Comparison of Calibration Methods Used for Rietveld Quantitative Phase Analysis of Cement and Fly Ash

Y Q Wei\textsuperscript{1,2}, W Yao\textsuperscript{1} and C Y Wang\textsuperscript{2}

\textsuperscript{1} Key Laboratory of Advanced Civil Engineering Materials of Ministry of Education, Tongji University, Shanghai, China
\textsuperscript{2} School of Civil Engineering, East China University of Technology, Nanchang, China
E-mail: yq.wei@tongji.edu.cn

Abstract. The overestimated contents of crystalline phases in polycrystalline powder samples containing amorphous phases must be calibrated when they are done by using Rietveld phase analysis (RPA) for quantitative X-ray diffraction patterns of samples. It has been indicated that there are two methods for this calibration are verified with nice accuracy involving internal standard method (ISM) and G-factor method (GFM) that have been applied to the RPA of both cement and fly ash that contain amorphous mine phases. However, the consistency between these two methods in quantitative determination of phase contents in silicate materials has not yet been discussed. Therefore, the accuracy and consistency between them in quantifying standard mixtures, cement and fly ash were evaluated experimentally. Results indicate that (1) both ISM and GFM gained the very nice accuracy and consistency for the ternary standard mixture, and also the good consistency for cement clinker and fly ash; (2) relatively, GFM is suitable for systems with any content of amorphous phases while ISM is preferably suitable for the system with much more amorphous phase contents, e.g. more than 50\% in weight (denoted as wt.\% henceforth), by adding the suggested 10wt.\% of Al\textsubscript{2}O\textsubscript{3} as internal standard:(3) ISM is not suggested to be used for quantifying the system containing less than 10w.t \% of amorphous phases, and the wisely higher addition of internal standard, such as 20\%, should be employed when it applied to quantifying the system with amorphous phases from 10wt.\% to 50 wt.\% in content.

1. Introduction
Conventional X-Ray diffraction (XRD) is commonly used for the phase determination of polycrystalline powder samples. The specific determination methods include traditional internal standard method, absorption diffraction method, peak method and reference intensity method. In most cases, these methods can only achieve semi-quantitative analysis of phases [1], because of the overlapped peaks of different phases, the preferred orientation and the information that is not fully utilized in the diffraction pattern. The Rietveld Quantitative Phase Analysis (RQPA or RPA) method [2] effectively solves the above problems by means of crystal structure refinement, physical correction and full-spectrum fitting, and it makes XRD convenient and reliable in quantitative analysis of polycrystalline systems [3]. The RPA method was first introduced by Taylor [4] in 1990 to the quantitative analysis of phases of Portland cement and, and then widely recognized in the quantitative analysis of cement mineral phases with the gradually improvement of both the Alite (C\textsubscript{3}S) superstructure model [5, 6] and other crystal structure models, and also the refinement procedures. However, The premise for applying the RPA method to the quantitative phase analysis of
polycrystalline systems is the fact that the sample does not contain amorphous phases, otherwise the crystal phase content will be overestimated. Previous studies [1, 7-9] have shown that cement contains amorphous phases, so it is necessary to correct the quantitative results of cement when using RPA. Aranda [10] introduced and used for the first time the Internal Standard Method (ISM) to quantify the mineral phase of clinkers containing amorphous phases when using RPA, verifying that the absolute accuracy of the amorphous phase content quantified by ISM can reach 1%. After that, this method was applied to the quantitative phase determination of cement and fly ash, and also the measurement of their hydration degree by Korpa [8] and Palomo [11]. Another method for correcting the quantitative results of RPA is the G-factor method (GFM), also known as the external standard method, which was first proposed by O’Connor et al. [12] in 1988 but used delay recently by Jansen et al. [13-16] for quantitative phase analysis of cement, fly ash and early hydration products of cement due to the need for real-time analysis. When Jansen [16] used the GFM to calibrate the quantitative phase results of cements, it was found that the amorphous phase was not detect obviously. This is in contradiction with the results of Yao Wu et al. [9] who found that cements used were detected to contain distinct amorphous phase with higher content by using ISM to quantitatively study the phase composition of cement clinkers. Therefore, a comparison between ISM and GFM was conducted to test the consistency of the two calibration methods in application to calibrating phase content of cement clinker and the fly ash. This paper firstly quantitatively analyzed binary and ternary standard mixture systems (without amorphous phase) to test both accuracy and accuracy of the two methods. And then the consistency of the two methods in calibrating quantitative results for cement clinker and fly ash systems. The results will help us fully understand the respective characteristics of the two methods, and select the appropriate method to quantitatively characterize cement, fly ash and its hydration process according to the actual situation.

2. Experimental

2.1. Materials

Cement clinker was provided by Hailuo Cement Co., Ltd., and Fly ash (Class Ⅰ) provided by Huaneng Thermal Power Plant. The chemical compositions of them were determined by quantitative X-ray fluorescence spectrometry (XRF), and the results were shown in Table 1. Zinc oxide (ZnO) as working chemical was provided by Tianjin Chemical Reagent Research Institute, which is in white powder, and its purity is higher than 99.95%. Alumina (Al$_2$O$_3$) as spectrum pure in white powder, and dihydrate gypsum (C$\text{H}_2$) as analytical reagent with purity higher than 99.99%. were provided by Sinopharm Chemical Reagent Co., Ltd. The XRD spectra of the three chemicals were plotted in Figure 2.

| Sample  | MAC$^{[17]}$ (cm$^2$/g) | Fly ash (wt.%) | Clinker (wt.%) |
|---------|----------------------|----------------|---------------|
| Na$_2$O | 25.00                | 0.45           | 0.61          |
| MgO     | 28.69                | 1.23           | 0.79          |
| Al$_2$O$_3$ | 31.66              | 28.98          | 5.48          |
| SiO$_2$ | 35.90                | 54.70          | 23.1          |
| P$_2$O$_5$ | 39.43              | 0.18           | 0.07          |
| SO$_3$  | 44.26                | 0.58           | 0.62          |
| K$_2$O  | 122.32               | 1.65           | 0.76          |
| CaO     | 124.78               | 4.48           | 64.8          |
| MnO     | 211.70               | 0.06           | 0.08          |
| Fe$_2$O$_3$ | 214.68             | 5.24           | 3.15          |
| LOI/C   | 4.51                 | 2.45           | 0.55          |

2.2. Sample preparation
It takes the block cement clinker and weighs 20 g of cement clinker intermediate particles and milled it by hand for 20 min; then, the milled clinker, fly ash, zinc oxide, aluminium oxide and dihydrate gypsum are respectively sieved through a 45 $\mu$m sieve. In order to ensure the authenticity of the sampling information, the fly ash and clinker sieve residue need to be dry-milled, and the milling and sieving steps should be repeated until all the samples are sieved out. Then mixing 2 g of Al2O3 and 2 g of ZnO and marking it as 5A+5Z; mixing 2g of Al2O3, 2g of ZnO and 1g of CSH2, as 4A+4C+2S; weighing 4g of fly ash, as FA; mixing 3.6g of fly ash and 0.4g of Al2O3, as FA+10A; then all sample are placed into agate mortars respectively with added acetone, and wet-milled for 10 min. Then placed them into a constant temperature and humidity drying oven at a temperature of 25 oC and relative humidity of 0% for 3 h. Finally, the sample placed into a standard sample tank with backpressure loading method. The mixing, preparation and loading steps of each sample need to be repeated three times.

2.3. Data collection and analysis

The instrument for collecting data is a Japanese D/Max-RB type X-ray diffractometer with CuK$\alpha$ radiation, Ni plate filtering, operating voltage of 40 KV, tube current of 100 mA, and optical system DS = SS = 1°, RS = 0.3 mm, graphite monochromator, scintillation detector, etc. The instrument uses a step-and-scan method with a step size of 0.024°, a count time of 0.6s per step, and a diffraction angle ranging from 7° to 41°. The acquired map was imported into the finishing fitting software Topas academic V 4.1 for refinement. The mineral crystal structure used was described in the literature [18]. During the finishing process, the sample displacement, preferential orientation and other corrections were performed as needed. Repeat three times for each sample and average as the final result.

3. Results and discussion

The standard mixture system was quantified by different calibration methods. The results are shown in Table 2.

| Phase content in binary system | Phase content in ternary system |
|-------------------------------|-------------------------------|
| (MAC=40.22 cm$^2$/g, G=6.62E-11 cm$^3$) | (MAC=44.85 cm$^2$/g, G=7.19E-11 cm$^3$) |
| Phase | Known | GFM | RPA | ISM | Known | GFM | RPA | ISM |
| A | 31.66 | 50.0 | 51.3 | 50.9 | 50.0 | 40.0 | 39.3 | 39.9 | 40.0 |
| Z | 48.78 | 50.0 | 49.5 | 49.1 | 46.5 | 40.0 | 38.9 | 39.5 | 39.6 |
| CSH$_2$ | 63.38 | 0.0 | 0.0 | 0.0 | 0.0 | 20.0 | 20.3 | 20.6 | 20.6 |
| Am/ | (0.8) | 0.0 | 3.5 | 0.0 | 1.47 | 0.00 | (0.2) |

3.1. Analysis of calibration calculation error of internal standard method

Due to the dilution of the internal standard, the intensity of the diffraction peak of the sample decreases, and it was very likely that the diffraction pattern of the internal standard was too strong to mask some important information of the diffraction pattern of the sample; therefore, the content of the internal standard must be control. Bensted [1] gives a recommended dosage of about 10%-15% (by weight, the same below). However, the low internal standard content makes the traceability of the internal standard too sensitive, it will cause a large error when the quantitative accuracy of the internal standard cannot be guaranteed. The following will focus on the sensitivity of internal standard tracer, that is the calibration error due to the low amount of standard addition.

In this paper, we use the literature [18] to generate the relationship between the internal standard post-refinement increment ($W_{\text{Std-Rietveld}} - W_{\text{Std}}$) and the amorphous content (shown in Figure 1), as shown in Figure 1-a, when the internal standard addition amount is 10%, if the absolute error of the RPA quantitative result ($W_{\text{Std-Rietveld}}$) is 1%, the maximum quantitative error of the amorphous phase content will be as high as 10%, which means that the internal standard method does not have a resolution for polycrystalline powders with an amorphous content of less than 10%, more clearly, the internal standard method cannot detect a sample having an amorphous content of less than 10%. Even with a 20% addition of the internal standard,
the maximum quantitative error of the amorphous phase content is 6.0%. However, as the content of the amorphous phase in the sample increases, this error gradually decreases.

For samples with an amorphous phase content higher than 50% (shown in Figure 1-b), when the RPA quantitatively produces a 1% quantitative error, and the calibration error of the 20% internal standard dosage is reduced to 1.95%, if the tolerance is ±2%, then the accuracy of the measurement can be met; for amorphous content greater than 60%, the calibration error of 10% internal standard dosage is 1.9%, which also meets the accuracy requirements.

Therefore, it is necessary to estimate the amorphous content of the sample in advance to ensure the calibration accuracy. When the amorphous content is less than 50%, the internal standard method is not recommended; when the amorphous content is higher than 50%, it is necessary to add 20% of the internal standard for calibration; when the amorphous content is higher than 60%, it is necessary to add 10% of the internal standard.

3.2. Internal standard method and G-Value method for quantitative consistency of cement clinker

Cement clinker is a typical polycrystalline system. It has been studied [8, 16] that its amorphous phase content is between 0% and 20%, so if the internal standard method may cause a large error in the quantitative content of amorphous content. However, in order to compare these two methods, the internal standard method was still used and 20% of the standard alumina was added to the clinker for tracing or calibration, for comparing with the quantitative results without the standard and the results are shown in Table 3. In these two systems, the results of the G-value method (C system) and the internal standard method (C+20% A system) are in good agreement, and the amorphous content of the internal standard method does not appear large error, showing the accuracy and precision of RPA quantification. The absolute deviation between the quantitative and amorphous phases of each crystal phase is within 1%; from the quantitative results of the G-value method, it is known that the maximum deviation (1.7%) between each other occurs on the C3S phase, but it is considered that the absolute content of the crystal phase is high in the system (about 50%), so this result is acceptable. As expected, in the C system, due to the existence of the amorphous phase, compared with the G-value method, the quantitative results of RPA clearly overestimate the content of each crystal phase, and the overestimation is 18%-20.5%. In the C+20A system, the absolute deviation of the amorphous phase content quantified by the internal standard method and the G-value method is the largest, which is 1.7%. The main reason of the absolute deviation is that the G-value method determines the amorphous content is the 100% content minus the sum of the contents of the crystal phases calibrated by the G-value method, which was a cumulative value, and there is an accumulation of errors, but after being evenly distributed to each crystal phase, the absolute deviation of the crystal contents from each other is within 1%. It should be noted that the dilution effect on the sample is not shown in the quantitative amount, because the amount of the internal standard was controlled. This can also be seen intuitively in Figure 3. The characteristic peak of the internal standard is relatively low and is not the characteristic peaks of the main crystal phases in the clinker overlap.
3.3. Internal standard method and G-value method for consistency of fly ash quantitative

Table 3. Quantitative results of fly ash by a variety of methods (Unit: wt. %)

| Phases     | GFM   | GFM   | ISM   |
|------------|-------|-------|-------|
|            | Content in FA | Content in FA +10A |
|            | MAC=48.52 cm2/g | MAC=46.83 cm2/g |
|            | G=6.62E-11 cm5 | G=7.19E-11 cm5 |
| Mullite    | 19.1  | 17.5  | 19.1  |
| Quartz     | 7.9   | 8.2   | 8.9   |
| Anhydrite  | 0.3   | 0.5   | 0.5   |
| Hematite   | 1.7   | 1.4   | 1.6   |
| Calcite    | 1.1   | 1.1   | 1.2   |
| A          | 0.0   | 9.2#  | 26.2# |
| Am/Error   | 69.9  | 71.3  | 68.7  |

*a stands for the content of A before corrected. 26.2# stands for the content of A by RPA

Class I fly ash is low calcium fly ash, which is a vitreous ash-based material with a small amount of glass and it has been shown to have a glassy content of 66.6%-86% [8, 19, 20]; according to the analysis of 1.2.2, it is determined that the phase content of 10% alumina is calibrated and compared with the quantitative results without the standard system, the results are shown in Table 4. It can be seen that in both systems, the results of the G-value method (FA system) and the internal standard method (FA+10A system) are in good agreement, and the quantitative results of the crystal phase and the amorphous phase are absolutely
deviated from each other within 1.2%; within the FA+10A system, due to the accumulation of errors, the maximum deviation of 2.6% of the phase content determined by the internal standard method and the G-value method still occurs in the amorphous content, which is different from the mullite in the fly ash. The apportioned deviation is 1.6%, the most likely reason is that the characteristic peak of the internal standard alumina at about 35.1 ° coincides with the characteristic peak of mullite (see Figure 4), so a certain fitting error is caused, which can also be seen by the G-value method quantitative alumina content in the system, and the absolute deviation from the actual content is 0.8%.

Another interesting phenomenon is that regardless of the standard mixture system, cement clinker or fly ash, when a certain standard is added, the content of each crystal phase calibrated by G-value method is generally slightly smaller than the content calibrated by the internal standard method, this is a systematic reduction and the proportion of reduction is also close, and the reduction is gradually increasing from the standard system, clinker system to fly ash system; according to formula (14), it can be seen that there are two reasons for the reduction of this system, one is the decrease of the absorption coefficient of the sample mass, and the other is the increase of the G value; the possibility of the first cause should be smaller, because the larger value of the deviation (2.6%, FA+10A) does not appear in the system with a large change in mass absorption coefficient (C+20A, Total MAC values as shown in Table 2 and Table 3), and within the same system, the mass absorption coefficient is basically stable; the change in G value is the main reason. It can be seen that the G value of the two tests (shown in Table 2 and Table 3, the time interval between the two tests is 10 days) is still very different. In addition, in this paper, the order of sampling is, firstly, the standard mixed sample, next, the cement clinker, and then, the fly ash, which coincides with the above-mentioned decreasing order, indicating that the true G value gradually decreases with time. And the quantification is still using the first calibration of the G value, resulting in a systematic reduction in the quantitative results. In fact, Jansen [15] did find that the G value decreases over time when studying the G-value method. In view of this, it is necessary to shorten the G-value measurement time and the sample test time as much as possible when using the G-value method.

4. Conclusion
1) It is necessary to estimate the approximate content of the amorphous phase in the sample, which is helpful to select the appropriate calibration method and internal standard dosage to minimize the experimental error; For samples with an amorphous phase content of less than 10%, a G-value is recommended; When the amorphous phase content is 10%-50%, if the internal standard method is used, it is recommended that the internal standard content is 20%; The amorphous phase content is greater than 50%, and the recommended internal standard content is 10%.

2) For the standard sample mixed sample, the G-value method yields a fairly accurate quantitative result; in the binary standard mixed sample, the internal standard method will cause a large error of the overall system due to its small quantitative error and all passed to other phases; When the number of standard phases in the mixture increases, the systematic error caused by the internal standard will decrease due to the apportionment; In the ternary standard mixture system, both methods obtained consistent and accurate quantitative results.

3) For polycrystalline systems such as cement clinker and fly ash, both the internal standard method and the G-value method can obtain satisfactory quantitative results, and the quantitative results of the two are consistent, because more crystal phases can share the cumulative error.

4) It should be noted that the sample test interval needs to be shortened as much as possible, when using the G-value method, to avoid the actual G-value reduction, which would result in the quantify of the crystal phase content to be small and cause an increase in cumulative error or the amorphous phase content.

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