



Project Summary

Fundamental Studies of Sorbent Calcination and Sulfation for SO₂ Control from Coal-Fired Boilers

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Results are presented from a laboratory-scale investigation of the reactivity of calcium-based sorbents for SO₂ capture after calcination at furnace operating temperatures (1200-1950°C). This work was undertaken to provide fundamental information for developing SO₂ emission control technology in pulverized-coal-fired utility boilers. Pulverized sorbents (<100 μm diameter) were calcined by injection into a laboratory gas flame reactor. Experimental variables were time, temperature, gas composition, limestone type, and particle size. Samples were collected for analysis of surface area, extent of calcination, particle size distribution, and reactivity toward SO₂.

Also investigated were fuel-rich sulfur capture, regeneration of sulfur species into the gas phase, and the effects of fly ash on specific surface area and SO₂ capture.

Particle heating, calcination, and surface area development occurred typically in 25-35 ms. Measured surface areas increased with decreasing calcination temperature; the range for a calcite, Vicron 45-3, was 3-15 m²/g at 1200-1830°C. Surface areas for dolomite reached 25 m²/g. The general order of SO₂ reactivity was dolomite >calcium hydroxide> calcite. Fly ash materials reduced both the surface area and the SO₂ reactivity of the sorbents tested: calcite was affected the most, and dolomite the least. An approximately linear correlation was found between SO₂ reactivity and specific surface area which covered both limestones and limestone/mineral mixtures.

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

Injecting pulverized limestone sorbents into the radiant section of a pulverized-coal-fired boiler, as a way to control SO₂, is being investigated by EPA. This program is largely a development effort designed to elucidate the principal controlling parameters of SO₂ capture and, as a result, allow for process optimization and generalization.

The goal of the present task is to obtain information on the high-temperature short-residence-time reactions involving sorbents under conditions typical of those existing in coal flames.

The objectives addressed are:

1. To determine the physical and thermal phenomena occurring during high-temperature calcination of calcium-based sorbents.
2. To determine the interrelationship between these physical changes and the ability of the sorbent to absorb sulfur compounds.
3. To determine the impact of controllable parameters on physical structure changes; e.g., sorbent type, sorbent size, temperature, stoichiometry, and gas-phase composition.

The approach employed in this effort was to inject a variety of pulverized sorbents into the high-temperature region of a laboratory gas flame. By providing high temperatures ($>1200^{\circ}\text{C}$) and moderate concentrations of H_2O and CO_2 , the gas flame simulated the environment in the radiant zone of a boiler furnace. Several diagnostic techniques were used to relate the changes occurring during calcination to the ability of the sorbents to absorb SO_2 . Both *in-situ* and laboratory analyses were performed in determining the physical and chemical changes of the particles during the short residence times at high temperatures. The experimental conditions, controlled by the laboratory flame environment, were varied to assess the impact of gas-phase temperature and stoichiometry on sorbent properties. Measured physical changes were compared with the ability of the sorbent to absorb SO_2 . In this manner, physical changes were linked to the sulfur reactivity of the sorbent.

Experimental Apparatus and Techniques

The experimental phase of this program involved injecting calcium-based sorbents into high-temperature flames. Physical and chemical processes occurring as a result of sorbent injection into a flame were studied on-line and by subsequent laboratory analysis. Temperature and time in the flame were the most important factors in determining the eventual characteristics of the sorbent.

Sorbent particles were injected into a one-dimensional laminar flame reactor. This flame thermal decomposition reactor (TDR) consists of a sintered bronze, flat-flame burner downfired into a 10-cm square stainless steel chimney. High quality fused silica windows are mounted on two opposing sides of the chimney for visualization measurements. The chimney also provides access for thermocouple measurements as well as sampling, both through ports in the wall and through the bottom of the chimney.

Batch sampling of solids from the flame reactor for physical and chemical analyses was performed with an isokinetic water-cooled stainless-steel probe. The solids were collected in a large-volume filter holder using filter elements with $0.8\ \mu\text{m}$ pore size. The probe was operated above the dew point of the sampled gas ($\sim 70^{\circ}\text{C}$) by restricting the cooling water flow rate. The filter was maintained at 100°C by keeping it in an electric oven.

To determine the ability of flame-injected sorbents to uptake SO_2 , a

"dispersed-phase SO_2 reactivity probe" was constructed. This probe extracted samples from the TDR in the dispersed phase and quenched them to 650°C to prevent further calcination or sintering. The sorbent stream was then drawn into a heated zone where it was mixed with SO_2 and allowed to react. After a fixed residence time, the sorbent passed through a cooled zone and was collected on a microporous glass fiber filter. The reaction zone was heated by a tube furnace which maintained a temperature of $1100 \pm 30^{\circ}\text{C}$ at its midpoint. These conditions were reproducible independent of the TDR flame condition.

Limestone sorbents were generally selected from those used previously in pilot- or bench-scale sorbent study programs. A high-calcium limestone, Vicron 45-3 (mean size $11\ \mu\text{m}$), was used as the base-case sorbent for this program. Also employed were calcium hydroxide (mean size $12.5\ \mu\text{m}$), a fertilizer grade dolomite ($34\ \mu\text{m}$), Marblewhite 125 ($30\ \mu\text{m}$, essentially a larger size cut of Vicron), and a Michigan marl ($18\ \mu\text{m}$), an impure limestone containing metal oxides and an organic component (approximately $\text{CH}_{0.8}\text{N}_{0.041}$) which accounts for nearly 5 percent of the sorbent mass.

Results and Discussion

This section is divided into: calcination studies, surface area studies, sulfur capture, alternate sorbents, mineral matter effects, and a summary.

Calcination Studies

Prior to this study there was a distinct absence of time-to-calcine data for pulverized sorbents for temperatures and gas-phase compositions similar to those found in the radiant zone of pulverized-coal-fired furnaces. Much of the previous data was collected at lower temperatures and/or with larger particle sizes in inert (typically N_2 or air) atmospheres. To investigate the times to calcine under conditions representative of those in furnaces, Vicron 45-3 limestone was injected into a series of hydrocarbon and hydrogen flames in the TDR. Solid samples were then collected at various distances (residence times) and analyzed for degree of calcination. Figure 1 shows the calcination of Vicron 45-3 at various residence times in four methane/air flames. The rate of calcination increases with increasing peak temperatures, and significant extents of calcination are attained in times less than 100 ms at all temperatures.

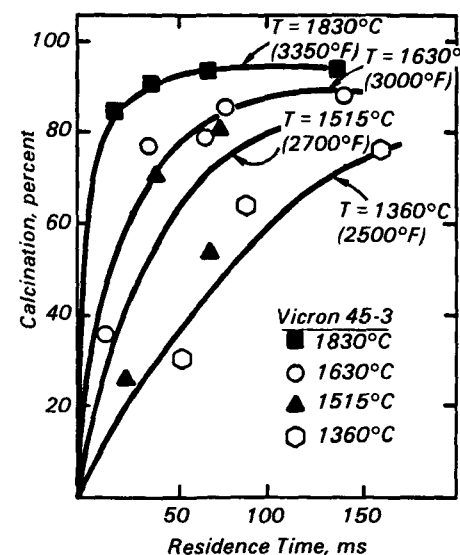


Figure 1. Calcination dependency on residency time for Vicron 45-3 injected into four methane/air flames in the TDR.

The present data are consistent with those of earlier studies. Figure 2 shows an Arrhenius plot of the present data as well as earlier differential reactor data and dispersed-phase data. The zero-order kinetic rate constant recommended earlier predicts a shorter time than was observed for calcination at furnace temperatures because, at these temperatures, the particle heatup time has become a significant portion of the total time required for calcination.

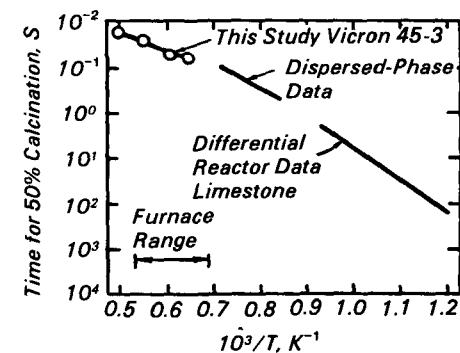


Figure 2. Comparison of present study with other data for calcination of Vicron 45-3 and similar limestones.

Surface Area Studies

Several sorbent properties are believed to have significant influence on sorbent reactivity toward SO_2 , including pore size, total porosity, total specific surface area,

and degree of crystallinity. Also important is the initial sorbent particle size, which is chosen at the outset. These properties, however, manifest themselves in the total specific surface area, which is a readily measurable parameter.

Samples for surface area analyses were collected at various residence times for Vicron 45-3 injected into four methane/air flames identical to those represented in Figure 1. The data are shown in Figure 3. The surface areas measured here (5-10 m²/g) are low relative to those reported for similar stones in lower temperature work and suggest that the calcine is not very reactive.

To test fragmentation of the sorbent during calcination, three samples of Vicron 45-3 were collected in the TDR: the first, collected without a flame; and the other two, collected at long residence time (>150 ms) from methane flames providing peak particle temperatures of 1360°C and 1830°C. All three sorbent size distributions, as determined by X-ray sedimentation, are shown in Figure 4. This shows that fragmentation does occur, and that it increases with increasing temperature. This degree of fragmentation is inadequate to account for the increase in surface area during calcination.

Sulfur Capture

If limestone activation is related to surface area, Figure 3 suggests that reactivity (or calcium utilization) should increase as the peak calcination temperature is reduced. Sulfation test results for Vicron 45-3 in the dispersed-phase SO₂ reactivity probe, immediately following calcination in the TDR, are shown in Figure 5. Although the utilization efficiency does increase somewhat with decreasing calcination temperature, the effect is not as dramatic as the differences in surface areas might suggest. The scatter in the low-temperature data occurs because the ability of the sorbent to calcine effectively is more sensitive to spurious pulses in the sorbent feed rate at these conditions. The higher utilization values are considered more reliable because those samples showed extents of calcination more representative of previous data for samples collected under identical conditions.

Experiments were conducted, with the TDR under both reducing and oxidizing conditions, to determine if sulfur capture at a given flame temperature depended on its capture as H₂S (to form CaS, as in the reducing region of a burner flame) or as SO₂ (to form CaSO₄, as in the oxidizing

region of a burner environment). In these tests, the TDR was operated with a H₂S-doped methane flame, with flame stoichiometry varied (from oxidizing to reducing) by substituting nitrogen for some of the combustion air. The results—over the temperature range 1250 to 1400°C—show that, at a given temperature, calcium utilization after 150 ms residence time is essentially independent of sulfur captured as H₂S or SO₂.

Although sulfur capture by limestone under fuel-rich conditions occurs with effectiveness similar to fuel-lean capture,

one potential limitation is the extent to which the fuel-rich product, CaS, might be oxidized to CaO and SO₂ in the subsequent fuel-lean region of an actual staged combustion boiler furnace. To test for this, a powdered CaS, similar in size to Vicron 45-3, was injected into four fuel-lean methane/air flames. Insufficient data were collected for a detailed analysis of the kinetics of the oxidation reaction, but the data in Figure 6 demonstrate the rapid regeneration of most of the sulfide at furnace temperatures. This level of sulfide regeneration in such a short time

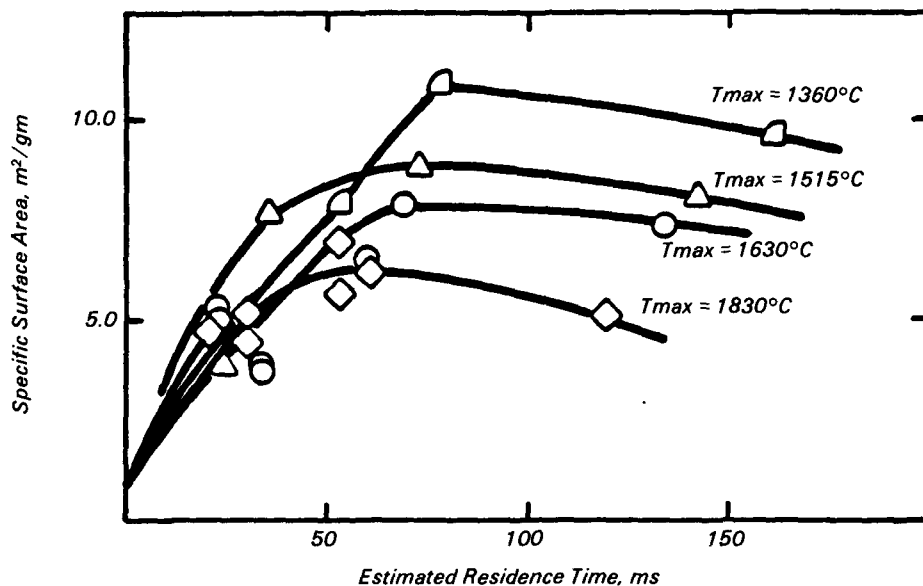


Figure 3. Specific surface area for Vicron 45-3 injected into methane/air flames.

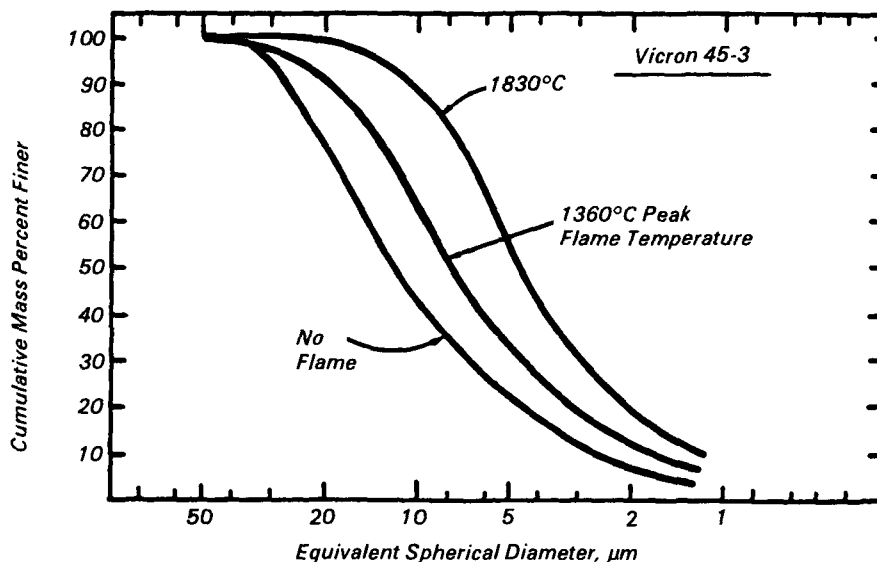


Figure 4. Effect of peak calcination temperature on the ultimate particle size distribution of Vicron 45-3 injected into methane/air flames.

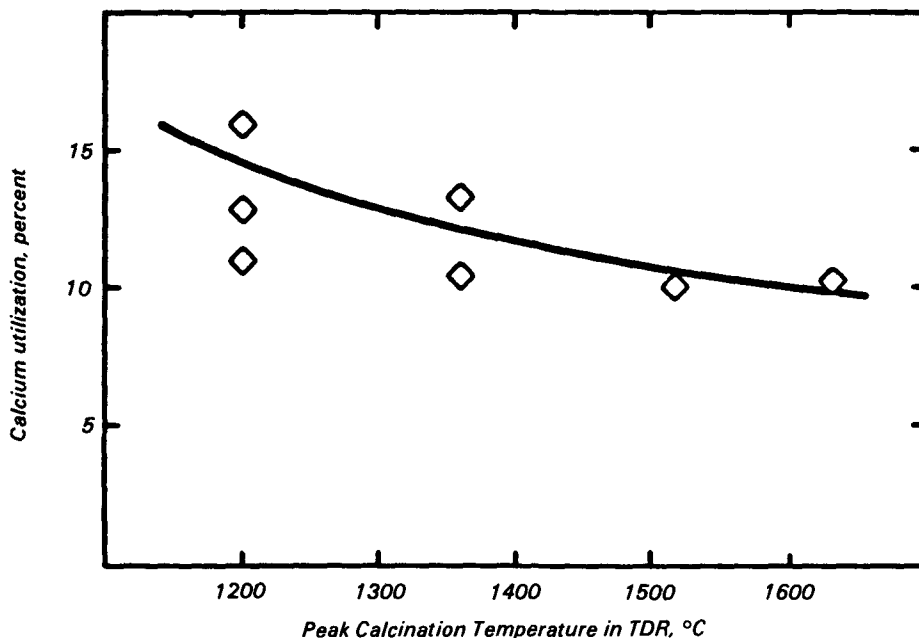


Figure 5. Calcium utilization efficiency of Vicron 45-3 in reactivity probe. Residence time, 600 ms; nominal reaction zone temperature, 1100°C; 6% SO₂ by volume.

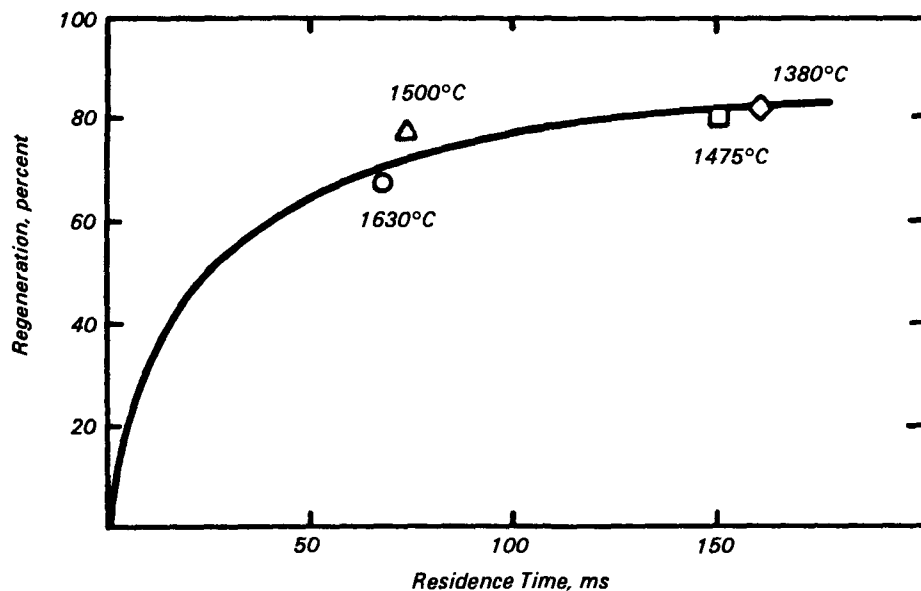


Figure 6. Regeneration of CaS with time in the TDR for fuel-lean methane flames.

(<100 ms) may render the fuel-rich capture process unacceptable unless solids are removed before tertiary air injection.

Alternate Sorbents

The calcitic limestone (Vicron 45-3) was used as a baseline because of its high calcium content, low cost, and the general availability of similar stones.

Sorbents other than Vicron 45-3 may respond quite differently when injected into high-temperature gases. In addition, their reactivity toward SO₂ sorption may relate to specific surface area in a different way. The sorbents chosen for study here have been used previously in bench- and pilot-scale studies and are representative of the major classes of limestones. In addition to Vicron 45-3, another high-

purity calcite having a larger particle size, Marblewhite 125, was investigated. Other calcium-based stones (marl, dolomite, and calcium hydroxide) were tested also.

Figure 7 shows the trends in surface area development and calcination for four alternate sorbents in a 1515°C methane/air flame in the TDR. In this flame the residence times were longer enough in some cases that a slight decline in specific surface area is suggested for all of the sorbents except dolomite. In addition, the extent to calcination rises rapidly at short times for all sorbents, corresponding to the initial particle temperature rise time of about 80 ms. After the initial rise the extent of calcination increased only slowly in the relatively cooler downstream gases. The effect of temperature on surface area was qualitatively the same for the alternate sorbents as for Vicron 45-3, increasing with decreasing flame temperature.

Two of the alternate sorbents, dolomite and calcium hydroxide, were also tested for sulfation in the dispersed-phase reactivity probe following calcination in the TDR. Figure 8 compares the results of these tests with Vicron 45-3 data and with the (unsulfated) surface areas measured when the sorbents were calcined in the TDR under similar conditions of TDR residence time and temperature. For each sorbent, both specific surface area and calcium utilization efficiency increased monotonically with decreasing calcination temperature. However, although Ca(OH)₂ and Vicron 45-3 had very similar surface areas over the range of study, Ca(OH)₂ had a significantly higher calcium utilization efficiency.

Mineral Matter Effects

The effects of coal-ash on limestone reactivity were investigated. To simulate the effects of ash, kaolin, a mineral common in coal ash, was added to Vicron 45-3 to make a 5 percent by weight mixture. The mixture was then injected into several flames and samples were collected for surface area analysis. The results are shown in Figure 9. Kaolin severely reduced the specific surface area of Vicron 45-3 at every condition studied.

Several sorbent mineral mixtures were also tested for sulfation in the dispersed-phase SO₂ reactivity probe. Figure 10 shows the effect of kaolin on the reactivities of dolomite, Ca(OH)₂, and Vicron 45-3. These data should be compared with the results for the pure sorbents in Figure 8. Kaolin has essentially no effect on dolomite and Ca(OH)₂. However, the utilization of Vicron 45-3 was severely

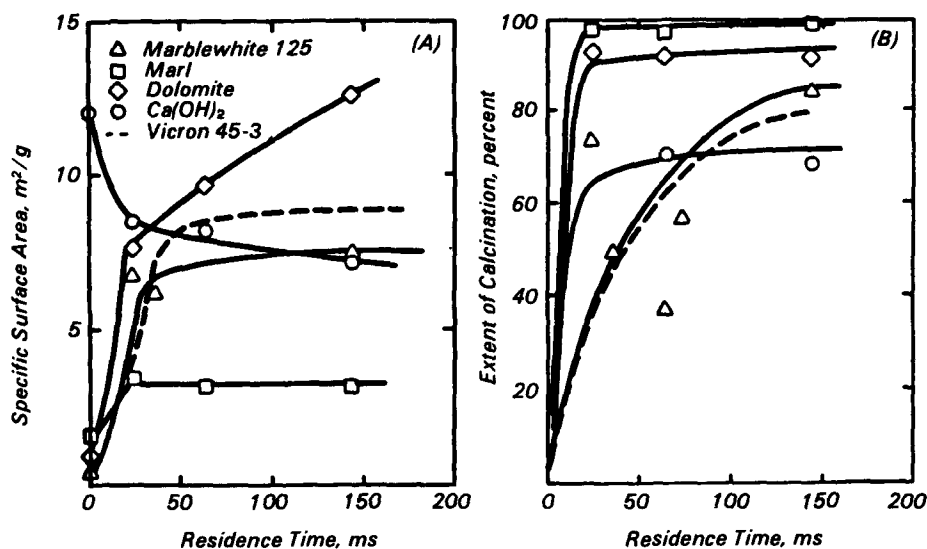


Figure 7. Specific surface area (A) and percent calcination of alternate sorbents (B). Peak calcination temperature 1515°C in the TDR.

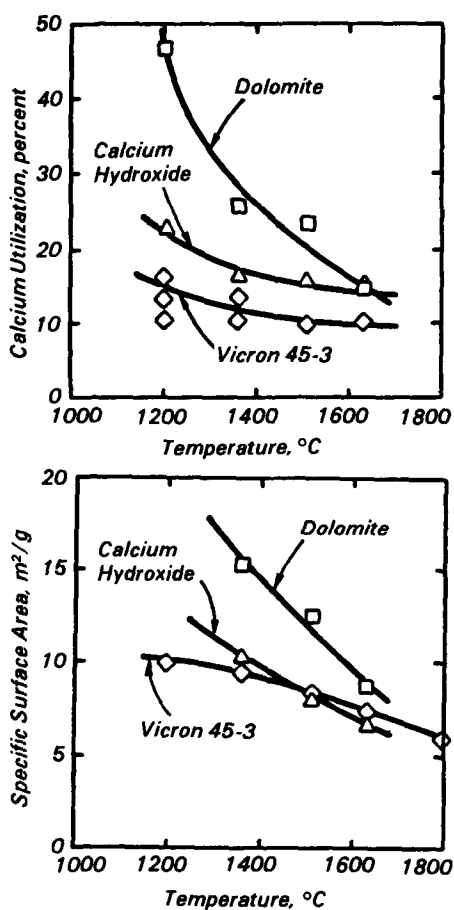


Figure 8. Comparison of surface area development and calcium utilization efficiency as a function of calcination temperature for three sorbents.

reduced, in parallel with the effect that kaolin had on surface area.

Summary

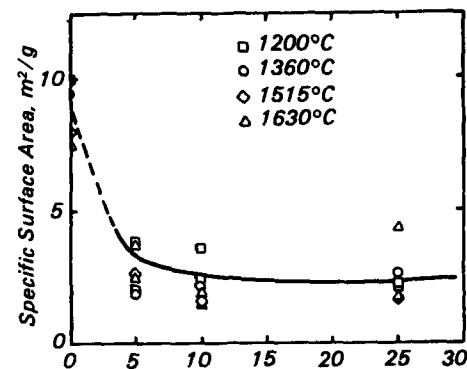
Measurements of the specific surface area of heat-treated sorbents, and of the reactivity of such sorbents for capturing sulfur, have indicated the following points: 1. The physical structure of sorbents (particle size, extent of calcination, specific surface area) after high-temperature heat treatment depends on the sorbent type and peak calcination temperature. 2. The specific surface area as measured by BET techniques provides a reasonable indication of the ability of the calcined sorbent to capture sulfur. 3. The specific surface areas measured for different sorbents calcined under furnace conditions (1200-1800°C) are relatively low (4-15 m²/g) and are inversely related to the maximum temperature that the sorbent has experienced.

The overall effect of surface area on sorbent reactivity toward SO₂ is shown in Figure 11. Although there may be individual trends for each sorbent and sorbent/mineral mixture, the data as a whole demonstrate that reactivity is directly a function of specific surface area after calcination for all sorbents studied.

Conclusions

In this study, the high-temperature short-time behaviors of calcium-containing sorbents were investigated in an environment which simulated the radiant zone of a pulverized-coal furnace. The

physical and chemical changes that influence the ability of the heat-treated sorbents to capture sulfur were measured. A new direct measuring technique was developed, based on the ability of the heat-treated sorbent to capture sulfur without having to quench the sample to ambient conditions. This technique utilized a reactivity probe which allowed the sorbent to be subjected to SO₂ under well-controlled dispersed-phase conditions. A variety of calcium-containing sorbents and mixtures of sorbent and mineral matter were investigated.



Wt-Percent Kaolinite in Vicron 45-3 Before Calcination

Figure 9. Effect of temperature on the ultimate specific surface areas of calcined Vicron 45-3/kaolin mixtures.

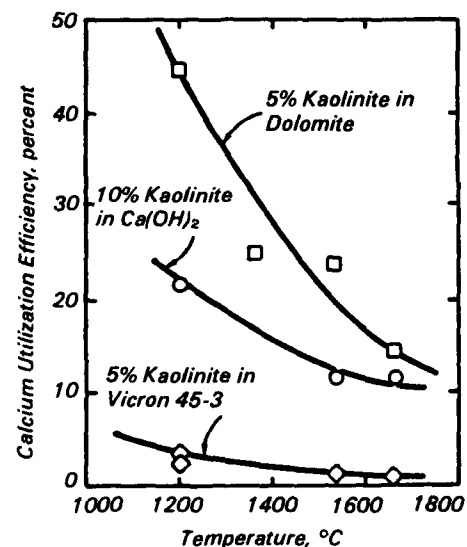


Figure 10. Effect of kaolin on the calcium utilization efficiency of three sorbents.

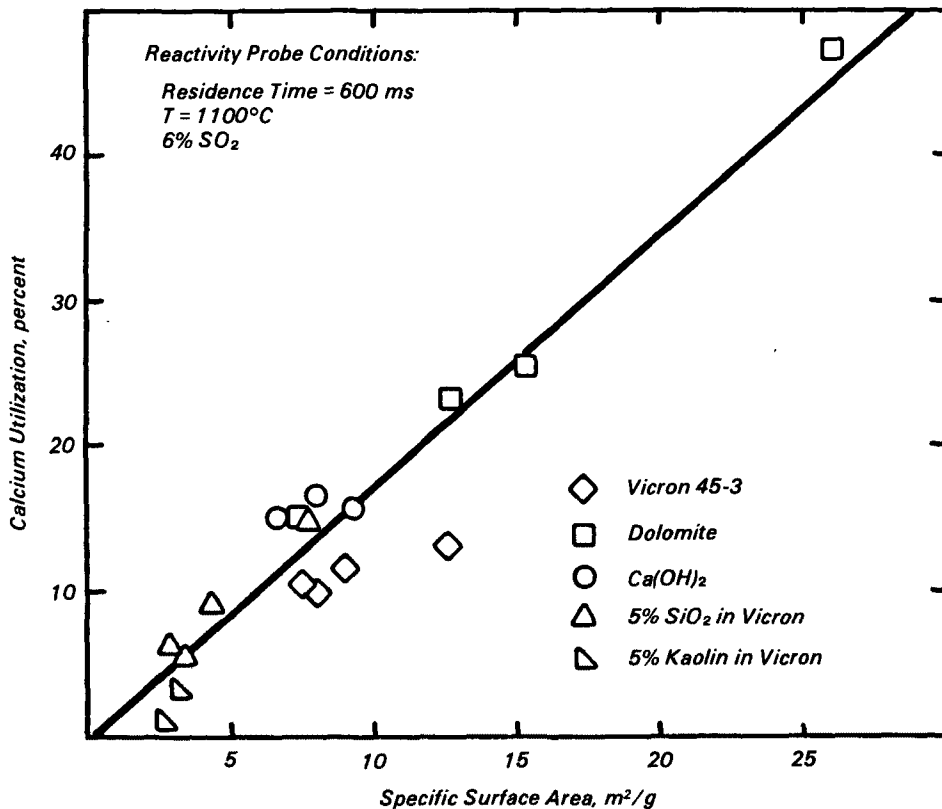


Figure 11. Calcium utilization efficiency of sorbents and sorbent/mineral mixtures as a function of specific surface area of sample calcined under identical conditions. Increasing specific surface area corresponds to decreasing peak calcination temperature for a given sorbent.

Conclusions from the results of this study are:

- At furnace temperatures (1200-1800°C) pulverized sorbents heat and calcine rapidly (<100 ms), although larger particles (>50 μm) may experience longer calcination times.
- Surface area develops in parallel with—and as a result of—calcination. For a given sorbent, higher surface areas are achieved at lower calcination temperatures.
- Thermal comminution of limestone is evident during calcination. However, it alone is not sufficient to account for the measured increase in specific surface area.
- Reactivity for sulfation, for a given sorbent, depends on the specific surface area of the sorbent after calcination, prior to exposure to SO₂.
- Certain minerals will effect a strong decrease in both surface area and SO₂ reactivity after calcination. The result is sorbent dependent.

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G. Blair Martin is the EPA Project Officer (see below).

The complete report, entitled "Fundamental Studies of Sorbent Calcination and Sulfation for SO₂ Control from Coal-Fired Boilers," (Order No. PB 85-221 729/AS; Cost: \$17.50, subject to change) will be available only from:

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