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CRYSTALLINITY DETERMINATION OF PURE PHASES USED AS STANDARDS FOR QXDA IN CEMENT CHEMISTRY

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ABSTRACT

The modified Ruland method was employed to determine the crystallinities of "pure phase" substances used as standards for quantitative x-ray diffraction analysis (QXDA) in order to improve the accuracy of x-ray quantitative analyses, especially for the crystalline phases whose pure phase standards with high crystallinity are not available and the amorphous phases whose contents are determined by difference from the QXDA determinations of the crystalline phases. It was found that most of the synthetic "pure phases" had the crystallinities less than 95% and some of the clinker minerals and the crystalline hydrates of Portland cement less than 90%. The effect of the "pure phase" crystallinity on accuracy of QXDA was discussed.

Introduction

The mineralogy of cement materials is an important factor which influences their properties. Quantitative x-ray diffraction analysis (QXDA) is often applied to determine the relative amount of crystalline phases or amorphous phases in cements, cement pastes and mineral additions [1-5]. Aldridge [6,7] and Taylor [8] reviewed the methods used for QXDA of the major clinker minerals (C_3S, C_2S, C_3A and C_4AF) and the crystalline hydrates (CH, ettringite, etc.) of Portland cement, and compared them with other techniques of quantitative phase analysis. Although XRD is generally considered as a good method of quantitative phase analysis, large errors are not uncommon in experimental data. Valid comparison of results from different laboratories is often impossible because most of the results are of low accuracy [6].

Nevertheless, if the results of QXDA are considered to be relative to the data of the pure phases used as standards in the analysis rather than to be absolute, it is not too difficult in practice to make the relative accuracy of x-ray quantitative measurement better than 5% for most of the crystalline phases in cement chemistry. Many experimental errors which do not concern the pure phase standards can be eliminated or minimised by the proper sample preparation techniques, such as, grinding the sample particles to less than 5μm, minimising the preferred orientation of the crystalline particles (or using the Rietveld method suggested by Hill et al[9]), and eliminating other experimental errors which will alter the observed intensities. In addition, errors can be introduced during data treatment but this also can be minimised by, for example, avoiding the use of overlapping diffraction lines (or using whole pattern matching techniques [9-11]), and employing the appropriate techniques for subtraction of the background. Therefore, the low accuracy of QXDA data may, to a considerable extent, result from a fact that many synthetic pure phases which are used as standards in the quantitative analysis of cement materials do not satisfy the requirements for the accurate quantitative analysis of XRD. There are two main sources of errors relating to the synthetic pure phases:

Inappropriate Choice of Standard Materials. Ion substitution and polymorphism widely present in the crystalline phases in cements and cement pastes can change their observed intensities of XRD. A systematic error may be caused by the difference in the type of ion substitution or the polymorphic form between the synthetic pure phase standard and the corresponding phase in the practical sample. Gutteridge [11] established a database of the synthetic pure phases as the primary standards for most of the cement minerals and portlandite which took into account the varieties of possible ion substitutions and polymorphism. The deviations of XRD intensities between the measured phase and the standard caused by compositional or polymorphic difference can be avoided by selecting the primary standard from the database which corresponds most closely to the measured phase in the polymorphic form or the type of substitution.

Presence of an Amorphous Component in Standard Material. Odler et al[12] noted that the intensities of the diffraction lines of synthetic ettringite varied sensitively, not only with its composition, but also its mode of preparation. They attributed the latter to the effect of crystallinity on the diffracted x-ray intensities. In fact, this kind of crystallinity effect in synthetic pure phase is commonly present in QXDA. It is also hard to say that the variations of XRD intensities of the synthetic pure phases attributed in reference[11] and [12] to ionic substitutions are not partly due to differences in crystallinity. Therefore, even though the measuring error may be reduced by the proper choice of standard, it will not be completely eliminated if the crystallinity effect is not taken into account. Nevertheless, few data for crystallinity parameters for the pure phase standards of QXDA are available. Consequently, the quantitative determination of the compounds that are difficult or impossible to obtain in a pure and highly crystalline state, will suffer from a large systematic error due to the crystallinity effect. If the amount of amorphous substance in a multiple-phase system needs to be determined by difference from the content of all the crystalline phases, a larger systematic error is easily produced because of an accumulation of the measuring errors of the crystalline phases induced by omitting the crystallinity effect.

The development of a standardless method for the determination of the crystallinities of the "pure phase" standards by XRD would represent a significant advance in quantitative phase analysis. Firstly, the accuracy of QXDA would be improved, especially for compounds difficult or even impossible to obtain pure and highly crystalline phases. Secondly, It would be unnecessary to spend much time and finance in preparation of the pure phases of high crystallinity because the lower crystallinity compounds could also be used as standards for accurate quantitative measurement. Thirdly, the quantitative analyses of amorphous substances in the multiple-phase samples might potentially reach the level of accuracy obtainable for crystalline phases. Finally, the crystallinity parameter might be used as a criterion to assess the quality of the pure phase for the purpose of QXDA.

In this paper, the modified Ruland method is employed to determine the crystallinities of the "pure phases" of some compounds which are commonly found in the field of cement and concrete. the accuracy of this method is assessed and the effect of the "pure phase" crystallinity on accuracy of the Reference Intensity Ratio (RIR) method of QXDA is discussed.

Experimental Methods and Conditions

Principle of The Modified Ruland Method. The Ruland method was originally developed by Ruland[13] to determine the absolute crystallinities of organic polymers. It is generally believed that Ruland method is the most reliable one for the determination of absolute crystallinity as it has a solid theoretical foundation. It was computerised by Vonk[14]. Subsequently, this method was modified by Vonk et al[15] to meet the needs of the crystallinity determination in a system where the chemical composition of the crystalline phase was different from that of the amorphous phase, such as, glass-ceramic materials.

In the modified Ruland method[15,16], the equation in which the crystallinity, X_C, of the sample is related to the data of x-ray diffraction can be expressed as follows if the sample only contains a crystalline phase and an amorphous phase:

$$R(S_p) \approx \frac{K(S_p)\cdot\langle Z_t\rangle}{X_c\cdot\langle Z_c\rangle} . \tag{1}$$

$R(S_p)$ is defined as:

$$R(S_p) = \frac{\int_{S_0}^{S_p} I(S)\cdot S^2\cdot dS}{\int_{S_0}^{S_p} I_C(S)\cdot S^2\cdot dS} , \tag{2}$$

where I(S) and $I_c(S)$ are the coherent intensities of x-rays diffracted by the sample and the crystalline phase respectively, S is the variable in the reciprocal space ($S=2\sin\theta/\lambda$, 2θ=Bragg angle and λ= wavelength of x-ray beam), S_0 corresponds to the starting angle of intensity measurement and S_p is the upper limit of S.

$\langle Z_t\rangle$ and $\langle Z_c\rangle$, standing for the average atomic numbers of the sample and the crystalline phase respectively, are given by:

$$\langle Z_t\rangle = \sum_i n_i\cdot Z_i^2 / \sum_i n_i\cdot Z_i \text{ and } \langle Z_c\rangle = \sum_j n_j\cdot Z_j^2 / \sum_j n_j\cdot Z_j , \tag{3}$$

where,
Z_i is the atomic number of the element i in the sample,
Z_j is the atomic number of the element j in the crystal,
n_i is the number of atoms of the element i in the chemical molecular formula of the sample,
n_j is the number of atoms of the element j in the molecular formula of the crystal.

$K(S_p)$ as a function of S_p has the following analytical expression:

$$K(S_p)=\frac{\int_{S_0}^{S_p} f_0^2(S)S^2dS}{\int_{S_0}^{S_p} f_0^2(S)D(S)S^2dS}, \tag{4}$$

where,
f_o is the average scattering factor per electron which approximately is a constant for all atoms in the system, D(S) is a disorder function which describes the reduction of $I_c(S)$ caused by deviations of the atoms from their ideal positions in the crystalline phase.

It needs to be borne in mind that the two conditions should be satisfied if the experimental x-ray intensities are applied to equation (2) for determination of the function $R(S_p)$: (a) no crystalline preferred orientation should be present in the sample; (b) the experimental angular range of the measurement (S_0,S_p) should be large enough to justify the substitution of a finite interval of the integration for the theoretical infinite one. In addition, the experimental x-ray intensities of the sample have to be converted to electron units, after corrected for polarisation, air and background scattering, etc.. The coherent intensities of the sample, I(S), are determined by subtraction of the incoherent intensities from the corrected experimental x-ray intensities in electron units. The crystalline peaks are separated from the amorphous contribution to the total x-ray scattering for determination of $I_c(S)$.

The chemical molecular formulae of the sample and the crystalline phase are requisite parameters for the crystallinity determination. If the chemical composition of the sample is identical to that of crystalline phase, as are most of the "pure phase" samples, the sample has the same molecular formula as the crystalline phase. If not, the chemical analysis of the sample needs to be performed for determination of the molecular formula of the sample.

It was found by Ruland[13] and Vonk[14] that the curve of $K(S_p)$ vs. S_p^2 can be properly approximated by a straight line or an upwards concave parabola which is generally expressed by:

$$K(S_p)=1+\frac{k}{2}\cdot S_p^2+c\cdot S_p^4, \tag{5}$$

where k and c are the positive constants. Equation (5) becomes a straight line of $K(S_p)$ vs. S_p^2 if c is equal to zero. If $K(S_p)$ in equation (1) is replaced by equation (5), equation (1) becomes:

$$R(S_p)\approx(1+\frac{k}{2}\cdot S_p^2+c\cdot S_p^4)\cdot(\frac{\langle Z_t\rangle}{\langle Z_c\rangle\cdot X_c}). \tag{6}$$

It is shown by equation (6) that the values of $R(S_p)$ vs. S_p^2 of a sample obtained from the experimental data of XRD will oscillate about an upwards concave parabola (sometimes a straight line). This parabola can be analytically expressed by:

$$Y(S_p)=\frac{\langle Z_t\rangle}{\langle Z_c\rangle}\cdot\frac{1}{X_c}+\frac{k}{2}\cdot\frac{\langle Z_t\rangle}{\langle Z_c\rangle}\cdot\frac{1}{X_c}\cdot S_p^2+\frac{c}{X_c}\cdot\frac{\langle Z_t\rangle}{\langle Z_c\rangle}\cdot S_p^4\,. \tag{7}$$

Equation (7) is determined by a least squares fit between the experimental data ($R(S_p)$, S_p^2) and the simulated parabola ($Y(S_p)$, S_p^2). The crystallinity X_c of the sample is simply obtained from: $X_c=<Z_t>/<Z_c>/Y(0)$. Fig. 1 demonstrates how the experimental values of $R(S_p)$ vs. S_p^2 oscillate about the upwards concave parabolas which are very close to straight lines for KCl sample.

The methods for all the above data correction and data treatment were described in detail by Vonk[14,15] and Benedetti et al[16]. A computer programming package was developed for the whole procedure of the crystallinity calculation in China Building Materials Academy.

Experimental Equipment and Conditions.

X-ray diffractometry. The quantitative analysis of x-rays was performed on a Rigaku Dmax-IIIA diffractometer, updated with a computer system for data collection and data treatment. The experimental conditions were as follows: Voltage = 37.5 kV; Tube current = 40 mA; Step width = 0.1°/step; Count time = 5 sec/step; the scanning interval = 5°-130°. A curved single crystal monochromator of graphite was installed in the receiving optical path.

Thermogravimetry (TG). Dupont 1090 synthetic thermal analysis instrument made in USA. was used for comparison of the quantitative results between XRD and TG.

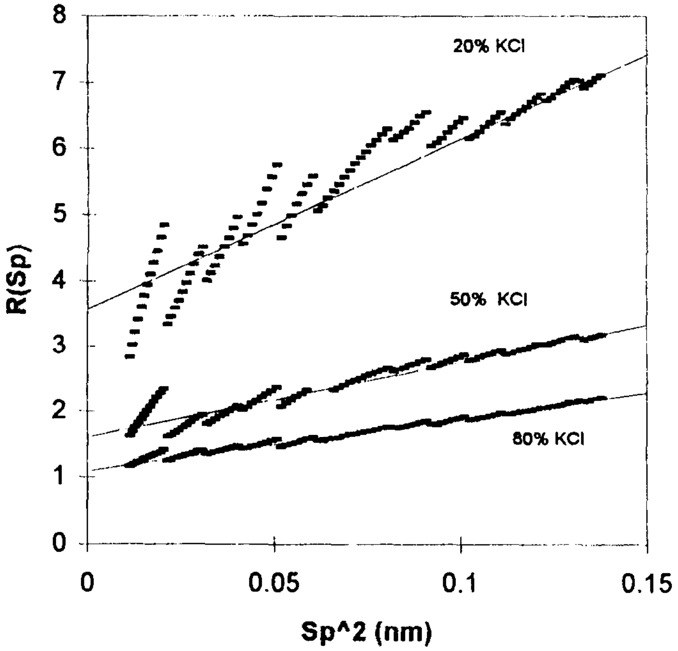

FIG. 1.
Variations of R vs. S^2 of KCl-glass Mixtures.

Standard substances for calibration. In order to examine the accuracy of the modified Ruland method for the crystallinity measurement, the pure potassium chloride was selected as standard substance because its perfectly crystallised grains with large size could be obtained conveniently. Another kind of pure substance, crystalline silicon, was also employed. Both standard substances were mixed with glass at the three levels of 20%, 50% and 80%. The industrial gypsums were chosen to compare the modified Ruland method with TG. The chemical compositions of the industrial gypsums and the glass are listed in Table 1.

Results and Discussion

Crystallinity Measurement. Fig. 1 shows the variations of $R(S_p)$ vs. S_p^2 for the KCl-glass mixtures. The solid curves represent the parabolas which fit the experimental data points by least squares procedure. Table 2 lists the analytical errors of the crystallinity determinations by the modified Ruland method. Although the oscillation of the data points around the fitting curves becomes serious as the crystal content in the sample decreases, the results of the crystallinity measurement do not significantly increase the absolute errors which keep less than 3%. The samples with glass contents below 50% keep the relative errors below 5% and the relative errors of the samples with 80% glass still lie below 10%. The well crystallised KCl presents a crystallinity of 99.36%, and the crystalline silicon, 96.8%. The modified Ruland method provides the $CaSO_4$ $2H_2O$ contents in the industrial gypsums very close to which does TG. Therefore, it is considered that the modified Ruland method is an appropriate technique for determining the crystallinity of the "pure phases" used for QXDA.

Table 3 lists the crystallinities of some "pure phase" substances collected or prepared by our laboratories which are determined by the modified Ruland method. Most of the so called "pure phases" have crystallinities below 95%. The crystallinities of hydration products, alite, C_4AF, etc. are below 90%. It is noted that crystallinity is often sensitive to the conditions and the skills of pure phase preparation. The three "pure" β-C_2S phases are prepared in the two different laboratories. The β-C_2S phases are stabilised by the element boron or phosphorus

TABLE 1

Chemical Compositions

Oxides	Gypsum from Hebei	Gypsum from Shanghai	Glass*
CaO	32.05	32.54	
Al_2O_3	0.35	0.03	22
SO_3	41.11	45.00	-
SiO_2	0.53	-	53
Bound Water	17.91	20.60	-
LOI	5.01	0.2	-
Fe_2O_3	0.11	-	-
MgO	2.43	-	22
B_2O_3	-	-	2
P_2O_5	-	-	5

* the ingredients of the raw materials

TABLE. 2

Error Analysis of the Crystallinities Measured by the Modified Ruland Method

Sample	Glass content	Measured value	Average value	Real value	Absolute error	Relative error	Comment
KCl		98.98 100.75 98.36	99.36	-	-	-	
	20	81.47 80.00 80.67	80.71	79.52	1.19	1.5	
	50	47.45 47.13	47.92	49.68	-2.39	-4.8	
	80	18.88 18.04 19.07	18.66	19.87	-1.21	-6.1	
Si	0	96.5 96.6 97.2	96.8	-	-	-	
	20	75.9 75.3 74.1	75.1	77.4	-2.4	-2.3	
	50	45.1 48.5 46.3	46.6	48.4	-1.8	-3.7	
	80	18.6 17.3 17.3	17.5	19.36	-1.86	-9.6	
gypsum A			88.82	87.36*	1.46**	1.6**	Hebei
gypsum B			98.7	98.4*	0.3**	0.3**	Shanghai

* determined by using TG.

** the deviations from the results of TG.

when they are cooled from high temperature to normal temperature. The crystallinities give the marked differences between the three β-C_2S, although the diffraction peaks of quartz (SiO_2) and f-CaO do not appear on the spectrums of XRD for all of them. Similarly, distinct differences in crystallinity can be observed between the synthetic ettringites. The suspensions containing $Ca(OH)_2$, $Al_2(SO_4)_3 \cdot 18H_2O$ and $CaSO_4 \cdot 2H_2O$ in proportion are agitated for 3 days to make ettringite (1), and for 5 days to make ettringite (2) and (3). Ettringite (2) and (3) are prepared by the same procedure but by two different operators. It is clear that the crystallinities of at least some synthetic pure phases are difficult to control during their preparation. Thus the crystallinity determination is an effective measure for overcoming this problem and improving the accuracy of QXDA of these phases.

Effect of Crystallinity of the Pure Phase Standard on Accuracy of QXDA (The RIR Method). The Reference Intensity Ratio (RIR) method is widely applied in QXDA. The most general definition of the Reference Intensity Ratio, RIR, is given by Hubbard and Snyder[17]

TABLE 3
Crystallinities of "Pure Phases"

Compound	Crystallinity	Comment
β-C_2S (1)	98.7	P as stabiliser*
β-C_2S (2)	92.0	B as stabiliser*
β-C_2S (3)	84.7	B as stabiliser*
Alite	88.2	*
C_4AF	87.7	*
C_3A	93.3	*
$C_4A_3\bar{S}$	92.9	*
α-C_2S	91.0	*
ettringite (1)	64.8	*
ettringite (2)	88.7	*
ettringite (3)	74.5	*
$Ca(OH)_2$	85.9	chemical reagent
$CaSO_4.2H_2O$	96.9	chemical reagent
$CaCO_3$	97.4	chemical reagent
α-SiO_2	93.2	from Hunan
α-Al_2O_3	92.4	*
TiO_2 (anatase)	93.0	from Shanghai

* prepared in China Building Materials Academy

$$RIR_{k,s} = \frac{I_{ik}}{I_{js}} \cdot \frac{I_{js}^{rel}}{I_{ik}^{rel}} \cdot \frac{X_s}{X_k} \tag{8}$$

where,

$RIR_{k,s}$ = the Reference Intensity Ratio, a constant relating to the properties of the phase k and the phase s (including the densities) and usually, also to the instrumental parameters,

X_k = the weight percentage of the phase k in the measured sample,

X_s = the weight percentage of the internal standard phase s in the sample,

I_{ik} = the XRD intensity of the line i of the phase k,

I_{js} = the XRD intensity of the line j of the phase s,

I_{ik}^{rel} = the intensity of the line i of the phase k relative to its 100% line ,

I_{js}^{rel} = the intensity of the line j of the phase s relative to its 100% line.

Equation (8) can be rearranged for the quantitative determination of the phase k in a sample when $RIR_{k,s}$ and X_s are the known parameters:

$$X_k = \frac{I_{ik}}{I_{js}} \cdot \frac{I_{js}^{rel}}{I_{ik}^{rel}} \frac{X_s}{RIR_{k,s}} . \tag{9}$$

According to equation (8), the RIR value can be experimentally determined by measuring the intensity ratios, $\frac{I_{ik}}{I_{js}}$ and $\frac{I_{ik}^{rel}}{I_{js}^{rel}}$, of the diffraction lines of the phase k and the internal standard phase s in a synthetic sample in which the pure phase k is mixed with the internal standard phase s in a known proportion. In fact, equation (8) and (9) are based on an assumption that both of the pure phase k and the internal standard phase s have crystallinities of 100%. If, currently, we consider the crystallinities of the "pure phase" k and the internal standard phase s as X_{ck} and X_{cs} rather than one hundred percent, the RIR value after the crystallinity correction, $RIR_{k,s}'$, can be given by:

$$RIR_{k,s}' = \frac{I_{ik}}{I_{js}} \cdot \frac{I_{js}^{rel}}{I_{ik}^{rel}} \cdot \frac{X_s \cdot X_{cs}}{X_k \cdot X_{ck}} \; . \tag{10}$$

Equation (9) after the crystallinity correction becomes:

$$X_k' = \frac{I_{ik}}{I_{js}} \cdot \frac{I_{js}^{rel}}{I_{ik}^{rel}} \frac{X_s \cdot X_{cs}}{RIR_{k,s}'} \; , \tag{11}$$

where X_k' is the weight percentage of the measured phase after the crystallinity correction. The absolute measuring error and the relative measuring error of the measured phase caused by the crystallinity effect can be derived from equation (9) and (11). When X_s and X_{cs} keep constant, the absolute error is:

$$X_k - X_k' = X_k' \left(\frac{1 - X_{ck}}{X_{ck}}\right) \; , \tag{12}$$

and the relative error is:

$$\frac{X_k - X_k'}{X_k'} = \frac{1 - X_{ck}}{X_{ck}} \; . \tag{13}$$

It is demonstrated by equation (12) and (13) that the systematic errors produced by the crystallinity effect are always positive. The absolute error is proportional to the weight percentage of the measured phase and the relative error. If X_{ck} is 90%, the absolute systematic error will exceed 3%, provided that X_k' is larger than 27%. The relative error is only dependent on the crystallinity of the pure phase standard of the measured compound. As X_{ck}=90%, the relative error will be over 10%. If X_{ck} is 80%, the relative error will be 25%. Apparently, it is necessary to perform the crystallinity correction before QXDA, when the crystallinity of pure phase standard is below 90%, as are those of alite, C_4AF, ettringite, CH, etc. in table 3. If the quantitative analysis with high quality is required, then most of the pure phase standards need the crystallinity correction.

As the measured phase is an amorphous substance, the absolute error and the relative error caused by the crystallinity effect are expressed by:

$$X_{am} - X_{am}' = -\sum_k (X_k - X_k') = -\sum_k X_k' \left(\frac{1 - X_{ck}}{X_{ck}}\right) \tag{14}$$

and

$$\frac{X_{am}-X_{am}'}{X_{am}'}=\frac{-\sum_{k}(X_k-X_k')}{1-\sum_{k}X_k'}=\frac{-\sum_{k}X_k'\left(\frac{1-X_{ck}}{X_{ck}}\right)}{1-\sum_{k}X_k'} \tag{15}$$

where the weight percentages of the amorphous substance before and after the crystallinity correction (X_{am} and X_{am}') are equal to $1-\Sigma X_k$ and $1-\Sigma X_k'$ respectively. The crystallinity effect always gives a negative systematic error to the result of QXDA of amorphous phase. The absolute measuring error of amorphous phase is a sum of those of all the crystalline phases in the system. Therefore, the crystallinity effect seriously influences the absolute accuracy of QXDA of amorphous phase. The relative error rises rapidly with increase of the total content of the crystalline phases in the sample. As the total content of the crystals is over 50%, the relative measuring error of amorphous phase will exceed the average relative measuring error of the whole crystalline phases. The crystallinity correction, in no doubt, is more important to the quantitative analysis of amorphous phase, particularly when the content of the amorphous phase is below 50%.

An Example of Practical Measurement. The industrial sulphoaluminate cements are employed to examine the deviations caused by the crystallinity effect in the practical quantitative measurement by using the RIR method. The sulphoaluminate cement clinker is mainly composed of the minerals $C_4A_3\bar{S}$ and C_2S, in addition to a little anhydrite, MgO, etc.. Gypsums with the different levels are blended into the clinker to make the cements with the different properties. Table 4. lists the quantitative results of $C_4A_3\bar{S}$ of the sulphoaluminate cements, using the RIR method with and without the crystallinity correction. The amount of $C_4A_3\bar{S}$ are also calculated from the data of chemical analysis, based on an assumption that all Al_2O_3 in the cement clinker is exhausted to form $C_4A_3\bar{S}$. The results of QXDA with the crystallinity correction match those calculated from the chemical composition very well. Nevertheless, the data of QXDA without the crystallinity correction show about 9% systematically higher than those from the chemical calculation. According to the assumption of the $C_4A_3\bar{S}$ calculation, the calculated result should present a maximum quantity of $C_4A_3\bar{S}$ which possibly exists in the sulphoaluminate cement. Therefore, the results with the crystallinity correction more approach the real values than those without the crystallinity correction.

TABLE 4

QXDA of $C_4A_3\bar{S}$ in Sulphoaluminate Cements

Cement	CR	QXDA	QXDAc	RD	RDc
C0	58.8	63.0	58.4	7.1	.7
C5	55.9	61.4	56.8	9.9	1.8
C15	50.0	54.9	50.84	9.8	1.7
C25	44.1	47.3	43.8	7.2	-0.7
C45	32.3	36.0	33.3	11.3	3.1

Cx= the different cements, where x is the gypsum level of the cement,
CR= the result calculated from the chemical composition.
QXDA= the result determined by the RIR method without the crystallinity correction.
QXDAc= the result determined by the RIR method with the crystallinity correction.
RD= the relative deviation of QXDA from CR.
RDc= the relative deviation of QXDAc from CR.

Conclusions

1. The modified Ruland method is a satisfactory technique to determine the crystallinities of the "pure phase" substances as standards for QXDA.
2. Most of the "pure phase" substances, which are prepared in the laboratories, show crystallinities less than 95% and some important synthetic cement minerals and crystalline hydrates such as alite, C_4AF, ettringite, CH, etc., less than 90%.
3. The influence of pure phase crystallinity on the absolute and the relative accuracy of QXDA can be determined by equation (12) and (13).
4. When the amount of amorphous phase is measured by difference from QXDA determinations of the whole crystalline phases in the system, the absolute measuring error caused by the crystallinity effect is a sum of the absolute measuring errors of the whole crystalline phases (equation (14)), and its relative measuring error (equation (15)) will be over the average relative measuring error of the whole crystalline phases provided that the amount of amorphous phase is below 50%.

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