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Project Summary

The Influence of Sorbent Physical Properties Upon Reactivity With Sulfur Dioxide

J. A. Cole, J. C. Kramlich, W. R. Seeker, and G. D. Silcox

Sulfation behavior was measured at 1000 and 1200°C for eight calcium oxide sorbents which were well characterized in terms of particle size, pore structure, and specific surface area. Sulfation results were compared with predictions of a simple mathematical model which applied the measured sorbent characteristics. The comparisons, intended to provide direction for model development, suggest need for model improvement in areas such as global kinetics at short times, and accountability for changes in structure due to sintering during sulfation.

Subsequently, the effects of the high temperatures on the surface areas of the sorbents in the absence of sulfation were also determined. Surface areas were marginally higher for the larger sorbents after 1000°C injection; but, in general, no correlation between particle size and surface area loss could be found. Surface area decay was shown to be very rapid in the first 200 ms, and subsequently very slow.

Differences between carbonate and hydrate sorbents' reactivities were investigated using aerodynamically size-classified materials: hydrates were found more reactive on an equal pre-reactor size basis. Also, no thermal comminution of the hydrate particles was noted within the high temperature environment. Thus, the superiority of hydrates on a common prefiring size basis cannot be explained in terms of

their fragmentation into smaller particles upon firing.

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

This report gives results of a determination of the influence of sorbent particle size on reactivity toward SO_2 in an isothermal environment. Two aspects of sorbent size were identified as important for current modeling efforts and general understanding: (1) the direct influence of particle size on the reactivities of constant surface area precalcined limes, and (2) the relationship between particle size and the relative reactivities of calcium hydroxides and calcium carbonates. The critical objective of the particle size studies was to identify the region of transition between pore and product-layer diffusion control. The transition occurs as particle size is reduced because the maximum distance that an SO_2 molecule has to diffuse through the prestructure of the calcine is limited by the particle radius.

In the first task (Task 5), the approach was to measure the reactivities of high surface area precalcines (prepared from calcium carbonate) having a wide range

of particle sizes. The precalcines had nearly constant initial surface areas of 25-32 m²/g. Sorbents were injected into an isothermal, laminar drop-tube reactor (ITR) downfired with an SO_2-doped methane flame. Reactivity was determined by gas analysis as SO_2 capture vs. time at 1000 and 12000°C. Solid samples were collected for surface area measurement in order to test the existing model assumptions about surface area loss and to provide input to further model development.

In the second task (Task 20), SO_2 capture was measured for raw carbonates and hydrates which had been aerodynamically classified into narrow size cuts. Having compared the reactivities on an equal size basis, one size cut from a carbonate and from a hydrate were tested for in-situ particle size using a cascade impactor sampling system.

Figure 1. X-ray sedimentation particle size distributions for precalcined sorbent. The range of uncertainty, based on porosimetry analyses, is indicated by the arrows at the median diameter for each material.

Precalcined Sorbent Studies

Eight precalcined sorbents were studied in Task 5. These materials were obtained as raw calcium carbonates from Pfizer Minerals and Pigments Division. The first five were aerodynamically classified from Marblewhite 125 (MW 125), a commercial limestone. The remaining three sorbents were precipitated calcium carbonates (PCCs). All sorbents were calcined to high surface areas in dry air at 700°C using a previously developed calcination procedure. Two of the MW 125 sorbents, 10 and 20 µm, were prepared by calcination to high surface area followed by sintering at 950°C for 30 minutes in flowing dry air. All of the sorbents were greater than 97% calcined. Particle size distributions determined by X-ray sedimentation are shown in Figure 1 for the precalcines. Arrows on each curve indicate the estimated uncertainties in the size distributions due to pore filling by the sedimentation medium. Time-resolved SO_2 capture tests with precalcined sorbents were carried out at a firing rate of 4.6 kW (HHV) with 4200 ppm SO_2 (dry, 0% O_2).

High Surface Area Precalcines

Time-resolved sulfation data for the precalcines at 1000°C are shown in Figure 2. Except for the Albagloss precalcine, most of the sorbent reaction occurs within the first 250 ms after injection. Figure 3 shows similar data generated at 1200°C. Again, most of the
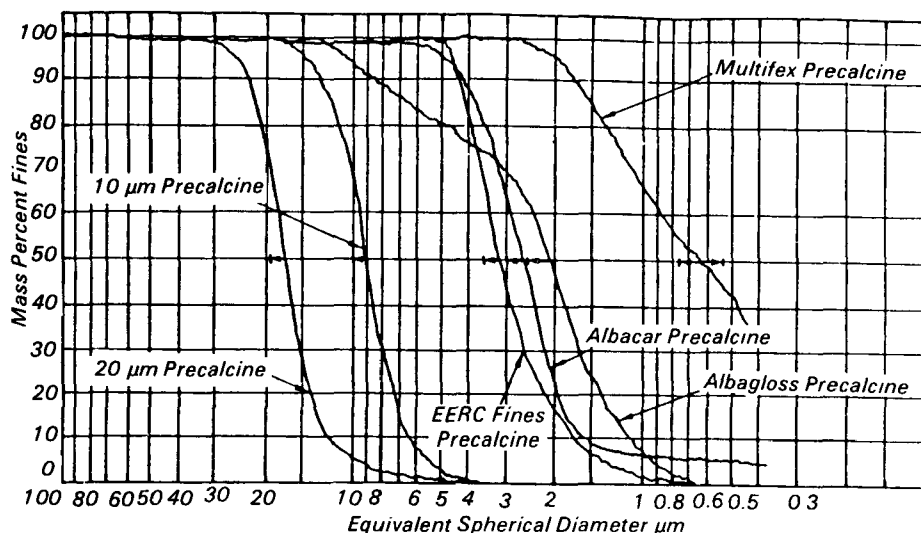
sulfation occurs at very short times. Taken together, the two data sets exhibit the following behavior:

● In going from 1000 to 1200°C, the larger sorbents (20, 10, 2 µm) and the Albagloss either increased in utiliza-

□ 20 µm, 27 m²/g
○ 10 µm, 32 m²/g
◇ 2 µm nominal, 27 m²/g
◮ Albacar 2 µm nominal, 27 m²/g
◻ Albagloss 0.8 µm nominal, 27 m²/g
◭ Multifex 0.07 µm nominal, 25 m²/g

tion, or stayed the same. The smaller sorbents (Albacar, Multifex) showed a slight decrease in utilization. (Because of its high aspect ratio, there is some ambiguity in defining the correct particle size for the Albacar as discussed below.)

□ 20 µm, 27 m²/g
○ 10 µm, 32 m²/g
◇ 2 µm nominal, 27 m²/g
◮ Albacar 2 µm nominal, 27 m²/g
◻ Albagloss 0.8 µm nominal, 27 m²/g
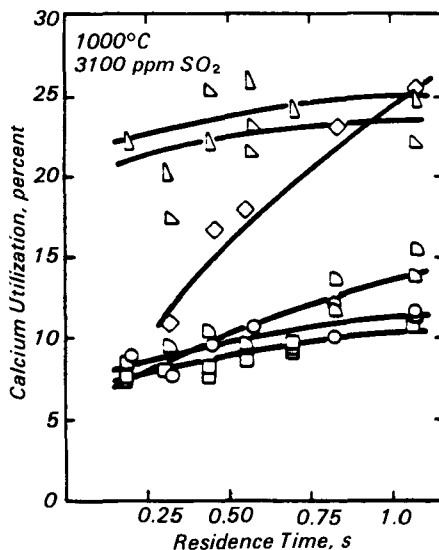◭ Multifex 0.07 µm nominal, 25 m²/g

Figure 2. Isothermal reactivity of calcined sorbents at 1000°C in the EER isothermal reactor at Ca/S = 1.0.
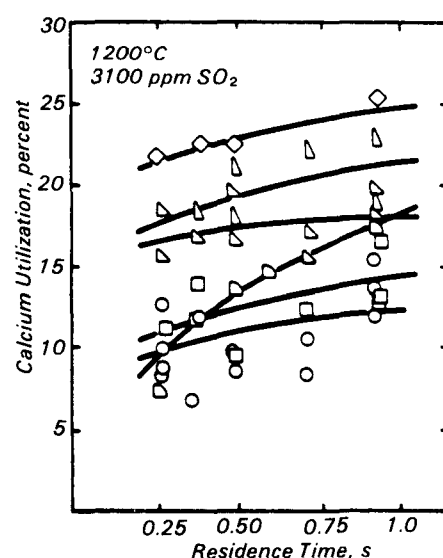

Figure 3. Isothermal reactivity of calcined sorbents at 1200°C in the EER isothermal reactor at Ca/S = 1.0.

● Two of the materials, the 2 μm Marblewhite precalcine at 1000°C and the Albagloss at 1200°C, show a markedly higher reactivity at longer times relative to the other standards.

The Albacar has a needle-like structure with a diameter of 0.5-0.7 μm and a length of 2-4.5 μm. Thus, the Albacar presents a minimum dimension that is less than that of the Albagloss. The key question is whether the material is better represented in terms of reactivity by its nominal size as reported by the Sedigraph (2 μm) or by its minimum diameter (0.5-0.7 μm). Since the models predict that the size dependence is governed mainly by the relationship between the particle interior and its closest surface, then the 0.5-0.7 μm would be the more appropriate dimension for characterizing sulfation behavior. Both dimensions will be considered in analyzing size dependence.

The dependence of ultimate utilization on particle size is shown in Figure 4. The Albacar is plotted as two points to illustrate each of the interpretations of its size. The data support the conclusion that finer particle size promotes improved utilization at both temperatures. Direct use of the grain model against the data indicates that pore diffusion ceases constraining the process below 1-2 μm. The data do not clearly replicate this trend. Rather, there appear to be differences between the precalcines that are not fully characterized by the particle size, surface area, or pore size measurements. This is supported by the anomalous behavior noted above in Figures 2 and 3.

At 1200°C the data generally show less variation in utilization with particle size. The grain model vastly overpredicts the capture which illustrates the necessity of including a sintering step in the calculation to correctly predict high temperature behavior. For both 1000 and 1200°C, there are sufficient uncontrolled differences between the sorbents (manifested as apparent data scatter) to prevent verification of the grain model conclusion that pore resistance becomes insignificant below about 1 μm.

Low Surface Area Precalcines

Time-resolved sulfation data for the low surface area precalcines are shown in Figure 5. Grain model predictions for each are the solid curves on each graph. These results are significant because the measured SO_2-capture levels were
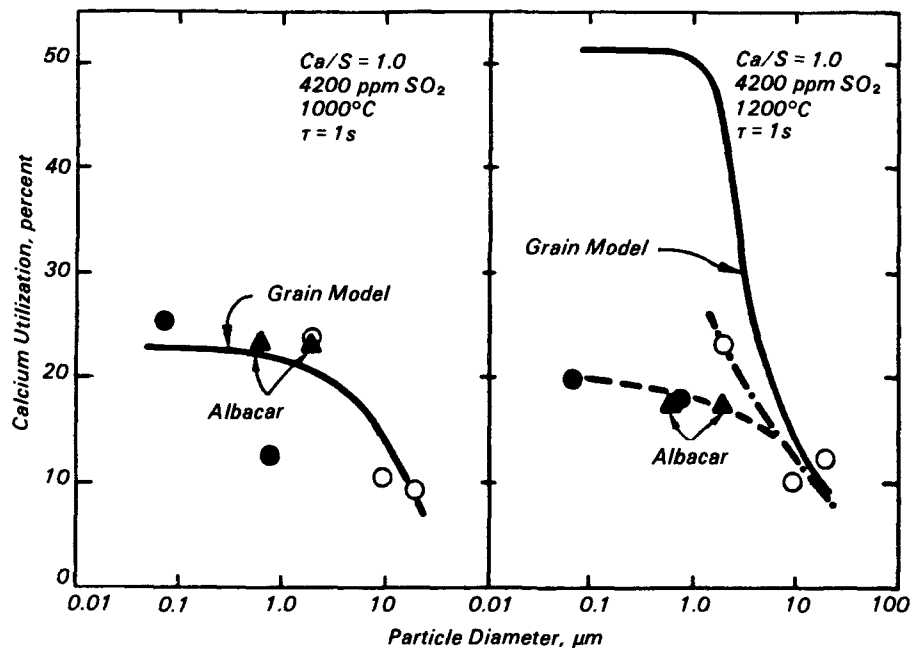
Figure 4. A summary of the sulfation vs. particle size data for precalcined materials. The solid lines are the grain model predictions. Solid symbols represent precipitated calcium carbonates, and open symbols represent MW 125.
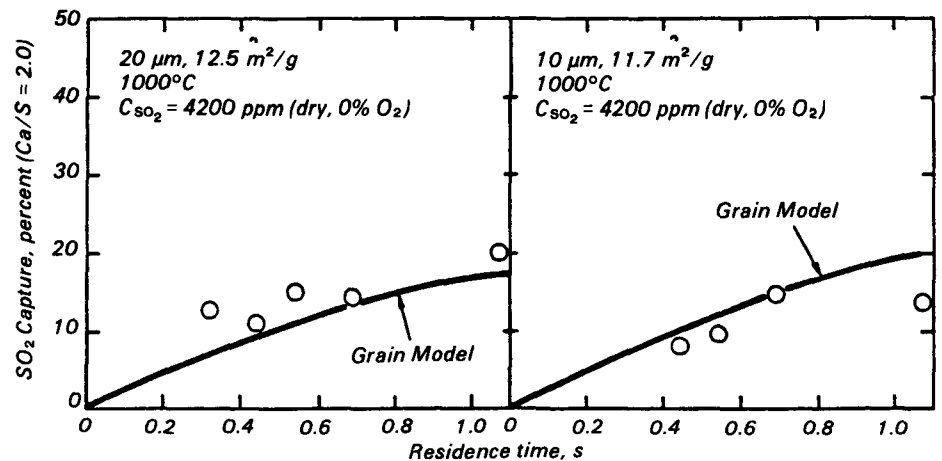
Figure 5. Time-resolved SO_2 capture by low surface area 10 and 20 μm precalcines. Grain-model predictions based on sorbent properties and reactor conditions are shown.

reduced only slightly by the large decrease in surface area (compare to Figure 2). Parametric modeling studies had predicted that, in the pore diffusion control regime, surface area would have a small impact on sorbent reactivity.

Precalcines Sintering Tests

Surface areas were measured for precalcines sampled from the ITR at 1000 and 1200°C without SO_2. Time resolved data were obtained using the 10 μm, 32 m²/g MW 125 precalcine, while samples

using the remaining sorbents were collected at 1 s residence time. The time-resolved data are shown in Figure 6. This demonstrates not only a significant loss of surface area, but also a significant difference between the extent of sintering at the two temperatures. These data also imply that surface area loss at these temperatures is faster at short times and approaches a steady state value in only a few hundred milliseconds. Data from the remaining sorbents also show greater surface area loss at 1200°C.

However, no correlation was found between surface area loss and particle size. The latter finding may simplify the manner in which sintering is incorporated into models of the sulfation process.

Hydrate Carbonate Studies

Intrinsic differences between the reactivities of hydrate and carbonate sorbents were examined using three hydrate and two carbonate sorbents prepared by aerodynamic classification of (respectively) Linwood atmospheric hydrate and Vicron 45-3 carbonate. These studies were performed at 1100°C with a reactor firing rate of 9.4 kW and 3000 ppm SO_2 (dry, 0% O_2). Figure 7 shows the ITR data and compares them with similar results obtained in the EER Controlled Temperature Tower (CTT). The ITR data corroborate the CTT data, but no inference should be made about the relative magnitudes of the two data sets because the CTT data were obtained under non-isothermal conditions and at a much longer residence time. These data are all presented as SO_2 capture vs. the mass mean particle diameter (determined by X-ray sedimentation). Recognizing that hydrates are more reactive on a constant prereactor size basis, tests were carried out to measure the in-situ sorbent particle sizes by cascade impactor sampling.

The 8.8 μm carbonate and 9.4 μm hydrate, because of their proximate sizes, were chosen for cascade impactor sampling. The samples were collected at a residence time of 475 ms on the impactor sampling system. The results of the impactor sampling tests are shown in Figures 8 and 9. Two tests were run with each sorbent, indicated by the open and closed symbols on the graphs. Also shown are the curves obtained by X-ray sedimentation (Sedigraph).

The agreement between the impactor sizing and the Sedigraph is far better than expected. Within the range and accuracy of the cascade impactor data, no change in particle size distribution is evident for either sorbent. One implication, of course, is that for this reactor operating condition the Sedigraph particle size is sufficient for a correlation like that shown in Figure 7.

Conclusions

Sulfation tests using size-classified precalcines confirmed the dependence of calcium utilization on particle size. The results suggested that influences beyond
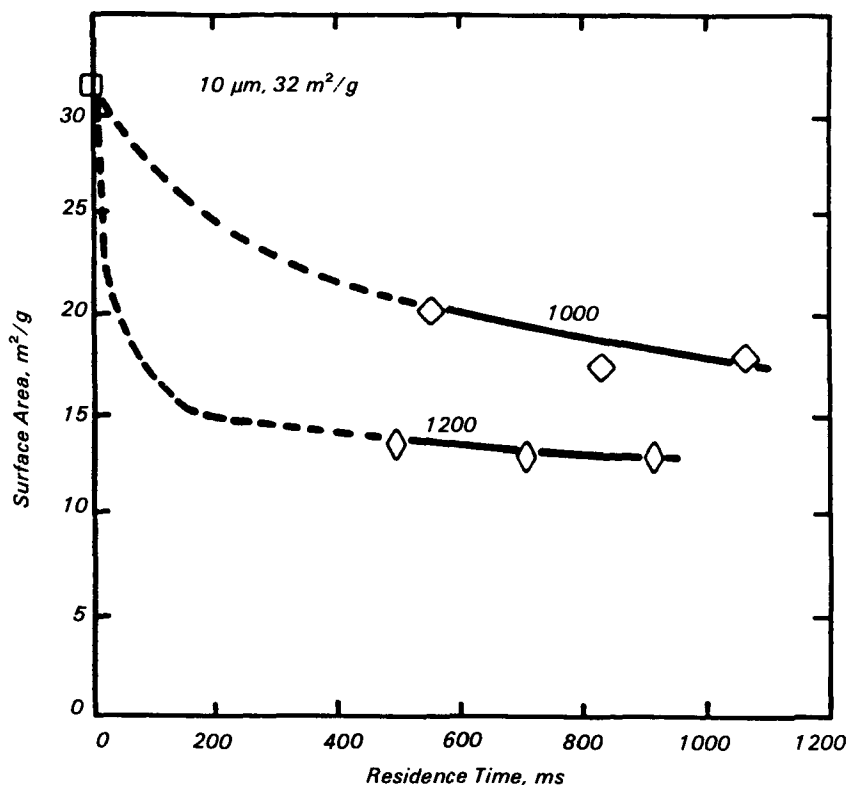

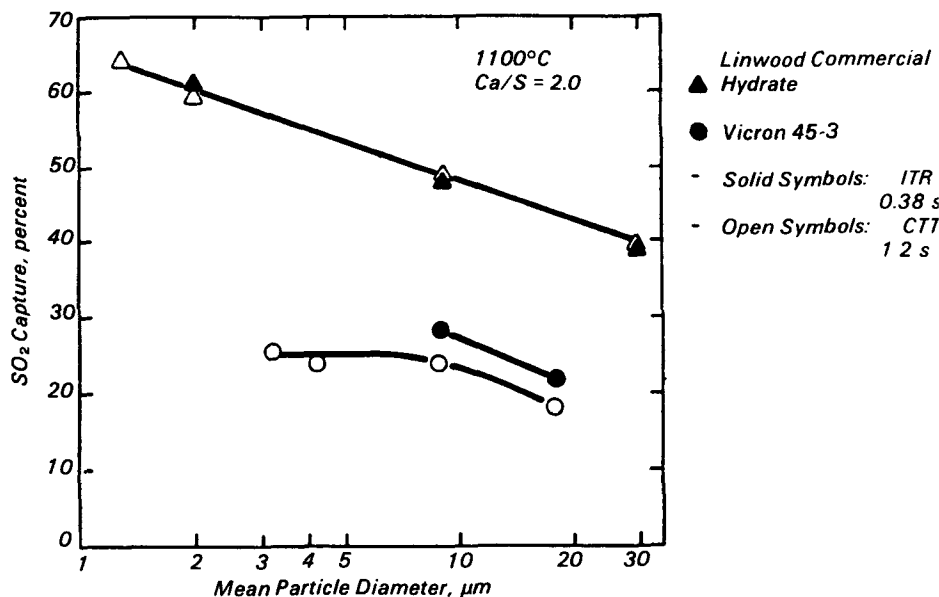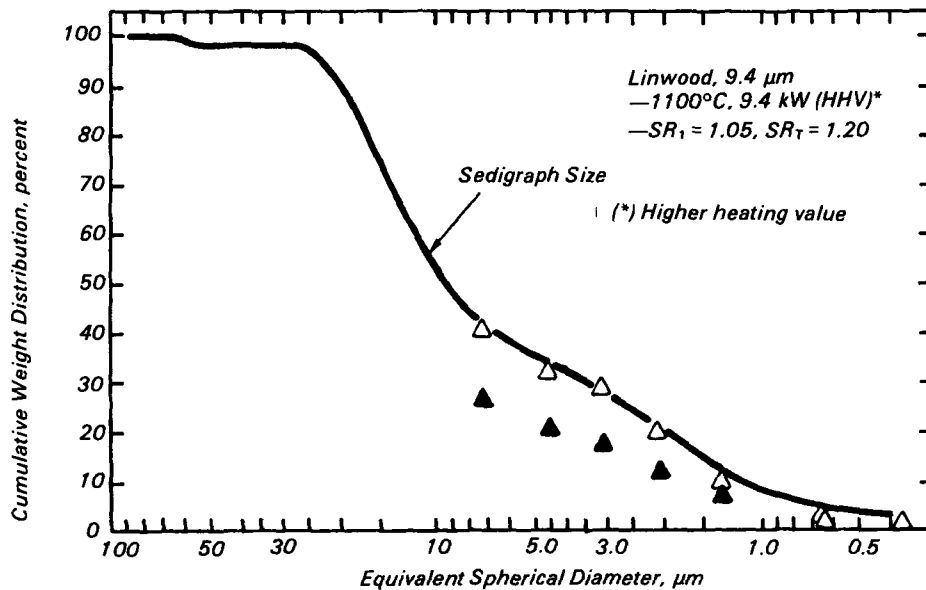Figure 6. Surface area profiles for 10 μm, 32 m^2/g precalcine at 1000 and 1200°C.

Figure 7. Particle size dependence of SO_2 capture by Linwood atmospheric hydrate and Vicron 45-3. The open symbols represent data taken on the Controlled Temperature Tower.

Figure 8. Comparison of in-situ particle size for 9.4 μm Linwood hydrate (determined by cascade impactor sampling) with the prereactor particle size determined by Sedigraph analysis. Open and solid symbols represent independently repeated runs.
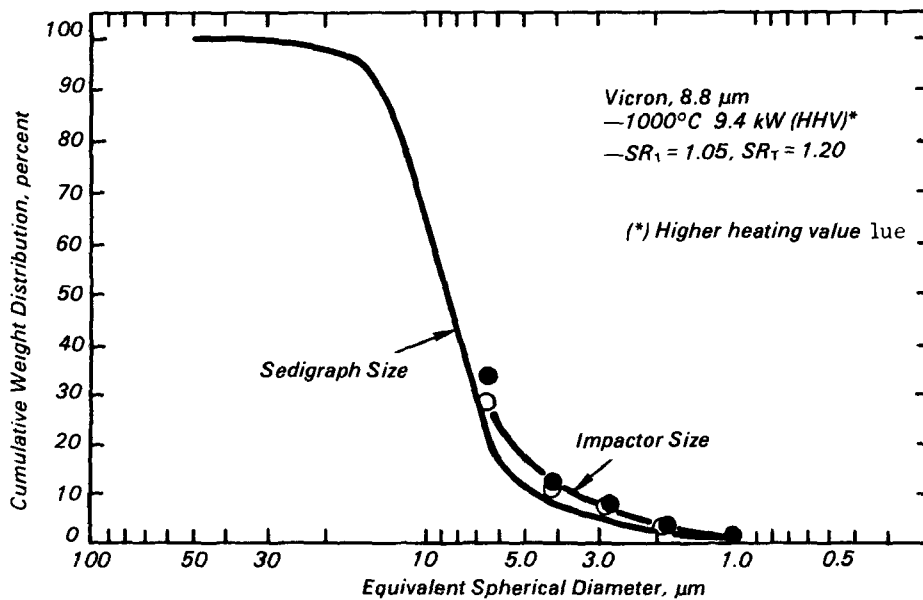
Figure 9. Comparison of in-situ particle size for 8.8 μm (determined by cascade impactor sampling) with the prereactor particle size determined by Sedigraph analysis. Open and solid symbols represent independently repeated runs.

particle size, pore structure, or surface area had an influence on utilization. Due to this variability, it was not possible to verify conclusively that the size for pore/product transition was correctly selected by the grain model. At 1200°C the model overpredicted the capture, a point which indicates the necessity of including sintering in the model. At the higher temperature, 1200°C, the results were less conclusive: the model overpredicted the observed capture for small particle sizes. In addition, two separate size vs. capture trends were indicated by the data, one for the PCC precalcines and the other for the MW 125 precalcines. Low surface area precalcines were used to study sulfation under reduced pore diffusion resistance. However, as the grain model had predicted, the decrease in surface area had only a small impact on the reactivities of the larger diameter precalcines.

Surface area sampling tests bring into question the model assumption of constant surface area. The data showed both residence time and temperature effects on surface area. The parametric tests, however, showed no impact of particle size on surface area loss.

The hydrate/carbonate reactivity tests showed that, on a common size basis, hydrates are more reactive than carbonates. The impactor data demonstrated that thermal comminution of the large hydrate fraction does not occur during exposure to the reactor gas. Thus, the enhanced reactivity of hydrates is not indicated to be due to thermal fragmentation within the reactor.

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Brian K. Gullett is the EPA Project Officer (see below).

The complete report, entitled "The Influence of Sorbent Physical Properties Upon Reactivity with Sulfur Dioxide," (Order No. PB 88-143 987/AS; Cost: $19.95, subject to change) will be available only from:

> *National Technical Information Service*
> *5285 Port Royal Road*
> *Springfield, VA 22161*
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