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THE EFFECT OF SODIUM CHLORIDE ON THE SURFACE AREA OF CALCINED LIMESTONE. PART 1

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ABSTRACT

The effect of sodium chloride on the specific surface area and average pore radius of limestone is studied. It is found that sintering takes place with increased calcination time, and sodium chloride addition. The specific surface area is inversely proportional to the amount of sodium chloride added to the Greer limestone. Therefore, mean pore radius is directly proportional to the amount of sodium chloride addition. The optimum amount of sodium chloride addition for the maximum sulfation capacity is 0.43 wt.%.

INTRODUCTION

It is important to control potentially harmful sulfur dioxide emitted to the atmosphere during combustion of fossil fuels. One of the developing technologies of sulfur dioxide removal is its reaction with calcined limestone in a fluidized-bed combustor. After calcination CaO in the limestone reacts with SO_2 and O_2 to form stable $CaSO_4$, leaving exhaust gases that are relatively free of sulfur.

In pilot plant studies of Shelton [1] and Pope, Evans, and Robins, Inc. [2] adding salt to fluidized-bed combustors was demonstrated to be a way of decreasing the levels of SO_2 in off-gases. Bardakci [3] and Shearer et al. [4] studied the effect of sodium chloride on the calcination and sulfation of limestone in fluidized-bed combustion. They showed that the presence of salt induces structural rearrangement in the stones that can lead to an optimum pore distribution for SO_2/O_2 reaction mixtures.

In this study the surface areas of calcined limestone with and without sodium chloride, and average pore radii which are determined from the extent of calcination and surface area measurements are presented.

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Wheeler [5] developed the following equation to calculate the average pore radius, r, from the surface area, S_g, porosity, ϵ, and particle density, ρ_p, of the porous solid structures:

$$r = \frac{2\epsilon}{S_g \rho_p} \tag{1}$$

Hartman and Coughlin [6] developed the following equation to calculate the porosity of calcined limestone:

$$\epsilon = 1 - (1 - \epsilon_{LS})\rho_{LS}\frac{y}{M_{CC}}\left[V_{CC} - X_{CO}(V_{CC} - V_{CO})\right] - (1 - \epsilon_{LS})\left(1 - y\frac{\rho_{LS}}{\rho_{CC}}\right) \tag{2}$$

EXPERIMENTAL

Greer limestone was ground with a mortar and pestle to particles of diameter between 210 and 500 μm (65 to 32 mesh). These particles in combustion boats (size A, No. 7-651 Combax), were dried in a furnace at 150°C for 2 h. After 2 h of drying, the Greer limestone and the boats were placed in a desiccator where anhydrous $CaSO_4$ was used as desiccant. Boats were tare weighted (about 0.5 g), then Greer limestone was placed in each boat. Boats with the Greer limestone particles were weighted again. These boats were placed in an oven which was preheated to 850°C and nitrogen gas was passed through the oven at a rate of about 400 cm^3 min^{-1}. The calcination was carried out at 850°C under N_2 atmosphere. At 0.5, 1, 2, 4, 8 and 24 h, respectively, two boats were taken out of the oven and placed in the desiccator. After 20 min of cooling each boat was reweighted. Limestone powder was transferred to a tared sample cell. The empty boat and the sample cell were reweighted and the integrated amount of gas absorbed by the sample is determined using a Quantachrome Monasorb Surface Area Analyzer, Model MS-4 (Quantachrome Corporation, NY). From the above measurements the percentage weight loss and the surface area were determined.

In order to add salt (NaCl) to a sample, about 15 g of dried Greer limestone particles were weighted. The proper amount of salt in order to have 0.1, 1 or 5% salt addition to the sample was placed in a small container and was dissolved in the smallest amount of deionized water possible. This solution was added to the Greer limestone particles and the container was washed with a small amount of deionized water which was also added to the Greer limestone sample and mixed with a spatula. The sample was dried in an oven at 150°C. The calcination experiment was carried out with this sample as explained before, then the surface areas were determined. From the weight loss the extent of $CaCO_3$ calcined was calculated. Then the porosity of calcined pellet was calculated using eqn. (2), and the average pore radius was calculated using eqn. (1).

RESULTS AND DISCUSSION

Figures 1, 2, 3 and 4 show the surface area and weight loss curves as a function of calcination time for the Greer limestone with 0, 0.1, 1 and 5 wt.% salt addition, respectively. Complete calcination took about 4 h for all of the samples except that the samples with 1 wt.% salt addition took less than 1 h to be calcined. Surface areas of each sample were increased during the calcination. After the calcination was completed, the surface areas started to decrease because of sintering. During sintering, smaller crystallites are combined to give larger crystallites thus giving a structure with lower surface area and larger pore openings. The average surface areas of all of the samples after 24 h in the oven are shown in Table 1. Examination of the surface areas after 24 h of calcination shows that the surface areas are inversely proportional to the amount of sodium chloride added, thus indicating that sodium chloride addition accelerates the sintering phenomenon.

Figure 5 shows the calculated average pore radius, as a function of calcination time and percentage sodium chloride added. Average pore radius decreases during the calcination due to the increased surface areas, but then increases due to the sintering and reduction of surface area. Shearer et al. [4]

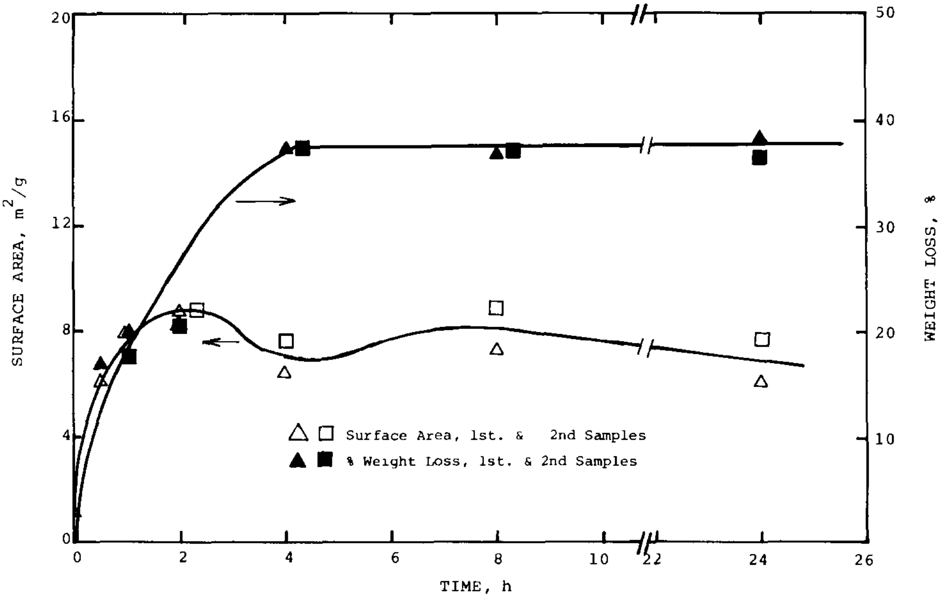

Fig. 1. Surface area and percentage weight loss for Greer limestone as a function of calcination time (no salt added, run No. S1).

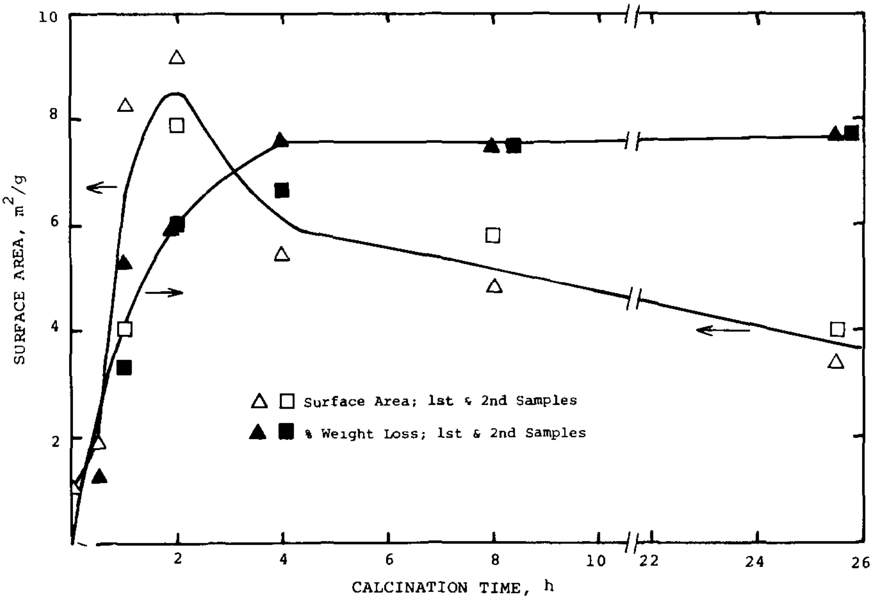

Fig. 2. Surface area and percentage weight loss for Greer limestone as a function of calcination time (0.1% salt added, run No. S4).

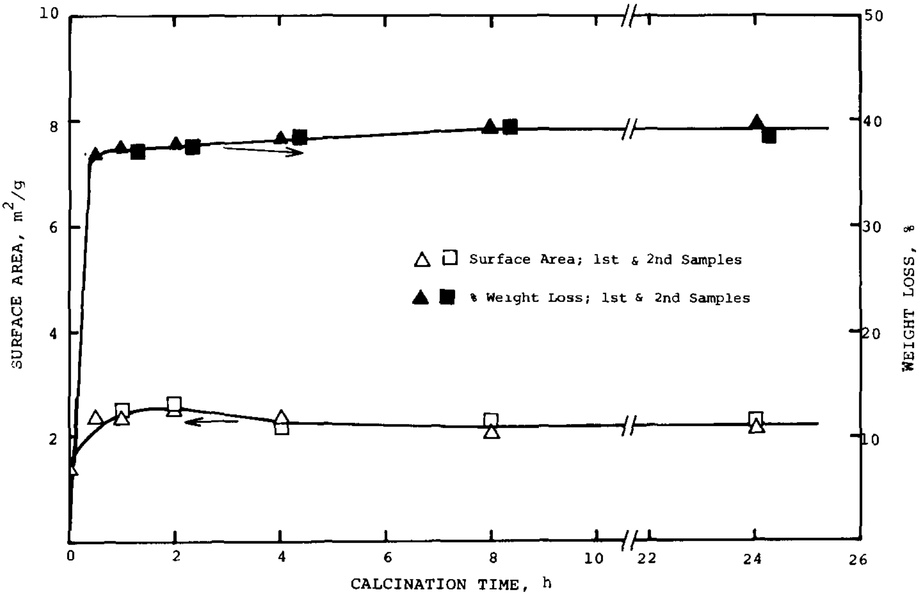

Fig. 3. Surface area and percentage weight loss for Greer limestone as a function of calcination time (1% salt added, run No. S3).

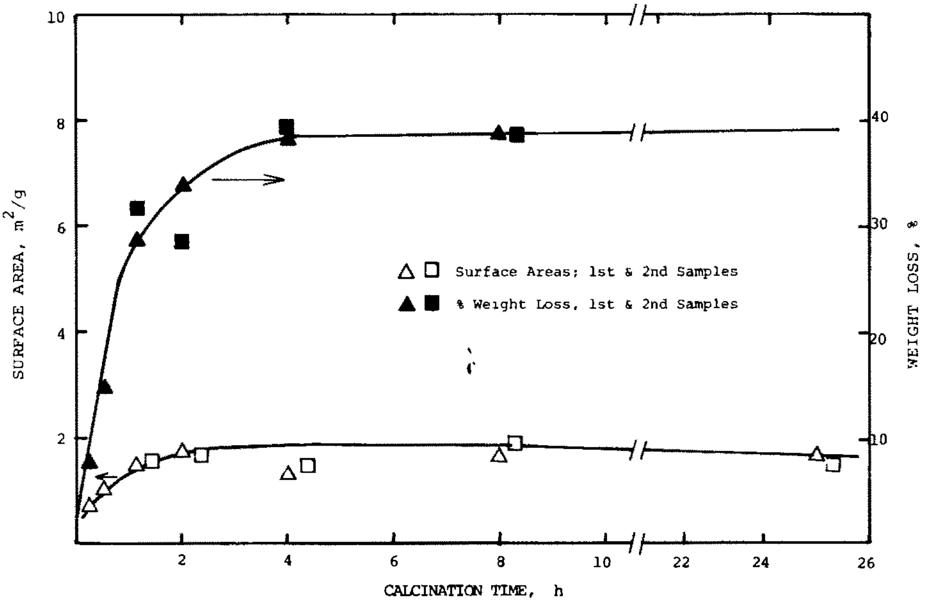

Fig. 4. Surface area and percentage weight loss for Greer limestone as a function of calcination time (5% salt added, run No. S5).

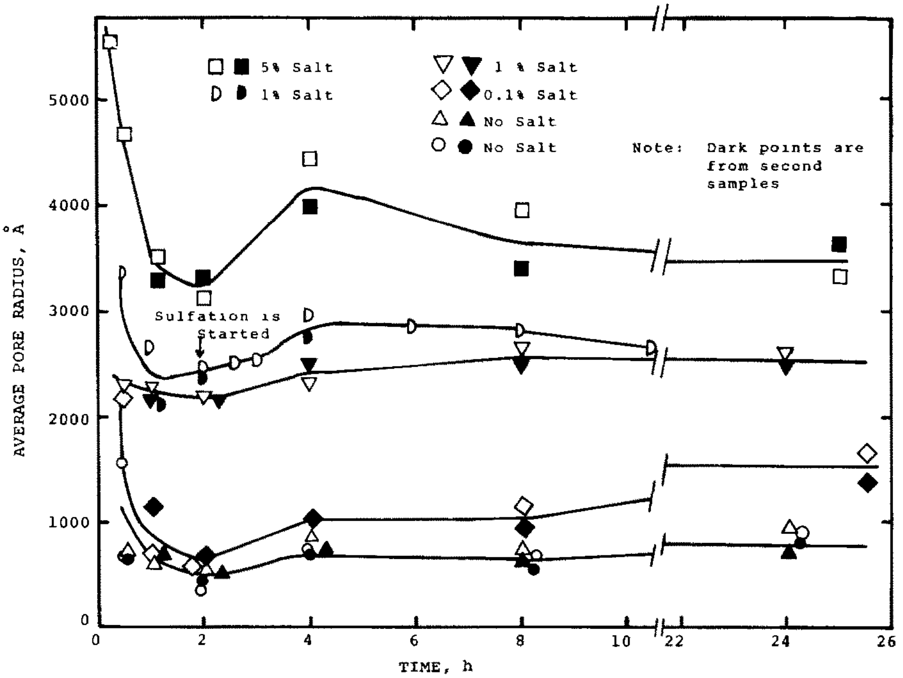

Fig. 5. Average pore radius as a function of calcination time and percentage sodium chloride added.

TABLE 1

Average surface areas of calcinea Greer limestone sample after 24 h

Sample, Greer limestone	Surface areas (m^2 g^{-1})
0% NaCl	7.04
0.1% NaCl	3.63
1% NaCl	2.12
5% NaCl	1.60

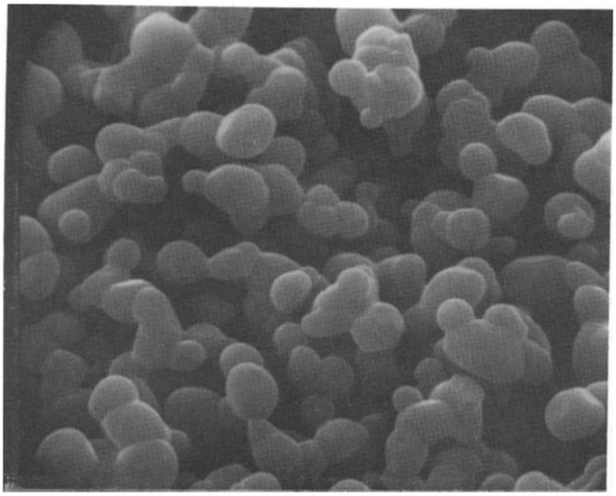

Fig. 6. $CaCO_3$, calcined 4 h at 1100°C (5% NaCl), 5700×.

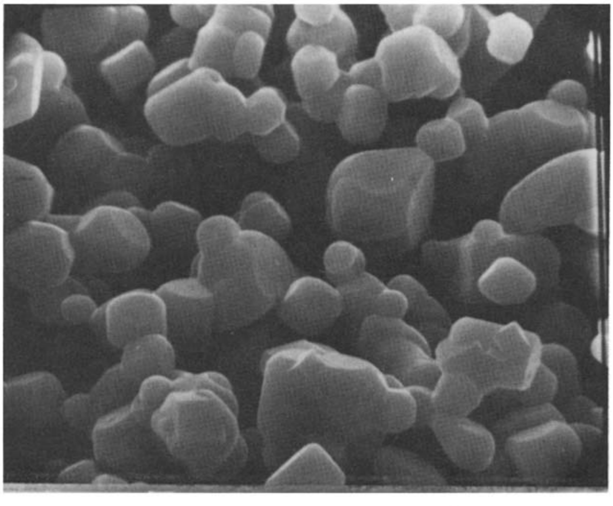

Fig. 7. $CaCO_3$, calcined 4 h at 1100°C (10% NaCl), 5700×.

found that the reactivity of calcined limestone to capture SO_2 reached a maximum with a salt content near 0.5 wt.% for most of the stones. They also reported that the optimum average pore radius is 0.15 μm or 1500 Å. In Fig. 5 this study also shows that in order to get an average pore radius of 1500 Å the added salt should be between 0.1 and 1.0 wt.%. At 4 h calcination time a linear extrapolation of the data gives 0.43% added salt.

Additionally, reagent-grade $CaCO_3$ with 5 and 10 wt.% salt were ground and calcined for 4 h at 1100°C. The scanning electron microscope pictures of these samples are shown in Figs. 6 and 7. In these figures, the white-colored parts are the crystals and the dark sections are the pore openings. Examination of these figures clearly shows the enlargement of crystallites and pore openings. Thus, the crystallite size and pore openings increase as the added weight percentages of salt were increased from 5 to 10 wt.%.

CONCLUDING REMARKS

The treatment of the Greer limestone with NaCl before calcination results in structural changes. Sintering takes place with increased calcination time. This sintering is accelerated with increasing NaCl addition. The sintering is a result of the increased ionic mobility. This takes place by combining smaller crystallites into larger crystallites and smaller pore openings to larger pore openings. This action also decreases the surface area available for any subsequent reaction of calcined limestone, but increases the effective diffusivity of gases through the porous matrix.

NOMENCLATURE

M	molecular weight
r	average pore radius (cm)
S_g	specific surface area ($cm^2\ g^{-1}$)
V_{CC}	molar volume of calcium carbonate (36.92 $cm^3\ mol^{-1}$)
V_{CO}	molar volume of calcium oxide (16.97 $cm^3\ mol^{-1}$)
X_{CO}	extent of calcination
y	calcium carbonate content in Greer limestone (wt.%)

Greek symbols

ϵ	porosity of calcined limestone
ρ_p	density of the calcined Greer limestone ($g\ cm^{-3}$)
ρ	density

Subscripts

CC	calcium carbonate
CO	calcium oxide
LS	Greer limestone

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