Quantification analysis of Cement materials

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Abstract

X-ray diffractometry is widely used for quality control and process control in cement. This article presents an accurate and precise quantification method for free lime in a clinker material and an accurate quantification method of the admixtures in a blended cement. The partial accumulation measurement was used to make a calibration curve including a scale factor to improve the accuracy and precision of the quantitative method. Analytical result of free lime showed good agreement with its preparation value and had a small standard deviation. The reference intensity ratio method combined with the WPPF method was applied to admixture quantification in a blended cement for accurate quantification. The quantitative values of the admixtures in the simulation sample with a three-component system showed good agreement with the preparation values.

1. Introduction

Cement, one of the gray materials in concrete, is made by combining gypsum and admixtures. The cement manufacturing process consists of three processes: raw material process, calcination process, and finishing process(1). In the raw material process, clinker raw material is formulated by mixing and grinding limestone, clay, silicate, iron, and so on. This mixture is called a preparation material. In the calcination process, clinker is made by calcination of the preparation material. In the finishing process, cement is made as a final product by adding gypsum and a small amount of mixed compositions (limestone, blast furnace slag, silica admixtures, and fly ash) to clinker. Elemental analysis by an X-ray fluorescence spectrometer (XRF) is used for process and quality control in these processes.

There are several types of cement, including portland cement (so-called cement), blended cement (blast furnace slag cement, silica cement, and fly ash cement), and eco-cement. Which one is utilized depends on the purpose. Characteristics of cement depend on the quantified ratio (mineral composition) of the substituent minerals. Conventionally, the Bogue method(2), a theoretical calculation using elemental analysis results, was used to control the mineral compositions. However, the actual mineral compositions often differ from the calculated mineral compositions since the method does not consider the effect of minor components in the cement or the calcination condition of the clinker. In recent years, the control of mineral compositions by X-ray diffractometer (XRD) has been viewed as important and is used especially during the calcination and finishing processes. The content of free lime, a minor component, is now regarded as being as important as those of the major components such as alite (C_3S: $3CaO{\cdot}SiO_2$), belite (C_2S: $2CaO{\cdot}SiO_2$), aluminate (C_3A: $3CaO{\cdot}Al_2O_3$) and ferrite (C_4AF: $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$). Free lime (CaO) is unreacted calcium oxide that remains after the calcination process. This is generated when the calcination conditions in a rotary kiln are not sufficient for all the calcium oxide in the preparation material to react with silicon oxide or aluminum oxide. Evaluation of free lime content is very important in controlling the calcination condition. In general, an accuracy and precision of 0.1 mass% or better is required, since free-lime content is controlled between 0.3–2.0 mass% in many cases. Free lime should be analyzed quickly because it is hygroscopic; it changes to calcium hydrate by reacting with moisture in the air. The analysis is also important from the quality-control point of view because volume expansion during hydration can cause cracks in concrete. In the finishing process, evaluation of the amorphous admixture (blast furnace slag, silica fume, and fly ash) is just as important as the evaluation of cement minerals. In recent years, utilization of waste materials, such as blast furnace slag, silica fume, and fly ash, is increasing due to the growing requirement for environmental load reduction. An example is cement mixed with blast furnace slag ("blast furnace slag cement"). It has better characteristics, including lower hydration heat and higher chemical resistivity, than portland cement. The amorphous content in blast furnace slag should be evaluated accurately because these characteristics depend on the mixing rate of the blast furnace slag, which is amorphous. In this article, we present a quantification method for free lime and the amorphous phase by XRD.

2. Accurate and Precise Evaluation of Free Lime Content

2.1 Experiment

Accurate and precise evaluation of free lime within 0.1 mass% is needed in the calcination process to control performance of the rotary kiln and volume expansion of concrete by hydration reaction. The

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titration methods described by ASTM C114-18(3) and JCASI-01: 1997(4) are used for the quantitative analyses of free lime at many cement factories; however, the operator must decide the final point of the reaction by visual observation of color changes. Therefore, there might be a systematic error due to the operator.

XRD, including Rietveld refinement(5), can be applied to the quantification analysis of free lime(6). However, the accuracy and precision of the analysis should be within 0.1% because the free-lime content is generally no more than about 0.3–2.0 mass%. We used partial integrated measurements to improve the precision of the analysis. To improve the accuracy, we applied a scale factor calculated by Rietveld refinement to prepare the calibration curve. A total of seven calibration standard samples were prepared by adding 0.1, 0.3, 0.5, 0.7, 1.0, 2.0 and 3.0 mass% of CaO reagent (Mitsuwa Chemicals Co., Ltd, 99.99%) to the research cement (Japan Cement Association). Also, samples based on the 601A-1 and 601A-2 (Japan Cement Association) cement standards were prepared by mixing 1.0 mass% of the CaO reagent to confirm the accuracy of the calibration curve made using the scale factor. The CaO reagent was calcined at 1000°C to obtain pure CaO because CaO might have been changed to $CaCO_3$ or $Ca(OH)_2$. The calibration samples and analytical samples were prepared using an agate mortar with hexane by mixing. A MiniFlex (Rigaku) desktop X-ray diffractometer equipped with high-speed, one-dimensional detector D/teX Ultra2 and Cu target was used for these measurements, operating at 40 kV and 15 mA (600 W). The integrated user privileges, measurements, analyses, data visualization and reporting software SmartLab Studio II was used for analysis.

2.2 Accurate improvement of quantification of minor components for Rietveld refinement by the partial accumulation measurement

WPPF (Whole Powder Pattern Fitting) used in powder X-ray diffractometry is a least-squares fitting method between theoretical diffraction calculated from lattice constants and the observed patterns. The fitting method using integrated intensities of each diffraction peak calculated from a crystal structure model is called Rietveld refinement. In Rietveld refinement, crystalline phases contained in a sample are quantified using equation (1) by optimizing a scale factor of crystalline components.

$$X_i = \frac{s_i Z_i M_i V_i}{\sum_j s_j Z_j M_j V_j} \tag{1}$$

X_i is the weight fraction of the analyte component i, S is the scale factor, Z is the number of molecules within a unit cell, M is the molecular weight, and V is the volume of the unit cell derived from the lattice constants.

Measurement can take a long time because a wide-range diffraction pattern is needed for Rietveld refinement (e.g. $2\theta = 10$–$90°$); however, rapid measurement is required for hygroscopic samples. In recent years, high-intensity data can be obtained in a shorter measurement time compared to conventional apparatuses by using a benchtop X-ray diffractometer equipped with a high-speed detector. However, the quantification precision for minor components such as free lime is not enough due to requirements of the S/N ratio of the diffraction peak. To improve the quantification precision by Rietveld refinement, a diffraction pattern with low noise (less affected by statistical fluctuation) is needed. Also, a long measurement time is needed to increase the S/N ratio by obtaining higher intensity in all diffraction areas. Here, the partial accumulation measurement, where weak diffraction peaks from minor phases are re-measured after collection of the wide-range diffraction pattern, is applied. This method improves the analysis accuracy for minor phases with a shorter overall measurement time by improving the S/N ratio of diffraction peaks originating from minor phases.

A schematic diagram of partial accumulation measurement is shown in Fig. 1. In a partial accumulation measurement, 1) After obtaining a wide-range diffraction pattern; 2) Repeat measurement of only diffraction peaks originating from a minor phase; 3) Merge data of (1) and (2); 4) Normalize data from (3). By this procedure, the S/N ratio of diffraction peaks originating from the minor phase can be improved in a shorter measurement time.

To validate the benefits of the partial accumulation measurement, quantification precision of Rietveld refinement was confirmed with and without (general measurement) the partial accumulation measurement for the same sample. For the general measurement, the entire diffraction pattern was measured in 8 min. For the partial accumulation measurement, the entire diffraction pattern was measured in 4 min and diffraction peaks of CaO (200) and (220) were measured for an additional 4 min, resulting in the same total data collection time. Table 1 shows the comparison of the quantification precision for free lime from Rietveld refinement. The quantification precision by the partial accumulation measurement was improved compared to the general measurement because the standard deviation in the fivefold simple repetition measurement by the partial accumulation method showed a smaller value than for the general measurement. Therefore, the partial accumulation method is effective for measuring free lime included as a minor phase.

2.3 Accurate quantitative analysis of free lime using the scale factor calibration curve method

There are problems with Rietveld refinement, as well as the calibration curve method, to achieve accurate quantitative analysis of free lime by XRD. In Rietveld refinement, total quantitative values of quantified phases are normalized to 100 mass%. This means that if unidentified or amorphous phases are included in a sample, they cause an error in the quantitative values.

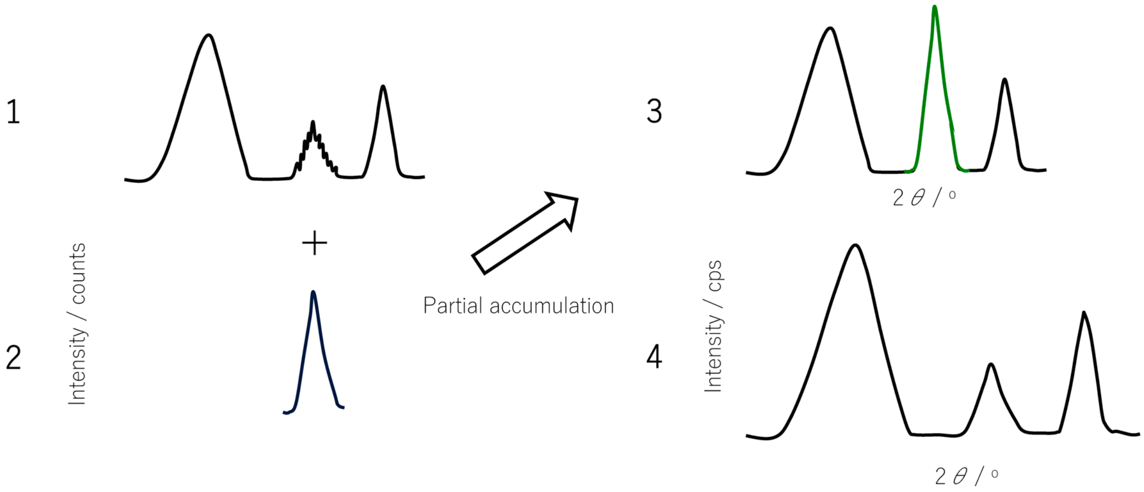

Fig. 1. The schematic diagram of partial accumulation measurement.

Table 1. Comparison of quantification precision between the general measurement and the partial accumulation measurement.

Measurement method	Quantitative value 1 (mass%)	Quantitative value 2 (mass%)	Quantitative value 3 (mass%)	Quantitative value 4 (mass%)	Quantitative value 5 (mass%)	Mean value (mass%)	Standard deviation (σ)	RSD (%)
General measurement	1.17	1.17	1.11	1.11	1.11	1.13	0.03	2.90
Partial accumulation measurement	1.16	1.14	1.16	1.12	1.11	1.14	0.02	2.00

Standard deviation (n=10)

RSD: Relative Standard Deviation / % (n=10)

This error especially affects quantitative values of minor phases. Accurate quantitative analysis for minor phases might be difficult because many phases are contained in cement. On the other hand, the calibration curve method has been used as a classical quantification method for minor phases. Quantitative analysis is performed by preparing a calibration curve showing the correlation between the integrated intensity of a diffraction peak and the concentration of a quantified phase. The error in quantitative results related to unidentified or amorphous phases does not happen in the calibration curve method because a quantitative value of one crystalline phase is obtained using a specific diffraction peak. This enables more accurate evaluation compared to Rietveld refinement, even for minor phases if an independent diffraction peak can be obtained. However, in the case of free lime, independent diffraction peaks are not obtained because diffraction peaks of free lime overlap with diffraction peaks of the clinker components. Fig. 2 shows the diffraction pattern around $2\theta=37°$, where the diffraction peak of free lime having the strongest intensity appears, along with the calculated diffraction peaks from free lime, belite and aluminate as the main components in cement.

In this situation, an independent diffraction peak of free lime cannot be selected since the diffraction peak of free lime overlaps with the diffraction peak of belite. Therefore, accurate evaluation using the calibration curve method with integrated intensities is difficult because any variation in the belite concentration affects the decomposition of the diffraction intensity of free lime. To verify peak overlap, quantification analysis of free lime was performed in two cement samples having different belite concentrations by the calibration curve method using the relationship between concentration and integrated intensity of CaO. As a result, the analysis result was shown as 1.16 and 1.13 mass%, compared to the preparation value of 1.00 mass%. This means that an accurate quantification analysis within 0.1 mass% order was not performed (Table 2). To solve this issue, we considered that a scale factor obtained by Rietveld refinement could be applied to the calibration method instead of the integrated intensity of the diffraction peak.

The scale factor is a parameter used to convert relative calculation intensity to absolute observation intensity, and it increases or decreases depending on the integrated intensities of each crystalline phase. A scale factor optimized by Rietveld refinement can be treated as an integrated intensity after peak decomposition. Using a scale factor for the calibration curve instead of an integrated intensity, an accurate quantification value might be obtained without overlap correction even though a diffraction peak of an analyte phase overlaps with coexisting components.

To improve the quantification precision of free lime, the partial accumulate measurement was applied for sample measurements. The calibration curve using the scale factor (Fig. 3) shows good linearity from 0.1 to

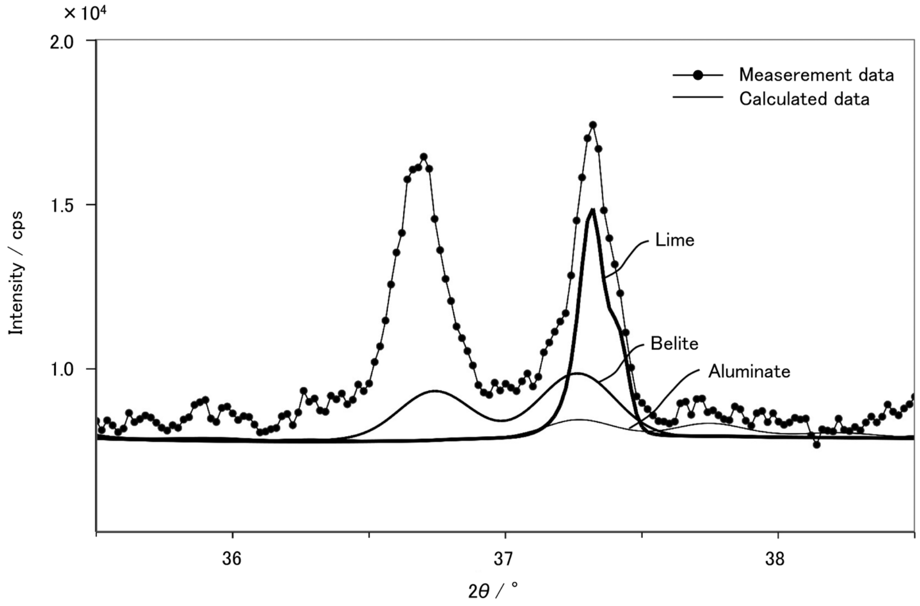

Fig. 2. Overlapping of diffraction peaks between free lime and other components.

Table 2. Quantification result of free lime in two cement samples having different matrices by the calibration curve method.

Amount of lime added (mass%)	Mean value (mass%)	Standard deviation (σ)	|Mean value-amount of lime added| (mass%)
1.00	1.16	0.02	0.16
1.00	1.13	0.04	0.13

Table 3. Quantification result of free lime in two cement samples having different matrices by the calibration curve method using the scale factor.

Amount of lime added (mass%)	Mean value (mass%)	Standard deviation (σ)	|Mean value-amount of lime added| (mass%)
1.00	1.03	0.02	0.03
1.00	1.02	0.03	0.02

3.0 mass% of CaO concentration. Table 3 shows the analysis results of free lime in two cement samples having different matrices by the calibration curve shown in Fig. 3. The quantification values of free lime resulting from fivefold simple repeat measurements showed good agreement with the preparation values, in addition to good repeatability. As a result, evaluation of free lime with accuracy and precision was achieved by combining the partial accumulation measurement and the calibration curve using the scale factor.

3. Accurate Evaluation of Amorphous Components in Mixed Cement

3.1 Experiment

There are several types of cement in concrete materials used for different applications. CO_2 is mostly emitted during the calcination process in cement manufacturing ($CaCO_3 \rightarrow CaO + CO_2$). To control the emission rate of CO_2, decreasing the cement amount per concrete unit is an effective method. Blended cement is a mixture of cement and blast furnace slag, and CO_2 emission in cement manufacturing can be decreased depending on the mixture amount of blast furnace slag since calcination is not needed. By expanding the use of blended cement, non-fuel CO_2 emission is expected to be reduced⁽⁸⁾. Also, blended cement has several advantageous characteristics compared to normal cement. For example, blast furnace slag cement, frequently used in blended cement, has characteristics of low heat of hydration, high chemical resistivity, and so on compared to normal cement, and those characteristics depend on the mixed quantity of the blended materials. Blast furnace slag, silica fume, and fly ash used as materials in blended cement are mostly amorphous; therefore, accurate evaluation of amorphous content is very important.

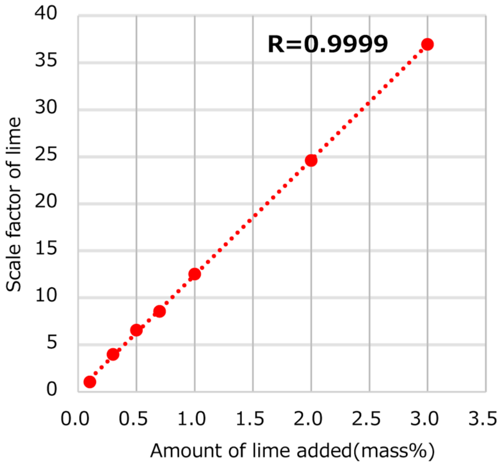

Fig. 3. Calibration curve of free lime using the scale factor.

Quantification of the amorphous component can be performed by combining Rietveld refinement and the internal standard method(9). In the internal standard method, an internal standard material with a known amount is added to the sample. Amorphous concentration can be quantified from the preparation amount and the Rietveld analysis result of the internal standard and the weight fractions X_i of contained crystalline phases calculated from equation (1).

$$C_i = \frac{X_i \times 100}{C'_{\mathrm{STD}}} \times C_{\mathrm{STD}} \qquad (2)$$

$$C_A = 100 - C_{\mathrm{STD}} - \Sigma C'_j \qquad (3)$$

In equations (2) and (3), C_A is the residual content including the amorphous phase (mass%), C_{STD} is the concentration of the internal standard (mass%), C'_{STD} is the calculated concentration of the internal standard analyzed by Rietveld refinement (mass%), and C_i is the quantitative value of crystalline phase i corrected by the internal standard material (mass%). Corundum (α-Al_2O_3) is typically used as an internal standard material because it is not contained in cement and is a stable material at ordinary temperature and normal pressure. The internal standard method is the traditional method for amorphous quantification, but its operation is tedious because the internal standard material needs to be mixed into the cement samples. SmartLab Studio II can be used for amorphous quantification method using standardless amorphous quantification without mixing samples by setting the RIR (Reference Intensity Ratio) value(11) of the amorphous pattern (halo) during the quantification analysis by the WPPF method(12). By the RIR method, a quantification analysis method using X-ray diffractometry, crystalline and amorphous phases can be quantified without adding an internal standard material into a sample or requiring the preparation of a calibration curve. The RIR value is calculated as the intensity ratio of the analyte component and corundum mixed in an equal amount. The weight fraction is calculated using equation (4) by the RIR method.

$$W_i \propto \frac{I_i^{\max}}{R_i} \qquad (4)$$

W_i is the mass fraction of the analyte component i, $I_i^{\max}$ is the strongest intensity, R_i is the RIR value. The amorphous phase is quantified by equation (5) combined with Rietveld refinement by setting the RIR value of a halo during quantification by WPPF.

$$W_{\mathrm{A}} = \frac{S_{\mathrm{A}}/R_{\mathrm{A}}}{\Sigma S_i/R_i} \qquad (5)$$

W_A is the weight fraction of the amorphous phase, S_A is a scale factor calculated by Rietveld refinement, and R_A is the RIR value.

The three types of simulation blast furnace slag cement having 40.0, 42.5 and 45.0 mass% of the blast furnace slag mixed with the research cement (Japan Cement Association) as matrix were prepared to use the RIR method as the amorphous quantification method. Also, two types of simulation mixture cements having mixing ratios of 4.5 : 4 : 1.5 and 5 : 2 : 3 of cement : blast furnace slag : fly ash were prepared to consider applying the RIR method to a mixture cement with three components. The experimental condition of the mixing, apparatus (X-ray tube, tube voltage, and current), and software were the same as 2.1.

3.2 Quantification method of amorphous phase in mixture cement by the RIR method

Blast furnace slag cement is classified into three types: A type (having 5 to 30% of the blast furnace slag concentration), B type (having 30 to 60%), and C type (having 60 to 70%). Currently, B type is the most popular blast furnace slag cement, with a typical slag content from 40 to 45%. Fig. 4 shows the Rietveld refinement result of blast furnace slag cement prepared with 40.0 to 45.0% slag contents. Table 4 shows the quantification analysis result of the blast furnace slag by the RIR method/Rietveld refinement. The template function of SmartLab Studio II was used for the Rietveld refinement. In Rietveld refinement, quantitative values

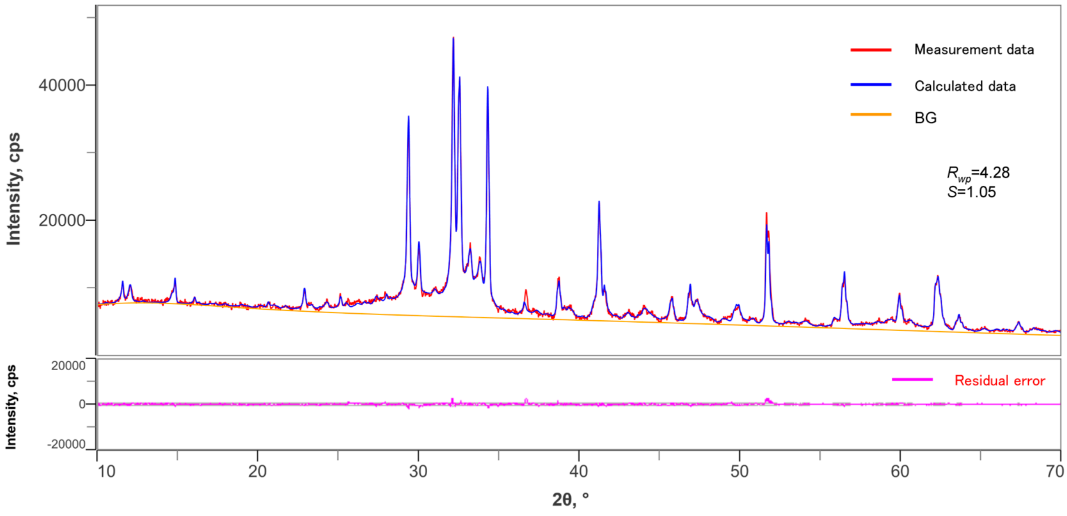

Fig. 4. Rietveld refinement result of the blast furnace slag cement.

Table 4. Quantification result of the blast furnace slag cement by Rietveld refinement.

Amount of blast furnace slag added (mass%)	40.0	42.5	45.0
Quantitativ value of blast furnace slag (mass%)	40.3	42.5	45.4

Table 5. Quantification result of the simulation mixing cement by Rietveld refinement.

Amount of mixture added (mass%)	Blast furnace slag : Fly ash 15 : 40	Blast furnace slag : Fly ash 30 : 20
Quantitativ value of mixture (mass%)	14.76 : 40.7	29.94 : 20.0

might be different although the same measurement data were used because the obtained quantification values depend on analysis conditions. Therefore, first of all, the sample having 40 mass% of slag content was analyzed. Then, the template prepared from the Rietveld refinement condition of 40 mass% of slag content was applied to other samples. The slag preparation values and quantitative values by Rietveld refinement were shown in good agreement due to using the same initial values and analysis conditions by the template function (Table 4).

Recently, in addition to two-component mixing cements, which have a cement and one type of additive, research has been conducted into three-component cements, which consist of a cement and two types of mixtures (13). Table 5 shows the analysis result of the three types of mixture cement. The fly ash content was calculated as total concentrations of the crystalline and amorphous phases because quartz and mullite as the crystalline phases were contained in the fly ash in addition to the amorphous phase. The blast furnace slag and fly ash contents were shown to be in good agreement with the preparation values by setting the RIR values for the amorphous phases in the blast furnace slag and fly ash and using the template function (Table 5). Therefore, the easy and accurate evaluation of amorphous phase content is achieved by setting the RIR value of an amorphous phase during quantification analysis by the WPPF method without mixing an internal standard material or requiring the preparation of a calibration curve. Moreover, the same results can be obtained by using the template function in spite of different analytes.

4. Summary

We presented the evaluation examples of free lime and the blended cement by X-ray diffractometry. Accurate and precise evaluation of free lime content in clinker as a minor component is enabled by combining the partial accumulation measurement and the scale factor calibration method. Moreover, accurate and precise evaluation of mixtures (blast furnace slag and/or fly ash) is enabled by setting the RIR value of halo during quantification analysis by the WPPF method. X-ray diffractometry can be applied for the evaluation of cement materials effectively.

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