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# THE CHARACTERIZATION OF A SOLID SORBENT WITH CRYSTALLITE SIZE AND STRAIN DATA FROM X-RAY DIFFRACTION LINE BROADENING

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## INTRODUCTION

EPA's Air and Energy Engineering Research Laboratory is currently investigating the injection of dry calcium hydroxide [$Ca(OH)_2$] into coal fired electric power plant burners for the control of sulfur dioxide ($SO_2$) emissions. The overall chemistry for the process is:

| HYDROXIDE PRODUCTION | BURNER REACTIONS |
|---|---|
| $CaCO_3 \rightarrow CaO + CO_2$ | $Ca(OH)_2 \rightarrow CaO + H_2O$ |
| $CaO + H_2O \rightarrow Ca(OH)_2$ | $CaO + SO_2 \rightarrow CaSO_3$ |
| | $2CaSO_3 + O_2 \rightarrow 2CaSO_4$ |

It has been found that the reactivity of the $Ca(OH)_2$ can vary considerably, depending on the limestone source. Furthermore, the time, temperature, and pressure conditions under which the $Ca(OH)_2$ is produced can have an effect on reactivity. Finally, it has been found that the addition of surfactants, during the production of the $Ca(OH)_2$, can enhance the reactivity. With all of these variables, the choice of materials and conditions for maximum efficiency is a formidable challenge. The use of full-scale furnaces, for the evaluation, is infeasible because of the expense. Bench-scale furnaces can produce relative ratings for sorbents, but are still very resource intensive for the level of testing needed. Laboratory characterization of sorbent material with techniques such as microscopic mineralogic examination, scanning electron microscopy, Brunauer, Emmett, and Teller surface measurements, thermogravimetric analysis, and differential thermal analysis has been explored, but none have proven to give conclusive results.

This situation has led to the investigation of x-ray diffraction (XRD) line broadening for sorbent characterization. It has long been known that the shape of XRD peaks is influenced by instrument factors, crystallite size, and lattice deformations. It was theorized that these microstructure factors could be a major factor in the differences between the reactivity of $Ca(OH)_2$ sorbents. The Warren-Averbach method[1] accomplishes separation of size and strain effects by first doing a Fourier transformation of the XRD peaks from the subject sample and a standard material which has relatively little peak broadening, due to crystallite size and microstrain. The Fourier coefficients of the sample are divided by the coefficients of the standard to deconvolute the component shape contributed by the instrument factors. The contributions due to size and strain can then be separated because the coefficients for strain effects are dependent on reflection order while those for size are not.

## EXPERIMENTAL

For this study, seven different $Ca(OH)_2$ sorbent materials were evaluated for percent conversion (100 x moles of calcium reacted with $SO_2$ divided by moles of calcium available) in an isothermal flow reactor operating at 1000 °C with 0.3 percent $SO_2$ and 1 second residence time. The XRD analysis was done on a Siemens D-500 diffractometer with a copper target source running at 50 kV and 40 mA. The entrance aperture was 1 deg., and the detector slit was 0.05 deg. A scintillation detector, equipped with a graphite monochrometer, was used. The subject $Ca(OH)_2$ phase was identified as JCPDS 4-733 which has a hexagonal structure. The standard material was zinc oxide, JCPDS 36-1451, which also has a hexagonal structure. The peak data are given in Table 1.

A total of 257 steps were counted for each peak. The data were processed with the CRYSIZ program which was written by Gerhard Zorn and is furnished as part of the Siemens DIF-500 operating system, version 1.1. Before running CRYSIZ, the raw data were smoothed by using the FIT program to fit it with a split Pearson seven function. The output from the CRYSIZ program consists of microstrain as a function of column length from 1 to a maximum of 100 nm, the average column length, the column length occurring with the maximum frequency, the width at half maximum of column length distribution, the relative frequency of column lengths as a function of column length, and the cumulative frequency of column lengths as a function of column lengths. The three functions of column length can be plotted on the system plotter.

Table 1. Experimental Conditions

| PHASE | MILLER INDICES | PEAK DEGS. | SCAN RANGE-DEGS. | FWHM DEGS. | I/Io | COUNT SECS. | STEP DEGS. |
|---|---|---|---|---|---|---|---|
| $Ca(OH)_2$ | 101 | 34.08 | 30.20-37.88 | 0.3-0.6 | 100 | 5 | 0.03 |
| | 202 | 71.76 | 68.00-75.68 | 0.4-0.9 | 12 | 30 | 0.03 |
| ZnO | 101 | 36.26 | 33.54-38.66 | 0.116 | 100 | 5 | 0.02 |
| | 202 | 76.77 | 74.34-79.46 | 0.121 | 5 | 20 | 0.02 |

Table 2. Experimental Data

| SAMPLE nm | PERCENT CONVERSION | 202 PEAK HALF WIDTH DEGS. | AVERAGE COLUMN LENGTH nm | STRAIN @ AVERAGE COLUMN LENGTH | STRAIN @ MAX FREQ COLUMN LENGTH | MAXIMUM DETERMI-NABLE COLUMN LENGTH |
|---|---|---|---|---|---|---|
| Reagent | 14.6 | 0.448 | 20.1 | 1.33 | 2.03 | 64 |
| Koping | 21.7 | 0.67 | 15.0 | 1.63 | 2.32 | 48 |
| Linwood | 22.1 | 0.582 | 13.6 | 1.76 | 2.19 | 44 |
| 0% Lig. | 23.5 | 0.693 | 13.9 | 1.83 | 2.54 | 44 |
| 4% Lig. | 25.6 | 0.78 | 11.9 | 2.06 | 2.74 | 36 |
| 1.5% Lig. | 27.8 | 0.835 | 11.9 | 2.29 | 2.92 | 32 |
| Fredonia | 31.4 | 0.875 | 11.1 | 1.95 | 3.54 | 44 |

## RESULTS AND CONCLUSIONS

The experimental data in Table 2 were taken from the output of the CRYSIZ program. Seven samples with reactivity data were available. The samples labeled Lig. had various amounts of Lignosite (a by-product of the paper industry) added in processing. The relation of the microstructure data to sorbent reactivity was tested by plotting the percent conversion for the samples versus the XRD data (Figs. 1-5).

The reactivity was seen to be directly proportional to the RMS strain at average column length and RMS strain at the column length of maximum frequency of occurrence (Figs. 3 and 4). The strain is a measure of potential energy stored in the crystal lattice due to disorder. This strain could provide the potential energy necessary to overcome the energy of reaction. The reactivity was seen to be inversely proportional to the crystallite column dimensions (Figs. 2 and 5). This would be reasonable because the smaller dimensions could indicate higher surface area and consequently more intimate gas

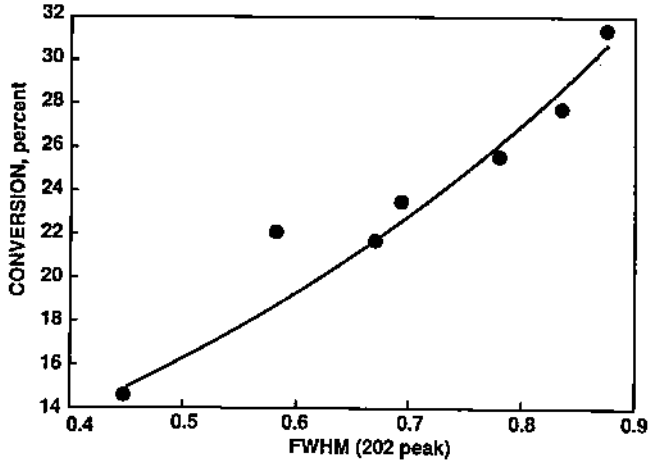


Fig. 1. Percent conversion vs. diffraction peak half width.

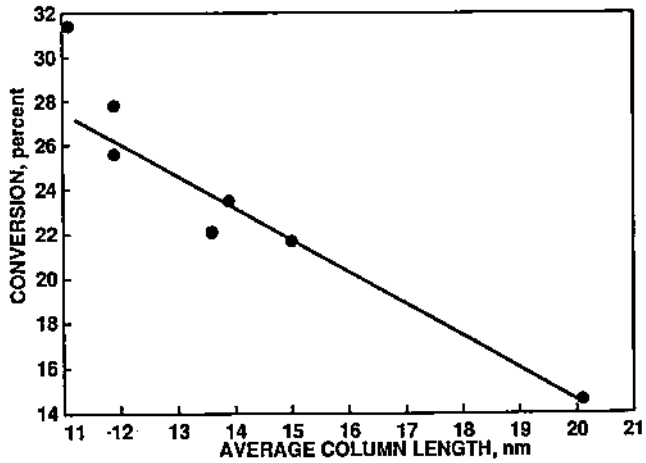


Fig. 2. Percent conversion vs. average column length.

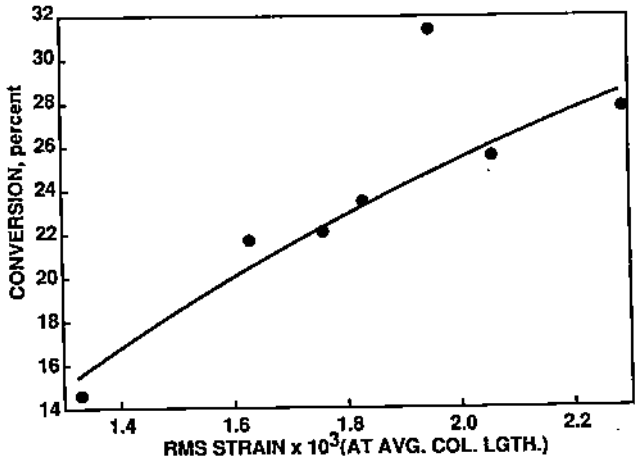


Fig. 3. Percent conversion vs. RMS strain at average column length.

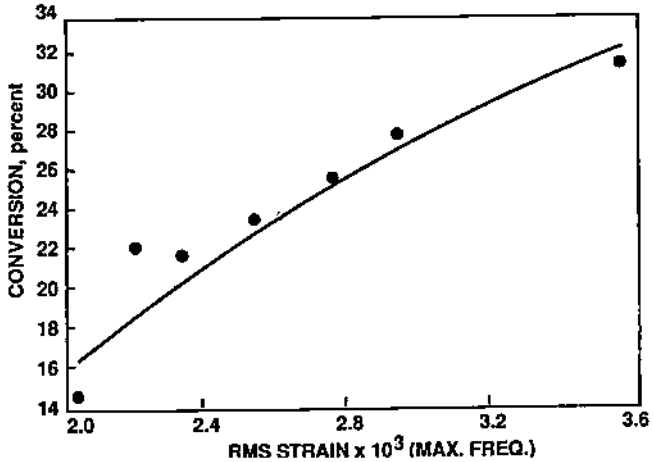


Fig. 4. Percent conversion vs. RMS strain at column length of maximum frequency of occurrence.

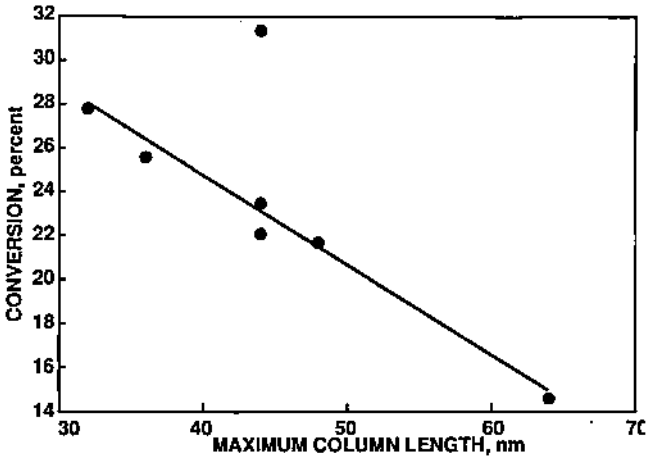


Fig. 5. Percent conversion vs. maximum determinable column length.

contact. The diffraction peak FWHM is directly proportional to reactivity because it reflects the contributions of increasing strain and decreasing crystallite dimensions (Fig. 1). In the two plots, Figs. 3 and 5, one sample lies too far above the regression line. The diffraction peaks for this sample apparently have been seen to be made up of contributions from a broad peak and a narrow peak, indicating the presence of two discrete phases. It is expected that future work will reveal an acceptable method for weighting the contributions. Future work will also be directed toward evaluating the relative contributions of size and strain as a function of column length.

REFERENCES

1. B. E. Warren, "X-ray Diffraction," Addison-Wesley, Reading, Massachusetts, 1969.