Fuel 105 (2013) 314–317

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Quantitative Rietveld analysis of the crystalline and amorphous phases in coal fly ashes

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HIGHLIGHTS

- ▸ X-ray diffraction (XRD) is used to quantify the phases in coal fly ashes.
- ▸ A non-standard Rietveld-based method is employed.
- ▸ In this method, the XRD signal from the amorphous phases has to be calibrated.
- ▸ The crystalline and amorphous phases in the fly ashes are simultaneously quantified.
- ▸ This approach provides fast, reliable and consistent phase quantifications.

ARTICLE INFO

Article history:
Received 10 February 2012
Received in revised form 20 June 2012
Accepted 21 June 2012
Available online 10 July 2012

Keywords:
X-ray diffraction
Fly ash
Rietveld method
Mineralogy

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

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http://dx.doi.org/10.1016/j.fuel.2012.06.090

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, Al_2O_3, or CaF_2 [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 Lutterotti 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 $Z_aM_aV_a$ 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 $Z_aM_aV_a$ enters in the expression for the calculation of the relative weight fraction of the unknown phase W_a within the mixture [17,19].

$$W_a = S_a(Z_aM_aV_a)/\sum_k S_k(Z_kM_kV_k), \tag{1}$$

where S_k denotes the Rietveld scale factor for the kth phase, Z_k represents the number of formula units in the unit cell, M_k is the molecular mass of the kth 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–C4 and T1–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 Kβ 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 s 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 where 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

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 CaF_2 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

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