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THE EFFECTS OF $CaCl_2$ ON LIMESTONE SULFATION IN FLUIDIZED-BED COAL COMBUSTION

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ABSTRACT

In an investigation into the effects of $CaCl_2$ on the sulfation of limestones in a laboratory furnace simulating fluidized-bed coal combustion conditions, small additions of $CaCl_2$ (< 1 mole%) to the limestone prior to calcination were found to increase the extent of sulfation by changing the limestone pore structure. These changes were effected by trace amounts of liquid in the system in a synthetic SO_2/O_2 flue gas at 850°C. At much higher concentrations of $CaCl_2$, large amounts of a liquid phase are produced, containing a substantial quantity of dissolved CaO and leading to greatly enhanced sulfation when exposed to SO_2/O_2. The use of $CaCl_2$ additive in fluidized-bed combustion would reduce the quantity of limestones required to meet air pollution standards for SO_2 and also reduce the quantity of solid waste generated.

INTRODUCTION

Recent interest in the use of alkali salts as additives for improving the efficiency of particulate limestone in removing SO_2 from flue gases in FBC has prompted a search for additives other than NaCl and other sodium-containing compounds [1]. There is concern that increased levels of sodium would contribute to hot corrosion problems.

In laboratory experiments, $CaCl_2$ was found to be as effective as NaCl in enhancing sulfur dioxide retention by limestone [2]. It has been routinely used as a freeze-proofing agent for coal storage piles [3]. The concentrations used for freeze-proofing are similar to the quantities of $CaCl_2$ found to be effective in this work. The lime industry has used $CaCl_2$ as well as many other additives to effect changes in physical properties and reactivities of calcined limes [4—6]. This is a report of an investigation of the effects of $CaCl_2$ on limestone sulfation and the mechanisms proposed to explain that interaction.

EXPERIMENTAL

Calcination and sulfation of a large number of naturally-occuring limestones were performed in controlled-atmosphere horizontal tube furnaces with and without added $CaCl_2$. Reagent grade $CaCl_2$ was used throughout. The salt was mixed with the limestone particles as aqueous slurries which were subsequently evaporated to dryness. Water of hydration was found to have no marked effect on reactivity since it was lost at low temperatures before decomposition of the limestone began.

A 1-g sample of 18—20-mesh stone was placed in a monolayer in a shallow quartz boat which was put inside a furnace at 850°C. Synthetic flue gases flowing at 500 cm^3 min^{-1} were used. Calcination was in 5% O_2, 20% CO_2, 75% N_2 and sulfation was done sequentially in the same gas mixture with 0.3% SO_2 added. Calcination times were 1 h, and sulfation reactions were allowed to proceed for 6 h.

A mercury porosimeter was used to determine pore distributions in calcined stones and to allow the average pore diameter to be determined for each sample. Scanning electron microphotographs were also taken so that untreated and treated stones could be compared visually.

RESULTS AND DISCUSSION

Figure 1 is a series of scanning electron microphotographs of limestone ANL-9501 after calcination, some untreated and some treated with $CaCl_2$. It shows the increasing effects of larger amounts of $CaCl_2$, with lime particles eventually fusing as more liquid phase is produced (Fig. 1). Figure 2 presents magnified views of limestone 9501, showing the fusion of particles that occurs at high concentrations of $CaCl_2$.

Figure 3 is a plot of average pore diameter vs. conversion of CaO to $CaSO_4$ for untreated limestones, limestones treated with 0.1 mole% $CaCl_2$, and limestones treated with 0.5 mole% $CaCl_2$. The distribution of data points has two areas representing increased sulfation. The first occurs near 0.3 μm and reaches a maximum sulfation in the range of 50—60% conversion of the available CaO to $CaSO_4$. The second increase in sulfation begins at average pore diameters of 1 μm and above, with conversions to sulfate continually increasing; apparently, conversion would eventually reach 100% if quantities of salt were larger or reaction time longer, as indicated by data (not included here) for pore diameters up to 5 μm.

The first effect of $CaCl_2$ at very low $CaCl_2$ concentrations is similar to that observed for NaCl additions [7] in which an increase in average pore diameter is caused by enhanced mobility of system constituents. Trace amounts of localized liquid phase catalyze the decomposition of $CaCO_3$ and the recrystallization of CaO. Large pores grow at the expense of small pores, and there is continuous growth of CaO crystallites. When sulfation is begun, this new pore structure is permeable to SO_2/O_2 mixtures, allowing more $CaSO_4$ to form; eventually an impervious layer forms to seal off residual CaO from further reaction. Figure 4 shows the relationship of the extent of conversion to sulfate and surface area (calculated from mercury porosimetry data) for many limestones. At this low concentration of salt (0.1 mole%) a maximum near 50% conversion is possible for all stones considered regardless of the original surface area of the calcined stones. At concentrations of

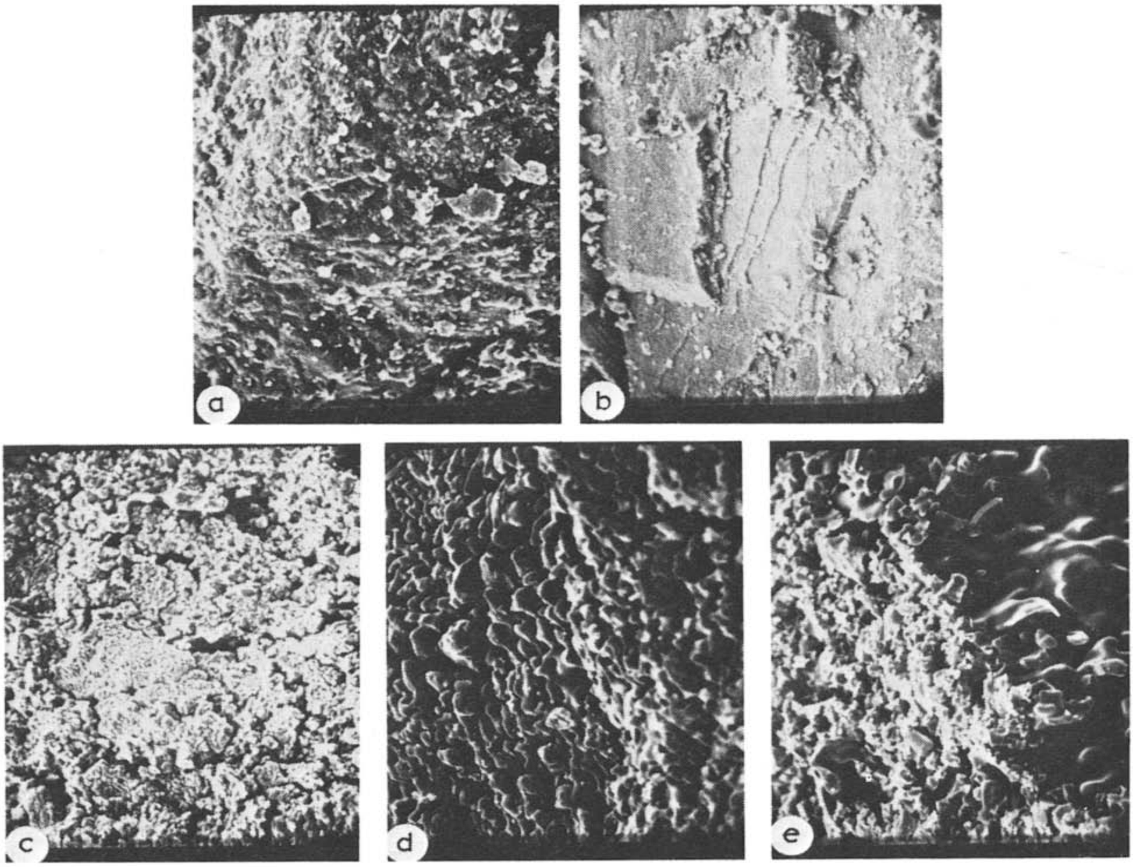

Fig. 1. Cross-sections of limestone ANL-9501 particles after calcination at 850°C in 5% O_2, 20% CO_2, balance N_2. (a) 9501 calcined for 2 h (×700); (b) 9501 calcined for 6 h (×700); (c) 9501 + 0.1 mole% $CaCl_2$ calcined for 1 h (×700); (d) 9501 + 0.5 mole% $CaCl_2$ calcined for 1 h (×650); (e) 9501 + 1.0 mole% $CaCl_2$ calcined for 1 h (×675).

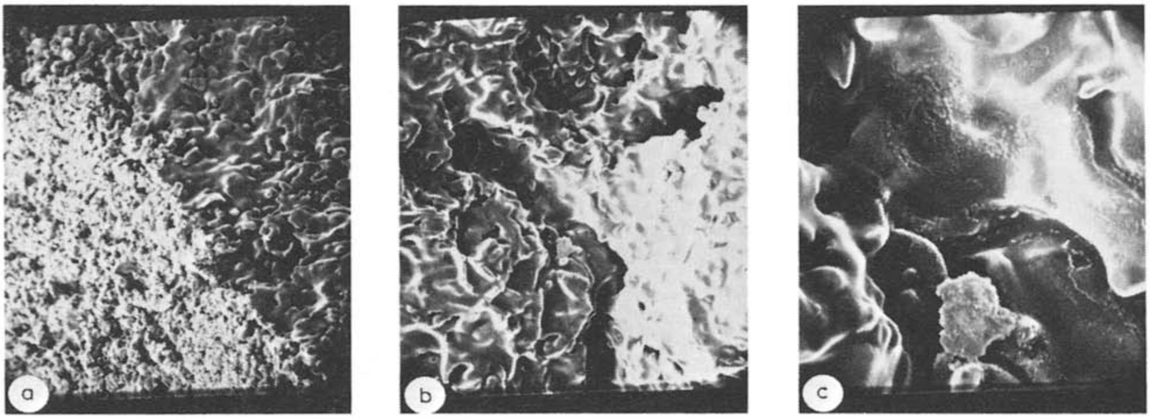

Fig. 2. Limestone ANL-9501 with $CaCl_2$ calcined 1 h at 850°C in 50% O_2, 20% CO_2, balance N_2. (a) 9501 + 1.0 mole% $CaCl_2$ (×520); (b) 9501 + 2.0% $CaCl_2$, junction of two particles (×520); (c) 9501 + 2.0% $CaCl_2$, junction of two particles (×1920).

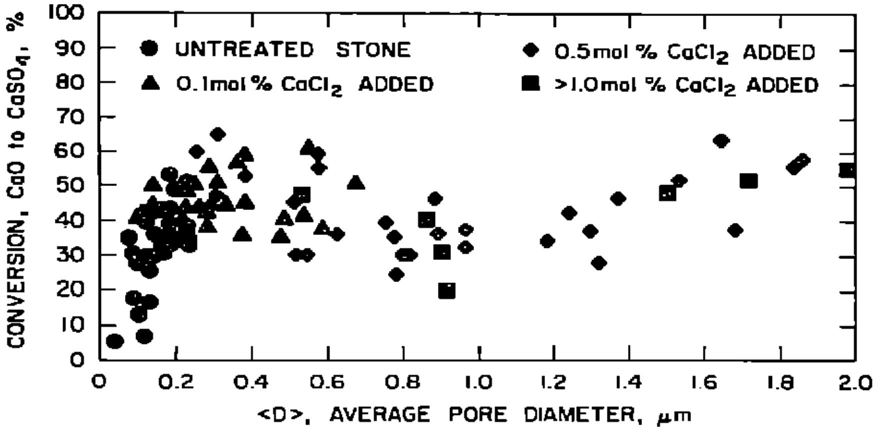

Fig. 3. Conversion to sulfate vs. average pore diameter for limestones treated with $CaCl_2$ at 850°C and sulfated for 6 h in 0.3% SO_2, 5% O_2, 20% CO_2, balance N_2.

$CaCl_2$ above 0.1 mole%, no relation of conversion to surface is found due to disruption of the crystal structure by dissolution.

Comparing the behavior of $CaCl_2$ and NaCl, the second increase in sulfation observed with increasing $CaCl_2$ levels is not observed with NaCl [7]. The phase diagram for CaO—$CaCl_2$ shows that a large amount of CaO is soluble in $CaCl_2$ and produces a very low-melting system. It is postulated here that the second increase in sulfation is due to the production of major amounts of liquid phase able to dissolve CaO, which would then be a more readily sulfatable species. Precipitation of the $CaSO_4$ formed would allow more CaO to dissolve; thus, sulfation could proceed indefinitely as long as there is enough $CaCl_2$ to produce a liquid phase.

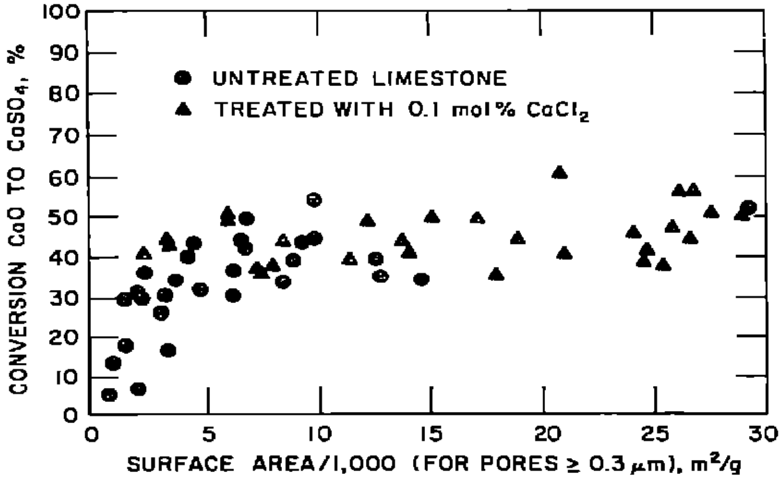

Fig. 4. 6-h conversion to sulfate with 0.3% SO_2 (6 h) vs. surface area of calcines for pores ≥ 0.3 μm in limestone calcined at 850°C 1 h in 5% O_2, 20% CO_2, balance N_2.

SUMMARY AND CONCLUSIONS

Calcium chloride, when used as an additive in fluidized-bed coal combustion, promotes the capture of SO_2/O_2 by both limestones and dolomites. At low concentrations of $CaCl_2$, a trace amount of liquid is present which essentially catalyzes sintering, producing larger pores and large crystallites. The larger pores are more capable of accepting large $CaSO_4$ molecules without being blocked off. At higher levels of salt addition, the effect of a decrease in grain surface area begins to predominate over improved gaseous permeability and the reactivity of the stone decreases. At still larger $CaCl_2$ concentrations ($\geqslant$2 mole%) large quantities of CaO can be dissolved in the $CaCl_2$, creating a very low-melting system containing large amounts of liquid phase. This facilitates reaction of dissolved CaO with gaseous SO_2/O_2. Even larger salt additions allow eventual sulfation of all of the available CaO. The amount of salt necessary to produce these effects varies with the original concentrations of impurities in the limestone and dolomites.

The effectiveness of $CaCl_2$ as an additive for increasing the capture of SO_2 by limestones, coupled with the fact that it is less corrosive than NaCl [8], argues for its use in fluidized-bed coal combustion. Study of porosity and laboratory reactivity data should enable boiler operators to determine empirically the range of concentrations which will maximize sulfur dioxide capture for specific limestone. By increasing the sulfation capacity of the limestones, the use of $CaCl_2$ as an additive can reduce the quantity of limestone required to meet SO_2 air pollution standards and reduce the amount of solid waste generated.

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