Determination of preferred orientation degree of portlandite by using rocking curve of diffraction line

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It is pointed out by theoretical analyses that calculating the preferred orientation degree of portlandite within the interfacial zone between cement paste and the aggregate, according to the currently accepted formula, can only be used as a qualitative method. The authors propose a method using the rocking curve of the diffraction line for determining the preferred orientation degree of portlandite and obtaining more precise results. This method can be used as a quantitative one.

1. INTRODUCTION

The preferred orientation of crystals in polycrystalline materials may have significant influence on the macro-scopic properties of these materials. In the study of cement-based materials, many researchers have found, by analysing X-ray diffraction lines, that the most characteristic feature of the microstructure within the weakest zone of bonding (transition zone) between cement-paste and aggregate is the preferred orientation of portlandite (crystalline $Ca(OH)_2$) with its c axis normal to the aggregate surface. Furthermore, the degree of preferred orientation in the zone is an important index to measure the properties of the interfacial zone. Thus, evaluating the degree of preferred orientation is the most important task for further studying the relationship between the structure of the interfacial zone and the bond properties within the interfacial zone.

2. PREVIOUS METHODS

2.1 Review of methods for determining preferred orientation

The phenomenon of preferred orientation of crystals exists widely in polycrystalline materials. Many re-searchers have studied for a long time to find a method for evaluating the preferred orientation. In 1924 a German metallurgist, Weller [1], proposed a pole-figure method and in 1940 Barrett et al. [2] proposed an inverse pole figure method. However, neither method can evaluate the texture quantitatively. Later, in the middle of the 1960s, Bunge [3] and Roe [4] proposed separately two methods using the orientation distribution function, with which the evaluation of crystalline preferred orientation can reach the quantitative level. But these two methods

were most complex and they can hardly be used widely in routine research work.

For polycrystals with a simpler structure, some scholars have proposed evaluating the degree of preferred orientation by measuring the diffraction intensities of crystalline planes in textured materials. For example, the formula of Mueller et al. [5] gives

$$P_{hkl} = \frac{I_{hkl}/I_{R,hkl}}{(1/n)\Sigma(I_{hkl}/I_{R,hkl})} \qquad (1)$$

in which I_{hkl} is the intensity of the (hkl) reflection from a textured specimen and $I_{R,hkl}$ is the intensity of the (hkl) reflection from a random specimen; the subscript R indicates the factors that are different for the random sample. n is the number of reflections.

Morris's formula [6] gives

$$P_{hkl} = \frac{I_{hkl}/I_{R,hkl}}{\Sigma(A_{hkl}I_{hkl}/I_{R,hkl})} \qquad (2)$$

in which A_{hkl} is the area of a spherical polygon associated with (hkl) expressed as a fraction of the total area. The value of A_{hkl} for different planes can be obtained by calculation [6].

The formula of Morta et al. [7] gives

$$P_{hkl} = \frac{\Sigma(N_{hkl}I_{hkl}/I_{R,hkl})}{(\Sigma N_{hkl}I_{hkl}/I_{R,hkl})} \qquad (3)$$

in which N_{hkl} is the multiplicity factor of (hkl).

In addition, for a compound with laminated structure, Lotgering [8] proposed a corresponding definition of pre-ferred orientation and a method of X-ray determination. His definition of a preferred orientation F is

$$F = \frac{P - P_0}{1 - P_0} \qquad (4)$$

where P_0 and P are the ratios of intensities of the (001) diffraction line and the total diffraction line, for a random material and a textured one, respectively. P_0 and P are as follows:

$$P_0 = \frac{\Sigma I_{R,001}}{\Sigma I_{R,hkl}} , \qquad P = \frac{\Sigma I_{001}}{\Sigma I_{hkl}}$$

The four methods mentioned above for evaluating the degree of preferred orientation share a common disadvantage: that the value of the orientation degree calculated from these formulae depends on the number of planes selected. Because these methods require the intensities of as many planes as possible, very low intensities of diffraction line may be included. This affects significantly the precision of calculating the result, as already pointed out by others [9]. Furthermore, for evaluating the degree of preferred orientation, the methods cannot be used for hardened cement paste due to the overlap of the diffraction lines of different crystals. Taking C_3S as an example,* its diffraction lines are disturbed by CSH at 0.304 and 0.276 to 274 nm, by portlandite at 0.261 nm and by ettringite at 0.218 nm.

2.2 Discussion of the formula for evaluating the degree of preferred orientation currently used

For the transitional zone between cement paste and aggregate, the preferred orientation is currently evaluated by the method proposed by Grandet and Ollivier [10]. Measuring the intensities of the diffraction line on the (001) and (101) planes of portlandite, the preferred orientation degree I_{CH} of portlandite can be calculated according to the formula

$$I_{CH} = \frac{I_{001}/I_{101}}{0.74} \tag{5}$$

Equation 5 has been widely used to evaluate the orientation degree of portlandite within the interfacial zone since the 7th International Congress on Cement Chemistry in 1980.

Equation 5 was proposed by Grandet and Ollivier [10], but they did not discuss it or give a definitively physical meaning to it. The equation was obtained according to the relationship between the intensities (001) and (101) of random portlandite. The physical meaning can be obtained by the following analysis. When the crystal exists in a random state in a space, the intensity of a group of (hkl) planes is as follows [11]:

$$I_{R,hkl} = \left(\frac{e^4}{m^2c^4}\right)\left(\frac{I_0\lambda^3}{32\pi r}\right)\left(\frac{N_{hkl}F^2_{hkl}}{v^2}\right)$$

$$\phi(\theta)e^{-2M}\left(\frac{1}{2\mu_R}\right)v'_{R,hkl,n} \tag{6}$$

*C = CaO, S = SiO_2, H = H_2O.

where e,m are the electronic charge and mass, respectively, I_0 is the intensity of the incident X-rays, λ is the wavelength of the incident X-rays, c is the velocity of light, V is the unit cell volume, N_{hkl} is the number of equivalent planes, F_{hkl} is the structure amplitude, e^{-2M} is the temperature-correction factor, $\phi(\theta)$ is the Lorentz polarization factor $(1 + \cos^2 2\theta)/\sin^2\theta \cos\theta$, μ is the linear absorption factor of the specimen, r is the radius of the cylindrical film, $V'_{R,hkl,n}$ is the diffraction volume of the (hkl) planes parallel to the surface of the specimen and $I_{R,hkl}$ is the absolute diffraction intensity.

The corresponding equation for a textured specimen is

$$I_{hkl} = \left(\frac{e^4}{m^2c^4}\right)\left(\frac{I_0\lambda^3}{32\pi r}\right)\left(\frac{N_{hkl}F^2_{hkl}}{v^2}\right)$$

$$\phi(\theta)e^{-2M}\left(\frac{1}{2\mu}\right)v'_{hkl,n} \tag{7}$$

Dividing equation 7 by Equation 6 yields

$$\frac{I_{hkl}}{I_{R,hkl}} = \frac{\mu_R}{\mu}\frac{v'_{hkl,n}}{v'_{R,hkl,n}} \tag{8}$$

For eliminating the error caused by the unequal volume V between the random and the textured specimen, $V'_{hkl,n}$ and $V'_{R,hkl,n/m}$ must be divided by V and V_R, respectively. Here, V corresponds to the volume of the diffraction phase. Thus

$$v_{hkl,n} = \frac{v'_{hkl,n}}{v} \qquad v_{R,hkl,n} = \frac{v'_{R,hkl,n}}{v_R}$$

According to the definition of the orientation factor P_{hkl},

$$P_{hkl} = \frac{V_{hkl,n}}{V_{R,hkl,n}}$$

Equation 8 can be written as follows:

$$\frac{I_{hkl}}{I_{R,hkl}} = \frac{\mu_R}{\mu}\frac{V}{V_R}\frac{V_{hkl,n}}{V_{R,hkl,n}} = \frac{\mu_R}{\mu}\frac{V}{V_R}P_{hkl}$$

Summing over all the measured reflections, this results in the following equation:

$$\Sigma\frac{I_{hkl}}{I_{R,hkl}} = \frac{\mu_R}{\mu}\frac{V}{V_R}\Sigma P_{hkl} \tag{10}$$

Dividing Equation 9 by Equation 10 yields

$$P_{hkl} = \frac{I_{hkl}}{I_{R,hkl}}\frac{\Sigma P_{hkl}}{\Sigma(I_{hkl}/I_{R,hkl})} \tag{11}$$

Similarly, for the plane $(h'k'l')$ we have

$$P_{h'k'l'} = \frac{I_{h'k'l'}}{I_{R,h'k'l'}}\frac{\Sigma P_{h'k'l'}}{\Sigma(I_{h'k'l'}/I_{R,h'k'l'})}$$

$$= \frac{I_{h'k'l'}}{I_{R,h'k'l'}}\frac{\Sigma P_{hkl}}{\Sigma(I_{hkl}/I_{R,hkl})} \tag{12}$$

Dividing Equation 11 by Equation 12 yields

$$\frac{P_{hkl}}{P_{h'k'l'}} = \frac{I_{hkl}}{I_{R,hkl}} \frac{I_{R,h'k'l'}}{I_{h'k'l'}}$$

For crystalline portlandite, letting (hkl) be (001) and (hkl) be (101), the final result is as follows:

$$\frac{P_{001}}{P_{101}} = \frac{I_{001}/I_{101}}{0.74} = I_{CH} \qquad (13)$$

Thus it can be seen that the degree of preferred orientation of portlandite defined by Equation 5 is essentially the ratio of orientation factor for plane (001) to that of plane (101). If $P_{101} = 1$, i.e. plane (101) is considered in random orientation, the I_{CH} value calculated from Equation 5 represents the orientation degree of plane (001). However, this is in fact impossible, because the space distributions of all planes change as preferred orientation of any crystal takes place. The diffraction intensities of all planes then change. Once the preferred orientation occurs on a plane (hkl), not only is the diffraction line of the plane itself strengthened, but the diffraction lines of all the planes are changed. It can be seen spatially that, as the preferred orientation occurs on a plane (hkl) of a crystalline grain, any plane at an angle of $\beta = 90°$ to the orientation plane (hkl) will experience a negative orientation, and the intensities of diffraction lines will be weaker. So-called negative orientation is when the volume of crystalline grain in which the normal of the plane is parallel to the normal of the sample surface is less than that of a random sample; as the angle β approaches 0° the intensity of the diffraction line of the plane will be strengthened. These two effects are proportional to the orientation degree of crystals. For portlandite the angle between plane (101) and plane (001) is 57.63°, i.e. greater than 45°. Thus, when plane (001) takes a preferred orientation, the plane (101) will take a negative orientation at a certain level, and cause the diffraction line of the plane (101) to weaken. Moreover, the weakening level is proportional to the degree of preferred orientation of plane (001). Therefore, the orientation degree of portlandite calculated by Equation 5 will be higher than that of the real value. In view of this, the method for evaluating the orientation degree of portlandite proposed by Grandet and Ollivier can only be used as a qualitative one.

3. QUANTITATIVE MEASUREMENT OF PREFERRED ORIENTATION IN PORTLANDITE BY USING POLYCRYSTALLINE ROCKING CURVE

The diffraction line of portlandite in the interfacial zone between cement paste and aggregate is different from that of a random sample. Two things account for this occurrence: one is the preferred orientation of crystalline grains which changes the diffraction intensities of each plane, and the other is the overlap of the diffraction peaks reflecting from the CH (101) plane and those of other

minerals. For evaluating the preferred orientation, the intensity and the half-maximum line width of the diffraction line cannot be purely used as evaluating indexes. For this reason, we propose a method for evaluating the preferred orientation of crystals within the interfacial zone by using the polycrystalline rocking curve.

3.1 Brief introduction of principle

The rocking curve is an X-ray diffraction curve reflecting the distribution state of a certain crystalline plane relative to the sample surface. In an ideal situation, the horizontal divergence angle of an incidental beam is $\alpha = 0°$. In the experiments, plane (hkl) of a crystalline grain was regulated at an angle 0° to the incidental beam in an X-ray diffractometer. Then the X-rays reflected from the sample were measured directly with a Geiger counter placed at 2θ positions for crystals in which plane (hkl) was parallel to the sample surface. With the other conditions constant, a set of diffraction lines can be obtained by regulating the angle ω between the sample surface and the diffraction plane. For the random sample, the rocking curve is in theory a horizontal line, due to the distribution of (hkl) planes homogeneously in the space. When $\omega = \theta$ or θ, the incident and diffraction beams are completely absorbed and the intensity of the diffracted beam will be zero. The rocking curve of a textured sample, in which the normals of the textured crystalline planes are parallel to that of the sample surface, will form a Gauss-like distribution curve (Fig. 1). The stronger the preferred orientation of plane (hkl), the sharper the rocking curve, i.e. the narrower the half-maximum line width.

3.2 Operating procedure

First, the 2θ value of the CH (000) diffraction peak on the X-ray spectrum was examined routinely with θ–2θ co-rotary scanning. Then the Geiger counter was fixed at $2\theta = 18.10°$ or so. Loosing the θ–2θ co-rotary device,
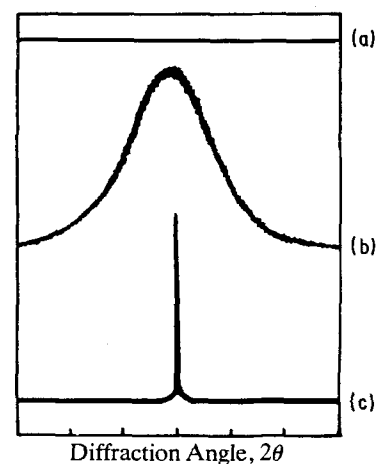

Fig. 1 The relationship between the polycrystalline rocking curve of the hkl plane and its preferred orientation: (a) ideal randomly oriented sample, (b) sample with preferred orientation, (c) completely oriented sample.

with the specimen face at an angle $\theta = 19°$ to the incident beam, we scanned to zero degrees. Thus the rocking curve was obtained.

Commonly, the horizontal divergence angle α does not equal zero, due to the divergence of the incident beam, effectively replacing $\alpha/2$ for the rocking curve ($1/2°$ in this experiment) with a higher angle. In the range θ to $\theta + \alpha/2$ the rocking curve reaches the maximum intensity. Of course, decreasing α may improve the curve, but this will decrease the intensity of the incident beam and not improve the analysis of the curve. Therefore, the angle must be chosen reasonably. In this experiment $\alpha = 1°$ was chosen and better results obtained.

3.3 Experimental results and discussion

From X-ray diffraction theory, the width of the diffraction line has a relationship with the specimen size and the X-ray scatter level. The fining of crystals and inhomogeneous microstress can broaden the diffraction line. However, the intensity of diffraction may not influence the half-maximum line width. For a rocking curve, its half-maximum line width may be slightly influenced not only by the factors mentioned above, but also by the orientation degree. The influence of crystalline grain size and microstress on the half-maximum line width may not be taken into account due to the broader line width. When the size of the specimen and experimental conditions remain constant, the change of the half-maximum line width caused by attenuation due to the focusing deviation to the circle of the goniometer may remain constant. Therefore, it is suggested that the half-maximum line width of a rocking curve depends only on the state and level of the
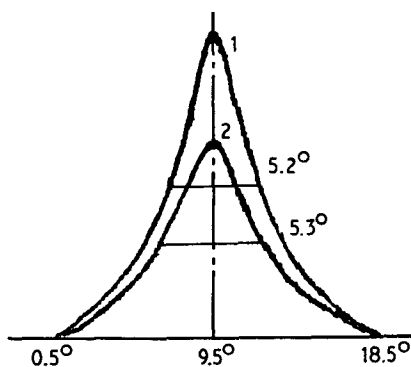

Fig. 2 The effect of $Ca(OH)_2$ content in a specimen on the half-maximum line width: (1) pure $Ca(OH)_2$ powder, (2) 80% $CaCO_3 + 20\% Ca(OH)_2$.

orientation of crystal grains along the specimen surface and not on the quantity of crystal and size of the crystal grains.

For improving the situation mentioned above, the specimen was prepared according to the method suggested by NBS in 1976 [14]. It was covered with a polyvinyl film to prevent the falling out of the powder sample, and to lighten the surface orientation due to preparing the specimen. The data obtained are listed in Table 1 and Fig. 2. The data prove that the above discussion is correct.

On the basis of this, we can assume that the CH in the bulk cement paste is in random orientation and can be used as a standard specimen for evaluating CH orientation degree, from the point of view mentioned above, we propose a formula to calculate the preferred orientation of crystals:

$$I_{CH} = \frac{B_{bulk}}{B_i} \qquad (14)$$

where I_{CH} is the orientation degree of CH, B_{bulk} is the half-maximum line width of the rocking curve for bulk cement paste and B_i is the half-maximum line width of the rocking curve for the ith layer within the interfacial zone. When $I_{CH} = 1$, orientation of the specimen is random; $I_{CH} = \infty$ means complete orientation of the specimen.

3.3.1 *Physical meaning of Equation 14*

In Equation 6, the first term is the physical constant, the second is the experimental constant, the third is the crystalline structure parameters of the specimen, the fourth is the Lorentz polarization factor related to angle θ, the fifth is a correction term for X-ray intensity attenuation, and V is the phase volume participating in the diffraction from the specimen. In a given experimental condition, the five terms mentioned above, for a given material and diffraction line, are constant and can be expressed in a constant K_1. Then

$$I = K_1 \frac{V}{\mu}$$

Thus

$$S_i = K_1 \frac{V_i}{\mu_i} K_2 \frac{2\theta}{\pi} \qquad (15)$$

$$S_R = K_1 \frac{V_R}{\mu_R} K_2 \frac{2\theta}{\pi} \qquad (16)$$

where V_i is the diffraction volume of CH in the textured specimen, V_R is the diffraction volume of CH in the

Table 1 Half-maximum line width of the samples with different content of $Ca(OH)_2$

Sample	Half-maximum line width (deg)
Chemically pure $Ca(OH)_2$ powder	5.2
80% $CaCO_3 + 20\% Ca(OH)_2$ powder	5.3

random specimen, S_i is the area of the rocking curve for the textured specimen, S_R is the area of the rocking curve for the random specimen and K_2 is a factor for the intensity attenuation caused by X-ray divergence, in measuring the rocking curve, depending on the slit width chosen in the experiment.

Similarly

$$I_{i,\max} = K_1 \frac{V'_{i,hkl,n}}{\mu_i} K_3 \qquad (17)$$

$$I_{R,\max} = K_1 \frac{V'_{R,hkl,n}}{\mu_R} K_3 \qquad (18)$$

where $I_{i,\max}$ is the maximum height of the rocking curve in the textured specimen, $I_{R,\max}$ is the maximum height of the rocking curve in the random specimen and K_3 is the proportional factor of diffraction intensity to the diffraction peak height. Because the peak height varies with the experimental conditions, K_3 depends on it.

Dividing Equation 15 by Equation 16 yields

$$\frac{S_i}{S_R} = \frac{V_i}{V_R} \frac{\mu_R}{\mu_i} \qquad (19)$$

Dividing Equation 17 by Equation 18 yields

$$\frac{I_{i,\max}}{I_{R,\max}} = \frac{V'_{i,hkl,n}}{V'_{R,hkl,n}} \frac{\mu_R}{\mu_i} \qquad (20)$$

Dividing Equation 20 by Equation 19 yields

$$\frac{I_{i,\max}}{I_{R,\max}} \frac{S_R}{S_i} = \frac{V'_{i,hkl,n}}{V'_{R,hkl,n}} \frac{V_R}{V_i} \qquad (21)$$

According to the Royer integral breadth definition (see Fig. 3)

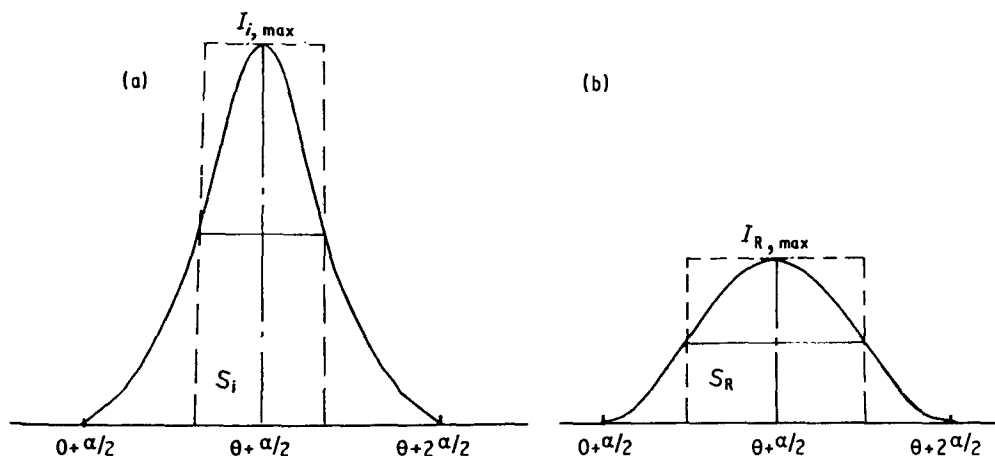$$B_i I_{i,\max} = S_i \qquad (22)$$

$$B_R I_{R,\max} = S_R \qquad (23)$$

Then from Equations 21, 22 and 23 it follows that

$$\frac{B_R}{B_i} = \frac{V'_{i,hkl,n}}{V'_{R,hkl,n}} \frac{V_R}{V_i} = \frac{V_{i,hkl,n}}{V_{R,hkl,n}} = P_{hkl}$$

Therefore

$$P_{hkl} = \frac{B_R}{B_i}$$

As the rocking curve is a symmetrical Gauss-like curve, the half-maximum line width of the curve nearly equals the integral width. Therefore, it is reasonable to use B_R/B_i as an evaluating index for the preferred orientation degree of polycrystals.

3.3.2 Comparison of methods

For comparing these two methods, i.e. Grandet and Ollivier's method and the rocking curve method, the following experiments were carried out.

On a polished marble block ($2\,\text{cm} \times 2\,\text{cm} \times 1\,\text{cm}$) an equally sized specimen of cement paste with W/C = 0.3 was poured to form a cube. After three days of hydration the composite cube was split along the interface [12]. According to Chang [13] the depth of diffraction transmission by the X-rays is about $10\,\mu\text{m}$. In testing, the fracture surface was scraped $10\,\mu\text{m}$ each time layer by layer. The testing specimen was installed in a plate rotary specimen apparatus to eliminate the influence of in-homogeneous surface on the intensity. The experimental data are listed in Table 2 and Figs 4 and 5.

The distribution of preferred-orientation CH within the interfacial zone measured by two methods is shown in Fig. 6. From the figure, we know that the width of the interfacial zone determined by the rocking curve is smaller than that from Grandet and Ollivier's method. This confirms the previous theoretical analysis, i.e. that the orientation degree determined according to Grandet and Ollivier is slightly higher. In addition, the fluctuation of the testing points from the distribution is smaller with the rocking curve than with Grandet and Ollivier's method. This indicates that the rocking curve eliminates

Fig. 3 Schematic diagram or rocking curves: (a) within the interfacial zone, (b) in the bulk cement paste.

Table 2 Use of the rocking curve and Grandet and Ollivier's method to determine the orientation degree of each layer within the interfacial zone

	Layer No.					
	1	2	3	4	5	6
Distance from the fracture surface (μm)	0	10	20.8	31.4	41.9	0
Half-maximum line width	3.8	4.3	5.3	6.2	6.2	–
$I_{CH} = B_{bulk}/B_i$	1.63	1.44	1.17	1.00	1.00	–
Peak height of CH (001) (cm)	14.3	5.6	3.0	2.4	2.2	0.3
Peak height of CH (101) (cm)	9.1	4.3	3.3	3.2	3.1	0
$I_{CH} = I_{001}/I_{101}/0.74$	2.1	1.76	1.23	1.01	0.96	–

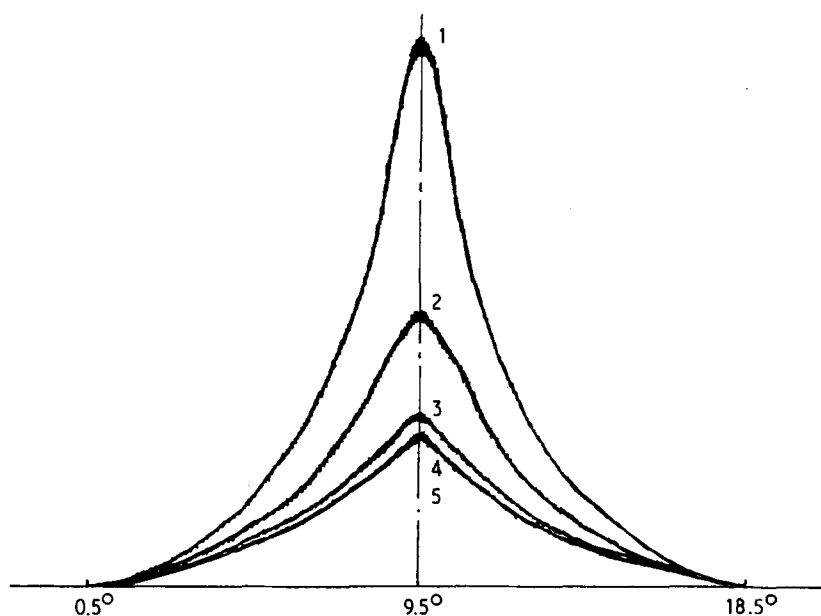| Remarks	Within the cement paste interfacial zone			In bulk cement paste		On marble side

Fig. 4 Half-maximum line width for the (001) plane of portlandite in different layers. The ordinate numerals are in accordance with those in Table 2.
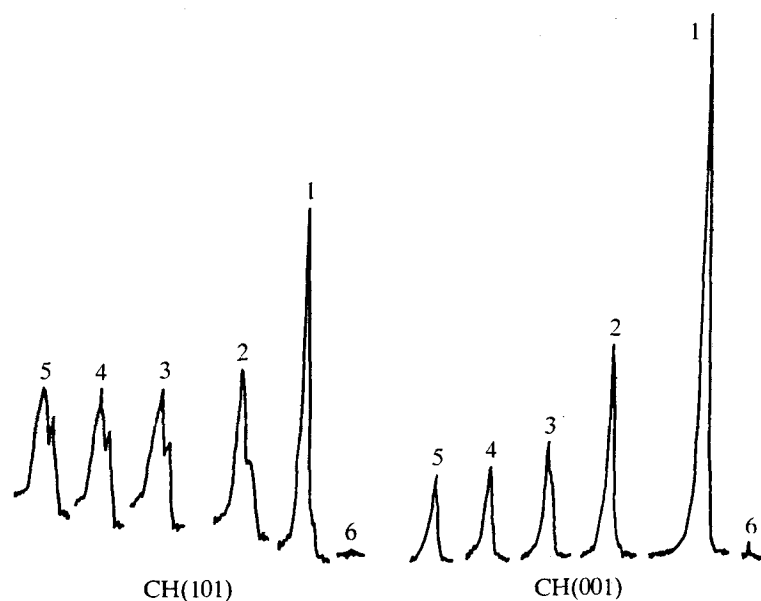

CH(101)   CH(001)

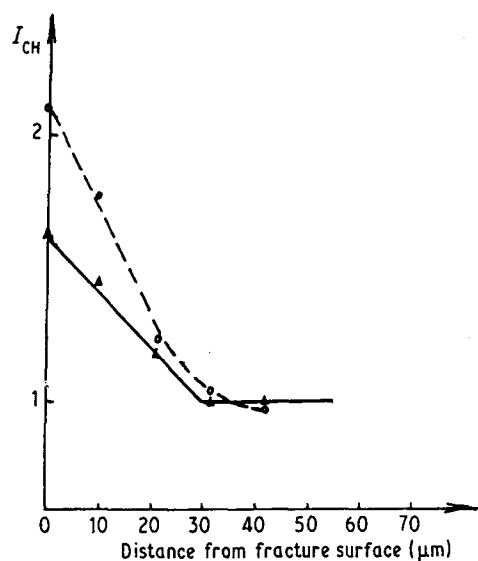Fig. 5 Peak of X-ray diffraction line for planes (001) and (101) of portlandite in different layers.

Fig. 6 The distribution of preferred orientation of portlandite within the marble–cement paste interfacial zone (W/C = 0.3, 3 days). ($\bigcirc$) $I_{CH} = (I_{001}/I_{101})/0.74$, ($\blacktriangle$) $I_{CH} = B_{bulk}/B_i$.

the fluctuation of the data points measured by Grandet and Ollivier's method, in which the intensity of the peak height (1 0 1) cannot be measured correctly.

4. CONCLUSION

Evaluating the degree of preferred orientation of portlandite within the transition zone between cement paste

and aggregate, the method using the rocking curve of the diffraction line is more precise than that proposed by Grandet and Ollivier. Due to its simplicity, it can be used widely in evaluating the degree of preferred orientation for crystals with the same preferred orientation axes.

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