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Abstract

X-ray diffraction (XRD) is a prominent technique to characterise cement-based materials. The combination of the Rietveld refinement with the Partial Or No Known Crystal Structure (PONKCS) approach now enables the quantification of both crystalline phases and amorphous contribution of SCMs. This paper describes the application of Rietveld-PONKCS to determine the amount of reacted glass powder (GP) in blended cement pastes. The accuracy and precision of the method were compared to the results of independent methods such as selective acid dissolution, thermogravimetric analysis (TGA) combined to energy-dispersive spectroscopy (EDS) or inductively coupled plasma (ICP) applied to GP-lime mixtures. For blended cement, the consistency of the method was internally checked using the standard addition method. Overall, an average precision of 1.6 wt.% and accuracy better than 1.5 wt.% were found for Rietveld-PONKCS applied to GP containing systems.

Keywords

X-ray diffraction, PONKCS, amorphous supplementary cementitious materials, soda-lime glass powder, blended cement

1. Introduction

Contributing to the efficient use of natural resources, the cement industry provides an added-value recovery option for various wastes and industrial by-products (e.g. thermal power plant fly ashes or post-consumption glass powder). Theses supplementary cementitious materials

(SCMs) are usually high-potential reactive materials used as an addition or in substitution to cement [1]. Their reaction mechanisms occur in synergy with the cement hydration and induce changes in the amounts and the types of the formed hydrates, the porous network, and therefore the durability of the concrete [1–5]. However, the use of novel pozzolanic SCMs is rather restricted to low substitution rates due to the challenges in understanding their reactivity in blended cementitious systems [1,6]. Therefore, further increase in SCMs dosages is closely linked to the development of techniques that accurately quantify their reactivity and their impact on the phase assemblage in the cementitious matrix [6]. In this context, different methods have been employed to assess the extent of SCMs' reaction. Nevertheless, most methods are subject to limitations and cannot be relevant for all SCMs currently available and under development. Direct and indirect methods for the determination of the SCMs hydration degree have been reviewed by several authors (e.g. RILEM TC 238-SCM committee) [7–9]:

- The selective dissolution approach has been by far the most reported in the literature over the past decades [10–15]. This method consists fundamentally of a preferential acid dissolution of the cement and hydrates while keeping the unreacted SCM particles intact. However, the application of this method has been associated with important uncertainties and showed considerable discrepancies with other methods [6,8,14,16]. These non-quantifiable errors are mainly related to the incomplete dissolution of the clinker and its hydrates and/or the partial dissolution of the SCMs [7,14,16].
- Backscattered electron image analysis (SEM-IA) is restricted by the resolution limit of the SEM to particles with a size greater than ~2 µm. Therefore, in addition to being time-consuming, this approach is irrelevant to fine materials such as silica fume or metakaolin [6,9,16].
- Different portlandite consumption approaches have been developed as indirect methods to estimate the pozzolanic reaction of SCMs in cement pastes. The stoichiometric amount of SCM required to react can be retrieved using the portlandite consumed (measured by thermogravimetric analysis) and the Ca/Si ratio of the C-S-H (often measured by EDS). However, this approach is sensitive to even relatively small errors in the measurement of portlandite content or Ca/Si ratio, and might lead to large uncertainties [8].

- Nuclear magnetic resonance (^{27}Al and ^{29}Si) spectroscopy is one of the direct methods that can be used with good accuracy. However, in addition to being time demanding, the NMR equipment is not readily available [17].
- Additionally, other indirect methods (such as calorimetry, chemical shrinkage, and bound water) are also commonly used to assess the reacted amounts of SCMs. Nonetheless, the translation of the results of these methods in terms of degree of hydration is still an outstanding issue [18,19].

The analysis of X-ray diffraction (XRD) patterns is another prominent technique in the characterisation of crystalline phases. Due to the ease and speed of the measurement, this technique has been applied to cement based materials [20–25]. Moreover, given the robustness of today's computation tools, the full-pattern Rietveld [26] quantification method can reliably deal with complex diffraction patterns with strong overlapping peaks. However, the Rietveld method can only be applied to crystalline phases with known structures. Therefore, other techniques are commonly combined with Rietveld refinement in order to determine the amount of amorphous/unidentified phases, such as the internal standard method or the external standard method (G-factor method) [27–29]. These approaches can determine the total content of amorphous phases but fail to distinguish the contributions of each amorphous material. For this purpose, Scarlett and Madson [30] have developed a direct approach for quantitatively analysing phases with "Partial Or No Known Crystal Structure" (PONKCS). This approach can be used for the quantification of amorphous phases, which are then defined as a "set of related peaks". Recently, the PONKCS method has been successfully adopted to measure the reaction's degree of supplementary cementitious materials in blended cement, since they are predominately amorphous [6–8,31–33].

Though the use of this method for conventional SCMs has been previously assessed [6–9,33,34], further work is required for the application the Rietveld-PONKCS approach to quantify the degree of reaction of alternative cementitious materials, such as Glass Powder (GP). GP is obtained by micronizing post-consumption soda-lime glass bottles and its use in concrete offers a viable opportunity to answer the current demand of highly sustainable concrete [5,35,36]. The predominant amorphous phase, mainly composed of silica, provides the required components to exhibit high pozzolanic properties. Therefore, an optimal industrial use of GP depends on improving the understanding of its reaction in blended-cement systems. In this respect, the present study explores the reliability and precision of Rietveld-PONKCS method for the quantification of glass powder (GP) degree of reaction in

binary systems. Moreover, the results of this XRD-based technique are compared to other independent methods such as selective acid dissolution and portlandite consumption. The consistency of the PONKCS measurements is verified first on synthetic systems consisting of portlandite and glass powder pastes, and then on cement pastes in order to test the relevance of this technique compared to the widespread methods.

2. Materials and methods

2.1 Materials and sample preparation

The study focuses on the measurement of the degree of reaction of post-consumption soda-lime glass powder, as a supplementary cementitious material (SCM). The hydration of GP was investigated within Portlandite pastes ($Ca(OH)_2$, also known as CH) and commercially available Ordinary Portland Cement (OPC) pastes. Table 1 presents chemical and mineral compositions of the raw materials, as obtained by X-ray Fluorescence and X-ray Diffraction with Rietveld quantification. Table 2 shows the physical properties obtained by laser granulometry, pycnometry, Blaine, and nitrogen adsorption tests. The Mass Absorption Coefficients (MAC, also μ) were calculated from chemical compositions and the international tables of crystallography for CuKα radiation [37], with the Loss of Ignition (LOI) attributed to water.

Table 1. Chemical and mineral compositions of used materials

	SiO_2	CaO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	P_2O_5	SO_3	MgO	TiO_2	LOI*	MAC
CH	--	73.98			—			0.07	0.11		25.79	93.55
GP	71.11	10.04	1.81	0.36	13.06	0.56	0.02	0.14	1.21	0.06	1.79	44.89
OPC	19.52	60.57	4.41	2.63	0.31	0.90	0.89	4.01	2.84	0.21	2.74	93.91

* Loss on ignition at 1000°C

	C_3S	C_2S	C_3A	C_4AF	CH	Calcite	Quartz	Gypsum	Bassanite	Periclase	Amorphous*
CH					95.1	0.8	—				4.1
GP					—	0.5	0.7				98.9
OPC	52.1	11.5	4.3	8.6	—	3.3	0.3	3.4	2.6	0.6	12.8

* Amorphous or/and unidentified obtained using external standard

Table 2. Physical properties of used materials measured by laser granulometry, pycnometry, Blaine and BET tests.

	D_{50} (μm)	Density	Blaine (m^2/kg)	BET (m^2/g)
CH	5.3	2.23	—	—

GP	10.2	2.54	593	0.70
OPC	16.3	3.11	395	1.26

Pastes of glass powder and $Ca(OH)_2$ were prepared with a propeller mixer (2 min, 2000 rpm) under nitrogen atmosphere, with GP:CH mass ratios of 1:3, 1:1, and 3:1. The water-to-binder (w/b) mass ratio was fixed to 0.75 to obtain a sufficient workability. The samples were cast into sealed containers and preserved in a desiccator until testing ages of 7, 14, 28, 56, and 91 days. Before each test, the samples were ground to an average diameter of d_{50}=40 µm, and the hydration was stopped using two solvent exchanges (isopropanol and diethyl ether). The solvents were removed first by filtration and then by vacuum drying. On the other hand, three sets of cement pastes were prepared with partial substitution (wt.%) of Portland cement (OPC) by glass powder at different rates: the system OPC with 100% Portland cement, the system 10GP with 10% of glass powder (90% OPC) and the system 20GP (80% OPC+20% GP), as reported in Table 3. The cement pastes were prepared with a w/b mass ratio of 0.485 using a high-shear mixer. The same conservation and hydration stoppage procedures, used for CH mixtures, were applied to GP-OPC systems.

Table 3. Mix design for CH and OPC pastes

$Ca(OH)_2$ mixes	GP:CH ratio	W/B	Cement pastes	GP:OPC ratio	W/B
25GP	25:75	0.75	OPC	0:100	0.485
50GP	50:50	0.75	10GP	10:90	0.485
75GP	75:25	0.75	20GP	20:80	0.485

2.2 Thermogravimetry

Thermogravimetric analyses (TGA) were conducted using a TA instrument SDT Q600. The analysis was run with ~50 mg samples over a temperature range of 30–1000°C with a heating rate of 20°C/min. N_2 was used as a purging gas at a rate of 50mL/min. TGA investigations allowed the determination of bound water and the mass loss corresponding to the portlandite decomposition. The bound water content was used to normalise the initial content of reactants and calculate the MAC of hydrated samples, which was necessary for the quantification of XRD patterns using the external standard method.

2.3 Selective acid dissolution and ICP-AES

Selective dissolution was used to determine the amount of unreacted GP in hydrated samples. The method was first carried out on anhydrous (raw) materials to test the effectiveness of the technique and to measure their dissolution. The values of the insoluble residues (97.9% for GP and 0.1% for CH) were used later to correct the unreacted GP measured in hydrated mixes. The dissolution was performed as follows: 1g (±0.0005g) of sample after hydration stoppage was placed in a beaker with 3 ml of HNO_3 and 97 ml of distilled water. The acid attack was continued for 30 min under continuous stirring. In order to determine the residue, the solution was first filtered using a 0.7-1 μm ashless filter paper, the residue with the filter was placed in a crucible, put in a furnace at 1000°C and then weighed.

On the other hand, the filtrate (100 ml) was diluted with distilled water to reach 1 L and analysed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The concentrations of silicon, sodium and calcium elements were quantified using an ULTIMA 2000 ICP-AES (Jobin Yvon Horiba).

2.4 X-ray diffraction data collection

A PANalytical X'pert Pro MRD diffractometer was used to acquire the X-ray powder diffraction patterns at 50 mA and 40 kV. Measurements were performed on flat surfaces of back-loaded samples with a Bragg-Brentano (θ-2θ) geometry, using Soller slits of 0.04 rad, incident divergence and anti-scatter slits of 0.5°. A PIXcel 1D detector with an active length of 3.347 °2θ was used for the data collection. The acquisition was performed over an angular range of 5 to 70°2θ with a step size of 0.0263°2θ and a counting time of 176 s (i.e. 720 ms/step), resulting in a time of 30 min per scan. During the scans, the samples were spun at 8 rpm around the vertical goniometer axis to improve particle statistics. A corundum powder (α-Al_2O3) was used as an internal and external standard (Alfa Aesar, crystallinity calibrated to 98.2% using the NIST SRM676a standard). The standard was frequently tested to consider the attenuation of the X-ray tube intensity.

2.5 Quantitative XRD analysis

The XRD experimental patterns were modelled using Xpert HighScore Plus 4.7a from PANalytical. The approach used for the profile fitting can be divided into three key steps, as proposed by Stetsko et al. [32]:

a) Traditional Rietveld with only the crystalline phases

In this step, a high order Chebyshev polynomial background (a 6^{th} order in this study) is required to exclude all the amorphous content from the calculation. During the refinement,

some parameters were subject to restrictions to avoid an unrealistic fit with aberrant values for the crystal parameters. Therefore, the lattice parameters variation was limited to a range of 1% and the Full Width at Half-Maximum (FWHM) to a range of 0.0001–0.2. The peak shape and the preferential orientation parameters were adjusted iteratively on raw materials only when necessary (i.e. in the case of a high weighted profile residue or a high goodness of fit) and then kept constant for the rest of the analysis. Following the refinement, the scale factors and cell volumes were used to estimate the absolute weight fraction of each phase using the external standard method (Eq. 1). The mass attenuation coefficient (MAC, μ) for each sample was derived from XRF chemical composition for anhydrous samples, and by a combination of XRF and TGA for hydrated samples.

$$w_\alpha = \frac{S_\alpha . (ZMV)_\alpha}{S_{ES} . (ZMV)_{ES}} \frac{\mu_{sample}}{\mu_{ES}} w_{ES,crist} \quad (1)$$

$$w_{amorphous} = 1 - \sum_{\alpha}^{np} w_\alpha \quad (2)$$

Where:

w_α : Weight fraction of phase α

$w_{amorphoi}$: Weight fraction of the total amorphous content

$S_{\alpha,ES}$: Refined scale factor of phase α, or of external standard (ES)

Z, M, V : Number of formula units per unit cell, the mass of the formula unit and the unit cell volume

$\mu_{sample,ES}$: Mass absorption coefficient of phase α (or ES)

$w_{ES,crist}$: Crystallinity of the external standard

np : Number of phases included in the calculation

b) Definition and calibration of the PONKCS pseudo-structure

The use of a PONKCS phase allows the quantification of a specific amorphous material (e.g. SCMs), by fitting a pseudo-structure to the amorphous contribution of the material to the

XRD pattern (see Fig 1). The pseudo-phase can be defined using an existing "hkl phase" with partial structure information or a newly defined set of related peaks with no structure information [30]. It is also worth mentioning that the amorphous hump can be fitted easily with a variety of space groups. Another parameter affecting the accuracy of the PONKCS phase quantification is the choice of the background. Different choices of the background have been reported in the literature. Madsen et al. [38] used a third order Chebyshev polynomial with a 1/2θ parameter, while Snelling et al. [6] reported that a first order Chebyshev polynomial with a 1/2θ parameter gives the best fit. On the other hand, Stetsko et al. [32] recommended the use of a first-order polynomial background. Otherwise, the background can also be fitted manually, but this will alter the inter-laboratory reproducibility of the method since it depends mainly on the user's judgement.

In this study, the glass powder was defined as a single phase using a set of pseudo-Voigt peaks while the C-S-H was modelled using an "hkl file" based on Tobermorite 14 Å crystal structure [39]. The diffuse scattering signals of amorphous phases were then refined using the Pawley curve fitting algorithm on a 100% anhydrous GP sample for glass powder (see Fig. 1) and a 180 days hydrated sample of silica fume and portlandite (ratio of 1 to 3) for C-S-H. In this study, a first-degree polynomial background with a 1/2θ parameter produced the most reliable fit when using the PONKCS phases. Therefore, this type of background was adopted for all analyses, i.e., for both raw materials and hydrated samples.

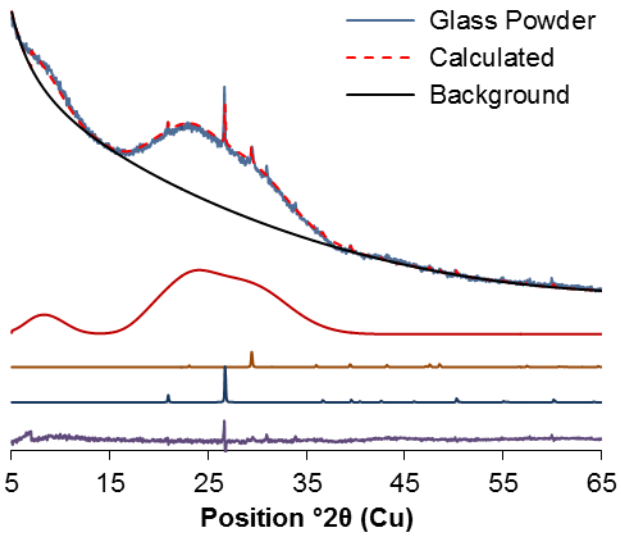

Fig. 1. Decomposition of a pure glass powder XRD pattern

After the definition of the PONKCS phase, the quantification required the calibration of the pseudo-phase. Therefore, the "ZMV constant" was determined by the internal standard method (Eq. 3) using a 50:50 reference mix of the glass powder and the highly crystalline corundum. It is worth mentioning that the ZM and V values have no physical meaning; they represent an empirical definition of the pseudo-phase for use in the Rietveld refinement.

$$\frac{W_\alpha}{W_{\text{strd}}} = \frac{S_\alpha (ZMV)_\alpha}{S_{\text{strd}} (ZMV)_{\text{strd}}} \quad \textbf{(3)}$$

On the other hand, the C-S-H weight percent in the hydrated samples was determined by difference using the external standard method (instead of a calibration constant for the C-S-H PONKCS phase). This approach was preferred to account for the expected variation of C-S-H composition over the hydration time.

c) Insertion of the calibrated PONKCS phase in the refinement

With the ZMV constant, all the parameters needed to quantify the PONKCS phase are available. The new phase can then be implemented in the Rietveld refinement of an unknown sample, and its weight percentage is calculated based on the defined ZMV constant and its refined scale factor. During the refinement with the PONKCS phase, the refined parameters obtained for the crystalline phases in "step a" were kept constant, while only the background was changed to a polynomial with a 1/2θ parameter and the PONKCS phase was included in the refinement. In the second iteration, all the scale factors were refined simultaneously.

2.6 SEM-EDS (QEDS)

The scanning electron microscopy was carried out with a Hitachi S-3400 N SEM equipped with an Oxford Inca Energy 250 energy-dispersive spectrometer (EDS). The hydration was stopped by solvent exchange in isopropanol, which allowed the removal of free water. The samples were coarsely ground and mixed in a fast-setting epoxy resin. Once the resin has hardened, the specimens were planarized using a 600 grit SiC paper then polished using a perforated cloth with 3 µm and 1 µm diamond suspensions with isopropanol as a lubricant. Before the analysis, the samples were degassed under vacuum for 2h and coated with about 15 nm of carbon to avoid surface charging during SEM analysis. The observations were performed with a magnification of 400× and an accelerating voltage of 15 kV, allowing the analysis over a region of interest of 300 µm × 240 µm.

The chemistry of around 700 micro-volume was investigated using an energy-dispersive X-ray spectroscopy (EDS) point analysis. A counting time of 20 s per spot was employed to

obtain quantifiable and high quality spectra. Afterwards, the quantitative analyses (QEDS) were achieved by post-processing the EDS spectra with the NIST software DTSA-II and using synthetic standards to calibrate the quantification (pure C_2S for *Ca* and *Si*, pure C_3A for *Al*, olivine for *Mg* and *Fe*, anhydrite for *S*, orthoclase for *K*, tugtupite for *Na* and *Cl*, and sphene for *Ti*). Finally, invalid measurements due to micro-cracked products and local charging were eliminated based on the Duane-Hunt limit.

3. Results

3.1 Calibration of the PONKCS method for GP

The repeatability (95% confidence interval) and the accuracy (i.e. bias between the PONKCS measures and the true weighed values) of the developed quantification method were first evaluated on simple anhydrous binary systems. Homogenised mixes of varying proportions of GP and corundum/portlandite were prepared to calibrate the pseudo-phase (see table 4). Triplicate measurements were done on arbitrary samples, prepared separately with the same composition, to assess the error related to the sample preparation (i.e. repeatability of the measurement). The decomposition of the calculated patterns, showing the contribution of each phase, is illustrated in Fig 2.

Table 4. Composition of the anhydrous systems employed to assess the accuracy and precision of the PONKCS method applied to GP.

Dry samples	GP	CH	Corundum
10GP90Corr (x3)	10		90
20GP80Corr (x3)	20		80
30GP70Corr	30		70
50GP50Corr (x3)	50		50
70GP30Corr	70		30
90GP10Corr (x2)	90		10
25GP75CH	25	75	
50GP50CH (x3)	50	50	
75GP25CH	75	25	

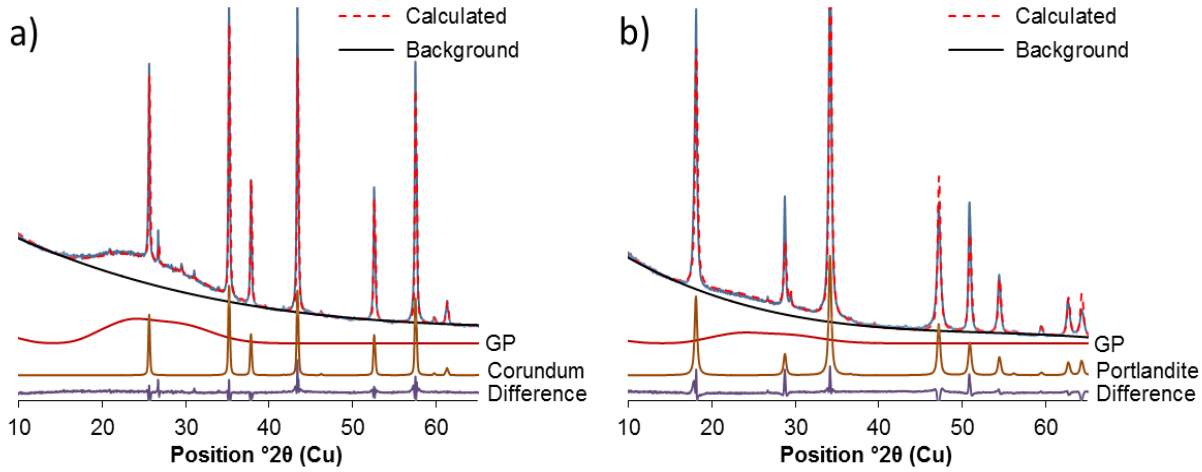

Fig. 2. XRD pattern decomposition of preblended anhydrous samples: a) 50GP50Corr and b) 25GP75CH. The experimental and calculated patterns are shown respectively in blue and dashed-red lines.

For the mixes performed in triplicate, the results showed a 2σ repeatability of 0.65% on average, without exceeding 0.93%. Moreover, the average measured-weighed bias was 0.9 wt.% (max 1.5 wt.%). Considering that the sample homogenisation may be more limiting than the XRD analysis procedure itself [6], it can be concluded that the method shows a high precision and a high accuracy in the quantification of GP in anhydrous mixes (within 1.5% of the weighed amount of SCM). The correlation between the measured and weighed amounts of GP is shown in Fig 3.

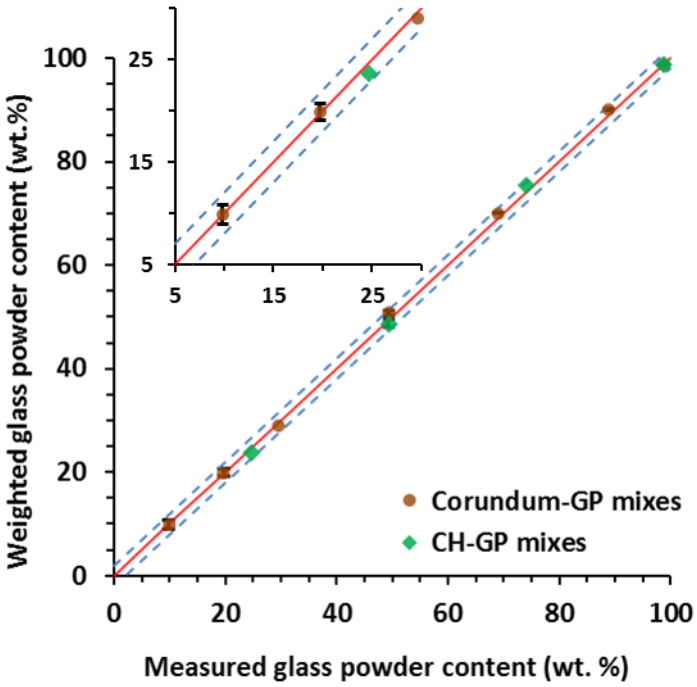

Fig. 3. Correlation between the weighed and measured glass powder content (wt. %) in the simulated anhydrous mixes with corundum and portlandite. The red line shows the 1:1 correlation while the dashed blue lines represent a tolerance interval of +/- 2 wt. %. The error bars describe the repeatability of the measurement.

3.2 Assessment of the PONKCS reliability in hydrated systems with GP

The hydration of cement leads to the formation of amorphous products, mainly C-S-H. This adds a level of complexity to quantitative analysis of the degree of reaction of SCMs due to the potential overlap between the SCMs and C-S-H amorphous humps. To address this issue, the Rietveld-PONKCS method was tested for different blended systems of increasing complexity: first, for hydrated mixes of GP and portlandite simulating the pozzolanic reaction (with 25, 50 and 75% GP), and then for blended cement pastes with 10% and 20% GP replacements to analyse the reactivity of the glass powder in cementitious matrices. As an example, Fig. 4 depicts the deconvolution of XRD patterns of hydrated GP-CH systems after 28 days of hydration. An increase of residual amorphous GP in increasing initial GP content is clearly shown in Fig. 4 and the results are further discussed in the next subsections, along with results of other independent methods used to cross-check the Rietveld-PONKCS analyses.

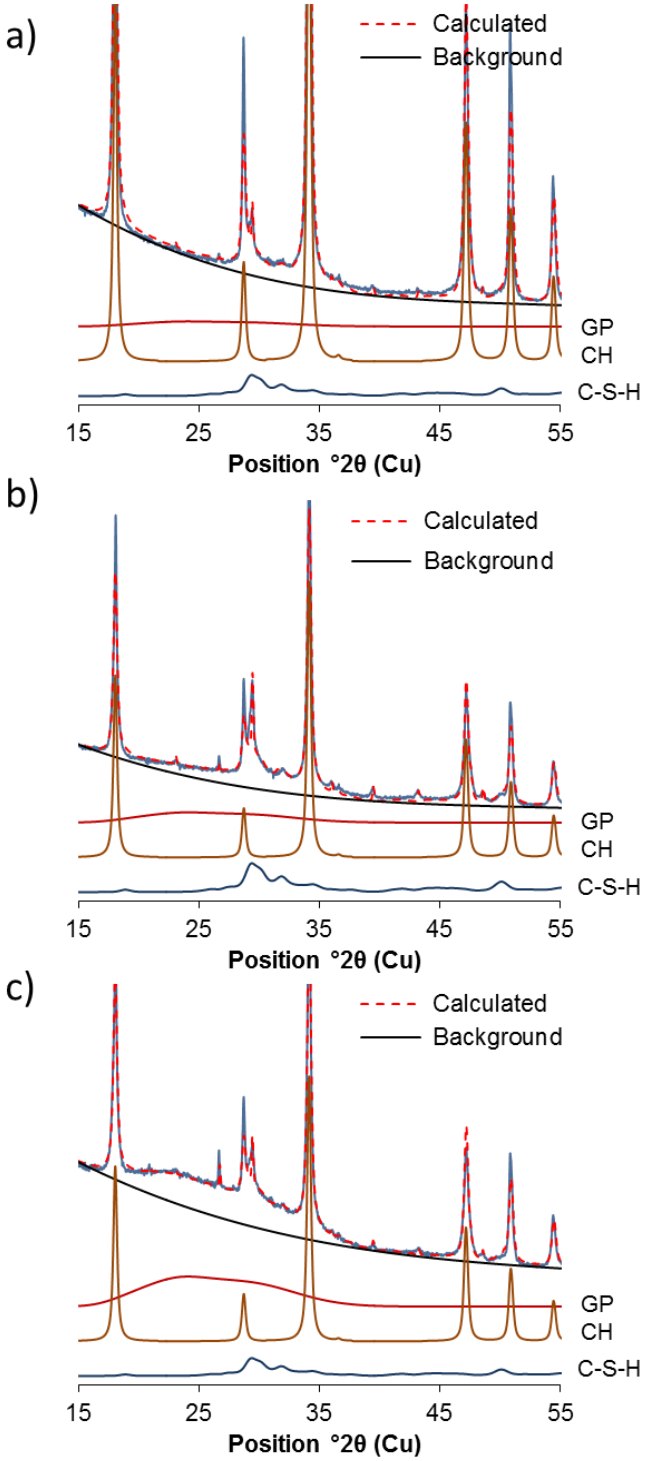

Fig. 4. XRD pattern decomposition of 28-day hydrated GP-CH systems: a) 25GP and b) 50GP and c) 75GP.

3.2.1 Comparison of independent methods for the quantification of GP in synthetic systems

a) Direct methods for the quantification of unreacted GP

The Rietveld-PONKCS method was first applied to simple hydrated mixes of GP and portlandite, and the extent of reaction of GP was determined at 7, 14, 28, 56, and 91 days. The degree of reaction of GP, normalised to the initial amount in the mix (i.e., corrected with the

bound water), was compared in Fig 5 with the results of the insoluble residue after acid dissolution. Overall, the two methods show very comparable results, with an average difference of the unreacted GP content of 0.7 wt.% (max 2.1 wt.%).

It is worth mentioning that due to the variation of GP content in the mixes, a variation in the hydrate composition is also expected. However, the aim of this paper is the quantification of the degree of reaction of GP, whereas the hydration products are further discussed in [40].

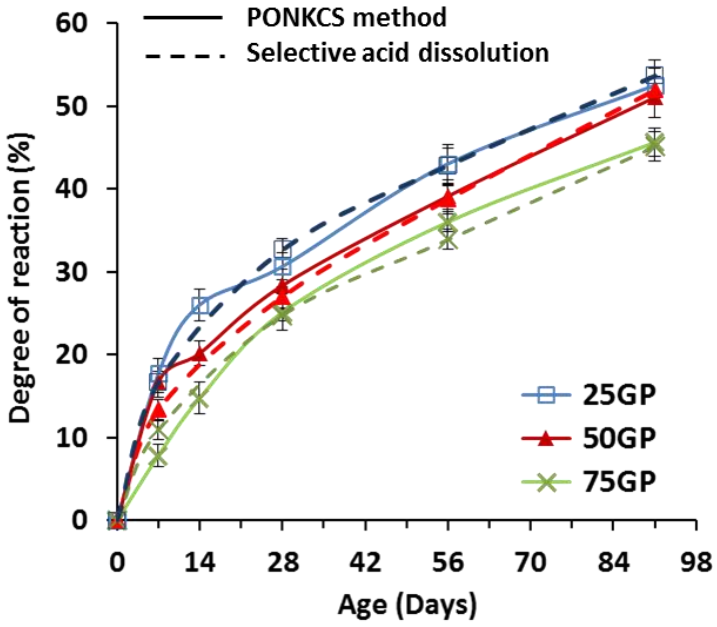

Fig. 5. Comparison of the degree of reaction of GP measured by Rietveld-PONKCS and by acid dissolution methods. The error bars show ranges of measurements.

b) Indirect methods and mass balance analyses

The amount of reacted SCMs can also be obtained indirectly based on the consumed portlandite (often measured by TGA) and the composition of the formed hydrates. The degree of reaction of SCMs is then calculated based on the amount of silica required to react with portlandite to reach the measured Ca/Si of the C-S-H. This method assumes that the totality of the dissolved silica from the SCM reacts with portlandite to form C-S-H. In the case of simple CH-GP systems, this assumption is realistic and therefore the degree of reaction (i.e. the reacted amount) of GP can be retrieved using equation 4.

$$\alpha_{GP} = \frac{W_{CH\ consumed,TGA}\ \frac{w_{CaO,CH}}{M_{CaO}}}{\left(Ca/Si_{CSH} - \frac{w_{CaO,GP}}{w_{SiO2,GP}}\ \frac{M_{SiO2}}{M_{CaO}}\right).f.\frac{w_{SiO2,GP}}{M_{SiO2}}} \quad (4)$$

With:

α_{GP} : Degree of hydration

$W_{CH\ consumed,TGA}$: Weight of consumed CH

$w_{oxide,material}$: Weight percentage of oxide (CaO, SiO_2) in material (CH, GP)

M_{oxide} : Molar mass of oxide

f : Mass fraction of SCM = (1-$w_{bound\ water,TGA}$)*initial ratio in dry blend

$w_{bound\ water,TGA}$: Bound water calculated using TGA

Therefore, in the opposite of cement blends where the stoichiometry of SCM reaction is usually assumed due to the complexity of the system [8], the composition of the hydrates in synthetic mixes of GP and CH can be determined correctly. In this aim, two independent methods were employed at the ages of 28, 56, and 91 days of hydration.

First, the composition of the hydrates was determined with EDS by investigating the chemistry of approximately 700 points per sample. Statistical analyses (multivariate Gaussian mixture modelling) were then carried, according to the method proposed by Wilson et al.[41–43], to isolate a cluster of hydration products and determine its mean composition (*Si/Ca*; *Si/Na*; *Si*/(*Ca*+*Na*); *SOX*) and covariance matrix, as shown in Fig 6.

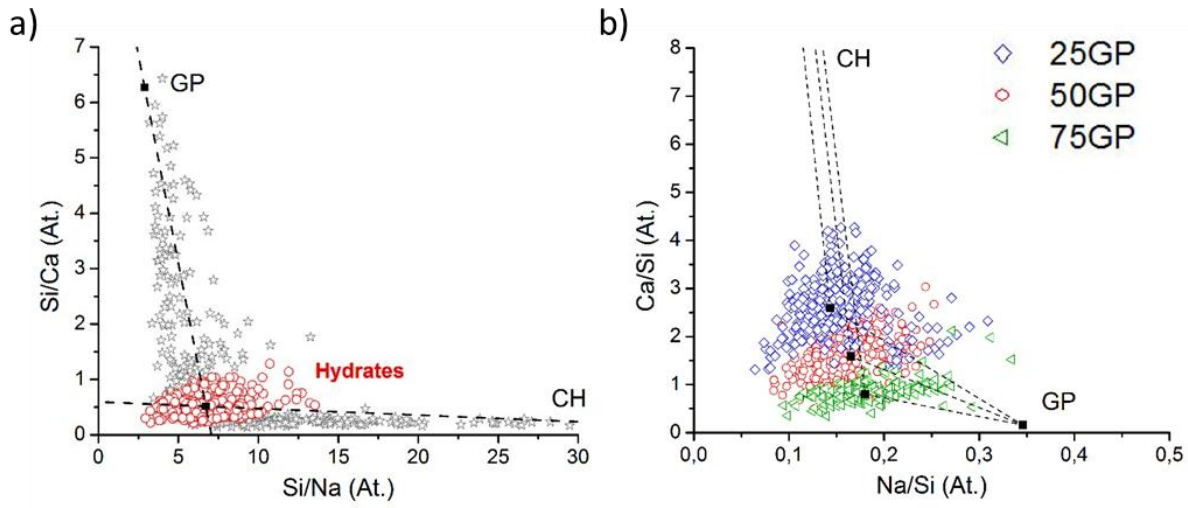

Fig. 6. Results of the statistical clustering: a) an example result of the deconvolution method adopted to separate the cluster associated to the hydrates, b) the hydrate clusters for the three systems CH-GP after 91 days of hydration.

Secondly, the filtrates after the acid dissolution were diluted to reach 1 L then analysed using ICP to measure the amounts of Si and Ca. Knowing that the GP remains undissolved after the acid attack, the elements in the solution are mainly provided by the dissolution of the reaction products and the unreacted calcium hydroxide. Therefore, using the results of the TGA to take into account the amount of unreacted CH, the average composition of the product can be determined. These techniques will be, respectively, referred to as TGA/QEDS and TGA/ICP. Fig. 7 displays the evolution of unreacted GP content in each system as a function of time obtained by the studied techniques.

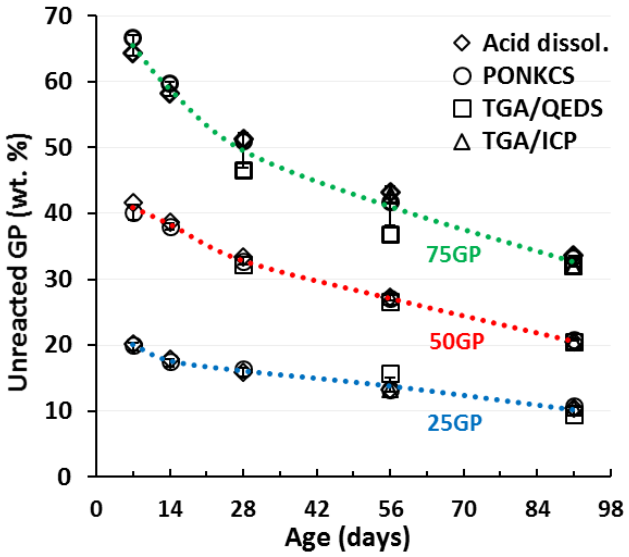

Fig. 7. Comparison of the unreacted amount of GP determined by acid dissolution, Rietveld-PONKCS and indirectly using TGA/QEDS and TGA/ICP. Dotted lines and error bars show the mean value and the standard deviation of the four methods.

c) Precision and accuracy of the PONKCS method

The accuracy of PONKCS method was assessed by comparing its results to the global mean of the four methods (since the real amount of unreacted GP is not known), while the precision was evaluated by calculating the standard deviation (2σ or 95% confidence interval). As shown in Fig. 8, a level of precision (2σ) of 1.2 wt.% and a measurement accuracy of 0.5 wt.% in average (max 1.4 wt.%) were found for the unreacted amount of GP in the hydrated GP-CH systems. It was also observed that the accuracy of the PONKCS method tends to decrease when the mixes contain high amounts of GP. Overall, the Rietveld-PONKCS method provided the most consistent results among the studied methods while the TGA/QEDS showed the largest disparities. This might be related to accumulation of errors,

since relatively small errors in the determination of the reacted CH content (TGA) can lead to significant changes in the unreacted amount of GP. Furthermore, the accurate determination of the composition of hydration products (i.e., the average Ca/Si ratio) can be a difficult task due to the variability and heterogeneity of the systems.

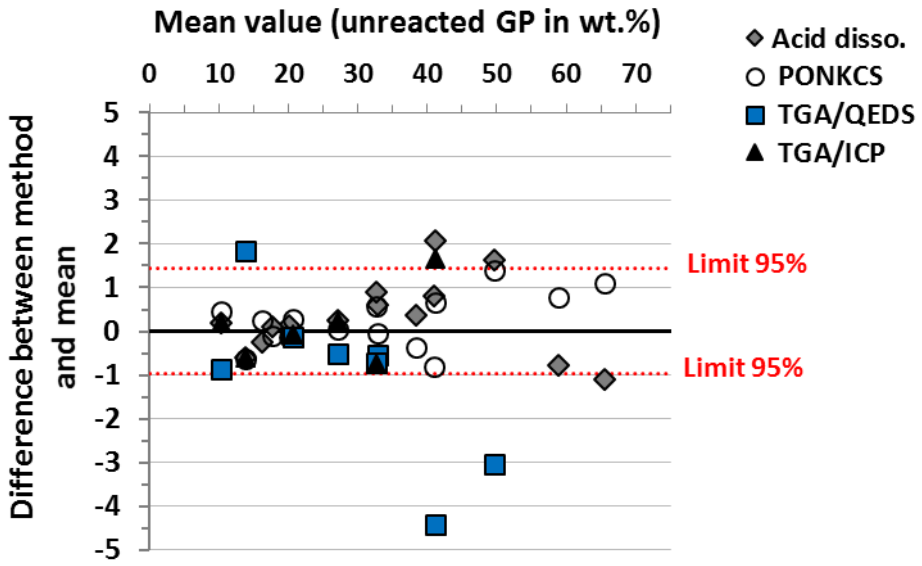

Fig. 8. Scatter plot of the difference between the measured unreacted amounts of GP and the mean value of the methods, as function of the mean value. Dotted red lines represent the 95% confidence interval for the unreacted amount of GP determined using the PONKCS method.

d) Sensitivity analysis and propagation of uncertainties

The PONKCS and acid dissolution methods allow direct quantification of the unreacted GP content, whereas the other two approaches involve a combination of methods. Thus, even small experimental errors (e.g. on the Ca/Si ratio of the C-S-H and/or the unreacted GP content) could lead to higher discrepancies on the degree of hydration, especially when the initial GP content is low. As shown in Fig. 9, direct methods for the measurement of the degree of reaction of GP (e.g. acid dissolution, Rietveld-PONKCS) provided the most consistent results while the indirect method showed relatively larger uncertainties. For the Rietveld-PONKCS method, an average precision of 3.8% and an accuracy of 1.7% (max 3.4%) were found for the measurement of the degree of reaction. On the other hand, the error of TGA/QEDS on the measurement of the degree of reaction of GP was assessed to 6.6% (max 13.3%). In this case, the combined small errors on TGA and/or QEDS measurements have higher impact on the degree of reaction of SCMs.

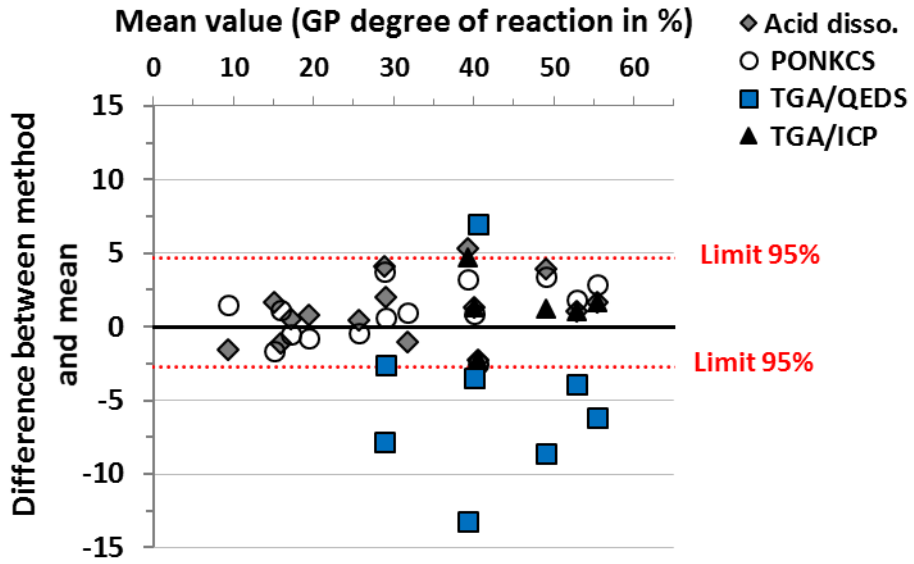

Fig. 9. Scatter plot of the difference between the GP degree of reaction and the mean value of the methods as function of the mean value. Dotted red lines represent the 95% confidence interval for degree of reaction of GP determined using the PONKCS method.

Following the determination of the degree of reaction of GP using Rietveld-PONKCS and acid dissolution, equation. 4 was used to back calculate the Ca/Si ratio of the C-S-H using the reacted amount of portlandite (TGA). Afterwards, the Ca/Si ratio of the products, obtained by these indirect methods, is compared to the results of direct measurements (QEDS and ICP). The results, shown in fig. 10, highlight the sensitivity of the degree of reaction to even small variations in the measured Ca/Si ratio. An average error of 0.21 on the Ca/Si ratio of products was assessed for the Rietveld-PONKCS approach. Also, it should be noted that the characterisation of the silica-rich rims, which appears around hydrating GP particles [35,40], is a limiting parameter for the accurate measurement of the Ca/Si ratio of the products using the EDS point analysis. This might explain the differences with the other techniques.

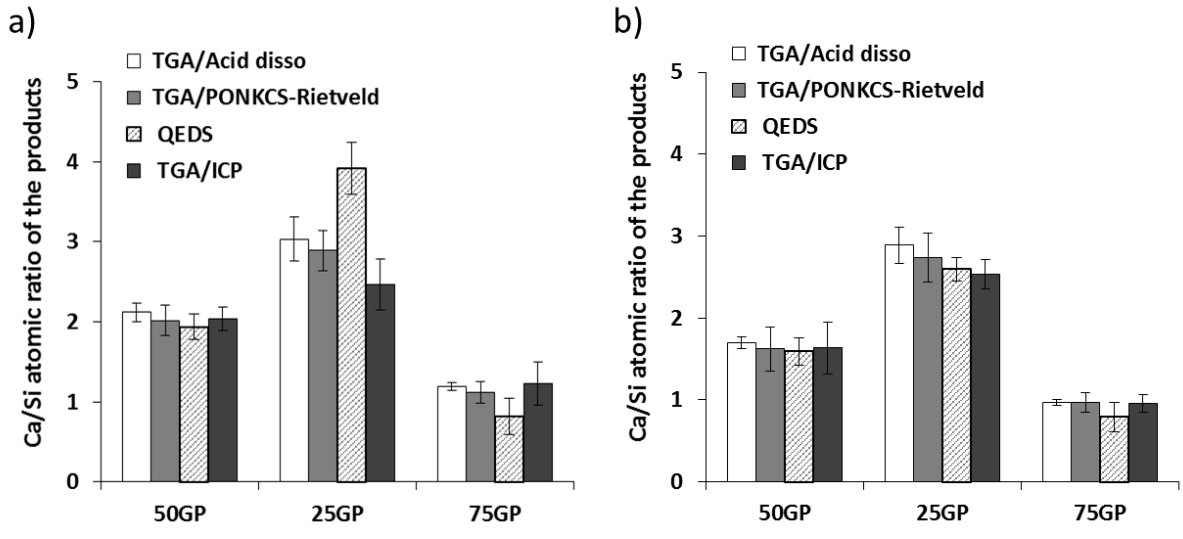

Fig. 10. Comparison of the Ca/Si ratios obtained by the different methods at (a) 56 and (b) 91 days of hydration for the studied systems.

3.3 Application to OPC-GP systems

3.3.1 Hydrated blended-cement paste with 20% GP replacement

The combination of the Rietveld-PONKCS and the external standard method can provide a wealth of information concerning the hydrates assemblage in blended cement pastes. In fact, the changes in the phase composition of the blended cementitious matrix, due to the reactivity of amorphous SCMs, can be retrieved, both qualitatively and quantitatively (± 1–3 wt.%). Fig. 11 illustrates the time resolved evolution of the hydrate phase assemblage formed in the system 20GP (in wt.%). It should be noted that the term "amorphous" in Fig. 11 refers to poorly crystalline hydrates (e.g. C-S-H, Fe-containing siliceous hydrogarnet, AFm, hydrotalcite-like phase), which cannot be discerned individually on the XRD patterns. Overall, the results show a slow hydration kinetics of GP, with ≈50 wt.% residual unreacted GP at 300 days (only ≈5% has reacted after 1 day). On the other hand, more than 90% of the cement clinker has reacted to form C-S-H, portlandite and ettringite, as the main hydration products. The plausibility of the quantified GP reactivity is assessed subsequently using the standard addition method.

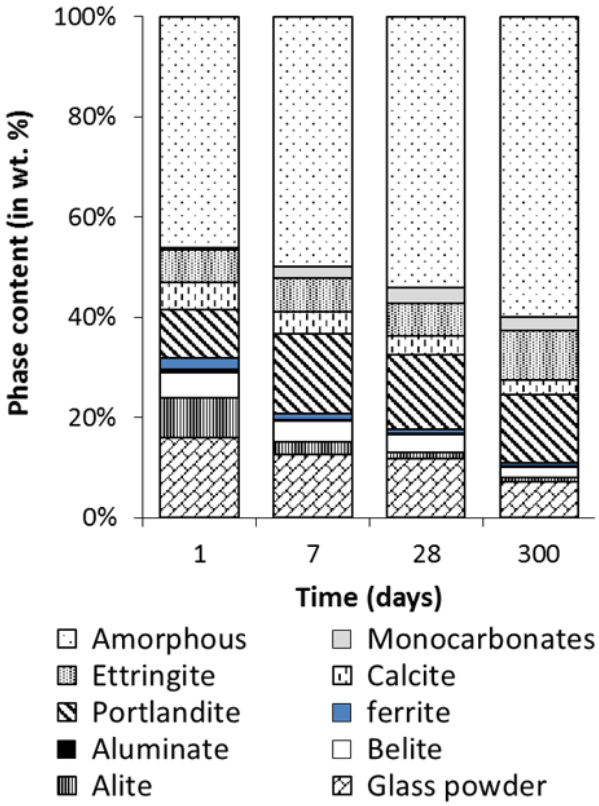

Fig. 11. Evolution of the phase assemblage in hydrating blended cement paste consisting of 80% OPC and 20% GP as a function of time. The amount of reacted GP is quantified using the PONKCS methods while the amorphous phase (which includes C-S-H, Fe-containing siliceous hydrogarnet, AFm, hydrotalcite-like phase) was determined using the external standard method.

3.3.2 Accuracy of the quantification of GP in cement pastes

For the hydrated blended cement, the accuracy of the method of PONKCS was assessed with the standard-addition method, i.e., by measuring the total GP content in mixtures of 182-day hydrated systems (OPC, 10GP and 20GP) with additional 20 and 40 wt.% glass powder. The positive value for the extrapolate intercept with the x-axis of the systems with additions thus provides an estimation of the GP in the original sample [6]. As shown in Fig. 12, the intercepts compare very well with the GP content directly measured by Rietveld-PONKCS, with a difference of 0.4 wt% on average and 0.5 wt.% at maximum. These differences are much smaller than the precision range (i.e. 95% confidence interval) of the method that was assessed to 1.6 wt.% on average (max 3.4 wt.%), using independent replicates.

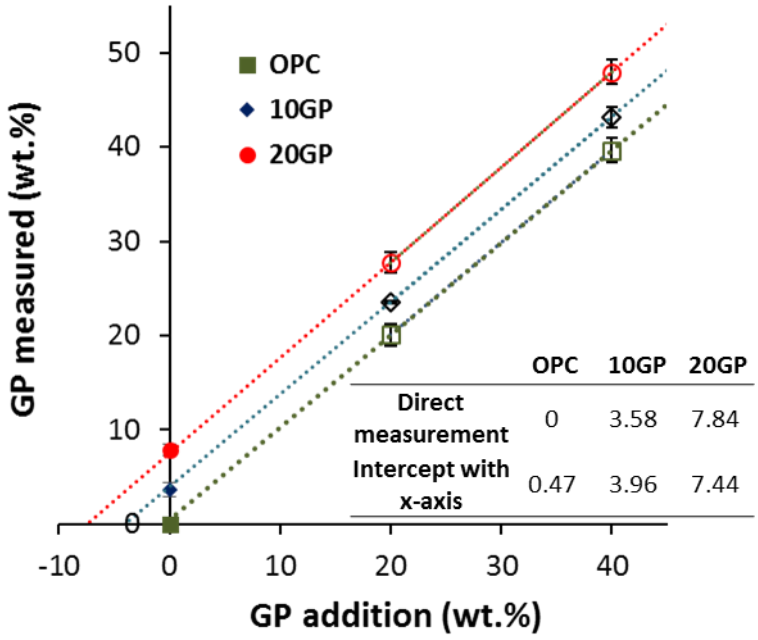

Fig. 12. Measured amount of GP using Rietveld-PONKCS method as a function of the additional GP mixed with ground samples of 182 days hydrated blended systems (OPC, 10GP and 20GP). The error bars show the repeatability of the measurement while the positive value for the intercept with the x-axis gives an estimation of the GP content in the original samples.

4. Discussion

This paper presents an assessment of the accuracy and precision of the Rietveld-PONKCS method for the quantification of amorphous phases in anhydrous and hydrated systems. The proposed approach allowed a direct determination of the contribution of amorphous SCMs and C-S-H (by difference using a standard) in hydrating binders. The glass powder content in blended and hydrated systems of increasing complexity was investigated by cross-checking the results of independent characterisation techniques. For anhydrous binary mixes consisting of GP-CH/Corundum, the quantification method produced high accuracy, with a weighed-measured bias fewer than 1.5 wt.%. For hydrating synthetic mixes of CH and GP, the correctness of the method was assessed by comparison to the global mean of the four studied approaches. Overall, the results of the Rietveld-PONKCS method compared well to the results of acid dissolution and TGA/ICP methods. The average differences between the mean of the methods and the result of each method were respectively 0.5, 0.7 and 0.6 wt.% for Rietveld-PONKCS, acid dissolution and TGA/ICP. On the other hand, TGA/QEDS analyses provided the largest variation among the studied approaches, with an average difference with the mean of 1.5 wt.% (max 4.4 wt.%). However, it should be emphasised, as aforementioned, that the accuracy was discussed in this study only in terms of comparison to the global mean

(the real amount of unreacted GP remains unknown). Finally, in the GP-blended cement pastes, the accuracy was estimated to 0.4 wt.% using the standard-addition method.

In the case of GP, a global level of precision lower than 3 wt.% was found for the Rietveld-PONKCS method for both anhydrous and hydrated blends. However, even small errors on the unreacted GP content could lead to larger disparities in the degree of reaction of GP. For instance, in the extreme case of the 10GP system hydrated for 182 days, a measurement error of ±1 wt.% in the GP content could result in a scatter of ±15% in degree of reaction. Consequently, it should be acknowledged that the accuracy of the Rietveld-PONKCS method for GP can drop acutely at high degrees of reaction or/and low replacement rates (e.g. below 10 wt.%) due the estimated precision of 2-3 wt.%. In this case, several replicate testing are needed to improve the statistical certainty and the reliability of the results. Furthermore, it is worth mentioning that even though the Rietveld-PONKCS method showed promising results for glass powder and that no specific hypothesis on the materials composition was necessary for its application, these results might not be reproducible for other SCMs. First, the glass powder has a homogeneous composition, thus it is realistic to assume that the calibrated phase is still representative of GP even after its partial dissolution. Second, the overlap between the GP and C-S-H peaks is minimal, thus the decomposition of the XRD pattern is relatively easy. These conditions do not necessarily apply for materials such as fly ash due its heterogeneity [44] or slag due to the important overlap between its diffuse hump and the C-S-H contribution [7]. Similar observations were reported by previous work on the PONKCS method [6,33].

In addition, an improvement of the quantification could be achieved by calibrating the PONKCS phase on pre-blended sample with a similar composition of the unknown sample, instead of a sample containing only the phase of interest. To explore this approach, the pseudo-phase of GP was recalibrated using a sample of 182-day hydrated OPC mixed with 20 wt.% GP addition before the application to GP-blended cement pastes. Notably, no significant change was observed on the ZMV value of GP, even if this procedure allowed taking into consideration the presence or the absence of elements absorbing X-rays such as calcium, iron and potassium. Moreover, the incorporation of minor elements (such Al, Na, Mg…) in the C-S-H structure may lead to a change in the C-S-H XRD profile. Therefore, additional improvements of the fit could also be reached with a more adapted C-S-H peak phase profile for hydrated blended cements [6,45].

Overall, it can be concluded that the Rietveld-PONKCS method enables a direct quantification of amorphous phase with a similar accuracy to other techniques such as

selective acid dissolution and TGA/ICP. Furthermore, the Rietveld-PONKCS has notable advantages compared to other techniques. First, the method after calibration requires only X-ray diffraction pattern to quantify both the crystalline and amorphous phases in the sample. Second, the direct quantification of GP avoids the accumulation of errors, which is encountered in indirect methods. Third, the method can also be applied to other SCMs, provided a homogeneous composition and no overlap of its amorphous hump with that of the C-S-H. Finally, additional work is still required to attain a more widespread use of the method, with investigations of the interlaboratory consistency and reproducibility. Eventually, further work will aim at developing and testing an optimised analysis protocol with guidelines and specifications concerning: the definition of the background, the number of refined parameters and their variation range, the definition and the calibration of the pseudo-phase, the size of particles, the limitations of the method, and more.

5. Conclusion

In this work, the Rietveld-PONKCS method was applied for the quantification of the degree of reaction of glass powder in anhydrous and hydrated binary pastes of CH-GP and OPC-GP. The following conclusions can be drawn according to the main findings of this study:

1. The precision (repeatability) of the measurement of GP content by the Rietveld-PONKCS method was assessed to 1.6 wt.% on average while the accuracy (bias) of the method was lower than 1.5 wt.%.
2. The Rietveld-PONKCS method showed a similar accuracy to acid dissolution and TGA/ICP. On the other hand, the indirect method based on TGA/QEDS produced the largest disparities. This is likely related to the complexity of the determination of Ca/Si and to the sensitivity of the approach to errors in the Ca/Si ratio and portlandite consumption.
3. The main advantages of the Rietveld-PONKCS method are the ease and speed of the analyses, the fact that it is a direct measurement and that no assumptions are required (errors are not accumulated), and the comprehensive information which can be retrieved from a single experimental test (XRD analysis).
4. Despite the apparent simplicity of the PONKCS method, the analyst experience and a good knowledge in crystallography are prerequisite to reach a good analytical accuracy and meaningful results. In addition, further effort and crosschecking work

519 are necessary for the development of an optimised and standardised analysis
520 procedure.
521 Given the promising results of the Rietveld-PONKCS approach, this method is expected to
522 quickly become a standard tool in the material science of cement and concrete, with its
523 particular use to evaluate the reactivity of amorphous SCMs. Moreover, the choice of high
524 quality SCMs can be facilitated through the assessment of their influence on the hydrates
525 phase assemblage and, with further development, the prediction of their impact on the long
526 term properties of concrete.

527

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