THE COMPARISON OF SEVERAL STANDARD MATERIALS AND TECHNIQUES FOR THE WARREN-AVERBACH DETERMINATION OF MICROSTRUCTURE CHARACTERISTICS OF CALCIUM HYDROXIDE SORBENT MATERIALS

Frank E. Briden

U.S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

INTRODUCTION

The Air and Energy Engineering Research Laboratory (AEERL) has been investigating the injection of dry calcium hydroxide into combustion streams for the removal of sulfur oxides. It has been known, for some time, that the reactivity of $Ca(OH)_2$ with sulfur oxides varies over a wide range for different batches of calcium hydroxide. The reactivity is a critical factor in the economics of the process. Because of this it is desirable to have a method to predict the reactivity of calcium hydroxide batches. The reactivity can be affected by many factors including the origin of the calcium carbonate mineral from which the hydroxide is produced, the production conditions, and the concentration of additives used for reactivity enhancement. It has been theorized that all of the preceding contribute to such physical characteristics as surface area, particle size, and porosity. The examination of these physical characteristics has provided the basis for understanding the reaction processes but has not provided all the factors necessary to correlate intrinsic sorbent characteristics with reactivity.

The application of microstructure factors derived from X-ray Diffraction Line Profile (XLP) for the characterization and reactivity prediction of calcium-hydroxide sorbent materials was first reported by Briden and Natschke (1). In that study, the XLP derived microstructure factors from several calcium-hydroxide factors were found to be related to their reactivities. In the study, the microstructure factor mean column length (CL) was seen to be inversely proportional to reactivity while the strain at the mean CL was seen to be directly proportional to reactivity. When the method was applied to more widely varying batches, the relation was not as consistent. The original data had been generated, using bulk sample holders and zincite as the instrument line-broadening standard. At this point, it was decided to investigate the effects of the choice of standards, the use of thick samples versus thin, and the simultaneous use of more than one microstructure factor in reactivity prediction.

EXPERIMENTAL

The experimental data were taken on a Siemens D-500 diffractometer. The x-ray source was a copper-target tube running 50 kV and 40 mA. The tube had a fine focus with a beam size of 0.4 x 12 mm and a take-off angle of 6° resulting in an effective beam width of 0.040 mm. The collimation was a 1° divergence slit, a 2.4° incident-beam Soller slit, a 1° scatter slit, and after the sample another 1° scatter slit, a 2° Soller slit, a 0.05° receiving slit, a 0.15° monochrometer slit, and a graphite monochrometer. A scintillation detector was used.

The bulk sample holders were end loaded and about 2 mm deep. The thin sample holders were zero background quartz plates. The thin-mount samples were slurried in amyl acetate and then the slurry was

spread over the plate and allowed to evaporate. The samples were not ground in order to preserve the, as received, crystallite size and strain conditions. In general, the samples would pass a 44 μm mesh sieve.

The data were processed on the system DEC 11/73, with an RSX11M operating system using the Siemens DIFFRAC 500, version 1.1 software. For the Warren-Averbach method (2) used to separate crystallite size and strain effects, it was necessary to use diffraction peaks of at least two orders of the same reflection. For $Ca(OH)_2$ (JCPDS No. 4-733), the only pair of reflections readily available are the 101 and 202 because of low intensities and interferences. The standards used to compensate for instrument line shape effects were LaB_6 (SRM 660), Si (SRM 640B), CaF_2 (Spex TMI-10, Lot 01841P), α-Al_2O_3 (Norton 871), and ZnO (Fisher Reagent, Lot 80186).

RESULTS AND DISCUSSION

In order to use the Siemens computer program CRYSIZE to determine microstructure factors with the Warren-Averbach method, it is first necessary to fit the diffraction peak with one of several functions available in the program FIT. This process improves the Warren-Averbach analysis by the reduction of random noise and the elimination of interference from foreign peaks. In all cases, the Pearson 7 or Split Pearson 7 functions were used. Six microstructure factors from the CRYSIZE output were examined. The first three were the mean CL (the mean distance across the crystallites in the 101 direction), the mode CL (CL occurring with the greatest frequency in the 101 direction), and the maximum calculated CL (the highest CL determined at the iteration limit of the CRYSIZE algorithm in the 101 direction). Also the root mean square strains (RMSS) for the three respective CLs were examined. The six microstructure factors were determined for six commercial $Ca(OH)_2$ sorbent products [Linwood, Marblehead, Kemidol, Snowflake, Modified Marblehead, and Illinois State Geological Survey (ISGS) Mixture] plus a more crystalline, reagent grade material from Alfa Chemical Company (Lot 8171481). The six microstructure factors and the full width at half maximum (FWHM) for the 101 and 202 peaks for the products are listed in Table 1. The products are listed from left to right in order of increasing reactivity [weight of $Ca(OH)_2$ converted to $CaSO_4$ divided by the total weight of $Ca(OH)_2$ used times 100]. The reactivities were obtained on the EPA innovative furnace reactor with a flow rate sufficient to give a residence time of 0.75 s between 538 and 427 °C with an SO_2 concentration of 3,000 ppm (3). In general, it can be seen that the CL factors decrease with increasing reactivity while the root mean square strains increase with increasing reactivity.

It had been anticipated that the microstructure factors would be very dependent on the mass absorption coefficient of the standard materials. When the mean CLs for the different $Ca(OH)_2$ products were plotted versus the FWHM of the second order standard peaks, a fairly good progression of increasing mean CL with increasing FWHM was observed (Figure 1). However, it was also observed that the CLs were not falling in order of the standard mass absorption coefficients. It appears that the mass absorption coefficient effects are outweighed by whatever other factors influenced the FWHM. The lowest mean CLs were obtained with CaF_2. However, it is noted that, even though the absolute values are different, the relative rankings for a given standard are the same except in the case of Kemidol and Snowflake which are extremely close. Of course, these $Ca(OH)_2$ samples all had very broad peaks and the difference between them and the standards was very large.

The RMSS values at the mean CLs were also plotted versus the FWHM of the second order standard peaks (Figure 2). The data point for the Kemidol sample with Al_2O_3 standard is obviously in error. In general the RMSS is seen to decrease with increasing FWHM of the second order standard peaks. The CLs obtained with Si are much lower than predicted. This, quite likely, indicates that the Si has a relatively high RMSS. Some of the strains are slightly higher for CaF_2 while some are slightly higher for LaB_6 indicating that, within experimental error, their strains are small but equivalent. As with the CLs, the absolute strain values vary with the FWHM but the relative order for the samples is constant.

The previous work (1) on relating microstructure factors to reactivity was limited to the consideration of one factor at a time. As more widely varying sorbent products have been investigated, it has become quite obvious that fairly wide deviations from the regression may occur. Because of this, it was attempted to perform the regression with more than one microstructure factor. Of course, the more factors considered the better the agreement that may be obtained. However, because of the limited size of data sets that become available for testing, it was considered that no more than two factors at a time should be used.
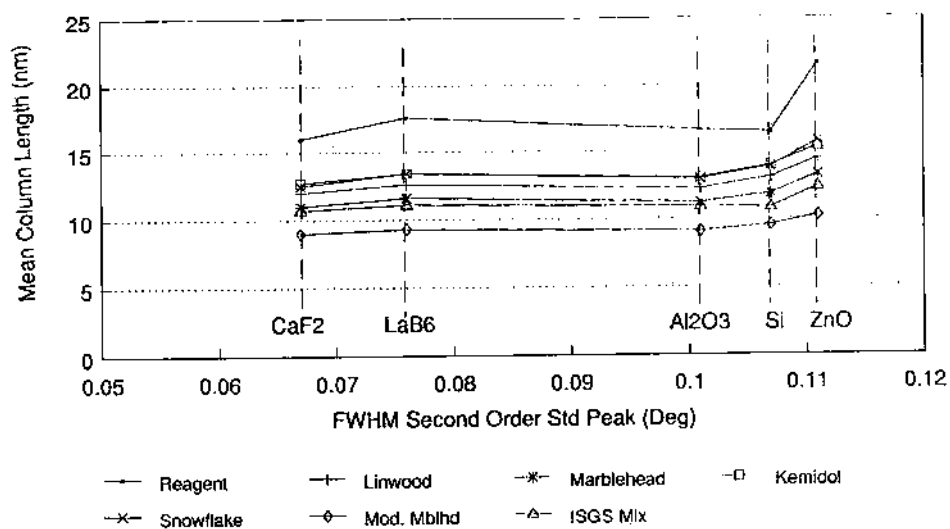
Figure 1. Mean CLs for Seven Ca(OH)₂ Products Calculated With Five Standard Materials Versus the FWHM of the Second Order Standard Peaks.

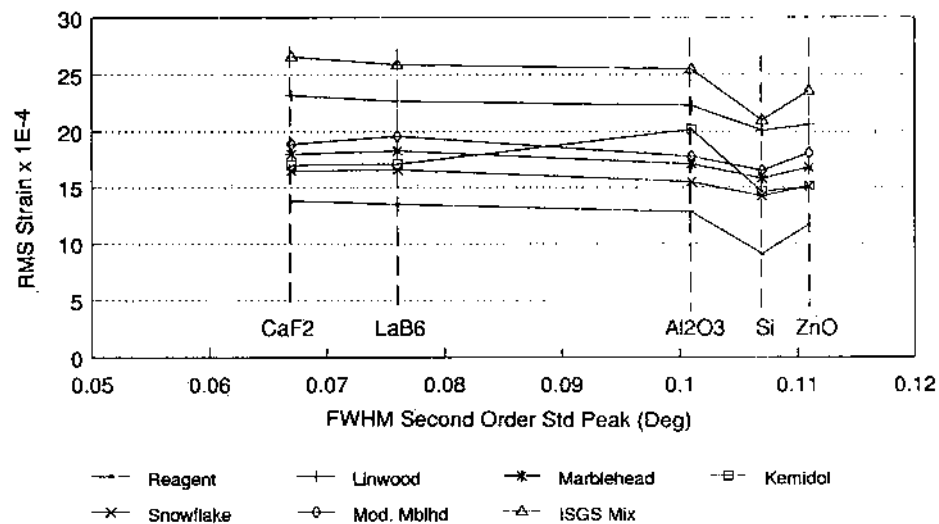

Figure 2. RMS Strain at the Mean CL for Seven Ca(OH)₂ Products Calculated with Five Standard Materials Versus the FWHM of the Second Order Standard Peaks.

TABLE 1. Ca(OH)$_2$ MICROSTRUCTURE FACTORS FROM X-RAY DIFFRACTION LINE PROFILES
(WITH CaF$_2$ STANDARD AND BULK MOUNT)

XLP Factor	Reagent	Linwood	Marblhd	Kemidol	Snowflake	Mod. Marblhd	ISGS Mix
% Reactivity	37.0	56.8	58.3	59.7	60.4	67.4	73.4
Mode CL (nm)	7.9	6.2	5.7	6.8	6.3	5.1	6.0
Mean CL (nm)	16.0	12	11.0	12.7	12.5	9.0	10.7
Max CL (nm)	64	36	44	48	48	36	32
RMSS Mode	0.00173	0.00263	0.00197	0.00216	0.00179	0.00225	0.00329
RMSS Mean	0.00138	0.00232	0.00180	0.00171	0.00165	0.00189	0.00266
RMSS Max	0.00091	0.00170	0.00127	0.00113	0.00119	0.00119	0.00174
101 XRD Peak FWHM (Deg)	0.290	0.4523	0.433	0.387	0.3685	0.540	0.5125
202 XRD Peak FWHM (Deg)	0.4405	0.7288	0.0691	0.634	0.603	0.8405	0.825

Tables 2 through 4 show the linear correlation coefficients for the six factors regressed, one and two at a time, over the seven products, for the standards CaF$_2$, LaB$_6$, and Al$_2$O$_3$. In these tables, the coefficients on the diagonals are for the single factors alone. The balance of the coefficients are the result of regressions of the factors taken two at a time. For all of these standards, the mean CL and the maximum CL are the best single predictors of reactivity. Of the strain factors, the strain at the average CL is the best predictor. It is not fully accurate to compare the magnitude of these strain coefficients to the size coefficients because it has been seen that the functions relating strain to reactivity are not linear and these coefficients came from linear regressions of size and strain. Preliminary calculations have shown that, when strain regression is treated as a second degree polynomial, the coefficients will improve. It would be logical to assume that any scheme to reliably predict reactivity should be based on both size and strain components. The mean CL and the strain at the mean CL are consistently high for all three standards.

The original work had started with bulk sample holders. It was desired to compare the results from the bulk sample holders with those from the thin mounts on zero background quartz plates. Table 5 presents the mean CL factors determined for CaF$_2$ and LaB$_6$ standard with bulk and thin samples. The absolute values for LaB$_6$ for bulk and thin samples are, in general, larger than those for CaF$_2$. The order for both thin samples is almost identical and likewise the order for both bulk samples is almost identical. However, the order for the bulk samples is quite different from the order for the thin samples. Table 6 gives the correlation coefficients for the regression of the microstructure factors for CaF$_2$ standard calculations for the thin samples. It is seen here that the single factor correlations are significantly lower than those for the bulk samples (Table 2). The mean CL correlation is only 0.61 for thin samples where it was 0.77 for the bulk samples. Because of the low correlations for the single factors (those on the diagonals) it was surprising to find that several of the regression pair correlations were significantly higher than those for the bulk samples. Of particular interest is the pair of factors maximum CL and RMSS at maximum CL. The first had a single factor correlation coefficient of 0.69 and the other 0.03 but when regressed together they had the highest correlation of 0.93. A theory that this evidence could support is that the better resolved thin sample peak allows the separation of the peak profile parameters which contribute to the two factors. In cases where the separate correlations are low but the simultaneous regression for the pair is high, the two factors could be synergistic so that the contribution of each factor depends directly or inversely on the contribution of the other.

CONCLUSIONS

1.   When different standards were compared for Ca(OH)$_2$ analysis, the CLs varied in a similar manner to the standard peak widths. The CaF$_2$, LaB$_6$, Si, and Al$_2$O$_3$ standards all gave quite comparable results. The absolute values obtained varied a little but the relative order in the series was hardly affected.

TABLE 2. CORRELATION COEFFICIENTS FOR THE REGRESSION OF REACTIVITY OF $Ca(OH)_2$ SORBENT ON MICROSTRUCTURE FACTORS FROM X-RAY DIFFRACTION LINE PROFILES (CaF_2 STANDARD AND BULK MOUNT)

Factor	Mode CL	Mean CL	Max CL	RMSS Mode	RMSS Mean	RMSS Max
Mode CL	0.65	0.85	0.80	0.82	0.78	0.73
Mean CL		0.77	0.85	0.85	0.84	0.82
Max CL			0.79	0.79	0.81	0.84
RMSS Mode				0.46	0.51	0.46
RMSS Mean					0.50	0.57
RMSS Max						0.38

TABLE 3. CORRELATION COEFFICIENTS FOR THE REGRESSION OF REACTIVITY OF $Ca(OH)_2$ SORBENT ON MICROSTRUCTURE FACTORS FROM X-RAY DIFFRACTION LINE PROFILES (LaB_6 STANDARD AND BULK MOUNT)

Factor	Mode CL	Mean CL	Max CL	RMSS Mode	RMSS Mean	RMSS Max
Mode CL	0.70	0.85	0.81	0.75	0.81	0.77
Mean CL		0.79	0.84	0.80	0.84	0.83
Max CL			0.79	0.89	0.80	0.83
RMSS Mode				0.51	0.58	0.51
RMSS Mean					0.58	0.70
RMSS Max						0.40

TABLE 4. CORRELATION COEFFICIENTS FOR THE REGRESSION OF REACTIVITY OF $Ca(OH)_2$ SORBENT ON MICROSTRUCTURE FACTORS FROM X-RAY DIFFRACTION LINE PROFILES (Al_2O_3 STANDARD AND BULK MOUNT)

Factor	Mode CL	Mean CL	Max CL	RMSS Mode	RMSS Mean	RMSS Max
Mode CL	0.64	0.86	0.79	0.74	0.83	0.73
Mean CL		0.77	0.82	0.81	0.86	0.82
Max CL			0.78	0.79	0.78	0.82
RMSS Mode				0.35	0.52	0.39
RMSS Mean					0.52	0.53
RMSS Max						0.38

TABLE 5. COMPARISON OF CRYSTALLITE MEAN CLs (nm) IN THE 101 DIRECTION OBTAINED WITH CaF_2 AND LaB_6 STANDARDS WITH BULK AND THIN FILM MOUNTS

Standard/ Mount	Reagent	Linwd	Marblhd	Kemidol	Snowflk	Mod Marblhd	ISGS Mix
CaF_2 Bulk	16.0	12.0	11.0	12.7	12.5	9.0	10.7
CaF_2 Film	16.4	14.0	12.2	9.3	14.7	11.2	9.3
LaB_6 Bulk	17.6	12.6	11.6	13.4	13.4	9.3	11.1
LaB_6 Film	17.6	14.3	12.6	9.0	15.2	11.4	9.5

TABLE 6. CORRELATION COEFFICIENTS FOR THE REGRESSION OF THE REACTIVITY OF
$Ca(OH)_2$ SORBENT ON MICROSTRUCTURE FACTORS FROM X-RAY DIFFRACTION LINE
PROFILES (CaF_2 STANDARD, FILM MOUNT)

Factors	Mode CL	Mean CL	Max CL	RMSS Mode	RMSS Mean	RMSS Max
Mode CL	0.10	0.89	0.89	0.01	0.89	0.19
Mean CL		0.61	0.90	0.63	0.69	0.74
Max CL			0.69	0.81	0.69	0.93
RMSS Mode				0.01	0.25	0.11
RMSS Mean					0.23	0.24
RMSS Max						0.03

2.   The present data indicate that crystallite size is inversely proportional to the first order of reactivity. The root mean square strains appear to be directly proportional to reactivity with a second degree function. When the microstructure factors are used to predict reactivity of solids for gases, the results are improved considerably by regressing two factors at a time.

3.   The use of thin samples gave a different order of mean CLs than those obtained for a series of bulk samples. The single factor correlation coefficients were lower for thin samples than bulk samples. However, when the thin sample results were regressed two at a time, higher correlations were achieved for some pairs than for those obtained for bulk samples. It is hypothesized that the thin samples gave better resolved peaks allowing the separation of factors which were synergistically related.

The assistance of David Natschke and Shawn Karns of Acurex Corporation, in collection and reduction of data, is deeply appreciated.

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