

**QUANTITATIVE RIETVELD ANALYSIS OF THE CRYSTALLINE AND AMORPHOUS PHASES IN
COAL FLY ASHES**

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ABSTRACT:

X-ray powder diffraction (XRD) in combination with the Rietveld method was used to evaluate the proportion of crystalline and amorphous (glassy) phases in fly ashes produced in pulverized-coal-combustion (PCC) power plants. The quantification of amorphous phases through the Rietveld method is most usually carried out i) by using an internal standard or ii) by using a poorly-crystalline phase to represent the amorphous phase in the lineshape calculations. In the present work, we explore the usefulness of an alternative method that relies on the calibration of the broad XRD signal arising from the amorphous phase. This procedure, which does not require any spiking of the samples, provides a suitable alternative to evaluate in an easy, fast and consistent manner the amount of crystalline and amorphous phases in the fly ashes.

1- INTRODUCTION

For an efficient disposal or reuse of the fly ashes produced in coal combustion and gasification power plants, it is of chief importance to carry out an accurate characterization of the chemical composition and mineralogy of the ashes. High proportions (commonly >60%) of an Al-Si glassy matrix containing minor and variable contents of Ca, Fe, Na, K, Ti, Mg, and Mn, with minor and variable amounts of a number of crystalline phases (most commonly quartz, mullite, lime, hematite, magnetite, feldspars, gypsum and traces of anhydrite, alkali sulfates, calcium silicate and aluminate, sillimanite, cristobalite-tridymite, wollastonite, and Fe-Al spinels) are the main components of pulverised-coal-(co)-combustion (PCC) fly ashes [1-7]. The amorphous Al-Si glass strongly influences the reactivity of the fly ashes and plays a key role in their subsequent applications as a pozzolanic additive, for the synthesis of zeolites, or for the fabrication of geopolymers [2, 6].

X-ray powder diffraction (XRD) is a standard tool to investigate the mineralogy of fly ashes from coal power plants [2-7]. Different methods have been employed to quantify from the XRD spectra the proportion of the crystalline phases as well as of the amorphous (glassy) content of the fly ashes [8-14]. Reference Intensity (RI) methods, in which the samples are spiked with a known mass of internal standard, allow the determination of the proportions of the different crystalline phases from the intensity ratio between the (usually most intense) peak of each crystalline phase and that of the internal standard [15-16]. The fly ash glass content is then indirectly derived from the difference with the content of the crystalline phases. In turn, standard-addition methods allow one to assess the content of a given phase by adding different known amounts of that phase and constructing a calibration curve. Standard-addition methods also enable one to determine the amorphous content of the fly ashes, provided that a reliable standard for the amorphous phase is available [14]. However, both the RI and the standard-addition methods usually require a large number of steps and are limited to a small number of crystalline phases. Furthermore, these quantitative methods cannot effectively deal with micro-absorption or preferred-orientation effects. In the case of the RI method, previous calibration experiments are usually required in order to obtain accurate RI ratios for each mineral phase relative to the internal standard, making this

method significantly cumbersome.

Over the last two decades, the Rietveld method has been increasingly used as a fast and reliable means to evaluate the content of the crystalline and amorphous phases in materials, chemical mixtures or geological specimens [17]. First devised by Hugo Rietveld for the characterization of crystalline compounds by neutron diffraction, the Rietveld method allows one to obtain refined structural data or quantitative information on powder samples through a least-squares fitting of the measured diffraction patterns. For this purpose, theoretical line profiles are calculated by using structural data (i.e., space group, lattice parameters, atomic positions, etc.) in combination with a lineshape model that takes into account the influence of different instrumental and sample-related effects on the peak profile of the diffraction reflections [17].

Several works have relied on Rietveld full-pattern fitting methods to carry out quantitative analyses of the crystalline phases and the amorphous proportion in fly ashes from XRD data [11-13]. The quantification of the fly ash glass content with the Rietveld method is usually performed by spiking the samples with a known proportion of an internal standard such as ZnO, Al₂O₃, or CaF₂ [11-12]. Ward and French [12] showed that it is also possible to determine the glass content of the fly ashes with the Rietveld method without the need of any spiking. For this purpose, these authors used the XRD pattern of a poorly crystalline silicate phase (metakaolin or tridymite) in order to represent the glassy phase. This approach, previously used by Lutteroti *et al.* [18] to quantify the amount of silicate glass in ceramic materials, was shown to provide good estimates of the proportions of the crystalline and amorphous phases in the fly ashes. The level of consistency achieved with the method of Ward and French [12] seems to depend on the origin of the samples investigated (i.e., on the chemistry of the samples). While the usefulness of Rietveld-based analyses to determine the glass content and also the glass composition of the fly ashes was clearly shown in that work, the calculation of the XRD spectrum for the glassy phase by using a poorly crystalline reference pattern is not straightforward. Information about the atomic positions, average bond lengths and micro-crystal size is required as an input for this type of full-profile analysis, but these data cannot be easily extracted from the fitting procedure alone.

Alternatively, it is possible to carry out quantitative Rietveld analyses of phases that have

an unknown (or amorphous) crystal structure by using a simple calibration procedure [19]. This type of approach, based in the extraction of the intensity of the XRD peaks of the unknown phase, simply requires the calibration of the product $Z_a M_a V_a$ for the unknown phase, where Z_a , M_a and V_a are, respectively, the number of formula units, molecular mass of the formula unit and volume of the unit cell of the unknown phase, labeled as a . The product $Z_a M_a V_a$ enters in the expression for the calculation of the relative weight fraction of the unknown phase W_a within the mixture [17,19]

$$W_a = S_a(Z_a M_a V_a) / \sum_k S_k(Z_k M_k V_k), \quad (1)$$

where S_k denotes the Rietveld scale factor for the k -th phase, Z_k represents the number of formula units in the unit cell, M_k is the molecular mass of the k -th formula unit, and V_k is the unit cell volume. The summation of Eq. (1) goes through all crystalline and amorphous phases in the mixture. For the calibration procedure, which allows one to relate the scale factor of the unknown phase (S_a) to its actual weight percent in the samples, the diffraction pattern from a well-characterized sample containing the unknown phase is required [19].

In the present work, we explore the usefulness of this calibration method to assess the proportion of crystalline and amorphous phases in fly ashes produced in PCC power plants. The aim of the present study is to evaluate if this procedure, which does not require any spiking of the samples (with the exception of the sample(s) used for calibration), is capable to provide results that are consistent with those obtained with other quantitative approaches.

2- MATERIALS AND METHODS

Nine samples of fly ashes from Spanish and Dutch coal (co)-combustion PCC power plants are used in the present work. The samples are labeled as C1 to C4 and T1 to T5. All the fly ashes investigated were produced at combustion temperatures of 1400-1500 °C in different PCC plants fed with coal, coal/petroleum coke, and coal/biomass blends. Details on the chemical and mineralogical composition of these fly ashes are reported elsewhere [14]. Table 1 displays the weight fraction of the two majority phases (quartz and mullite) as well as the amorphous content of the samples, determined with the RI method in Ref. [14]. Note that the present work is restricted to PCC samples, which display a similar mineralogy, carbon content, loss-on-ignition content, and

Si/Al ratios [14]. Fly ashes produced with other combustion processes, such as fluidized bed combustion (FBC), exhibit a different chemical composition and mineralogy and would require a separate full-pattern analysis.

For the XRD measurements, all samples were pulverized (<5 μm) and carefully homogenized. XRD scans were acquired by using a Bruker-AXS (Siemens) D5005 powder diffractometer equipped with a 2.2 kW sealed Cu x-ray source, a graphite monochromator to filter out the Cu $K\beta$ radiation, and a NaI(Tl) scintillation detector. The scans were performed between 4° and 60° 2θ with a 0.05° step size and a counting time of 3 seconds per step. While lower step sizes and longer integration times are typically considered for Rietveld analyses, standard step sizes and integration times were deliberately employed here in order to assess the usefulness of the Rietveld approach for a fast determination of the fly ash glass content.

Rietveld full-pattern analyses were performed with the TOPAS 4.2 program (Bruker AXS, 2003-2009). For the analyses, the XRD broad signal from the amorphous phase was fitted with a split pseudo-Voigt (SPV) function. To reduce the number of adjustable parameters, the Lorentz fraction for the left and right SPV profiles were respectively taken as 1 and 0.5, as these two values were found to give good agreement between calculated and experimental XRD curves for all the samples investigated. The peak position, the area and the right and left width of the SPV function were left as free parameters. Given that the $Z_a M_a V_a$ product has no physical meaning [19], the area under the curve of the SPV function was directly used as effective scale factor for the amorphous phase. The XRD reflections for the crystalline phases were adjusted with conventional pseudo-voigt functions, whereas a first-order polynomial function was found to yield a good fit of the background signal. Following the discussion of Scarlett *et al.* [19], for the calibration of the $Z_a M_a V_a$ factor of the amorphous matrix we used T2 fly ash as calibration sample, since accurate data about the content of mullite, quartz, and fly ash glass obtained with both the RI method and the standard-addition method was available for this sample [14]. Once the $Z_a M_a V_a$ factor for the glass was obtained, Rietveld-based quantifications were carried out for the rest of XRD scans. The proportions of the crystalline and amorphous phases were thus obtained. To check for the reliability of the structural data corresponding to the mullite phase, single- and binary-phase Rietveld analyses of XRD scans

of mullite and 50:50 mullite/fluorite mixtures were carried out (not shown). The refined cell volume and resulting crystal density of mullite turned out to be in agreement with published values [11], and excellent quantitative results for the binary mixtures were obtained.

3- RESULTS AND DISCUSSION

As discussed in detail elsewhere [14], the XRD spectra reveal that quartz (Qz) and mullite (Mu) are the two main crystalline phases in the PCC fly ashes studied in this work, with concentrations up to ~5%(Qz) and 16.3% (Mu) in weight percent as obtained with the RI method with CaF_2 as internal standard. Weak peaks arising from small amounts of anhydrite, calcite, microcline-orthoclase, hematite, and magnetite also show up in some of the XRD scans of the PCC samples. The RI method indicates that the concentration of these phases is lower than ~1% in all fly ash samples, with the exception of C2 fly ash, which was found to contain slightly higher amounts (3.4%) of hematite (Hem) and magnetite (Mag). From the RI ratios, it is concluded that the amorphous content of the samples is in the range 80-97% [14].

Figure 1 shows the powder diffraction pattern of T2 fly ash, dominated by the main reflection of quartz at 26.6° (in 2θ). Peaks from mullite and hematite, as well as the broad signal from the amorphous matrix, also appear in the spectrum. As described in the previous section, this pattern was used to calibrate the product $Z_a M_a V_a$ for the amorphous phase as required for the Rietveld quantifications. For this purpose, a value of $W_a = 89.5\%$ for the weight fraction of the amorphous phase as obtained by Font *et al.* [14] for T2 fly ash was employed. From the fit, the weight fraction of quartz (5.5%), mullite (3.9%), and hematite (0.7%) was also obtained for this fly ash. These values are in good agreement with those reported by Font *et al.* [14] (Qz 5%, Mu 5.9%, Hem 0.3%).

As can be seen in Fig. 1, the calculated XRD lineshape resulting from the fitting procedure closely matches the experimental spectra. The inset of Fig. 1 shows an expanded view of the broad signal measured from T2 fly ash corresponding to the amorphous phase (crosses). Note that the peaks from the crystalline phases are not visible in the inset because of the particular scale used in the plot. The figure also shows the SPV profile resulting from the fitting procedure. The SPV

function and the hump arising from the amorphous phase show good agreement over the entire angular range of the measurement.

Rietveld quantitative analyses were subsequently performed for the rest of fly ash samples by using the $Z_a M_a V_a$ factor extracted from the fit to the XRD pattern of T2 fly ash. The weight fractions for the main crystalline phases as well as for the amorphous phase thus obtained are given in Table 1. The values extracted with the RI method [14] are also given for comparison purposes. As can be seen in the table, the Rietveld-based approach yields values for both the glass and quartz contents that are in good agreement ($\pm 4\%$ and $\pm 1.3\%$ for glass and quartz, respectively) with those obtained with the more involved internal reference methods. Only C1 fly ash exhibits some minor discrepancy in the quartz content, which we attribute to an underestimation of the value given by the RI method owing to the weak XRD signal of the main peak of quartz. With regard to mullite, it should be realized that, with the exception of T1 fly ash, the mullite content values obtained with the RI method are consistently larger ($\sim 3\text{-}5\%$) than those obtained with the Rietveld method. We attribute these differences to the fact that the main XRD doublet from mullite at 26.2° (in 2θ) is fairly weak and superimposed to the main peak of quartz at 26.6° , which complicates the evaluation of the mullite weight fraction with the RI method. However, it cannot be ruled out that the Rietveld approach gives rise to underestimated mullite content values owing to distortions in the crystal structure of the mullite phase in the fly ashes.

In all cases, the calculated XRD peak profile resulting from the Rietveld fits closely matched the experimental spectra, with weighted-pattern residuals (R_{wp}) in the 13%-18% range for all fly ashes including the calibration sample (T2 fly ash). Minority phases such as hematite, magnetite or anhydrite were also taken into account in the Rietveld analyses (for instance, as discussed above, hematite in the case of T2 fly ash). The resulting weight fractions for these phases were, in most cases, lower than 1% and, therefore, have not been included in Table 1. In the particular case of C2 fly ash, the hematite and magnetite contents ($\sim 4\%$) extracted from the Rietveld full-pattern matching were also in good agreement with the results (3.4% for both phases) of Font *et al.* [14].

Figure 2 shows a comparison between the fly ash glass content obtained with the RI and

the Rietveld calibration approach used in this work. In the figure, the dotted line is the result of a linear fit, with correlation coefficient $R=0.946$, that has been forced through the origin. The slope of the linear fit is equal to 1.013, i.e., an average 1.3% above the RI data, which confirms the high consistency of the Rietveld determination. As can be seen in the plot, the data obtained with both methods on the samples with the highest glass contents (>90%) is highly consistent. In the samples with lower proportions of amorphous phase, the values extracted with the RI method tend to be slightly lower (~3-4% in most cases). Given that these samples exhibit the largest proportions of mullite, these small differences can partly be attributed to the different values of mullite content obtained with the RI and the Rietveld method (see discussion above), leading to underestimated values of the fly ash glass content.

From the above results, it is clear that the calibration method provides a reliable means to obtain a fast evaluation of the weight percent of both the crystalline and amorphous phases in coal (co)-combustion PCC fly ashes. The method may in principle be easily extended to any type of fly ash regardless of their origin (for instance, FBC ashes) provided that an appropriate mineralogical characterization of one or more samples is available for calibration purposes. With regard to this, it should be noted that the consistency of this approach could be increased by using several samples for calibration.

The requirement of the preliminary calibration step might be viewed as a potential limitation of the method. One should realize that no assumptions about the crystalline structure of the amorphous phase are needed with the present approach. This is in contrast to other methods that rely on poorly-crystalline silicate phases like metakaolin or tridymite to represent the amorphous phase [12]. With the present approach, information about the crystallite size, fly ash composition or atomic positions is not required as an input for the full-pattern model.

In order to compare the two Rietveld approaches, we have performed Rietveld quantitative analyses of the PCC fly ashes studied in this work by using tridymite in order to represent the glassy phase (see Ward *et al.* [12]). Applying this method with the TOPAS 4.2 program, we find that a careful adjustment of the micro-crystallite size values required in the component convolutions for the calculation of the XRD signal from the amorphous phase is required in order to obtain

consistent results. Once such adjustment is done, good agreement between the fly ash glass content obtained with the two Rietveld methods is obtained. However, it is found that the XRD lineshapes corresponding to the poorly-crystalline tridymite phase do not perfectly match the humps arising from the glassy phase. In contrast, if the micro-crystal size is left as a free fitting parameter, very good agreement between experimental and calculated curves is found. In this case, however, the amorphous weight proportions thus obtained turn out to sizably underestimate the glass content in all fly ashes. This is in contrast to the calibration approach used in the present work, which yields very good agreement between calculated and experimental spectra, and high consistency between the Rietveld and the RI quantitative values is also obtained.

4. CONCLUSIONS

Although the quantification of the amorphous content with the Rietveld method is usually performed by using an internal standard, quantitative Rietveld analyses without any sample spiking can still be carried out provided that the XRD signal from the amorphous phase is calibrated. In this work, the usefulness of this calibration approach in order to evaluate the amorphous content in fly ashes by means of the Rietveld method was explored. The calibration of the XRD signal from the amorphous phase provides a reliable determination of the weight fraction of both the crystalline and amorphous phases in coal fly ashes. This method, which may be easily extended to the quantification of the amorphous content in any type of mixture, becomes particularly useful in the context of industrial characterization, as it provides fast quantitative data without the need of any particular sample processing.

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TABLES

Table 1. Content of quartz, mullite, and amorphous glass in (co)-combustion PCC fly ashes as obtained with the Rietveld method. For comparison, data obtained in Font *et al.* [14] with the reference intensity (RI) method using CaF₂ as an internal standard are also given. In the case of the calibration sample (T2), the content of quartz, mullite and glass was obtained with the standard addition method. With the exception of sample T2, the glass content values have been rounded to the nearest integer.

Sample	Glass (%)		Quartz (%)		Mullite (%)	
	RI	Rietveld	RI	Rietveld	RI	Rietveld
T2 (calibration)	89.5 ^a	89.5	6.0 ^a	5.5	3.5 ^a	3.9
T1	80	77	3.2	4.5	15.8	18.5
T3	86	89	2.2	3.1	10.6	7.7
T4	80	84	2.8	3.6	16.3	11.0
T5	84	87	2.7	3.2	12.4	8.9
C1	94	93	0.8	3.3	4.4	3.1
C2	80	83	2.5	1.9	9.3	5.6
C3	97	98	1.3	1.3	<0.1	<0.1
C4	93	92	1.6	1.7	4.6	2.0

^aValues for the calibration sample (T2) were obtained with the standard addition method (see Font *et al.* [14])

FIGURE CAPTIONS

Figure 1. Rietveld plot (10-55°) for the T2 fly ash, used to calibrate the XRD signal from the amorphous phase in the PCC fly ashes ($R_{wp}=14.7\%$). The amorphous content of this sample was accurately determined with independent methods in Font *et al.* [14]. The inset shows an expanded view of the fit with a split pseudo-Voigt function (solid line) of the broad XRD signal (hump) arising from the amorphous phase (crosses). Due to scaling reasons, the XRD peaks arising from the crystalline phases are not visible in the inset.

Figure 2. Determination of the fly ash glass content with the Rietveld method (solid circles) as a function of the glass content obtained with the reference intensity (RI) method. Following Ref. [19], for the full-pattern matchings the intensity of the amorphous XRD signal has been calibrated by using the XRD spectrum of fly ash T2. Data for this sample is also given (star). The dotted line is the result of a linear fit to the data. The slope of the linear fit, which has been forced through the origin, is equal to 1.013.

FIGURES

FIGURE 1

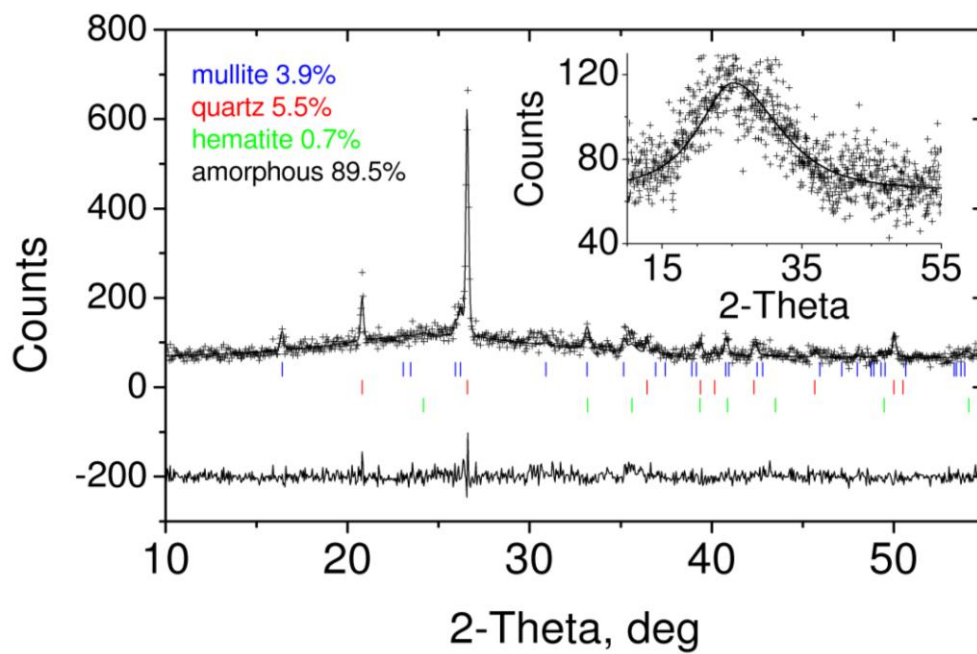


FIGURE 2

