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# Comparative Study of the Reactions of Metal Oxides With $H_2S$ and $SO_2$

Authors:
Sotirchos, S.V.

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Department of Chemical Engineering
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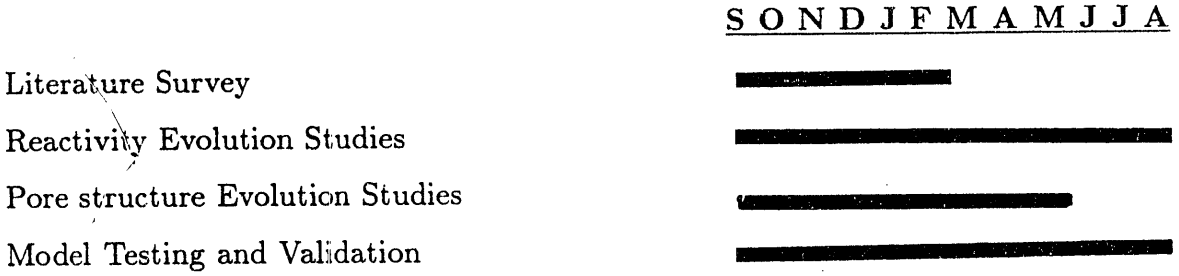
# COMPARATIVE STUDY OF THE REACTIONS OF METAL OXIDES WITH $H_2S$ and $SO_2$

## CONTRACT INFORMATION

| | |
|---|---|
| **Contract Number** | DE-FG22-90PC90301 |
| **Contractor** | University of Rochester<br>Department of Chemical Engineering<br>Rochester, NY 14627 |
| **Contractor Project Manager** | Prof. Stratis V. Sotirchos |
| **Principal Investigator** | Stratis V. Sotirchos |
| **METC Project Manager** | Mr. V. P. Kothari/Dr. Kamal Das |
| **Period of Performance** | Sept. 15, 1990 to Sept. 14, 1993 |
| **Schedule and Milestones** | |

**1991-1992 Program Schedule**



## OBJECTIVES

The primary objective of this project is 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 oxides of zinc, iron, and/or copper will be used as model systems in our experimental studies, which will include reactivity evolution studies and pore structure characterization using a variety of methods. Our work will focus on oxides that can react (sufficiently fast) both with $SO_2$ and $H_2S$. We intend 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.

## 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.

## PROJECT DESCRIPTION

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 $H_2S$. During the first period of this project, we concentrated on the experimental investigation of the reaction of $ZnO$-based sorbents with $SO_2$ and the reaction of $CaO$-based sorbents with $H_2S$. Two commercially available zinc oxide sorbents and calcines prepared from three limestones of high (>95%) calcium carbonate content were used in the experiments. 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. We also worked on the development of a grain-based mathematical model for gas-solid reactions with solid product, which allows for partial overlapping (sintering) of the grains that make up the porous solid, and carried out a detailed study of the measurement of effective diffusion coefficients in porous solids using the diffusion-cell method. Details on the partially overlapping grain model are given by Efthimiadis and Sotirchos (1992a).

The $ZnO$-$SO_2$ reaction was found to take place with very low rate, and thus only the $CaO$-$H_2S$ reaction data were analyzed. Very strong dependence of the overall reaction rate of the calcines and of its evolution with the progress of the reaction on particle size was observed. 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) from the study of the sulfation of the same solids. In both cases, the reactivity of the sorbent was found to increase, in general, with increasing average grain in the precursor stone, and the same behavior was also exhibited by the calcination rates of the precursors. Very good agreement was obtained between model and experiment using parameter values consistent with those needed to describe the sulfation of the same solids. 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. More details on these results are given by Efthimiadis and Sotirchos (1992b) and Sotirchos and Zarkanitis (1992).

Unfortunately, the immense volume of information that was collected from our studies and the studies of other research groups 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. For example, pressurized fluidized-bed combustion (PFBC) units normally operate under a pressure of 16 atm, which for an average $CO_2$ content of 15% gives a partial pressure of $CO_2$ in the reactor of about 2.4 atm. Thermodynamic calculations show that the temperature for $CaCO_3$ calcination in the presence of 2.4 atm of $CO_2$ must be larger than 980 °C, that is, well above the temperature range (750-950 °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 under high pressure PFBC conditions, favorable desulfurization is known to occur in PFBC units (Bulewicz et al., 1986; Murthy et al., 1979). Analogous observations apply to coal gas desulfurization ($H_2S$ removal) by limestone addition at high pressures.

In view of the above observations, it was decided to work on the comparative experimental investigation of the direct reaction with $H_2S$ and $SO_2$ of the three limestones that 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 $CaCO_3$, as it was done in the studies of Snow et al. (1988) and Tullin and Ljungstrom (1989) for the limestone-$SO_2$ reaction. Some of our results for the direct reaction of limestones with $SO_2$ will be discussed in the following section.

## RESULTS

### 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, 1992). 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 $\mu$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 $\mu$m) 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 $^o$C. The inlet gases were composed of a mixture of 70% $CO_2$ (99.99% purity), and 30% air (containing 0.5% or 2% $SO_2$). The sample was heated to the desired reaction temperature of 750 $^o$C or 850 $^o$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.

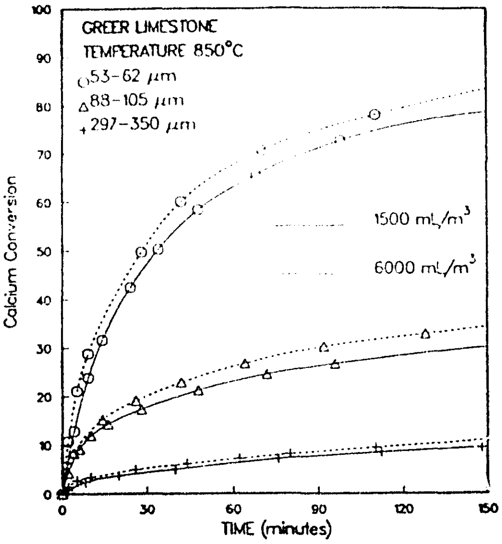


**Figure 1. Conversion vs. time results during direct sulfation at 850 $^o$C of Greer limestone particles**

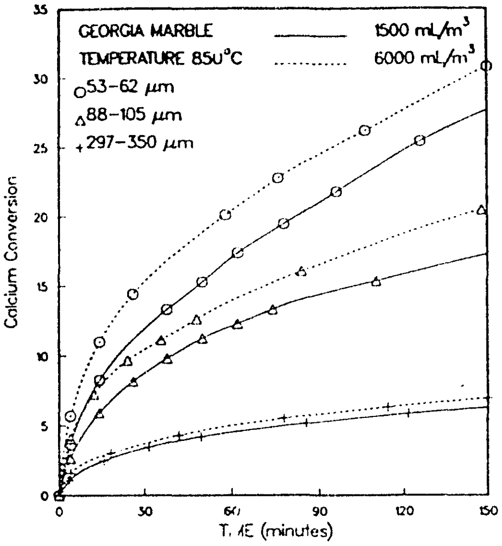


**Figure 2. Conversion vs. time results during direct sulfation at 850 $^o$C of Georgia marble particles**

## Reactivity Evolution Results

Figures 1-3 present conversion vs. time data for the direct sulfation at 850 $^o$C of 53-62, 88-105, and 297-350 $\mu$m 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. It is obvious from the results of Figures 1-3 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.

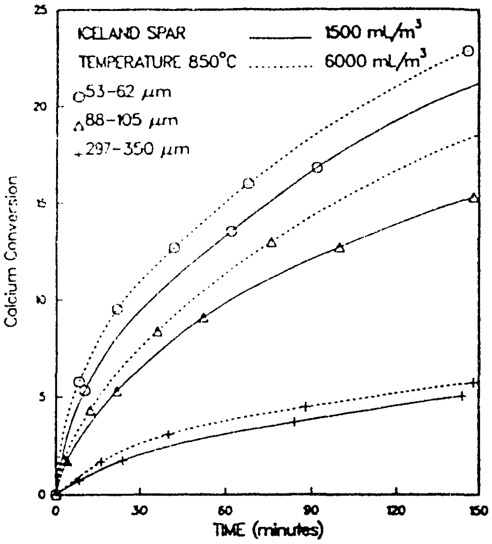


**Figure 3. Conversion vs. time results during direct sulfation at 850 °C of Iceland spar particles**

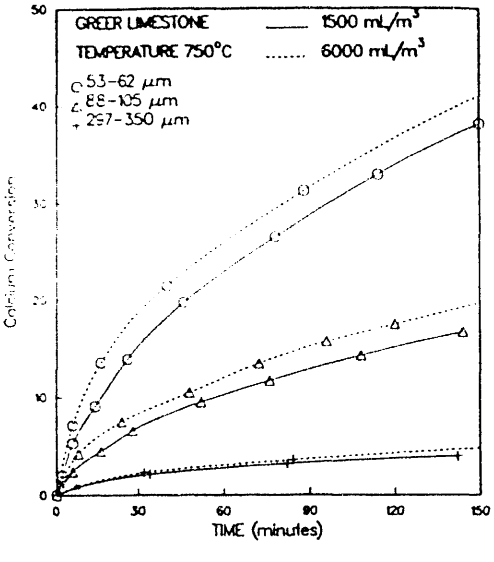


**Figure 4. Conversion vs. time results during direct sulfation at 750 °C of Greer limestone particles**

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.

Qualitatively similar results were obtained for the direct sulfation of the three solids (for the same particle sizes and $SO_2$ concentrations as in Figures 1-3) at 750 °C. The conversion vs. time curves for the Greer limestone sample are shown in Figure 4. Comparison of Figures 1 and 4 shows that 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. 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 °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.

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.

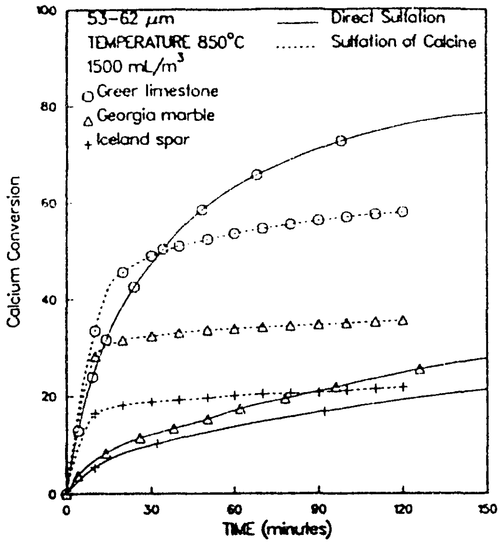


**Figure 5. Comparison of the conversion evolution curves during direct and indirect sulfation of 53-62 $\mu$m particles at 850 $^oC$**

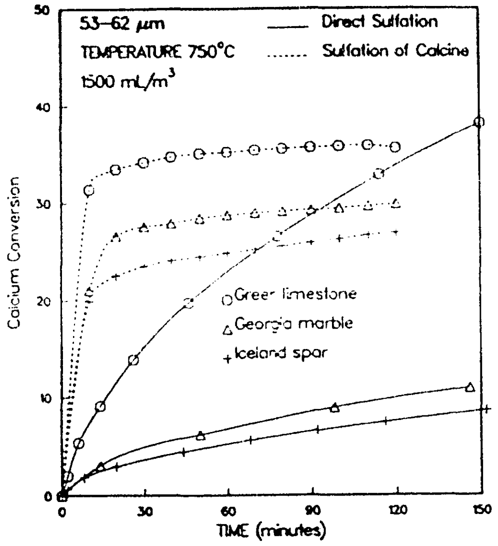


**Figure 6. Comparison of the conversion evolution curves during direct and indirect sulfation of 53-62 $\mu$m particles at 750 $^oC$**

Figures 5 and 6 compare at 850 and 750 $^oC$, respectively, the conversion vs. time curves that we measured in this study for the direct reaction of 53-62 $\mu$m 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 Figures 5 and 6 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 Figure 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 Figures 5 and 6 cannot be used to determine the effect of temperature on the reaction of calcined limetones since the calcines of each figure were produced at different temperatures, and as a result, they have different pore structures. Zarkanitis and 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.

## Pore Structure Results

Mercury penetration and gas adsorption were used to analyze the structure of the solids. 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 only. 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.

Very small porosities and surface areas were determined for the precursors from the $N_2$ sorption data. Specifically, the porosity for pores of radius smaller than 100 nm were found to be 0.015, 0.007, and 0.004 for Greer limestone, Georgia marble, and Iceland spar, respectively, whereas the corresponding values of surface area were 0.91, 0.31, and 0.23 $m^2/g$. 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. It is interesting to note that the reaction rates and the sulfation efficiencies, both for direct and indirect (after calcination) sulfation (see Figures 5 and 6), 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 probably 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.

The analysis of the sorption isotherm of a Greer limestone sample exposed to the reactive mixture for only 1 min showed that its cumulative porosity was much smaller than that of the unreacted precursor. This was also found to be the case for a sample that was heat-treated under $N_2$ and $CO_2$ at the reaction temperature (see Figure 7). The pore size distribution of the heat-treated precursor 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 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 580-585 °C. During heat treatment at 850 °C, molten phosphorous pentoxide 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.

Figure 7 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, 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 Figure 7 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.

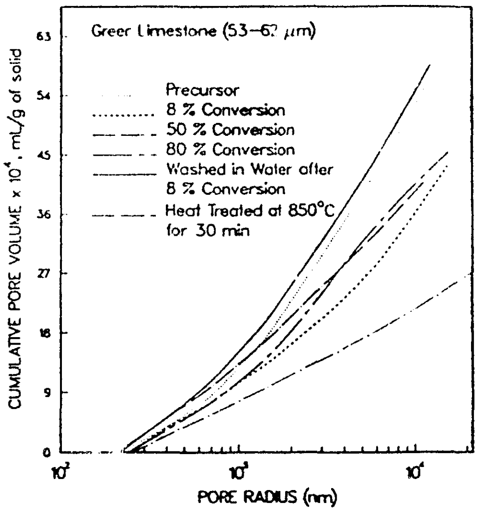


**Figure 7. Effects of conversion on the pore size distribution of Greer limestone particles (53-62 $\mu$m) during direct sulfation at 850 °C**

The $CaSO_4$ product of the 8% converted sample of Figure 7 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 level, while gas sorption analysis (see Figure 7) 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).

## Analysis of the Reactivity Data

The initial reaction rates were used to determine the intrinsic reaction rate constant and the order of the reaction with respect to $SO_2$. Details on parameter estimation are given in Krishnan and Sotirchos (1992a). 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 following values were estimated for the reaction rate constant (in $\mathrm{mol}^{0.6}/\mathrm{cm}^{0.8}\cdot\mathrm{s}$): $9.06\times10^{-6}$ (750 °C) and $3.83\times10^{-5}$ (850 °C) for Greer limestone; $3.04\times10^{-6}$ (750 °C) and $9.53\times10^{-6}$ (850 °C) for Georgia marble; $2.28\times10^{-6}$ (750 °C) and $7.77\times10^{-6}$ (850 °C) for Iceland spar.

Assuming Arrhenius-type dependence of the rate constants on temperature, the above values of rate constant 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 this reaction with respect to the reaction temperature than that observed for the reaction of CaO with $SO_2$.

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. A variable diffusivity shrinking-core model was thus developed and used to analyze the experimental data. 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.

Figure 8 shows the variation of effective diffusivity ($D_e(l)$) 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 mL/m$^3$ of $SO_2$. The variation of the diffusivity 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 $\mu$m, and thus, $D_e(l)$ values are shown only within this window of product layer thickness. On the other hand, Greer limestone particles reacted at 850 °C developed a product layer thickness of approximately 6 $\mu$m during 150 min sulfation.

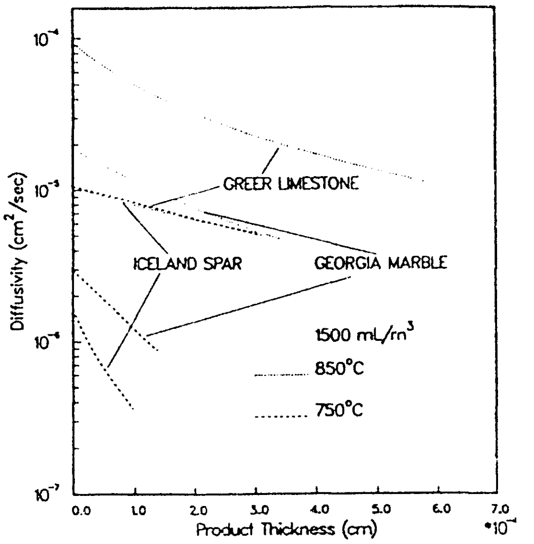


**Figure 8. Effective diffusivity vs. depth in the product layer for reaction under 1500 mL/m$^3$ of $SO_2$**

The results of Figure 8 and those obtained for the variation of the effective diffusivity for a bulk concentration of 6,000 mL/m$^3$ of $SO_2$ (Krishnan and Sotirchos, 1992b) showed that the value of effective diffusivity in the product layer for the limestone-$SO_2$ reaction falls 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 effective diffusivity at the maximum depth is at least two to three orders of magnitude higher than the product layer diffusivity for the $CaO$-$SO_2$ reaction, which has a value of $10^{-12}$ m$^2$/s on the average (Sotirchos and Zarkanitis, 1992). The higher diffusivity of $SO_2$ 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 $SO_2$ even though it involves essentially nonporous solids. The effective diffusivity at a certain depth was always the highest for Greer limestone, with Iceland spar displaying the lowest value. The same order of variation was followed by the rates of the indirect and direct sulfation reactions (see Figures 5 and 6) and 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).

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 (see Figure 8). 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.

## FUTURE PLANS

In the coming year, we will concentrate on the completion of the study of the direct reaction of limestones with $SO_2$ and $H_2S$ under simulated high pressure conditions. We will also complete the investigation of the changes that the mass transport resistance in the pore space of calcined limestones undergoes during sulfidation and carbonation. Finally, we intend to carry out some experiments on the reactions of supported $CuO$ sorbents with $H_2S$ and $SO_2$.

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