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Project Summary

Fundamental Studies of Dry Injection of Calcium-Based Sorbents for SO₂ Control in Utility Boilers

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A research program was conducted to determine the mechanisms which limit the extent of reaction between sulfur dioxide (SO_2) and calcium-based sorbents [$CaCO_3$ and $Ca(OH)_2$] by measuring the in situ physical structure and reactivity of sorbent injected into a combustion environment for residence times as short as 35 ms. Four models of the sulfation reaction were used to guide the research and interpret the data. The extent of sorbent utilization was found to be limited by porosity losses during the sorbent activation process. In-situ porosities a fraction of that theoretically possible were measured in the absence of SO_2. At temperatures below 1000°C, this porosity loss was determined to be caused by CO_2-activated sintering. The presence of SO_2 during calcination reduced the extent of porosity loss and at optimal temperature sulfation conditions no loss in porosity was observed. At temperatures above 1200°C, porosity losses may result from an increased rate of thermal sintering or a decrease in the rate of the sulfation reaction. Calcines from $CaCO_3$ suffered greater losses in porosity than those from $Ca(OH)_2$ which, along with the larger $CaCO_3$ particle size, accounts for the substantial differences in SO_2 capture between these two sorbents.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Upper furnace injection of calcium based sorbents to adsorb SO_2 has been studied extensively in recent years. A complete understanding of the fundamental physical and chemical processes which occur at furnace temperatures has not, however, been achieved. Previous studies of the sulfation process and well established theories have allowed the rates of external mass transfer, pore diffusion, and product layer diffusion to be calculated. These processes coupled with the chemical reaction, the unknown physical structure of a calcined sorbent, and the extremely high rate of the overall process (the reaction is primarily over within a few hundred milliseconds) make it difficult to determine which of these mechanisms controls the extent of sorbent utilization. Other studies have determined the physical structure of calcined sorbent but only at times much longer than those available in full scale utility boilers. This program was designed to determine the physical structure of calcined sorbents at these early times so

that the mechanisms that limit sorbent utilization can be understood and higher levels of SO_2 capture achieved.

Experimental Facilities

Fundamental experiments were conducted in three research facilities: the Isothermal Reactor (ITR); the Short Time Reactor (STR); and the Controlled Temperature Tower (CTT). Firing rates in these three facilities range from 9.4 kW for the ITR to 26.4 kW for the CTT.

The ITR is an electrically heated drop-tube furnace down-fired by a premixed flat-flame burner. Sampling residence times normally range from 100 to 500 ms with isothermal operating temperatures of 800-1500°C. The STR is a back-fired furnace which operates isothermally at temperatures of 930-1370°C with residence times of 35-400 ms. The STR can operate either isothermally or under quenched conditions and can fire coal as well as gaseous fuels. The CTT is a back-fired reactor designed to simulate the time-temperature histories of a wide variety of coal-fired boilers. The CTT can also fire either gas or coal.

The ITR was used to obtain data on SO_2 capture as a function of time, temperature, and sorbent type. This information was supplemented with data obtained from the CTT on the influence of quench rate on SO_2 capture. To determine the in-situ physical structure of calcined sorbent, solids were sampled from the STR as a function of time, temperature, SO_2 concentration and sorbent type. A CO flame was used during solid sampling to allow sorbent to be obtained without the presence of H_2O in the sampling system while still providing a sulfation environment similar to that in a coal or natural gas fired furnace. Surface area, porosity, and pore size distribution were determined for sorbent collected from the STR.

Modeling

The complexity of the sulfation reaction requires that models of the sulfation process be used to define which process controls the extent of sorbent utilization. Four sulfation modeling approaches were considered in this program: a grain model, a pore tree model, and two distributed pore models. Each model assumes that sorbent particles are spherical and fully calcined prior to the onset of sulfation. In addition, an activation model of the calcination reaction based on the grain model was utilized.

The activation model was developed to simulate simultaneous calcination and surface area loss. It considers $CaCO_3$ decomposition at the $CaO/CaCO_3$ interface, diffusion of CO_2 through the CaO to the particle surface, diffusion of CO_2 from the particle surface to the bulk gas, and continuous, finite rate surface area loss for the calcined material (sintering). The calcination process is represented by a spherical, shrinking core model with the intrinsic calcination rate dependent only on the chemical rate. The sintering rate is assumed to depend on CO_2 concentration and surface area.

All of the sulfation models include the following sequential mechanisms: external mass transfer; pore diffusion; solid state diffusion; heterogeneous chemical reaction; and product layer buildup on the internal surfaces. Each model, however, view the physical structure of the calcine differently.

The grain model treats the CaO particle as an agglomerate of CaO grains whose distribution of sizes is set to match the measured BET surface area. The pore tree model describes the sorbent pore structure as a set of trees of various sizes whose trunks are located at the particle surface. The size distribution of the pores is proportional to $1/r_p^3$, where r_p is the pore radius. Two versions of the distributed pore model were considered: one viewed the pore structure as being made up of an interconnected network of pores, and the other viewed the pore structure as having non-intersecting pores. Both distributed pore models use experimentally determined pore size distributions.

Results

Influence of Temperature

Capture of SO_2 for sorbents sulfated in the ITR and for the Linwood hydroxide sulfated in the STR fired with a CO flame shows that a maximum in SO_2 capture occurs between 1100 and 1200°C. The activation and grain models indicate that the surface area of a sorbent will increase to a maximum immediately upon calcination and then rapidly decrease to an equilibrium value within a few tenths of a second. The surface area of the Linwood hydroxide sampled from the STR, both with and without SO_2 present, does not show this. The surface area of these samples did not significantly vary with either time or temperature. The measured porosity of these solids, plotted in Figure 1, also did not vary with time or temperature and are

much less than the porosity theoretical[ly] possible from $Ca(OH)_2$ (0.49).

The porosity of the calcined sorbe[nt] sampled from the STR with SO_2 prese[nt] has, however, been reduced from i[ts] original value by the buildup of th[e] $CaSO_4$ product layer within the por[e] structure. These original porosities, whic[h] can be calculated when the extents [of] sorbent utilization are known, are plotte[d] in Figure 2. A maximum in calculate[d] original porosity is observed betwee[n] 1100 and 1200°C which is nearly equa[l] to the theoretical porosity of $Ca(OH)_2$. [At] lower and higher temperatures th[e] calculated original porosities were les[s] than the theoretical value. A compariso[n] of these calculated original porosities t[o] the measured porosities without SO_2 present (Figure 1) reveals that when SO_2 is present the extent of porosity loss fro[m] the theoretical porosity is either reduce[d] or prevented.

This dependency of the calculate[d] original porosity on temperature and th[e] presence of SO_2 allows a new hypothesi[s] to be proposed:

The process which causes this porosit[y] loss (sintering) occurs at approximatel[y] the same temperature as the sulfatio[n] reaction. Porosity loss and sulfatio[n] may therefore be viewed as processe[s] which compete for available sulfatio[n] sites. When the mechanism whic[h] causes porosity loss is fast compare[d] to sulfation, the loss in porosity result[s] in low sorbent utilization. Whe[n] sulfation is fast, porosity loss does n[ot] occur and greater levels of sorbe[nt] utilization result.

The dependence of porosity loss o[n] temperature could be caused by either [of] two scenarios. At low temperature[s] (~970°C) the sulfation reaction is slo[w] due to kinetic and diffusional limitation[s] and a large loss in porosity occurs. [At] intermediate temperatures (~1180°C) the sulfation reaction is fast enough t[o] prevent porosity losses. At highe[r] temperatures (>1200°C) the increasin[g] rate of $CaSO_4$ decomposition reactio[n] results in a net decrease in the rate of th[e] overall sulfation reaction, and porositie[s] again drop.

The most likely mechanism respon[sible] for this porosity loss is eithe[r] thermal or CO_2 activated sintering. EPA'[s] B. K. Gullett conducted a similar set [of] experiments in an electrically heate[d] nitrogen (CO_2 free) flow furnace a[t] 1000°C. The measured porosities (with[out SO_2) and the calculated origina[l] porosities (with SO_2) showed n[o]
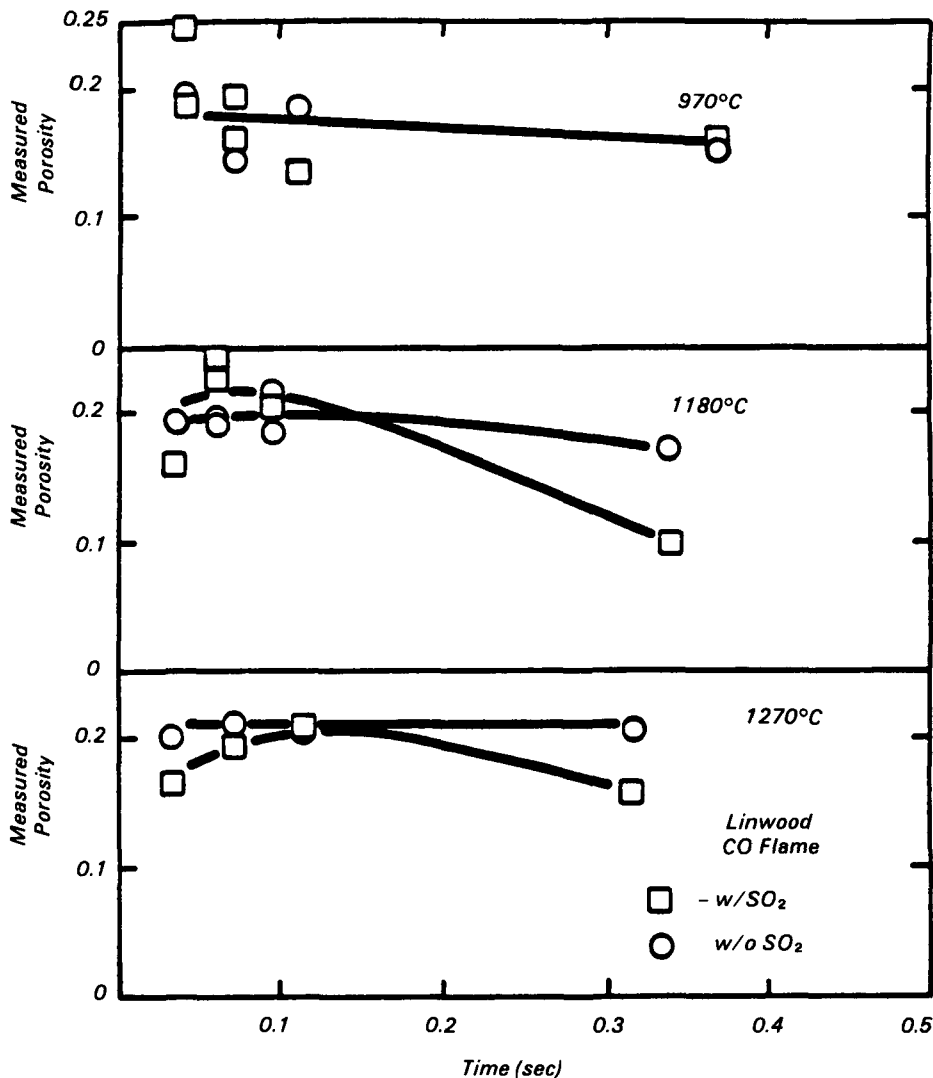
Figure 1. *Measured porosities of sorbent sampled from the STR.*

Influence of Mixing Rate

Mixing of sorbent is known to influence the extent of SO_2 capture. A venturi throat in the ITR provides a completely mixed stream within 7-10 ms, while a straight throat doesn't provide complete mixing until 24-40 ms. Use of the faster mixing throat results in significantly increased levels of SO_2 capture. It was concluded that slower mixing in an isothermal furnace affects SO_2 capture by:

(1) Delaying the onset of sulfation.

(2) Exposing the sorbent to a distribution of temperatures. When mixing is slow, eddies within the sorbent/air jets may obtain temperatures between the jets' initial temperature and the furnace temperature. While at these intermediate temperatures the sorbent will calcine and obtain an original porosity (see Figure 2) different than sorbent which calcines at the furnace temperature. The distribution of original porosities will result in a lower average porosity and lower average sorbent reactivity.

(3) Allowing incomplete mixing to occur. Mixing which is not complete at the end of a furnace may result in eddies with high levels of sorbent (and depleted of SO_2) and eddies containing low levels of sorbent (and high levels of SO_2).

The ITR fitted with the venturi throat has extremely rapid mixing and none of these phenomena are likely to influence SO_2 capture. When fitted with the straight throat, factors (1) and (2) above affect capture.

Influence of Quench Rate

SO_2 capture at higher quench rates result from two mechanisms:

(1) The time available at temperatures where sulfation occurs is reduced.

(2) A finite mixing time exposes the sorbent to a distribution of temperatures. Calcination occurs at a range of temperatures, and a distribution of original porosities results. The lower average sorbent porosity leads to lower sorbent reactivity and lower SO_2 capture. This effect also results in a shift in the temperature where the maximum SO_2 capture occurs.

When this second mechanism was included in the interconnected distributed pore model, it is able to account for the
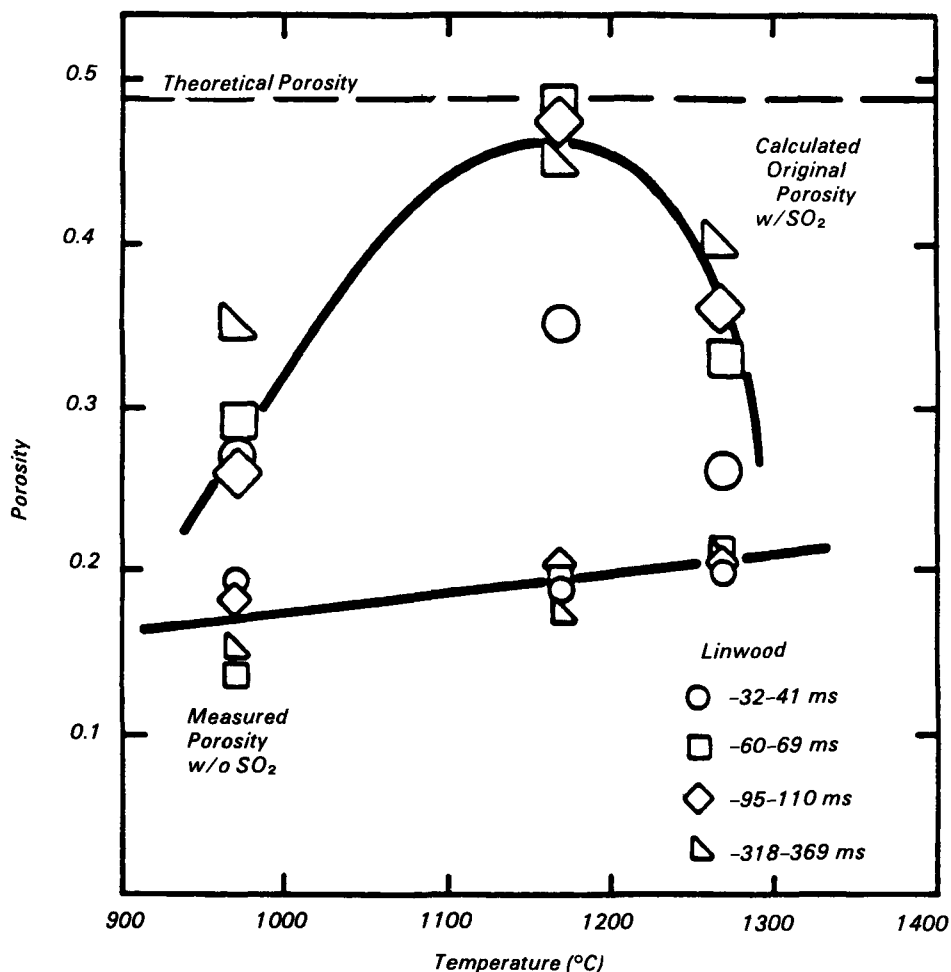
significant drop in porosity from the theoretical porosity of a calcined hydroxide within the first 500 ms. Porosity losses therefore occur only in the presence of CO_2, indicating that CO_2-activated sintering is responsible for porosities less than the theoretical value (at the low temperature range).

The second scenario describing the dependence of porosity loss on temperature is that at the lower temperatures (970°C) the high rate of CO_2-activated sintering is responsible for porosity losses. At the intermediate temperatures (~1180°C) the rate of CO_2-activated sintering slows, and porosity losses no longer occur. At higher temperature range, porosity loss is caused by an

increasing rate of thermal sintering rather than a decreasing rate of sulfation. Data are not currently available to determine which hypotheses is correct.

A modeling approach was developed based on the data obtained in this study. Pore size distributions from the earliest time sampled and an average calculated porosity at each temperature were used as inputs for the interconnected distributed pore model. The results, plotted as solid lines in Figure 3, match the data extremely well. To predict SO_2 capture at the highest temperature (1270°C), the equilibrium concentration of SO_2 above $CaSO_4$ had to be included in the model, as indicated by the dashed line.

Figure 2. Measured porosities and calculated original porosities.

differences in SO_2 capture due to quench rate.

Influence of Sorbent Type

$Ca(OH)_2$ from different commercial sources are known to vary in their ability to capture SO_2. Capture by a Mississippi hydroxide in the STR is significantly less than capture by the Linwood hydroxide. The calculated original porosities for the Mississippi hydroxide, plotted in Figure 4, are less for those than for the Linwood hydroxide. Interconnected distributed pore model predictions indicate that the differences in capture by these two hydroxides result from the slightly larger particle size of the Mississippi $Ca(OH)_2$ and from the greater porosity loss it experiences.

The difference in SO_2 capture between carbonates and hydroxides was investigated in the STR with a CO flame. It has been hypothesized that lower levels of

capture by carbonates result from their large particle size. Calculation of their original porosities, plotted in Figure 5, reveals that carbonates are subject to greater losses in porosity than hydroxides. Predictions by the interconnected distributed pore model indicate that lower SO_2 capture by carbonates results (approximately) equally from their larger particle size and their greater porosity loss. Analysis of the porosity data also indicates that those portions of the carbonates which calcine most rapidly have low original porosities while those fractions calcining more slowly have the theoretical porosity of a calcined calcium carbonate.

Influence of Physical Structure

Average pore diameters for the Linwood hydroxide sampled from the STR without SO_2 present, varied as a function of temperature but not as a

function of time. Pore size distributio corrected to a constant porosity a plotted in Figure 6 for the Linwo hydroxide. Above 80 Å, the distributio are about the same while at below 80 the distributions are scattered. determine the extent that the differences make in SO_2 capture, t pore size distributions in Figure 6 we entered in the interconnected distribut pore model. The results of the calculations, presented in Figure indicate that the observed differences pore size distributions have litt influence on SO_2 capture. To furth determine the influence of pore si distribution on sulfation pore si distributions from the Linwood sorbe sampled at 970°C and 1270°C, t Vicron 45-3 carbonate, the Mississip hydroxide, and the Fredonia hydroxi sampled from a nitrogen reactor 1000°C were corrected to a consta porosity and used as inputs for t model. The predictions exhibit no mo than 6% variation in SO_2 capture. T variations in sorbent pore size distributi resulting from different sulfatic conditions therefore have no significa effect on SO_2 capture.

Conclusions

The goal of this program was determine the mechanism(s) which lin calcium utilization. This was accor plished by investigating the relationsh between sorbent physical structure a various sulfation parameters. In-si sorbent physical structure was dete mined by sampling from the Short Tin Reactor (STR), an isothermal react fired with a CO flame. The use of a C flame allowed sorbent to be sampled the absence of H_2O which was shown degrade calcined sorbent durir sampling.

Investigation of the influence injection temperature on SO_2 capture a sorbent physical structure revealed th calcination of sorbent in a combustic environment resulted in positi dramatically less than theoretical possible – 0.49 for $Ca(OH)_2$. Th presence of SO_2 was found to reduce t extent of or completely prevent porosi loss, depending on the injectic temperature. The cause of this porosi loss was determined to be CO activated sintering. A hypothesis w proposed based on this information:

Porosity loss and sulfation may viewed as processes which compe for available sulfation sites. When t mechanism which causes porosity lo

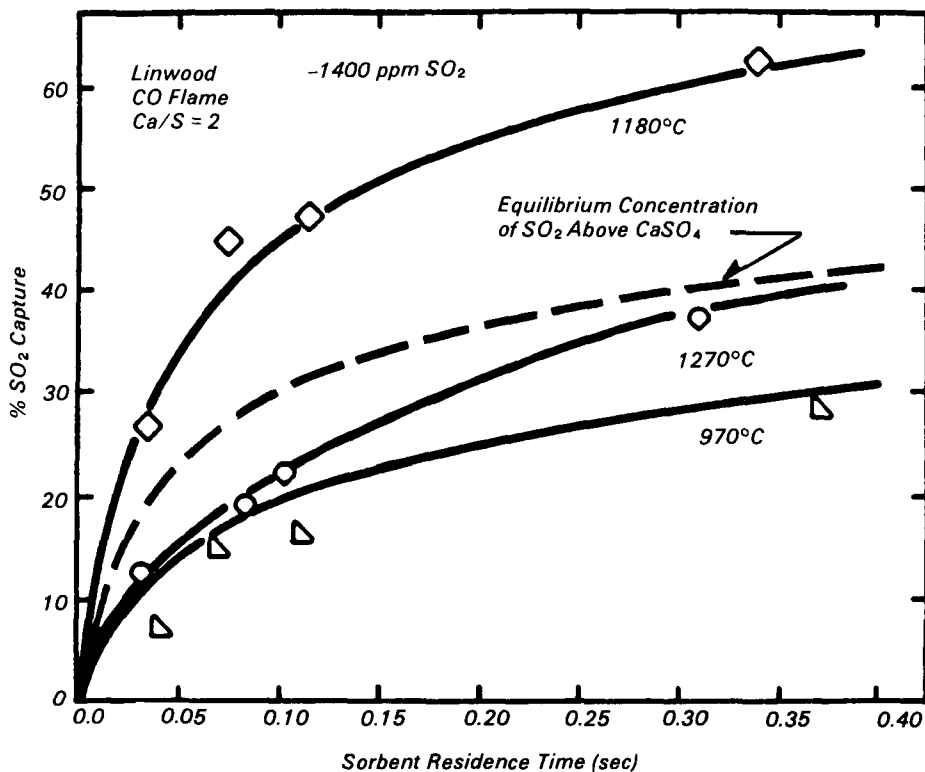**Figure 3.** Interconnected distributed pore model predictions based on calculated original porosities.

cining at longer times obtained the theoretical porosity of a carbonate (0.54).

Modeling indicated that, although average pore diameters varied as a function of temperature (but not as a function of time), the observed variations in pore size distribution had little effect on SO_2 capture when corrected to a constant porosity. The use of pore size distributions from carbonates and from a sorbent sampled from a nitrogen environment did not change the predicted levels of SO_2 capture.
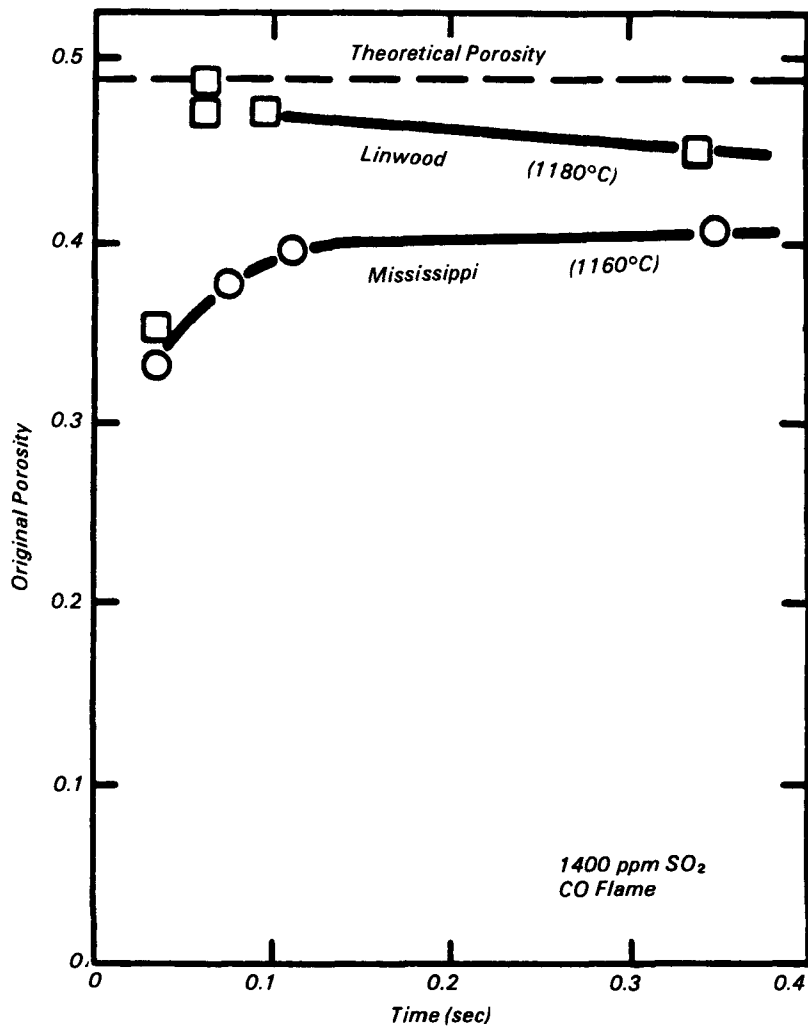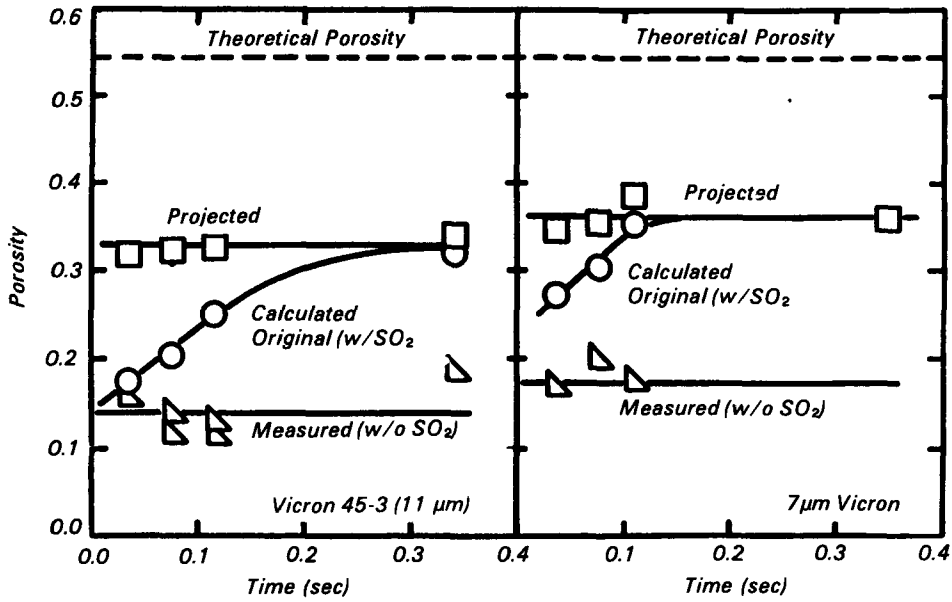
is fast compared to sulfation (at low temperatures, $\sim 970\,^\circ$C), the loss in porosity results in low sorbent utilization. When sulfation is fast ($\sim 1180\,^\circ$C), porosity loss does not occur and greater levels of sorbent utilization result. At higher temperatures ($> 1200\,^\circ$C) the increasing rate of $CaSO_4$ decomposition reaction results in a net decrease in the rate of the overall sulfation reaction and porosities again drop.

It was also noted that, at the higher temperature range porosity losses may result from an increased rate of thermal sintering rather than a decrease in the rate of the sulfation reaction. A distributed pore model, which used the measured pore size distributions and these porosities, was able to adequately predict the observed SO_2 capture without the use of adjustable parameters.

Mixing was found to influence SO_2 capture by (1) delaying the sulfation reaction, and (2) altering the extent of porosity loss by changing the sorbent thermal history. In an isothermal environment with slow mixing, transient

temperatures (between a sorbent's initial temperature and the ambient temperature) may occur resulting in a porosity loss not directly related to the injection temperature.

In a quenched environment, mixing which occurs over a period of time will expose the sorbent to a distribution of temperatures and a resulting distribution of porosity losses. This results in (1) an average porosity different from the isothermal case (for a given injection temperature) and a resulting different capture and (2) a shift in the temperature where maximum SO_2 capture occurs.

The extent of porosity loss and sorbent particle size were found to be the primary factors which determine sorbent reactivity. Different hydroxides experienced significantly different levels of porosity loss, and carbonates suffered dramatically greater losses in porosity than did hydroxides. The degree of porosity loss in carbonates varied with time. Those portions of a carbonate which calcined under 35 ms had a porosity equal to that of a carbonate calcined without SO_2 present (the lowest porosity possible), while portions cal-

Figure 4. Calculated original porosities of two hydroxides.

Figure 5. Measured porosities of solids sampled without SO_2 and calculated original porosities of solids sampled with SO_2 corrected for extent of calcination. The projected original porosities were calculated by assuming that the uncalcined portion of the collected sorbent would have a porosity of 0.54 upon complete calcination.
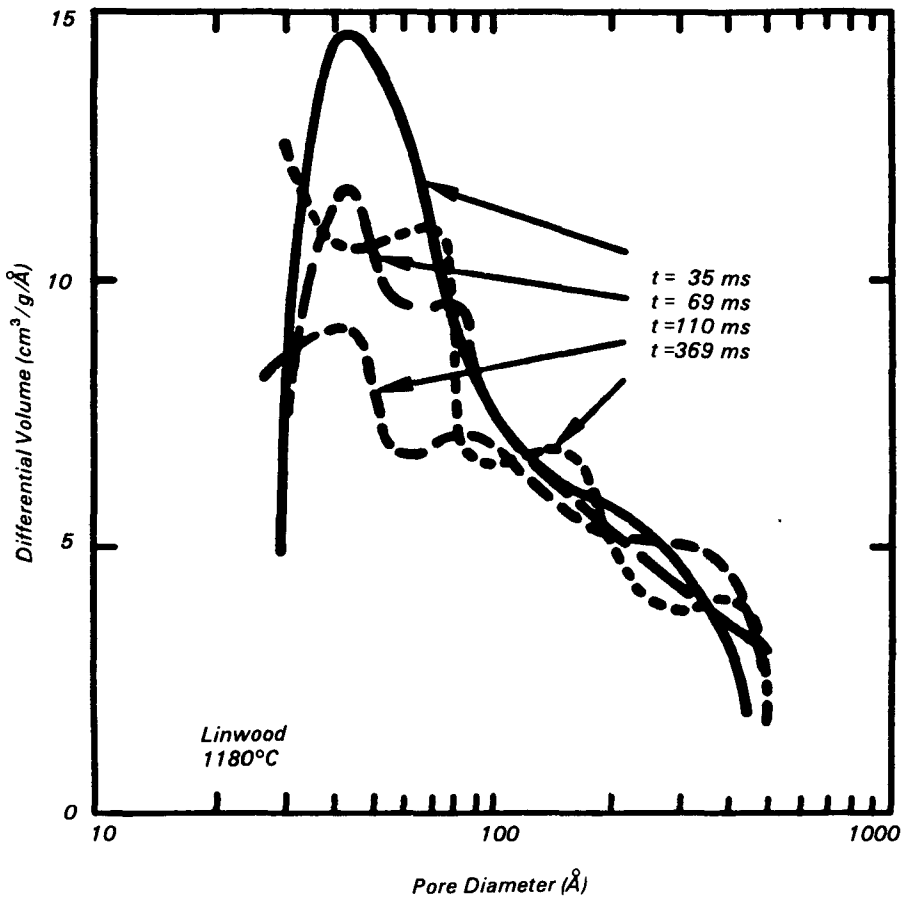
Figure 6. Pore size distributions corrected to a constant porosity.
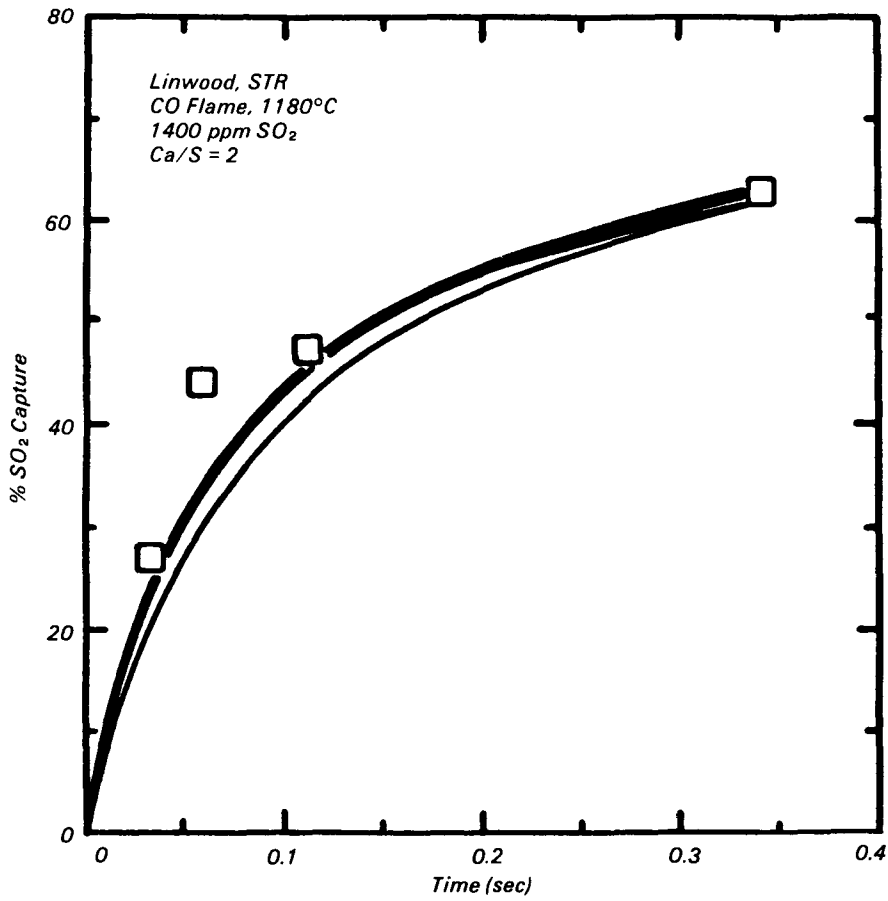
Figure 7. Predictions of the interconnected distributed pore model based on pore size distributions from Figure 6.

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EPA/600/S2-88/069