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Role of Porosity Loss in Limiting SO_2 Capture by Calcium Based Sorbents

The extent of high temperature (900–1,300°C), short time (<1 s) SO_2 capture was found to be limited by temperature-dependent losses in the porosity of calcium based sorbents. At 970°C these porosity losses were caused by CO_2-activated sintering. Sulfation of the sorbents either prevented or reduced the extent of porosity losses. Differences in SO_2 capture between hydroxides from different commercial sources, and significantly lower levels of capture by calcium carbonates compared to hydroxides were attributed to differences in particle size and the degree of porosity loss.

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Introduction

The emission of SO_2 from the combustion of high sulfur coals in industrial boilers and furnaces is generally accepted as a major contributor to acid rain. Although flue gas scrubbers adequately control SO_2 emissions, their high cost has discouraged their installation on older units. Consequently, there is considerable interest in the development of low cost SO_2-control technologies such as upper furnace injection of dry calcium-based sorbents.

When $CaCO_3$ or $Ca(OH)_2$ is injected into a high temperature environment, it rapidly calcines (or dehydrates) to form CaO:

$$CaCO_3(s) = CaO(s) + CO_2(g) \tag{1}$$

$$Ca(OH)_2(s) = CaO(s) + H_2O(g). \tag{2}$$

The differences in molar volume between the parent sorbent and the calcine (CaO) result in the formation of highly porous particles. Theoretical porosities of 0.54 and 0.49 can be calculated for calcines from carbonates and hydroxides, respectively, if the initially nonporous particles are assumed to maintain their original particle size. The actual porosity of the calcine is, however, dependent on calcination conditions. Dogu (1981) found that a 1.5 cm limestone calcined below 950°C attained the theoretical porosity (when corrected for impurities), while above 950°C, porosity decreased linearly with temperature. Fischer (1955) measured the porosity of 2.54 cm calcite stones and found that both temperature and heating rate influenced porosity. These losses in porosity from the theoretical value are generally accepted to result from thermally induced sintering mechanisms.

Thermal sintering, a process where many small crystals grow into fewer larger crystals, reduces the specific surface area of a calcine and can result in a measurable decrease in particle size (Murray, 1956). Nicholson (1965) notes that sintering induced by high temperatures takes place by three mechanisms:

- When the ratio of the temperature to the Tammann temperature is less than 0.2, crystal adhesion takes place.
- From 0.2 to 0.5, surface diffusion dominates the sintering process.
- When the ratio is greater than 0.5, bulk diffusion occurs.

The sintering rate of CaO may be significantly accelerated by the presence of CO_2 and H_2O (Borgwardt et al., 1986). These gaseous species promote sintering by forming short-lived compounds [$CaCO_3$ or $Ca(OH)_2$] which create "bridges" between adjacent CaO crystals. When the gaseous specie leaves the crystal structure, the CaO molecules reorganize into a structure which minimizes the free energy of the crystal surfaces. Sintering activated by CO_2 or H_2O will only occur over a limited range of temperatures. When temperatures are too high, the "bridge" specie will be too thermodynamically unstable to occur, and when temperatures are too low, the rate at which the gaseous species enter the CaO crystal structure will be too slow for sintering to be appreciable in the times considered here. The rate of moisture-activated sintering will be greatest near the decomposition temperature of $Ca(OH)_2$, approximately 580°C, while CO_2-activated sintering will be important near the decomposition temperature of $CaCO_3$, approximately 900°C. The overall sintering rate of CaO in a combustion environment is, therefore, the sum of three types of sintering (thermal, H_2O promoted, and

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CO_2 promoted), each of which will be active over specific temperature ranges.

When a calcine is exposed to SO_2 and O_2 at high temperatures, $CaSO_4$ will be formed on the calcine's internal and external surfaces:

$$CaO(s) + SO_2(g) + \tfrac{1}{2} O_2(g) = CaSO_4(s).$$

The rate of this reaction is slow below 900°C, due to kinetic and diffusional limitations, and above 1,300°C, $CaSO_4$ is unstable and the reaction will not occur. Virtually all of the calcine's surface area resides in its internal pore structure (for particles smaller than 1 μm, external surface area becomes important) and the sulfation reaction, therefore, occurs internally. The increase in molar volume from the solid reactant to the product results in a filling of the pore structure and, due to rapid reaction rates and pore diffusional resistances, may lead to plugging of the outer layers of the calcine while leaving the interior unreacted.

The theoretical extent of sulfation is directly related to a calcine's porosity. If it is assumed that the product ($CaSO_4$) fills the entire pore structure evenly, then utilization of a calcine, X, can be related to its initial porosity, ϵ_0, and its porosity at any time, $\epsilon(t)$:

$$X = \frac{\epsilon_0 - \epsilon(t)}{(\alpha - \epsilon_0)(\alpha - 1)} \tag{3}$$

where α is the ratio of the molar volumes of $CaSO_4$ and CaO. The maximum possible utilization of calcines from $CaCO_3$ and $Ca(OH)_2$ with their theoretical porosities would be 55 and 46 percent, respectively.

The importance of the calcine's physical structure for SO_2 capture has been documented by numerous researchers. Bortz and Flament (1984), Cole et al. (1987), Newton (1987), and others have studied the influence of a calcined sorbent's physical structure at short times (<1 s) in combustion environments. The use of sorbents calcined before exposure to SO_2, allows physical characteristics of the calcines (porosity, pore size distribution, and surface area) to be measured and used as inputs for computer model predictions of SO_2 capture by these precalcined sorbents (Newton, 1987).

Predictions of SO_2 capture by raw (uncalcined) sorbents are hampered, however, since the physical properties of the *in-situ* calcine in a combustion environment are not known. Determination of those properties is difficult since the presence of combustion products during sampling (primarily H_2O) promotes rehydration and sintering which significantly alter the calcine's physical structure. One approach for avoiding this problem would be to sample solids calcined in an inert environment (N_2, He, etc.). Sintering activated by CO_2, however, occurs at approximately the same temperature range as the sulfation reaction, and it is likely that combustion gases influence the *in-situ* structure of a calcine during sulfation. The physical properties measured by this approach would not be representative of those occurring in a combustion environment.

This study was conducted to determine the physical properties of sorbents calcined and sulfated in a combustion environment. The use of an experimental reactor fired with a CO flame allowed solids to be sampled without having H_2O present in the sampling system, while providing levels of CO_2 representative of those found in combustion systems.

Experimental Systems

Measurements of SO_2 capture and solid samples were obtained using the Short Time Reactor (STR) illustrated in Figure 1. The STR has a reaction zone 10 cm in diameter by 122 cm in length, and can be operated from 930 to 1,370°C. Two auxiliary burners are back-fired through annular channels around the main combustion chamber to provide an isothermal reaction zone. Solid samples and SO_2 measurements can be obtained at residence times from 30 to 400 ms when fired at 17.6 kW.

Sorbent was pneumatically injected into the reactor through a radial dispersion injector which ensured complete mixing of the sorbent with the gas phase. Gas samples were taken with a phase discrimination probe (which separates reactive particles from the gas stream), passed through a permeation dryer, and analyzed with a DuPont nondispersive UV SO_2 analyzer.

Solids were sampled from the reactor with an air-cooled isokinetic probe and collected on a filter maintained at 130 to 180°C. Previous work (Cole et al., 1987) has shown that significant rehydration with accompanying surface area loss is likely to occur in sampling systems, due to the presence of fuel hydrogen. The STR was fired, therefore, with a CO flame. It was verified early in this study that the physical structure of calcined sorbent was not altered in the sampling system and that SO_2 capture in CO- and natural gas-fired reactors was comparable. Surface area, porosity, and pore size distribution were determined by nitrogen porosimetry. Porosities were calculated by assuming that only those pores smaller than approximately 10% of the sorbent particle diameter constitute the internal porosity of the calcined sorbent. Three sorbents were used in the study: a Linwood hydroxide [$Ca(OH)_2$, 2.2 μm mass mean diameter (mmd)], a Mississippi hydroxide [$Ca(OH)_2$, 3.1 μm mmd], and Vicron 45-3 ($CaCO_3$, 11 μm mmd). For a more detailed description of the experimental details, see Newton et al. (1988).

In addition to the STR, a small amount of data were taken in an "inert calciner," which is similar in construction to the STR but electrically heated so that measurements could be taken using inert gases.

Results and Discussion

Capture of SO_2 by the Linwood hydroxide is plotted in Figure 2 as a function of time, at a calcium-to-sulfur ratio of 2. Capture occurs rapidly within the first 100 ms and then proceeds at a

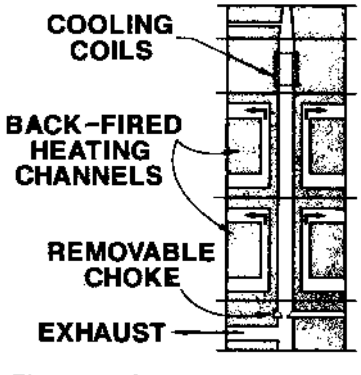

Figure 1. Cross-section of STR.

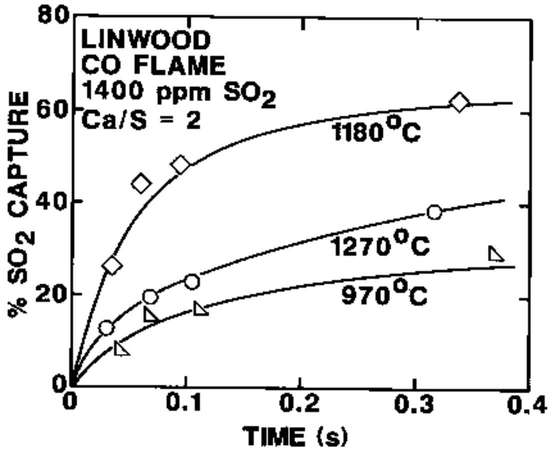

Figure 2. SO_2 capture by Linwood calcium hydroxide in CO-fired STR.

substantially slower rate at longer residence times. Plotting these data as a function of temperature, Figure 3, reveals a maximum in capture between 1,100 and 1,200°C. This type of time and temperature dependence is typical for the CaO-SO_2 reaction and has been observed in many earlier studies (Cole et al., 1987; Newton, 1987).

Surface area

Sorbent was sampled from the STR (both with and without SO_2 present in the reactor) at times and temperatures corresponding to the data in Figure 2. It has been postulated that the sorbent surface area should be greatest immediately upon calcination and then decrease rapidly over a period of several hundred milliseconds (0.3–0.5 s) to some equilibrium value (Silcox et al., 1989). Plots of the measured surface areas, shown in Figure 4, indicate that they did not vary significantly over the range of times and temperatures tested.

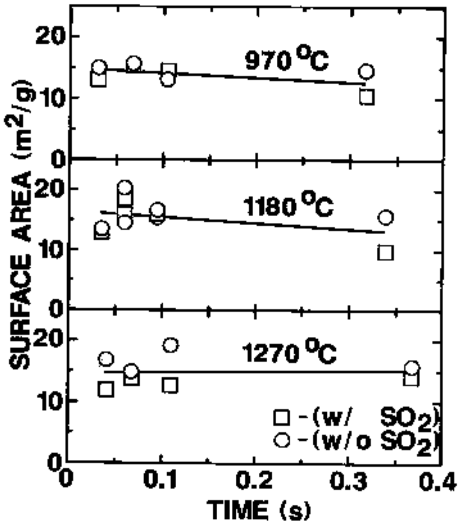

Figure 4. Measured surface areas of flash calcined Linwood calcium hydroxide.

Pore structure

The *in-situ* pore structure of sorbent calcined in a combustion environment has not previously been determined accurately. Pore size measurements taken of sorbents calcined in inert environments may not be representative of those taken in a combustion environment, while those taken from a combustion environment are suspect since the presence of water in the sampling system is known to alter the calcine's physical structure during sampling. The use of a CO-fired furnace allowed pore size distributions to be determined for calcines sampled from a combustion environment without the presence of water in the sampling system.

It has been hypothesized that sintering will result in pore structures whose pores increase in size as temperature is increased (Newton, 1987). Average pore diameters of the Linwood hydroxide sampled in the absence of SO_2, plotted in Figure 5, show this to be true. These average pore diameters did not, however, vary with time. This indicates that the sintering responsible for these variations in pore structure occurs rapidly only during an initial short period (<35 ms) and proceeds at a much slower rate, if at all, at longer times.

Porosity

Hydroxides. Measured porosities of these same samples, plotted in Figure 6, also exhibited no significant trends with time or

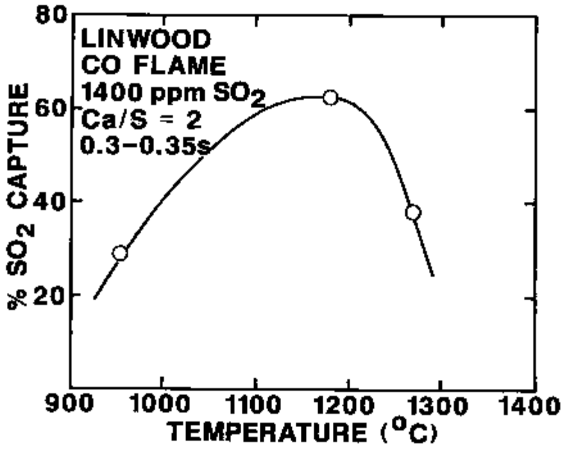

Figure 3. SO_2 capture by Linwood calcium hydroxide vs. temperature.

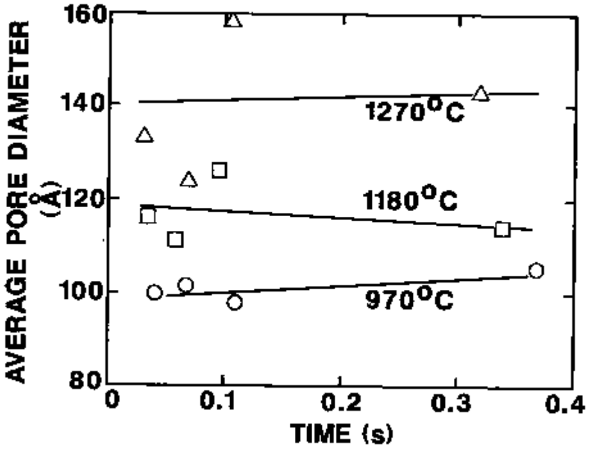

Figure 5. Measured average pore diameters of flash calcined Linwood calcium hydroxide.

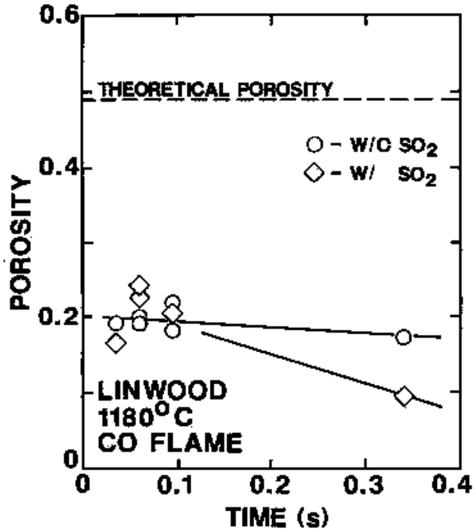

Figure 6. Measured porosity of Linwood calcium hydroxide vs. porosity theoretically possible.

temperature. The comparatively low value of porosity at 1,180°C and the longest time is due to the high level of utilization which is filling the pore structure and reducing porosity. The measured porosities of sorbent sampled with SO_2 in the reactor are not representative of the calcine's initial porosity since the higher molar volume of the product of the sulfation reaction, $CaSO_4$, results in measured porosities lower than the initial porosity. This initial porosity, ϵ_0, can be calculated from Eq. 3 if the extent of sorbent utilization is known. Calculations of this initial porosity, or the "calculated original porosity," based on the data in Figures 2 and 6, are presented in Figure 7 as a function of temperature. The dashed line in Figure 7 represents the theoretical porosity of a calcined $Ca(OH)_2$: 0.49.

For the range of temperatures considered, the measured porosity of sorbent sampled without SO_2 present in the reactor was substantially less than theoretically possible. At 970°C, the calculated original porosity of sorbent sampled *with* SO_2 present in the reactor is also less than theoretically possible, although it is significantly greater than the measured porosity of sorbent sampled *without* SO_2 in the reactor. At 1,170°C, the calculated original porosities are approximately equal to the porosity theoretically possible, and at the higher temperature, 1,270°C, the calculated original porosities of sorbent sampled *with* SO_2 in the reactor were, again, less than theoretically possible but greater than the measured porosity of sorbent sampled *without* SO_2. In summary, the presence of SO_2 reduced the extent of porosity loss, and at the optimum sulfation temperature, completely prevented porosity losses.

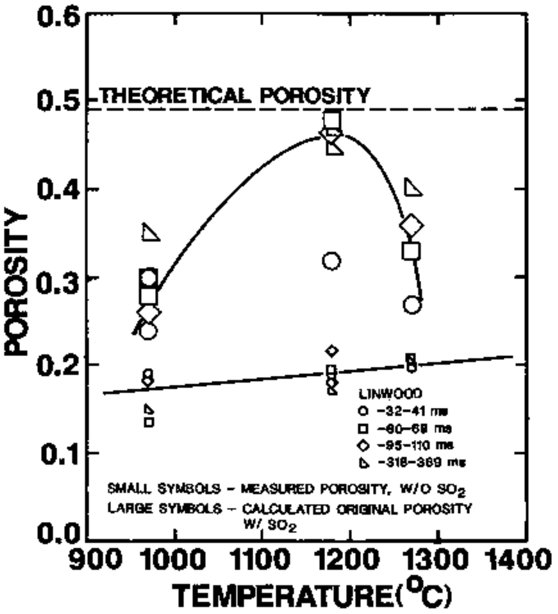

Figure 7. Measured and calculated original porosity of Linwood calcium hydroxide.

One interpretation of these data would be that the calcine pore structure collapses around the sulfated sorbent and is merely a reflection of total sorbent utilization. The data in Figure 6, however, indicates that porosity losses are very rapid and occur at times under 35 ms when sorbent utilization is relatively low. A more likely interpretation is that sulfation of a calcined hydroxide at early times reduces or prevents the observed porosity losses.

The cause of this porosity loss is most likely either thermal or CO_2-activated sintering. A similar set of data was taken in the "inert calciner," operated with an electrically heated N_2 environment (CO_2-free). At 970°C, a temperature at which calculated original porosities were significantly less than the theoretical value, a measured porosity of 0.38 was determined for Linwood hydroxide sampled *without* SO_2 present in the CO_2-free inert calciner. This porosity is greater than the porosity of sorbent sampled under similar conditions in the presence of CO_2, and is approximately equal to the calculated original porosity of sorbent sampled with SO_2, shown in Figure 7. This indicates that CO_2-activated sintering is responsible for the low measured porosities of sorbent sampled without SO_2 present in the reactor.

The mechanism which prevents the extensive porosity losses of sorbent sampled in the absence of SO_2 is not known. One possibility is that the formation of a layer of $CaSO_4$ creates a diffusional barrier which reduces CO_2 access to the CaO crystal structure. A second possibility is that, once CO_2 has entered the CaO crystal structure, the layer of $CaSO_4$ prevents the forma-

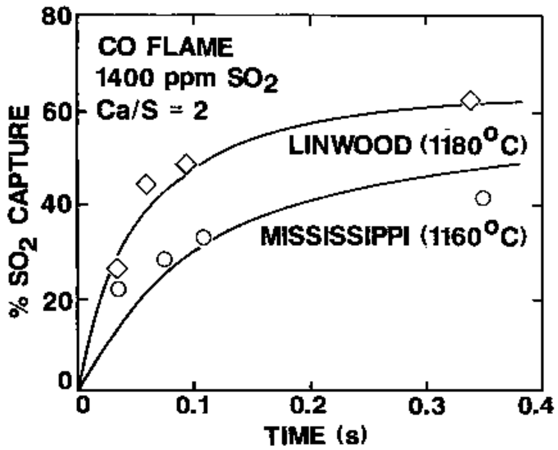

Figure 8. SO_2 capture by calcium hydroxides from different commercial sources.

tion of the transient $CaCO_3$ "bridges" between adjacent CaO crystals.

Hydroxides from different manufacturers are known to vary in their ability to capture SO_2 (Newton et al., 1988). To provide insight into this phenomenon, SO_2 capture and sorbent structure were characterized for a Mississippi hydroxide which consistently yielded lower capture levels than the Linwood. Capture of SO_2 by the Mississippi hydroxide in the CO-fired STR is shown in Figure 8. Calculated original porosities for these two sorbents, plotted in Figure 9, reveal that the Mississippi hydroxide is subject to a greater degree of porosity loss than the Linwood hydroxide. This greater porosity loss coupled with the slightly greater particle size of the Mississippi hydroxide (4.1 vs. 2.2 µm) probably accounts for its lower levels of SO_2 capture.

Porosity

Carbonates. Numerous studies have documented that SO_2 capture by calcium carbonates is substantially less than capture by calcium hydroxides, a phenomenon which has often been attributed to the larger particle size of carbonates. To verify this, sorbent was sampled from the CO-fired STR, and SO_2 capture measurements were taken as a function of time at the optimum sulfation temperature (1,160°C) with Vicron 45-3 (11 µm) and a 7 µm size cut of the Vicron 45-3. Capture by the 7 µm Vicron, shown in Figure 10, was greater than that by the parent Vicron (11 µm) but still substantially less than capture by the Linwood hydroxide.

Plotted in Figure 11, porosities of the two sized Vicron carbonates sampled *without* SO_2 present in the reactor were, as with the Linwood hydroxide, substantially less than the porosity theoretically possible, or 0.54 for $CaCO_3$. To calculate the original porosity of calcined and *sulfated* $CaCO_3$, the extent of calcination (plotted in Figure 12) must also be considered since carbonates calcine at substantially lower rates than hydroxides. Plotted in Figure 11, the calculated original porosities of the two Vicron sorbents increase and approach steady-state values of 0.32–0.36. Two observations can be made from these data.

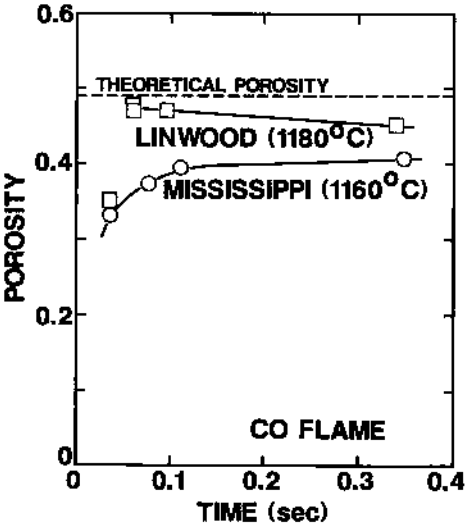

Figure 9. Calculated original porosities of flash calcined calcium hydroxides from different commercial sources.

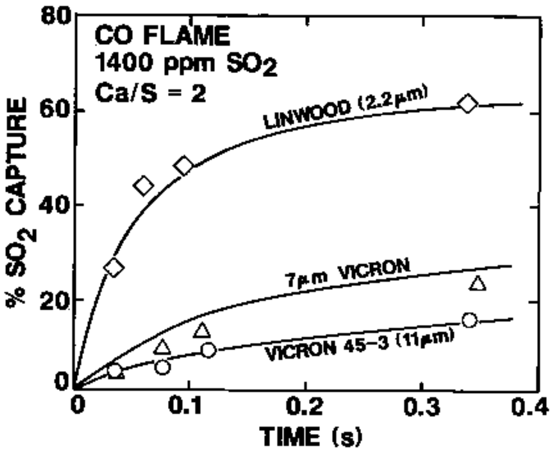

Figure 10. Comparison of SO_2 capture by calcium hydroxide and calcium carbonates.

First, the steady-state calculated original porosities of the two carbonate sorbents sampled *with* SO_2 present in the reactor, are much less than the porosity theoretically possible for $CaCO_3$. This is in contrast to the Linwood hydroxide, which had a maximum in calculated original porosity at the optimum sulfation temperature approximately equal to its theoretical value. Carbonates, therefore, appear to be more susceptible to porosity losses during sulfation than hydroxides. This extensive porosity loss during sulfation, coupled with the larger particle size of the carbonates, accounts for their lower levels of SO_2 capture compared to hydroxides. This greater degree of porosity loss by carbonates may result from:

1. Differences between the crystal structure of CaO from calcium carbonates and hydroxides, which allow CO_2 to more easily diffuse through the crystal structure of CaO from $CaCO_3$. (Gullett and Bruce, 1987, offer evidence which suggests that the pores in these two types of CaO are, in fact, shaped differently).
2. The presence of CO_2 from the decomposition of $CaCO_3$

Either of these mechanisms could lead to increased rates of CO_2-activated sintering and greater degrees of porosity loss.

The second observation made from the data in Figure 10 is that the extent of porosity loss is not constant with time. The increasing calculated original porosities indicate that those portions of the carbonates which calcine at later times do not experience the same degree of porosity loss as those which calcine rapidly. If it is assumed that the uncalcined portions have the theoretical porosity of a calcined carbonate (0.54), projected original porosities ($\epsilon_{0,p}$) at complete calcination can be calculated as a function of time:

$$\epsilon_{0,p} = \epsilon_m x + 0.54(1 - x), \tag{4}$$

where ϵ_m is the measured porosity, and x is the extent of calcination. The projected values, also shown in Figure 11, are constant with time, thus indicating that the fraction calcined after 35 ms obtains the theoretical porosity of a carbonate. It is that portion which calcines rapidly that is subject to porosity losses. By 35 ms, the calcining carbonate has undergone a moderate level of sulfation which may prevent any further collapse.

Summary

The use of a CO-fired reactor allowed calcines (CaO) of $CaCO_3$ and $Ca(OH)_2$, to be sampled without significantly alter-

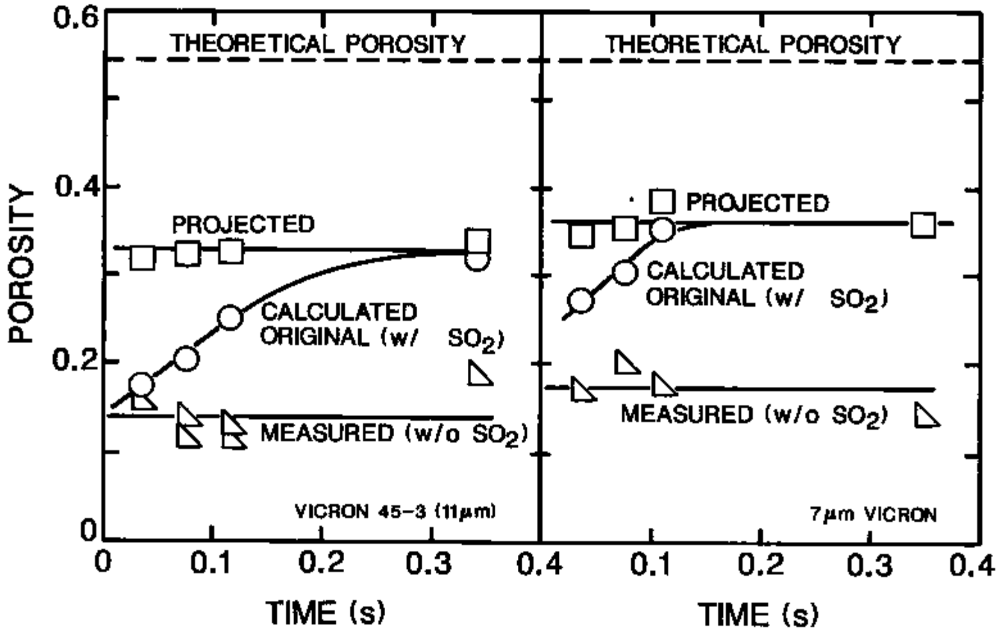

Figure 11. Measured porosity, calculated original porosity, and projected original porosity.
Assuming the uncalcined fraction will have the theoretical porosity of calcium carbonates.

ing their physical structure. Determination of physical properties revealed that sorbents injected into a high temperature combustion environment obtain porosities significantly less than theoretically possible. This porosity loss was greatest in the absence of SO_2. For the calcined Linwood hydroxide, however, when SO_2 was present, the extent of porosity loss was either reduced or, at the optimum sulfation temperature, completely prevented. Data taken from a CO_2-free reactor, electrically heated to 970°C, indicated that these porosity losses result from CO_2-activated sintering. Sulfation may prevent porosity losses due to CO_2-activated sintering either by forming a $CaSO_4$ diffusional barrier which reduces access of CO_2 to the CaO crystal structure, or by interfering with the formation of transient $CaCO_3$ "bridges" which are necessary for CO_2-activated sintering to occur.

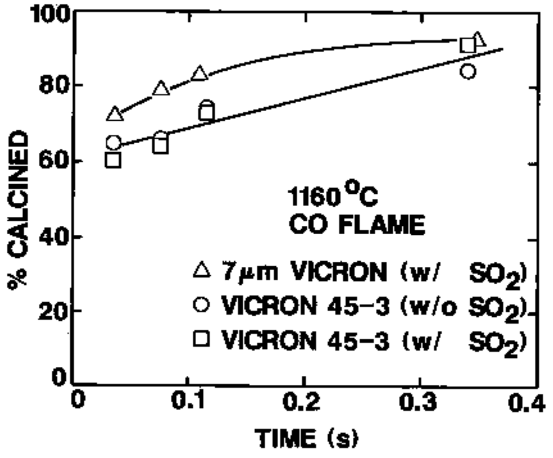

Figure 12. Extent of calcination for two calcium carbonates.

Slightly lower levels of SO_2-capture by a hydroxide from a different commerical source, a Mississippi hydroxide, were attributed to a greater particle size and slightly greater extent of porosity loss during sulfation.

Carbonates suffered substantially greater degrees of porosity losses than the hydroxides. This extensive porosity loss during sulfation, coupled with the larger particle size of the carbonates, accounts for their significantly lower levels of SO_2 capture compared to hydroxides. Analysis of the porosity data for the carbonate sampled from the reactor indicated that the fraction of sorbent which calcines rapidly, suffers porosity losses, while the fraction which calcines more slowly, attains the porosity theoretically possible for $CaCO_3$. At the longer times the calcine/carbonate has undergone a moderate level of sulfation which may prevent any further porosity losses.

Acknowledgment

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