

CCA-391

545.824:546.41—36

Original Scientific Paper

## Correction of Preferential Crystallite Orientation in X-ray Quantitative Analysis. Quantitative X-ray Determination of $\text{Ca}(\text{OH})_2$

A. Bezjak and I. Jelenić

Research Department, Association of Yugoslav Cement Producers, Zagreb, Croatia, Yugoslavia

Received October 15, 1965

The work deals with the problem of preferential orientation of crystallites in quantitative X-ray analysis. A new method has been worked out theoretically and practically for the correction of reflection intensities from polycrystalline samples with preferentially oriented crystallites. Equations are included for the determination of correction parameters. Practical application of the new method is demonstrated on quantitative X-ray analysis of calcium hydroxide. The work includes a calibration graph for the determination of coefficient  $\alpha$ , comparing corrected and uncorrected values of analytical intensities of  $\text{Ca}(\text{OH})_2$ .

Quantitative X-ray analysis has become rather important in the determination of constituents in multiphase systems. Methods have been worked out for the application of quantitative X-ray analysis to special systems with the intention of obtaining more precise data. Regardless of the considerable number of works published on the general and special application of quantitative X-ray analysis there are still some unsolved or only partially solved problems, so sometimes this extremely important and unique method is not accurate enough.

Such a crucial problem which has yet to be solved for the quantitative X-ray analysis of the phase composition in multiphase systems is the question of preferential orientation of crystallites in the examined sample. This problem is more important in spectrometric analysis than in the photographic technique. As today due to its considerable advantages diffractometric analysis is gaining ground, an answer should be found on the phenomenon of preferential orientation of crystallites in quantitative X-ray analysis. Preferential orientation in the specimen leads to an increased intensity of basal reflections and a diminution of other reflections. This diminution or increase depends on the degree of the preferential crystallite orientation in the specimen and as the degree is influenced by various agents it has not always the same value and so the intensity data are not reproducible.

So far the problem of preferential orientation has mainly been solved by a special technique of sample preparation which consists in pulverizing the specimen to a size of the order  $< 5 \mu$  and in a special technique of mounting the specimen in the holder. Yet, when crystallites have a specially expressed plane or lathlike habit and a pronounced cleavage the preferential orientation in the sample cannot be avoided nor a satisfactory reproducibility of intensity

data for particular diffraction maxima achieved. This is the reason why such specimens are unsuitable for quantitative X-ray determination.

This work presents theoretically and practically a method which offers a correction of the intensity data for particular reflections in a polycrystalline specimen exhibiting a preferred orientation. The calculations are made from experimental data obtained from the intensity of reflections, considering both those increased and those diminished by the preferential orientation. The worked out theory has been applied in practice to quantitative X-ray analysis of calcium hydroxide where the crystallites are characterized by a hexagonal plane habit and therefore have a tendency to orient preferentially which leads to an error in quantitative determination.

Copeland and Bragg<sup>1</sup> who developed a method for quantitative analysis of calcium hydroxide in hydrated cement, tried to avoid the preferential orientation of crystallites by a special technique of specimen preparation, *i. e.* by attempting to eliminate this orientation in the sample. They checked the accuracy of single analytical data by comparing the results obtained from increased reflections to those from diminished reflections, both brought about by preferentially oriented crystallites in the specimen.

This work describes a more general method which can find wider applications in practice.

#### THEORETICAL

Quantitative X-ray analysis is based on the known Alexander and Klug<sup>2</sup> equation:

$$\frac{I_i}{I_s} = \alpha X_i \quad (1)$$

where  $I_i$  = intensity of the  $i$ -th reflection of the quantitatively examined substance

$I_s$  = intensity of the standard reflection

$\alpha$  = coefficient of proportionality

$X_i$  = concentration of  $i$ -th component

This equation refers to the method of internal standard. In practice, quantitative analysis by means of this equation becomes impossible if during the preparation of specimen the  $I_i$  changes because of the preferentially oriented crystallites.

However, for such preferentially oriented specimens another equation analogous to equation (1) can be derived:

$$\frac{(I_p)_o}{I_s} = \alpha X_i \quad (2)$$

In equation (2)  $(I_p)_o$  stands for the intensity of the  $p$ -th reflection for all specimens demonstrating the same degree of preferred orientation. Mostly, however, in specimen preparation the same degree of preferential orientation is not always achieved and this results in the change of intensity  $I'_p$ .

We can take that

$$(I_p)_o = f \cdot I'_p \quad (3)$$

In this relation  $I'_p$  signifies the intensity of a selected reflection, if the degree of preferential orientation in the specimen differs from the degree for which the intensity of the selected reflection is expressed as  $(I_p)_0$ . In equation (3)  $f$  is the factor term for reciprocal dependence of the mentioned intensities, *i. e.* the factor by which  $I'_p$  should be multiplied to obtain  $(I_p)_0$ . This factor  $f$  is not constant but dependent on the degree of the preferred orientation of crystallites. In order to solve the problem of determining the  $f$  factor following considerations have been made.

In X-ray analysis according to Bragg-Brentano principle on a flat and mounted powder sample those planes only are reflected which lie parallel to the sample plane. In the usual way of preparation crystallites with laminated (plate-like) structures such as calcium hydroxide and clay minerals are preferentially oriented in such a way that their basal planes come parallel to the sample plane. As a result the intensity of basal reflections becomes intensified whilst that of all the other reflections weakens. This consequently indicates that there is an interdependence between the intensification of basal reflections and the weakening of all the other reflections.

Therefore the intensities of all the reflections in the specimen containing preferentially oriented crystallites can be divided into two groups. The intensities of the first group become stronger if the degree of preferential orientation of crystallites in the specimen increases (they are mostly basal reflections). The intensities of these reflections are expressed by  $I_p$  if the degree of preferential orientation of crystals in the specimen equals zero and if the degree is bigger than zero they are expressed by  $I'_p$ . For the second group of reflections the intensities become less with the increased degree of preferred orientation. They are expressed by  $I_{np}$  if the degree of preferential orientation equals zero and by  $I'_{np}$  if this degree is bigger than zero.

In the case when an  $x$ -th part of the total number of crystals has a preferred orientation then

$$I'_p = (1 - x) \cdot I_p + \beta x I_p = (1 - x + \beta x) \cdot I_p \quad (4)$$

and

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

where  $x$  = part by weight of the specimen crystals which have oriented preferentially

$I_p$  and  $I_{np}$  = intensities of reflections obtained on a specimen with randomly oriented crystals, *i. e.* intensities corresponding to normal Debye-intensities.

In a specimen with preferred orientation the normal Debye intensities are diminished for the factor  $(1 - x)$  ( $x$  being the measurement of the degree of preferential orientation of crystals), because the part of randomly oriented crystals also diminished for the same factor. The intensity  $I'_p$  in a specimen with preferentially oriented crystals increases for the member  $\beta x I_p$ . The coefficient  $\beta$  is the factor for converting the intensity of the Debye reflection  $I_p$  into the intensity of the corresponding reflection which results from a large number of preferentially oriented small monocrystals.  $\beta$  depends on the reflection angle and the X-ray characteristics of the substance so it must be separately determined for every component and every reflection.

By eliminating  $x$  in the equations (4) and (5) (Appendix-I) we have:

$$\frac{I'_p}{I_p} = \beta + (1 - \beta) \cdot \frac{I'_{np}}{I_{np}} \quad (6)$$

This linear dependence can be written in another form (Appendix-II).

$$\frac{I_p}{I'_p} = aq + b \quad (7)$$

where  $q = \frac{I'_{np}}{I'_p}$

Equation (7) shows the linear dependence of  $\frac{I_p}{I'_p}$  upon the quotient  $\frac{I'_{np}}{I'_p}$ .

$\frac{I'_{np}}{I'_p}$  is the ratio of the reflection intensities of the two different groups for the same specimen and  $\frac{I_p}{I'_p}$  the ratio of reflection intensities of the first group in a randomly and a preferentially oriented specimen.

If the basic intensity is taken as the one with a definite degree of preferred orientation of crystallites  $(I_p)_o$ , then the equation (7) by substituting

$$I_p = \frac{1}{K} (I_p)_o \quad (8)$$

can be transformed into

$$\frac{(I_p)_o}{I'_p} = Kb + Kaq$$

or if  $A = Ka$  and  $B = Kb$  then

$$\frac{(I_p)_o}{I'_p} = Aq + B \quad (9)$$

or

$$(I_p)_o = (Aq + B) I'_p \quad (10)$$

where

$$Aq + B = f \quad (11)$$

The conversion of the intensity  $I'_p$  into  $(I_p)_o$  is made by means of equation (10). For this conversion the constants  $A$  and  $B$  must be known and they are found by a separate previous determination.

An analogous correction can be made for  $(I_{np})_o$  too.

$$\frac{(I_{np})_o}{I'_{np}} = A' + B' q' \quad (12)$$

$$(I_{np})_o = (A' + B' q') \cdot I'_{np} \quad (13)$$

where

$$q' = \frac{1}{q} = \frac{I'_p}{I'_{np}}$$

The constants  $A'$  and  $B'$  are also obtained experimentally.

## EXPERIMENTAL

The explained theory was applied in practice for quantitative X-ray analysis of calcium hydroxide.

Calcium hydroxide was prepared by the reaction of calcium oxide with water at the temperature of  $100^{\circ}\text{C}$ . Thus obtained precipitate of calcium hydroxide was separated by quick filtration and dried in a desiccator over KOH to constant weight.

The diffraction patterns were obtained with Philips Geiger counter diffractometer. The radiation was  $\text{CuK}\alpha$ . X-ray tube operated at 36 KV and 18 mA, X-ray beam was collimated by means of  $1^{\circ}$  divergent and scatter slits and a 0.2 mm receiving slit. Scanning speed was  $1/4^{\circ} 2\theta$  per minute and the chart paper speed 400 mm per hour.

To determine the coefficients A and B in equation (9) and (10) a mixture of calcium carbonate and calcium hydroxide was prepared at the ratio of 1 : 1. Calcium carbonate was used as standard. Five X-ray pictures of the prepared sample were made with a different degree of preferred orientation of crystallites. The difference in the degree of the preferred orientation was achieved by different techniques in specimen preparation. In the analysis the following reflections were used: for calcium hydroxide

index	d
001	4.90 Å
101	2.628

and for calcium carbonate the reflection belonging to  $d = 3.035 \text{ Å}$ .

Table I shows the ratios of intensity for calcium hydroxide to standard intensity of calcium carbonate.

TABLE I

$I'_p/I_s$ ( $I'_{001}/I_{\text{CaCO}_3}$ )	$I'_{np}/I_s$ ( $I'_{101}/I_{\text{CaCO}_3}$ )	$q = \frac{I'_{np}}{I'_p}$
0.866	0.624	0.720
0.495	0.738	1.490
1.090	0.578	0.530
0.576	0.720	1.250
0.616	0.708	1.150

TABLE II

X	$I'_p/I_s$	$I'_{np}/I_s$	$q = \frac{I'_{np}}{I'_p}$
0.05	0.354	0.336	0.950
0.05	0.300	0.308	1.030
0.10	0.740	0.536	0.726
0.10	0.720	0.491	0.682
0.15	1.070	0.838	0.778
0.15	1.040	0.750	0.715
0.20	1.520	0.956	0.630
0.20	1.260	1.068	0.850
0.25	1.550	1.281	0.825
0.25	2.060	1.270	0.620
0.30	2.240	1.520	0.679
0.30	2.140	1.500	0.701

The calibration graph for the determination of coefficient  $\alpha$  with the method of internal standard was made by means of calibration mixtures of calcium hydroxide, the standard substance and a diluents. Sodium chloride was used as internal standard and white cement as diluents. Mixtures were prepared with 5, 10, 15, 20, 25 and 30% of calcium hydroxide and 10% of the standard. Two samples were made from every mixture and two independent diffraction patterns were obtained. Table II

shows the ratios of intensities  $\frac{I_{001}}{I_{\text{NaCl}}}$ ,  $\frac{I_{101}}{I_{\text{NaCl}}}$  and  $\frac{I_{101}}{I_{001}}$ .

#### RESULTS

The constants A and B were determined from data quoted in Table I. The value of intensity  $I'_p$  taken for  $(I_p)_o$  is the intensity of the lowest degree of preferred orientation, *i.e.*  $q = 1.490$ . To avoid errors likely to happen because of differences in absorption and in the compactness of sample the inten-

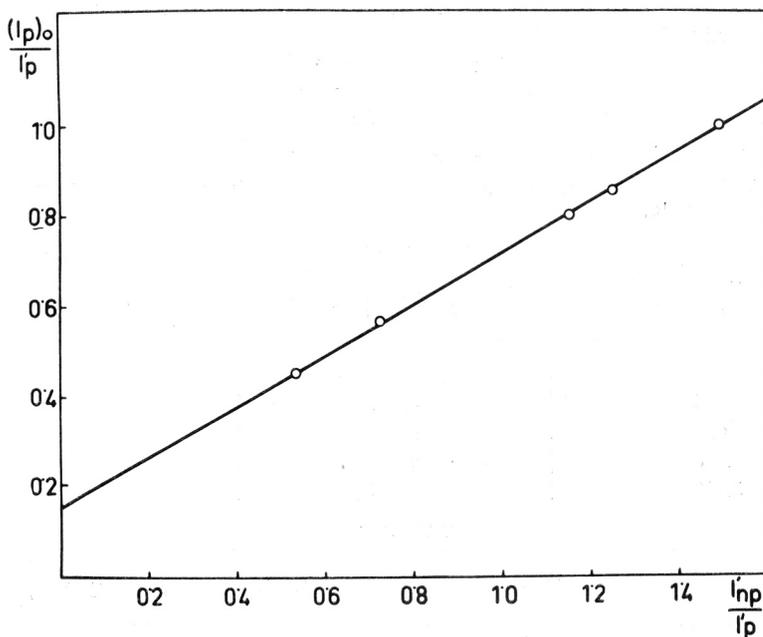


Fig. 1. Calibration graph to determine A and B of  $\text{Ca(OH)}_2$ .

sities were compared to the strongest intensity of calcium carbonate. For such comparison the equation (9) takes the form

$$\frac{(I_p)_o/I_s}{I'_p/I_s} = Aq + B \quad (14)$$

Table III gives the data for the calculation of coefficients A and B.

The least square method was used for the determination of the coefficients A and B;  $A = 0.561$  and  $B = 0.153$ . Figure 1 shows the line from which coefficients A and B were determined.

TABLE III

$\frac{(I_p)_o/I_s}{I'_p/I_s}$	$q = \frac{I'_{np}}{I'_p}$
0.570	0.720
1.000	1.490
0.455	0.530
0.860	1.250
0.803	1.150

TABLE IV

X	$q = \frac{I'_{np}}{I'_p}$	$f = Aq + B$	$I_p/I_s$	$(I_p)_o/I_s$
0.05	0.950	0.686	0.354	0.244
0.05	1.030	0.730	0.300	0.219
0.10	0.726	0.561	0.740	0.416
0.10	0.682	0.535	0.720	0.385
0.15	0.778	0.589	1.070	0.632
0.15	0.715	0.555	1.040	0.582
0.20	0.630	0.507	1.520	0.770
0.20	0.850	0.631	1.260	0.790
0.25	0.825	0.615	1.550	0.960
0.25	0.620	0.501	2.060	1.020
0.30	0.679	0.535	2.240	1.210
0.30	0.701	0.547	2.140	1.170

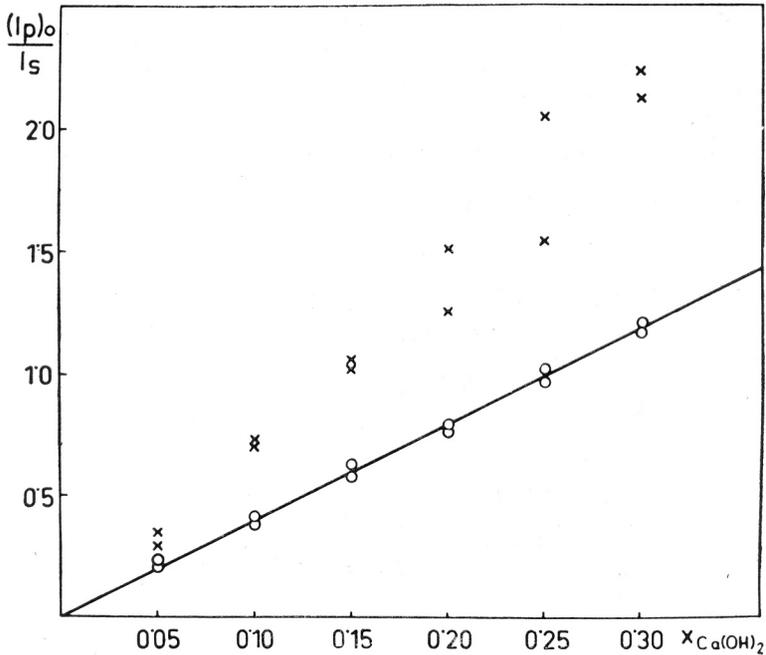


Fig. 2. Calibration graph for quantitative determination of  $Ca(OH)_2$ .

o — corrected intensities  
 x — uncorrected intensities

Equation (10) was used for the correction of experimentally obtained intensities when preparing the calibration graph. Table IV contains data for the concentration of calcium hydroxide ( $X$ )  $q$ ,  $f$ ,  $I'_p/I_s$  and  $(I_p)_0/I_s$ .

Fig. 2 shows the calibration graph for the quantitative determination of  $\text{Ca}(\text{OH})_2$ . The diagram was obtained from data of corrected intensities. Coefficient  $\alpha$  is 4.0. This value is also found by the least square method.

#### DISCUSSION

As demonstrated on Figure 2 satisfactory results in quantitative X-ray analysis can be obtained by correcting the intensities caused through preferred orientation of crystals in the sample. Without such correction the calibration line can be determined only with a very crase standard deviation. The correction is specially important for quantitative analysis of calcium hydroxide in unknown mixtures, the error caused by preferred orientation of crystallites being hard to define in such a case.

The presented method has another advantage, namely the possibility to analyze a sample with a high degree of preferred orientation which gives more precise data on the intensities. This is specially important when there are low concentrations of calcium hydroxide because preferred orientation increases its analytical 001 reflection.

At the present stage the only serious disadvantage of the proposed method occurred in case when  $I'_{np}$  cannot be determined. When discussing this method it should be noted that all the oriented crystallites do not contribute to the total intensity as measured by spectrometric analysis. This is due to the statistical orientation of crystallites oriented round the most favourable position. It can be assumed that this statistical distribution of orientation is not necessary the same for all substances, but it will always be nearly identical for the same material. The influence of this statistical distribution on the intensity is included in the coefficient  $\beta$  so that this coefficient has a wider significance than it has been pointed out in the theoretical part.

New methods are in progress to eliminate the mentioned difficulties which may occur under certain circumstances.

#### APPENDIX

I. Two fundamental equations for correction of preferred orientation are

$$I_p' = (1 - x + \beta x) I_p \quad (\text{A.1})$$

and

$$I_{np}' = (1 - x) I_{np} \quad (\text{A.2})$$

from A.2 we get

$$x = 1 - \frac{I_{np}'}{I_{np}} \quad (\text{A.3})$$

and by substituting  $x$  in (A.1)

$$\frac{I_p'}{I_p} = \frac{I_{np}'}{I_{np}} + \beta \left( 1 - \frac{I_{np}'}{I_{np}} \right) = \beta + (1 - \beta) \frac{I_{np}'}{I_{np}} \quad (\text{A.4})$$

II. Multiplying equation (A.4) by  $\frac{I_p}{I_p'}$

$$1 = \beta \frac{I_p}{I_p'} + (1 - \beta) \frac{I_{np}'}{I_{np}} \cdot \frac{I_p}{I_p'} = \beta \frac{I_p}{I_p'} + (1 - \beta) \frac{I_p}{I_{np}} \cdot \frac{I_{np}'}{I_p'} \quad (\text{A.5})$$

and dividing (A.5) by  $\beta$

$$\frac{1}{\beta} = \frac{I_p}{I'_p} + \frac{1-\beta}{\beta} \frac{I_p}{I_{np}} \cdot \frac{I'_{np}}{I'_p} \quad (\text{A.6})$$

or when  $\frac{\beta-1}{\beta} \cdot \frac{I_p}{I_{np}} = a$  and  $\frac{1}{\beta} = b$

we obtain

$$\frac{I_p}{I'_p} = a \frac{I'_{np}}{I'_p} + b \quad (\text{A.7})$$

and finally

$$\frac{I_p}{I'_p} = aq + b \quad (\text{A.8})$$

where  $\frac{I'_{np}}{I'_p} = q$  (A.9)

III. Multiplying equation (9) (Theoretical part)

by  $\frac{1}{q}$

$$\frac{(I_p)_e}{I'_p} \cdot \frac{1}{q} = A + B \frac{1}{q} \quad (\text{A.10})$$

or

$$\frac{(I_p)_e}{I'_p} \cdot \frac{I'_p}{I'_{np}} = A + B \frac{1}{q} \quad (\text{A.11})$$

$$\frac{(I_p)_e}{I'_{np}} = A + B \frac{1}{q} \quad (\text{A.12})$$

when  $(I_p)_e = k(I_{np})_e$  we have

$$\frac{(I_{np})_e}{I'_{np}} = \frac{A}{k} + \frac{B}{k} \frac{1}{q} \quad (\text{A.14})$$

$\frac{A}{k} = B'$  and  $\frac{B}{k} = A'$  are constants. If  $\frac{1}{q} = q'$

we finally get

$$\frac{(I_{np})_e}{I'_{np}} = A'q' + B' \quad (\text{A.15})$$

#### REFERENCES

1. L. E. Copeland and R. H. Bragg, *Anal. Chem.* **30** (1958) 196.
2. H. P. Klug and L. E. Alexander, *The X-ray Diffraction Procedures*, John Wiley, New York 1954, p. 412.

#### IZVOD

**Korekcija s obzirom na preferiranu orijentaciju kristalita u rendgenskoj kvantitativnoj analizi. Rendgenska kvantitativna analiza  $\text{Ca}(\text{OH})_2$**

A. Bezjak i I. Jelenić

Rad obrađuje problem preferirane orijentacije kristaliteta u kvantitativnoj rendgenskoj analizi. Teoretski i praktički je razradena nova metoda za korekciju intenziteta refleksa s polikristaliničnih uzoraka koji sadrže preferirano orijentirane

kristalite. Izvedene su jednadžbe za određivanje korekcionog faktora. Praktična primjena nove metode prikazana je na kvantitativnoj rendgenskoj analizi kalcijevog hidroksida. Dobiven je baždarni dijagram za određivanje koeficijenta  $\alpha$  uz usporedbu korigiranih i nekorigiranih vrijednosti analitičkog intenziteta.

ISTRAZIVACKI ODJEL,  
UDRUZENJA PROIZVOĐAČA CEMENTA  
ZAGREB

Primljeno 15. studenoga 1965.