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Influence of Particle size in Quantitative X-Ray Analysis of Substances with a Pronounced Disposition for Preferential Orientation of Crystallites. Quantitative X-Ray Determination of Calcium Hydroxide

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The paper deals with the influence of particle size in quantitative X-ray analysis of substances with a pronounced disposition of crystallites to orient preferentially. Dependence of the broadening of diffraction maxima on the degree of preferential orientation of crystallites is proved experimentally. An equation has been derived to correct the broadening of diffraction maxima to the value belonging to randomly oriented specimen. Such a correction is needed to find out the dependence of the coefficient of proportionality α (reflection intensity/weight fraction) on the particle size of crystallites. This dependence is expressed by equation $B_1 \cdot \alpha = \text{const.}$ which is the result of experiments carried out in quantitative X-ray analysis of calcium hydroxide.

INTRODUCTION

The height and breadth of diffraction maxima of any crystalline substance are closely connected with the particle size of crystallites on which the X-rays diffract: the smaller the crystallites the lower and broader their diffraction maxima.

These intensity variations which result from different particle size of crystallites in different samples of the same compound demand special attention in the course of quantitative determination, especially if the heights of diffraction maxima are included in the calculation. In that case the coefficients of proportionality α between the analytical reflection intensity and the weight fraction are not the same for all specimens of the compound because there are differences with regard to particle size of crystallites. The mentioned coefficients have therefore to be determined separately for samples with different particle size of crystallites. This experimental way makes it possible to ascertain the dependence of these coefficients on the particle size of crystallites.

Difficulties caused by differences in particle size of crystallites are even more complicated in compounds with a pronounced disposition of crystallites to orient preferentially because such crystallites and the randomly oriented ones do not contribute equally to the breadth of diffraction maxima, as observed in the experimental work on calcium hydroxide. This fact also must be taken into consideration in X-ray quantitative determination when peak heights are used.

THEORETICAL PART

The particle size of crystallites in a sample and the breadth of the diffraction maxima are connected, as already known, by Scherrer's equation

$$D = \frac{K \cdot \lambda}{\beta \cos \Theta} \tag{1}$$

where

D — mean particle size of crystallites,

β — broadening of diffraction maxima corrected for instrumental broadening,

K — constant comprising the form of crystallites and the way D and β are defined.

This expression makes it possible to define the mean particle size of crystallites in a sample from experimental data on the breadth of diffraction maxima.

The breadth of the diffraction maximum, which becomes stronger due to preferential orientation of crystallites in the sample, is influenced both by the mean size of randomly oriented and that of preferentially oriented crystallites. If these two mean sizes were equal or if the crystallites would orient regardless of their size, the degree of preferential orientation would not effect the breadth of a certain diffraction maximum. It was noticed, however, that the diffraction maxima which increase through intensified preferential orientation become more and more narrow as the degree of the orientation increases. This leads to the conclusion that it is mostly the larger crystallites that orient preferentially. It is obvious that the experimentally obtained breadth of diffraction maximum on samples with preferentially oriented crystallites cannot represent a direct value for the particle size determination because this breadth depends also on the degree of preferential orientation. The breadth of a diffraction maximum should therefore be defined for a sample containing randomly oriented crystallites. As such a sample is not available in the case of well developed and larger crystallites, the breadth of diffraction maximum for a sample with randomly oriented crystallites must be determined from experimentally obtained breadth of diffraction maxima belonging to samples with a different degree of preferential orientation of crystallites. To this purpose the breadth of a diffraction maximum was theoretically analyzed for preferentially oriented crystallites.

According to this theoretical analysis the experimentally obtained integral breadth of a diffraction maximum (denoted with $\overrightarrow{B}$ on Fig. 1) can be expressed

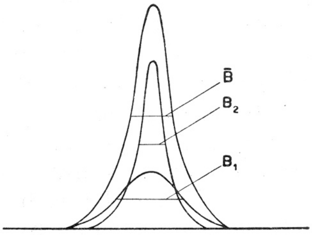


Fig. 1. Breadth of diffraction maxima resulting from the fraction of randomly oriented crystallites (B_1) and preferentially oriented crystallites (B_2). $\overrightarrow{B}$ experimentally determined breadth.

by its area and height. The height of diffraction maximum (I'_p) which increases with the intensification of preferential orientation of crystallites in a sample can be defined by the expression deduced in the work on correction of intensity with regard to preferential orientation of crystallites[1]:

$$I'_p = (1 - x) \cdot I_p + \beta x I_p = (1 - x + \beta x) I_p \tag{2}$$

where

I_p — height of diffraction maximum which increases through intensified preferential orientation for a randomly oriented sample,

x — fraction of crystallites which orient preferentially,

β — factor of proportionality between the reflection intensity on a powder sample and that on a monocrystalline one.

The area of the considered diffraction maximum, *i. e.* its integral intensity, equals the sum of integral intensities of diffraction maxima caused by the preferentially and the randomly oriented fractions respectively:

$$(1 - x) I_p B_1 + \beta x I_p B_2 \tag{3}$$

where

B_1 — breadth of diffraction maximum which increases through the intensification of preferential orientation and belongs to the randomly oriented fraction of crystallites,

B_2 — breadth of diffraction maximum which increases through the intensification of preferential orientation and belongs to the preferentially oriented fraction of crystallites.

Consequently the integral breadth ($\overline{B}$) of experimentally obtained diffraction maxima which increase through intensified preferential orientation can be expressed by

$$\overline{B} = \frac{(1 - x) I_p B_1 + \beta x I_p B_2}{(1 - x + \beta x) I_p} \tag{4}$$

From one of the fundamental equations in the earlierly mentioned work[1] showing the change of the reflection intensity caused by the change in the degree of preferential orientation of crystallites, namely:

$$I'_{np} = (1 - x) I_{np} \tag{5}$$

where

I'_{np} — reflection intensity which decreases due to the intensification of preferential orientation of crystallites for a sample with preferentially oriented crystallites,

I_{np} — intensity of the same reflection for a sample with randomly oriented crystallites

we obtain the expression

$$1 - x = \frac{I'_{np}}{I_{np}} \tag{6}$$

Introducing this expression into equation (2) we have

$$\beta x = \frac{I'_p}{I_p} - \frac{I'_{np}}{I_{np}} \tag{7}$$

and substituting the expression for $1 - x$ and βx into equation (4) we get the following linear dependence between the integral breadth of diffraction maximum and the ratio of intensities:

$$\overline{B} = B_2 + \frac{I'_{np}/I_{np}}{I'_p/I_p}(B_1 - B_2) = B_2 + \frac{I_p}{I_{np}}(B_1 - B_2) \cdot q \tag{8}$$

The I_p/I_{np} (*i. e.* the ratio of intensity which increases and that which diminishes with the increase in the degree of preferential orientation for a randomly oriented sample) being a constant and known value for every substance, it is possible by applying Eq. 8 to determine the breadth of the diffraction maximum B_1 belonging to a randomly oriented sample from experimental data for $I'_{np}/I'_p = q$ and $\overline{B}$ obtained on samples with different degrees of preferential orientation of crystallites.

This breadth must be determined for all types of a compound for which the coefficient α is being determined in order to find out the interdependence of these two values, *i. e.* the function

$$B_1 = f(\alpha) \tag{9}$$

The theory here exposed has been experimentally verified in quantitative X-ray determination of calcium hydroxide.

EXPERIMENTAL PART

To deal with the problem of the combined effect, *i. e.* preferential orientation plus influence of particle size and form of crystallites in quantitative X-ray analysis of calcium hydroxide, it was necessary to prepare several types of the compound.

The starting substance was calcium oxide obtained by heating calcium carbonate *p. a.* at 1600° C.

Samples were prepared by:

— precipitation from water at 100° C. The precipitate was separated by quick filtration (CH-1)[2]

— hydration of calcium oxide in moist atmosphere at room temperature (CH-2)[2]

— hydration of calcium oxide in moist atmosphere at 40° C (CH-3)

— paste hydration (CH-4)

Samples of calcium hydroxide were dried in a desiccator over KOH to prevent contamination with carbon dioxide. On X-ray examination all samples were free of calcium oxide while calcium carbonate was present in one sample only (CH-1), where it was chemically determined as amounting to 2%. Consequently the calibration curve for this type of calcium hydroxide was corrected to 98%. In preparation of calibration mixtures quartz (SiO_2 *p. a.*) was used as internal standard (particle size less than 5 μ) and cement clinker and slag as diluents.

X-ray charts were obtained on *Philips* Geiger counter diffractometer. The radiation was *CuK α*. X-ray tube operated at 40 kV and 20 mA. X-ray beam was colimated by divergent and scatter slits 1° and 0.2 mm. Scanning speed was 1/4° 2 Θ per mm., and paper speed 800 mm./h.

As analytical reflections we took for

$Ca(OH)_2$ $d = 4.90$ Å (I_p)
$d = 2.682$ Å (I_{np})
SiO_2 $d = 3.35$ Å (I_s)

For every calibration mixture X-ray charts were made on two samples prepared by a different mounting technique. The intensities were determined by measuring the height of diffraction maxima.

The breadth of diffraction maxima was determined for all types of calcium hydroxide which served in the preparation of calibration mixtures. X-ray charts were made and the heights of analytical reflections measured for every type of calcium hydroxide on a number of samples obtained by different mounting techniques. Instead of measuring integral breadth we measured the breadth of diffraction maximum in the middle of the reflection height.

This approximation of the breadth of diffraction maxima is deduced from a great number of experimental data which showed that there is a linear dependence between approximative breadth and the ratio I'_{np}/I'_{p}. The results are presented on Table I.

TABLE I

Types of $Ca(OH)_2$	I'_{np}/I'_{p}	$\overline{B}_{101}$ (°2 Θ)	$\overline{B}$ (°2 Θ)	$\overline{B}_{corr.}$ (°2 Θ)
CH-1	1.18	0.253	0.229	0.232
	0.86	0.262	0.196	0.196
	0.34	0.262	0.159	0.159
	1.45	0.262	0.247	0.247
	0.94	0.296	0.243	0.216
CH-2	1.64	0.619	0.638	0.638
	1.65	0.600	0.615	0.619
CH-3	1.66	0.460	0.471	0.471
CH-4	1.58	0.244	0.229	0.219
	1.35	0.229	0.184	0.189
	1.47	0.240	0.206	0.201
	1.37	0.235	0.206	0.206
	1.19	0.236	0.188	0.186
	1.12	0.235	0.188	0.188

RESULTS

The correction of analytical reflection intensities for preferential orientation by means of the correction factor

$$f = A \frac{I'_{np}}{I'_{p}} + B$$

was described in earlierly published works[1,3]. The values for correction constants A and B are given as $A = 0.646$, $B = 0.048$[3]. These constants enabled us to correct the experimentally obtained intensity ratios I'_{p}/I_{s} to $(I_{p})_{o}/I_{s}$, *i. e.* to the degree of preferential orientation corresponding to $I'_{np}/I'_{p} = 1.490$.

Thus corrected intensity ratios were then used for the construction of calibration curves for all the four types of calcium hydroxide. Figures 2—5 represent these calibration curves. Different coefficients of proportionality α were obtained and they are given in Table II.

In the theoretical part expressions have been derived which provide means to determine the breadth B_1 for randomly oriented crystallites according to

Eq. 8 from the mean broadening B at different degrees of preferential orientation in crystallites, *i. e.*

$$\overline{B} = B_2 + \frac{I'_{\mathrm{np}}}{I'_{\mathrm{p}}} \cdot \frac{I_{\mathrm{p}}}{I_{\mathrm{np}}} (B_1 - B_2)$$

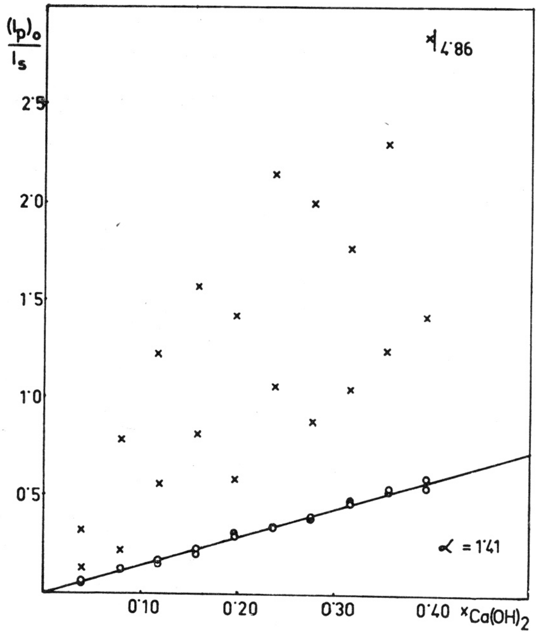


Fig. 2. Calibration graph for CH-1.

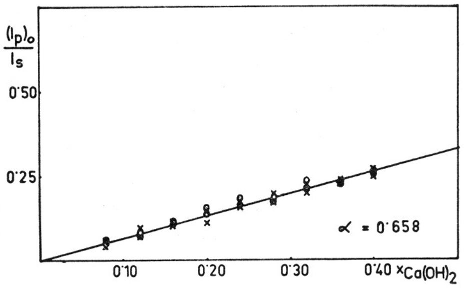


Fig. 3. Calibration graph for CH-2.

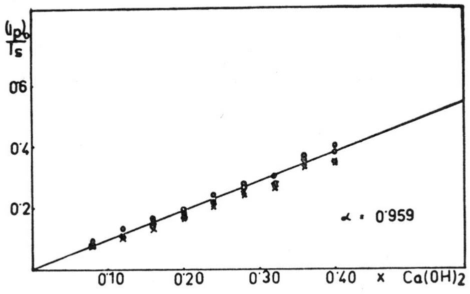


Fig. 4. Calibration graph for CH-3.

In this equation $I_{\mathrm{p}}/I_{\mathrm{np}}\,(B_1 - B_2)$ is constant, so the equation is a linear one where $I'_{\mathrm{np}}/I'_{\mathrm{p}}$ and $\overline{B}$ are variables which have to be determined experimentally.

It was presumed that under constant experimental conditions randomly oriented crystallites will induce no broadening of the (*101*) reflection. However, a slight broadening was noticeable in connection with different preparation techniques (compact-incompact), so a correction of mean breadth $\bar{B}$ was made by using equation

$$\bar{B}_{\mathrm{cor}} = \frac{\bar{B} \times (\bar{B}_{\mathrm{comp}})_{101}}{(\bar{B}_{\mathrm{incomp}})_{101}} \qquad (10)$$

where

$\bar{B}_{\mathrm{comp}}$ — represents the value for $\bar{B}$ on the sample with the highest degree of preferential orientation.

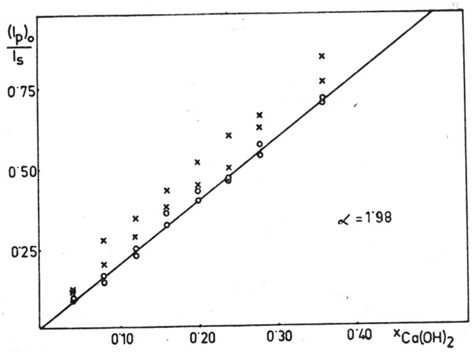


Fig. 5. Calibration graph for CH-4.

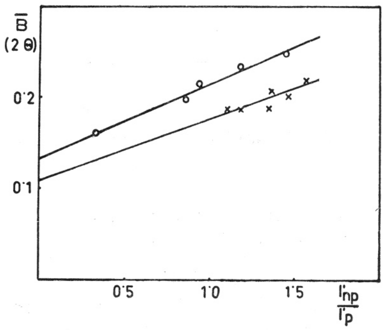


Fig. 6. Dependence of breadth $\bar{B}$ on ratio $I'_{\mathrm{np}}/I'_{\mathrm{p}}$.

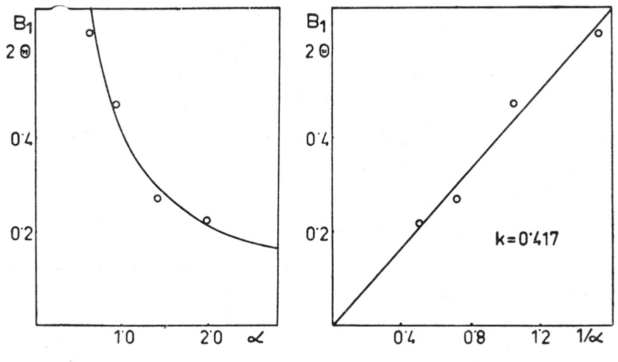
TABLE II

Types of $Ca(OH)_2$	α
CH-1	1.410
CH-2	0.658
CH-3	0.959
CH-4	1.980

TABLE III

Types of $Ca(OH)_2$	B_1 ($^{0}2\,\Theta$)	α
CH-1	0.27	1.410
CH-2	0.62	0.658
CH-3	0.47	0.959
CH-4	0.22	1.980

Curves for CH-1 and CH-4 were calculated by the least squares method from corrected values for $\bar{B}_{\mathrm{cor}}$ and the measured intensity ratios $I'_{\mathrm{np}}/I'_{\mathrm{p}}$ (Fig. 6). In these samples variations in preparation technique brought about differences in the degree of preferential orientation. Types CH-2 and CH-3 were not preferentially oriented, so the broadening of diffraction maxima was constant. For samples CH-3 no preparate was obtained with a ratio $I_{\mathrm{np}}/I_{\mathrm{p}}$ smaller than 1.65. This being the maximum ratio for $I'_{\mathrm{np}}/I'_{\mathrm{p}}$, we concluded that there is no preferential orientation at that ratio. Values for B_1 and the coefficients α are presented in Table III.



a b

Fig. 7a and b. Dependence of coefficient of proportionality (α) on the breadth B_1.

DISCUSSION

X-ray investigations made to determine the influence of particle size of crystallites in quantitative analysis of calcium hydroxide demonstrated two essential points: first that there exists a direct dependence between the breadth of diffraction maximum and the degree of preferential orientation of crystallites, and second, that a rule for interdependence of the breadth of diffraction maxima and the coefficient of proportionality α between the weight fraction and the intensity (height) of diffraction maxima can be established only if the breadth of a diffraction maximum has been determined for a randomly oriented sample. It has been experimentally demonstrated that

$$B_1 \cdot \alpha = \text{const.} \tag{11}$$

Functional dependences for B_1 on α and B_1 on $1/\alpha$ are presented in Figs. 7a and 7b. Such a dependence was expected because the total intensity of scattered X-rays in a region of Bragg's angles is proportional to the volume fraction of the component, regardless of the particle size of its crystallites or the breadth of the diffraction maxima. In other words, the integral reflection does not depend on the particle size of crystallites, as already known. Consequently, in the construction of calibration curves from integral reflection and identical coefficient α would be obtained for all types of calcium hydroxide if preferential orientation of crystallites had been completely avoided in all samples. As this is practically impossible, another way of analysis has to be adopted.

From the results of these investigations on the influence of preferential orientation and particle size of crystallites in quantitative X-ray analysis of calcium hydroxide we can recommend the following way of quantitative determination. The standard substance in the amount added to calibration mixtures for construction of calibration curves to determine the coefficient α is admixed to a sample with an unknown content of $Ca(OH)_2$. A series of samples with different degrees of preferential orientation is then prepared from this mixture. The X-ray charts of the samples furnish data on the intensities (heights) and breadth of reflections which become stronger and those which diminish because of preferential orientation. From these data and after the previously published procedure[3] we determine the intensity of the analytical reflection belonging to a sample with a selected, definite degree of preferential orientation for which calibration curves have been constructed, and coefficients α determined. The breadth of analytical diffraction maximum which belongs to randomly oriented samples (B_1) is then determined by combining the data for heights and breadth of diffraction maxima in the way described by the present work (Eq. 8). The coefficient α belonging to this breadth is then read from the functional dependence (11). The concentration of calcium hydroxide in an unknown sample is calculated from the determined coefficient α and the analytical reflection intensity reduced to a definite degree of preferential orientation of crystallites by means of equation

$$\frac{(I_p)_o}{I_s} / \alpha = x_{CH}$$

In the recommended procedure the intensities of diffraction maxima are presented by their heights. An analysis with integral reflections, *i. e.* areas, would do better for calibration because, if previously corrected for preferential orientation, would give the same coefficient α for all types of calcium hydroxide. In our opinion the calculation with heights is a better procedure, especially if $Ca(OH)_2$ is determined in systems where its diffraction maxima are partly overlapped by diffraction maxima of other components. In order to use the integral reflection intensities in quantitative X-ray analysis of calcium hydroxide we need know the simultaneous influence of the degree of preferential orientation and of the particle size of crystallites on the changes in ratio of integral intensities of different reflections. This problem is the subject of our further investigation.

The work carried out so far induces us to conclude that the problem of quantitative X-ray analysis of calcium hydroxide is a very complex one and that several different phenomena have to be taken into account. Even the two essential problems: *i. e.* the disposition to orient preferentially and the influence of particle size of crystallites are complicated and reciprocally dependent. The change in the breadth of diffraction maximum can be brought about by the change in the degree of preferential orientation only when the particle size of crystallites in a sample differs considerably. The distribution of particle size and the form of crystallites influence the ability for preferential orientation and the fraction of crystallites which are so oriented. The fact that different samples with identical mean particle size have different dispositions to orient preferentially can be explained only by joint consideration of particle size distribution and of the form of crystallites belonging to different specimens. Likewise it can happen that a sample with smaller crystallites will display a stronger disposition to orient preferentially. In our opinion this dependence between the degree of preferential orientation of crystallites and the broadening of diffraction maximum should supply important data for the calculation of particle size distribution functions and its application will most likely be used also outside quantitative X-ray analysis.

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IZVOD

Utjecaj veličine čestica u kvantitativnoj rendgenskoj analizi supstancija s izrazitom sposobnošću preferiranog orijentiranja kristalita. Kvantitativno rendgensko određivanje kalcijevog hidroksida

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Razrađena je metoda pomoću koje se mogu eliminirati greške koje nastaju kod kvantitativne rendgenske analize supstancija s izrazitom sposobnošću preferiranog orijentiranja kristalita zbog razlika u veličini čestica. Eksperimentalno je dokazana funkcionalna ovisnost između proširenja difrakcijskog maksimuma i stepena preferirane orijentacije kristalita. Izvedena je jednadžba iz koje se može odrediti širina difrakcijskog maksimuma za kaotično orijentirani uzorak. Ovu je širinu (B_1) potrebno odrediti da se ustanovi ovisnost kalibracione konstante (α) o veličini kristalita. Nađeno je da se ta ovisnost može izraziti jednadžbom: $B_1 \cdot \alpha =$ konst. Mjerenja su izvršena na kalcijevom hidroksidu.

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