Comparative SO_2 Reactivity of CaO Derived from $CaCO_3$ and $Ca(OH)_2$

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Experimental data on sulfation rates of CaO particles derived from $CaCO_3$ are compared to those derived from $Ca(OH)_2$ using a product layer diffusion control model differing only in the shape of the CaO grain. Both the model and the experimental data indicate slightly higher reactivity for the $Ca(OH)_2$-derived oxide due to the observed difference in grain shape. This effect is considered as a contributor to the greater performance of $Ca(OH)_2$ in pilot-scale SO_2 removal studies.

Introduction

In an effort to develop a low-cost, retrofit technology for control of sulfur dioxide (SO_2) emissions from coal-fired utility plants, boiler injection of dry calcium-based sorbents to form calcium sulfate ($CaSO_4$) has been widely studied. The effects of such parameters as injection temperature, sorbent surface area, and SO_2 concentration on the reaction between the active species, calcium oxide (CaO), and SO_2, are well documented. One such parameter of particular interest is the chemical parentage of the active sorbent. In pilot-scale studies, CaO derived from hydrated lime, $Ca(OH)_2$, has been found to be more reactive than that from the respective limestone, $CaCO_3$ (Cole et al., 1986; Beittel et al., 1985). Three reasons have been suggested for this superiority of $Ca(OH)_2$-derived calcines (termed h-CaO) over their carbonate analogues (termed c-CaO):

1) The activation rate for production of reactive h-CaO is much faster than the activation, or calcination, rate that forms c-CaO, allowing the sulfation reaction to begin sooner.

2) The inherent particle size of h-CaO is much smaller than that of c-CaO, thus lessening mass transfer resistances.

3) Structural differences lend a greater reactivity to h-CaO.

Maline and Pershing (1987) studied the short-time sulfation rates of similarly sized ($\simeq 5\ \mu m$) $CaCO_3$ and $Ca(OH)_2$ based sorbents. They reported that, at short residence times (<100 ms), sulfur capture was independent of sorbent type, indicating that the overall sulfation rate is not affected by the faster activation rate exhibited by the h-CaO. Furthermore, Gullett and Bruce (1987) noted superior reactivity for h-CaO over c-CaO of the same porosity using CaO samples, eliminating activation rates from consideration. Borgwardt et al. (1987) investigated the sulfation rates at 1,073 K of CaO materials made from six calcium carbonates and their respective calcium hydroxide analogues prepared at conditions sufficient to yield identical surface areas of approximately 23 m^2/g. Using the product layer diffusion model formulated by Bhatia and Perlmutter (1981, 1983), they extracted nearly identical values for the product layer diffusivities of both c-CaO and h-CaO. They concluded that no inherent kinetic differences existed between the two sorbent types. Performance differences at the pilot scale were attributed to the smaller mean h-CaO particle size resulting from fragmenting of the larger CaO particles during the highly exothermic hydration reaction. In contrast, Gullett et al. (1988) measured the extent of sulfation of c-CaO and h-CaO precalcines of the same surface area as a function of particle size at varying residence times, finding that, in general, for each particle size the h-CaO reacted to a greater extent than did the c-CaO. While the rate of conversion to $CaSO_4$ was indeed shown to be primarily a function of particle size, clearly other factors, presumably structural differences, contributed to the observed enhancement of the h-CaO sulfation reaction.

Gullett and Bruce (1987) measured the pore volumes and pore size distributions of high porosity c-CaO and h-CaO samples using nitrogen porosimetry. While the distributions themselves were quite similar, the shape of the adsorption/desorption isotherms suggested a difference in the shape of the pores; c-CaO suggested the openings between packed spheres while h-CaO approximated slits or the gaps between plates when

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interpreted in accordance with Gregg and Sing (1982). This finding was in agreement with the pore structures suggested by Beruto et al. (1980). Gullett and Bruce further reported that available porosity was filled by product more slowly for h-CaO, allowing a higher conversion to $CaSO_4$, presumably due to this pore structure difference.

In this work, sulfation data were obtained for both c-CaO and h-CaO at varying porosities and temperatures. Results were analyzed using a conventional spherical grain model for c-CaO and a flat plate model for h-CaO. Both models were developed for sulfation reaction control by product layer diffusion, based upon modelling (Sotirchos and Yu, 1985) and experimental (Borgwardt and Bruce, 1986; Borgwardt et al., 1987) evidence for the rate controlling step. Values for the solid diffusivity, SO_2 concentration, and activation energy were obtained from conversion data extrapolated to the zero porosity case where pore plugging effects are absent. The greater than three times larger volume of the $CaSO_4$ product can build up between adjacent grains, plugging pores and increasing the solid diffusion distance through the reactant. The model was then expanded to fit higher porosities using a modified effectiveness factor to express pore plugging limitations.

The effect of modelling h-CaO as a flat plate structure results in higher conversion at the same surface area than that of c-CaO modelled as a spherical grain. As surface area and temperature are increased, this effect becomes more pronounced, partially accounting for the reactivity advantage of $Ca(OH)_2$ over $CaCO_3$ sorbents.

Experimental Method

The parent sorbent used in this research was Fredonia White limestone containing 95% by mass $CaCO_3$. Sorbents produced from this parent material were identical to those tested by Gullett and Bruce (1987). Samples of approximately 15 mg of sorbent sized to a nominal diameter of 2.8 μm were spread evenly on a quartz wool bed. The high gas throughput, small sample size, and small particle size serve to eliminate bulk gas, film, and pore diffusion resistances as well as maintain differential conditions with respect to SO_2 concentration. The bed was supported in a quartz carrier and inserted into a fixed bed isothermal reactor described by Borgwardt et al. (1984). The samples were calcined under a flowing N_2 atmosphere at temperatures varying from 1,073 to 1,273 K for 120 s and allowed to sinter under a stagnant N_2 atmosphere for varying times, producing a range of porosities. The carrier was transferred to an identical second reactor at the desired reaction temperature, allowed 1 min for temperature equilibration, and exposed to 23 std L/min process flow consisting of 0.3% SO_2 and 5% O_2 (from dry air) with a N_2 balance for times up to 600 s. Table 1 summarizes the range of experimental conditions. Samples were then removed and analyzed for degree of conversion to $CaSO_4$ by dissolving totally in deionized water with a small amount of 1N HCl. Molar ratios of $SO_4^{=}$ and Ca^{++} ions were then determined by ion chromatography and atomic absorption spectroscopy, respectively.

Table 1. Experimental Conditions

Sorbent Type	Porosity Range (5 Samples)	Reaction Temp., K	Reaction Times, s (7 Times)
c-CaO	0.03 to 0.48	1,073	0 to 600
c-CaO	0.03 to 0.41	1,173	0 to 300
c-CaO	0.03 to 0.34	1,273	0 to 100
h-CaO	0.06 to 0.50	1,073	0 to 600
h-CaO	0.06 to 0.44	1,173	0 to 300
h-CaO	0.06 to 0.36	1,273	0 to 100

Porosity and surface area for each set of reaction conditions were determined using a Micromeritics Digisorb 2600 Autoanalyzer. Surface area was determined using the standard Brunauer-Emmett-Teller (B.E.T.) method. Porosities were obtained by measuring the adsorbed N_2 at a relative pressure of 0.985, corresponding to the volume in pores with nominal openings of 1,400 Å or less. Pore volumes of selected samples were independently verified using mercury porosimetry. Experimental variability in measured surface area and porosity was accounted for by developing the relationships presented in Figure 1. Values were determined on composites of four 100 mg samples carried through the reaction procedure up to the point of SO_2 exposure, then removed from the reactor and cooled under flowing N_2.

Results and Discussion

In conjunction with the grain shape suggested by adsorption/desorption isotherms for c-CaO, the expression relating conversion, X, to time, t, for spherical grains of radius, r, controlled by product layer diffusion is given below (Levenspiel, 1972)

$$k_s t = 1 - 3(1 - X)^{2/3} + 2(1 - X) \tag{1}$$

with

$$k_s = (6MD_e C)/\rho r^2) \tag{2}$$

Noting that for uniformly sized spheres,

$$r = 3/(S\rho) \tag{3}$$

and expressing the temperature dependence of the diffusion through the forming product layer (Jost, 1960) as

$$D_e = D_o \exp\left[-E/RT\right] \tag{4}$$

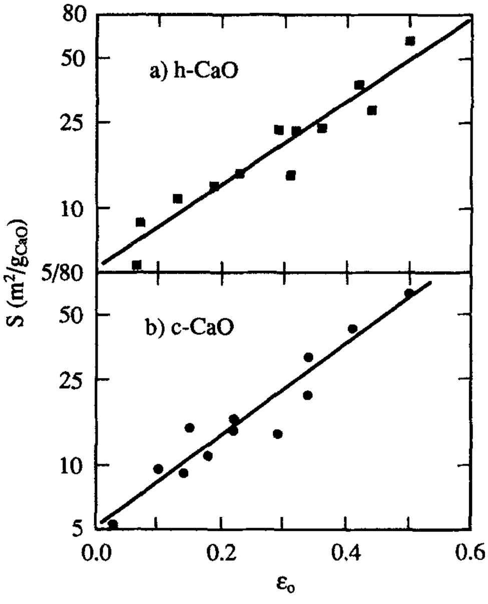

Figure 1. Experimental surface area/porosity relationships for a) h-CaO and b) c-CaO prior to SO_2 exposure.

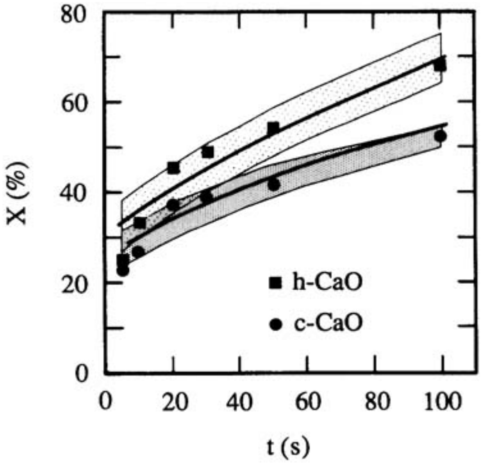

Figure 2. Fit of product layer diffusion models to experimental data for h-CaO and c-CaO at 1,273 K, $S = 27\ m^2/g$, $\epsilon_o = 0.34$.

Equation 2 can be rewritten as

$$k_s = 0.667 M D_o C \rho S^2 \exp\left[-E/RT\right] \qquad (5)$$

For a flat plate grain shape, as suggested by the h-CaO isotherms, the X vs. t curve for product layer diffusion control is given as

$$k_p t = X^2 \qquad (6)$$

with

$$k_p = (2 M D_e C)/(\rho L^2) \qquad (7)$$

where $L = 1/2$ the plate width.

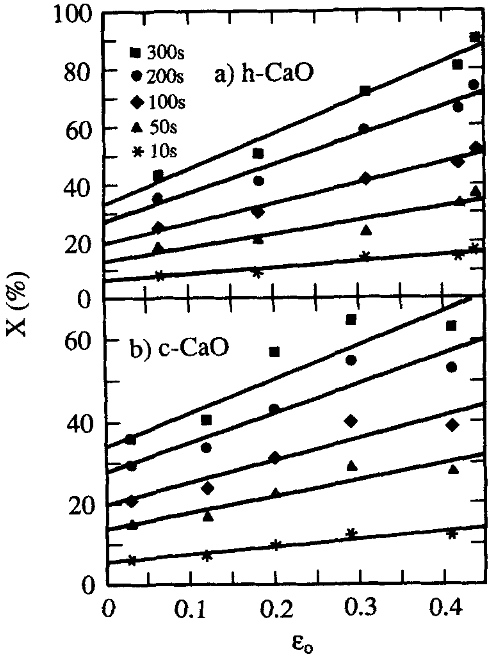

Figure 3. Linear approximation for conversion at 1,173 K and varying time for a) h-CaO and b) c-CaO.

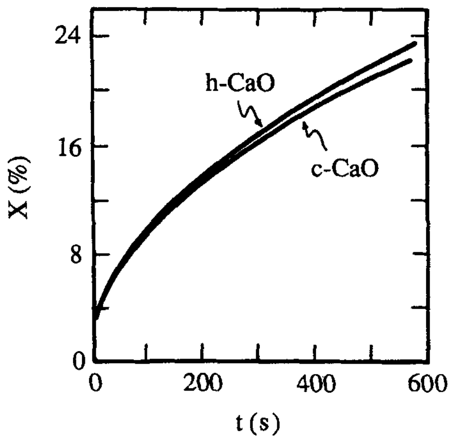

Figure 4. Reaction response for zero porosity sorbents predicted by models at 1,073 K.

For uniform plates,

$$2L = T_p = 2/(S\rho) \qquad (8)$$

Substituting into Eq. 7 gives

$$k_p = 2 M D_o C \rho S^2 \exp\left[-E/RT\right] \qquad (9)$$

The X vs. t experimental data from precalcinated c-CaO runs were fitted using the spherical grain diffusion model as in Borgwardt and Bruce (1986). Data from h-CaO runs were in turn fitted to the plate model, reflecting the slit-shaped pores indicated from the N_2 adsorption isotherm shape. In each case, the data were fit through the origin to satisfy the condition of zero conversion at zero time. Examples of the fit for one porosity and one temperature for each sorbent along with estimates of the associated errors representing 90% confidence intervals are presented in Figure 2. The figure clearly shows a reactivity advantage for h-CaO over c-CaO at longer times despite nearly identical surface areas and porosities. To eliminate any possible effects of pore plugging, the fitted data were then extrapolated to a theoretical porosity of zero using a linear approximation as shown in the example in Figure 3. From the theoretical zero porosity data, rate constants k_s (for c-CaO) and k_p (for h-CaO) were extracted at each temperature investigated. Figure 4 pre-

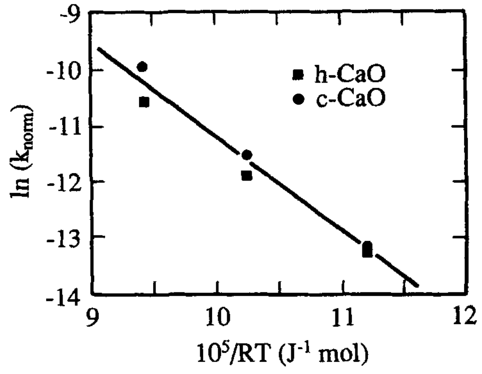

Figure 5. Arrhenius plot of zero porosity conversion data.

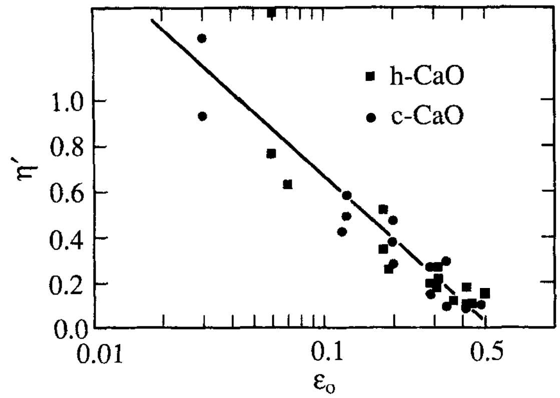

Figure 6. Relationship between η' (k_{obs}/k_{pred}) and initial porosity for h-CaO and c-CaO sorbents.

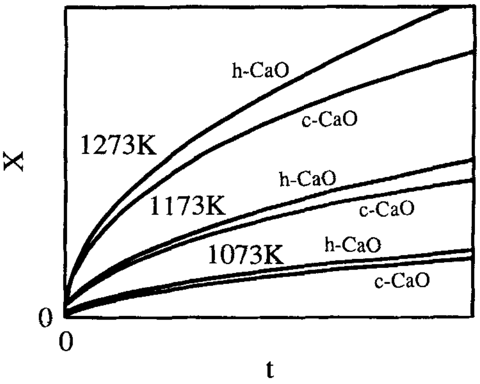

Figure 8. Trends predicted by model for h-CaO and c-CaO at 1,073, 1,173 and 1,273 K for arbitrary initial surface area and reaction time.

sents the fitted curves at 1,073 K, one of the three temperatures tested. Reactivity differences between h-CaO and c-CaO at zero porosity are minimal due to the low values for the initial surface areas (5.2 and 5.0 m^2/g, respectively).

From Eqs. 5 and 9 a plot of ln $(k_s/0.667S^2)$ or ln $(k_p/2S^2)$ vs. 1/RT will yield an intercept of ln $(MD_oC\rho)$ and a slope of $-E$, assuming that D_o and E are the same for both sorbent types. Determining the value of $MD_oC\rho$ in this manner avoids the necessity for evaluating the order of the SO_2 concentration dependence, a matter of some debate among researchers, as long as the concentration is constant throughout the experiments. Figure 5 presents this plot, resulting in the following expressions for the rate constants:

$$k_s = 124S^2 \exp\left[-164{,}300/RT\right] \tag{10}$$

and

$$k_p = 372S^2 \exp\left[-164{,}300/RT\right] \tag{11}$$

The value obtained for the activation energy (164,300 J/mol) compares favorably with that of Borgwardt and Bruce (1986) under similar experimental conditions (153,200 J/mol), and agrees with the range normally seen for diffusion of ions due to thermally induced lattice defects (Bénière and Catlow, 1983).

Utilizing Eqs. 10 and 11, predicted k values, k_{pred}, for porosities greater than zero were then calculated. Comparison with the experimental values, k_{obs}, showed that as porosity (and surface area) increased, the ratio of k_{obs} to k_{pred} decreased due to effects of pore plugging from formation of the more voluminous $CaSO_4$ product. Pore plugging occurs due to product layer buildup between adjacent grains and results in longer solid diffusion distances for the reactant, which act to slow the reaction (Bhatia and Perlmutter, 1981). As porosity and surface area increase, pore sizes decrease allowing pore plugging to occur more readily. This leads to competition between increased reactivity due to a higher surface area and decreased reactivity due to pore plugging. The effects of pore plugging on the reaction are accounted for empirically by noting the relationship shown in Figure 6 between the k_{obs}/k_{pred} ratios and the porosities of the data. Use of an empirical effectiveness factor, η', obtained from

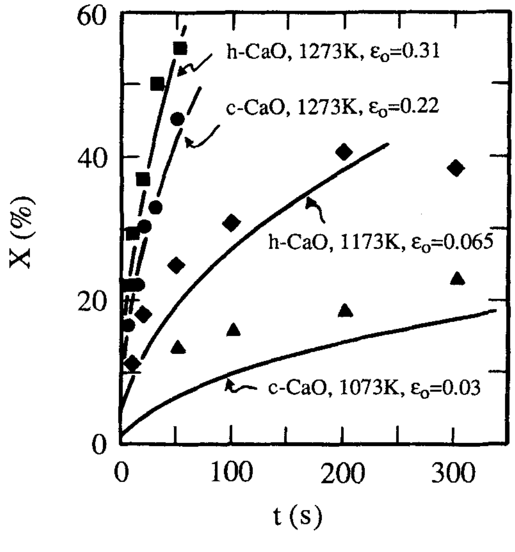

Figure 7. Comparison of model predictions with experimental data.

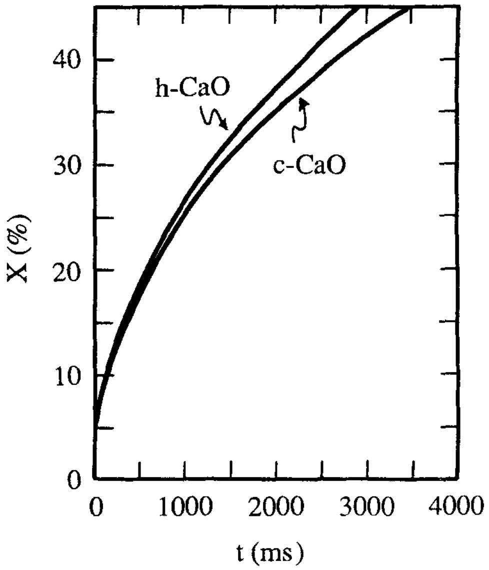

Figure 9. Model predictions of h-CaO and c-CaO conversions (S = 25 m^2/g CaO) at 1,473 K simulating furnact injection temperatures.

this relationship allows the model to closely predict the observed X vs. t curves. Figure 7 compares the experimental data with the model for a wide range of porosities and temperatures.

Close examination of the conversion vs. time expressions for c-CaO and h-CaO obtained by combining Eqs. 10 and 1 and Eqs. 11 and 6, respectively, shows that, for sorbents of the same surface area under identical reaction conditions, a higher reactivity is predicted for h-CaO. Furthermore, it can be seen that the difference in degree of reaction increases with sulfation time and temperature, Figure 8. At 1,073 K and moderate surface area, reactivity differences are insignificant as reported by Borgwardt et al. (1987). However, as the temperature increases, reactivity differences are more pronounced. Still, at the temperatures and residence times expected in a realistic furnace environment, the same surface area results in only slight conversion differences, Figure 9. Reactivity differences predicted by extrapolating results of this work to the high temperatures and short times experienced in a furnace are less than the experimental error associated with such short time measurements. While greater reactivity is seen for h-CaO due to grain structure differences at longer times such as those investigated in this work, particle size differences between commercially available c-CaO and h-CaO probably account for the bulk of the noted reactivity differences in furnace applications at the short times available for sulfation. These results are consistant with those reported for pilot scale tests by other investigators (Beittel et al., 1985; Cole et al., 1986).

A last piece of evidence for the models' interpretation of structural differences between h-CaO and c-CaO precalcines is found in recent scanning electron photomicrographs mentioned by Milne and Pershing (1987). These high resolution photographs clearly indicate an open plate-like structure for the h-CaO which contrasts radically with the more amorphous, sphere-like, c-CaO structure. This agrees with earlier reported SEM analyses by Gooch et al. (1986). These results, along with the aforementioned isotherms, validate the use of divergent rate expressions for the product layer diffusion equation.

Conclusions

Three explanations have been given for the superior performance of hydrated limes, $Ca(OH)_2$, over limestones, $CaCO_3$, in high temperature sorbent injection applications. The first of these explanations, differences in calcination rates between the two sorbents, has been shown in previous investigations to be unimportant by examination of short time reactivity data. The typically smaller particle size of hydrated sorbents has also been clearly shown by other researchers to be the major contributor to their higher reactivity but does not fully explain this phenomenon. Structural comparisons indicate that $Ca(OH)_2$ in the reactive state exhibits a plate-like structure in sharp contrast to the more sphere-like shape of calcined $CaCO_3$. Results of our research indicate that this plate structure results in a faster rate of diffusion of reactant through the growing $CaSO_4$ product layer during sulfation yielding higher ultimate conversions as sulfation times are extended and available pore volume is filled. This effect is exaggerated at longer times and higher temperature regimes, resulting in greater sulfur capture by $Ca(OH)_2$.

Notation

C = SO_2 concentration
D_e = effective product layer diffusivity
D_o = Arrhenius frequency factor
E = activation energy
k_{norm} = normalized rate constant
k_{obs} = rate constant determined from experimental data
k_{pred} = rate constant predicted by model
k_p = rate constant for product layer diffusion model with plate-like grains
k_s = rate constant for product layer diffusion model with spherical grains
L = 1/2 plate thickness
M = molecular weight of CaO
r = radius of spherical grain
R = universal gas constant
S = specific surface area prior to sulfation
t = time
T_p = plate thickness
T = absolute temperature
X = conversion
ϵ_o = porosity prior to sulfation
η' = empirical effectiveness factor
ρ = density of CaO

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