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THE OPTIMAL TEMPERATURE OF SULFUR RETENTION

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ABSTRACT

The effects of calcination temperature on the development of pore size and on the SO_2 sorption capacity have been investigated It has been shown that the optimal temperature of sulfur retention observed in a fluidized-bed combustor can very possibly be due to pore size variations because of calcinations at different temperatures

INTRODUCTION

In a fluidized-bed combustor (FBC), an optimal temperature for maximum sulfur retention has been observed. Generally, these temperatures lie between 830 and 900°C. Increasing or decreasing the combustion temperatures results in lower sulfur retentions. Among the various explanations proposed for such phenomena are the existence of the oxidation and reduction zones in the bed [1], the disproportionation reaction of $CaSO_3$ [2], etc. The pore structure of calcined limestone has been shown to be strongly affected by the calcination conditions [3], i.e. the environment of CO_2 partial pressure. The higher the CO_2 partial pressure, the larger the pore size distribution. The reason for this is that CO_2 partial pressure retards the calcination rate, allowing the larger pores to develop. In an atmospheric fluidized-bed combustor, the CO_2 partial pressure generated at atmospheric pressure is about 0.15 atm. This value, relative to the equilibrium CO_2 partial pressure for $CaCO_3$ conversion to CaO (Fig. 1) [4], is higher at lower temperature. The larger the difference of these values, the less retardation on the $CaCO_3$ conversion to CaO. Since CO_2 partial pressure is lower at lower temperature, the retardation effect on calcination is higher at lower temperatures. Thus when calcination occurs at higher temperatures, the lime sorbent will have a lower capacity for SO_2. Combining this effect with the fact that increasing temperature increases the reaction rates, a temperature maximum could conceivably occur for a given solid residence time in the bed.

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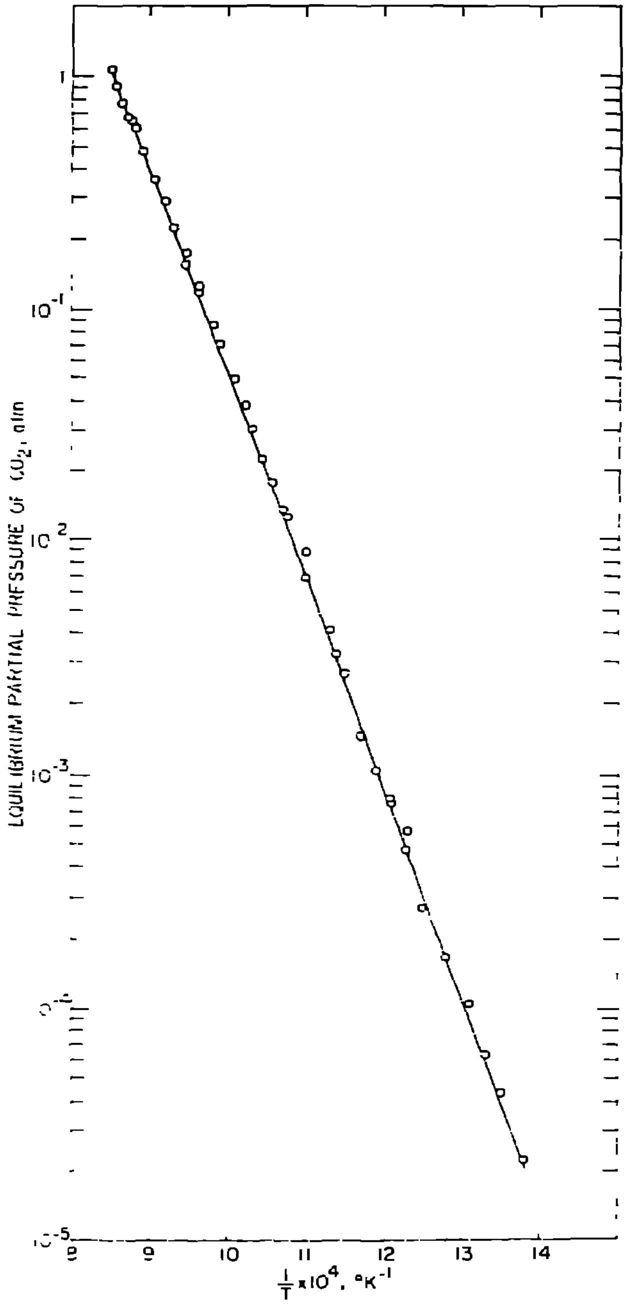

Fig. 1. Equilibrium CO_2 partial pressure for $CaCO_3$ conversion to CaO.

EXPERIMENTAL

A DuPont thermo-analyzer Model 951 was used for the sulfation rate measurements. Detailed experimental and calculation procedures and the apparatus used for the measurements have been described elsewhere [5,6]. A small quartz boat with an area of about 0.6 cm^2 was used as the sample holder. A quartz tube packed with alumina chips and housed in a clamshell furnace served as the preheater for the reactant gases. About 60 mg of uncalcined Greer limestone (16/20 Tyler mesh) was spread in a thin layer in the quartz boat. The limestone was calcined isothermally in 15% CO_2 and 85% N_2. It was then sulfated isothermally with a simulated combustion gas (0.25% SO_2, 5% O_2, and 94.75% N_2) flowing at a velocity of about 10 cm sec^{-1} over the sample surface. This velocity was predetermined to be sufficiently high to minimize gas film diffusion rates.

Two sets of experiments were designed to test the above theory. In the first set, limestone samples were calcined and sulfated at the same temperature in the simulated fluidized-bed condition. In the second set of experiments, limestone samples were all calcined at 1000° C, thereby producing the same pore size distribution. Sulfation temperatures were then varied from 750 to 1000° C.

RESULTS AND DISCUSSION

Figure 2 shows the overall rate of the sulfation reaction for limestone calcined at the sulfation temperatures. The percent of sulfation after 2 h from Fig. 2 was plotted against temperature in Fig. 3. A peaking temperature of 875° C is observed, which is very close to the value obtained from FBC tests.

Figure 4 gives the sulfation rates for Greer limestone calcined at 1000° C. Note that after about 20% sulfation the rates drop sharply regardless of the sulfation temperatures. Plotting the extent of sulfation after 2 h versus temperature as shown in Fig. 5, the sulfation capacity levels off at above 850° C. No peaking temperature is observed. It is reasoned that in about 2 h the sulfation was sufficient to plug the transport pores because of the larger molar volume of $CaSO_4$ to CaO, thereby stopping further noticeable increase in reaction rates.

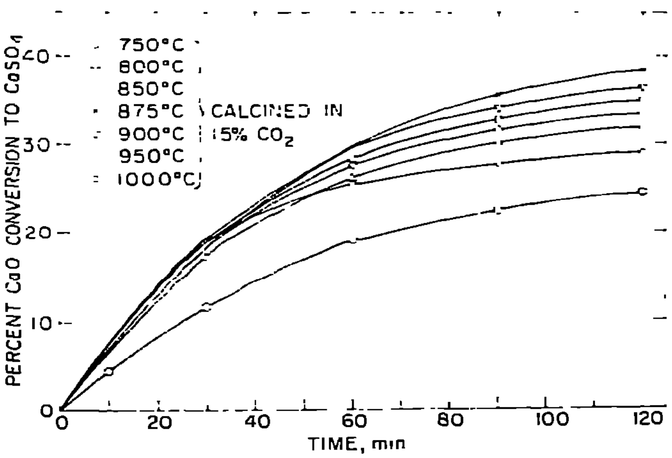

Fig. 2. The effect of temperature on limestone sulfation rate with calcination at the sulfation temperature.

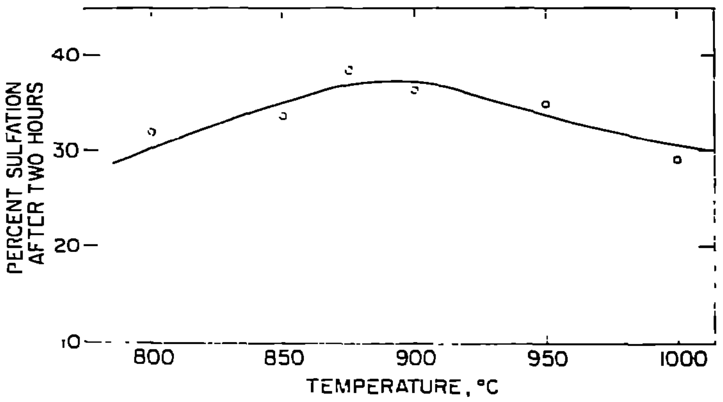

Fig. 3. The effect of temperature on calcium utilization in sulfation with calcination at the sulfation temperature.

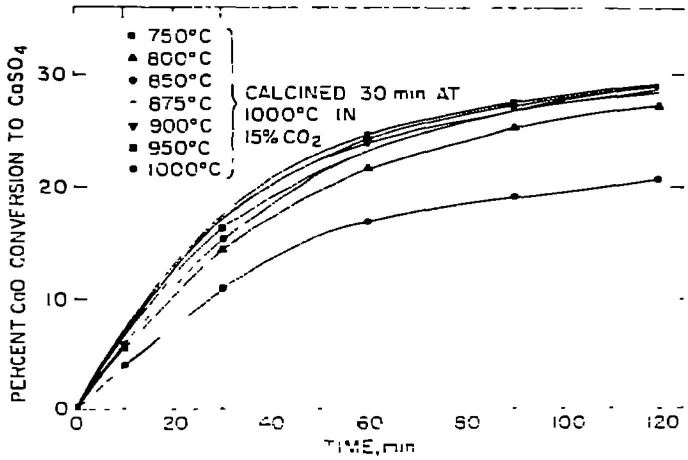

Fig. 4. The effect of temperature on limestone sulfation rate with 30 min calcination at 1000°C.

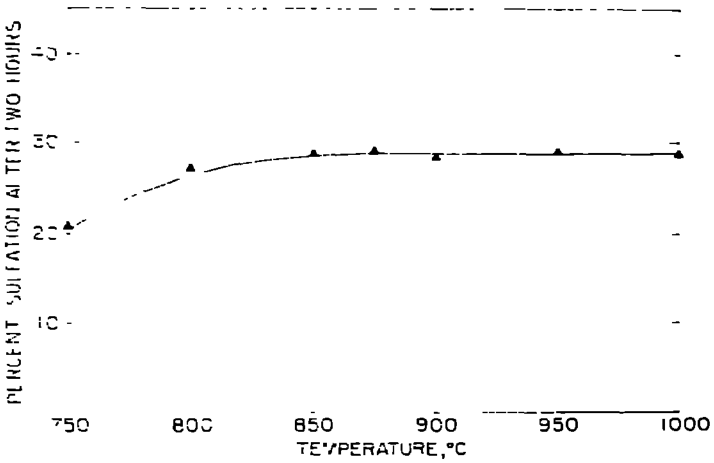

Fig. 5. The effect of temperature on calcium utilization in sulfation with 30 min calcination at 1000°C.

By comparing Figs. 3 and 5, it is clear that the temperature maximum observed in a FBC is possibly due to pore size variations because of calcinations at different temperatures. To further confirm the postulated mechanism, tests of precalcined limestone samples in a fluidized bed are necessary.

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