

## A THERMOGRAVIMETRIC STUDY OF THE EFFECT OF PORE VOLUME-PORE SIZE DISTRIBUTION ON THE SULFATION OF CALCINED LIMESTONE\*

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### ABSTRACT

The sulfation of calcined limestones, whose pore volume-pore size distributions had been adjusted by varying the calcination atmosphere, was studied in a TG apparatus. For all the stones tested, it proved possible to improve the capacity of the calcine for fast reaction with sulfur dioxide. Electron microprobe studies showed that the enhanced sulfation occurred via increased inter- and intragranular diffusion. The results show why pressurized sulfation can lead to greater sorbent utilization, and how the capacity of limestones as SO<sub>2</sub> removal agents in high temperature gas cleaning may be enhanced.

### INTRODUCTION

When limestone is used to remove sulfur dioxide from hot combustion gases, the rate of the reaction and its relation to the capacity or utilization of the limestone is a critical process variable. Despite the enormous number of laboratory studies on the sulfation of calcined lime and bench scale or pilot plant investigations using this reaction, insufficient attention has been paid to the relation between the calcination of the parent limestone and the subsequent reaction of its product lime with sulfur dioxide. In earlier work<sup>1</sup>, it was shown that the rate of the sulfation reaction depended on the partial pressure of carbon dioxide in the original calcination environment. It was postulated that the pore structure of the calcines was modified by the calcination treatment so as to improve the capacity of the sorbent for reaction at a rate fast enough to be used in a technically feasible process.

In this work, the pore volume hypothesis previously advanced was tested by studying the sulfation reaction in a TG apparatus, using a variety of sorbents whose physical characteristics were well-defined. The effect of temperature on the sulfation of limestone calcines was also studied. The object of the study was to understand the mechanism of the sulfation reaction and to relate TG experimental data obtained

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under close stimulation of practical conditions to process performance, specifically in a fluidized bed combustion system.

## EXPERIMENTAL

The apparatus used was a Dupont 951 thermobalance which, when modified as described by Ruth<sup>2</sup>, was capable of operation in flowing sulfur dioxide at elevated temperatures. The balance, controlled by a Dupont 990 console, was attached to a data acquisition system controlled by a Mostek microprocessor (Fig. 1). The microprocessor was programmed by a Wang 2200 calculator to control the flow of weight and temperature data from two analog Dupont recorders (one from a balance contained in a custom built pressure shell capable of operating at 10 atm) to a Fluidyne multichannel interface. Here, the signals were digitized and, then, saved on tape. The microprocessor's control of data acquisition released the Wang calculator for data reduction and plotting, if desired. The Wang was equipped with 16 K memory, cassette tapes, a CRT display and a printer.

Data saved by the microprocessor were reread by the Wang for reduction. Each weight datum was read to  $\pm 5 \mu\text{g}$ . This corresponds to 0.03% sulfation of a typical 10 mg sample of calcium oxide. The temperature was measured by a chromel-alumel thermocouple. During a typical isothermal sulfation experiment, the standard

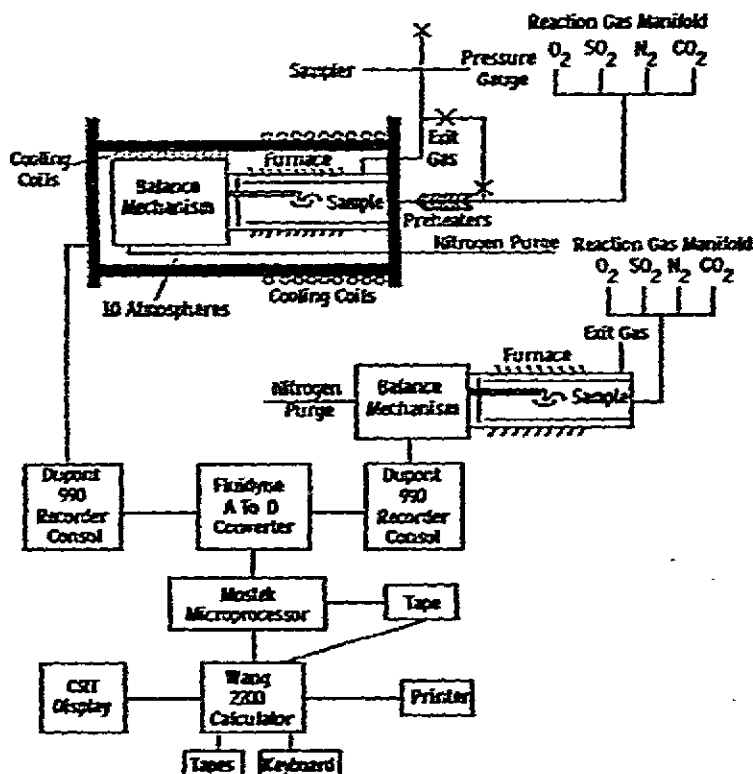


Fig. 1. Schematic of the TGA and data acquisition system.

TABLE 1

## SORBENTS USED IN SULFATION STUDIES

<i>Limestone</i>	<i>Source</i>	<i>Use in pilot plant fluid bed tests</i>	<i>Grain size (<math>\mu\text{m}</math>)</i>
Carbon	The Carbon Limestone Company, Lowellville, Ohio	Babcock and Wilcox	47
Greer	Greer Limestone Company, Morgantown, W. Va.	Pope, Evans and Robbins Argonne National Labs.	11
Grove	M. J. Grove Lime Company, Fredrick, Md. (quarried in Stephens City and Middleton, Va.)	National Coal Board, Argonne National Labs. Pope, Evans and Robbins Exxon	6-24
Canaan Dolomite	Pfizer Minerals, Pigments, and Metals, Gibsonburg, Ohio (quarried in Canaan, Conn.)	Combustion Power Co.	~ 300

TABLE 2

## CHEMICAL ANALYSIS OF SORBENTS

	<i>Sorbent</i>			
	<i>Carbon limestone</i>	<i>Greer limestone</i>	<i>Grove (1359) limestone</i>	<i>Canaan dolomite</i>
CaO (wt. %)	50.46	37.97	53.98	30.67
MgO (wt. %)	0.68	1.1	0.70	20.22
CO <sub>2</sub> (wt. %)	40.95	31.84	43.22	48.53
Al <sub>2</sub> O <sub>3</sub> (wt. %)	2.6	9.8	< 0.4	0.08
Fe <sub>2</sub> O <sub>3</sub> (wt. %)	2.0	3.7	1.0	0.43
SiO <sub>2</sub> (wt. %)	3.4	15.4	< 0.1	0.39
Na <sub>2</sub> O (wt. %)	0.046	0.561	0.0081	0.017
K <sub>2</sub> O (wt. %)	0.422	2.29	0.11	0.048
Cl (wt. %)	0.0034	0.011	0.0017	0.0044
Sum	100.6	102.7	99.52	100.4
Ignition wt. loss (%)	42.70	32.44	42.43	45.76

deviation of the temperature readings was 1.1 °C (0.04 mV). About 100 data points, selected at 1% weight change intervals, were reduced for each run. The fraction of the sorbent sulfated was calculated from the input calcium content of the limestone (as determined from EDTA titration).

Natural limestone samples characterized in Tables 1 and 2 were sized to the desired range, 1000–1190  $\mu\text{m}$ . Samples weighing about 19 mg were placed in a platinum mesh screen, suspended from the balance arm. Reactant gas flow rates were measured with rotometers. Special gas mixtures of CO<sub>2</sub> in N<sub>2</sub> and SO<sub>2</sub> in N<sub>2</sub> were purchased with analyses.

Calcines were prepared in two ways: on the thermobalance and in a batch fluid bed reactor (atmospheric pressure). On the thermobalance, the limestone was heated at a rate of  $10^{\circ}\text{C}/\text{min}$  to the calcination temperature,  $760\text{--}950^{\circ}\text{C}$ . The sulfating gas atmosphere ( $0.5\% \text{SO}_2$ ,  $4\% \text{O}_2$  in  $\text{N}_2$ ) was introduced at a flow rate of  $200 \text{ ml}/\text{min}$  after complete calcination. Calcines were also prepared in  $70 \text{ g}$  batches in the fluid bed unit. Before TG sulfation, these calcines were heated to temperature at a rate of  $10^{\circ}\text{C}/\text{min}$ . The results for three limestones and a dolomite, calcined under a variety of conditions (including 20 calcines prepared in a fluid bed unit) for over 60 TG experiments are detailed in a contract report to EPRI<sup>3</sup>. The calcines prepared in the thermobalance were representative of those from the fluid bed unit.

Sulfations were typically continued until the rate of  $\text{SO}_2$  sorption fell below  $0.1\% \text{ Ca}$  sulfating per minute. The basis for this choice was a first-order model for fluidized bed desulfurization, assuming uniform sulfur generation throughout the bed<sup>4</sup>. With limestone reacting at  $0.1\% \text{ Ca}/\text{min}$ , in  $0.5\% \text{SO}_2$  on the thermobalance,  $80\%$  sulfur removal would be maintained in a  $4 \text{ ft.}$  bed fluidized at  $8 \text{ ft.}/\text{sec}$ . Although this rate criterion was used to evaluate sorbent utilization (Fig. 2), the TG data collected could be utilized for any rate or time criteria.

Mercury penetration porosimetry was used to measure the pore volume-pore size distribution of calcines prepared in the fluid bed unit. The surface area of the calcines was measured by a B.E.T. adsorption isotherm.

Sulfated samples from the TGA were split and mounted under a microscope in an epoxy resin so as to examine a cross-section from the surface to the center of

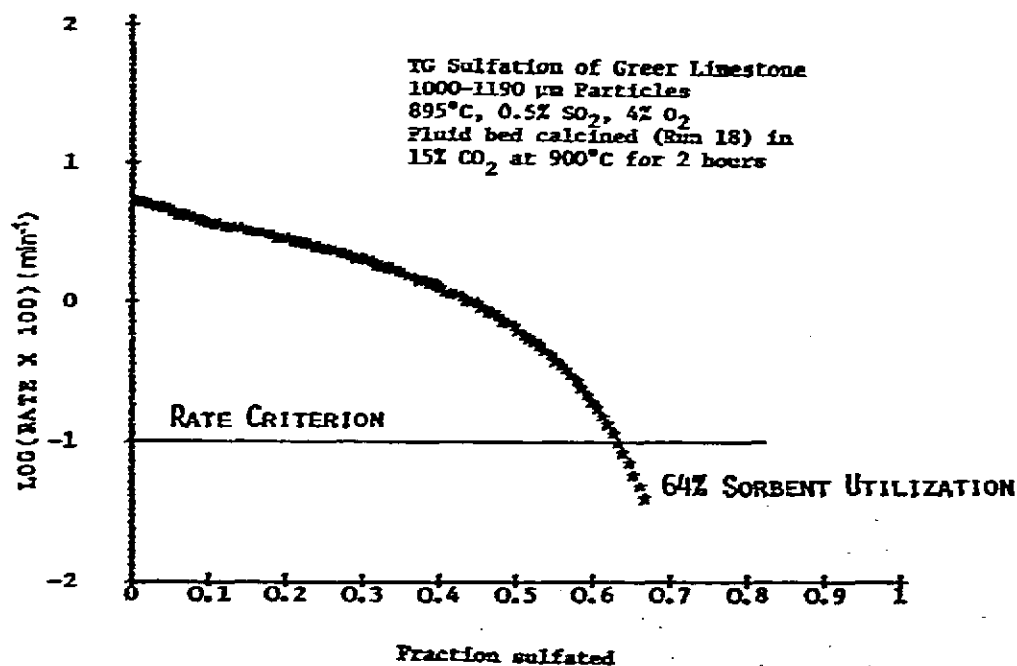


Fig. 2. TG rate criterion for sorbent utilization evaluation.

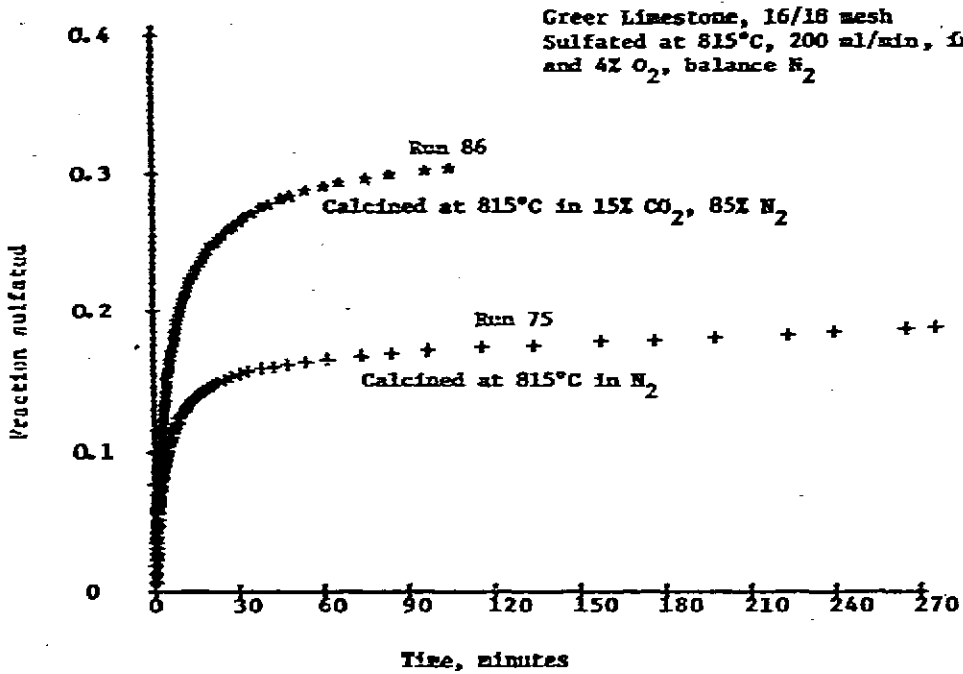


Fig. 3. The effect of calcination atmosphere on the sulfation of Greer limestone.

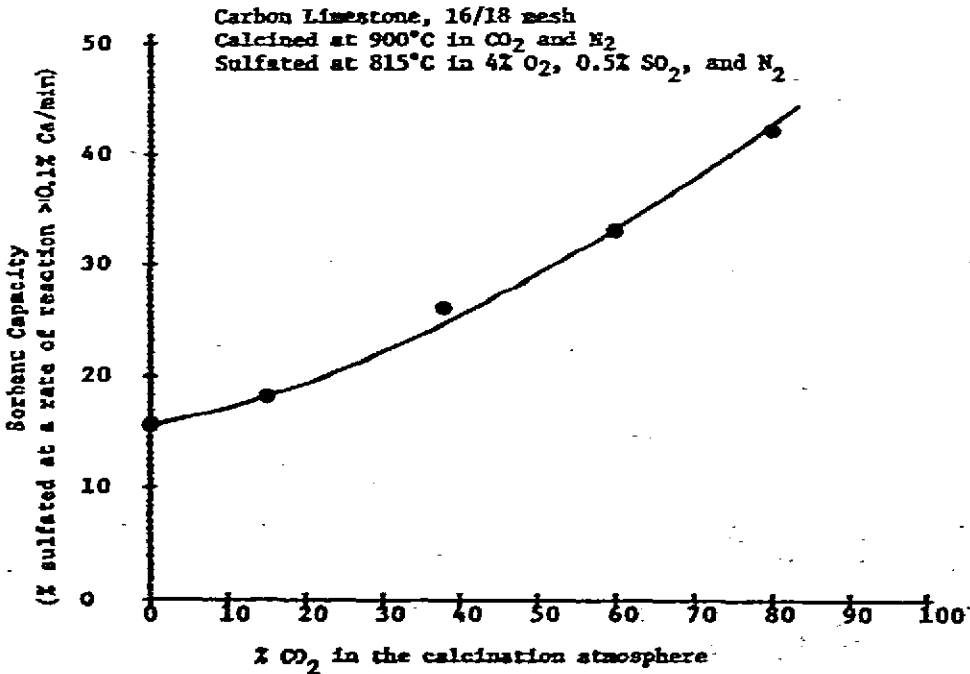


Fig. 4. The effect of calcination atmosphere on the utilization of Carbon limestone.

the particle. Electron microprobe sulfur scans were examined to define sulfur penetration patterns.

RESULTS

Controlled calcination in a CO<sub>2</sub> atmosphere improved the subsequent utilization in the sulfation reaction of all sorbents tested. Limestone capacities could be at least doubled (depending on the sorbent type) by increasing the CO<sub>2</sub> pressure in the calcining atmosphere.

In Fig. 3, the sulfation history of Greer limestone is shown after calcination in two environments. Calcination in 15% CO<sub>2</sub> improved the calcium utilization from 17% (for a calcine prepared in nitrogen) to 30%. The utilization of Carbon limestone as a function of CO<sub>2</sub> in the calcining atmosphere is shown in Fig. 4. The range of sorbent utilization varies from 16% when calcined in a nitrogen atmosphere to 40% when calcined in 0.8 atm of CO<sub>2</sub>. The calcination in 0.8 atm CO<sub>2</sub> required 2.5 h for 90% CO<sub>2</sub> loss, as compared with 25 min in nitrogen.

Calcination in an atmosphere containing CO<sub>2</sub> typically produced calcines with

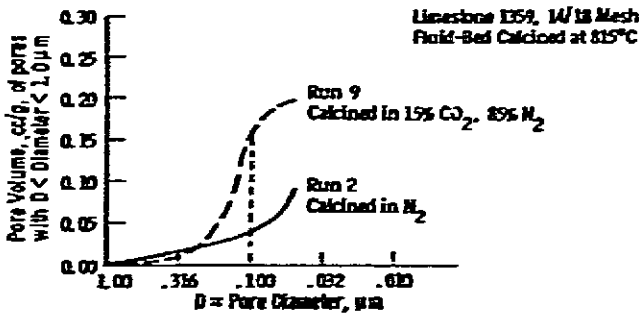


Fig. 5. The effect of calcination atmosphere on the pore volume distribution of limestone 1359 calcines.

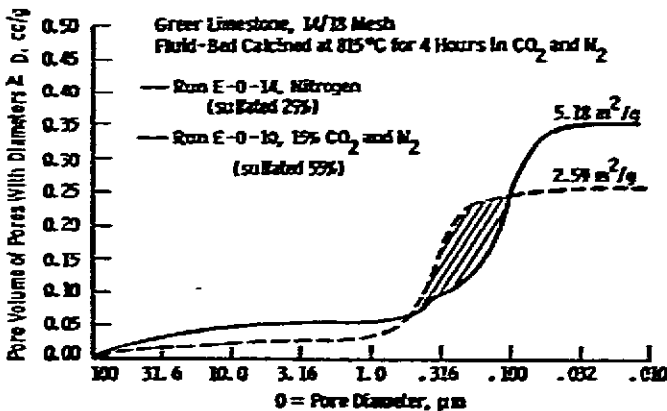


Fig. 6. The effect of calcination atmosphere on the pore volume distribution of Greer limestone calcines.

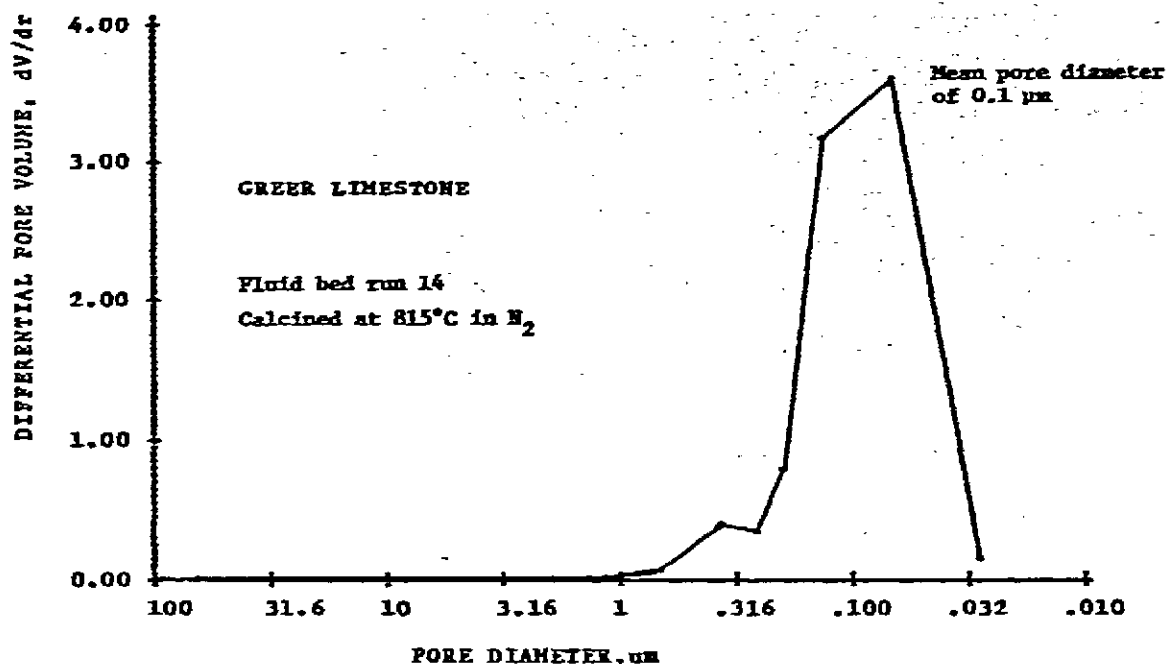


Fig. 7. The mean pore diameter of a calcine as determined from a differential pore volume curve.

pores of larger diameters than those of the calcines prepared in nitrogen. The pore volume-pore size distribution, shown in Fig. 5, for limestone 1359 shows a shift to pores of diameters  $> 0.1 \mu\text{m}$  when the calcine is prepared in  $\text{CO}_2$ .

The improved utilization of Greer limestone with pore structure change upon slow calcination in  $\text{CO}_2$  is illustrated in Fig. 6. When calcined in 15%  $\text{CO}_2$ , the mean pore diameter (as determined by a maximum in the differential pore volume curve, Fig. 7), shifted from  $0.1 \mu\text{m}$  to  $0.5 \mu\text{m}$ , increasing the sorbent's utilization from 29 to 55%. It should be noted that the overall porosity and the surface area of the calcine prepared in nitrogen was greater than those for the  $\text{CO}_2$  calcine. The sulfation capacity was improved when the pore volume and surface area were decreased in concert with a shift from finer to wider-mouthed pores.

High sorbent utilization is dependent on a pore structure which allows sulfur penetration into the sorbent particle and into the individual sorbent grains. For large-grained sorbents, such as Canaan dolomite with  $300 \mu\text{m}$  grains, sulfur diffusion into the individual grains limits conversion. Figure 8 illustrates almost exclusive intergranular sulfation of the stone. Slow calcination in  $\text{CO}_2$  improves the pore structure of sorbents to allow better utilization within the grains. Figure 9 shows how sulfur penetration into  $40 \mu\text{m}$  grains of Carbon limestone was enhanced by precalcination at  $900^\circ\text{C}$  in 60%  $\text{CO}_2$ .

#### Temperature

The influence of temperature on the sulfation of limestone was found to be dependent on the pore structure of the calcine involved. The optimum temperature

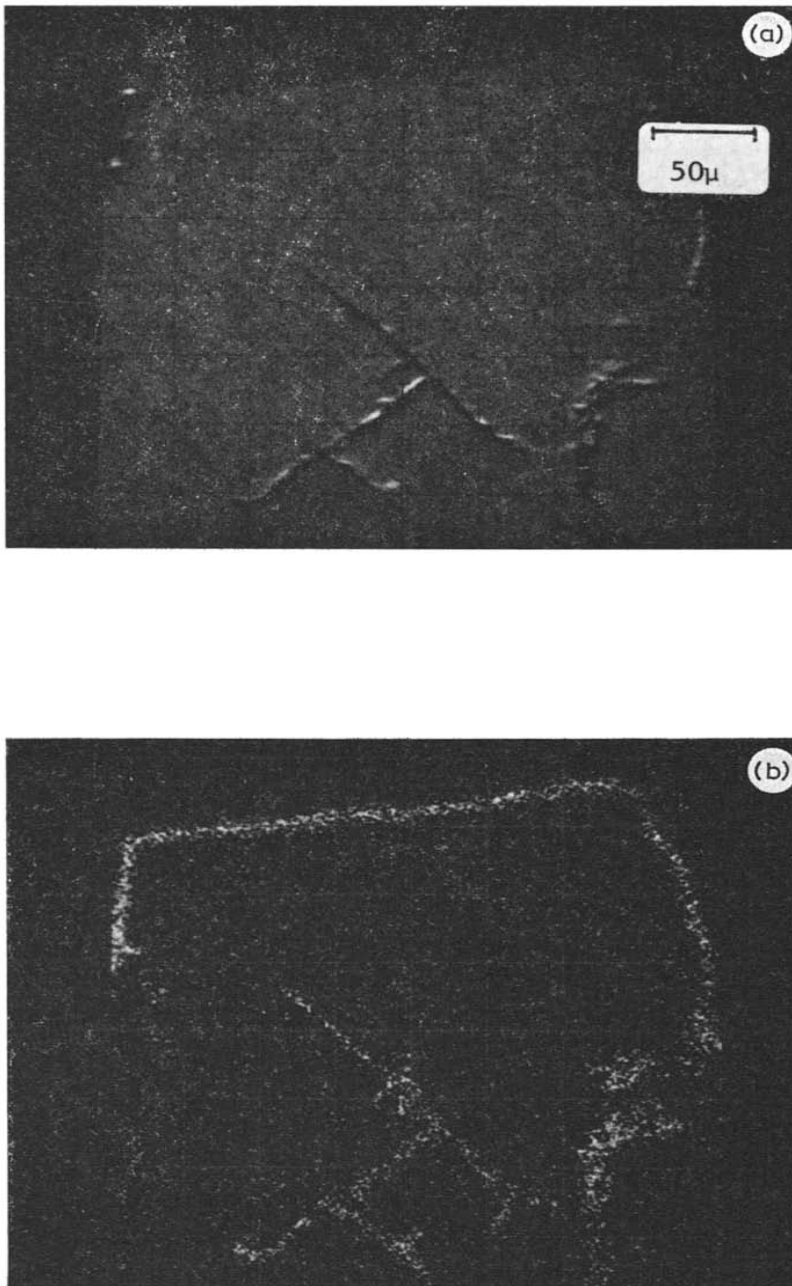
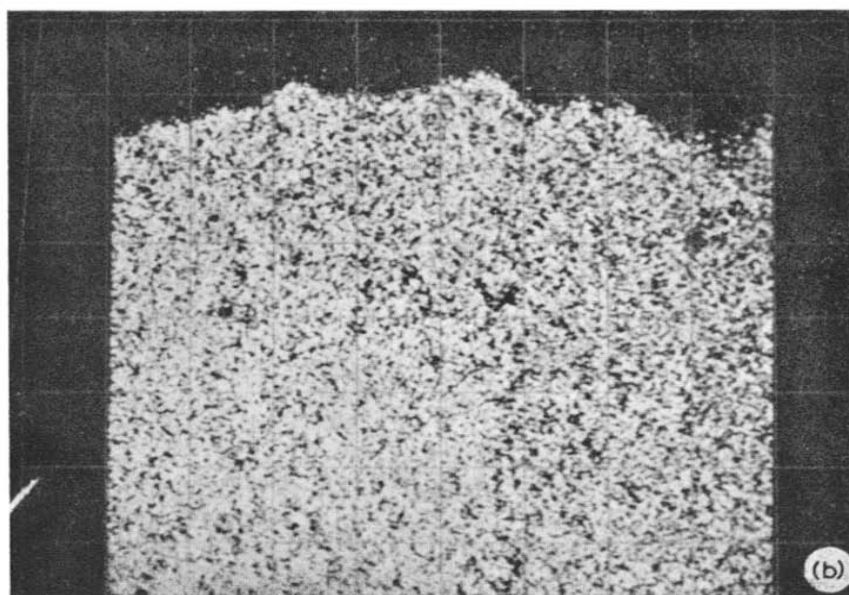
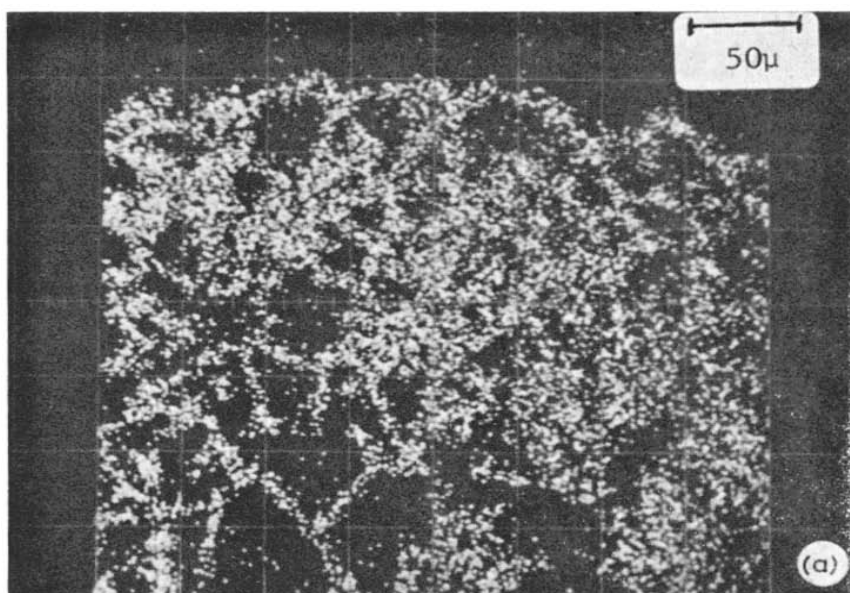


Fig. 8. Sulfur penetration at the periphery and grain boundaries of Canaan dolomite (300  $\mu\text{m}$  grains). (a) Photomicrograph of scanned area. (b) Sulfur scan.

for limestone sulfation shifted to a higher temperature when a calcine with a wider mean pore diameter was used. For Greer limestone, the variation in sorbent utilization with temperature is illustrated for two calcines in Fig. 10. The calcine prepared at 815°C in  $\text{N}_2$  had pores with diameters in the range of 0.05–0.1  $\mu\text{m}$ . The calcine





**Fig. 9.** Improved intragranular sulfur penetration in Carbon limestone resulting from precalcination in  $\text{CO}_2$  (1000  $\mu\text{m}$  particles). (a) Sulfated 23% in 200 min at 815°C in 4%  $\text{O}_2$  and 0.5%  $\text{SO}_2$  after calcination at 815°C in  $\text{N}_2$ . (b) Sulfated 40% in 100 min at 815°C in 4%  $\text{O}_2$  and 0.5%  $\text{SO}_2$  after controlled calcination at 900°C in 60%  $\text{CO}_2$  and  $\text{N}_2$ .

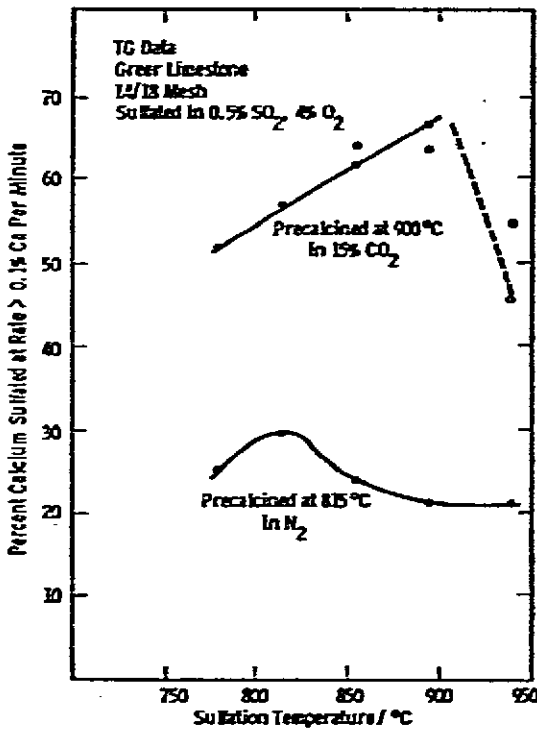


Fig. 10. The effect of temperature on the utilization of two calcines of Greer limestone.

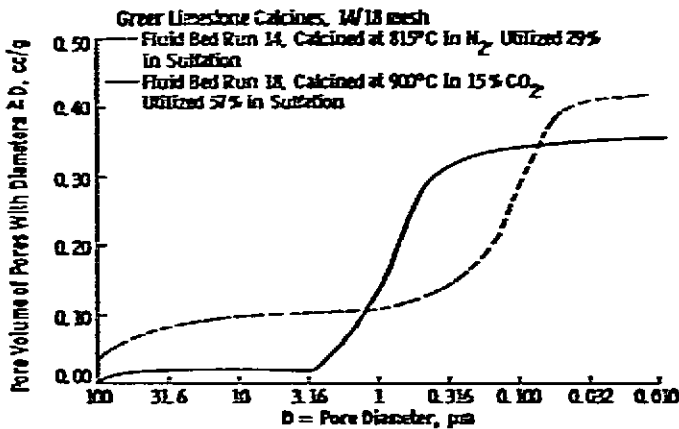


Fig. 11. The pore volume distribution of two Greer limestone calcines.

prepared at 900°C in an atmosphere containing 15% CO<sub>2</sub> had wider-mouthed pores, in the range 0.5–2 μm diameter (Fig. 11).

The fine-pore calcine was 20–30% utilized in sulfation. Electron microprobe sulfur scans show uniform sulfur distribution to 300 μm penetration in the 500 μm radius particle when sulfated at 815°C (Fig. 12). However, when the small-pore calcine was sulfated at 895°C, the sulfation occurred solely at the sorbents periphery, forming a 50 μm shell of sulfate. With increasing temperature, sulfur penetration into the solid decreased.

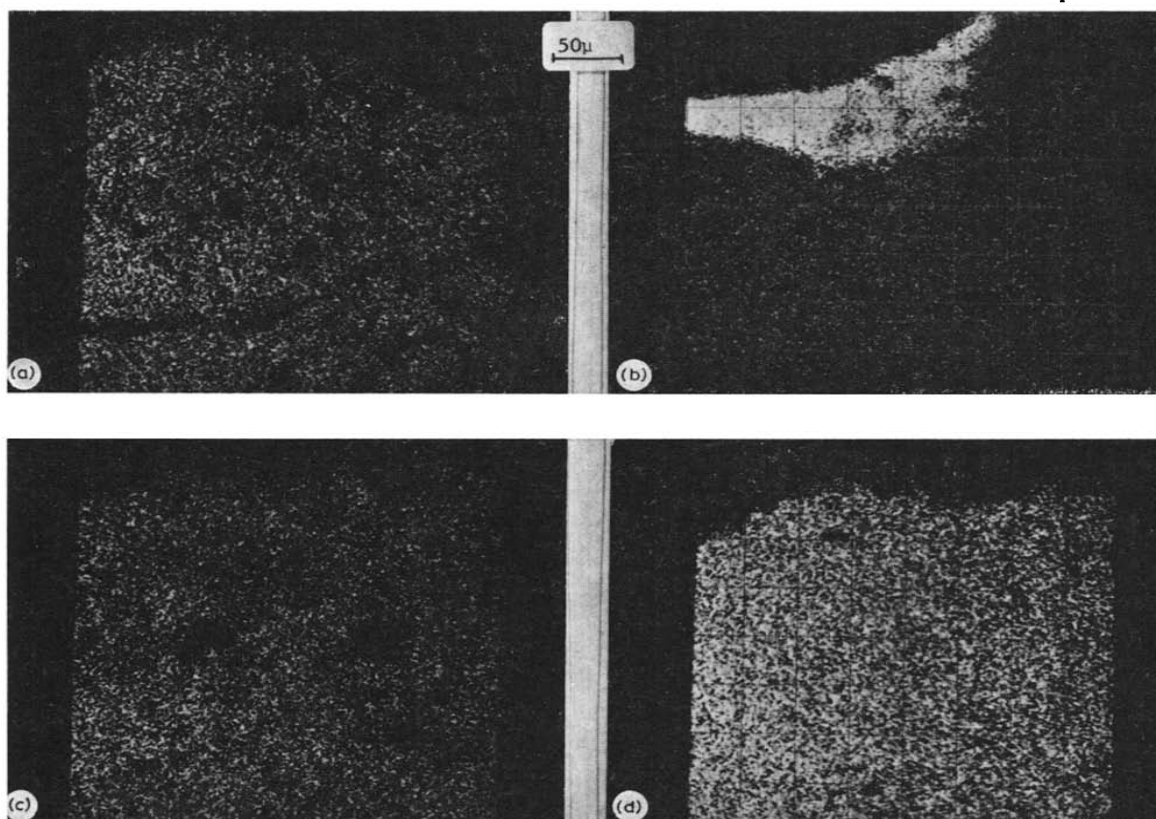


Fig. 12. The effect of precalcination on the sulfur penetration into Greer limestone at high temperatures (1000–1410  $\mu\text{m}$  particles, TG sulfated in 0.5%  $\text{SO}_2$ , 4%  $\text{O}_2$  in  $\text{N}_2$ ). (a) Calcined at 815°C in  $\text{N}_2$ , sulfated 28% at 815°C. (b) Calcined at 815°C in  $\text{N}_2$ , sulfated 22% at 895°C. (c) Calcined at 900°C in 15%  $\text{CO}_2$ , sulfated 52% at 780°C. (d) Calcined at 900°C in 15%  $\text{CO}_2$ , sulfated 67% at 895°C.

In contrast, the wider-pore calcine provided adequate passageways for  $\text{SO}_2$  diffusion into the center of the sorbent, before even the fast reaction at 900°C could form a sulfate shell. Electron microprobe scans show fairly uniform sulfur penetration throughout the wide-pore particle after both high- and low-temperature sulfation.

#### DISCUSSION

The data reported confirm that pore volume distribution and grain size are determining factors for the utilization of calcined lime. Potter<sup>5</sup> found that the pore volume of various limestone calcines measured by mercury intrusion was the single most important property in accounting for a wide range of sorbent reactivities in a fixed bed unit. Borgwardt and Harvey<sup>6</sup> reported that calcined sorbents with pores smaller than 0.2  $\mu\text{m}$  had reactivities that were very sensitive to particle size. Harvey and Steinmetz<sup>7</sup> found that the capacities of limestones were related to the porosity of pores  $>0.9 \mu\text{m}$  as measured by image analysis. They also characterized limestone

capacities with respect to grain structure. Porous grain structures were found to be more reactive than tightly interlocking mosaic structures.

In extension of this earlier work, it has been shown that slowing the calcination reaction produces a shift in the pore distribution of calcines toward pores of larger mean diameter. The importance of pore diameter results from the greater molar volume of calcium sulfate product relative to either the parent limestone or lime. The accumulation of product at pore mouths seals the pathway by which sulfur dioxide would otherwise enter the grains or penetrate, intergranularly, the interior of the particle. The wider these pore mouths, the greater the extent of sulfation before they become blocked. Slow calcination apparently allows the calcium oxide lattice to grow and consolidate, so that fine pores coalesce to form wider pores. During the calcination of the relatively large particles in atmospheres containing  $\text{CO}_2$ , diffusion of  $\text{CO}_2$  through the product layer became progressively slower as reaction proceeded. In comparing the rates of calcination in an atmosphere of nitrogen and an atmosphere of  $\text{CO}_2$ , the change in rate should be accounted for by increased diffusional resistance from the change in the carbon dioxide partial pressure gradient across the reactant interface. In fact, the decelerating effect of carbon dioxide is greater than expected, supporting the idea of a reduced total pore volume, further increasing the resistance to diffusion.

The interaction between the pore volume distribution of the calcine and the optimum sulfation temperature may be ascribed to a competition between reaction and diffusion. Sulfur dioxide which arrives at pore mouths can suffer one of two fates. It can react chemically with the walls of the pores or it can diffuse down the pores towards the center of the sorbent before sulfating. Reaction and diffusion are competing processes in determining the ultimate sulfur distribution across a cross-section of the sorbent. Hartman and Coughlin<sup>8</sup> consider these competing processes in their model of sorbent sulfation. The effects demonstrated here cover significant changes in the relative importance of these processes. For narrow-mouthed pores, it is evident that raising the temperature from 815 to 900°C increases the reaction rate so the chemical reaction dominates over diffusion and most of the sulfur is found at the pore mouths. However, by widening the pore mouths, it proved possible to redress the balance. Despite the higher reaction rate at 900°C, the sulfur was able to diffuse into wider pores, resulting in a more even sulfur distribution across the particle's radius.

#### APPLICATION

In fluidized bed combustion for electric power generation, environmental constraints are met by burning coal in a fluidized bed of limestone. Current Environmental Protection Agency new source performance standards are met with a Ca/S ratio of  $>3:1$  (meaning less than one third of the lime is sulfated). Increasing the limestone utilization (reducing the quantity of limestone used) not only saves sorbent purchasing, transportation, storage and handling costs (as well as spent

sorbent processing and handling costs), but is necessitated by proposed reduction in EPA emission standards or the use of dirty, higher sulfur, coals.

During atmospheric combustion with 20% excess air, the partial pressure of  $\text{CO}_2$  generated from combustion and calcination accumulates to 0.15 atm in the effluent. The equilibrium concentration of  $\text{CO}_2$  at  $850^\circ\text{C}$  is about 0.5 atm. Limestone could be precalcined slowly in a separate unit or a compartment adjacent to the combustor under a partial pressure of  $\text{CO}_2$  closer to the equilibrium to increase the sorbent's efficiency. Recent fluidized bed results have confirmed thermogravimetric data. Improved sulfur retention was found in the Exxon miniplant after batch precalcination of limestone under  $\text{CO}_2$  partial pressures similar to those studied here<sup>9</sup>. Since high partial pressures of  $\text{CO}_2$  are generated under pressurized combustion, sorbents should calcine at a slower rate and have enhanced capacities (provided the average  $\text{CO}_2$  level is less than the equilibrium for calcination). In general, pressurized operation has led to improved sorbent utilization in pilot plant tests.

Wider pores formed during calcination under high  $\text{CO}_2$  pressures enable sorbents to react more completely at high sulfation temperatures, where fast reaction rates would block the entrances of smaller pores and quickly cause diffusion of  $\text{SO}_2$  through product sulfate to limit reaction. Therefore, precalcination of sorbents may enable the temperature range of atmospheric fluidized bed combustion to be extended into higher regions where improved combustion efficiency can be obtained, as well as good sorbent utilization. Once again, pressurized fluidized bed combustors show improved sorbent utilization at higher temperatures ( $900^\circ\text{C}$ ) where atmospheric pressure units show poor utilization.

#### CONCLUSION

Calcining limestone slowly in an atmosphere containing  $\text{CO}_2$  improves the sorbent's sulfation capacity by creating a superior pore distribution in the sorbent. The optimum pore distribution for a sorbent permits sulfur penetration into the individual oxide grains as well as throughout the particle's interior. It is, therefore, dependent on the sorbent grain structure.

The postulated mechanism explains the optimum temperature noted in practice for desulfurization and the data obtained offer a critical test for the validity of reaction rate models.

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