



## Project Summary

# Fundamental Studies of Calcium-Based Sorbents for SO<sub>2</sub> Control from Coal-Fired Boilers

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Laboratory-scale controlled-temperature experiments were used to study aspects of SO<sub>2</sub> capture by calcium-based sorbents in a flame/gas environment. Experimental parameters were sorbent type, temperature, residence time, and the effects of mineral additives, or promoters, on sorbent reactivity. The data revealed that isothermal capture is greatest at 1000°C, above which 1000°C sintering of the sorbent can occur which reduces sorbent utilization. High surface area precalcined sorbents achieved moderately higher ultimate utilizations than their parent carbonates, but their real advantage was more rapid sulfation at lower temperatures where raw stones were limited by calcination. At 900 and 1000°C the time for calcination for carbonate sorbents was significant. Pressure hydrated (Type S) dolomitic limes consistently achieved the highest utilizations. The results suggest that—at ideal sulfation conditions (1000°C, isothermal residence times greater than 1 s, no deactivation of the sorbent by coal ash minerals)—the best calcium utilizations achievable would be about 25-30% with the raw limestone tested (Vicon 45-3), about 30-35% with the raw dolomite tested, and about 40% with both precalcined dolomite (precalcined to a surface area of 60 m<sup>2</sup>/g) and pressure-slaked dolomitic lime. Adding Cr<sub>2</sub>O<sub>3</sub>, alkali metal salts, and certain other promoters increased the utilization of limestone. Cr<sub>2</sub>O<sub>3</sub> effected a fac-

tor of 3.5 increase in utilization after calcination at 1600-1700°C.

*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

Dry injection of calcium-based sorbents is being studied as a way to control SO<sub>2</sub> emissions from pulverized-coal-fired utility boilers. The current objective for the technology is to achieve intermediate levels of SO<sub>2</sub> removal (50-60%) when retrofit onto existing boilers, thus serving as a potential component of an acid rain control strategy.

In the present task, an isothermal drop-tube furnace and a non-isothermal flame reactor were used to study aspects of SO<sub>2</sub> capture in the dispersed phase under controlled conditions, over a range of temperatures representative of a utility furnace environment. The objectives were:

- To determine the sulfur capture reactivity of a wide variety of calcium-based sorbents—including hydrates and high surface area precalcines, as well as carbonates—over a range of temperatures and residence times. This study included assessment of surface area/

reactivity development (during calcination), surface area decay (due to sintering and sulfation), and the sulfation reaction itself.

- To observe physical changes in the sorbent which could be linked to its reactivity.
- To study the effects of mineral matter in either deactivating sorbents, or enhancing their reactivity.

## Experimental

### Apparatus

Discussed here are reactors and sorbent precalcination apparatus.

### Reactors

Two experimental reactors were used in this program. The principal reactor used was the isothermal reactor (ITR), a dispersed-phase, isothermal, drop-tube furnace. The ITR was down-fired using SO<sub>2</sub>-doped gaseous fuel, with electrical wall heating to maintain constant temperature over the reactor length. Sorbent particles injected down through the burner at the top of the unit could have residence times of about 0.5-3.0 s by vertically adjusting an isokinetic, water-cooled, stainless steel sampling probe extending up through the reactor bottom.

The second reactor was a non-isothermal flame reactor, a down-fired unit which could expose sorbents to high temperatures (>1200°C) for short residence times (<0.25 s). The feed sorbents were entrained in a fuel/air premixture prior to injection to ensure rapid heating to peak reactor temperature; heat loss through the reactor walls then resulted in a steep temperature dropoff.

Solids from the flame reactor were generally sampled using a dispersed-phase quartz SO<sub>2</sub> reactivity probe. Samples of dispersed sorbent—calcined in the flame reactor, but not sulfated—were collected in the probe, quenched to 650°C, then exposed to SO<sub>2</sub> under controlled conditions (1100°C, 0.6 s, 6% SO<sub>2</sub>). This reactivity probe permitted sorbents, calcined under a range of conditions in the flame reactor, to be sulfated under constant conditions, so that reactivities (in terms of calcium utilizations) could be compared directly.

### Sorbent Precalcination Apparatus

In order to generate high-surface-area precalcined materials for testing in the reactors, a transpired bed calciner

was developed. The apparatus is a 20-cm diameter stainless-steel can inside a large box furnace. The can has a heavy lid with a single hole for thermocouple access and to allow sweep gas and CO<sub>2</sub> to escape. Raw sorbent is spread in a thin bed on a 400 mesh stainless steel screen. Sweep gas, N<sub>2</sub>, is preheated and passed up through the sorbent bed at controlled flow rates and controlled temperatures.

### Sorbents

The baseline sorbents used in this study were Vicron 45-3 (a calcitic limestone having a mean size of 11 μm) and D3002 (a dolomite with a mean size of 12 μm). These sorbents were also tested following precalcination: precalcine surface areas of 40 m<sup>2</sup>/g were typical for Vicron (referred to as V40); and 60 m<sup>2</sup>/g, for D3002 (referred to as D60). A pressure-hydrated dolomitic lime (mean size 1.0 μm, referred to as Type S (supplied by Warner), was also tested. Several other sorbents were also tested.

In most reactor tests, run results were determined by analyzing sorbent samples from the reactors. These solids analyses included measurements for carbon (carbonate), hydrogen (hydroxide), total sulfur (sulfate) and total calcium, in order to permit determination of the extent of calcination and the calcium utilization (percent calcium as sulfate). Other analyses performed on some samples included specific surface area (nitrogen absorption) and pore size distribution (mercury porosimetry).

## Results and Discussion

### Non-Isothermal Reactor

The report presents histograms of the reactivity for eight sorbents flame-treated in the thermal decomposition reactor at peak temperatures of 1200 and 1500°C, and then sulfated in the dispersed-phase reactivity probe at the standard 0.6 s/6% SO<sub>2</sub> condition. The sorbents included two raw limestones, two dolomites, three hydroxides, and one limestone precalcined to a surface area of 34 m<sup>2</sup>/g. For all sorbents tested, the reactivity decreased by 25-50% when the flame temperature was increased. Previous measurements have indicated that this can be attributed to decreased specific surface area due to more rapid sintering at increased temperature. However, the *relative* reactivity of the flame-treated sorbents is insensitive to flame temperature: only two of the sorbents changed positions

relative to each other at the higher temperature. The limestones were generally the less reactive after flame treatment, followed by hydroxides; the dolomites were the most reactive. The single 34 m<sup>2</sup>/g precalcine (produced from Vicron limestone) was found to be more reactive than the raw limestone from which it was produced. Thus precalcining provided an increased reactivity that was not completely lost when flame-treated for short times (<200 ms).

### Isothermal Reactor (ITR)

Sorbent utilizations in the ITR were determined by sulfur analyses on the sorbent particles after exposure in the reactor. Following the testing described in this report, it was discovered that the utilizations reported here are generally high, by a factor as high as 2, as a result of sulfur uptake by the sorbent in the ITR solids sampling system. These erroneously high utilization values do not change the basic conclusions of this study; however, this error should be borne in mind when the utilization values reported below are compared against values from other investigators.

Calcium utilization was measured as a function of residence time in the ITR for five sorbents at temperatures of 900, 1000, 1100, and 1200°C. In each case the initial SO<sub>2</sub> concentration in the burned gases was 3600 ppm, and the sorbent feed rate was adjusted to ensure a calcium-to-sulfur ratio (Ca/S) of less than 1.0 so that the measured calcium utilization would not be affected by SO<sub>2</sub> depletion in the reactor.

### Effects of Residence Time and Sorbent Types

At 900°C (Figure 1), the utilizations of the D60 precalcine and the Type S hydrate are distinctly the greatest at all residence times; the V40 precalcine is the next most reactive. The raw Vicron and dolomite are the least reactive, especially at low residence times; the roughly 0.5 s delay in the onset of sulfation for the raw sorbents is undoubtedly due to the time required for particle heatup and calcination at this relatively low temperature. The precalcines being already calcined, do not experience this delay, and have almost reached their ultimate sulfation level before the raw stones have even started sulfating. The Type S sorbent also appears to experience no delay due to calcination (dehydration); the hydrator of the hydrate requires a lower temperature, and is less endothermic, than the

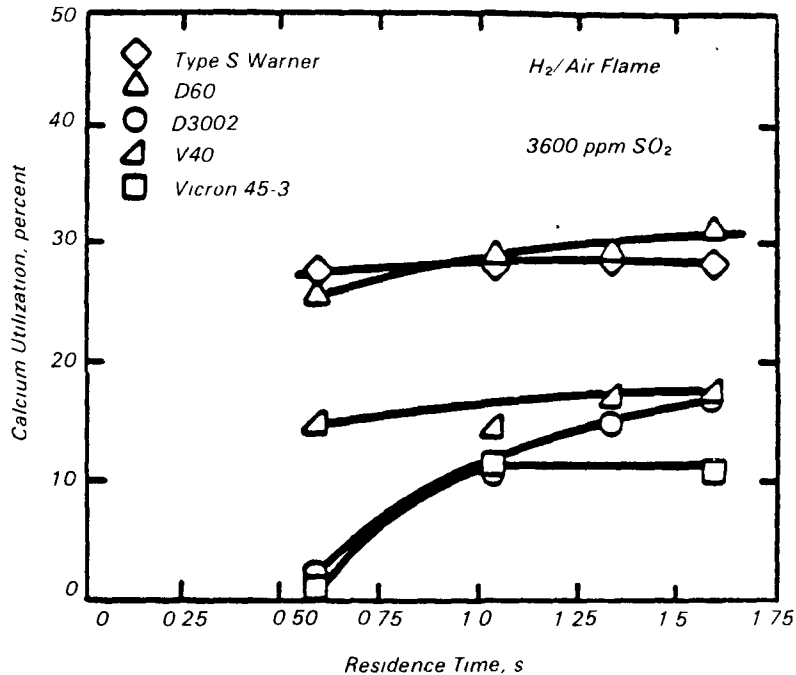


Figure 1. Calcium utilization profiles for five sorbents at 900°C

calcination of the raw carbonates, so that (even at 900°C) dehydration appears to offer no impediment to sulfation.

All five sorbents appear to be approaching an effective "ceiling" on utilization at residence times above about 1 s. This ceiling—at far less than 100% utilization—reflects a significant slowing of the sulfation rate, presumably due to increases in pore diffusion resistance (as internal sorbent pores become blocked due to sulfation and thermal sintering) and to increases in product layer diffusion resistance (as the sulfate layer becomes thicker). The D60 and the Type S sorbents achieve the highest utilization before leveling off (about 30%); the V40 and the raw dolomite reach a lower utilization (less than 20%); and the raw Vicron had the lowest ceiling of all (about 10%). The raw Vicron was only half calcined at 900°C; this is undoubtedly one explanation for the low utilization achieved by the limestone. Insofar as pore diffusion and product layer diffusion resistances are responsible for the apparent utilization ceiling, the utilizations can be increased by going to even finer particle sizes than those tested here.

At 1000°C (Figure 2), all five sorbents display a dramatic increase in reactivity compared to that experienced at 900°C.

However, the relative order of reactivity has changed to Vicron 45-3 < V40 < D3002 < D60 < Type S, reflecting a large increase in the relative reactivity of D3002. Both of the raw sorbents still exhibit some delay in SO<sub>2</sub> uptake due to calcination, but the delay is not as severe as that experienced at 900°C. The Vicron, which was only half calcined at 900°C, is essentially fully calcined at 1000°C.

The apparent ceilings on calcium utilization are much higher for each sorbent at 1000°C relative to 900°C, with the Type S achieving utilizations of over 40% after 1 s. After 1.5 s, the utilization of the raw dolomite is approaching that of the D60 precalcine; after 0.75 s, the V40 utilization levels off at a value perhaps only 2 to 3 percentage points above the raw Vicron. Thus, at this temperature, it would appear that the primary value of a precalcine would be where only short residence times are available, and delays due to calcination cannot be accepted.

### Temperature Effects

Figure 3 summarizes the sulfur capture of the five sorbents as a function of temperature. The data shown in Figure 3 were taken from utilization profiles (analogous to Figures 1 and 2) at the residence time of 1.0 s. The most signif-

icant aspect of Figure 3 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. The maximum is thought to be a result of the tradeoff between sintering and reaction kinetics. It is interesting that the optimum temperature is the same for five different sorbents.

### Cr<sub>2</sub>O<sub>3</sub> Addition

Figure 4 shows calcium utilization for Vicron 45-3 injected into the ITR alone, and mixed with 6 wt% Cr<sub>2</sub>O<sub>3</sub>. For these tests, the ITR was operated at a constant furnace temperature of 1100°C, but the flame temperatures were varied as shown, resulting in a ramped temperature profile from flame temperature to 1100°C. All tests employed 3600 ppm SO<sub>2</sub>. As expected, the utilization of Vicron 45-3 decreased with increasing flame temperature. This reflects both a decrease in surface area upon calcination and, in some cases, a shorter residence time in the sulfation window where sulfation will occur with reasonable kinetics (about 1250 - 1000°C). With the Vicron/Cr<sub>2</sub>O<sub>3</sub> mixture, however, the utilization initially increased as the flame temperature was increased. Subsequently, the utilization decreased until, at a 1950°C flame temperature, the utilization was nearly equal to that of Vicron 45-3 alone. If the ratio of the Vicron/Cr<sub>2</sub>O<sub>3</sub> utilization to the Vicron-only utilization is calculated, this ratio is found to be highest (at a value of 3.5) at a flame temperature of 1600-1700°C. Both the temperature and the magnitude of this maximum in the utilization ratio agree with data obtained in a bench-scale boiler simulator furnace.

### Additional Minerals

Fourteen additional minerals were screened to determine their potentials as sorbent reactivity promoters. The materials, in 5 wt% mixtures with Vicron 45-3, were exposed to 3600 ppm SO<sub>2</sub> under the 1100°C isothermal condition as well as with a 1360°C flame fired into the ITR at a furnace temperature of 1100°C.

Figure 5 shows the results of isothermal tests at 1100°C in bar-graph form. The open section of each bar is the utilization achieved in 0.92 s; the solid portion represents the additional utilization up to 1.4 s. The horizontal lines are the averages of four replicates of the utilizations measured for unpromoted Vicron

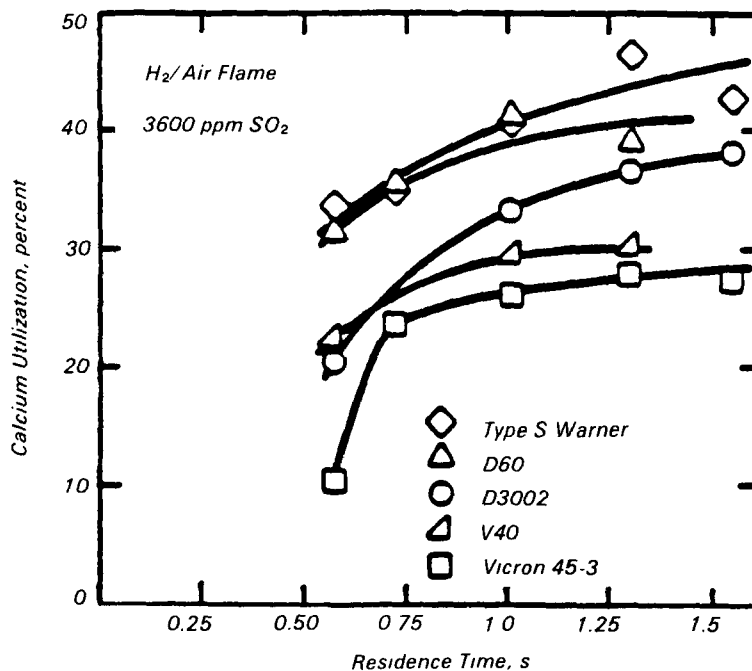


Figure 2. Calcium utilization profiles for five sorbents at 1000°C.

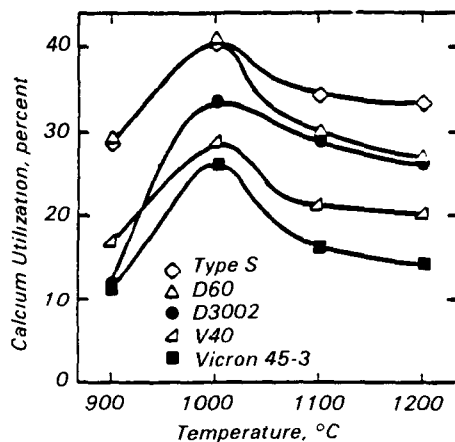


Figure 3. Relative levels of calcium utilization at 1.0 s by five sorbents as a function of isothermal reaction/calcination temperature.

45-3 at the two residence times. Down-pointing vertical arrows adjacent to the data for  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{MoS}_2$  show what their calcium utilizations would be if the sulfur initially present in the additives remained with the additive, and was not released by the additive and captured by the calcium. For the  $\text{Li}_2\text{CO}_3$  mixture, the utilization measured at 1.4 s was lower than that at 0.92 s.

Among the minerals tested, the alkali metal salts as a group showed the most promise as promoters; and lithium, the lightest alkali, produced the greatest enhancement.

Every additive tested, except  $\text{MoS}_2$ , caused a net increase in utilization (compared with unpromoted Vicron) after 1.4 s. The magnitudes of the increases are not as great as were observed with  $\text{Cr}_2\text{O}_3$ ; however, all of the results are above the 95% confidence limit based on the four replicate samples of Vicron 45-3 collected at 1.4 s.

The same promoters were tested under nonisothermal conditions using a 1360°C flame with the ITR walls still at 1100°C. The calcium utilization by unpromoted Vicron 45-3 was considerably lower at this condition than an 1100°C isothermal. This was due in part to thermal deactivation, but also stems from the substantially shorter time that the sorbent had in the sulfation window. The total residence time of the sorbent in the ITR was 0.6 s; however, much of this time the temperature was above 1250°C. The percentage improvement in utilization effected by many of the promoters at 1360°C (relative to unpromoted Vicron) was well above that for the same promoters at 1100°C. However, at the higher temperature, the benefits of improved promoter activity have been offset by increased sintering (and perhaps by the reduced time in the sulfation window); as a result, the absolute value of the utilization at 1360°C never exceeds that at 1100°C for any one promoter.

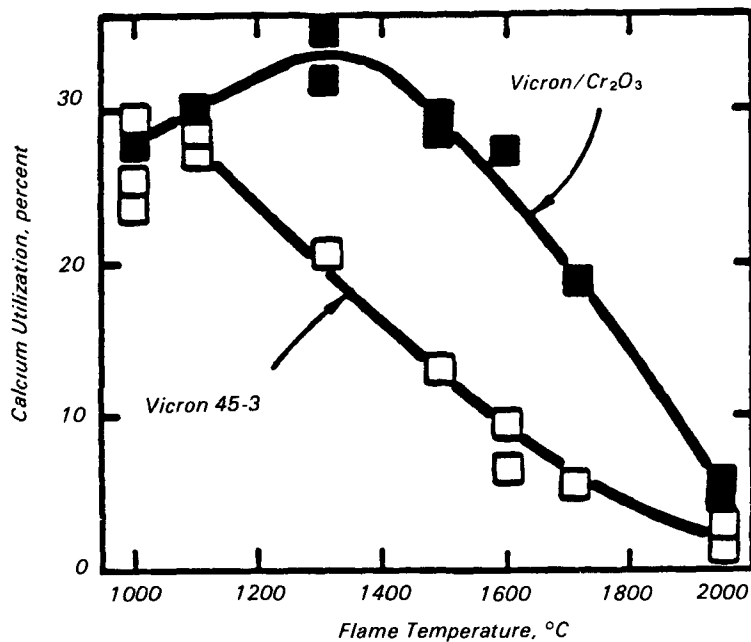


Figure 4. Calcium utilization of Vicron 45-3 with and without Cr<sub>2</sub>O<sub>3</sub> as a function of initial flame temperature. 1100°C wall temperature, 3600 ppm SO<sub>2</sub>.

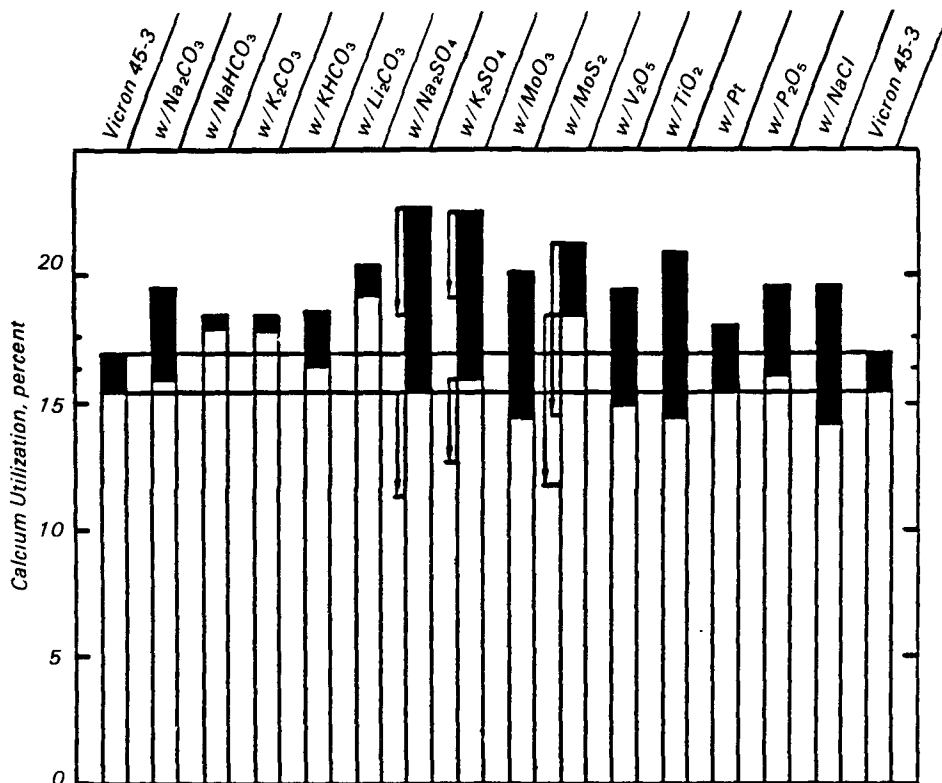


Figure 5. Calcium utilization by Vicron 45-3 in the presence of promoters under isothermal conditions in the ITR. 1100°C, 3600 ppm SO<sub>2</sub>. The open portion of each bar presents utilization achieved in 0.92 s. The solid portion shows the additional utilization at 1.4 s. For Li<sub>2</sub>CO<sub>3</sub>, the data at 0.92 s were higher than at 1.4 s. Arrows adjacent to Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, and MoS<sub>2</sub> designate the correction for the sulfur content of the additives.

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*The complete report, entitled "Fundamental Studies of Calcium-Based Sorbents for SO<sub>2</sub> Control from Coal-Fired Boilers," (Order No. PB 87-152 500/AS; Cost: \$24.95, subject to change) will be available only from:*

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