QUANTIFICATION OF AMORPHOUS CONTENT IN COMBUSTION BY-PRODUCTS: AN OVERVIEW

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ABSTRACT

The presence of the amorphous phases has a great effect on the pozzolanic, chemical and mechanical properties of combustion by-products. Traditional quantitative phase identification of combustion by-products by the Rietveld refinement method fails to consider the presence of the amorphous and unidentified phases. Several direct and indirect analytical methods which are used to determine the amorphous phases and assess their performance via X-ray diffraction have been discussed with their benefits, limitations and applicability.

Keywords: Combustion by-products; amorphous content; analytical techniques;

1. INTRODUCTION

The combustion by-products refer to ash deposits, fly ash, bottom ash and other residues from burning solid fuels for producing power or steam. [1] These by-products often contain crystalline and amorphous phases. There are several approaches to characterize the amorphous phases in the sample including the X-ray diffraction (XRD) method [2-4], differential scanning calorimetry (DSC) [5], solution calorimetry (SC) [6], isothermal microcalorimetry (IMC) [7], nuclear magnetic resonance (NMR) [7], Fourier transform infrared spectroscopy (FTIR) [8] and Raman spectroscopy (RS) [9]. The combination of these techniques [2-4, 10-17] can be also used to determine the amorphous content in the sample. [18] The commonly used characterization methods for amorphous phases have been summarized in **Table 1**.

Table 1. The commonly used characterization methods for amorphous phases

Method	Detection limit/%	Sample weight/mg	Phase detection	Remarks	References
XRD	0.4–10	300-400	Crystalline	Diffraction affected by the properties of the sample	[2-4]
DSC	1–20	4-10	Both	crystallinity measured at melting point; thermal changes during the scan;	[5]
SC	0.5-1.8	10-70	Both	Difficulty in quantification of some processes	[6]
IMC	0.5-5	20-300	Amorphous	Careful selection of experimental conditions; Lack of specificity;	[7]
NMR	0.5-3	500-700	Both	Applicable only to organic compounds	[7]
FTIR	1-2	5-50	Both	Quantitative subtraction of overlap from the matrix required	[8]
RS	1	2000	Both	used as complementary quantification method to IR	[9]

XRD is the most commonly used analytical method for quantitative analysis of crystalline and amorphous phases in these by-products. The presence of non-crystalline materials creates a broad hump in the diffraction diagram which is called amorphous halo. [19] The position and width of the amorphous halo indicate the distribution of the interatomic distances in the crystal structure. The area under the amorphous halo relies on the quantity of the amorphous materials in the sample and can be used to semi-quantitatively determine the amorphous content. [19, 20] The characteristics of the amorphous and crystalline phases

are considered to be crucial factors which have a great effect on the pozzolanic, chemical and mechanical properties of these by-products. [21] As the melting and sintering, slagging and fouling involve the formation of amorphous phases in the combustion by-products, it is important to use a method to determine the amorphous content. [3, 19] The different methods with the software used and different standards for determining the amorphous content in the combustion by-products have been summarized in **Table 2**. The commonly used analytical methods with their benefits and limitations have been reviewed in this paper.

Table 2. Different methods for determining amorphous content in combustion by-products

Authors	Samples	Software	Methods	Standards	%
Yan et al. (2018) [2]	coal fly ash	TOPAS	Rietveld-Internal	ZnO	10
Liu et al. (2018) [3]	slag	Topas	Rietveld-Internal	Al_2O_3	50
Zhao et al.(2017) [4]	fly ash	TOPAS	Rietveld-Internal	Al_2O_3, SiO_2	10, 20, 30
Hoppe et al.(2017) [10]	Rice-Husk Ashes	-	Rietveld-Internal	LiF	10
Ye and Radlinska (2016) [11]	Fly ash, slag	Jade	Rietveld-Internal	Nickle	15
Singh and Subramaniam (2016b) [12]	alkali activated fly ash	TOPAS 4.2	Rietveld-External	Al_2O_3	30
Snellings (2014b) [22]	Cements, fly ash	-	PONKCS	-	20
Ibanez et al.(2013) [13]	coal fly ashes	TOPAS	Rietveld-Internal	CaF_2	30
Bayuseno et al. (2010) [14]	MSWI bottom ash	SIROQUANT	Rietveld-Internal	CeO_2	20
Ural (2007) [15]	Turkish coals	SIROQUANT	Rietveld-Internal	ZnO	50
Whitfield and Mitchell (2003) [16]	cements and clinkers	TOPAS	Rietveld-Internal	Al_2O_3	25, 50
Winburn (1999) [17]	combustion by-products	GSAS	Rietveld-Internal	TiO_2, ZnO, Al_2O_3	10, 20, 50

2. SUMMARY OF THE ANALYTICAL METHODS

There are many methods to determine the amorphous content in the mixture using XRD methods, including the single peak approach and the whole pattern approach. In the first method, the estimation of the amorphous content is obtained from a limited 2θ data point. In the latter method, a choice between the pattern summation methods and the crystal model based on the Rietveld method are needed to be made. [18] Quantification of amorphous and crystalline phase content depends on the determination of the diffraction intensity of each phase to the whole diffraction pattern in a mixture. Two evaluation methods are used to determine the amorphous content. [23] The limitations and benefits of these methods are compared and some recommendations are made. Successful determination of amorphous content requires careful consideration in finding suitable methods for a given sample. This paper discusses and evaluates the capabilities, advantages and limitations of these methods.

2.1. Single peak method

This method is based on the measure of one or more diffraction peaks for each phase. It uses a single diffraction peak to achieve the amorphous content rather than using the whole diffraction pattern. [18] It assumes that the diffraction intensity of these peaks is representative for each individual phase. This method relies on the direct evaluation of the diffraction intensity

of amorphous phases to the whole diffraction pattern. This can be achieved by simple numerical approach or profile fitting. The general procedure is as follows: [18, 23] An advantage of this method is that it does not necessarily need the background determination, especially for those unreliable and difficult distinctions between the background and amorphous intensities. There is no need to determine all mineral phases in the mixture. This method requires pure standards with a known amount. Neither the instrument setup or the sample properties must change between the unknown measurements and calibration, otherwise the calibration is invalid. [23]

2.2. Whole pattern phase analysis methods

These methods depend on the comparison of the observed diffraction data with the measured patterns or calculated patterns (based on Rietveld method). In the Rietveld method, diffraction patterns are calculated using the structure factors determined by the measure from the actual sample or the crystal structure information. These methods use measured diffraction data from data libraries which provide standard diffraction pattern of each phase. The following methods are used to characterize the amorphous content based on the Rietveld refinement method. [18]

2.2.1. Rietveld method

The output of A Rietveld quantitative phase analysis is a set of crystalline phase scale factors. The weight fraction of a crystalline phase (W_α) in the sample is determined as, [24] $W_\alpha = \frac{S_\alpha(ZMV)_\alpha}{\sum_{j=1}^{n} S_j(ZMV)_j}$. Where Z is the number of formula units in a unit cell, V is the volume of a unit cell, M is the molecular mass of the given formula unit and S is the refined scale factor. This assumed that all the phases are crystalline in the mixture and the weight fractions sum the analysed concentrations to unity. In the presence of non-included or amorphous components, the values may be overestimated concerning the true concentrations. This method is used as a direct approach for quantitative analysis of amorphous content. The amorphous content can be determined by the Rietveld method using the algorithm of Hill and Howard [24] as this method treated all the phases as crystalline and included these phases in the analysis. [23]

2.2.2. Internal standard method

The internal standard method (or spiking method) is more experimentally-demanding and uses a crystalline standard phase in a known amount (W_{st}). This crystalline standard should be free of amorphous content or the non-diffracting content must be known. The mixture should be homogenized as small particles. A general procedure for the Rietveld refinement analysis of the amorphous content was outlined elsewhere. [25] This method determines the overall unaccounted content (including the amorphous phases and the unidentified crystalline phases) called ACn (amorphous and crystalline not-qualified). This method highlights the contribution of the amorphous phases and any unidentified crystalline phases. [26] The W_α is determined as, [24] $W_\alpha = W_{st} \frac{S_\alpha(ZMV)_\alpha}{\sum_{st}[S_{st}(ZMV)_{st}]}$. Where S_{st} is the refined scale factor of the standard phase. The addition of a standard phase may be problematic for low-content phases. Some authors outlined a procedure for the refinement analysis to study the effects of the systematic errors. [25] Two powder diffraction patterns are required to be collected. Firstly, a powder diffraction pattern of the sample is collected and the crystalline phases are determined. Secondly, a powder diffraction of the sample mixed with internal standard is collected. The weight fraction of the internal standard (W_{st}) is determined. Due to the presence of ACn phases, the refined weight fractions are overestimated.

2.2.3. External standard method

This method is indirect and follows a similar procedure of the internal standard method. The weight fraction of the crystalline phases is determined on an absolute scale and the amorphous content is obtained by difference. Unlike the internal standard method, this approach uses an external standard material.[27] Either a pure standard material or a phase with a known quantity in the mixture is used as an external standard to determine a normalization constant (K) which is used to calculated the weight fractions on an absolute scale, [23] $W_\alpha = \frac{S_\alpha(ZMV)_\alpha \cdot \mu_m^*}{K}$. Where μ_m^* is the mass absorption coefficient of the mixture. K only relies on the instrumental parameters and is independent of the sample-related parameters. Only the unidentified and amorphous contents are determined.

2.2.4. PONKCS method

In this direct method, those phases with partial or no known crystal structure (PONKCS) are characterized by the measured structure factors rather than the calculated ones. This method overcomes the difficulties which require a known crystal structure. The intensity contributions of the amorphous and the crystalline phases to the whole diffraction pattern can be characterized by Le Bail fitting, Pawley or single line methods. [28] In the method, the amorphous and crystalline phases are characterized by empirical or calculated structure factors. For those using empirical structure factors, the calibration constants (ZMV) must be derived. ZMV can be obtained by a known mixture of a crystalline or amorphous component and an internal standard. $(ZMV)_\alpha = \frac{W_\alpha}{W_s} \frac{S_s}{S_\alpha}(ZMV)_s$. Where W_α and W_s are the known weight fractions of the sample (α) and the standard (S), respectively. S_α and S_s are the refined scale factors of the sample (α) and the standard (S), respectively.

This approach provides a direct measure of the amorphous content and combines the results with the analysis of crystalline phases in the mixture. A one-time calibration for every single standard mixture is sufficient. A good recommendation is to create a comprehensive database with the PONKCS phases for the refinement of the crystal structures. [18, 23]

2.2.5. Linear calibration model (LCM) method

Unlike the external and internal methods, this method is direct and discards the information related to the

crystalline phases but it is still based on the analysis of a wide range of diffraction points and uses some refined parameters. [18] The diffraction intensity contribution of an amorphous component to the whole diffraction pattern is modelled through Le Bail, Pawley or single line fitting methods. Only the refined scale factors are used in the analysis. A linear calibration model associated with the quantity of the amorphous content ($W_{amorphous}$) and the scale factor can be derived from the relationship between the concentration and peak intensity. [29] $I_{amorphous} = C_{amorphous} \frac{W_{amorphous}}{Q_{amorphous}\mu_m^*}$. Where $C_{amorphous}$ is a constant for the group of reflections for amorphous phases, $W_{amorphous}$ is the weight fraction of an amorphous phase, $Q_{amorphous}$ is the density of an amorphous phase, μ_m^* is the mass absorption coefficient of the mixture. This allows the derivation of a linear calibration model to relate the refined scale factor (S) to the amorphous content ($W_{amorphous}$),

$W_{amorphous} = A \cdot S - B$. Where A and B are the slope and the residual offset of the calibration, respectively.

2.2.6. Degree of crystallinity (DOC) method

This method is straightforward and direct, compared to other methods discussed. This approach is based on the estimation of the total diffraction intensity or area contributed to the whole diffraction pattern by each phase in the mixture. The degree of crystallinity (crystalline index, DOC) is then determined from the total areas under the defined amorphous and crystalline phases, $DOC = $ crystalline area/(crystalline area + amorphous area). The weight fraction of the amorphous phase can be determined from $W_{amorphous} = 1 - DOC$. This method can only be applied if the crystalline components have the same chemical compositions in the sample. If this is not fulfilled, the absolute values will be obtained from the standard calibration. [23]

Table 3. Summary of the methods for determining the amorphous content

Method	Approach	Standardisation	Multiple amorphous	Benefits	Limitations
Single peak	Direct	Calibration suite	Yes	Capable for a few phases and no need to determine all mineral phases	Unreliable if the overlap is difficult to distinguish
Rietveld	Direct	No	Yes	Determine more than one amorphous component without any calibration	Not accurately represent the sample with short-range order
Internal	Indirect	Internal standard	No	Can be used in many Rietveld analysis software	Relies on the acquisition of an appropriate absorption contrast
External	Indirect	External standard	No	The samples are not contaminated in this method	Only the unidentified and amorphous contents are determined
PONCKS	Direct	Single mixture	Yes	Suitable for significant errors due to the microabsorption and the crystalline phases with known structures.	Needs the availability of a standard material to derive an empirical ZMV
LCM	Direct	Calibration suite	Yes	Can be applied when there is a minimal variation of absorption contrast between the phases	Only suitable for the mixture similar to the calibration series
DOC	Direct	Case dependent	Yes	Available in many software programs	An additional step is needed if chemical compositions of the crystalline phase are different from the whole sample

3. DICUSSIONS AND APPLICATIONS OF THE ANALYTICAL METHODS

Some of the applications of these methods in the combustion by-products are summarized in **Table 4**. Yan et al. [2] quantitatively studied the effects of NaOH and temperature on the formation of amorphous phases and analyzed the amorphous and crystalline phases in coal fly ash using Rietveld-Internal method. The results showed the Rietveld-internal method is effective in determining the amorphous and crystalline phases. Liu et al. [3]

studied the amorphous phases in slag using Rietveld-internal approach. The results showed that the amorphous content was quite high in the slag. Zhao et al. [4] quantitatively and accurately assess the amorphous and crystalline phases in fly ash using Rietveld-XRD/internal methods. The results showed that the amorphous content was sensitive to the minor phases. Hoppe et al. [10] studied the effects of amorphous content on the reactivity of rice husk ashes. The results showed that the lime consumption is insignificantly influenced by the specific surface area and amorphous content. The decrease in amorphous silica increased the

reaction potential. Ye and Radlinska [11] investigated the alkaline activation on the nature of amorphous phase using Rietveld-internal methods. The results showed that the nature of amorphous and crystalline phases was dependent on the sample age, activation and slag-fly ash ratio. Singh and Subramaniam [12] quantitatively analyzed the amorphous content in alkaline activation fly ash. The results showed that the amorphous phase was correlated with the compressive strength. Snellings et al. [22] quantified the amorphous content in cements and fly ash using PONKCS-XRD methods. The results showed that the presence of multiple amorphous phases would reduce the accuracy with an acceptable data. Ibanez et al. [13] evaluated the amorphous and crystalline phases in coal fly ashes via Rietveld-internal methods. They found a useful calibration method to assess the amorphous content. Bayuseno et al. [14] used Rietveld-internal methods to analyze the amorphous and inorganics in MSWI bottom ash. The results showed that the decrease in amorphous content caused formation of ettringite, rosenhahnite and hydrocalumite. Ural [15] quantified the amorphous and mineral phases in coals by Rietveld-internal methods. The results showed that the presence of the amorphous phases attributed to the differences and quality between coals. Whitfield and Mitchell [16] quantified the amorphous content is clinkers and cements by Rietveld-internal methods. The results showed that the presence of amorphous content affected the reactivity of samples. Winburn [17] developed the Rietveld-internal method to quantify the amorphous and crystalline phases in coal combustion by-products. The results showed that the errors of amorphous content could be reduced with smaller particle sizes and a linear absorption coefficient.

Table 4. The amorphous and crystalline phases in different combustion by-products with remarks

Authors	Samples	Crystalline phases	Amorphous content (%)	Remarks
Yan et al. (2018) [2]	coal fly ash	Mullite, quartz, zincite	39.4, 33.18, 55.8, 61.2,	Effects of NaOH and temperature on amorphous phases
Liu et al. (2018) [3]	slag	Merwinite, gehlenite, periclase	97.94	Amorphous content was quite high
Zhao et al.(2017) [4]	fly ash	Mullite, quartz, lime, rutile, calcite	70.4, 75.3	Amorphous content is sensitive to minor phases
Hoppe et al.(2017) [10]	Rice-Husk Ashes	Quartz, cristobalite	76.7, 70.8, 69.7, 66.1	A decrease in amorphous content increased in reactivity
Ye and Radlinska (2016) [11]	Fly ash, slag	Quartz, mullite, hematite, zeolite	82.6-98.6	The nature of amorphous content was dependent on several factors
Singh and Subramaniam (2016b) [12]	alkali activated fly ash	Zeolite, mullite, quartz, hematite, rutile	39.8-48.1	Amorphous phases in correlation with compressive strength
Snellings et al. (2014b) [22]	Cements, fly ash	Quartz, mullite, calcite, arcanite, ferrite	92.6, 98.7	Presence of multiple amorphous phases reduce the accuracy
Ibanez et al.(2013) [13]	coal fly ashes	Quartz, mullite hematite	89.5	A useful calibration method was developed for assessing the amorphous content
Bayuseno et al. (2010) [14]	MSWI bottom ash	Quartz, corundum, ettringite, calcite	24.5, 33.5	the decrease in amorphous content caused formation of ettringite, rosenhahnite and hydrocalumite
Ural (2007) [15]	Turkish coals	Quartz, illite, albite, pyrite	63.9-83.5	Presence of amorphous content attributed to the quality and differences between coals
Whitfield and Mitchell (2003) [16]	cements and clinkers	Rutile, quartz, anhydrite, gupsum	21.0-43.3	Presence of amorphous content affected the reactivity of samples.
Winburn (1999) [17]	combustion by-products	Quartz, mullite, hematite, periclase	68.6, 71.1	Smaller particle sizes increased the accuracy of amorphous content

4. CONCLUSIONS

The methods discussed above are capable of determining the amorphous contents in the sample. The benefits and limitations for the analytical methods should be considered when choosing a suitable method for a given sample (as summarized in Table 3). When the intensity contributions of the amorphous phases to the whole diffraction pattern are not clear, the indirect method, such as external or internal standard method should be used. If the calibration standards and samples contain amorphous material, the accuracy will decrease. This also works for the materials with perfect crystalline.

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