8: Comparison of the pore size distributions, determined from N_2 sorption data, of fully sulfided Greer limestone and Georgia marble samples at $750^\circ C$ and 6000 ppm H_2S .

Figure 6.9: Comparison of conversion vs. time results for direct sulfidation of Georgia marble at 750°C and $1500 \text{ ppm } \text{H}_2\text{S}$ with those obtained for direct sulfation (Krishnan and Sotirchos (1993a)).

size distributions of the precursor stones have been discussed in detail by Krishnan and Sotirchos (1993a). The results of Fig. 6.10 show that the pore size distributions of the precursor, heat-treated sample, and 80% sulfated sample represent very low porosity and are not very different. The directly sulfided sample is much more porous than the heat-treated solid and the sulfated sample, and therefore, its product layer must offer less resistance to mass transport than the sulfated layer.

The measured porosity for the sulfided solid is well below the value that would result if the overall particle size remained unchanged. The solid product (CaS) occupies less space than a stoichiometrically equivalent amount of solid reactant ($CaCO_3$). Specifically, the ratio of the molar volume of product to that of reactant is about 0.7, and thus, the sulfided layer should be approximately 30% porous if there were no particle shrinkage (most probably the result of sintering of CaS) during sulfidation. A different situation is encountered in the case of sulfation where the solid product ($CaSO_4$) is bulkier than the reactant (the ratio of the molar volume of the solid product to that of the solid reactant is about 1.24), and thus, an increase in the overall particle size must occur even if a nonporous product layer is formed during sulfation. Because of this difference, the product layer thickness is larger for the same conversion level in the case of the sulfation reaction, and this along with smaller porosity of the product layer leads to a much higher overall resistance for diffusion from the external surface of the particles to the unreacted core. To all these one should also add the fact that a larger molecule (SO_2) is involved in the sulfation reaction.

We mentioned earlier that several reactions involving limestones may occur in a gasifier. The $CaO-H_2S$ reaction and the $CaCO_3-H_2S$ reaction are the primary routes of desulfurization in coal gasifiers. In contrast to the direct sulfidation where, as we have seen in Figs. 6.8 and 6.10, the solid is initially nonporous and develops limited porosity in the course of the reaction, the $CaO-H_2S$ reaction involves a solid with a well developed porous structure and, hence, high internal surface area. The existence of high surface area in the calcined solid enables its sulfidation to proceed with a much higher rate than the limestone- H_2S reaction. Some comparative results are shown in Fig. 6.11 for Georgia marble reacted at $750^\circ C$ under 3000 ppm of H_2S . Whereas all CaO present in the calcines

Figure 6.10: Pore size distributions of partially sulfated (directly) and fully sulfided (directly) Greer limestone. Direct sulfidation was carried under 6000 ppm of H_2S at $750^\circ C$. Direct sulfation was carried under 6000 ppm of SO_2 at $850^\circ C$.

is converted to CaS for all particle sizes, only part of $CaCO_3$ is sulfided within the time interval shown in the figure. These results lend further support to the conclusion that the mechanisms of desulfurization under calcining and noncalcining conditions differ radically and that the fundamental knowledge that exists in the literature on the $CaO-H_2S$ reaction can only be of limited help in understanding the mechanism of the limestone- H_2S reaction.

6.6. Product layer diffusivities and discussion

Because of the low porosity of the precursor stones, the limestone- H_2S reaction starts with H_2S reacting with $CaCO_3$ mainly at the periphery of the particles to form CaS , the solid product. Further sulfidation can take place only by diffusion of H_2S through the product layer and reaction with $CaCO_3$ at the interface between reacted and unreacted solid. If the particles react in a shrinking core fashion, the product layer exists in the form of a shell next to their external surface. A mathematical model describing the shrinking core behavior observed during direct sulfation of limestones was developed by Krishnan and Sotirchos (1993b). A diffusion coefficient varying with the distance from the external surface of the particles and nonlinear kinetics were employed in that model, but preliminary computations for limestone sulfidation showed that satisfactory agreement between model and experiment could be obtained for constant diffusion coefficient in the product layer. Equations for a shrinking core model with constant diffusivity in the product layer are given in several sources of the literature (e.g., Szekely et al. (1976) and Levenspiel (1972)). For linear kinetics and spherical particles, the relation between time and conversion is given by

$$\tau = 1 - \rho + \frac{\phi^2}{2}(1 - \rho^2) + \frac{\phi^2}{(1 - Z')}\left(\frac{1}{2} - \frac{1}{Sh_e}\right)((Z' + (1 - Z')\rho^3)^{2/3} - 1) \quad (6.4)$$

where

$$\tau = tv'_s k_s c_b / a_0; \quad Sh_e = k_g a_0 / D_e \quad (6.5a, b)$$

$$\phi^2 = k_s a_0 / D_e; \quad \rho = a_c / a_0 \quad (6.6a, b)$$

and the overall conversion X is given by

$$X = 1 - \rho^3 \quad (6.7)$$

Figure 6.11: Comparison of the conversion vs. time curves for the $\text{CaO-H}_2\text{S}$ (Efthimiadis and Sotirchos (1992)) and the $\text{CaCO}_3\text{-H}_2\text{S}$ (this study) reactions. In both cases, the data are for 3000 ppm H_2S and 750 °C. The calcines were prepared at the same temperature under 100% N_2 .

D_e is the effective diffusivity of H_2S through the product layer, v'_s is the volume of the unreacted solid (including the pore space) per mole of solid reactant, a_0 and a_c are the initial radius and the unreacted core radius of the particles, respectively, and Z' is the stoichiometric volume ratio of the solid product-solid reactant pair, that is, the volume of reacted solid per unit volume of stoichiometrically equivalent amount of unreacted solid.

v'_s can be estimated from the initial composition and porosity of each limestone, whereas the estimation of Z' also requires the porosity of the reacted layer. We have the equations:

$$v'_s = \frac{v_{CaCO_3}}{(1 - \epsilon_s)\psi_{CaCO_3}} \quad (6.8)$$

$$Z' = \frac{(1 - \epsilon_s)}{(1 - \epsilon_p)}(1 + (Z - 1)\psi_{CaCO_3}) \quad (6.9)$$

v_{CaCO_3} is the molar volume of $CaCO_3$, Z is the ratio of the molar volume of CaS to that of $CaCO_3$, ψ_{CaCO_3} is the volume fraction of $CaCO_3$ in the solid phase of the limestone precursor, and ϵ_s and ϵ_p are the porosities of the unreacted and completed reacted solid, respectively. For high $CaCO_3$ content and low unreacted and reacted solid porosities, Eqs. (6.8) and (6.9) suggest that v'_s and Z' can be approximated by v_{CaCO_3} and Z , respectively.

The following observation may be used to check the assumption that the direct sulfidation of limestones proceeds in a shrinking core fashion. Different size particles develop product shells of different thickness at the same conversion level. It can be shown that for slab geometry particles, the variation of the product layer thickness with time is independent of particle size if the effective diffusivity in the product layer depends on the distance from the external surface of the particles only. This is also true for other particle geometries at relatively low conversion levels, that is, before the effect of the curvature of the particles becomes significant. The variation of the product layer thickness with time for Georgia marble reacted at $750^\circ C$ under 3000 ppm of H_2S is displayed in Fig. 6.12. The curves shown in the figure have been obtained from the experimental conversion vs. time results with the product layer thickness computed from the expression $d = a_0[(Z' + (1 - Z')(1 - X))^{1/3} - (1 - X)^{1/3}]$. Nearly identical variation of the product layer thickness with time is seen for all particle size ranges in Fig. 6.12, indicating that

the hypothesis of a shrinking core behavior for the reaction of Georgia marble with H_2S is correct. Similar behavior was observed for the product thickness vs. time curves of all cases investigated in this study.

The only parameter that remains to be determined from the experimental results is the effective diffusivity of the reactive gas (H_2S) through the product layer surrounding the core of unreacted limestone. We estimated the effective diffusivity by matching the model predictions (Eq. (6.12)) with the experimental conversion-time curves through a least squares error minimization procedure. In estimating D_e at a certain temperature, all conversion vs. time results available at this temperature (i.e., for all particles and concentrations) were employed. Table 6.3 lists the effective diffusivity values we estimated. The highest value of effective diffusivity was obtained for Georgia marble reacted at $750^\circ C$, twice the value determined for Greer limestone reacted at the same temperature. This result agrees with the behavior seen in Fig. 6.7, where the overall reactivity of Georgia marble is initially lower than that of Greer limestone but surpasses it as the conversion increases, the product layer becomes thicker, and diffusion in the product layer becomes the controlling step. At $650^\circ C$, Greer limestone reached slightly higher conversion than Georgia marble at all times, and this fact is reflected in having comparable diffusivity values for the two solids. The value of D_e for Iceland spar is at both temperatures much smaller than the values for Greer limestone and Georgia marble, indicating that its lower overall reactivity (see Fig. 6.7) is due not only to its lower intrinsic reactivity but also to the higher resistance of its product layer to H_2S transport.

In our study of the direct sulfation of limestones (Krishnan and Sotirchos, 1993), we found that the overall sulfation reactivity and the effective diffusivity in the product layer decreased in the order Greer limestone $\rightarrow$ Georgia marble $\rightarrow$ Iceland spar, that is, in the order of increasing grain size in the precursor and decreasing porosity (see Table 6.1). On the basis of this observation, it was postulated that the petrographic structure of a limestone plays a very important role in determining its product layer structure and, hence, its overall sulfation reactivity. Similar conclusions were reached from the study of the sulfation of the calcines of the same solids (Sotirchos and Zarkanitis, 1992). The overall reactivity also increased in the same order during sulfidation of calcined particles in the

Figure 6.12: Product layer thickness vs. time for the three particle size ranges of Georgia marble assuming shrinking core behavior.

53-62 and 88-105 μm size ranges (Efthimiadis and Sotirchos, 1992), but larger particles exhibited the behavior seen here for direct sulfidation at large reaction times, that is, the Georgia marble sample reacted faster than the other two.

Limestone	Temp. ($^{\circ}\text{C}$)	D_e (cm^2/s)	σ^2/a_0 (cm^{-1})
GL	750	5.26×10^{-5}	665.72
	650	46.67×10^{-6}	4180.41
GM	750	1.11×10^{-4}	204.05
	650	6.25×10^{-6}	2749.33
IS	750	7.14×10^{-6}	2378.62
	650	1.82×10^{-6}	7838.83

Table 6.3: Effective diffusivities for H_2S through the product layer and values of σ^2/a_0 for the different types of limestones at 750°C and 650°C . GL=Greer limestone, GM=Georgia marble, and IS=Iceland spar.

Effective diffusion coefficients, for diffusion in the pore space of the calcines, larger than those used for sulfation of the same sorbents (Zarkanitis and Sotirchos, 1992) had to be employed by Efthimiadis and Sotirchos in order to be able to reproduce the indirect sulfidation data using a pore-based mathematical model. Since Georgia marble particles tend to explode during heating under CO_2 at high rates – because of the decomposition of the MgCO_3 contained in them – Efthimiadis and Sotirchos postulated that the apparently aberrant behavior of large Georgia marble particles was due to the development of cracks in their interior during heating which decreased the resistance for mass transport in their pore space. The formation of these cracks did not have such a dramatic effect on the sulfation behavior of the particles because sulfation leads to complete pore plugging and, as a result, even these large pores are eventually filled with solid product. This explanation may also be applicable to the observed differences between direct sulfation (Krishnan and Sotirchos, 1993b) and direct sulfidation (present study) in the variation of reactivity and effective diffusivity in the product layer among the three samples. As we mentioned earlier,

the direct sulfation involves formation of a bulkier, than the reactant, solid product, which causes plugging of any initially present pores, while sulfidation is accompanied by reduction of volume which, if particle shrinkage did not occur, would yield a porous sulfided product having about 30% porosity.

Figs. 6.2-6.4 compare the predictions of the shrinking core model, for the effective diffusivities of Table 6.3, with the experimental conversion vs. time curves for reaction at 750°C and 3000 ppm of H_2S . Very good agreement between theory and experiments is seen to exist for all three limestones, and similar behavior was observed for reaction at 650°C . The predictions of the model were also tested by comparing the theoretical and experimental product layer thickness vs. time curves. Such a comparison is made in Fig. 6.13 for the smallest size range ($53\text{--}62\ \mu\text{m}$) for the three limestones reacted at 750°C and under 3000 ppm of H_2S . As in the case of the conversion vs. time curves, the model reproduces satisfactorily the experimental data for the whole duration of the experiment.

The results of Figs. 6.2-6.4 and 6.13 point to the conclusion that a constant effective diffusivity shrinking core model can adequately describe the direct sulfidation of limestones. However, a closer look at the experimental and theoretical conversion vs. time curves of Figs. 6.2-6.4 reveals that in all cases the mathematical model tends to overestimate the conversion at the early stages of the reaction and overpredict it after some reaction time. This behavior suggests that the overall resistance to mass transport in the product layer decreases as the reaction progresses. The decrease in the mass transport resistance is most probably caused by the formation of a more open product layer with increasing conversion, which causes the diffusion coefficient to increase away from the external surface of the particles. On the contrary, the analysis of direct sulfation data for the same limestones revealed a progressively increasing mass transport resistance (Krishnan and Sotirchos, 1993). This opposite behavior is not surprising considering that the way of formation of the product layer during direct sulfation – where the nascent product layer pushes against a progressively thicker product layer – is in contrast to that in direct sulfidation – where the product shell collapses with the progress of reaction.

From the extracted values of effective diffusivities and the intrinsic reaction rate constants obtained earlier, it is possible to determine which mechanism controls the direct

Figure 6.13: Comparison of the theoretical (continuous curves) and experimental (distinct data points) product layer thickness vs. time results for the small particles of the three solids directly sulfided at 750°C under 3000 ppm of H_2S .

sulfidation process using the ratio of the reaction time for complete conversion under mass transport control to that for reaction in the kinetically controlled regimes (Szekely et al. (1976)). For a first order reaction and negligible external diffusional limitations (i.e., $Sh_e = \infty$), it follows from Eq. (6.4) that this ratio is given by

$$\sigma^2 = \frac{1}{2} \phi^2 \left(\frac{Z' - Z'^{2/3}}{Z' - 1} \right) = \frac{1}{2} \frac{k_s a_0}{D_e} \left(\frac{Z' - Z'^{2/3}}{Z' - 1} \right) \quad (6.10)$$

The overall reaction can be considered to be under total kinetic control for $\sigma^2 < 0.1$ and under total diffusional control for $\sigma^2 > 10$. Values of σ^2/a_0 for $Z' = 1$ (i.e., of $k_s/(6D_e)$) in cm^{-1} are reported in Table 6.3 for the various cases we studied. It follows from these values that at $650^\circ C$ the reaction was controlled by diffusion in the product layer in all cases except for the 53-62 μm size range of Georgia marble which yields a value of 7.9 for σ^2 . On the other hand, at $750^\circ C$ the reaction was under complete diffusion control only for the larger two size ranges of Iceland spar and the 297-350 μm size range of Greer limestone. All other cases were reacted in the intermediate regime where both kinetics and diffusion in the product layer are controlling the process.

Much lower product layer diffusivities were estimated by Krishnan and Sotirchos (1993b) from the analysis of reactivity vs. time data for direct sulfation. Specifically, for Greer limestone and Iceland spar the diffusivities in the sulfated layer at the onset of the reaction – a variable product layer diffusivity was used for direct sulfation – are lower by about a factor of 5 than the sulfided layer values of Table 6.3, whereas for Georgia marble the difference is about an order of magnitude. This result and the formation of a thicker product layer during direct sulfation provide an explanation for the lower direct sulfation rates of the three solids (see Fig. 6.9 for Georgia marble). The values of effective diffusivities through the product shell developed during indirect sulfidation of the limestones (i.e., sulfidation of the calcines) are two to three orders of magnitude lower than the values of Table 6.3 (Efthimiadis and Sotirchos, 1992). Similar differences were noted (Krishnan and Sotirchos, 1993b) between the product layer diffusivities of the direct and indirect sulfation of the three samples. Nevertheless, the existence of a pore network in the interior of the calcined particles enables the reaction to take place throughout the intraparticle space, leading to higher reaction rates than in the case of direct reaction

despite the smaller product layer diffusivities. Of course, for calcine sulfation this happens before plugging of the pore space with solid product and formation of inaccessible pore space lead to stoppage of the sulfation reaction.

Arrhenius-type dependence of the product layer diffusivity on temperature was assumed, and the results of Table 6.3 were used to determine the activation energy. The highest value of 53.78 kcal/mole was obtained for Georgia marble, followed by Greer limestone with 38.61 kcal/mole and Iceland spar with 25.55 kcal/mole. These values are by almost an order of magnitude higher than the activation energies of the direct sulfidation reaction, in agreement with our earlier observation that the influence of temperature on the process becomes stronger as the conversion increases and the role of diffusion in the product layer becomes more important. Efthimiadis and Sotirchos (1992) reported much lower values for the product layer diffusivities of the $CaO-H_2S$ reaction, namely, 13, 16, and 13 kcal/mole for Georgia marble, Greer limestone, and Iceland spar, respectively. Activation energies comparable to the values of Table 6.3 were estimated by us in our previous study of the direct sulfation of the same stones (Krishnan and Sotirchos (1993b)). This results indicates that temperature has similar influence on the product layer diffusivity during direct sulfidation and sulfation.

The large differences in the values of the product layer diffusivities at the two temperatures (650 and 750°C) for the limestone- H_2S reaction cannot be justified by the effect of temperature on the diffusion process since the diffusivity values of Table 6.3, in conjunction with the pore structure characterization data, suggest that diffusion occurs in the Knudsen diffusion regime. Therefore, the product layer structure must be strongly influenced by the temperature of the reaction. This conclusion is in agreement with observations made by Attar and Dupuis (1979) in their study of the direct sulfidation of calcites. At temperatures higher than 640°C, they noticed a sudden rise in the rate of the $CaCO_3-H_2S$ reaction accompanied by separation of the CaS crystals formed on the $CaCO_3$ surface.

6.7. Summary

The reaction between $CaCO_3$ and H_2S was studied by employing three solids of high calcium carbonate content, a microcrystalline limestone (Greer limestone), a coarsely-

grained marble (Georgia marble), and a single-crystal calcite (Iceland spar), and carrying out the reaction in the presence of CO_2 to prevent the decomposition of $CaCO_3$ to CaO . The effects of particle size, temperature, and H_2S concentration were investigated. Very strong influence of particle size and temperature on the behavior of the process was revealed by the experimental data. The concentration of the gaseous reactant was found to affect linearly both the intrinsic kinetics of the reaction and the process of diffusion in the intraparticle space. Because of the very low porosity of the three solids, the reaction was assumed to proceed in a shrinking core fashion, and the initial reaction rate data were used to estimate the intrinsic reaction rate constant. It was found that the intrinsic reaction rate constant decreased in the order Greer limestone $\rightarrow$ Georgia marble $\rightarrow$ Iceland spar at both temperatures, that is, in the same order as the intrinsic rate constant of the direct sulfation reaction (Krishnan and Sotirchos, 1993a).

The characterization of the pore structure of fully sulfided solids using mercury porosimetry and N_2 adsorption-desorption data revealed that the reacted solids possessed little porosity, much smaller than the 30% (approximately) value that would have resulted if the overall size of the particle did not change during sulfidation. A shrinking core model based on the assumption of a homogeneous product layer (and therefore of a constant effective diffusivity in the product shell) was employed to analyze the direct sulfidation data and to estimate the effective diffusion coefficient through the product layer. From the estimated values of effective diffusivity and intrinsic reaction rate constant, it was determined that in most cases studied the limestone- H_2S reaction was controlled by diffusion in the product layer, while in the rest it was under the control of both intrinsic kinetics and diffusion in the product layer. The product layer diffusivities for Greer limestone and Georgia marble were found to be comparable but higher than those determined for Iceland spar. This result agreed with the variation of the overall reaction rate among the three solids, especially at high conversion levels where the process was controlled by diffusion in the product layer.

The values of effective diffusivities through the product layer of direct sulfidation were found to be higher than those in the product layer of direct sulfation, in agreement with the higher overall reactivity of the former reaction. Also, they were much higher than

the product layer diffusivities for sulfidation of the calcines and exhibited much higher sensitivity to temperature than them. Since this strong dependence on temperature cannot be justified by the diffusion process itself – the diffusivity values in the product layer of direct sulfidation suggest that diffusion occurs in the Knudsen regime – we concluded that the structure of the product layer formed during direct sulfidation varies with the reaction temperature.

Very good agreement was obtained between theory and experiment for all cases, and it was thus concluded that a shrinking core model with a constant effective diffusivity can adequately describe the direct sulfidation process. The agreement between theory and experiment could be improved by employing a variable diffusivity shrinking core model, with decreasing mass transport resistance with progress of reaction. In contrast, an increasing mass transport resistance with progress of reaction was observed for the direct sulfation of limestones (Krishnan and Sotirchos, 1993). It is believed that the different way of formation of the product layer (outward expansion during direct sulfation vs. inward shrinkage during direct sulfidation) is the main cause for the different evolution of intraparticle mass transport resistance with the progress of reaction during these two processes.

6.8. Notation

Symbols that do not appear here are defined in the text.

a	radius of the particle, cm
a_0	initial radius of the particle, cm
a_c	radius of unreacted core, cm
c_b	concentration of H_2S in the bulk, mol/cm^3
c_s	concentration of H_2S at the surface of the particle, mol/cm^3
D_e	effective diffusivity of H_2S in the product layer, cm^2/s
k_g	external mass transfer coefficient, cm/s
k_s	intrinsic reaction rate constant, cm/s
n	order of reaction with respect to H_2S
Sh_m	effective Sherwood number defined by Eq. (6.5b)
t	time, s

v'_s	volume of unreacted core per mole of $CaCO_3$, cm^3/mol
X	conversion of the reacting solid
Z'	volume of reacted solid phase per unit volume of unreacted solid phase (including pore volume)

Greek

ϕ^2	Thiele modulus defined by Eq. (6.6a)
ρ_c	dimensionless radius of unreacted core, a_c/a_0
σ^2	shrinking core reaction modulus defined by Eq. (6.10)
τ	dimensionless time defined by Eq. (6.5a)

6.9. Literature References

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7. EXPERIMENTAL VALIDATION OF A MATHEMATICAL MODEL FOR FIXED-BED DESULFURIZATION

7.1. Introduction

The tendency of various metal oxides to react with sulfur-containing compounds is used to remove such species (primarily H_2S) from coal-derived gas at high temperatures. Several supported or unsupported oxides, in single or mixed form, have been studied experimentally in the literature as candidate sorbents for hot coal gas desulfurization (for example, see studies by Caillet and Harrison (1982), Yumura and Furimsky (1985), Tamhankar et al. (1986), Gangwal et al. (1989), and Efthimiadis and Sotirchos (1991)). In most cases ZnO has been used as one of the active components of the sorbent, since many studies have shown that its use leads to very low equilibrium H_2S concentrations in the exit stream of the desulfurization reactor. Coal gas desulfurization is carried out in fixed-bed reactors, but other reactor configurations, such as moving and fluidized-bed reactors, are currently under study and development (Jain et al. (1990) and Lee et al. (1990)). Fixed-bed reactors are also used, almost exclusively, in experimental studies of the performance of coal gas desulfurization sorbents.

Mathematical models for fixed-bed reactors are very useful in design and scale-up studies, especially if they are capable of predicting the behavior of these units for different conditions from those at which they were tested and validated. They are also indispensable for the analysis of experimental data from lab-scale fixed-bed reactors employed in laboratory studies since, because of the very high rate of reaction of metal oxides with H_2S , it is practically impossible to achieve differential operation of such reactors. Desulfurization in fixed-beds is a complex process requiring consideration of a large number of subprocesses for its description. One has to consider mass transport in the particles, mass transport through the product layer formed in the interior of the particles, reaction at the unreacted- reacted solid interface, and evolution of the physical microstructure of the reacting particles. Since the concentrations of sulfur-containing pollutants in coal gas streams are typically low, small amounts of heat are released during the reaction, and consequently, consideration of heat transport is not necessary for the description of the

process. A mathematical model for a fixed-bed desulfurization reactor, therefore, consists of three submodels, one for describing mass transport and reaction in the bed, another for mass transport and reaction in the particles, and a third for local reaction and structure evolution within the particle or pellet.

The equations for mass transport and reaction in the fixed-bed are relatively well-defined. Thus, what really differentiates one fixed-bed model from another is the submodel used to describe the behavior of the individual sorbent pellets or particles in the bed. If one wants to avoid the complication of developing a theoretical single pellet model and testing it, the only available alternative is to use experimental data for single pellets or differential reactors to develop an experimental single pellet model, that is, a correlation for the dependence of the average reaction rate of the pellets (or particles) on solid conversion, temperature, and reactant concentration. Of course, such a model will be useful only if the conditions used in the operations of the fixed-bed are within the range used to develop the experimental model. Such an approach was taken, among others, by Park et al. (1984) in their study of the oxidation of reduced iron oxide with water vapor, a problem fundamentally similar to that of metal oxide sulfidation.

The performance of a mathematical model for coal gas desulfurization in fixed beds is examined in this study. The mathematical model is developed along the lines of fixed-bed desulfurization model by Sotirchos and Zarkanitis (1989). The random pore and grain models of Sotirchos and Yu (1985, 1988) for gas-solid reactions with solid product were used by Sotirchos and Zarkanitis to describe the behavior of individual pellets, but in our model, we will make use of the generalized random pore model of Yu and Sotirchos (1987), a model for reaction and structure evolution in porous media of pore-network structure undergoing a gas-solid reaction with solid product. Past studies on the sulfidation of two zinc oxide sorbents in a thermogravimetric analysis system (Efthimiadis and Sotirchos, 1991) showed that this structural model can successfully describe the behavior of single particles over a broad range of operating conditions. The fixed-bed desulfurization model is evaluated using experimental data for sulfidation of ZnO sorbents in a fixed-bed reactor, obtained in our laboratory at various combinations of operating conditions using the same two sorbents used in our past studies. No adjustable parameters are used in the comparison of

model predictions and experimental data since all parameters needed for the description of individual particles using the generalized random pore model have been determined independently from thermogravimetric analysis data.

7.2. Materials

The sorbents used in this study were mixtures of metal oxides with ZnO being the main constituent and other compounds (Al_2O_3 , SiO_2 , CaO , and MgO) being present in smaller amounts. The fresh materials were obtained from United Catalysts in the form of 3/16" extrusions with the commercial names: catalysts G-72D and C7-2. The unreacted materials showed some weight loss during the heat-treatment under nitrogen flow, most probably caused by removal of volatile compounds (binder solid and humidity). For this reason, the unreacted solids were heat-treated for 30 min at $600^\circ C$ before each sulfidation experiment. The compositional analysis of the two sorbents showed that 89% of sample G-72D and 78% of sample C7-2, on a weight basis (after heat treatment), was zinc oxide. The rest was mainly alumina and silica in sample C7-2 and alumina in sample G-72D. The extrusions were crushed and divided into particle size ranges using mechanical sieving.

Zinc Oxide Sample	G-72D	C7-2	C7-2*
Total Pore Volume (Hg porosimetry), cm^3/g	0.178	0.289	0.275
BET Surface Area, m^2/g	26.57	27.72	25.52
Most Probable Radius (Hg Porosimetry), $\text{\AA}$	115	200	200
Most Probable Radius (N_2 Adsorption), $\text{\AA}$	125	180	200

Table 7.1: Physical properties of the unreacted heat-treated sorbents. (*=Second batch of sorbent C7-2).

Particles of 297-350 μm were used in the characterization of the pore structure of the solids. In Table 7.1 we summarize the physical properties of the unreacted heat-treated materials. Pores in the range of 10,000-20 $\text{\AA}$ were accounted for in the estimation of the pore volumes of Table 7.1 that were obtained from the mercury porosimetry data. The

physical properties of the micropores (pores of radius less than 20 Å) were computed using the t-method (De Boer et al., 1965). The small micropore volume and surface area of both materials and the pore size distributions of the solids (to be presented later in Figs. 7.13 and 7.14) showed that the pore space of both samples consists primarily of mesopores (pores with radius in the range 20-500 Å) and macropores (pores with radius larger than 500 Å). The BET surface area of the two sorbents is almost the same, but there is a significant difference in their pore volumes and most probable pore radii. (The most probable radius is the value where the slope of the cumulative pore volumes vs. pore radius curve has its maximum value). Sample C7-2* corresponds to a different batch of catalyst C7-2. It can be seen from the Table 7.1 that there are negligible differences between the physical properties of the two batches of sample C7-2. Moreover, when samples of the two batches were sulfided under identical reaction conditions, the conversion vs. time curves were, within experimental error, identical. A detailed investigation of the pore structure of unreacted sorbents G-72D and C7-2 and their sulfides was carried out in another study by Efthimiadis and Sotirchos (1991).

7.3. Apparatus and Procedure

Sulfidation experiments were carried out isothermally in a fixed-bed reactor system, which is shown in Fig. 7.1. The reactor was a quartz tube of 1.5 or 0.75 cm I.D. mounted vertically in a 3-zone furnace, which maintained a uniform temperature profile in the reactor. The sorbent was placed in the quartz tube between two zones of spherical quartz beads (1 mm in diameter) of about 2 cm in height each. The sorbent bed was supported by quartz wool placed at the bottom of the lower zone of quartz beads and at the top of the upper zone. The configuration of the reactor allowed the measurement of the reactor temperature using two thermocouples, one introduced through the upper fitting of the tube, as shown in Fig. 7.1, and the other through the fitting at its bottom. In a typical experiment, the thermocouple tips were placed outside the bed at a distance of a few mm from the quartz wool. However, in two runs the upper thermocouple was placed in the middle of the sorbent bed in order to measure the variation of the temperature in the sorbent bed during the reaction. The temperature difference between the indication of

this thermocouple and that at the entrance of the reactor was less than 3°C at all times, implying that small amounts of energy were released by the exothermic reaction at the reaction conditions of our study.

The fixed-bed reactor of Fig. 7.1 was loaded with particles of 210-250, 297-350, and 710-850 μm . The bed voidage was computed from the dimensions of the sorbent bed, the weight of the solid, and the bulk density of each sorbent (2.7 g/cm^3 for sample G-72D and 2.0 g/cm^3 for sample C7-2), the latter determined from the skeletal density and porosity of the unreacted materials. It was found that the bed voidage was approximately 40% for the two reactor tubes and for all particles sizes used in this study. This value agrees with the experimental data of Dixon (1988) on the dependence of the void fraction in fixed-beds on the particle to tube diameter ratio.

The gas distribution system involved a system of on/off and metering valves, arranged to control the flow rate and composition of the gas stream entering the reactor. The reactive gas was a mixture of 10,500 ppm H_2S in nitrogen, which could be further diluted with nitrogen as shown in Fig. 7.1. Standard correlations for flow through particle beds were used to estimate the pressure drop in the bed; it was found to be negligible for all particle sizes and conditions used in our studies. The gas stream leaving the reactor was divided into two streams. The first (about 90-95% of the main stream) was sent to the vent, while the second was used for gas analysis by sending it through the sampling loop of the injection system of a chromatograph. The injection system consisted of a 6-port valve attached to an electric actuator. A programmable integrator (Chromjet of Spectra Physics) was used for automatic injection and analysis of gas samples every 3 min. The same reactor configuration could also be used for fluidized-bed experiments. Much larger flow rates were used to fluidize the particles during such experiments. The cyclone in Fig. 7.1 was used to separate and collect the fines produced by attrition of the sorbent particles during fluidization.

The gas chromatograph was a Varian 3300 equipped with FPD and TCD detectors. The analysis was carried out isothermally at 90°C with helium as the carrier gas. Preliminary experiments showed that there was a linear relation between the square root of the integrated H_2S peak and the concentration of the injected samples when the H_2S content

Figure 7.1: Schematic of the fixed-bed reactor and the gas analysis system.

of the stream was lower than 2,000 ppm. Thus, low H_2S concentrations were detected by the FPD, while higher H_2S concentrations were measured by the TCD, which could also detect nitrogen and water vapor. The weight of the sulfided sorbent was measured at the end of the experiment, and its difference from the initial sorbent weight (after the loss of the volatile compounds) was used to estimate the average conversion of the sorbent in the bed. This value was, within 1% error, in agreement with the average conversion determined from the variation of the H_2S concentration of the effluent stream of the reactor with time. Samples of reacted material were collected from different parts of the bed and were analyzed by mercury porosimetry and gas adsorption (N_2 at 77 K). A Micromeritics Autopore II 9220 mercury porosimeter and a Quantachrome Autosorb 1 volumetric adsorption unit were used for the characterization of the samples.

7.4. Single Particle Behavior

Gas-solid reactions of the form $Solid + Gas \rightarrow Solid + \dots$, with $\dots$ denoting other gas species participating in the reaction, were modelled by Yu and Sotirchos (1987) in the so-called generalized random pore model. This model accounts for structural changes in the interior of the porous solid, diffusion of the gas species in the pore space and in the product layer, and chemical reaction at the interface between the unreacted and the sulfided solid. The pore space of the solid is assumed to consist of cylindrical pore segments arranged in the form of a three-dimensional lattice. The population of pores is described using the experimentally determined pore size distribution of the unreacted solid (from mercury intrusion data). The equations describing structural changes in the interior of the solid reactant with the progress of the reaction and variation of the intraparticle diffusion coefficient with the local conversion in the particle can be found in the works of Yu and Sotirchos (1987) and Zarkanitis et al. (1990).

The equations that describe diffusion of a gaseous species in a spherical porous particle and reaction with the solid are written using dimensionless quantities as follows:

$$\frac{\partial(\omega_p \epsilon_p y_p)}{\partial \tau_p} = \frac{1}{\Phi^2} \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial}{\partial \rho} (\delta^e y_p) \right) - \nu_A \kappa_v y_p \quad (7.1)$$

$$\frac{\partial \xi}{\partial \tau_p} = \frac{1}{(1 - \epsilon_0)} \kappa_v y_p \quad (7.2)$$

y_p is the concentration of the reactive gas, ρ is the radial distance in the particle, δ^e is the effective diffusivity, κ_v is the volume-based reaction rate constant, ε_0 and ε_p are the porosities of the unreacted and reacted particle, respectively, ξ is the local conversion of the particle, ν_A is the stoichiometric coefficient of the reactive gas, and τ_p is the time. Eqs. 7.1 and 7.2 are written for a first-order reaction with respect to the gaseous reactant, since this was found to be the case for the reaction of sorbents G-72D and C7-2 with H_2S in our previous studies (Efthimiadis and Sotirchos, 1991). The boundary and initial conditions for Eqs. 7.1 and 7.2 are:

$$\frac{\partial y_p}{\partial \rho} = 0|_{\rho=0}; \quad \frac{Sh^e}{\delta^e}(1 - y_p) = \frac{\partial y_p}{\partial \rho}|_{\rho=1} \quad (7.3a, b)$$

$$y_p = 0 \text{ and } \xi = 0 \text{ at } \tau_p = 0 \quad (7.4a, b)$$

The dimensionless quantities shown in Eqs. 7.1-7.4 are defined by the equations:

$$\rho = \frac{r}{a}; \quad y_p = \frac{c_p}{c_b}; \quad \delta^e = \frac{D^e}{D_0^e}; \quad \kappa_v = \frac{k_v}{k_{v0}}; \quad \omega_p = v_s c_b; \quad (7.5a - e)$$

$$\tau_p = v_s k_s S_0 \int_0^t c_b dt'; \quad \Phi^2 = a^2 \frac{k_s S_0}{D_0^e}; \quad Sh^e = \frac{k_g a}{D_0^e} \quad (7.6a - c)$$

The symbols used in Eqs. 7.5 and 7.6 are explained in the notation section of this paper.

Experimental data obtained during the sulfidation of G-72D and C7-2 particles of 53-350 μm were used in previous studies (Efthimiadis and Sotirchos, 1991) to test the applicability of the generalized random pore model to zinc oxide sulfidation. Excellent agreement was found to exist between model predictions and experiment. However, in some of the fixed-bed experiments, the C7-2 particles were larger than those used in our previous sulfidation studies. Therefore, additional sulfidation experiments were performed in the thermogravimetric analysis system using particles of 600-710 and 710-850 μm . C7-2 samples of about 3 mg were reacted with 0.5% H_2S diluted in nitrogen at 200 ml/min flow rate (at standard conditions). Details about the TGA reactor are given elsewhere (Efthimiadis and Sotirchos, 1991). The TGA experimental data were successfully reproduced by the generalized pore model without using any adjustable parameters since the two parameters needed for the application of the mathematical model (diffusion coefficient

in the product layer and coordination number of the pore network (i.e., average number of pores per node)) had been determined in previous studies (Efthimiadis and Sotirchos, 1991) by fitting the model predictions to the experimental data for particles in the size range 53-350 μm . Experimental and predicted conversion vs. time curves for sulfidation at 600°C of C7-2 particles in the size range 210-850 μm are shown in Fig. 7.2.

In the sulfidation of ZnO sorbents, as well as in most gas-solid reactions, the time associated with structural changes in the interior of the particles is much larger than the time associated with the establishment of the steady state profile of the reactive gas concentration in the particles (pseudosteady-state approximation). As a result, the transient term in Eq. 7.1 can be set equal to zero. The average reaction rate per unit of particle volume, $\bar{R}_v$, is then related to the concentration of H_2S in the surrounding gas phase (i.e., in the bed) by the equation:

$$\bar{R}_v = \bar{k}_v(\bar{\xi})c_b \quad (7.7)$$

The average conversion of a particle ($\bar{\xi}$) and the average volumetric reaction rate constant in a particle ($\bar{k}_v(\bar{\xi})$) can be computed from the local conversion (ξ) and reaction rate constant ($k_v(\xi)$) using the equations:

$$\bar{\xi} = \int_0^1 \xi \, d\rho^3 \quad (7.8)$$

$$\bar{k}_v(\bar{\xi}) = \int_0^1 k_v(\xi) y_p \, d\rho^3 \quad (7.9)$$

Shown in Fig. 7.3 is the variation of the volumetric reaction rate constants with the conversion at 600°C for various particle sizes of the two sorbents used in our experiments. The evolution of the average volumetric reaction rate with the average conversion in particles sulfided at 500°C was similar to that of Fig. 7.3. The volumetric reaction rate constants in Fig. 7.3 were normalized with respect to the initial volumetric reaction rate constant in the absence of intraparticle diffusional limitations ($k_{v0} = k_s S_0$). Therefore, the initial value of $\bar{k}_v(\bar{\xi})/k_{v0}$ is equal to the initial effectiveness factor, and as a result, in the absence of initial intraparticle diffusional limitations it should be unity. Increasing the

Figure 7.2: Comparison of the reactivity data obtained in a differential reactor at 600°C with the mathematical model predictions.

particle size intensifies the intraparticle diffusional limitations and leads to lower average reaction rate for the same average conversion in the particle. According to the results of Fig. 7.3, the average reactivity of sorbent G-72D not only is lower than that of sorbent C7-2 (same size particles) but decreases faster with the conversion as well. As the results of Table 7.1 show, sample G-72D has less pore volume per unit mass and smaller most probable radius than sample C7-2. Moreover, it was found from the analysis of the single particle sulfidation data that the effective diffusivity of H_2S in its pore space is smaller and decreases faster with the conversion than that in sample C7-2 (Efthimiadis and Sotirchos, 1991).

7.5. Mathematical Model for a Fixed-Bed Reactor

The development of a mathematical model for a fixed-bed reactor is facilitated greatly by assuming that the concentration in the bed changes negligibly within a distance equal to the particle or pellet size. The average local reaction rate and conversion at any point in the bed are then equal to the average reaction rate and conversion of a particle, which experiences ambient conditions identical to those at the same point of the bed. The average local reaction rate and conversion in the bed are given by Eqs. 7.8 and 7.9, and as a result, it is necessary to solve the structural and particle model equations at every point in the bed in order to determine their values. For a first-order reaction — as it is the case here — it is not necessary to solve these two models simultaneously with the bed equations if the pseudosteady-state approximation is used for diffusion in the product layer and diffusion and reaction in the pore space. The structural model is solved first to create a database for the particle problem, which is then solved to create a database (for the variation of $\bar{k}_v$ with $\bar{\xi}$) for the bed model. This approach was used by Sotirchos and Zarkanitis (1989) in their fixed-bed desulfurization model.

The equations that describe the material balances of the gas and the solid reactant are in dimensionless form:

$$\epsilon_b \frac{\partial y}{\partial \tau} = \frac{\partial^2 y}{\partial x^2} - Pe \frac{\partial y}{\partial x} - \bar{\Phi}^2(\bar{\xi})y \quad (7.10)$$

$$\frac{\partial \bar{\xi}}{\partial \tau} = \omega \bar{\Phi}^2(\bar{\xi})y \quad (7.11)$$

Figure 7.3: Evolution of the average volumetric reaction rate constant with the average conversion in various particle sizes at 600°C.

where

$$y = \frac{c}{c_0}; \quad x = \frac{z}{L}; \quad Pe = \frac{uL}{D_b} \quad (7.12a, b, c)$$

$$\tau = \frac{tD_b}{L^2}; \quad \bar{\Phi}^2(\bar{\xi}) = \frac{(1 - \varepsilon_b)L^2 \bar{k}_v(\bar{\xi})}{D_b}; \quad \omega = \frac{v_s c_0}{(1 - \varepsilon_0)(1 - \varepsilon_b)} \quad (7.13a, b, c)$$

y is the concentration of the reactive gas in the bed, x is the axial distance in the bed, ε_b is the bed voidage, $\bar{k}_v(\bar{\xi})$ is the volumetric reaction rate, Pe is the Peclet number, and τ the reaction time. The symbols in Eqs. 7.12 and 7.13 are given in the notation section of this paper. The boundary and initial conditions used for Eqs. 7.10 and 7.11 are:

$$-\frac{\partial y}{\partial x} = Pe(1 - y) \quad \text{at } x = 0 \quad (7.14)$$

$$\frac{\partial y}{\partial x} = 0 \quad \text{at } x = 1 \quad (7.15)$$

$$y = 0 \quad \text{and} \quad \bar{\xi} = 0 \quad \text{at } \tau = 0 \quad (7.16a, b)$$

The numerical procedure followed for the solution of the above equations is described in detail by Sotirchos and Zarkanitis (1989).

Before we proceed with the presentation of the model predictions, we will briefly discuss some of the assumptions made in the development of the mathematical model for the bed. No energy balance was included in the bed model since the reactor was assumed to operate isothermally. As mentioned previously, the temperature rise in the bed was too small (less than 3°C) to justify use of a nonisothermal model. It is assumed that the bed voidage (ε_b) remains constant during the sulfidation reaction. Even though the solid product occupies more space than the solid reactant, this assumption is not unreasonable because reaction mainly occurs in the interior of the porous particles. The ratio of the internal surface area of the solids to the geometrical external surface area is about 4,000 for particles of $200 \mu\text{m}$ and larger for the other particle sizes used in this work. The axial dispersion coefficient, D_b , was estimated from the formula $D_b = \varepsilon_b \mathcal{D} / \eta$ for $\eta = 2$. $\mathcal{D}$ is the binary diffusion coefficient of H_2S in N_2 , and η is the tortuosity factor of the bed. We chose to work with this value of axial dispersion coefficients on the basis of the pulse chromatographic studies of Krishnan and Sotirchos (1990) for beds packed with zinc oxide particles of the same sizes as the ones used in our experiments.

The predictions of the mathematical model were found to be strongly influenced by the type of sorbent, size of sorbent particles, and residence time of reactive mixture in the sorbent bed. Fig. 7.4 presents simulation results for the reaction of 210-250 and 297-350 μm particles of samples G-72D and C7-2 with a mixture of 10,500 ppm H_2S in nitrogen at 600°C . The reaction times were normalized with respect to the minimum time required for complete conversion of the bed (t_0). The space velocity for all the cases of Fig. 7.4 was $20,000\text{ hr}^{-1}$ (based on the volume of empty bed at standard conditions), and the reactor diameter and length were 0.75 and 3.40 cm , respectively. For small H_2S concentration in the exit stream, t/t_0 gives a direct measure of sorbent utilization (sorbent used/initial bed load) in the bed. According to the results of Fig. 7.4, the sorbent utilization decreases with increasing particle size for a given breakthrough concentration. Moreover, it takes less time to get a certain concentration at the exit of the reactor when the reactor is loaded with G-72D particles.

The conversion profiles in the reactor for the four cases of Fig. 7.4 are shown in Fig. 7.5 at reaction times 0.3, 0.6, and 0.9 (t/t_0). Because of the high value of space velocity used to obtain the results of Fig. 7.4, the contribution of the axial dispersion term in the mass balance in the bed is negligibly small. As a result, with the exception of the early stages of the reaction, the concentration profiles in the bed are identical to those of Fig. 7.5. The behavior of the results of Figs. 7.4 and 7.5 for the breakthrough curves are in agreement with those of Fig. 7.3 for the variation of the volumetric reaction rate constant. (The k_{v0} values for the two sorbents do not differ significantly.) The sorbent utilization for a certain breakthrough concentration varies in the same order as the average reactivity of the particles, and the spread of the conversion profile in the bed increases with decreasing particle reactivity.

The performance of a sorbent bed loaded with 297-350 μm particles at 600°C , under different reactive gas flow rates corresponding to space velocities (S.V.) of 20,000, 10,000, and 2,000 hr^{-1} (at standard conditions) is examined in Fig. 7.6. The dimensions of the sorbent bed are the same as those in Fig. 7.4. Large residence times (small reactive gas flow rates) tend to reduce the spread of the conversion profile in the reactor and, hence, increase the utilization of the sorbent at the breakthrough point. Obviously, there is a

Figure 7.4: Breakthrough curves predicted by the mathematical model for sulfidation at 600°C of sorbent beds loaded with zinc oxide particles.

Figure 7.5: Conversion profiles in the sorbent bed at different reaction times for the cases presented in Fig. 7.4. —: G-72D, 297-350 μm ; - - -: G-72D, 210-250 μm ;: C7-2, 297-350 μm ; - · - ·: C7-2, 210-250 μm .

Figure 7.6: Effect of the space velocity (S.V.) of the reactive gas on the model predictions for sulfidation of 297-350 μm particles at 600°C.

trade-off between gas throughput in the reactor and sorbent utilization. Therefore, the conditions for optimal operation depend not only on the sorbent but on the economics of the overall process (sulfidation and regeneration) as well.

7.6. Sulfidation Experiments in a Fixed-Bed Reactor and Model Predictions

In this section, we present and discuss the breakthrough curves that were measured in our experiments and compare them with the predictions of the mathematical model. The application of the model involves no unknown parameters. The parameters of the sorbent bed (particle diameter, weight of the unreacted solid, and bed length and radius) and the operating conditions (temperature and reactive gas flow rate and composition) are directly measured. On the other hand, the parameters for the particle model (diffusion, reaction, and structure evolution equations) – which are needed to determine $\bar{k}_v(\bar{\xi})$ (using Eqs. 7.8 and 7.9) – are found from the analysis of the single-particle TGA reactivity data. Table 7.2 summarizes the reaction conditions for the various fixed-bed experiments discussed in this section. The reactive mixture was 1.05% H_2S in N_2 for all experiments, with the exception of run FB209, where a mixture containing 0.509% H_2S was used.

It should be pointed out that in addition to the particle sizes listed in Table 7.2, experiments were also carried out with 53-62 and 88-105 μm particles under various reaction conditions. It was observed that particles in these size ranges tended to agglomerate in the fixed-bed reactor, leading to significant pressure drop in the reactor. Problems of this kind were not encountered in beds loaded with particles larger than 200 μm .

No H_2S was detected by the FPD (flame photometric detector) before the breakthrough point in all our experiments, implying that the H_2S concentration in the exit stream of the reactor was below the detection limit of the detector (about 1 ppm). The equilibrium concentration for the reaction of ZnO with 10,500 ppm H_2S in nitrogen at 500 and 600°C was calculated using thermodynamic data from Barin and Knacke (1973). In accordance to our gas analysis measurements, lower H_2S concentrations than our detection limit (for example, 0.4 ppm at 600°C) were estimated from the thermodynamic calculations.

Run	Sorbent	Particle Size (μm)	Reactor I.D. (cm)	Reactor Length (cm)	Temp. ($^{\circ}C$)	Space Vel. (hr^{-1})
FB107	G-72D	297-350	0.75	2.8	500	5120
FB105	C7-2	297-350	0.75	2.8	500	4920
FB104	G-72D	297-350	0.75	2.5	600	5395
FB101	C7-2	297-350	0.75	2.8	600	4880
FB102	C7-2	210-250	0.75	2.8	600	4790
FB209	G-72D	210-250	1.5	2.5	600	14620
FB108	G-72D	297-350	0.75	2.5	600	1995
FB106	C7-2	297-350	0.75	2.5	600	2070
FB212	G-72D	297-350	1.5	5.4	600	1850
FB211	C7-2	297-350	1.5	2.5	600	16120
FB301	C7-2	710-850	1.5	9.4	600	3050
FB302	C7-2	710-850	1.5	8.7	600	3320

Table 7.2: Reaction conditions used in the sulfidation experiments.

The experimental and the theoretical results of Fig. 7.7 give breakthrough curves for samples G-72D and C7-2 at 500 and 600°C. The experimental data (the H_2S concentrations measured by GC analysis) are given by distinct points, while the model predictions are presented as continuous curves. (The results will be presented in the same way in all the other figures we will discuss in this section.) The experiments of Fig. 7.7 were performed using particles of 297-350 μm and space velocities of about 5,000 hr^{-1} . Very good agreement, both qualitative and quantitative, appears to exist between model and experiment in Fig. 7.7. This was found to be true for all cases considered in our study, a remarkable result considering that all model parameters were determined from independent experiments. Relatively large deviations between the theoretical and experimental results were observed only for small breakthrough concentrations, i.e., in the vicinity of the 'elbow' of the breakthrough curve. Even if the data for small concentrations were as reliable as those

for large concentrations, this behavior should not surprise us. The sulfidation of zinc oxide is a reversible reaction, and it is thus possible its actual kinetics for small concentration values to be much different from the irreversible, linear kinetics used in the mathematical model.

The results of Fig. 7.7 indicate that the reaction temperature has almost no effect on the experimental and theoretical data. This is in agreement with the weak effect of desulfurization temperature on the behavior of single C7-2 and G-72D particles that we observed in our TGA studies (Efthimiadis and Sotirchos, 1991). Weak influence of desulfurization temperature on the experimental data was also seen in fixed-bed experiments of other desulfurization studies such as the study of Yumura and Furimsky (1985) with zinc oxide sorbents and Gangwal et al. (1989) with zinc ferrite sorbents. We did not cover a larger temperature range in our experiments, because at temperatures higher than 600°C we may have sintering and zinc loss (above 650°C according to Tamhankar et al. (1986) and Gangwal et al. (1989)), whereas at temperatures below 500°C reactivity results may be corrupted by sulfur chemisorption in the sorbents (Efthimiadis and Sotirchos, 1991).

Since the residence time of the reactive mixture in the sorbent bed has strong effects on sorbent utilization (Fig. 7.6), experiments were carried out in the fixed-bed reactor of Fig. 7.1 over a broad range of space velocities (about $2,000\text{--}15,000\text{ hr}^{-1}$). The experimental data and the model predictions for a bed loaded with particles of the G-72D sample and sulfided at 600°C are shown in Fig. 7.8. Particles of $210\text{--}250\text{ }\mu\text{m}$ size were used in the FB209 run, while in all the other runs the reactor was loaded with $297\text{--}350\text{ }\mu\text{m}$ particles. The dependence of the breakthrough response of the fixed-bed desulfurization reactor on particle size and space velocity may also be seen in Fig. 7.9 for beds loaded with sample C7-2, but for a much broader range of particle size than for sample G-72D (Fig. 7.8). In agreement with the theoretical predictions of Figs. 7.4 and 7.6, the results of Figs. 7.8 and 7.9 show that an increase in the particle size or in space velocity increases the spread of the breakthrough curve and leads to lower sorbent utilization. It is interesting to note that a combination of smaller particle size and higher space velocity in run FB209 relative to the values used in run FB104 produces a breakthrough curve similar to that obtained in the latter case. The H_2S concentration used in run FB209 is half the value used in all

Figure 7.7: Comparison of the experimental data with the model predictions at different reaction temperatures.

other experiments but since the reaction is of first order with respect to the concentration of H_2S , results for different H_2S concentration can be compared with each other. Direct inspection of the fixed-bed model equations (Eqs. 7.10-7.16) reveals that the breakthrough curve expressed as y vs. t/t_0 is independent of the H_2S concentration at the inlet of the reactor.

It is clear from the comparison of model predictions and experimental data in Figs. 7.7-7.9 that the mathematical model successfully predicts the behavior of fixed-bed reactors loaded initially with fresh (unreacted) particles. In order to examine the ability of the model to describe the behavior of a fixed-bed reactor when desulfurization starts with a nonuniform conversion profile in the bed, we carried out experiments using beds loaded with partially reacted sorbents. Specifically, we stopped the reaction in runs FB301 and FB302 after significant H_2S concentration was detected at the outlet of the reactor (a few hundred ppm, as it can be seen in Fig. 7.9 for run FB302) by passing N_2 through the reactor. We then reversed the direction of flow in the bed and continued the sulfidation process under the reaction conditions used in the first step of the experiment. The experimental results obtained from these experiments are shown in Fig. 7.10, with the solid markers used for the concentrations measured during the first step of the experiments. In presenting the results, the start time for the second part of the experiments was set equal to the actual time when the first sulfidation step was stopped, t^* (τ^* in dimensionless form). The model predictions of Fig. 7.10 given by solid curves are for the first step of the experiments and were obtained by integrating the fixed-bed model equations with the initial conditions given by Eqs. 7.16a,b. The dashed curves give the model predictions for the second part of the experiment and were obtained by integrating the model equations with initial conditions:

$$y = 0 \text{ and } \bar{\xi} = \bar{\xi}^*(x) \text{ at } \tau = \tau^* \quad (7.16'a, b)$$

with $\bar{\xi}^*(x)$ being the concentration profile in the inverted bed at the end of the first part of the experiment, i.e., $\bar{\xi}^*(x) = \bar{\xi}(1-x, \tau^*)$. Good agreement is again observed to exist between model predictions and experimental results, especially in the most important part of the breakthrough curve, namely, that corresponding to low H_2S concentration in the outlet stream. The tendency of the mathematical model to predict sharper breakthrough

Figure 7.8: Experimental data and model predictions for sulfidation of the G-72D sample at 600°C.

Figure 7.9: Experimental data and model predictions for sulfidation of the C7-2 sample at 600°C.

curves in the high concentration region and, hence, faster completion of the reaction is due to overprediction of the reaction rate at high conversions by the particle model (see Fig. 7.2).

7.7. Analysis of the Pore Structure of the Sulfided Sorbents

The pore structure of the sulfided sorbents was characterized using mercury porosimetry and nitrogen adsorption at 77K. Samples of reacted particles were collected from the top, bottom, and middle section of the bed. N_2 pycnometry measurements, made in the adsorption unit were used to estimate the skeletal densities of the unreacted and fully sulfided solids. Heat-treated samples of samples G-72D and C7-2 had skeletal densities of 5.4 and 4.8 g/cm³, respectively. Lower densities were measured for the sulfided forms of the two sorbents (4 and 3.8 g/cm³ for sorbents G-72D and C7-2, respectively).

The pore volumes of the fully sulfided sorbents agreed well with those predicted from the porosities and compositions of the unreacted (heat-treated) samples under the assumption that there was no change in the overall dimensions of the particles during the reaction. This finding was used to determine the average conversion of the partially reacted samples using the pore volumes obtained from the mercury porosimetry data. The average conversion $\hat{\xi}$ of a sample collected between points x_1 and x_2 in the bed is obviously equal to

$$\hat{\xi} = \frac{1}{x_2 - x_1} \int_{x_1}^{x_2} \bar{\xi} dx \quad (7.17)$$

$\hat{\xi}$ is related to the average porosity $\hat{\epsilon}$ of the sample by the equation:

$$\hat{\xi} = \frac{\epsilon_0 - \hat{\epsilon}}{(1 - \epsilon_0)(Z - 1)} \quad (7.18)$$

where Z is the volume of fully reacted solid phase per unit volume of unreacted solid phase. Z is equal to 1.56 and 1.38 for samples G-72D and C7-2, respectively. The average conversion for the partially reacted samples that were collected from the top, middle, and bottom parts of the bed are shown by dashed straight lines in Figs. 7.11 and 7.12 for samples G-72D (run FB209) and C7-2 (run FB211). Each dashed line extends over the portion of the bed, in terms of distance, that each average conversion represents. The continuous solid curves give the conversion profile predicted by the mathematical model at

Figure 7.10: Comparison of the model predictions with the experimental data of two sulfidation runs at $600^\circ C$.

the time the sulfidation reaction was stopped. We see that in both figures the experimental average conversion histogram is in very good agreement with the theoretical conversion profile.

The cumulative pore volume vs. pore diameter curves for the partially reacted samples of Figs. 7.11 and 7.12, determined from mercury intrusion porosimetry data, are given in Figs. 7.13 and 7.14, respectively. Shown in the figures are also the pore volume distribution curves for the unreacted sorbent (solid curves). The results of Figs. 7.13 and 7.14 show that the total pore volume decreases with increasing conversion, while the most probable pore radius of the pore volume distributions shifts toward larger pore sizes. The decrease in the total pore volume is expected since the reaction involves a solid product (ZnS) which occupies more space than the oxide from which it results. This cannot be said, however, about the displacement of the pore size distribution toward large pores. If the pore structure of the sorbents evolves only because of the reaction of H_2S with ZnO , the size of each pore should become progressively smaller as ZnO is replaced by ZnS and the pore volume distribution should move toward smaller pores. Shift of the pore size distribution toward larger pores was also observed by Grindley (1988), who performed mercury porosimetry measurements on sulfided and regenerated zinc ferrite pellets in a fixed-bed reactor.

The behavior of the pore volume distribution curves of Figs. 7.13 and 7.14 is in disagreement with the results we obtained in another study (Efthimiadis and Sotirchos, 1991) on the evolution with the conversion of the pore volume distribution of partially reacted samples of the same sorbents prepared in a fluidized-bed reactor. Pore volume distribution curves for partially reacted and fully sulfided samples of sorbent C7-2 from that study are shown in Fig. 7.15. These samples were prepared using the experimental arrangement of Fig. 7.1 with the fixed-bed replaced by a fluidized-bed reactor. Specifically, about 5 g of 710-850 μm particles were sulfided up to four different conversion levels using 1.05% H_2S in N_2 flowing at 3.5 l/min (standard temperature and pressure). The pore volume distribution of the unreacted sorbent and of the fully sulfided sorbent in the fixed-bed reactor (see Fig. 7.14) are also shown in Fig. 7.15 for comparison. As the results of Fig. 7.15 show there is no shift of the pore volume distribution of the samples prepared in

Figure 7.11: Comparison of the predicted by the mathematical model conversion profile in the sorbent bed of the FB209 run (sample G-72D) and the experimentally determined average conversion of segments of the sorbent bed.

Figure 7.12: Comparison of the predicted by the mathematical model conversion profile in the sorbent bed of the FB211 run (sample C7-2) and the experimentally determined average conversion of segments of the sorbent bed.

Figure 7.13: Porosimetric cumulative pore volume vs. pore diameter curves of unreacted G-72D sorbent and those of solid samples collected from the top, middle, and bottom of the sorbent bed of run FB209.

Figure 7.14: Porosimetric cumulative pore volume vs. pore diameter curves of unreacted C7-2 sorbent and those of solid samples collected from the top, middle, and bottom of the sorbent bed of run FB211.

Figure 7.15: Pore volume distributions of sample C7-2 sulfided in a fluidized and in fixed-bed reactor.

the fluidized-bed reactor toward larger pores. Actually, all samples appear to have similar cumulative pore volume distributions in the region of large pores.

All particles in a fluidized-bed reactor experience, on the average, the same reaction conditions, and as a result, partially reacted samples prepared in such a reactor consist of particles of the same conversion. Samples collected from a fixed-bed reactor, on the other hand, cover a range of conversion levels, which may be rather broad depending on the part of the bed they were taken from (see Figs. 7.11 and 7.12). This difference is important when comparing the pore volume distributions of partially reacted samples of the same conversion from the two reactors, but it alone cannot explain the observed shift of the pore volume distribution of the fixed-bed samples toward large pores. However, since no mixing takes place in the fixed-bed reactor, with the exception of the layer of particles located at the entrance of the reactor, all other particles see the reactive mixture for the first time after they spend some time – which is roughly proportional to their distance from the entrance in the reactor – exposed to the product stream of the reaction, namely, a stream containing a% H_2O for a reactive mixture containing a% H_2S . Analysis of the pore structure of C7-2 particles (710–850 μm) exposed at 600°C to a stream containing 1% H_2O for 2 hr showed shifting of the pore size distribution towards larger pores, though to a less extent than in Fig. 7.13. In view of this finding, it was postulated that the displacement of the pore size distributions of the fixed-bed samples toward large pores is caused by structural changes occurring because of the exposure of the sorbent particles to water vapor. Water vapor is also present in the fluidized-bed reactor, but since the internal surface of all particles is covered by a progressively thicker layer of sulfided phase, the occurring structural changes are less extensive.

The initial pore size distributions used in the application of the mathematical model (solid curves of Figs. 7.13 and 7.14) give pore surface areas 22 and 23 m^2/g , for sorbent G-72D and C7-2, respectively (pores greater than 50 Å in radius). These values are close to the BET surface areas of the unreacted materials (see Table 7.1). BET surface areas of fully sulfided samples of the two sorbents are listed in Table 7.3. The generalized pore model predicts that the surface area of the fully sulfided G-72D and C7-2 sorbents should be 16 and 18 m^2/g , respectively. The smaller experimental values of internal surface area for

the sulfided sorbents are not unexpected considering the displacement of the experimental pore volume distributions toward larger pores. Another reason for this discrepancy may be the use of the pore size distribution extracted from mercury intrusion data in the mathematical model. This distribution corresponds to the true pore size distribution only for an ideal structure of infinitely long cylindrical pores. For an arbitrary structure, it gives a measure of the distribution of feeder pores through which mercury invades the interior of the sorbent, and as a result it is narrower and located at smaller pore sizes than the actual pore size distribution of the solid.

Material	Experiment	Surface Area (m^2/g)
G-72D	FB209	9.4
G-72D	FB212	7.9
C7-2	FB211	13.55
C7-2	FB101	15.83
C7-2	FB102	13.62

Table 7.3: BET surface areas of fully sulfided zinc oxide sorbents.

7.8. Summary and Conclusions

Two commercially available zinc oxide sorbents were reacted at high temperatures using H_2S-N_2 mixtures in a fixed-bed reactor. Particles in the size range of 210-850 μm were used in the experiments. Breakthrough curves were determined experimentally by chromatographic analysis of the stream leaving the reactor. The comparison of experimental data obtained under the same sulfidation conditions for the two sorbents showed that the pore structure of the sorbents plays a major role in determining sorbent utilization in the bed at the breakthrough point. Other parameters having strong effects on the behavior of the reactor were the size of the particles and the residence time of the reactive mixture in the reactor. Experiments at 500 and 600°C showed that the reaction temperature

influenced insignificantly the performance of the two solids as sorbents for H_2S removal.

Samples of fully or partially reacted particles collected from different parts of the fluidized-bed reactor were analyzed by mercury porosimetry and gas adsorption. The pore volume distribution of the reacted (partially and fully) samples was found to be shifted toward larger pores relative to the distribution of the unreacted solids. Such behavior was not seen in solids sulfided in a fluidized-bed reactor under the same conditions (temperature, pressure, and reactive gas mixture composition) as in the fixed-bed experiments. Since the particles in a fluidized-bed reactor remain exposed to the product stream of the reaction until the reaction front reaches them, it is believed that the displacement of their pore size distribution toward larger pores is caused by structural changes occurring because of their exposure in the water vapor produced by the sulfidation reaction.

The experimental results (breakthrough curves and pore structure data) were used to test the predictions of a mathematical model for fixed-bed desulfurization reactors. The behavior of each particle in the fixed-bed reactor was described using the generalized random pore model of Yu and Sotirchos (1987). Reactivity evolution data from thermogravimetric analysis experiments had been used in a past study to determine the values of the various parameters appearing in the generalized random pore model for each of the sorbents, and as a result, the application of the overall model to the fixed-bed data involved no unknown parameters. Very good agreement was observed between model predictions and experimental data for all cases examined in our study. The mathematical model reproduced successfully both the breakthrough curves and the solid conversion profiles in the fixed-bed reactor.

It must be pointed that it is not necessary to use a detailed model, like the one employed in this study, to describe the transport, reaction, and structure evolution processes in the pellets if our only objective is to use the overall mathematical model to correlate the experimental data. Since the general shape of the breakthrough curve is weakly influenced by the detail built into the pellet model, any model would succeed in reproducing the experimental curves provided that its parameters are allowed to vary from one experiment to another. For instance, Wang et al. (1990) used the unreacted-core model to describe the behavior of each pellet and obtained very good agreement between model results and

experimental data from a bench-scale reactor loaded with zinc ferrite or zinc titanate pellets. However, the the effective diffusivity values that had to be used to obtain good agreement between model and experiment were much different from those used in another study (Woods et al., 1991) to reproduce, using the unreacted-core model, sulfidation data for single pellets of the same sorbents from gravimetric experiments.

7.9. Notation

Symbols that do not appear here are defined in the text.

a	radius of the particle, cm
c	reactive gas concentration in the bed, mol/cm^3
c_0	initial reactive gas concentration in the bed, mol/cm^3
c_b	reactive gas concentration in the bulk phase, mol/cm^3
c_p	reactive gas concentration in the particle, mol/cm^3
D	bulk diffusion coefficient, cm^2/s
D_b	axial dispersion coefficient in the fixed-bed, cm^2/s
D^e	effective diffusion coefficient in the particle, cm^2/s
D_0^e	initial effective diffusion coefficient in the particle, cm^2/s
k_g	mass transfer coefficient, cm/s
k_s	reaction rate constant in the particle, cm/s
k_v	volumetric reaction rate constant in the particle, s^{-1}
k_{v0}	initial volumetric reaction rate constant in the particle, s^{-1}
$\bar{k}_v$	average volumetric reaction rate constant in a particle or in the bed, s^{-1}
L	length of the sorbent bed, cm
Pe	Peclet number (see Eq. 7.12c)
r	radial distance in a particle, cm
$\bar{R}_v$	average reaction rate per unit of particle volume, $mol/cm^3/s$
S_0	initial surface area, cm^2/cm^3
Sh^e	Sherwood number (see Eq. 7.6c)
t	time, s

t_0	minimum time for the complete conversion of the sorbent bed, s
u	superficial velocity in the reactor, cm/s
v_s	volume of the unreacted solid per mol of the solid reactant, cm^3/mol
x	dimensionless distance in the bed
x_i	dimensionless distance of point i in the bed
y	dimensionless concentration in the bed
y_p	dimensionless concentration in the particle
z	axial distance in the bed, cm
Z	volume of fully reacted solid phase per unit volume of unreacted solid phase

Greek

δ^e	dimensionless effective diffusivity
ϵ_0	porosity of the unreacted particles
ϵ_b	bed voidage
ϵ_p	porosity of the reacted particles
$\hat{\epsilon}$	average porosity of particles located in a segment of the sorbent bed
η	tortuosity factor for axial dispersion
κ_v	dimensionless reaction rate constant in a particle
ν_A	stoichiometric coefficient of the reactive gas
ξ	local solid conversion in a particle
$\bar{\xi}$	average solid conversion in a particle or in the bed
$\hat{\xi}$	average conversion of particles located in a segment of the fixed-bed
ρ	dimensionless distance in a particle
τ	dimensionless time for the fixed-bed reactor (see Eq. 7.13a)
τ_p	dimensionless time for the particle (see Eq. 7.6a)
Φ^2	Thiele modulus for the particle (see Eq. 7.6b)
$\bar{\Phi}^2$	Thiele modulus for the sorbent bed (see Eq. 7.13b)
ω	dimensionless parameter (see Eq. 7.13c)
ω_p	dimensionless parameter (see Eq. 7.5e)

7.10. Literature References

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8. A PARTIALLY OVERLAPPING GRAIN MODEL FOR GAS-SOLID REACTIONS

The reaction of gases with porous solids is among the most frequently encountered reactive systems in industrial applications. The products of a gas-solid reaction may consist of gases only (e.g., char combustion and gasification), or formation of other solid species with different properties from the solid reactant may take place (e.g., reaction of sulfur-containing gases with metal oxides and deposition of ceramic material in fibrous preforms). Regardless of whether a gasification or a solid product formation reaction is considered, a mathematical model must be used to describe the structural changes that occur in the interior of the porous solid in the course of the chemical reaction. The various mathematical models presented in the literature for this purpose are usually classified into two, rather broad, categories (Ramachandran and Doraiswamy, 1982): models based on the representation of the pore space of the porous media by a collection of hollow objects (pore models) and models based on the representation of the solid phase of the porous media by an assemblage of dense objects (grain models). Hybrid and other abstract representations of the pore structure of a porous medium are also possible (Bhatia, 1987), but most of the structural models of the literature fall into either of the above categories.

In a grain model, the pore structure of the reacting solid is typically viewed as consisting of uniform in size, unconsolidated (nonoverlapping) grains, usually of spherical shape, which react independently of each other in a shrinking core fashion (Szekely et al., 1976). Because of the simplicity of the grain model expressions for the variation of the structural properties of a reacting solid with the extent of the reaction, the models that are most frequently used in the literature for the analysis and interpretation of experimental data for gas-solid reactions are based on variants of the grain model. Among the most important modifications of the original formulation of the grain model by Barner and Mantell (1968) and Szekely and Evans (1970), one could mention the extension of the model to solids with distributed grain size (Szekely and Propster, 1975), the use of variable size grains to account for density differences between the solid product and the solid reactant (Georgakis et al., 1979), and the incorporation in the model of sintering effects on the structural changes of the solid (Ranade and Harrison, 1981).

The most important deficiency of the various versions of the grain model is the assumption of nonoverlapping grains at all conversion levels and all porosities, which leads to the prediction of monotonically decreasing reaction surface area with the progress of the reaction (reacted-unreacted solid interface for reactions with solid product or pore surface for gasification reactions). Moreover, there is a minimum close packing porosity for grains of a certain shape, and therefore, the assumption of unconsolidated grains for porosities below this threshold value is physically unrealistic. These shortcomings of the grain model can be removed by allowing the grains in the structure to overlap. A grain model for partially sintered spheres was developed by Lindner and Simonsson (1981) who represented the solid reactant as aggregates of spheres in an initial state of sintering. The derivation of approximations for the evolution of the structural properties of this structure with the extent of the reaction was accomplished by considering a sphere with an average number of nearest neighbors. The structural model of Lindner and Simonsson was modified by Alvfors and Svedberg (1988) to account for the presence of inert solids in the porous medium, and the modified model was used to study the sulfation of calcined limestones and dolomites. The notion of overlapping grains was further pursued by Sotirchos (1987) and Sotirchos and Yu (1988), who developed structural models for porous media that can be represented by a population of randomly overlapping grains of distributed size. Comparison of the predictions of the random grain model (Sotirchos and Yu, 1988) with those of the corresponding random pore model (Sotirchos and Yu, 1985) showed that grain structures react in a different manner from capillary structures. Sotirchos and Zarkanitis (1989) incorporated the random grain model in a design model for fixed-bed desulfurization reactors and showed that the grain size distribution may have a strong influence on the breakthrough behavior of the bed.

The assumption of freely overlapping grains makes possible the derivation of exact analytical expressions for the dependence of the structural properties of the porous medium on the conversion, but in actual porous media, the extent of grain overlapping should vary among different solids. For porous media prepared as powder compacts, in particular, the extent of grain overlapping should be a function of processing conditions and of procedures used for their preparation. A grain representation of a porous medium that is more flexible

than that of randomly overlapping grains is obtained when one considers a population of grains with each having a hard core surrounded by a penetrable soft shell. Only the soft shells of the grains can overlap with each other, when this population of grains is used to represent the structure of the porous medium. Obviously, at the limit of zero size of hard core one obtains the random overlapping grain model, while at the limit of zero thickness of soft shell, the nonoverlapping grain model results.

A special case of the partially overlapping grain model is obtained when all grains are assumed to have the same size and the same soft shell thickness or, equivalently, hard core size. Rikvold and Stell (1985) used the scaled-particle theory of Reiss, Frisch, and Lebowitz (1959) to develop expressions for the porosity and surface of D -dimensional partially overlapping spheres of uniform size and uniform hard core radius. (For $D = 2$, the obtained structure is that of parallel, partially overlapping cylindrical grains). Tomadakis and Sotirchos (1991a) used a Monte Carlo simulation scheme to compute the structural properties of partially overlapping cylinders ($D = 2$) and found that the relations proposed by Rikvold and Stell (1985b) provided an excellent approximation to the porosity of the structure in a rather wide range of porosity and cylinder to hard core radius ratio values. The surface areas predicted by the expression of Rikvold and Stell (1985b) were lower than the numerically computed values, but the agreement between the analytical results and the numerically computed values should be deemed satisfactory in view of the large computational times needed to obtain the latter.

A structure of partially overlapping spheres, with each sphere having the same radius and hard core radius, is used as basis in this study for the development of a partially overlapping spherical grain model for gas-solid reactions with solid product. The development of the mathematical model proceeds along the lines of the grain model of Sotirchos and Yu (1988). The expressions of Rikvold and Stell (1985a) are used to follow the variation of the porosity and surface area (reaction and pore surface area) with the extent of the reaction. In order to demonstrate the flexibility of the new model, a detailed parametric sensitivity analysis of its predictions is carried out, and the results are compared with those of the randomly overlapping and nonoverlapping grain models. Finally, the model is applied to the analysis of some experimental data for the sulfidation of zinc oxide, a

reaction used to remove sulfur-containing contaminants (primarily H_2S) from coal gas at high temperatures.

8.1. Local Reaction and Structure Evolution Model

Expressions for Porosity and Internal Surface Area

We consider a structure consisting of a population of uniformly sized, spherical grains of radius R . Each grain consists of a hard core of radius R_c and a penetrable soft shell. Such a structure can be obtained from an initial structure of randomly 'packed' nonoverlapping grains of radius R_c by letting the grains 'grow' from radius R_c to radius R . It thus makes sense to parametrize the system using the porosity of the structure made up of the hard cores of the grains ϵ_c and the grain growth variable δ , the latter defined as the ratio of grain radius to hard core radius.

For $\delta < 1$, the porosity and surface area of the porous medium are given by the expressions for hard (nonoverlapping) spheres, i.e.,

$$\epsilon = 1 - \frac{4\pi}{3}nR^3 \quad (8.1)$$

$$S = 4\pi nR^2 \quad (8.2)$$

with n being the number of grains per unit volume. As $\delta \rightarrow \infty$, i.e., $R_c \rightarrow 0$, then the structural properties of the solid are given by the equations for randomly overlapping grains, i.e.,

$$\epsilon = \exp\left(-\frac{4\pi}{3}nR^3\right) \quad (8.3)$$

$$S = \epsilon 4\pi nR^2 \quad (8.4)$$

For other values of δ and ϵ_c , we use the expressions derived by Rikvold and Stell (1985), which in terms of the quantities defined in this study have the form:

$$\begin{aligned} \epsilon = \epsilon_c \exp \left[-\frac{(\delta^3 - 1)(1 - \epsilon_c)}{\epsilon_c} \right] \\ \times \exp \left[-\frac{3(1 - \epsilon_c)^2}{2\epsilon_c^3} (2(\delta - 1)^3 + 3\epsilon_c(\delta - 1)^2) \right] \end{aligned} \quad (8.5)$$

$$S = \frac{3\epsilon(1 - \epsilon_c)\delta}{R\epsilon_c^3} [\epsilon_c^2 \delta^2 + (1 - \epsilon_c)(3(\delta - 1)^2 + 3\epsilon_c(\delta - 1))] \quad (8.6)$$

Eq. (8.6) follows from differentiation of Eq. (8.5) with respect to R , using the fact that $S = d\epsilon/dR$. For $\delta = 1$, Eqs. (8.5) and (8.6) reduce to those for nonoverlapping grains, i.e., (8.1) and (8.2), but they become indeterminate as $\delta \rightarrow \infty$.

Rikvold and Stell (1985a) derived Eqs. (8.5) and (8.6) by realizing that a structure of partially permeable spheres is isomorphic to a fluid of hard spheres of radius R_c into which one attempts to introduce a hard solute molecule of radius $(R - R_c)$. This problem forms the basis of the scaled-particle theory for hard sphere fluids of Reiss, Frisch, and Lebowitz (1959). The porosity of the partially overlapping sphere structure corresponds to the volume accessible to the center of the solute molecule, while its internal surface area corresponds to the surface accessible to the center of the solute molecule when it is in contact with at least one solvent molecule. Reiss et al. (1959) derived exact expressions for quantities equivalent to ϵ and S in terms of the contact correlation function G , that is, the radial distribution function of the solvent molecules around a solute molecule on contact between solvent and solute. Eqs. (8.5) and (8.6) are based on a quadratic approximation of G in terms of the inverse particle separation. This approximation yields exact results up to the third virial coefficient (Reiss et al., 1959), and it is commonly referred to as the scaled-particle approximation.

The porosity and surface area of a porous medium can be measured using gas adsorption and mercury porosimetry. For the case of nonoverlapping or randomly overlapping spheres, Eqs. (8.1) and (8.2) or Eqs. (8.3) and (8.4), respectively, may be used to determine the values of the two parameters, n and R , that define the population of the spherical grains. A structure of partially overlapping grains requires, as Eqs. (8.5) and (8.6) show, three parameters for its unique characterization, namely, ϵ_c , R , and δ , and consequently, additional information about the pore structure of the porous medium is needed in order to be able to specify these parameters. For man-made porous media prepared as powder compacts, the radius of the spherical grains is a known quantity, while for other porous solids, it may be determined from direct photomicrographic observation of their structure. Another alternative is to treat one of the three parameters of the partially overlapping grain model as a free parameter and thus provide the structural model that can be based on Eqs. (8.5) and (8.6) with more flexibility than the corresponding structural model for

non- or freely overlapping grains.

Figs. 8.1 and 8.2 present the variation of the porosity, ϵ , and dimensionless surface area, SR , of a structure of partially overlapping spherical grains with the grain growth variable, δ , for various values of hard core porosity. Since the hard cores of the grains cannot overlap, the hard core porosity can only take values larger than the porosity corresponding to a structure of ordered close packed spheres, ϵ_{ocp} ($= (1 - \pi/18^{1/2}) \cong 0.2595$). For $\delta = 0$, the porosity of the grain structure is equal to unity, while its internal surface area is zero (see Figs. 8.1 and 8.2). For δ values less than unity, the solid structure obviously consists of unconsolidated (nonoverlapping) grains, and the porosity and internal surface area are given by Eqs. (8.1) and (8.2), which in terms of ϵ_c , R , and δ can be written in the form

$$\epsilon = 1 - (1 - \epsilon_c)\delta^3 \quad (8.7)$$

$$S = \frac{3(1 - \epsilon_c)\delta^3}{R} = \frac{3(1 - \epsilon_c)\delta^2}{R_c} \quad (8.8)$$

As the radius of the grains and, hence, the growth variable increase, the porosity decreases becoming equal to the hard core porosity at $\delta = 1$.

The porosity and internal surface area predicted by Eqs. (8.5) and (8.6) become identically zero only for infinitely large values of the grain growth variable, regardless of the hard core porosity of the structure, while one would expect this to be the case only for randomly overlapping grains ($\epsilon_c = 0$). Nevertheless, as Figs. 8.1 and 8.2 show, the porosity and internal surface area of a partially overlapping grain structure given by Eqs. (8.5) and (8.6) become practically zero beyond a certain value of grain growth variable – which increases with increasing hard core porosity – and consequently, the above limitation of Eqs. (8.5) and (8.6) is not expected to influence in any way the predictions of the structural model we intend to build on them. Since the grains do not overlap for $\delta < 1$, the internal surface area always increases with increasing δ in this region. The internal surface area continues to increase as δ becomes greater than unity and the soft shells of the grains start to overlap with each other, but eventually, the loss of surface area because of grain overlapping offsets the gain caused by grain growth forcing the surface area of the solid to go through a maximum. For obvious reason, the position of the maximum moves towards smaller δ values with decreasing hard core porosity.

Figure 8.1. Variation of the porosity, ϵ , with the the grain growth variable (ratio of grain to hard core radius), δ , for several values of hard core porosity, ϵ_c .

Figure 8.2. Variation of the dimensionless surface area, SR , with the the grain growth variable (ratio of grain to hard core radius), δ , for several values of hard core porosity, ϵ_c .

Reaction and Structure Evolution Equations

We are now ready to proceed with the development of the structure evolution model for gas-solid reactions with solid product. We will consider the general gas-solid reaction

with $\cdots$ denoting other gases participating in the chemical reaction. The stoichiometrically equivalent molar volume of the solid product, $\nu_P v_P$, may be larger or smaller than the molar volume of the gaseous reactant, ν_S , leading to decrease or increase, respectively, of the porosity of the reacting porous medium. Sulfidation and sulfation of metal oxides are typical examples of reactions accompanied by decrease in the porosity, while the oxidation of metal sulfides exemplifies reactions producing more open pore structures. An extreme example of the latter type of reactions is the class of gasification reactions, which is also covered by Eq. (8.9) for ν_P equal to zero.

We define the stoichiometric volume ratio of the (solid reactant, solid product) pair, Z , as the ratio of stoichiometrically equivalent volumes of solid product and solid reactant ($Z = \nu_P v_P / \nu_S$). Z is in general different from unity or zero, and as a result, the internal structure of the reacting porous medium is characterized by two evolving interfaces, defining the reaction and pore surfaces of the solid. Each point of the reaction or pore surface moves with velocity proportional to the local reaction in the direction of the unit vector that is normal to the surface there. Therefore, each of these two surfaces can be represented by a population of grains that are concentric to those forming the initial structure and, hence, have the same hard core radius and hard core porosity.

Let R_0 be the initial grain radius, R_r the radius of the grains forming the reaction surface, and R_p the radius of the grains forming the pore surface. We express the intrinsic rate of the reaction, $\mathcal{R}_s$, in terms of the change in R_r as

$$\frac{dR_r}{dt} = -\nu_S \mathcal{R}_s(c_r, T) \quad (8.10)$$

where c_r is the concentration of the gaseous species at the reaction surface. Assuming that the concentration of the gaseous reactant is the same at all points of the product layer, between R_r and R_p , that are at the same distance in the radial direction from the pore or

reaction surface and solving the diffusion equation in the product layer, we find that

$$c_p - c_r = \frac{\nu_A}{D_P} \mathcal{R}_s(c_r, T) S_r \int_{R_r}^{R_p} \frac{dR}{S(R)} \quad (8.11)$$

c_p is the concentration of the gas in the pores, $S_{r,p}$ is the reaction or pore surface area, D_P is the diffusion coefficient of the gas in the product layer, and $S(R)$ is the surface area of the grain structure when the grain radius is R . Obviously, $S(R_{r,p}) \equiv S_{r,p}$. For a first-order reaction, combining Eqs. (8.10) and (8.11) gives

$$\frac{dR_r}{dt} = - \frac{v_S k_s c_p}{1 + \frac{\nu_A k_s}{D_P} S_r \int_{R_r}^{R_p} \frac{dR}{S(R)}} \quad (8.12)$$

The equation for the change of R_p results from a balance on the solid. We have that

$$\frac{dR_p}{dt} = - \frac{dR_r}{dt} [(Z - 1) \frac{S_r}{S_p}] \quad (8.13)$$

The initial conditions for Eqs. (8.12) and (8.13) obviously have the form:

$$R_r(0) = R_p(0) = R_0 \quad (8.14)$$

In dimensionless form, Eqs. (8.12)-(8.14) may be written as

$$\frac{dy_r}{d\tau} = - \frac{1}{1 + \beta (S_r/S_0) \int_{y_r}^{y_p} \frac{dy}{(S(R)/S_0)}} \quad (8.15)$$

$$\frac{dy_p}{d\tau} = - \frac{dy_r}{d\tau} [(Z - 1) \frac{(S_r/S_0)}{(S_p/S_0)}] \quad (8.16)$$

$$y_r(0) = y_p(0) = R_0 S_0 \quad (8.17)$$

with

$$y_{r,p} = R_{r,p} S_0; \quad \beta = \frac{\nu_A k_s}{D_P S_0} \quad (8.18a, b)$$

$$\tau = v_S k_s S_0 \int_{t_0}^t c_p dt' \quad (8.19)$$

The dimensionless structural model is independent of the reactive gas concentration and its variation with time, the initial internal surface area of the grain structure, and the molar volume of the solid reactant. The reaction rate constant, product layer diffusivity, and initial internal surface area have been grouped into the dimensionless parameter β , which can be viewed as a measure of the ratio of the magnitudes of the relative rates of reaction at the solid-solid interface and mass transport in the product layer. For $\beta = 0$, the rate of mass transport in the product layer is infinitely fast relative to the rate of reaction, and as a result, reaction occurs in the kinetically controlled regime. On the other hand, as $\beta \rightarrow \infty$, the overall rate of reaction becomes controlled by diffusion in the product layer.

With the initial porosity and internal surface area of the solid known, possibly from physical adsorption or mercury porosimetry measurements, $\delta_0 (= R_0/R_c)$ has to be specified to complete the description of the system, provided, of course, that values from the various kinetic and transport parameters are available. Using Eqs. (8.5) and (8.6) (for $\delta_0 > 1$) or eqs. (8.7) and (8.8) (for $\delta_0 < 1$, i.e., an initial structure of unconsolidated grains), we can compute the values of hard core porosity, ϵ_c , and initial grain radius, R_0 , for the chosen set of ϵ_0 , S_0 , and δ_0 values. Another option is to specify ϵ_c and solve the equations for δ_0 and R_0 . The evolution of the properties of the reaction surface and pore surface structures, subscripts r and p , respectively, are also followed using Eqs. (8.5) and (8.6) or (8.7) and (8.8). Since the grains representing the reaction and pore surface structure are concentric to those of the original structure, their hard core porosity and hard core radius are the same. The grain growth variable, $\delta_{r,p}$ that must be used in equations (8.5) and (8.6) or (8.7) and (8.8) to obtain the porosity and internal surface area is given by

$$\delta_{r,p} = \frac{R_{r,p}}{R_0} = \frac{y_{r,p}}{S_0 R_0} \quad (8.20)$$

For the dimensionless form of the model, it is necessary to define only the values of ϵ_0 and δ_0 in order to obtain a completely described structure. However, it should be kept in mind that the dimensionless reaction times can be compared to each other only for solids of the same initial internal surface area.

The mathematical model of Eqs. (8.15) and (8.16) is solved as an initial value problem consisting of three ordinary differential equations, the third differential equation obtained

by setting the integral appearing in the denominator of the right-hand side of Eq. (8.15) equal to an auxiliary variable g , i.e., by setting $g = \int_{y_r}^{y_p} \frac{dy}{S(R)/S_0}$. More details on the solution procedure may be found in the paper by Sotirchos and Yu (1988). Notice that by eliminating $d\tau$ from Eq. (8.16), a differential equation between y_r and y_p is obtained, which can be solved independently of Eq. (8.15), that is, independently of the processes of diffusion in the product layer and chemical reaction. The fractional conversion, ξ , of the solid is obtained from the porosity, ϵ_p , or the 'porosity' of the reaction surface structure, ϵ_r , by using the relationship

$$\xi = \frac{\epsilon_r - \epsilon_0}{\epsilon_0} = \frac{\epsilon_0 - \epsilon_p}{(Z - 1)(1 - \epsilon_0)} \quad (8.21a, b)$$

which results from an overall mass balance in the solid reactant and solid product. According to Eq. (8.21b), complete pore closure ($\epsilon_p = 0$) for conversions less than unity may take place for initial porosities smaller than $(Z - 1)/Z$ (obviously, for $Z > 1$).

8.2. Structural Model Results

The local reaction and structure evolution model developed in the preceding section suffices for the description of the behavior of a gas-solid reaction process under reaction conditions controlled by intrinsic kinetics and diffusion in the product layer, that is, in the absence of significant concentration gradients in the intraparticle space. Four parameters are involved in the dimensionless form of the structural model (see Eqs. (8.13)-(8.21)): ϵ_0 , extent of grain overlapping (quantified by ϵ_c or δ_0 for partially overlapping grains), β , and Z . Before proceeding with the presentation and discussion of our numerical results, we will briefly discuss our choices for the values of these parameters.

The initial porosity of porous media encountered in practical applications usually varies in the range [0.4, 0.6]. In order to simplify the investigation of the parametric sensitivity of the problem, the initial porosity will be fixed at 0.5 in all the numerical results that will be presented in our study. Four grain overlapping patterns will be employed in our analysis: i) the well-known nonoverlapping grain model (NOGM) in which the area and porosities of the pore and reaction surface structures are given at all porosity (or conversion) levels by Eqs. (8.1) and (8.2); ii) the randomly overlapping grain model (ROGM)

of Sotirchos and Yu (1988) in which the porosities and areas are given by Eqs. (8.3) and (8.4); iii) the partially overlapping grain model (POGM) with initially nonoverlapping grains ($\delta_0 = 1$); and iv) the partially overlapping grain model with $\delta_0 = 1.2$.

The stoichiometric volume ratio, Z , is zero for gasification reactions ($\nu_P = 0$ in Eq. (8.9)), but for gas-solid reactions with solid product formation, its value varies widely depending on the (solid reactant, solid product) pair; for example, $Z = 1.62$ for (ZnO , ZnS), $Z = 0.62$ for (ZnS , ZnO), $Z = 3.09$ for (CaO , $CaSO_4$), and $Z = 4.01$ for (MgO , $MgSO_4$). In our analysis for the parametric sensitivity of the problem, we will work with $Z = 2$, the largest Z value that permits complete conversion of the solid reactant for 0.5 initial porosity before complete pore plugging takes place, and $Z = 3$, a value characteristic of the sulfation of calcined limestones (see above), a gas-solid reaction of much importance in the control of SO_2 emissions from coal-fired power plants. Parameter β , which expresses how fast the intrinsic reaction is relative to the diffusion of the gaseous reactant through the product layer, can take any value between zero and infinity depending on the reaction conditions. We will present results for the two extremes of intrinsic reaction control and product layer diffusion control ($\beta = 0$ and $\beta = \infty$) and for an intermediate case ($\beta = 1$) where both the resistance for reaction and that for diffusion through the solid product are important.

Fig. 8.3 presents the variation of the internal surface area, normalized with respect to its initial value, with the porosity for a solid with 0.5 initial porosity for the four patterns of grain overlapping considered in our study. Internal surface area (normalized) vs. porosity curves for other initial porosities are shown in Fig. 8.4 for the case of partially overlapping grains with $\delta_0 = 1$. As it is indicated in Fig. 8.3, the surface areas for porosities less than the initial correspond to the pore surface areas (S_p) for gas-solid reactions with $Z > 1$, while those for porosities greater than the initial describe the evolution of the reaction surface area (S_r) or of the pore surface area for $Z < 1$. The surface area of the nonoverlapping grain model increases monotonically with decreasing porosity since the grains are assumed to react independently of each other (i.e., not to overlap) even for porosities smaller than the porosity corresponding to the densest ordered close packing of hard spheres, viz. 0.2595. All other patterns of grain overlapping give zero internal surface

Figure 8.3. Dependence of the evolution of the dimensionless internal surface area, S/S_0 , with the porosity of a grain structure with $\varepsilon_0 = 0.5$ on the extent of grain overlapping. —: nonoverlapping grains (NOGM); - - -: partially overlapping grains (POGM) with $\delta_0 = 1$;: partially overlapping grains (POGM) with $\delta = 1.2$; - · -: randomly overlapping grains (ROGM).

Figure 8.4. Evolution of the dimensionless internal surface area, S/S_0 , with the porosity of a grain structure with $\delta_0 = 1$ (i.e., $\varepsilon_c = \varepsilon_0$) for several values of initial porosity.

Figure 8.5. Variation of the pore and reaction surface areas with the conversion for $Z = 2$. The reaction surface area of partially overlapping grains with $\delta_0=1$ evolves in the same way as that of nonoverlapping grains. —: nonoverlapping grains (NOGM); - - -: partially overlapping grains (POGM) with $\delta_0=1$;: partially overlapping grains (POGM) with $\delta=1.2$; - · - ·: randomly overlapping grains (ROGM).

Figure 8.6. Variation of the pore and reaction surface areas with the conversion for $Z = 3$. The reaction surface area of partially overlapping grains with $\delta_0=1$ evolves in the same way as that of nonoverlapping grains. —: nonoverlapping grains (NOGM); - - -: partially overlapping grains (POGM) with $\delta_0=1$;: partially overlapping grains (POGM) with $\delta=1.2$; - · - ·: randomly overlapping grain model (ROGM).

area for zero and unity porosity, and therefore, they are consistent with the physics of the problem. It can be shown using Eqs. (8.3) and (8.4) that the maximum surface area for randomly overlapping grains occurs at $\epsilon = e^{-(2/3)} \cong 0.51$. In the partially overlapping grain model, the maximum surface area occurs at porosities smaller than the initial for $\delta_0 \leq 1$ (see Figs. 8.2 and 8.4) while for initially overlapping grain structures ($\delta_0 > 1$), the position of the maximum relative to the initial porosity depends on ϵ_0 and δ_0 .

The results of Figs. 8.3 and 8.4 are valid for any value of Z , but in order to follow the evolution of the pore and reaction surface areas with the conversion, these results must be used in conjunction with Eq. (8.21). Surface area vs. conversion curves for gas-solid reactions with $Z = 2$ and $Z = 3$ (i.e., the values that we will use in this study), constructed using Fig. 8.3 and Eq. (8.21), are shown in Figs. 8.5 and 8.6, respectively. For $Z = 2$, the porosity becomes exactly zero when complete conversion of the solid takes place, and as a result, both the pore and reaction surface areas of structures with overlapping grains (ROGM and POGM) are zero (Fig. 8.5). The maximum conversion that can be reached before complete pore plugging takes place ($\epsilon_p = 0$) for $\epsilon_0 = 0.5$ and $Z = 3$ (Fig. 8.6) is equal of 0.5 ($\xi_{max} = \frac{\epsilon_0}{(1 - \epsilon_0)(Z - 1)}$, see Eq. (8.21b)). For $Z = 3$, the pore surface area of structures with overlapping grains is zero at the maximum conversion, as in the case with $Z = 2$, but the reaction surface area is finite because of the presence of unreacted solid in the particles. For obvious reasons, the reaction surface area of partially overlapping grains with $\delta_0 = 1$ evolves in the same fashion as that of nonoverlapping grains.

Gas-solid reactions with $Z > \frac{1}{1 - \epsilon_0}$ will have surface area evolution histories similar, qualitatively, to those for $Z = 3$ (Fig. 8.6). The reaction surface areas of system, with $Z \leq \frac{1}{1 - \epsilon_0}$ will vary in a similar fashion as the corresponding curves of Fig. 8.2, while the qualitative variation of their pore surface areas – which will be finite at $\xi = 1$ – will depend on whether Z is greater or less than unity (see Fig. 8.3). The most interesting observation from the results shown in Figs. 8.3, 8.5 and 8.6 is that the reaction surface area at a certain conversion increases with increasing grain overlapping, while the opposite trend holds for the pore surface areas for gas-solid reactions with $Z > 1$. This behavior will be used later to explain the differences in the reaction vs. time histories of solids with different patterns of grain overlapping.

Figure 8.7. Conversion vs. time curves for insignificant diffusional limitations in the product layer ($\beta = 0$). The conversion evolution curves of nonoverlapping grains and partially overlapping grains with $\delta_0=1$ are the same. NOGM: nonoverlapping grains; POGM: partially overlapping grains; ROGM: randomly overlapping grains.

Conversion vs. time results for reaction conditions controlled by intrinsic kinetics ($\beta = 0$) are shown in Fig. 8.7. Since nonoverlapping grains (NOGM) and partially overlapping grains (POGM) with $\delta_0 = 1$, have the same reaction surface area (see Figs. 8.3, 8.5, and 8.6) and the resistance for diffusion through the product plays no role in the process, the conversion vs. time curves for these two patterns of structure evolution are identical. For the same reason, the conversion evolution results are independent of the value of the stoichiometric volume ratio (Z), although the latter still determines the maximum allowable conversion, as it is indicated in Fig. 8.7 for $Z = 3$. Since the local reaction rate is proportional to the internal reaction surface area (S_r) and the concentration at the reaction interface is the same as that in the pores, the reaction rate and, hence, the conversion of the solid follow the same trend as S_r with increasing overlapping, that is, they also increase.

Figs. 8.8 and 8.9 present conversion evolution histories for $\beta = \infty$, that is, under reaction conditions controlled by diffusion in the product layer. Since $\beta \rightarrow \infty$ is equivalent to letting the reaction occur infinitely fast relative to the diffusion of the gaseous reactant in the product layer (i.e., $k_s \rightarrow \infty$), it is necessary to redefine the dimensionless time as

$$\tau' = \lim_{k_s \rightarrow \infty} \frac{\tau}{\beta} = (v_S/v_A) D_P S_0^2 \int_0^t c_p dt' \quad (8.22)$$

Comparison of Figs. 8.8 and 8.9 reveals that the effects of grain overlapping on the conversion trajectories become stronger as the stoichiometric volume ratio (Z) increases. Moreover, the relative positions of the various conversion vs. time curves appear to be influenced by the Z value. In particular, it is interesting to observe that for $Z = 3$, the order of the four conversion vs. time curves is reversed relative to that seen in Fig. 8.7 for $\beta = 0$, that is, the conversion reached after some reaction time now decreases with increasing grain overlapping. These results can be explained with the aid of Figs. 8.5 and 8.6 for the variation of the surface areas with the conversion. As shown there, the pore surface area increases with decreasing grain overlapping (ROGM $\rightarrow$ POGM $\rightarrow$ NOGM), and therefore, more surface area is available for diffusion through the product layer for $R > R_0$, and the thickness of the product layer is smaller. These two factors gain importance as

Figure 8.8. Conversion vs. time curves under reaction conditions controlled by diffusion in the product layer ($\beta = \infty$) for $Z = 2$. NOGM: nonoverlapping grains; POGM: partially overlapping grains; ROGM: randomly overlapping grains.

Figure 8.9. Conversion vs. time curves under reaction conditions controlled by diffusion in the product layer ($\beta = \infty$) for $Z = 3$. NOGM: nonoverlapping grains; POGM: partially overlapping grains; ROGM: randomly overlapping grains.

Figure 8.10. Conversion vs. time curves under reaction conditions where both kinetics and diffusion in the product layer are important ($\beta = 1$) for $Z = 3$. NOGM: nonoverlapping grains; POGM: partially overlapping grains; ROGM: randomly overlapping grains.

Figure 8.11. Variation of the reaction rate ($\frac{d\xi}{d\tau}$) with the concentration for the cases of Fig. 8.10.

Z increases and the product layer becomes thicker, eventually offsetting the effect of the smaller reaction surface areas. The results of Fig. 8.9 for the NOGM and ROGM cases are qualitatively similar to those presented by Sotirchos and Yu (1988) for the $CaO-SO_2$ reaction. Introducing the values used by Sotirchos and Yu for the $CaO-SO_2$ reaction in the definition of β (Eq. (8.18b)), we find that in their computations β was equal to 141.

Results for a case in which both intrinsic kinetics and diffusion through the product layer are important are shown in Fig. 8.10 for $\beta = 1$ and $Z = 3$. Both S_r and S_p are important in this case, and as a result, the conversion vs. time trajectories for the various patterns of grain overlapping differ less than the corresponding curves in Figs. 8.7 and 8.9. The evolution of the conversion in Fig. 8.10 may be more easily followed and better understood by examining the variation of the reaction rate ($d\xi/d\tau$) with the conversion, shown in Fig. 8.11. Since nonoverlapping grains and partially overlapping grains with $\delta_0 = 1$ have the same and the smallest reaction surface area at all conversions, their reaction rates and, hence, conversions are smaller than those of the others and practically indistinguishable of each other at low conversions. As the conversion increases and the product layer thickens, diffusion in the product layer plays a more important role. Thus, the model of nonoverlapping grains (NOGM) that has the largest pore surface area starts to react faster and eventually reaches higher conversions than the other models.

8.3. Results Under Internal Diffusional Limitations

A model for intraparticle diffusion and reaction is needed in addition to the structural model if the gas-solid reaction occurs in the presence of significant concentration gradients. For small concentration of gaseous reactant and under isothermal conditions, the intraparticle diffusion and reaction model can be written, in dimensionless quantities and for spherical particles, in the following form:

$$\frac{\omega \partial(\epsilon_p x)}{\partial \tau} = \frac{1}{\Phi^2} \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial}{\partial \rho} (\delta^e x) \right) - \nu_A \kappa_v x \quad (8.23)$$

$$\frac{\partial \xi}{\partial \tau} = \frac{1}{(1 - \epsilon_0)} \kappa_v x \quad (8.24)$$

$$\frac{\partial x}{\partial \rho} = 0|_{\rho=0}; \quad \frac{Sh^e}{\delta^e}(1-x) = \frac{\partial x}{\partial \rho}|_{\rho=1} \quad (8.25a, b)$$

$$\rho = \frac{r}{a}; \quad x = \frac{c_p}{c_f}; \quad \delta^e = \frac{D^e}{D_0^e}; \quad \kappa_v = \frac{k_v}{k_{v0}}; \quad \omega = v_S c_f; \quad (8.26a - e)$$

$$\tau = v_S k_s S_0 \int_0^t c_f dt'; \quad \Phi^2 = a^2 \frac{k_s S_0}{D_0^e}; \quad Sh^e = \frac{k_g a}{D_0^e} \quad (8.27a - c)$$

c_f is the concentration in the bulk of the gas phase, a is the radius of the particle, r is the distance from the center of the particle, and k_g is the mass transfer coefficient.

The intraparticle effective diffusivity, D^e , and the volume-based reaction rate constant, k_v , are functions of the local conversion. It follows from Eqs. (8.12) and (8.15) that $\kappa_v (= k_v/k_{v0})$ is given by the equation

$$\kappa_v = \frac{S_r/S_0}{1 + \beta(S_r/S_0)} \int_{y_r}^{y_p} \frac{dy}{S(R)/S_0} \quad (8.28)$$

The effective diffusion coefficient is obtained from the well-known additivity-of-resistances (Bosanquet) formula, i.e.,

$$\frac{1}{D^e} = \frac{1}{D_K^e} + \frac{1}{D_B^e} \quad (8.29)$$

Recent Monte Carlo computations of effective diffusivities in fibrous media by Tomadakis and Sotirchos (1991b) have shown that Eq. (8.29) provides an excellent approximation to D^e over the whole diffusion regime. The Knudsen, D_K^e , and bulk, D_B^e , effective diffusivities are given by the equations

$$D_B^e = \frac{\epsilon}{\eta_B} \mathcal{D}; \quad D_K^e = \frac{\epsilon}{\eta_K} D_K(2\epsilon_p/S_p) \quad (8.30a, b)$$

$D_K(2\epsilon_p/S_p)$ is the Knudsen diffusivity in a cylindrical capillary of radius $(2\epsilon_p/S_p)$. In order to simplify the analysis of the results, it will be assumed that the tortuosity factors, η_B and η_K , are the same and independent of the porosity. The consequences of this assumption will be discussed later during the presentation of some numerical results for the $ZnO-H_2S$ reaction.

Eqs. (8.28)-(8.30) and the solution of the structural model can be used to determine the variation of κ_v and δ^e ($= D^e/D_0^e$) with the local conversion, ξ . With the functional dependence of these two parameters of the conversion known, the equations of the intraparticle diffusion and reaction model (Eqs. (8.23)-(8.25)) can be solved by using some discretization scheme to convert them into a system of ordinary differential equations and subsequent integration in time. For the results presented in this study, discretization was carried out using *B*-spline interpolation and collations (De Boor, 1978) and the resulting set of ordinary differential equations was integrated using a Gear-type solver (Gear, 1971).

With the initial bulk to Knudsen diffusivity ratio fixed, three additional parameters are involved in the diffusion and reaction model: Φ^2 , Sh^e , and ω . Since the diffusion coefficient in the intraparticle space much smaller than that in the bulk, the Sherwood number (see Eq. (8.27c)) is usually a very large number, and as a result, the concentration at the surface of the particles is equal to that in the bulk, i.e., $x|_{\rho=1} = 1$. Under the typical operating conditions encountered in most gas-solid reaction (e.g., hot gas and flue gas desulfurization) the value of ω varies in the range of $10^{-6} - 10^{-8}$. The time constant for diffusion in the intraparticle space (Eq. (8.23)) is thus much smaller than that associated with structural changes in the reacting solid (Eq. (8.24)), and consequently, the exact value of ω has practically no effect on the results of the diffusion and reaction model (pseudosteady-state approximation). It can be argued, therefore, that the initial Thiele modulus is the only parameter of practical significance encountered in the dimensionless form of the intraparticle model.

Fig. 8.12 presents the effects of intraparticle diffusion on the conversion vs. time results for a solid reacting in the Knudsen diffusion regime ($D_K^e \ll D_B^e$) with $\beta = 1$ and $Z = 3$, whose corresponding conversion evolution curves in the absence of intraparticle diffusion resistance are given in Fig. 8.10. The analogous results for the case with $\beta = \infty$ (Fig. 8.9), where local reaction and structure evolution is controlled by diffusion in the product layer, are shown in Fig. 8.13. Since $\beta \rightarrow \infty$ implies that $k_s \rightarrow \infty$, it is again necessary to modify the definition of all dimensionless parameters and variables (namely, τ , Φ^2 , and k_v) that involve k_s . This is done using the equation $Q' = \lim_{k_s \rightarrow \infty} \frac{Q}{\beta}$, with Q representing τ , Φ^2 , or κ_v . Thus, τ' is given by Eq. (8.22), with c_f in the place of c_p , and

$\Phi'^2 = a^2 \frac{D_P S_0^2}{\nu_A D_0^2}$. The average conversion, $\bar{\xi}$, of Figs. 8.12 and 8.13 is defined as

$$\bar{\xi} = \int_0^1 \xi d\rho^3 \quad (8.31)$$

The results of Figs. 8.12 and 8.13 were obtained by assuming that complete pore closure at the external surface takes place when the local conversion becomes equal to 0.49 – the maximum conversion possible is 0.50. Thus, notice that no reaction takes place in Figs. 8.12 and 8.13, that is, the conversion remains unchanged, after the time that corresponds to 0.49 conversion, for each case, in Figs. 8.10 and 8.9, respectively.

Comparison of the conversion trajectories of Fig. 8.12 with those of Fig. 8.10 shows that the effects of grain overlapping on the predictions of the overall model (structure evolution and diffusion and reaction) become stronger as the Thiele modulus increases and the intraparticle diffusional limitations intensify. Similar conclusions are reached by comparing the various conversion vs. time curves in Figs. 8.13 and 8.9. The most noteworthy observation from the results of Figs. 8.12 and 8.13 is that in the presence of intraparticle diffusional limitations the maximum conversion reached by the reacting particles decreases with decreasing grain overlapping although the observed behavior in the kinetically controlled regime is different and in the case of $Z = 3$ exactly the opposite. This behavior can be explained with the help of Fig. 8.14 which presents the variation of the effective Knudsen diffusivity with the conversion for the four patterns of grain overlapping. It is seen that the effective diffusion coefficient decreases with increasing grain overlapping – since D_K^e is proportional to $(1/S_p)$ and S_p increases with increasing overlapping (see Figs. 8.4 and 8.6). The intraparticle concentration and, hence, conversion gradients become larger as the grains are permitted to overlap more, and therefore, smaller average conversion is reached by the particles when plugging of the opening at their external surface takes place. Under strong internal diffusional limitations (e.g., $\Phi^2 = 10$), the average conversion decreases with increasing grain overlapping at all reaction times. If diffusion takes place in the bulk diffusion regime at all conversion levels, the effective diffusion coefficient will be independent of the extent of grain overlapping (for tortuosity factors depending on the porosity only), and consequently, the effects of the intraparticle diffusional limitations on

Figure 8.12. Average conversion vs. time curves under diffusional limitations in the intraparticle space for $\beta = 1$ and $Z = 3$ (see Fig. 8.10). $\omega = 10^{-7}$; $Sh^e = \infty$. —: nonoverlapping grains (NOGM); - - -: partially overlapping grains (POGM) with $\delta_0=1$;: partially overlapping grains (POGM) with $\delta=1.2$; -.-.: randomly overlapping grains (ROGM).

Figure 8.13. Average conversion vs. time curves under diffusional limitations in the intraparticle space for $(\beta = \infty)$ and $Z = 3$ (see Fig. 8.9). $\omega = 10^{-7}$; $Sh^e = \infty$. —: nonoverlapping grains (NOGM); - - -: partially overlapping grains (POGM) with $\delta_0=1$;: partially overlapping grains (POGM) with $\delta=1.2$; -.-.: randomly overlapping grains (ROGM).

Figure 8.14. Variation of the normalized effective Knudsen diffusivity (D^e/D_0^e) with the conversion for $Z = 3$.

Figure 8.15. Typical concentration and conversion profiles in the interior of the particles. $\beta = 1$; $Z=3$; $\delta_0 = 1$; $\Phi^2 = 10$.

the conversion vs. time curves will be qualitative different from those of Figs. 8.12 and 8.13. However, actual processes are expected to behave more like the cases of Figs. 8.12 and 8.13 since even if diffusion initially occurs in the bulk diffusion regime, the decreasing average pore opening ($\frac{4\epsilon_p}{S_p}$) will eventually bring it under Knudsen diffusion control.

Typical conversion and gaseous reactant concentration profiles in the interior of the reacting particles are shown in Fig. 8.15 for the case of Fig. 8.12 with $\delta_0 = 1$ (partially overlapping grains) and $\Phi^2 = 10$. It is seen that because of the decreasing intraparticle effective diffusivity with the local conversion, both profiles become steeper with the progress of the reaction. The evolution of the conversion and concentration profiles for the other cases of Fig. 8.12 and 8.13 is qualitatively similar to that shown in Fig. 8.15.

8.4. Application to the Reaction of ZnO Sorbents with H_2S

In order to demonstrate the flexibility of the partially overlapping grain model, in comparison to that of the two extremes of non- and randomly overlapping grains, we apply in this section the model to some experimental reactivity evolution data for the reaction of a zinc oxide sorbent (sorbent G-72D of United Catalysts) with H_2S . The physical structure of the solid was characterized by mercury porosimetry, gas adsorption, and nitrogen pycnometry. The sorbent has $\epsilon_0 = 0.51$, $v_s = 17 \text{ cm}^3/\text{gmol}$, $Z = 1.56$ and $S_0 = 27 \text{ m}^2/\text{g}$. (The v_s and Z values were estimated using the composition of the sorbent.)

The predictions of the diffusion, reaction, and structure evolution model of this study for nonoverlapping (NOGM) and partially overlapping (POGM) with $\delta_0 = 1$ grains are compared in Fig. 8.16 with experimental data for the reaction of ZnO particles (four size ranges) with 0.5% H_2S in N_2 at 600°C (see Fig. 4.15). The arithmetic mean of the two limits of the particle size range was used as particle size in our computations, and the effective diffusivity was computed using Eqs. (8.29) and (8.30) with $\eta_B = \eta_K = 3$. On the basis of the results from the analysis of the experimental data using the generalized random pore model, the product layer diffusivity (D_P) and the reaction rate constant (k_s) were set equal to $10^{-8} \text{ cm}^2/\text{s}$ and $4.3 \times 10^{-3} \text{ cm/s}$, respectively. The Sherwood number ($k_g a/\mathcal{D}$) was estimated using correlations for flow past spherical particles, and it was found to be almost unity for all particle sizes. In agreement with the general results of Fig. 8.12

Figure 8.16. Comparison of experimental conversion vs. time curves for ZnO sulfidation with results predicted by the mathematical model. 600°C ; 5000 ppm H_2S in N_2 .

Figure 8.17. Effects of the extent of grain overlapping on the variation of the effective diffusion coefficient with the conversion of the zinc oxide sorbent of Fig. 8.16.

and 8.13, the nonoverlapping grain model is more strongly influenced by the existence of intraparticle diffusional limitations, and thus tends to underestimate the average conversion of the large particles. The main reason for this kind of behavior lies again in the variation of the effective diffusion coefficient with the conversion, shown in Fig. 8.17. Diffusion in the intraparticle space practically takes place in the Knudsen diffusion regime – the initial value of $2\epsilon_p/S_p$ is 200 Å – and therefore, the effective diffusivity at nonzero conversions increases significantly with decreasing grain overlapping.

Since the variation of the effective diffusivity with the conversion turns out to be the most important of the factors that influence the predictions of the overall model in the presence of internal diffusional limitations, the theoretical results of Fig. 8.16 are strongly affected by the formula used to follow the dependence of the effective diffusivity in the structure of the solid. A constant tortuosity factor was used to obtain the results of Fig. 8.16, but since the structure of the solid becomes more tortuous as the porosity decreases, the tortuosity factor is in general an increasing function of the porosity (Tomadakis and Sotirchos, 1991a). Use of variable (and possibly different) tortuosity factors for the Knudsen and bulk diffusion regimes is not expected to change the qualitative trend seen in Fig. 8.17 although the δ_0 value that gives the best agreement between model and experiment will most probably be different.

8.5. Summary and Further Remarks

A mathematical model was developed for gas-solid reaction occurring in porous media whose structure can be visualized as an assemblage of partially overlapping (penetrable) spherical grains of uniform radius, each consisting of a spherical hard core, of the same radius for all grains, and a soft penetrable shell. The development of the diffusion, reaction, and structure evolution model was based on the randomly overlapping grain model of Sotirchos and Yu (1988) and the expressions derived by Rikvold and Stell (1985a) – on the basis of the scaled-particle theory of hard sphere fluids of Reiss et al. (1959) – for the porosities and surface areas of partially penetrable spheres. The partially overlapping grain model is considerably more flexible than the structural models that correspond to the extreme cases of nonoverlapping and partially overlapping grains. By varying the hard

core to grain radius ratio, it is possible to cover the whole space between these two extremes for a solid of given porosity and internal surface area.

A detailed parametric sensitivity analysis of the mathematical model, in terms of the various dimensionless parameters encountered in, was carried out for the case of gas-solid reactions with solid product. The flexibility of the mathematical model was demonstrated by applying it to a set of experimental data for the $ZnO-H_2O$ reaction. Our results showed that the effects of the extent of grain overlapping on the evolution of the overall reactivity of the solid with time are influenced in a rather complex fashion by the diffusional limitations in the product layer and in the intraparticle space. For fixed values of initial porosity and internal surface area, the conversion reached by the reacting solid increases with increasing grain overlapping in the absence of diffusion limitations, because of increasing reaction surface area. However, as the grains are permitted to overlap more, the pore surface area decreases, and this can lead to lower local reaction rates under strong diffusional limitations in the product layer. Smaller pore surface areas usually imply larger effective diffusion coefficients in the Knudsen regime, and as a result, the conversion reached by the reacting solid particles in the presence of strong intraparticle diffusional limitations decreases, in general, with decreasing grain overlapping.

We mentioned in the introductory section of our paper that a partially overlapping ('sintered') sphere model was developed by Lindner and Simonsson (1981) (PSSM model). The development of this model was based on the assumption that the structure of the unreacted solid could be represented by an aggregate of spherical grains in which each grain is in contact with n , on the average, other grains of the same initial radius, r_0 . The 'degree of sintering' was given by the distance d from the center to the plane of contact. For a given d/r_0 and ϵ_0 , n was determined by requiring that the model be consistent with the physical constraint of having zero surface area at zero porosity. Fig. 8.18 compares the variation of the internal surface area with the porosity of a structure of initial nonoverlapping grains with $\epsilon_0 = 0.5$ predicted by the Lindner and Simonsson model ($d/r_0 = 1$; $n = 5.57$) and the partially overlapping grain model ($\delta_0 = 1$). Since both models start with a structure of unconsolidated grains, the internal surface areas they predict for $\epsilon > \epsilon_0$ are identical, but significant differences are observed between the surface areas predicted by the two models

Figure 8.18. Comparison of the surface area vs. conversion curve predicted by the partially overlapping grain model (POGM) developed in this study for $\epsilon_0=0.5$ and $\delta_0=1$ with that given by the partially sintered sphere model (PSSM) of Lindner and Simonsson (1981) for the equivalent values of $\epsilon_0=0.5$ and $d/\tau_0=1$. Both models predict the same evolution of S for $\epsilon > \epsilon_0$.

below ϵ_0 . Since these surface areas are the pore surface areas for $Z > 1$, the conversion vs. time results of the two models in the presence of diffusional limitations (in the product layer or in the intra-particle space) are expected to differ significantly.

It can be shown using Eqs. (8.19), (8.21), and (8.23) in the paper by Lindner and Simonsson that the internal surface area for $d/r_0 = 1$ decreases with decreasing porosity for $n > 4$, which corresponds to $\epsilon_0 > 2/3$. On the other hand, the internal surface area given by Eq. (8.6) (in our study) for partially overlapping grains with $\delta_0 = 1$ goes through a maximum for all ϵ_0 . Thus, the only way to make the internal surface area vs. conversion curve of the PSSM model get closer to that of the POGM model for $\epsilon < \epsilon_0$ in Fig. 8.18 is to use in the PSSM model $d/r_0 > 1$. The pore surface of the PSSM model will then evolve as that of nonoverlapping grains until the point $d/r = 1$. (At $d/r = 1$ the derivative of the surface area vs. porosity curve is discontinuous because at this point each grain in the PSSM model comes in contact with a finite number of grains.)

8.6. Notation

Symbols that do not appear here are defined in the text.

- a radius of the particle, cm
- c_f gas concentration in the bulk, mol/cm^3
- c_p gas concentration in the pores, mol/cm^3
- c_r gas concentration at the reaction surface, mol/cm^3
- D bulk diffusion coefficient, cm^2/s
- D^e effective diffusion coefficient, cm^2/s
- D_B^e effective bulk diffusion coefficient, cm^2/s
- D_K Knudsen diffusion coefficient in a pore, cm^2/s
- D_K^e effective Knudsen diffusion coefficient, cm^2/s
- D_P diffusion coefficient in the product layer, cm^2/s
- k_s reaction rate constant, cm/s
- k_g mass transfer coefficient, cm/s
- k_v local volume-based reaction rate constant, s^{-1}

n	number of grains per unit volume
r	radial distance in a particle, cm
R	grain radius, cm
R_c	hard core radius, cm
$\mathcal{R}_s$	reaction rate per unit surface, $mol/cm^2/s$
S	internal surface area of a two-phase structure, cm^2/cm^3
Sh^e	Sherwood number (see Eq. (8.27c))
t	time, s
T	temperature, K
v_i	specific molar volume of solid i , cm^3/mol
x	dimensionless concentration in the particle
y	dimensionless radial distance in the grains
Z	stoichiometric volume ratio ($\nu_P \nu_P / \nu_S$)

Greek Letters

β	dimensionless parameter (Eq. 8.18b)
δ	grain growth variable
δ^e	dimensionless effective diffusivity
ϵ	porosity of a grain structure
ϵ_c	hard core porosity
η_B	tortuosity factor for bulk diffusion
η_K	tortuosity factor for Knudsen diffusion
κ_v	dimensionless reaction rate constant ($= k_v/k_{v0}$)
ν_A	stoichiometric coefficient of the reactive gas
ν_P	stoichiometric coefficient of the solid reactant
ξ	local solid conversion
$\bar{\xi}$	average solid conversion in a particle
ρ	dimensionless distance in a particle
τ	dimensionless time ($= \nu_S k_s S_0^2 \int_0^t (c_f \text{ or } c_p) dt'$)

- τ' dimensionless time $(= (v_S/\nu_A) D_P S_0^2 \int_0^t (c_f \text{ or } c_p) dt')$
 Φ^2 initial Thiele modulus $(= a^2 k_s S_0 / D_0^e)$
 $\Phi^{2'}$ modified initial Thiele modulus $(= a^2 D_P S_0^2 / (\nu_A D_0^e))$
 ω dimensionless parameter $(= c_f v_S)$

Subscripts

- 0 refers to $t = 0$ or to properties of the unreacted grain structure
 f refers to the bulk gas phase
 p refers to the pore surface or to the grains forming the pore surface
 r refers to the reaction surface or to the grains forming the reaction surface
 P refers to the solid product
 S refers to the solid reactant

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9. STEADY-STATE VS. TRANSIENT MEASUREMENT OF EFFECTIVE DIFFUSIVITIES IN POROUS MEDIA USING THE DIFFUSION-CELL METHOD

9.1. Introduction

The effective diffusivities of gases in porous media participating in gas-solid reactions, as well as their variation with the extent of the conversion of the solid for noncatalytic reactions, are among the most important parameters needed for the description of such processes. Knowledge of the effective diffusivity and its dependence on pore structure is also required in the analysis of experimental reactivity data for reactions between gases and porous solids obtained under significant diffusional limitations in the pore space. The particle-bed and the diffusion-cell method are most commonly used for the measurement of effective diffusion coefficients in porous media. In the particle-bed (or pulse-chromatographic) method, the effective diffusivity is extracted from the response of the exit concentration of a tracer gas in a packed bed of particles of the porous solid to a pulse change in the inlet concentration (Kucera, 1965; Schneider and Smith, 1968; Shah and Ruthven, 1977). Among the most important advantages of the particle-bed method over the diffusion cell method is that it can also be employed for porous media available in particle form only. Moment analysis of the response of the packed bed is the preferred method in the literature for estimation of the effective diffusivity from pulse-chromatographic data inasmuch as analytical expressions for the dependence of the moments of the response on the parameters of process can be derived if a linear convection and diffusion mathematical model is used for the bed – a reasonable approximation for low concentrations of diffusing gas.

Despite its appealing simplicity, the moments method may lead to inaccurate estimates of the effective diffusion coefficient because of the strong effect of experimental errors in the response curve (especially for large values of time) on the computed moments, and in particular on the second central moment that is usually used to estimate the effective diffusion coefficient. An alternative method of response analysis which does not present this disadvantage is the time-domain method, in which the effective diffusion coefficient and other transport parameters of the system (the axial dispersion coefficient,

for instance) are estimated by minimizing the difference between the experimental response and the response predicted by the mathematical model, usually, the integral square error (Boersma-Klein and Moulijn, 1979). Some of the problems met in the moments method can be avoided in the time-domain method by using only the part of the response that is free of large relative experimental errors.

In the diffusion-cell method, first proposed by Wicke and Kallenbach, 1941), streams of a binary mixture of a carrier gas and of the species whose diffusion coefficient we seek to determine are flown over the two sides of a pellet (slab-shaped sample) of the porous medium. The experiment is carried out under isobaric conditions because, otherwise, a flux model for simultaneous convection and diffusion in porous media has to be used to analyze the experimental data and isolate the diffusive contribution to the total mass transport flux. In contrast to the particle-bed method, diffusion-cell measurements can be carried out both under steady-state and transient conditions (Smith, 1981). In the steady-state version of the experiment, the mass transport flux is determined by measuring the concentration of the streams leaving the two sides of the diffusion cell and performing a simple mass balance on the tracer gas. When transient operation of the diffusion cell is employed, a concentration pulse is introduced in the stream that flows over one side of the porous sample, and the response of the concentration of the tracer gas in the exit stream of the other side is monitored, as in the case of the particle-bed method (Suzuki and Smith, 1972); Dogu and Smith, 1975); Baiker et al., 1982). Because of its simplicity, the moments method is again the preferred method of data analysis for transient diffusion-cell experiments. The sensitivity of the moments method to experimental errors in the response (noise, baseline shift, etc.) is not as large as that of particle-bed data because only the zero and first moments are now needed to get the effective diffusivity. Nevertheless, a time-domain method should again be preferred. Since only the zero and first moments of the experimental and theoretical responses are matched, the response curves in the time domain can be considerably different from each other.

It has been reported in the literature that effective diffusivities extracted from steady-state experiments in a diffusion cell may differ significantly from the values obtained from the analysis of pulse response data from particle-bed or diffusion-cell arrangements, even if

the same unit (i.e., diffusion cell) is used to obtain the steady-state and dynamic response data (McGreavy and Siddiqui, 1980; Baiker et al., 1982). Several explanations have been proposed to account for this discrepancy. These include: the existence of dead-end pores which should participate in the diffusion process under transient conditions but not under steady-state conditions; the effects of nonequilibrium adsorption, while equilibrated adsorption is usually assumed in the construction of the transient model; the effects of surface diffusion; and the effects of the dynamics of the entry and exit sections of the diffusion-cell or particle-bed apparatus, including those of the detectors used for concentration measurement, on the overall dynamics on the process and, hence, on the moments of the transient response to a concentration pulse. To all these explanations, one should add the possibility of erroneous determination of the moments of the response because of experimental errors.

Cui et al. (1989, 1990) recently showed that even in the absence of dead-end pores, surface diffusion and adsorption equilibration effects, and entry and exit section dynamics effects, effective diffusivities obtained from steady-state diffusion-cell experiments will always be different for solids with a distribution of pore size from those obtained from pulse-chromatographic (particle-bed) data through moments matching. The main reason for this difference is the use of a pseudohomogeneous model, that is, the use of a single effective diffusion coefficient to describe diffusion in an intrinsically inhomogeneous system which comprises subsystems (pores) of different diffusional resistances. For a simple pore structure consisting of parallel, noninteracting pores, Cui et al. showed that experiments under steady-state conditions yield, for diffusion parallel to the pores and in the absence of adsorption, the Johnson and Stewart, (1965) effective diffusivity, viz.,

$$D_s^e = \varepsilon \int_R D(R) \gamma(R) dR \quad (9.1)$$

$D(R)$ is the diffusivity in pores of radius R , ε is the porosity, and $\gamma(R)$ is the normalized porosity density function, that is, $\gamma(R)dR$ is the porosity fraction that belongs to pores with radius in the range $[R, R + dR]$. Matching of the moments of the transient responses of the inhomogeneous and homogeneous models, on the other hand, yields an effective

diffusivity given by

$$D_t^e = \varepsilon \left[\int_R \frac{1}{D(R)} \gamma(R) dR \right]^{-1} \quad (9.2)$$

Eqs. (9.1) and (9.2) give the same effective diffusivity only for solids with pores of uniform size. For solids with distributed pore size, the effective diffusivity of Eq. (9.2) is always smaller than that given by Eq. (9.1), by more than an order of magnitude for broad pore size distributions. Cui et al. (1989) postulated that for pore network models more complex than the parallel, noninteracting pore network, the differences between the steady-state (diffusion-cell) and transient (particle-bed) diffusivities for distributed pore size solids would undoubtedly be larger than those between the predictions of Eqs. (9.1) and (9.2).

The measurement of effective diffusivities using the diffusion-cell method under stationary and nonstationary conditions was examined by Burghardt et al. (1988) for bidisperse porous structures consisting of through macropores and dead-end micropores. Three different pore structures were considered in their analysis: a globular structure consisting of compacted microporous particles, a capillary structure with dead-end micropores emanating from the surface of a macroporous network, and a structure with dead-end micropores situated parallel to through macropores. It was found that the diffusion process in the dead-end micropores has no effect on the zero and first moments of the response of the diffusion cell, and as a result, matching of the first two moments yields the steady-state effective diffusivity. The micropore effective diffusivity appears in the second moment of the response, and the effective diffusivities obtained by second moment matching are lower than the value obtained from the stationary experiment. The theoretical conclusions of Burghardt et al. were in excellent agreement with their own experimental data for five different porous pellets.

An analysis of the relation between the effective diffusivities obtained from transient and steady-state mass transport experiments for solids with a pore size distribution using the diffusion-cell method is presented in this paper. The simple network of parallel (through) pores that was employed by Cui et al. (1989, 1990) in their study of the particle-bed method is used to represent the structure of the solid, and two models, differing in the complexity of the boundary conditions, are used to describe the diffusion-cell process. It is shown that in the case of transient diffusion-cell experiments, moment analysis of the tran-

sient responses (i.e., zero or first moment matching) yields the same result as steady-state diffusion-cell experiments. Despite having the same zero and first moments, the impulse responses of the inhomogeneous and pseudohomogeneous models differ significantly, but if a time-domain parameter estimation procedure is employed, the obtained effective diffusivity is, in general, larger than that resulting from steady-state experiments. It is finally shown that for more realistic pore structures, that is, pore structures exhibiting pore interlinking between the two sides of the solid sample, the difference between the responses of the homogeneous and inhomogeneous model, for the same zero and first moments, is smaller and approaches zero as the extent of pore communication is increased.

9.2. Description of the Diffusion-Cell System

A schematic diagram of a diffusion-cell arrangement is shown in Fig. 9.1. F_i are the flow rates of the gaseous streams that flow over the two sides of the porous slab, c_i are the concentrations of the diffusing species (solute) in the solute-carrier mixtures, V_i are the volumes of the dead-space regions ('mixing' chambers) next to the two faces of the porous slab, l is the slab thickness, and A is the cross-sectional area of the slab perpendicularly to the direction of diffusion, viz., the x -direction. In order to facilitate the analysis and interpretation of the results and avoid the use of a tortuosity factor, it is assumed that the pore space of the solid can be represented by an assemblage of cylindrical pores, arranged parallel to the direction of diffusion. The population of pores is described using the distribution density $\varepsilon(R)$, with $\varepsilon(R)dR$ being the porosity due to pores with size in the range $[R, R + dR]$. The normalized form of $\varepsilon(R)$ is denoted by $\gamma(R)$.

If a homogeneous model is used to describe the diffusion process in the porous medium, the mass balance for the solute in the solid in the absence of chemical reaction takes the form

$$\varepsilon \frac{\partial c_h}{\partial t} + \frac{\partial N_h}{\partial x} = 0 \quad (9.3)$$

where c and N are the concentration and flux of the solute, respectively, and subscript h is used to indicate that they refer to a homogeneous model. For a single pore of radius R ,

Figure 9.1: Schematic diagram of a diffusion-cell arrangement. The circled graph shows the local pore structure in enlargement.

on the other hand, the mass balance for the solute is written

$$\frac{\partial c(R)}{\partial t} + \frac{\partial N(R)}{\partial x} = 0 \quad (9.4)$$

with $c(R)$ and $N(R)$ being the concentration and flux of the solute in a pore of radius R . For small concentrations of solute and isobaric conditions, the fluxes (N_h and $N(R)$) can be related to the concentration gradients using the relations

$$N_h = -D^e \frac{\partial c_h}{\partial x}; \quad N(R) = -D(R) \frac{\partial c(R)}{\partial x} \quad (9.5a, b)$$

D^e and $D(R)$ are the diffusion coefficients of the solute in the porous medium (effective) and in a pore of radius R , respectively, both assumed independent of the concentration of the solute. Introducing Eqs. (9.5a,b) in Eqs. (9.3) and (9.4), the mass balance equations in the porous medium and in an individual pore become

$$\frac{\varepsilon \partial c_h}{\partial t} - D^e \frac{\partial^2 c_h}{\partial x^2} = 0 \quad (9.6)$$

$$\frac{\partial c(R)}{\partial t} - D(R) \frac{\partial^2 c(R)}{\partial x^2} = 0 \quad (9.7)$$

The average molar flux for the inhomogeneous system at some position x in the porous slab is obtained by averaging the flux for a single pore the same position over the pore size distribution, that is, we set

$$N_n = \int_R N(R) \varepsilon(R) dR \quad (9.8)$$

(Subscript n is used to indicate quantities that refer to the inhomogeneous system or model.)

Under steady-state conditions, we have that

$$\frac{\partial c_h}{\partial x} = \frac{\partial c(R)}{\partial x} = \frac{c_l - c_0}{l} \quad (9.9)$$

where c_0 and c_l are the concentrations of the solute at $x = 0$ and $x = l$. Equating the homogeneous and inhomogeneous model fluxes (Eqs. (9.5) and (9.8)) and using Eq. (9.9), we find that the steady-state effective diffusivity is given by

$$D_s^e = \varepsilon \int_R D(R) \gamma(R) dR \quad (9.10)$$

that is, Eq. (9.1).

9.3. Effective Diffusivities From Transient Experiments Using Moments Matching

In order to be able to extract effective diffusion coefficients from experimental data of transient experiments, a set of boundary conditions is needed to complete the mathematical model. The simplest set of boundary conditions is obtained by assuming that the volumes of the mixing chambers are negligibly small in comparison to that of the porous slab and that no flow takes place over the face of the slab at $x = l$, where measurement of the concentration response takes place. For an actual experimental arrangement, this situation corresponds to the case where a diffusion cell with a closed end is employed, the carrier-solute mixture is flown over the open end of the cell at a very high flow rate, and some concentration sensor is used to measure the concentration of the solute at the closed end (Suzuki and Smith, 1972). With these assumptions the boundary conditions take the form

$$c_h = c_0 = c_1; \quad c(R) = c_0 = c_1 \quad (\text{at } x = 0) \quad (9.11a, b)$$

$$N_h = 0; \quad N_n = 0 \quad (\text{at } x = l) \quad (9.12a, b)$$

$$c(R) = c_l, \quad \text{for all } R \quad (\text{at } x = l) \quad (9.13)$$

Eq. (9.13) states that the solute has the same concentration in all pores at the closed end of the diffusion cell. Using Eqs. (9.5) and (9.8), Eqs. (9.12) may be written in the equivalent form

$$\frac{\partial c_h}{\partial x} = 0; \quad \int_R D(R) \frac{\partial c(R)}{\partial x} \varepsilon(R) dR = 0 \quad (9.14a, b)$$

In the application of the moments method, the moments of the experimental response of a system (diffusion cell or particle bed) to some form of concentration input are set equal to those predicted by a homogeneous model for the system, and the resulting equations are used to estimate the unknown effective transport properties of the model. For the ideal case of a unit impulse (Dirac delta function) input, the moments of the response of the output, m_i , can be found from the transfer function between input and output, $G(s)$,

using the equation

$$m_i = (-1)^i \lim_{s \rightarrow 0} \frac{d^i G(s)}{ds^i} \quad (9.15)$$

It can easily be shown by taking the Laplace transform of Eqs. (9.6), (9.11a), and (9.14a) and solving the resulting equations that the transfer function for the homogeneous model is

$$G_h(s) = \frac{1}{\cosh(\sqrt{\frac{\varepsilon s}{D^e}} l)} \quad (9.16)$$

Using Eq. (9.16), we find that the zero moment of the impulse response is unity and that the first moment is given by

$$m_{1h} = \frac{\varepsilon l^2}{2D^e} \quad (9.17)$$

Similarly, solving Eqs. (9.7), (9.11b), (9.13), and (9.14b) in the s -domain we find that the transfer function for the inhomogeneous model has the form

$$G_n(s) = \frac{\int_R D(R) \sqrt{\frac{s}{D(R)}} \frac{1}{\sinh(\sqrt{\frac{s}{D(R)}} l)} \varepsilon(R) dR}{\int_R D(R) \sqrt{\frac{s}{D(R)}} \frac{\cosh(\sqrt{\frac{s}{D(R)}} l)}{\sinh(\sqrt{\frac{s}{D(R)}} l)} \varepsilon(R) dR} \quad (9.18)$$

Using Eq. (9.16), we find that the zero moment of the impulse response of the inhomogeneous system is unity, as in the case of the homogeneous model, and that the first moment is given by the expression

$$m_{1n} = \frac{l^2}{2 \int_R D(R) \gamma(R) dR} \quad (9.19)$$

Matching the first moments of the inhomogeneous ('experimental') and homogeneous model responses, i.e., setting $m_{1h} = m_{1n}$, we get

$$D_t^e = \varepsilon \int_R D(R) \gamma(R) dR \quad (9.20)$$

with subscript t used to denote effective diffusivities estimated from dynamic data. Eq. (9.20) clearly states that the effective diffusivity obtained using the moments method is identical to that obtained from steady-state experiments.

A question that naturally arises at this point is whether this conclusion is specific to the limiting case described by the boundary conditions given by Eqs. (9.11)-(9.14) or it also applies to the more general problem depicted in Fig. 9.1. If perfect mixing is assumed

in the dead-space regions adjacent to the porous slab, the boundary conditions for the homogeneous and inhomogeneous diffusion-cell models become of the form (Burghardt and Smith, 1979)

$$V_1 \frac{\partial c_0}{\partial t} = F_1(c_1 - c_0) - AN \quad (9.21)$$

$$c_h = c_0; \quad c(R) = c_0 \quad (\text{at } x = 0) \quad (9.22a, b)$$

$$V_2 \frac{\partial c_l}{\partial t} = F_1(c_2 - c_l) + AN \quad (9.23)$$

$$c_h = c_l; \quad c(R) = c_l \quad (\text{at } x = l) \quad (9.24a, b)$$

Eqs. (9.22b) and (9.23b) state that the concentrations of the solute in all pores at $x = 0$ and $x = l$, respectively, are the same. The flux N used in Eqs. (9.21) and (9.23) is given by Eq. (9.5a) for the homogeneous model and (9.8) and (9.5b) for the inhomogeneous model.

Assuming that the same concentration of solute is present initially in both streams, solution of Eqs. (9.6), (9.21), (9.22a), (9.23), (9.24a), and (9.5a) gives for the transfer function of the homogeneous model the result

$$G_h(s) = \frac{g_{1h}}{(1 + \tau_1 s + g_{2h})(\phi + \tau_2 s + g_{2h}) - g_{1h}^2} \quad (9.25)$$

with

$$g_{1h} = \frac{A}{F_1} D^e \sqrt{\frac{\varepsilon s}{D^e}} \frac{1}{\sinh(\sqrt{\frac{\varepsilon s}{D^e}} l)} \quad (9.26)$$

$$g_{2h} = \frac{A}{F_1} D^e \sqrt{\frac{\varepsilon s}{D^e}} \frac{\cosh(\sqrt{\frac{\varepsilon s}{D^e}} l)}{\sinh(\sqrt{\frac{\varepsilon s}{D^e}} l)} \quad (9.27)$$

$$\phi = F_2/F_1; \quad \tau_i = V_i/F_1 \quad (9.28a, b)$$

Using Eq. (9.16), we find that the zero and first moments of the impulse response of the homogeneous model are given by the relations (see also Burghardt and Smith, 1979)

$$m_{0h} = \frac{1}{1 + \phi(1 + \frac{F_1 l}{AD_e})} \quad (9.29)$$

$$m_{1h} = m_{0h}^2 [\tau_1(1 + \frac{\phi F_1 l}{AD_e}) + \tau_2(1 + \frac{F_1 l}{AD_e}) + \frac{A \varepsilon l}{F_1} + (1 + \phi) \frac{\varepsilon l^2}{2D_e} + \frac{\varepsilon \phi F_1 l^3}{6A(D_e)^2}] \quad (9.30)$$

Solution of the equations of the inhomogeneous model (Eqs. (9.7), (9.21), (9.22b), (9.23), (9.24b), (9.8), and (9.5b)) leads to the following transfer function between the input (c_1) and output (c_l) concentrations:

$$G_n(s) = \frac{g_{1n}}{(1 + \tau_1 s + g_{2n})(\phi + \tau_2 s + g_{2n}) - g_{1n}^2} \quad (9.31)$$

with

$$g_{1n} = \frac{A}{F_1} \int_R D(R) \sqrt{\frac{s}{D(R)}} \frac{1}{\sinh(\sqrt{\frac{s}{D(R)}} l)} \varepsilon(R) dR \quad (9.32)$$

$$g_{2n} = \frac{A}{F_1} \int_R D(R) \sqrt{\frac{s}{D(R)}} \frac{\cosh(\sqrt{\frac{s}{D(R)}} l)}{\sinh(\sqrt{\frac{s}{D(R)}} l)} \varepsilon(R) dR \quad (9.33)$$

Differentiating Eq. (9.31) and using Eq. (9.16), we derive the following expressions for the zero and first moments of the impulse response of the inhomogeneous model:

$$m_{0n} = \frac{1}{1 + \phi(1 + \frac{F_1 l}{AD_t^e})} \quad (9.34)$$

$$m_{1n} = m_{0n}^2 [\tau_1(1 + \frac{\phi F_1 l}{AD_t^e}) + \tau_2(1 + \frac{F_1 l}{AD_t^e}) + \frac{A \varepsilon l}{F_1} + (1 + \phi) \frac{\varepsilon l^2}{2D_t^e} + \frac{\varepsilon \phi F_1 l^3}{6A(D_t^e)^2}] \quad (9.35)$$

where D_t^e is the effective diffusivity given Eq. (9.20).

It is seen by comparing Eqs. (9.30) and (9.35) that by setting the effective diffusivity in the homogeneous model equal to that given by Eq. (9.20), its first moment becomes identical to that of the inhomogeneous model. Therefore, even for the general form of boundary conditions (Eqs. (9.21)-(9.24)), moment analysis of transient experimental data gives the same effective diffusion coefficient as steady-state experiments. Comparison of Eqs. (9.29) and (9.34) reveals that this choice of effective diffusivity also makes the zero moments of the two responses identical. This is a very important observation since the zero moment of the impulse response is the change of the steady-state concentration of the solute at $x = l$ for a unit step change in the input concentration at $x = 0$ (c_1).

In the chromatographic (particle-bed) method, pores of different size share the same concentration at the external surface of the particle, but otherwise, diffusion occurs independently in each pore. The contribution of the intraparticle diffusion process to the second central moment of the bed's response turns out to simply be the average of the diffusion time of a single pore over the pore size distribution (Villermaux, 1987; Cui et al., 1989). (The diffusion time is proportional to $a^2/D(R)$ (cf. Eq. (9.17)), with a being the radius of the particle.) The second central moment of the chromatographic response is thus influenced more strongly by the diffusivity of the small pores, and second moment matching leads to Eq. (9.2), which predicts much smaller effective diffusivities than the value resulting from diffusion-cell experiments (Eq. (9.10) or (9.20)). In the diffusion-cell method, however, there is interaction of the fluxes in different size pores at the end of the sample (see Eqs. (9.8), (9.12b), and (9.23)), and it is actually the large pores that serve as the main transport arteries of the system even under transient conditions. This interaction is further discussed in the following section, where the time domain responses of the homogeneous and heterogeneous models are compared.

9.4. Comparison of the Homogeneous and Inhomogeneous Model Responses in the Time Domain

It was pointed out in the introduction that matching the first two moments of the experimental and theoretical responses of a system does not guarantee good agreement between the concentration vs. time curves in the time domain. It is interesting, therefore, to investigate the relationship of the time-domain responses of the inhomogeneous ('experimental') and homogeneous models after their first two moments have been matched. In order to simplify the analysis, interpretation, and presentation of the results, we will focus on solids with discrete, bimodal distribution of pore size, i.e., solids for which

$$\varepsilon(R)dR = \varepsilon_1\delta(R - R_1) + \varepsilon_2\delta(R - R_2)$$

The impulse responses of the homogeneous and inhomogeneous models for the case of simple boundary conditions (with one of the ends of the diffusion cell closed and without dead space and mass transport limitations at its exposed end, Eqs. (9.11)-(9.14)) are shown in Fig. 9.2. The corresponding curves for a diffusion-cell with both ends exposed to gaseous

streams (boundary conditions given by Eqs. (9.21)-(9.24)) are shown in Fig. 9.3. The Fast Fourier Transform (FFT) method (specifically, a routine described by Press et al. (1986)) was used to invert the transfer functions given by Eqs. (9.16), (9.18), (9.25), and (9.31) and construct the response curves in the time domain. The results shown in the figure are for diffusion in the Knudsen regime in a solid with 0.5 total porosity, equal porosities of large and small pores, and pore size ratio equal to 10. For the case with the general form of boundary conditions (Fig. 9.3), the volumes of the mixing regions next to the two faces of the slab were taken as 1/10 of the volume of the slab, and the dimensionless parameters $AD(R_2)/F_i l$ were set equal to 3. In an actual experiment, the latter value would obtain, for instance, for $A = 2 \text{ cm}^2$, $D(R_2) = 0.5 \text{ cm}^2/\text{s}$, $l = 0.2 \text{ cm}$, and $F_i = 100 \text{ cm}^3/\text{min}$.

The response curves have been rendered independent of the type of the solute, sample thickness, and pore size by using the dimensionless time $tD(R_2)/l^2$ instead of the real time. Since diffusion occurs in the Knudsen regime, the diffusivity ratio is equal to the pore size ratio, i.e., $D(R_1) = D(R_2)/10$. Using this relationship and Eq. (9.10) or (9.20), we find that the effective diffusivity of the homogeneous model that is obtained from steady-state experiments or from transient experiments through moments matching is equal to $0.275D(R_2)$. Use of the particle-bed diffusivity expression of Cui et al. (Eq. (9.2)) gives about three times smaller effective diffusivity ($D^e = 0.090909 \cdot \cdot \cdot D(R_2)$). When the simple set of boundary conditions (Eqs. (9.11)-(9.14)) is employed, the first moment of the homogeneous model with effective diffusivity given by Eq. (9.2) is about three times larger than the first moment of the homogeneous model (2.75 vs. $0.90909 \cdot \cdot \cdot$, in dimensionless units). Thus, it is hardly surprising that the response curves of the homogeneous model with effective diffusivity given by Eq. (9.2) (chain-dot curves in Figs. 9.2 and 9.3) have practically no relation to the 'actual' response curves of the system, that is, the response curves of the inhomogeneous model (solid curves). It should be pointed out that the second moment of the inhomogeneous model is larger than that of the homogeneous model with D^e from Eq. (9.10) or (9.20), in agreement with the conclusions of Burghardt et al. (1988), but smaller than the value obtained when the chromatographic diffusivity (Eq. (9.2)) is employed. For instance, for the cases shown in Fig. 9.2, the second moment of the inhomogeneous model is $1.935 \cdot \cdot \cdot$, while that of the homogeneous model is 1.377 for D^e

Figure 9.2: Impulse response curves of the homogeneous and inhomogeneous models for a diffusion cell with a closed end (boundary conditions given by Eqs. (9.11)-(9.14)). $\varepsilon_1 = \varepsilon_2 = 0.25$; $R_1 = 0.1R_2$.

Figure 9.3: Impulse response curves of the homogeneous and inhomogeneous models for a diffusion cell with gaseous flow over both ends (boundary conditions given by Eqs. (9.21)-(9.24)). $\varepsilon_1 = \varepsilon_2 = 0.25$; $R_1 = 0.1R_2$; $\frac{V_i}{Al} = 0.1$; $\frac{AD(R_2)}{F_i l} = 3$.

from Eq. (9.20) and 12.60 for D^e from Eq. (9.2).

Although the impulse response of the homogeneous model (with D^e from Eq. (9.10) or (9.20)) has the same zero and first moments as the response of the inhomogeneous model, Figs. 9.2 and 9.3 show that there are significant differences between the response curves in the time domain. These differences are mainly due to the existence of two time constants, differing by an order of magnitude, for gaseous diffusion in the inhomogeneous (heteroporous) solid and the use of a single time constant in the homogeneous model. By using a single time constant, it is impossible to simultaneously capture the fast dynamics of the large pores and the slow response of the small pores, and as a result, the homogeneous model tends to underpredict the system's response for small and large values of time. This behavior is in qualitative agreement with some results obtained by Mo and Wei (1986) from the numerical solution of the diffusion equation on a lattice simulating the structure of a partially blocked ZSM-5 zeolite. Mo and Wei found that the steady-state effective diffusivity was the lower limit (for increasing time) of a transient effective diffusivity based on the instantaneous mass transport flux through the sample.

When only one end of the diffusion cell is exposed to a gaseous stream, the total flux at its closed end must obviously be zero at all times, and consequently, the diffusion flux in the small pores there must be the negative of the diffusion flux in the large pores. This situation is illustrated in Fig. 9.4 which presents dimensionless concentration profiles in the diffusion cell at various times following a step change (from zero) in the concentration of the tracer gas (solute) at its exposed end. The results of the figure show that the concentration gradient in the small pores at the closed end of the slab is always positive, and consequently, there is net flow of tracer gas in the small pores through both ends at all times. It is thus the large pores that serve as the transport arteries of the porous slab under unsteady conditions, and therefore, concentration equilibration in the small pores takes place much faster than it would if transport in them occurred independently of that in the large pores – as it is the case in particle-bed experiments (Eq. (9.2)).

Fig. 9.5 presents the evolution of the dimensionless concentration profiles in the two pore families following a step change (from zero) in the concentration of the tracer gas at $x = 0$ when both ends of the diffusion cell are exposed to flowing streams. Although in

Figure 9.4: Dimensionless concentration profiles in a diffusion cell with closed end (boundary conditions given by Eqs. (9.11)-(9.14)) at various times for a step change (of magnitude c_1) in the concentration of the stream flowing over its open end. Model parameters same as in Fig. 9.2. —: concentration in pores of radius R_2 ; - - -: concentration in pores of radius R_1 .

Figure 9.5: Concentration profiles in a diffusion cell with both ends exposed to gaseous streams (boundary conditions given by Eqs. (9.21)-(9.24)) at various times for a step change (of magnitude c_1) in the concentration of the stream flowing over one end. Model parameters same as in Fig. 9.3. —: concentration in pores of radius R_2 ; - - -: concentration in pores of radius R_1 .

this case the total diffusion flux at $x = l$ is not zero, the concentration gradient in the small pores at this point is again positive during the initial stages of the transient response of the system, and therefore, mass transport from one end of the slab to the other occurs through the large pores only. Only after the concentration profile gets close to steady state, the concentration gradient in the small pores at $x = l$ becomes negative, and direct contribution of these pores to the mass transport rate through the slab starts to take place. Both in Figs. 9.4 and 9.5, the concentration profile in the large pores becomes almost linear after the initial stages of the transient process, indicating that the diffusion process in the large pores is at pseudosteady state. This situation is obviously expected since the time constant for diffusion in the pores is inversely proportional to the pore size, and hence, it is an order of magnitude smaller for the large pores.

If the Fast Fourier Transform method is used to compute the concentration profiles shown in Figs. 9.4 and 9.5, complete response curves must be constructed at various positions within the cell. This turns out to be a computationally intensive task since both a very high sampling frequency and a large interval of time must be employed to capture the slow and fast dynamics of the local responses. For this reason, the results shown in Fig. 9.4 and 9.5 were obtained using cubic B-spline collocation (De Boor, 1978) to discretize the inhomogeneous model equations (Eqs. (9.7) and (9.11)-(9.14) or (9.21)-(9.24)) and time-integration of the resulting system of algebraic and ordinary differential equations with a Gear-type solver (Gear, 1971).

We have seen in Figs. 9.2 and 9.3 that despite having the same first two moments, the impulse responses of the homogeneous and inhomogeneous model exhibit marked differences in the time domain. It was thus decided to examine how the response curves of the homogeneous model for effective diffusivities obtained through a time-domain parameter estimation compare with that of the inhomogeneous model. Effective diffusivities were thus determined by minimization of the weighted integral square difference of the impulse responses of the homogeneous and inhomogeneous model, that is, by minimization of the functional

$$f = \int_0^{\infty} w(t)(y_n(t) - y_h(t))^2 dt \quad (9.36)$$

where $w(t)$ is the weight function: 1, t , or t^2 . The Fast Fourier Transform method was

used to obtain the homogeneous and inhomogeneous model responses, y_h and y_n , and as a result, the equivalent finite sum form of functional f was employed in the computations. The upper limit of the time interval used in the evaluation of the functional was set equal to 8 times the first moment of the normalized impulse response of the inhomogeneous model.

Method	$D_i^e/D(R_2)$	Zero Moment	First Moment
Moments	0.275	1.0	0.9090
$w(t) = 1$	0.4046	1.0	0.6178
$w(t) = t$	0.3673	1.0	0.6805
$w(t) = t^2$	0.30862	1.0	0.8100

Table 9.1: Effective Diffusivities from Moments Matching or Time-Domain Parameter Estimation on the Diffusion-Cell with Closed End.

The obtained diffusivities through the above parameter estimation scheme for the diffusion cells used to get the results of Figs. 9.2 and 9.3 are given in Tables 9.1 and 9.2. Shown in the tables are also the values of the first and zero moments of the homogeneous model for the estimated effective diffusivity. The impulse response curves of the homogeneous model for the effective diffusivities of Tables 9.1 and 9.2 are compared with the impulse response of the inhomogeneous model in Figs. 9.6 and 9.7. Notice that when both ends of the cell are exposed to flowing streams, both the first and the zero moments of the impulse response of the homogeneous model are functions of the effective diffusivity. Therefore, in this case one has the choice of using the impulse response or its normalized form in the parameter estimation scheme.

The results of Tables 9.1 and 9.2 show that time-domain parameter estimation gives effective diffusion coefficients larger, in general, than the value obtained through moments matching. The only exception is the case with $w(t) = t^2$ and the general form of boundary conditions (Table 9.2 and Fig. 9.7). The main reason for this occurrence is that the time-domain parameter estimation process – especially if the normalized form of the response is

Figure 9.6: Comparison of the impulse response of the inhomogeneous model with the impulse responses of the homogeneous model for effective diffusivities estimated through curve fitting using different weight functions in the expression for the square error (see Table 9.1). The diffusion cell has one of its ends closed, and the model parameters are the same as those of Fig. 9.2.

Figure 9.7: Comparison of the impulse response of the inhomogeneous model with the impulse responses of the homogeneous model for effective diffusivities estimated through curve fitting using different weight functions in the expression for the square error (see Table 9.2). The diffusion cell has both ends exposed to gaseous flow, and the model parameters are the same as those of Fig. 9.3. The chain-dotted ($-\cdot-$) curves were obtained by matching the normalized impulse responses of the inhomogeneous and of the homogeneous models.

used – places more weight on the initial response of the system where the impulse response has larger values. As more weight is put on the difference between the homogeneous and inhomogeneous impulse responses at large times, by using weight functions t and t^2 , the effective diffusivity becomes smaller and the response curve moves to the right – except when the normalized response is used with $w(t) = t$ in Table 9.2 and Fig. 9.7. Using $w(t) = t$ appears to give the best, in a qualitative sense, results, but it should be kept in mind that unless the effective diffusivity obtained via moments matching is used, the steady-state behavior will not be predicted by the homogeneous model. Only the effective diffusivity given by Eq. (9.10) or (9.20) reproduces the zero moment of the response, which as we have already mentioned is the steady state concentration at $x = l$ for $c_1 = 1$ and $c_2 = 0$.

Method	$D_i^e/D(R_2)$	Zero Moment	First Moment
Moments	0.275	0.3113	0.4858
$w(t) = 1$	0.3578	0.3411	0.4972
$w(t) = t$	0.3048	0.3232	0.4906
$w(t) = t^2$	0.2290	0.2894	0.4762
$w(t) = 1^*$	0.4805	0.3712	0.5067
$w(t) = t^*$	0.5082	0.3765	0.5082
$w(t) = t^{2*}$	0.4465	0.3641	0.5046

Table 9.2: Effective Diffusivities from Moments Matching or Time-Domain Parameter Estimation on the Diffusion-Cell with both ends open. (*Using the normalized form of the impulse response.)

For the simple set of boundary conditions (Eqs. (9.11)-(9.14)), the first moment is inversely proportional to the effective diffusivity (see Eq. (9.17)), and as a result, the relative differences among the first moments of Table 9.1 are proportional to those among the effective diffusivities. However, as the results for the first moments of Table 9.2 show, when both ends of the diffusion cell are exposed to flowing streams (the standard experimental arrangement), the sensitivity of the first moment to the effective diffusivity is considerably

weaker. This different behavior is due to the fact that the contributions of the dynamics of the mixing chambers to the overall first moment (see Eq. (9.30)) are weakly influenced by the effective diffusivity. There are two important consequences of this observation for those using transient operation of a diffusion cell to extract effective diffusivities. First, sufficient information on the dynamics of the mixing chambers must be available to obtain accurate effective diffusivity estimates. Second, small errors in the moments may produce large errors in the diffusion coefficient estimates.

9.5. Pore Interlinking and Mismatch between the Homogeneous and Inhomogeneous Model Responses

The parallel pore model does not offer an acceptable representation of the internal structure of porous media encountered in practical applications. Its main drawback is that it does not allow for pore communication in the interior of a porous sample, and as a result, the concentration fields in pores of different size interact only at the external surface of the sample. Real porous media, however, exhibit a highly interconnected pore structure – a point in the interior can be reached from almost any point of the external surface – and with such frequency that in most cases it is impossible to discern long uninterrupted pore segments between pore intersections. Thus, in this section we will examine how the mismatch between the responses of the inhomogeneous and homogeneous models (with D^e given by Eq. (9.10) or (20)) is affected by pore communication (pore interlinking) in the interior of the porous medium.

A simple porous medium with interconnected pores, probably the simplest, is obtained by considering a laminated structure in which each lamina is topologically equivalent to the parallel pore structure of Fig. 9.1, that is, it contains parallel, noninteracting pores arranged perpendicularly to its faces. Between two adjacent laminae, there exists a thin void layer whose sole function is to preserve the continuity of diffusion paths between adjacent laminae and equilibrate the concentration there. The assumption that the concentration is uniform in the region between adjacent laminae does not necessarily imply that there is no diffusion resistance in this region parallel to the faces of the slab. It simply means that over the smallest region of the face of each lamina that is statistically

representative of the cross-section of the pellet at large - that is, it contains a statistically representative sample of pore mouths - concentration differences are negligible. A structure consisting of k laminae of equal thickness l/k is schematically shown in Fig. 9.8. Obviously, if only one layer is considered, the parallel pore structure considered thus far in our analysis (Fig. 9.1) is obtained.

In the diffusion cell experiment, the laminated structure is assumed to be positioned in such a way that diffusion takes place parallel to the pores, as in Fig. 9.1. Eq. (9.7) now holds in the interior of each lamina, and Eqs. (9.11)-(9.14) or (9.21)-(9.24) are still the boundary conditions at the two faces of the porous slab. Let $c^i(R)$ be the concentration in the interior of the i th lamina in a pore of radius R . Continuity of flux and concentration at $x = \frac{il}{k}$ requires that

$$\int_R D(R) \frac{\partial c^i(R)}{\partial x} \varepsilon(R) dR \Big|_{x=(\frac{il}{k})^-} = \int_R D(R) \frac{\partial c^{i+1}(R)}{\partial x} \varepsilon(R) dR \Big|_{x=(\frac{il}{k})^+} \quad (9.37)$$

$$c^i(R) \Big|_{x=(\frac{il}{k})^-} = c^{i+1}(R) \Big|_{x=(\frac{il}{k})^+} = c_n^i \quad (9.39)$$

with c_n^i being the concentration, common for all pores, of the inhomogeneous model at $x = il/k$. Obviously,

$$c_n^0 = c_0; \quad c_n^k = c_l \quad (9.39a, b)$$

Using the solution of Eq. (9.7) in each layer, Eq. (9.37) takes the form

$$\alpha c_n^{i+1} - c_n^i + \alpha c_n^{i-1} = 0; \quad \alpha = g_{3n}/2g_{4n} \quad (9.40a, b)$$

with

$$g_{3n} = \int_R D(R) \sqrt{\frac{s}{D(R)}} \frac{1}{\sinh(\sqrt{\frac{s}{D(R)}} \frac{l}{k})} \varepsilon(R) dR \quad (9.41)$$

$$g_{4n} = \int_R D(R) \sqrt{\frac{s}{D(R)}} \frac{\cosh(\sqrt{\frac{s}{D(R)}} \frac{l}{k})}{\sinh(\sqrt{\frac{s}{D(R)}} \frac{l}{k})} \varepsilon(R) dR \quad (9.42)$$

Solving the difference equation described by Eq. (9.40a) and using Eq. (9.39) and the general form of boundary conditions, we get, after some manipulations, that

$$G_n(s) = \frac{c_l}{c_1} = \frac{f_1(\rho_2 - \rho_1)}{f_2 f_3 (\rho_2^k - \rho_1^k) - f_1 (f_2 + f_3) (\rho_2^{k-1} - \rho_1^{k-1}) + f_1^2 (\rho_2^{k-2} - \rho_1^{k-2})} \quad (9.43)$$

Figure 9.8: Schematic representation of a multilayered slab. The pore structure of each layer is the same as that shown in the circled graph of Fig. 9.1.

with

$$\rho_{1,2} = \frac{1 \pm \sqrt{1 - 4\alpha^2}}{2\alpha} \quad (9.44)$$

$$f_1 = \frac{A}{F_1} g_{3n}; \quad f_2 = 1 + \tau_1 s + \frac{A}{F_1} g_{4n}; \quad f_3 = \phi + \tau_2 s + \frac{A}{F_1} g_{4n} \quad (9.45a - c)$$

By setting $\tau_1 = \tau_2 = \phi = 0$ and letting $F_1 \rightarrow \infty$, Eq. 9. (43) gives the transfer function for the simple set of boundary conditions (Eqs. (9.11)-(14)), which turns out to be

$$G_n(s) = \frac{g_{3n}(\rho_2 - \rho_1)}{g_{4n}(\rho_2^k - \rho_1^k) - g_{3n}(\rho_2^{k-1} - \rho_1^{k-1})} \quad (9.46)$$

For $k = 1$, Eqs. (9.43) and (9.46) take the form of Eqs. (9.31) and (9.18), respectively. It is possible to further simplify Eqs. (9.43) and (9.46), but such a simplification is unnecessary for their inversion using the Fast Fourier Transform method.

The expressions for the first and zero moments of the impulse response of the transfer functions of Eqs. (9.43) and (9.46) are again derived using Eq. (9.16). After a number of algebraic manipulations, one finds that the zero and first moments of the impulse response of a multilayered slab are independent of the number of layers, k , for both types of boundary conditions. Thus, the zero moment of the impulse response of Eq. (9.46) is unity, its first moment is given by Eq. (9.19), and the zero and first moments of Eq. (9.43) are given by Eqs. (9.34) and (9.35), respectively. This result obviously implies that the effective diffusivity in a multilayered slab that is obtained through moments matching is independent of the number of layers and is given by Eq. (9.10) or (9.20).

Increasing the number of laminae in the slab increases the degree of interaction of pores of different size in the porous medium. The effects of pore interlinking on the response of the diffusion cell may therefore be investigated by examining how the number of laminae influences the behavior of the system. Figs. 9.9 and 9.10 present impulse response curves, constructed by inverting Eqs. (9.46) and (9.43), respectively, for various values of k , with each layer in the slab characterized by discrete, bimodal distribution of pore size. The pore size distribution and the other parameters of the cell are identical to those used to obtain the results of Figs. 9.2-9.7 for the single layer slab. It is seen that as the number of layers is increased and the degree of pore interaction between the two sides of the porous slab rises, the response of the diffusion cell (inhomogeneous model) gets closer

to that predicted by the homogeneous model using the effective diffusivity of Eq. (9.10) or (9.20) (dashed curve). Even with only two layers in the porous slab, that is, with the pores interacting only at a single point, there is a dramatic decrease in the difference between the inhomogeneous and the homogeneous model response. With both ends of the cell exposed, the response of the inhomogeneous system becomes almost identical, for most practical purposes, to that of the homogeneous model for less than 8 layers in the slab. However, since the two responses are further apart when the simple set of boundary conditions is used, it takes more layers for the difference between the two responses to be reduced to a similar extent in this case (compare Figs. 9.9 and 9.10). In the hypothetical situation of an infinite number of pore layers, a perfectly interconnected pore network obtains, in which the microscopic concentration field in each pore coincides with the macroscopic one given by the homogeneous model with D^e taken from Eq. (9.10) or (9.20).

The above observations point to the conclusion that under conditions of pore communication – as it is expected to be the case in an actual porous medium – the disagreement between the predictions of the homogeneous and inhomogeneous model might not be of such magnitude to justify the use of a complex inhomogeneous model to describe the diffusion process. It can thus be argued that provided that a diffusion flux model consistent with the topology of the pore structure of the porous medium is employed (Sotirchos, 1989), a pseudohomogeneous model employing effective values for the various transport properties may provide a satisfactory description not only of the steady-state but also of the transient processes occurring in a solid with distributed pore size.

9.6. Summary and Concluding Remarks

The relation between the effective diffusion coefficients of nonadsorbing gases obtained from steady-state and transient diffusion-cell experiments was investigated in this study. A simple geometrical model consisting of parallel noninteracting pores, of some pore size distribution (parallel bundle pore model), was used to represent the physical structure of the porous medium, and two different experimental arrangements were employed in the analysis of the system; namely, one in which the concentration of the tracer gas is monitored at a closed end of the diffusion cell and another in which gaseous streams flow over

Figure 9.9: Effect of the number of layers in a sample of fixed thickness on the impulse response of the homogeneous model (D^e from Eq. (9.10) or (9.20)) for a diffusion cell with closed end. Model parameters same as in Fig. 9.2.

Figure 9.10: Effect of the number of layers in a sample of fixed thickness on the impulse response of the homogeneous model (D^e from Eq. (9.10) or (9.20)) for a diffusion cell with both ends exposed to gaseous flow. Model parameters same as in Fig. 9.3.

both faces of the porous slab. The parallel pore model does not permit communication of pores in the interior of the porous slab, and thus, in order to examine the effects of pore interlinking on our conclusions, we also studied the diffusion problem in a laminated structure, in which the pore structure of each lamina is described by the parallel bundle pore model.

The analysis of the problem showed that the effective diffusivity determined by matching the zero and first moments of the experimental (inhomogeneous model) response of the diffusion cell with the corresponding moments of the response of the homogeneous model is identical to the effective diffusion coefficient derived from steady-state diffusion cell experiments. Because of the existence of different time constants for diffusion in a solid with a pore size distribution, the time-domain response predicted by the homogeneous model, which has a single time constant, is different from that of the inhomogeneous model. If a time-domain parameter estimation scheme is employed, the obtained effective diffusivities are, in general, larger than the steady-state value. These findings are in sharp contrast with the conclusions reached by Cui et al. (1989, 1990) from their analysis of particle-bed transient data, where it was found that effective diffusivities extracted from particle-bed experiments through moment matching for solids with distributed pore size and noninteracting pores (parallel bundle model) can be smaller, by a few orders of magnitude in some cases, than the steady-state diffusivities.

Allowing for pore communication in the interior of the porous solid causes a dramatic reduction in the difference between the responses of the homogeneous and inhomogeneous model in the time domain. It can thus be argued that the intrinsic inability of a pseudo-homogeneous model to describe diffusion and reaction in a physically inhomogeneous pore structure might not be an issue in practical applications, and that explanations for any discrepancies between transient and steady-state estimates of effective diffusivities from diffusion-cell experiments should be sought elsewhere. It should be pointed out that in their comparative study of measuring methods of effective diffusivities in porous catalysts, Baiker et al. (1982) obtained experimental results that are in agreement with the conclusions of my study and of the study of Burghardt et al. (1988). The steady-state diffusion-cell effective diffusivities in the industrial catalysts they studied were found to be

practically the same as, or in a few cases slightly smaller than, the transient effective diffusivities measured using the same unit. Only when the particle-bed method was used, the dynamic diffusivities were significantly smaller than the steady-state values, in agreement with the analysis of Cui et al. However, Baiker et al. concluded that the differences between the particle-bed and diffusion-cell results were within reasonable limits considering the sources of uncertainty in the bed experiments.

9.7. Notation

Symbols that do not appear here are defined in the text.

c	concentration, kmol/m^3
c_0	concentration at $x = 0$, kmol/m^3
c_l	concentration at $x = l$, kmol/m^3
c_i	inlet concentration of the stream flowing over face i of the slab, kmol/m^3
$c(R)$	concentration in a pore of radius R , kmol/m^3
$c^i(R)$	concentration in a pore of radius R in layer i of a multilayered slab, kmol/m^3
c_n^i	concentration at the interface of layer i and $i + 1$ of a multilayered slab, kmol/m^3
D^e	effective diffusion coefficient, m^2/s
D_s^e	steady-state effective diffusion coefficient, m^2/s
D_i^e	transient effective diffusion coefficient, m^2/s
f_i	parameters defined in Eq. (9.45)
F_i	flow rate of the stream flowing over face i of the slab, m^3/s
g_{ih}	parameters defined in Eqs. (9.26) and (9.27)
g_{in}	parameters defined in Eqs. (9.32), (9.33), (9.41), and (9.42)
$G(s)$	transfer function between c_l (output) and c_1 (input)
k	number of laminae in a multilayered slab
l	slab thickness, m
m_i	i th moment of impulse response, m^i
N	diffusion flux, $\text{kmol}/\text{m}^2 \cdot \text{s}$
$N(R)$	diffusion flux in a pore of radius R , $\text{kmol}/\text{m}^2 \cdot \text{s}$