

**Removal of H<sub>2</sub>S and SO<sub>2</sub> by CaCO<sub>3</sub>-Based  
Sorbents at High Pressures**

Semiannual Report

February 1999–July 1999

Prepared by:

Prof. Stratis V. Sotirchos

August 1999

Work Performed under Grant No.: DE-FG22-95PC95217

Performed for:

U.S. Dept. of Energy  
University Coal Research Program  
Pittsburgh Energy Technology Center  
Pittsburgh, Pennsylvania

Performed at:

University of Rochester  
Dept. of Chemical Engineering  
Rochester, NY 14627

## EXECUTIVE SUMMARY

The theoretical and experimental investigation of the mechanism of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  removal by  $\text{CaCO}_3$ -based sorbents (limestones and dolomites) in pressurized fluidized-bed coal combustors (PFBC) and high pressure gasifiers, respectively, is the main objective of this study. It is planned to carry out reactivity evolution experiments under simulated high pressure conditions or in high pressure thermogravimetric and, if needed, fluidized-bed reactor (high pressure) arrangements. The pore structure of fresh, heat-treated, and half-calcined solids (dolomites) will be analyzed using a variety of methods. Our work will focus on limestones and dolomites whose reaction with  $\text{SO}_2$  or  $\text{H}_2\text{S}$  under atmospheric conditions has been studied by us or other research groups in past studies. Several theoretical tools will be employed to analyze the obtained experimental data including a variable diffusivity shrinking-core model and models for diffusion, reaction, and structure evolution in chemically reacting porous solids.

During this reporting period, work was primarily done on the investigation of the effects of various operating and process parameters on the direct sulfidation of limestones, that is, their reaction with  $\text{H}_2\text{S}$  in the presence of  $\text{CO}_2$  at concentrations large enough to prevent the decomposition of  $\text{CaCO}_3$  to  $\text{CaO}$ . The two calcitic solids of high calcium carbonate content (over 97%) that were employed in the experiments that we described in past reports were also employed in these studies: a fine-grained limestone (Greer Limestone) and a solid supplied in the form of large single crystals (Iceland Spar). Experiments were carried out in a high pressure, thermogravimetric analysis system that we developed under this study. Results were obtained on the effects of the concentration of  $\text{H}_2\text{S}$ , particle size, temperature, and pressure. The results showed that the pressure influenced the behavior of the process mainly through its effects on the concentration of  $\text{H}_2\text{S}$ , and the rate of the reaction was found to be of first order with respect to this variable. The behavior of the process could be described satisfactorily by a shrinking core model with a product layer diffusivity that depended only on the temperature and did not vary with the distance from the external surface of the particles. The results on the effects of particle size, temperature, limestone sample, and concentration of  $\text{H}_2\text{S}$  were in agreement with those in a

past investigation of the direct sulfidation reaction of limestones in our laboratory at atmospheric pressure.

Some of the conclusions of our study on the direct sulfidation reaction of limestones were at variance with those reached from the study of the direct reaction of limestones with SO<sub>2</sub> in the previous reporting period, where the reaction rate was found to exhibit order equal to 0.4, a variable diffusivity (decreasing away from the external surface of the particles) had to be employed in the shrinking core model to describe the experimental data, and the product layer diffusivity was a strong function of the concentration of SO<sub>2</sub> in the gas phase. However, even in that case, the pressure appeared to affect the behavior of the process mainly through its effects on the concentration of the sulfur-containing gas (i.e., SO<sub>2</sub>).

**TABLE OF CONTENTS**

EXECUTIVE SUMMARY	ii
TABLE OF CONTENTS	iv
LIST OF FIGURES	v
1. BACKGROUND INFORMATION	1
2. WORK DONE AND DISCUSSION	7
3. SUMMARY	9
BIBLIOGRAPHY	10

**LIST OF FIGURES**

Figure 1. Dependence on the variation of the conversion with time for the Greer Limestone sample during direct sulfidation at 750 °C on the pressure, the H<sub>2</sub>S concentration, and the particle size.

Figure 2. Dependence on the variation of the conversion with time for the Iceland Spar sample during direct sulfidation at 750 °C on the pressure, the H<sub>2</sub>S concentration, and the particle size.

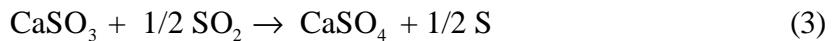
## 1. BACKGROUND INFORMATION

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  $\text{CO}_2$  pressure for decomposition of limestone ( $\text{CaCO}_3$ ) or dolomite ( $\text{CaCO}_3\text{MgCO}_3$ ) 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  $\text{CaCO}_3$  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. 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  $\text{SO}_2$  has been the subject of extensive investigation. In accordance with the above remarks, the experimental evidence in most of the studies of the literature 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; Vogel et al., 1977; Hasler et al., 1984; Simons and Garman, 1986; Yu, 1987; Gullett and Bruce, 1987; Zarkanitis and

Sotirchos, 1989; Zarkanitis, 1991). Unfortunately, the immense volume of information that has been accumulated over the years on the reaction of calcined limestones and dolomites with  $\text{SO}_2$  is not applicable to  $\text{SO}_2$  emissions control by limestones and dolomites under PFBC conditions. PFBC units normally operate under a pressure of 16 atmospheres, and for an average  $\text{CO}_2$  content of 15%, this implies that the partial pressure of  $\text{CO}_2$  in the reactor is 2.4 atm. Thermodynamic calculations show that the temperature for  $\text{CaCO}_3$  calcination in the presence of 2.4 atm of  $\text{CO}_2$  must be larger than 980 °C, that is, well above the temperature range (750-950 °C) encountered in a PFBC unit. Nevertheless, even though 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 and Kandefer, 1986; Murthy et al., 1979). For dolomites, the situation is somewhat different since half-calcination (formation of an  $\text{MgO}-\text{CaCO}_3$  product) is possible under 2.4 atm of  $\text{CO}_2$ . Even in this case, however, if the absorption of  $\text{SO}_2$  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  $\text{CaCO}_3$  with  $\text{SO}_2$  may involve various reaction steps (Van Houte et al., 1981):

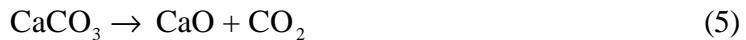


$\text{CaSO}_3$  decomposes at temperatures higher than 650 °C, and therefore, under typical operating conditions in a PFBC unit, the overall reaction may be written as:



For dolomites, one should also address the question of the reaction of MgO with SO<sub>2</sub>.

If the partial pressure of CO<sub>2</sub> within the bed varies, calcination of CaCO<sub>3</sub> may take place in regions where CO<sub>2</sub> pressures lower than the equilibrium pressure are prevailing. The calcination of CaCO<sub>3</sub> will yield a partially calcined product, the extent of calcination depending on the residence time of the solid in the low CO<sub>2</sub> concentration region. CaO formed in the solid will react with the SO<sub>2</sub> present in the bed in the same fashion as in the case of AFBC units:

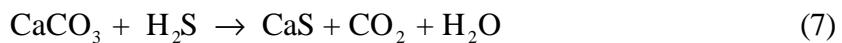


If the partially calcined solid moves into regions rich in CO<sub>2</sub>, where reaction (5) is favored to proceed from right to left, carbonation, i.e., recovery of CaCO<sub>3</sub>, will take place, with reaction (4) competing with reaction (5) for CaO. Decomposition of CaCO<sub>3</sub> may also take place even if there is no variation of the CO<sub>2</sub> 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<sub>3</sub> is stable, at the average partial pressure of CO<sub>2</sub> in the reactor, decomposition of CaCO<sub>3</sub> will occur. However, only small amounts of CaO have been found in the reactor by Ljungstrom and Lindqvist (1982), suggesting that direct sulfation of limestones (eq. (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<sub>2</sub> partial pressures above the equilibrium value existed in the form of CaCO<sub>3</sub>.

Studies of SO<sub>2</sub> removal at high pressures have been carried out both with carbonates and precalcined solids (Newby et al., 1980; Ulerich et al., 1982; Dennis and Hayhurst, 1984, 1987; Bulewicz et al., 1986). 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), for example, 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<sub>2</sub>. Working with a laboratory-size PFBC, Bulewicz et al. (1986) observed an increase in the sorption capacity of Ca-based sorbents (chalk, limestone, and dolomite) with an increase in pressure up to 2 atm, but further increase in pressure caused a reduction in the sorption capacity of all samples. Similar observations were made by Jansson et al. (1982). PFBC studies at Exxon (Hoke et al., 1977) showed better sulfur retention for precalcined limestones, but Stanton et al. (1982) observed no improvement in sorbent utilization by precalcination. Stanton et al. also reported that under weakly noncalcining conditions, a feed of uncalcined limestone gave better sulfur retention than what kinetic studies performed in a thermogravimetric apparatus predicted.

A situation similar to that prevailing in PFBC units is encountered in desulfurization in gasifier at high pressures. Fixed-bed and fluidized-bed gasifiers typically operate around 850 °C with a temperature at the exit of around 500-800 °C. The pressure of operation is in most cases in the 200-300 psi range, and at an average pressure of 250 psi, it turns out that the CO<sub>2</sub> partial pressure in the reactor is about 1.8 and 4.3 atm for air blown and oxygen blown gasifiers, respectively (based on a typical CO<sub>2</sub> content (mole/mole) of 11% and 26%, respectively (Grindley et al., 1985). Almost all observations made for SO<sub>2</sub> removal in PFBC reactors apply to H<sub>2</sub>S removal in high pressure gasifiers but with reactions (7) and (8) taking place (primarily) in a gasifier instead of (4) and (6):



Like in the case of sulfation, the main difference between the direct and indirect reactions is that a highly porous solid is involved in the indirect process while that participating in the direct reaction is essentially nonporous. In view of this difference, the information that is presently available on the sulfidation of limestone-derived calcines (e.g., see 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 limestones with  $\text{H}_2\text{S}$ . Few fundamental studies have been presented in the literature on the direct reaction of limestones with  $\text{H}_2\text{S}$ , and most of those have been carried out under low pressures (Borgwardt and Roache, 1984) or under conditions where both sulfidation reactions ((7) and (8)) could take place (Attar and Dupuis, 1979).

The direct sulfation or sulfidation of calcium carbonate-containing sorbents can be studied under atmospheric pressure provided that there is enough  $\text{CO}_2$  in the reactor to prevent decomposition of the carbonate (simulated PFBC or high pressure gasification conditions). Tullin and Ljungstrom (1989) performed sulfation experiments in a thermogravimetric analyzer (TGA) under conditions inhibiting calcination of  $\text{CaCO}_3$  and found that the sulfation rate of uncalcined  $\text{CaCO}_3$  was comparable with the sulfation rate of calcined material; they thus concluded that desulfurization in PFBC's is achieved by direct sulfation of limestones. Large amounts of sample and small particles (around 150 mg and 10-90  $\mu\text{m}$ ) were used by those authors in their experiments, and thus extracting any quantitative information is practically impossible (because of strong interparticle diffusional limitations). A similar procedure was employed by Snow et al. (1988) and Hajaligol et al. (1988), who also observed that the direct sulfation of  $\text{CaCO}_3$  can reach for some precursors higher conversions than the sulfation of the calcines ( $\text{CaO}$ ). High concentrations of  $\text{CO}_2$  (70%  $\text{CO}_2$  by volume) were also used by Borgwardt and Roache (1984) to study the direct reaction of limestone particles with  $\text{H}_2\text{S}$  at atmospheric pressure in a differential reactor. They employed a limestone precursor (Fredonia limestone) of relatively high porosity (about 8%), and thus, 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 (8)).

A detailed investigation of the direct sulfation of limestones with  $\text{SO}_2$  and  $\text{H}_2\text{S}$  under simulated high pressure conditions was carried out by our research group (Krishnan and Sotirchos, 1993a,b,1994) using three limestone specimens of high  $\text{CaCO}_3$  content. In accordance with the observations of Tullin and Ljungstrom (1989), Snow et al. (1988), and Hajaligol et al. (1988), our sulfation results (Krishnan and Sotirchos, 1993a,1994) showed that the direct reaction of calcium carbonate with  $\text{SO}_2$ , believed to be the dominant reaction in a PFBC, is qualitatively different from the reaction of limestone calcines. A similar conclusion was reached for the limestone- $\text{H}_2\text{S}$  reaction (Krishnan and Sotirchos, 1994). These results reinforced our early conclusion that the accumulated knowledge in the literature from the extensive study of the reaction of calcined limestones and dolomites with  $\text{SO}_2$  or  $\text{H}_2\text{S}$  cannot be used to derive any reliable conclusions for flue or coal gas desulfurization under high pressure conditions. Nevertheless, with the exception of the studies conducted under simulated high pressure conditions on a few limestones, no fundamental studies have been carried out in the literature on the reaction of limestones and dolomites with  $\text{SO}_2$  or  $\text{H}_2\text{S}$  under true high pressure conditions (i.e., at high pressures and in the presence of  $\text{CO}_2$ ). Moreover, even though the experimental data under simulated high pressure conditions have been extremely helpful in elucidating some of the phenomena encountered in the direct sulfation or sulfidation of limestones, it is questionable whether these results are directly applicable to reaction under true PFBC or high pressure gasification conditions, especially for solids with significant dolomitic content.

Based on the above observations, a research program has been proposed for the investigation of the mechanism of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  removal by limestones and dolomites at high pressures. Reactivity evolution experiments will be carried out using thermogravimetric and, if needed, fixed-bed and fluidized-bed reactor (high pressure) arrangements. Thermogravimetric experiments will be carried out under simulated high pressure conditions at atmospheric pressure using a unit currently available in our lab and at high pressures using a high pressure TGA proposed to be set up under this project. The pore structure of fresh, heat-treated, and half-calcined solids (dolomites) will be analyzed using a variety of methods. Our work will focus on limestones and dolomites whose reaction with  $\text{SO}_2$  or  $\text{H}_2\text{S}$  under atmospheric conditions has

been in detail investigated by either us or other research groups. The obtained experimental data will be analyzed using various theoretical tools developed by my research group for studying gas-solid reactions, and will be used as basis for the development of predictive single particle models for use in design models of combustors or gasifiers.

## 2. WORK DONE AND DISCUSSION

During this reporting period, work was primarily done on the investigation of the effects of various operating and process parameters on the direct sulfidation of limestones, that is, their reaction with  $H_2S$  in the presence of  $CO_2$  at concentrations large enough to prevent the decomposition of  $CaCO_3$  to  $CaO$ . The two calcitic solids of high calcium carbonate content (over 97%) that were employed in the experiments that we described in past reports were also employed in these studies: a fine-grained limestone (Greer Limestone) and a solid supplied in the form of large single crystals (Iceland Spar).

Experiments were carried out in a high pressure, thermogravimetric analysis system that we developed under this study. Results were obtained on the effects of the concentration of  $H_2S$ , particle size, temperature, and pressure. The results showed that all these operating conditions and parameters had very strong effects on the behavior of the process. The type of limestone also had a very strong influence on the reaction rate; specifically, the Iceland Spar sample presented much lower reactivity than the Greer Limestone material at the same conditions.

Figure 1 presents experimental results on the effects of particle size, pressure, and concentration at 750 °C on the conversion vs. time behavior of Greer Limestone, and Figure 2 presents the corresponding results for Iceland Spar. Qualitatively similar results were obtained at other temperatures. In all cases shown in these two figures, the solid samples were exposed during reaction to a mixtures consisting of 70%  $CO_2$  and 30%  $N_2$  containing 0.5% or 1%  $H_2S$ .

The concentrations of  $H_2S$  in the two pairs of  $H_2S$  mole fraction and pressure that are used in Figures 1 and 2 ({3,000 ppm  $H_2S$ , 1 atm} and {1,500 ppm  $H_2S$ , 4 atm}) differ by a factor of

2, and for this reason, the reaction time shown in the figures for the case with the larger concentration corresponds to the real time multiplied by a factor of 2. It is seen in both figures that the conversion vs. time curves of the two curves are very close to each other, and this indicates that the rates of the various subprocesses that are encountered in the overall direct sulfidation process of the particles depend linearly on the concentration of  $\text{H}_2\text{S}$ .

The following subprocesses are involved in the sulfidation process: the sulfidation reaction at the unreacted solid-reacted solid interface, the transport of the reactant ( $\text{H}_2\text{S}$ ) from the gas phase to the external surface of the particles, and the transport of the sulfiding species ( $\text{H}_2\text{S}$  or some other ionic species) from the external surface to the reaction interface. The rate of mass transport from the gas phase to the external surface of the particles depends linearly on the concentration of  $\text{H}_2\text{S}$ , but even if that were not the case, it would not have any effect on the behavior of the overall process since – as it can be easily verified using correlations of the literature for the Sherwood number of spherical particles – the corresponding resistance for mass transport is negligible. The initial overall reaction rates are only influenced by the intrinsic rate of the chemical reaction, and the analysis of the acquired data led to the result that the rate of the reaction is of first order with respect to the concentration of  $\text{H}_2\text{S}$ . Since the rate of the overall process was found to change linearly with the concentration of  $\text{H}_2\text{S}$ , one concludes in view of the above results, that the rate of mass transport through the solid product layer depends linearly on the concentration of  $\text{H}_2\text{S}$ . This in turn implies that if this rate is expressed in terms of the concentration of  $\text{H}_2\text{S}$ , the diffusion coefficient in the solid product layer should be independent of that variable.

A shrinking core model with diffusion coefficient depending only on the temperature of operation and having the same value at all positions within the solid product shell was used to model the sulfidation process. The predictions of the mathematical model are shown in Figures 1 and 2, and they hold for both cases considered in the figures ( $\{3,000 \text{ ppm H}_2\text{S}, 1 \text{ atm}\}$  and  $\{1,500 \text{ ppm H}_2\text{S}, 4 \text{ atm}\}$ ). (In accordance with the remarks made above, the time for the second case was multiplied by a factor of 2.) Very good agreement is seen to exist between the model results

and the experimental data. The reaction rate constant of the Greer Limestone sample was found to be by about a factor of 2 greater than that of Iceland spar, and both samples exhibited rather low activation energy of similar value, much lower than that of the direct sulfation reaction (about 16 vs. 120 kJ/mol). The product layer diffusivity for Greer Limestone was by a factor of 6-8 larger than that for Iceland Spar, and this was the main reason for the large differences in the sulfidation rates of same size particles of the two solids at the same conditions. The activation energy for the product layer diffusivity varied from about 100 kJ/mol for Iceland Spar to about 150 kJ/mol for Greer Limestone.

The results on the effects of particle size, temperature, and concentration of H<sub>2</sub>S on the direct sulfidation of limestones were in agreement with those obtained in a past investigation of the process at atmospheric pressure (Krishnan and Sotirchos, 1994). Considering that the effects of pressure on the process were found to be manifested only through its effects on the concentration of H<sub>2</sub>S, this is a very interesting finding because it suggests that the information of the literature on the direct-limestone reaction at atmospheric pressure can be used to derive conclusions on their performance at high pressures.

### 3. SUMMARY

The effects of various operating and process parameters on the direct sulfidation of limestones, that is, their reaction with H<sub>2</sub>S in the presence of CO<sub>2</sub> at concentrations large enough to prevent the decomposition of CaCO<sub>3</sub> to CaO. Two calcitic solids of high calcium carbonate content (over 97%) were employed in the experiments, and the reaction was studied in a thermogravimetric analysis system that can operate at pressures above atmospheric. Pressures in the 1-4 atm range were employed. The results showed that the pressure influenced the behavior of the process mainly through its effects on the concentration of H<sub>2</sub>S, and the rate of the reaction was found to be of first order with respect to this variable. The behavior of the process could be described satisfactorily by a shrinking core model with a product layer diffusivity that depended only on the temperature and did not vary with the distance from the external surface of the particles. The results on the effects of particle size, temperature, limestone

sample, and concentration of H<sub>2</sub>S were in agreement with those in a past investigation of the direct sulfidation reaction of limestones in our laboratory at atmospheric pressure.

For the next six-month period, we plan to conduct experiments on the effects of the effects of carbonation reaction on the sulfation of calcined limestones. As explained in the introductory section of this report, this situation may occur as calcined particles move into areas of the combustor where the concentration of CO<sub>2</sub> is above the equilibrium value for the calcination reaction at the prevailing temperature.

## **BIBLIOGRAPHY**

Attar, A., and F. Dupuis, Ind. Eng. Chem. Process Des. Dev., 18, 607 (1979).

Borgwardt, R.H. and R.D. Harvey, Environ. Sci. Technol., 6, 350 (1972).

Borgwardt, R.H. and N.F. Roache, Ind. Eng. Chem. Process Des. Dev., 23, 742-748 (1984).

Borgwardt, R.H., N.F. Roache, and K.R. Bruce, Environ. Progress, 3, 129-135 (1984).

Bulewicz, E.M., S. Kandefer, and C. Jurys, J. Inst. Energy, 188 (1986).

Dennis, J.S. and A.N. Hayhurst, Inst. Chem. Eng. Symp. Ser., 87, 61 (1984).

Dennis, J.S. and A.N. Hayhurst, Chem. Eng. Sci., 42, 2361 (1987).

Efthimiadis, E.A., and S.V. Sotirchos, Ind. Eng. Chem. Res., 31, 2311 (1992).

Grindley, T., S.S. Kim, E.E. Gorski, and G. Steinfeld, "Aspects of the Design of a Process Development Unit for High-Temperature Coal Gas Desulfurization," Technical Report, DOE/METC-85/6025, 1985.

Gullett, B.K. and K.R. Bruce, AIChE J., 33, 1719 (1987).

Hajaligol, M.R., J.P. Longwell, and A.F. Sarofim, Ind. Eng. Chem. Res., 27, 2203 (1988).

Hartman, M. and R.W. Coughlin, Ind. Eng. Chem., Process Dev., 13, 248 (1974).

Hartman, M. and R.W. Coughlin, AIChE J., 22, 490 (1976).

Hasler J.R. et al., "Testing of Limestone Samples from the TVA region as Sulfur Dioxide Sorbents in Atmospheric Fluidized Bed Combustors," Technical Report, Institute for Mining and Mineral Research, Univ. of Kentucky, 1984.

Hoke, R.C. et al., "Studies of the Pressurized Fluidized-Bed coal Combustion Process," Technical Report, EPA-600/7-77-107, September 1977.

Jansson, S.A., L.P. O'Connell, and J.E. Stantan, Proc. Int. Conf. Fluid. Bed Combust., 7, 1095 (1982).

Krishnan, S.V., Ph.D. Thesis, University of Rochester, 1993.

Krishnan, S.V. and S.V. Sotirchos, Can. J. Chem. Eng., 71, 244 (1993a).

Krishnan, S.V. and S.V. Sotirchos, Can. J. Chem. Eng., 71, 724 (1993b).

Krishnan, S.V. and S.V. Sotirchos, Ind. Eng. Chem. Res., 33, 1444 (1994).

Ljungstrom, E., and O. Lindqvist, Proc. Int. Conf. Fluid. Bed. Combust., 7, 465 (1982).

Murthy, K. S., J. E. Howes, and H. Nack, Environ. Sci. Technol., 13, 197 (1979).

Newby, R.A., N.H. Ulerich, and D.L. Keairns, Proc. Int. Conf. Fluid. Bed Combust., 6, 803 (1980).

Ruth, L.A., A.M. Squires, and R.A. Graff, Environ. Sci. Technol. 6, 1009-1014 (1972).

Simons, G.A. and A.R. Garman, AIChE J., 32, 1491 (1986).

Smith, D. et al., Proc. Int. Conf. Fluid. Bed Combust., 7, 439 (1982).

Snow, M. J. H., J. P. Longwell, and A. F. Sarofim, Ind. Eng. Chem. Res. 27, 268 (1988).

Sotirchos, S.V., and S. Zarkanitis, AIChE J., 38, 1536 (1992).

Stantan, J.E., S.N. Barker, R.V. Wardell, N.H. Ulerich, and D.L. Keairns, Proc. Int. Conf. Fluid. Bed Combust., 7, 1064 (1982).

Tullin, C., and E. Ljungstrom, Energy Fuels, 3, 284 (1989).

Ulerich, N.H., R.A. Newby, W.G. Vaux, and D.L. Keairns, Proc. Int. Conf. Fluid. Bed Combust., 7, 121 (1982).

Ulerich, N.H, E.P. O'Neill, and D.L. Keairns, "The Influence of Limestone Calcination on the Utilization of the Sulfur-Sorbent in Atmospheric Pressure Fluid-Bed Combustors," EPRI ER-426, Final Report, 1977.

Van Houte, G., L. Rodrique, M. Genet, and B. Delmon, Environ. Sci. Technol., 15, 327 (1981).

Vogel, G.J. et al., Quarterly Report (January-March 1977), prepared for DOE, Argonne National Laboratory, 1977.

Wen, C.Y., and M. Ishida, Environ. Sci. Technol., 7, 703( 1973).

Yen, J.H., K. Li, and F.H. Rogan, Chem. Eng. Comm., 10, 35-60 (1981).

Yu, H.C., Ph.D. Thesis, University of Rochester, 1987.

Zarkanitis S., Ph.D. Thesis, University of Rochester, 1991.

Zarkanitis, S., and S.V. Sotirchos, AIChE J., 35, 821 (1989).

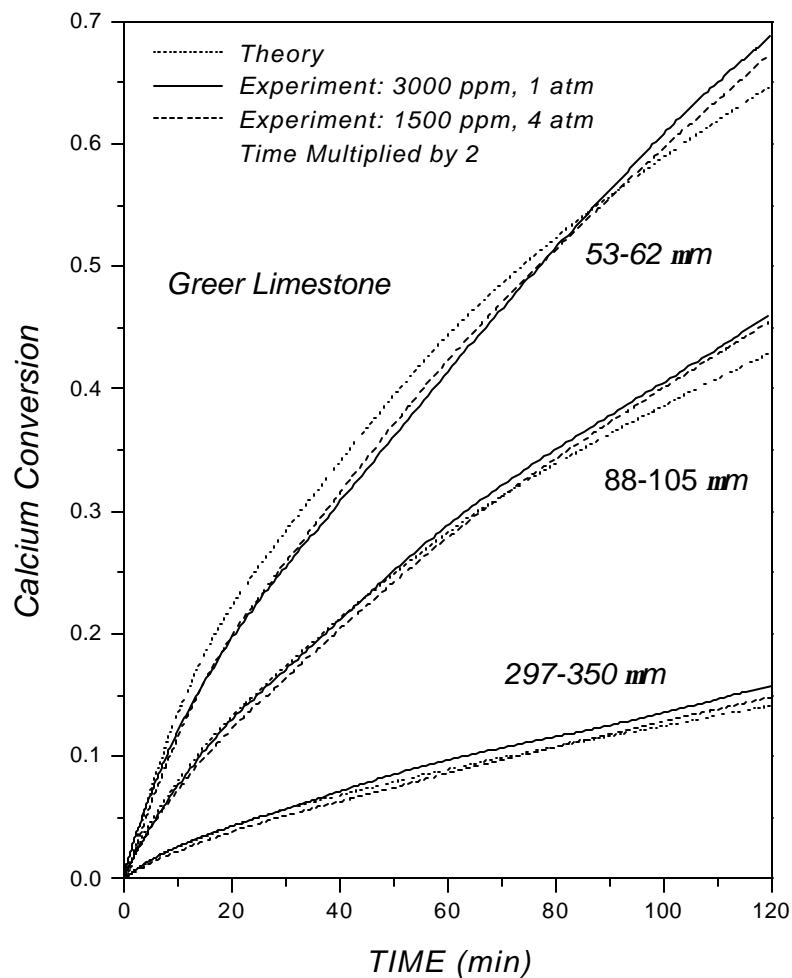


Figure 1. Dependence on the variation of the conversion with time for the Greer Limestone sample during direct sulfidation at 750 °C on the pressure, the  $\text{H}_2\text{S}$  concentration, and the particle size. For 4 atm pressure, the time has been multiplied by 2.

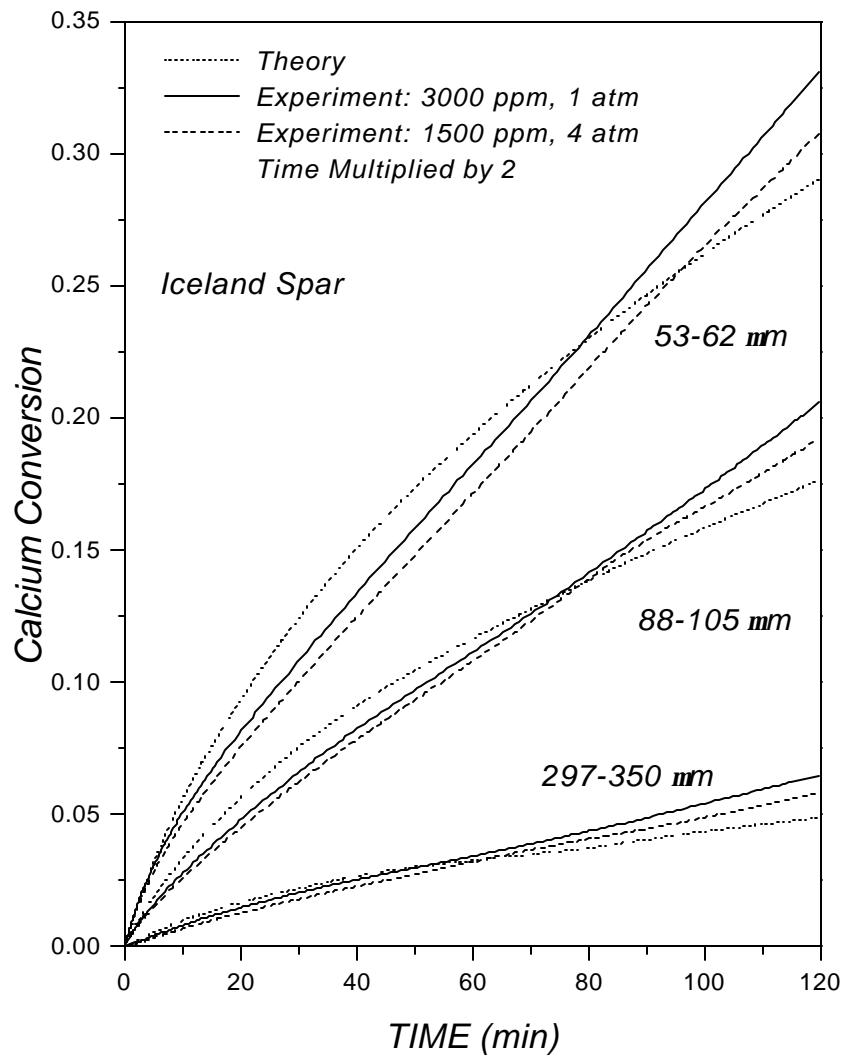


Figure 2. Dependence on the variation of the conversion with time for the Iceland Spar sample during direct sulfidation at 750 °C on the pressure, the H<sub>2</sub>S concentration, and the particle size. For 4 atm pressure, the time has been multiplied by 2.