# ISOTHERMAL FLAME STUDIES OF LIMESTONE PROPERTIES RELEVANT TO $SO_2$ REMOVAL FROM P.C. UTILITY BOILERS

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## Introduction

Dry-limestone injection provides an economically attractive means for $SO_2$ emissions control in pulverized-coal-fired (p.c.) utility boilers. The process is especially attractive as a retrofit for older boilers because of the potentially low capital costs relative to other $SO_2$ control technologies (1). In addition, the raw material is readily available and relatively inexpensive (2). Early demonstration tests, however, met with little success. For example, acceptable levels of $SO_2$ removal could not be achieved, even with a large stoichiometric excess of limestone (3).

In an attempt to enhance the capture of $SO_2$, research has been conducted under conditions representative of full-scale systems (4,5). Fundamental experimental and theoretical research has also been undertaken to examine the kinetics of calcination and sulfation (6-11).

The present effort was undertaken to investigate the conditions which will optimize $SO_2$ removal from flue gases by calcium-based dry sorbent injection. The conditions explored included time, temperature, and sorbent type and preparation. Sorbents were injected under experimental conditions which simulated, but did not duplicate, the environment of a p.c. utility boiler. The goal was to provide an environment representative of large-scale systems, but simultaneously well characterized, uniform and reproducible.

The approach to the present study was to utilize a laboratory-scale apparatus to study the sulfur capture reaction $CaO + SO_2 + 0.5\ O_2 \rightarrow CaSO_4$ under isothermal conditions in a flame-gas environment designed to simulate the radiant zone of a p.c. boiler. Powdered sorbents were injected and dispersed into a flow reactor doped with 3600 ppm $SO_2$ and down-fired by a flat-flame burner which provided residence times near 1.5 s for temperatures from 900-1200°C. $SO_2$ sorption was measured as a function of time, temperature, and sorbent characteristics.

## Experimental

Reactor. The reactor is a dispersed-phase Isothermal Flow Reactor (ITR). The ITR provides a relatively long (up to 3.0 s) isothermal zone in which sorbent chemistry

can be studied as a function of time, temperature, and environment. This reactor is unique because it provides a large volume for dispersal of sorbents at reasonable feed rates. This is necessary to permit solids sampling for chemical analysis within practical time frames.

The ITR (Figure 1) is an electrically heated, gas-downfired drop-tube furnace. It has a heated length of 90 cm and accommodates a 10-cm diameter alumina reaction tube. Heating is provided by silicon carbide globars located in three independently regulated heating zones 22.5- 45- and 22.5-cm long. The ITR has a maximum wall temperature of 1500°C.

The ITR is downfired by a porous bronze plug water-cooled flat-flame burner. Limestone was injected into the ITR along the axis of the reactor through the burner. The limestones were injected from a 1.1-mm i.d. tube, which produced a turbulent jet, effectively dispersing the materials over a wide cross section of the reactor. Residence times and heating rates of the particle streams were calculated based on confined jet mixing theory (12) and convective and radiative heat transfer calculations. Heating rates were on the order of $10^4$ K/s and total (end of reactor) residence times of 1.2 - 1.6 s were employed in the experiments described here. Solids sampling from the ITR was accomplished with an isokinetic water-cooled stainless steel probe. Sorbents were quenched rapidly and collected on a glass fiber filter located at the base of the probe. The probe is 1.2 m long and enables sample collection within 40 cm of the sorbent injection location.

Temperature profiles in the ITR are shown in Figure 2. Temperatures were measured using a 0.025-mm diameter butt-welded supported type S thermocouple. Radiation corrections to the thermocouple readings were applied only for non-isothermal reactor conditions, otherwise the corrections were smaller than +5°K. The profiles in Figure 2 are all for hydrogen-air flames. Methane was the fuel used for flame temperatures above 1350°C.

Sorbents. Limestone samples evaluated in this study are listed in Table 1. Each was characterized both before and after injection using several analytical techniques which are listed in Table 2. Most of the raw materials were analyzed for chemical composition, particle size distribution, and specific surface area. Samples collected from the reactors were analyzed for carbon (carbonate), hydrogen (hydroxide), total sulfur (sulfate) and total calcium. From these measurements the extent of calcination and calcium utilization (percent calcium as sulfate) were determined for most samples. In addition, the precalcined dolomite (D60) and precalcined Vicron 45-3 (V40) were characterized by specific surface area and pore size distribution before and after injection into the reactor.

Vicron 45-3 and D3002 served, respectively, as the baseline calcite and dolomite in this study. They both are comparable in mean size, specific surface area and both are high-purity minerals. It was from these limestones that the V40 and D60 precalcines were produced. Surface areas indicated for the precalcines are typical. However, the materials were produced in small batches and surface areas varied between batches. The type S material is a pressure-slaked dolomitic lime.

Table 1. PHYSICAL AND CHEMICAL PROPERTIES OF LIMESTONE SORBENTS

| Material | Composition | Mean Size, m | Surface Area $m^2/g$ | Chemical Analysis, wt% Ca | Mg |
|---|---|---|---|---|---|
| Vicron 45-3 | $CaCO_3$ | 11 | 0.6 | 39.0 | 0.49 |
| D3002 Dolomite | $CaCO_3 \cdot MgCO_3$ | 10 | 0.54 | 24.8 | 11.3 |
| D60 Precalcine | $CaO \cdot MgO$ | -- | 60.67 | --- | --- |
| V40 Precalcine | CaO | -- | 41.45 | --- | --- |
| Type S (Warner) | $Ca(OH)_2 \cdot Mg(OH)_2$ | 1.0 | 18.20 | 28.0 | 15.9 |

Table 2. ANALYTICAL PROCEDURES

| PROCEDURES | DETERMINATION |
|---|---|
| Brunauer, Emmett, Teller $N_2$ absorption isotherm | Specific Surface Area |
| Pekin-Elmer 240B | Carbon, hydrogen det. extent of calcination, hydration |
| Leco SC32 | Total Sulfur |
| ASTM D2795 Chelometric Tritration | Total Calcium |
| Sedigraph (X-ray sedimentation) | Particle size distribution, mean size |
| Mercury instrusion porisimetry | Pore size distribution, true porosity, porosity distribution |

## Results

Calcium utilization was measured as a function of residence time in the isothermal reactor (ITR) for the five sorbents at temperatures of 900, 1000, 1100 and 1200°C. In each case the initial $SO_2$ concentration in the burned gases was 3600 ppm and the sorbent feed rate was adjusted to ensure a calcium-to-sulfur ratio (Ca/S) less than 1.0 so that the measured calcium utilization would not be affected by $SO_2$ depletion in the reactor.

Sorbent Reactivity Ranking. At 900°C (Figure 3) the capture levels of the precalcines and type S are all greater than those of the raw sorbents, D3002 and Vicron 45-3. In part, this is due to the time required for the raw sorbents to calcine. At 1.6 s, the D3002 is still taking up $SO_2$ while the V40 capture profile has leveled off. The type S sorbent has a lower calcination temperature as well as a less endothermic calcination reaction than the raw sorbents. It may in fact calcine so quickly at 900°C that the calcination reaction presents no impediment to sulfation. Similarity in the reactivities of D60 and type S might be an indication of the surface area

attained by the type S material. The D60 and V40 are not expected to sinter (lose surface area) rapidly at this temperature.

At 1000°C (Figure 4) the relative order of reactivity has changed to Vicron 45-3 < V40 < D3002 < D60 < type S. This reflects a large increase in the relative reactivity of D3002. At 1.5 s, the calcium utilization of D3002 is approaching that of the D60 precalcine and from 0.75 s on the V40 remains just about 10 percent more reactive than Vicron 45-3. Both of the raw sorbents exhibit some delay in $SO_2$ uptake due to calcination, but it is not as severe as that experienced at 900°C. All five sorbents display a dramatic increase in reactivity between 900 and 1000°C.

At both 900 and 1000°C the data suggest that $SO_2$ capture occurs rapidly at first. The rate of sulfation then slows abruptly or, in some cases, approaches zero. Pore structure analyses of the D60 and V40 precalcines suggests an explanation for this behavior. The active surface area of the precalcines was found to occur in pores about 80 and 130 A° in diameter for the D60 and V40 precalcines, respectively. These pores represented porosities of 0.18 and 0.13 for the two sorbents. After low temperature sulfation (to avoid sintering) to about 25% utilization the porosities were reduced to 0.15 and 0.08 and the active pore diameter of the sulfated V40 was reduced to about 100 A°. Thus, pore plugging reduces the accessibility of the active sorbent surface to $SO_2$ thereby reducing the global sulfation reaction rate.

Temperature Effects. Figure 5 summarizes the ranking of reactivity of the five sorbents as a function of temperature. The data shown in Figure 5 were taken from smoothed-by-eye reactivity profiles at the residence time of 1.0 s. There is very little uncertainty associated with the ranking in Figure 5 because the slopes of calcium utilization profiles all were shallow at 1.0 s. What has not been taken into account is the delay of the onset of sulfation for Vicron 45-3 and D3002 due to slow calcination at 900 and 1000°C. Accounting for the delay would alter the shapes of the temperature/utilization profiles somewhat; however, it would not be reflective of the ultimate result of low-temperature injection into a p.c. utility boiler where calcination times may be a factor.

The most significant aspect of Figure 5 is the appearance of a maximum in the utilization achieved as a function of temperature. The location of the true maximum appears to be very near 1000°C but may be different for each sorbent. Although such a maximum might have been predicted as a result of the tradeoff between sintering and reaction kinetics, there was no suggestion that it would occur at the same temperature for five different sorbents.

## Conclusions

For simultaneous calcination and sulfation under isothermal conditions, hydroxides and precalcines had the greatest initial reactivity. At longer times and higher temperatures, however, the advantages of precalcines diminished. In general, dolomitic materials were more reactive than calcitic stones. The advantage of the hydrated dolomitic lime may, in part, have been due to a small mean particle size. For all materials the optimal calcination and sulfation temperature was 1000°C, reflecting a balance of slow reaction kinetics at lower temperatures and sintering (surface area loss) at higher temperatures. Conversion profiles exhibited a knee, shifting from rapid to slow or zero rate of conversion, consistent with measured internal pore plugging due to sulfation.

## Acknowledgments

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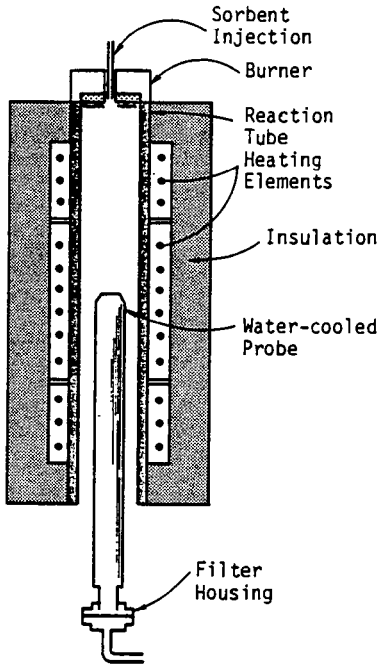


Figure 1. Schematic of the isothermal reactor with the burner and water-cooled probe installed.

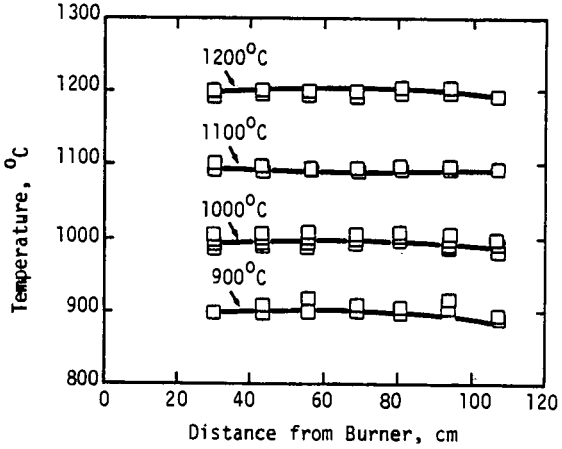


Figure 2. Temperature profiles in the isothermal reactor.

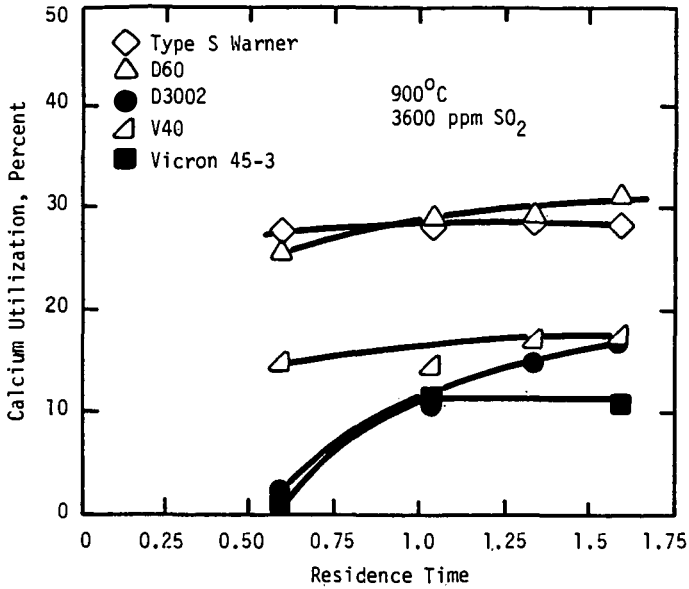


Figure 3. Calcium utilization profiles for five sorbents at 900°C, 3600 ppm $SO_2$.

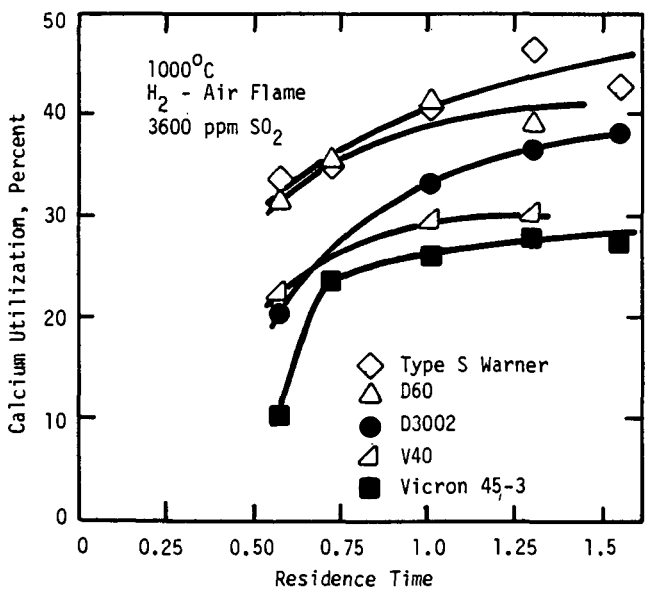


Figure 4. Calcium utilization profiles for five sorbents at 1000°C, 3600 ppm $SO_2$.

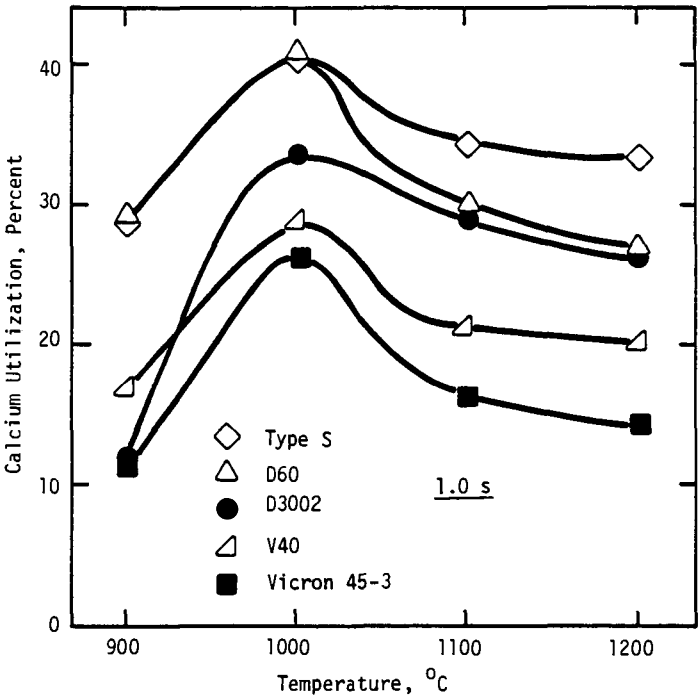


Figure 5. Relative levels of calcium utilization at 1.0 s by five sorbents as a function of isothermal reactor/calcination temperature.