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# C-S-H Quantification Using XRD: A Comparison of the Rietveld and PONKCS Methods

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## Abstract

The mineralogical quantification of cementitious materials can be performed using the Rietveld method, provided that suitable crystallographic data is available. X-ray amorphous phases, such as C-(A-)S-H, restrict the use of the Rietveld method because only very little crystallographic information is available. It is possible to get around this shortcoming using the PONKCS method (acronym for Partial Or No Known Crystal Structure) or employing the crystallographic data theorized by Richardson for C-S-H. This study examines the practical application of these two approaches to quantify the C-S-H phase of mature cement paste and the hydration monitoring of CEM I and C<sub>3</sub>S pastes. The quantifications obtained were compared to the TGA and hydration modeling results. It was shown that the two methods yield comparable and interchangeable results, each achieving an accuracy within 5% of the expected values.

## Keywords

X-ray diffraction  
C-S-H  
Cement  
Quantification  
PONKCS  
Rietveld

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## 1. Introduction

X-ray diffraction (XRD) is an analytical technique broadly used in material science for its sensitivity to crystallized phases and user-friendliness. It is extensively employed to gauge the mineralogy of cementitious materials (Aranda et al., 2012; Snellings, 2017). It is used primarily to identify and define all the phases of mineralogical assembly. XRD can also be used for quantitative phase analysis (QPA) owing to the fact that diffracted intensity and mass fraction are directly related (Cullity & Stock, 2014). As an example, the monochromatic intensity  $y_{mp}$  diffracted by a compound  $p$  in a mix may be written as in the following equation (Alexander & Klug, 1948):

$$y_{mp} = K_p \frac{X_p}{\rho_p \mu_s} \quad (1)$$

where  $K_p$  is a constant that depends on the diffractometer and the nature of the mineral phase  $p$ ;  $\rho_p$  and  $X_p$  are the density and mass fraction of phase  $p$ , and  $\mu_s$  is the mass absorption coefficient of the tested sample.

This feature has prompted the development of various types of quantitative approaches (Cullity & Stock, 2014; Hill & Howard, 1987; Madsen et al., 2011) based in the first instance on the intensity of a single peak, such as the internal or external standard approach, from which the reference intensity ratio method is derived (RIR) (Chung, 1974; Hubbard & Snyder, 1988; Saeki et al., 2024). It is essential to point out that although

these methods are not difficult to implement, they are very easily biased. As the peaks are compared to others, phenomena such as the preferential orientation or superposition of specific peaks may result in erroneous quantification (Chipera & Bish, 2013; Cullity & Stock, 2014; Hill & Howard, 1987). It follows that these methods must be seen as being semi-quantitative since they can only consider part of the observed diffractogram. This may result in a lack of accuracy and reliability in the quantification of a mineralogical assembly that is as complex as that of cementitious materials. Subsequent methods were based on factoring in the entire diffractogram, such as the method put forward by Rietveld (1967, 1969). This whole pattern-fitting method is based on the set of measured intensities, limiting the phenomena mentioned above. This numerical approach was initially proposed for structure refinement; its use for the quantification of mass fractions appeared later (Bish & Howard, 1988; Hill & Howard, 1987; O'Connor & Raven, 1988; Wiles & Young, 1981).

In practice, the quantification method known as Rietveld analysis is designed to assess the mass fractions  $X_i$  by minimizing the quadratic difference between the experimental diffractogram and the theoretical diffractogram re-calculated using all the available crystallographic data. This minimization is performed over the entire angular domain measured experimentally in an iterative approach. The principle involves refining certain variables of interest that contribute to the measured intensities: crystal lattices, scaling factors, atomic

displacement parameters, and the absorption properties of the compounds. (Aranda et al., 2012; Scrivener et al., 2017). This type of calculation implies that there is a need for crystallographic data for all the mineral phases. Based on the work of Aranda et al. (2012), Le Saoût et al. (2011) and Young (1995), a simplified Rietveld algorithm is suggested [Eq. (2)], showing all the refined parameters. The calculated intensity at the data point  $i$  is a sum of the refined crystal parameters and the background  $y_{ci}$ .

$$y_{ci} = y_{cbi} + \left[ \sum_p S_p \sum_q P_q L_q P_q |F_q|^2 (\varphi(\Delta\theta_{iq})) \right] \quad (2)$$

where  $y_{ci}$  represents the intensity calculated at the iteration  $i$ ;  $p$  the mineralogical compound under consideration, and  $q$  the Miller indices (h, k, l);  $S_p$  the scale factor;  $P_q$  the peak multiplicity factor;  $L_q$  the Lorentz and polarization factors;  $F_q$  the structure factor;  $\varphi$  a peak profile function;  $P_q$  the correction of the preferential orientation;  $y_{cbi}$  the intensity of the diffuse background. For more details about these parameters, please refer to Albinati and Willis (2006), Bish and Post (1989), Cullity and Stock (2014) and Young (1995).

The mass fraction  $X_i$  of each mineral phase is evaluated using the scale factors  $S_p$  (Aranda et al., 2012; Bish & Howard, 1988; Hill & Howard, 1987) obtained during Rietveld refinement. These scale factors are related to the phase concentrations through crystallographic parameters such as the unit cell volume, the number of formula units per cell, and molecular weight — provided that crystallographic data is available. The fit quality between the calculated and experimental diffractograms is typically assessed using agreement indices that measure the squared deviation between observed and calculated intensities. Among the most common are the weighted profile R-factor and the goodness of fit ( $\chi^2$ ), which are minimized during the refinement to improve the match between model and measurement (Toby, 2006; Young, 1995).

However, one of the main challenges that remains lies in handling many adjustable parameters. While modern software is user-friendly and computationally efficient, care must be taken to limit the degrees of freedom, ensure the plausibility of refined values, and avoid overfitting. Agreement indices alone are not sufficient to judge the physical consistency of a model (Scrivener et al., 2004; Toby, 2006). The Rietveld method has long proven its effectiveness and accuracy for crystalline phase assemblies. For poorly crystallized or amorphous mineralogical phases, the usual Rietveld analysis is difficult to perform since some of the input data (i.e., the crystallographic data) may be imprecise or even missing because of the low diffractive response of these amorphous phases under X-ray radiation. This limitation is particularly problematic for cementitious materials owing to the low molecular order, on the crystalline scale, of several mineralogical phases such as nanocrystalline calcium silicate hydrate C-S-H (Taylor et al., 1984), fly ash, metakaolin, or even slag (Taylor, 1997). Therefore, the Rietveld analysis applied to cementitious materials (including one or more amorphous compounds) is challenging. A few methods may bypass this issue, and readers are invited to consult Madsen et al. (2011) for further details. Nevertheless, the Rietveld analysis has been widely used for quantifying the mineralogical assembly of cementitious materials (Aranda et al., 2012; Le Saoût et al., 2011; Scrivener et al., 2004). In optimal conditions, quantifications can achieve an accuracy of approximately 0.2 wt.%, with typical values ranging between 1 to 2 wt.%. However, the precision tends to decrease for minor phases (De la Torre & Aranda, 2003; León-Reina et al., 2016; Zhao et al., 2018). Achieving this level of accuracy is time-consuming and demands substantial expertise in Rietveld QPA.

The presence of an amorphous phase may be addressed using an external standard (Goncharov & Zhutovsky, 2023; Jansen et al., 2011; Snellings, 2016) an internal one (Goncharov & Zhutovsky, 2023) but the most effective approach is the PONKCS method (Partial Or No Known Crystal Structure) that was successfully applied to several cementitious amorphous phases (Adu-Amankwah et al., 2022, 2023;

Goncharov & Zhutovsky, 2023; Li & Scrivener, 2025; Madsen et al., 2011; Mejdí et al., 2020; Naber et al., 2019; Scarlett & Madsen, 2006; Stetsko et al., 2017). This method does not require crystallographic data for the amorphous phase but uses a fitted profile as an input for the Rietveld analysis. The main difficulties that hinder the use of PONKCS are signal identification/acquisition and calibration. Firstly, the diffractogram must ideally be acquired using a sample of the pure amorphous phase and then calibrated by processing mixes of known mass fractions (Scarlett & Madsen, 2006; Stetsko et al., 2017). This approach may be complex since it requires a pure amorphous phase (C-S-H, for instance) available for the internal calibration, which restricts the user-friendliness and accessibility of the method. The main drawbacks of PONKCS are: (1) the calibration depends on the diffractometer that is used (and then any change in equipment requires a recalibration), and (2) the diffractogram of the amorphous material is fixed and cannot be modified in the QPA. In addition, internal and external standard approaches allow quantification of C-S-H together with other amorphous hydrates and unidentified phases, often resulting in an overestimated amorphous fraction and added experimental complexity or bias. Using known crystallographic data and a mineralogical analogue is an alternative to the PONKCS, internal and external standard approaches. Tobermorite has long been known to have a structure similar to C-S-H (Bonaccorsi et al., 2005; Grangeon et al., 2013; Richardson, 2014). Accordingly, a handful of studies have used tobermorite as a model for C-S-H in a Rietveld QPA and have succeeded in estimating the contribution of the amorphous phase after cross-analyses (Battocchio et al., 2012; Garbev et al., 2008; Geng et al., 2017; Mesecke et al., 2022; Renaudin et al., 2009). Recently, Richardson (2014) suggested a list of probable structural models for C-S-H based on clinotobermorite. These models reproduce several experimental findings and provide detailed crystallographic structures that can be used directly as input data for a Rietveld analysis. Although these models are often cited and used in the literature, this approach could be open to debate since there is still no consensus regarding the nanostructure of C-S-H. Nonetheless, these models establish a crystallographic structure that can be used in Rietveld QPA to simulate the contribution of C-S-H in a cementitious material. This approach could theoretically allow for a more direct, specific, and streamlined quantification of C-S-H, eliminating the need for standards or supplementary measurements.

This article proposes a straightforward and time-efficient approach for quantifying C-S-H in cementitious materials using Rietveld QPA and the structure models proposed by Richardson. The goal is to offer a reliable and accessible method that avoids complex or resource-intensive procedures. The simplified Rietveld approach, based on structural models proposed by Richardson, is compared to the PONKCS method. At the same time, the decision was made to simplify the sample preparation procedures (grinding) as much as possible to make the QPA procedure even more straightforward to perform. Finally, the resulting limited uncertainty of QPA makes it possible to validate *a posteriori* the assumptions and simplifications made.

## 2. Materials and methods

The first stage of the study consisted of preparing simple model mixes by mixing different products with different mass fractions. Three mixes were made (**Table 1**). The first (Mix. 1) incorporated common chemicals (NaCl + KCl) without any relationship to the cementitious materials, and the aim was to obtain a rough estimate of the quantification uncertainties. It should be noted that the choice of this mixture is not flawless, as these phases are sensitive to grinding. The second mix (Mix. 2) was prepared using portlandite and calcite, while the third (Mix. 3) was a simplified model of the mineralogical assembly of cementitious materials: it was a mix of C-S-H, portlandite, and a

**Table 1**

Sample summary of analyzed sample.

Type	Name	Composition	Comments	Age
Model mixes	Mix. 1	NaCl + KCl	ACS grade (purity > 95%)	
	Mix. 2	Ca(OH) <sub>2</sub> + CaCO <sub>3</sub>	ACS grade (purity > 95%)	
	Mix. 3	C-S-H + CH + C <sub>3</sub> S	(C/S) <sub>C-S-H</sub> = 1.4 [42]	
Hardened pastes	Hard. 1	w/c = 0.40	CEM I, Val d'Azergues cement plant*	13 years
	Hard. 2	w/c = 0.40	CEM I, Beffes cement plant	28 days
	Hard. 3	w/c = 0.50	90% C <sub>3</sub> S + 10% C <sub>2</sub> S	28 days
Hydrating pastes	Hydr. 1	w/c = 0.40	CEM I, Beffes cement plant	From 6 h to 28 d
	Hydr. 2	w/c = 0.50	90% C <sub>3</sub> S + 10% C <sub>2</sub> S	From 6 h to 28 d

\* Paste already studied in Auroy et al. (2015, 2018), Drouet et al. (2019) and Poyet et al. (2016)

**Table 2**

Phases structural data references (CCDC for C-S-H and COD for other phases). Complete C-S-H data files are available in Richardson (2014).

Phase	Database code number	Reference
C-S-H	From 1028747 to 1028762	Richardson (2014)
Portlandite (CH)	9000113	Henderson and Gutowsky (1962)
Alite (C <sub>3</sub> S)	1540704	Mumme (1995)
Belite (C <sub>2</sub> S)	9012789	Tsurumi et al. (1993)
Ettringite (AFt)	9012922	Hartman and Berliner (2006)
Monocarboaluminate (AFm)	1000459	François et al. (1998)
Hemicarboaluminate (AFt)	2105252	Runčevski et al. (2012)
Tricalcium aluminate (C <sub>3</sub> A)	1000039	Mondal and Jeffery (1975)
Ferrite (C <sub>4</sub> AF)	1008124	Bertaut et al. (1959)
Gypsum	5000039	Cole and Lancucki (1974)
Calcite	2100992	Maslen et al. (1993)

mix of 90 wt.% C<sub>3</sub>S and 10 wt.% C<sub>2</sub>S provided by Septdout Company<sup>1</sup> (see Notations). The C-S-H was obtained by grinding the C-S-H paste (C/S = 1.4) prepared in a previous work (Kangni-Foli et al., 2021). This paste was obtained by mixing stoichiometric quantities of C<sub>3</sub>S (from Mineral Research Processing) and colloidal silica (BASF) to obtain C/S = 1.4. Finally, the C/S ratio = 1.4 is lower than the values expected and encountered in the usual materials (between approximately 1.5 and 1.7 (Deschner et al., 2012; Gallucci et al., 2013; Lothenbach & Nonat, 2015), but this is the lowest C/S ratio that can be obtained in the laboratory by mineral synthesis without the parasitic presence of portlandite (Martín-Garrido et al., 2020). Please note that after grinding, the C-S-H paste was kept in a CO<sub>2</sub>-free glovebox (under N<sub>2</sub> atmosphere) at ambient temperature and dry conditions (the relative humidity was not measured but was between 0% and 5%). Subsequently, the powder samples were dry before they were used (XRD).

Secondly, three different hardened cement pastes were tested (**Table 1**): two pastes were prepared with two CEM I from two other cement plants (Hard. 1 and Hard. 2 from the Val d'Azergues and Beffes plants, respectively), and a paste obtained by hydration of the C<sub>3</sub>S and C<sub>2</sub>S mix (Hard. 3). Finally, 2 hydrating pastes were used for hydration monitoring: CEM I (Beffes, Hydr. 1) and C<sub>3</sub>S/C<sub>2</sub>S (Hydr. 2) pastes. We deliberately limited our approach to C<sub>3</sub>S and CEM I to avoid adding additional amorphous phases that could have interfered with the study (fly ash and/or slag for CEM III and CEM V).

The pastes were prepared by mixing the anhydrous binder with demineralized water in a mixer for 2 minutes at 250 rpm, followed by 3 minutes at 500 rpm for a batch volume equal to 2 liters. The fresh mix was subsequently poured into cylindrical plastic molds (diameter 15 mm, height 100 mm), closed before being sealed with Parafilm M, and stored in a nitrogen-regulated glove box at room temperature until analysis.

Before data acquisition, all samples were gently ground for about one minute using an agate mortar and pestle. Although grain size was not measured in this study—despite its known relevance for accurate QPA (Snellings, 2017)—the resulting powder is estimated to have an average particle size of around 100 to 200 μm. While optimal QPA typically requires finer powders (a few tens of microns) and specialized equipment (e.g., the McCrone mill), this level of preparation was deliberately avoided to maintain a simple, practical and quick approach.

The grinding procedure was applied consistently across all samples, and no significant variation was observed in the resulting diffractograms. Moreover, the limited uncertainty of the QPA results, discussed in the following sections, supports the validity of this simplified approach a posteriori. Grinding was carried out in open air, with minimal drying, to preserve hydration products such as AFt and AFm phases (Zhang & Glasser, 2000). Two different diffractometers were used: the Hard. 2 and Hard. 3 pastes were tested using a Panalytical Aeris Research Edition with Cu-Kα irradiation obtained at 40 kV and 15 mA. Data were collected between 2θ = 5 and 70° with a step of 0.011° for a total acquisition time of 2 hours; an incidence divergence slit was set at 0.25° while the receiving slit was set at 0.1° and a beam knife high was also used. All the other samples were tested using a Panalytical X'Pert with a Cu-Kα anode operated at 45 kV and 40 mA. The diffractograms were then acquired between 5° and 70° with a step of 0.011° for one hour; an incidence divergence slit was set at 0.5° while the receiving slit was set at 8 mm. The durations used (1 hour and 2 hours) were chosen to obtain diffractograms of comparable quality to maximize the signal-to-noise ratio. Both diffractometers were equipped with a PIXcel1D detector.

The QPA was performed using the Panalytical HighScore Plus v4.9 software (Degen et al., 2014) based on the recommendations in the reference volume (Snellings, 2017) using crystallographic data from the Crystallography Open Database (COD, 2025) and the structures suggested by Richardson (2014) for C-S-H, obtained on the basis of CCDC<sup>2</sup> (see Notations). The crystallographic structures used are summarized in **Table 2**.

For the C-S-H, all the structures proposed by Richardson were included in the Rietveld refinements and, in this context, the software (HighScore Plus from Malvern Panalytical) (Degen et al., 2014) automatically selected the most suitable structures to reproduce the experimental diffractograms. From a practical point of view, an initial simulation was run with all C-S-H structures. At the end of this simulation, all irrelevant structures (with zero or very low mass fraction; i.e., less than 1 wt.%) were removed and the simulation was restarted. Using an iterative approach and removing irrelevant structures at each iteration, we arrived at an effective description of C-S-H that required only four models (T5\_14sc, T5\_11SC, T3\_14sc, T11\_14sc). Subsequently, these four models proved sufficient to correctly describe

the contribution of C-S-H in all experimental diffractograms. Detailed information regarding their structures, including CaO/SiO<sub>2</sub> and H<sub>2</sub>O/SiO<sub>2</sub> ratios, can be found in the original publication (Richardson, 2014).

The AFm phases correspond to both monocarboaluminate and hemicarboaluminate. The polymorphism of the aluminum phases was not considered in this instance, despite the conclusions reached in other studies (de Noirfontaine et al., 2006; Taylor et al., 2000), due to the good agreement between the fitted model, the experimental data, and the QPA results. The quantitative analyses were performed following published studies (Albinati & Willis, 2006; Aranda et al., 2012; Scrivener et al., 2004; Snellings, 2017), and were similar for both the Rietveld and PONKCS methods. The background contribution of the 6-hour and 1-day hydrated samples was modeled using a ten-degree 1/20 polynomial to compensate the contribution of residual water on the observed pattern, phenomenon reported in Manjunath et al. (1973) and Snellings (2017). A four-degree polynomial was used for all the other samples. The March-Dollase algorithm (Dollase, 1986) was introduced to factor in the preferential orientation of portlandite.

A detailed summary of the strategies used for PONKCS analyzes is shown in Appendix 1.

Thermogravimetric analyses (TGA) were performed on freeze-dried samples using a Netzsch STA 409 PC LUX device. Ground samples (120 mg) were heated between 30 °C and 1150 °C at 10 °C/min. under nitrogen flow (80 mL/min.). The results were post-processed using Netzsch Proteus analysis software, with the tangential method to assess the quantity of portlandite (Lothenbach et al., 2017). Hydration was stopped prior to TGA analysis to ensure comparability of hydration monitoring across sample sets, which also enabled replicate measurements. For XRD, no pretreatment was applied to preserve ettringite (Zhou & Glasser, 2001), and samples were analyzed immediately after grinding to minimize rehydration, carbonation, or drying, following established guidelines (Snellings, 2017) and samples were analyzed immediately after grinding to minimize rehydration, carbonation, or drying. Freeze-drying was selected for TGA samples as an optimal balance between rapid hydration stoppage and efficient sample processing.

In parallel with the tests, the hydration speed and mineralogical assembly of some of the pastes were estimated using the hydration model suggested by Parrott and Killoh (1984) in the version modified by Lothenbach et al. (2008a, 2008b) using the Cemdata18 thermodynamic database

(Lothenbach et al., 2019) and the GEMs code (Blaser et al., 2015). This model is considered validated for describing the hydration kinetics of Portland cements and is therefore used as a reference in this study. All the results are given with reference to 100 g of dry binder.

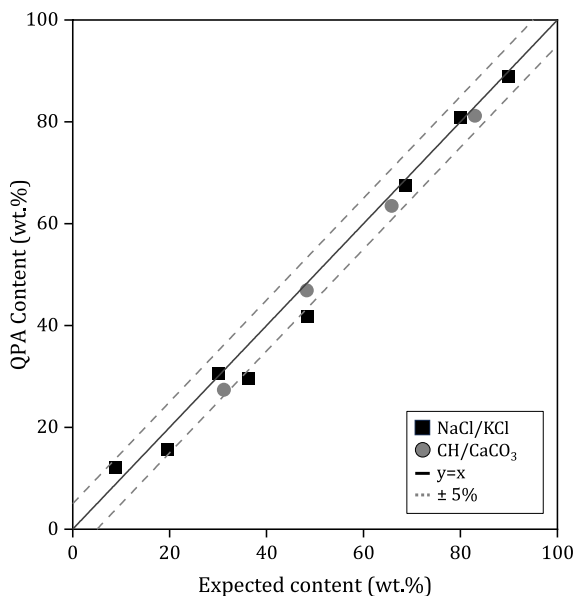
### 3. Results

#### 3.1 Model mixes

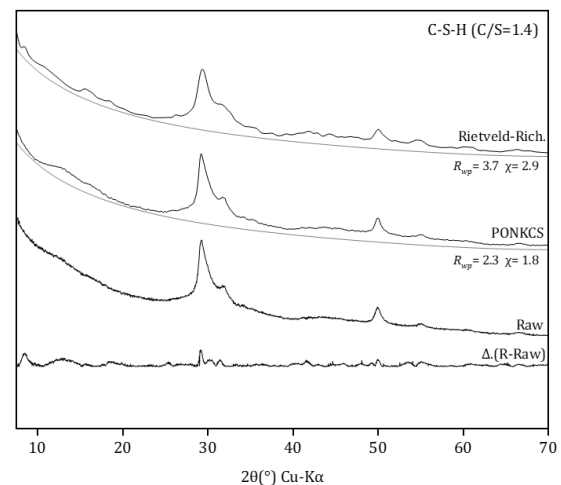
The Rietveld analysis was initially applied to the first two mixes of crystallized phases, Mix 1 (KCl + NaCl) and Mix. 2 (portlandite and calcite), to illustrate the approach and estimate roughly the uncertainty of the whole process (from sample preparation to QPA). The results obtained, as presented in Fig. 1, show that the Rietveld quantification gives a correct evaluation of the composition of the mixes and that the deviation from the experimental value is limited and is generally under  $\pm 5$  wt.%. However, using oxides instead of KCl and NaCl might have resulted in greater accuracy owing to these salt griding sensitivity.

#### 3.2 Description of C-S-H

Secondly, the two approaches (Rietveld with the structures suggested by Richardson and PONKCS) were used to reproduce the experimental diffractogram of the pure C-S-H paste (C/S = 1.4) (Kangni-Foli et al., 2021). All the results are shown in Fig. 2. The diffractogram obtained by the PONKCS method provides accurately describes the contribution of the amorphous material (the values of the agreement indices are low). This outcome was expected; the experimental diffractogram is simulated by the composition of a significant number of elementary peaks, which were generated by creating a virtual crystallographic structure recalibrated for this purpose, as illustrated in Fig. A1 in the Appendix. For the Rietveld approach, the software algorithm adjusted the crystallographic structures suggested by Richardson to reproduce the experimental diffractogram. The result is satisfactory in overall terms (agreement indices values fall close to those obtained with PONKCS) insofar as the major peaks are reproduced (around 30°, 32°, 50° and 55°). Some minor contributions appear (at around 15° and 40°, for instance), induced by the crystal structures that were considered. These contributions, however, are not very intense and appeared later to have a negligible effect on the diffractogram in cementitious material



**Fig. 1** Composition determined by Rietveld QPA versus the weighed amounts in the phase mixtures.



**Fig. 2** C-S-H paste (C/S = 1.4), comparison of calculated and experimental diffractograms ( $\Delta$  stands for the difference between the calculated diffractogram and the experimental one). Top diffractogram (Rietveld-Rich) is a blend of C-S-H contributions: T11\_14sc (5.3%) T5\_14sc (7.2%), T5\_11sc (61.4%), T3\_14sc (26.1%).

(due to the background and presence of other mineral phases, which will reduce the C-S-H contribution to the diffractogram).

### 3.3 Application to mature cement pastes

The two approaches — Rietveld-Richardson and PONKCS — yield qualitatively and quantitatively similar results on all the mature cement pastes (Hard. 1, Hard. 2, and Hard. 3). Qualitatively, their calculated diffractograms closely match the measured ones, as illustrated by the example of C<sub>3</sub>S pastes (Hard. 3, Fig. 3(A)). In both methods, the calculated contribution of the C-S-H phase to the measured diffractogram is identical to the two approaches considered.

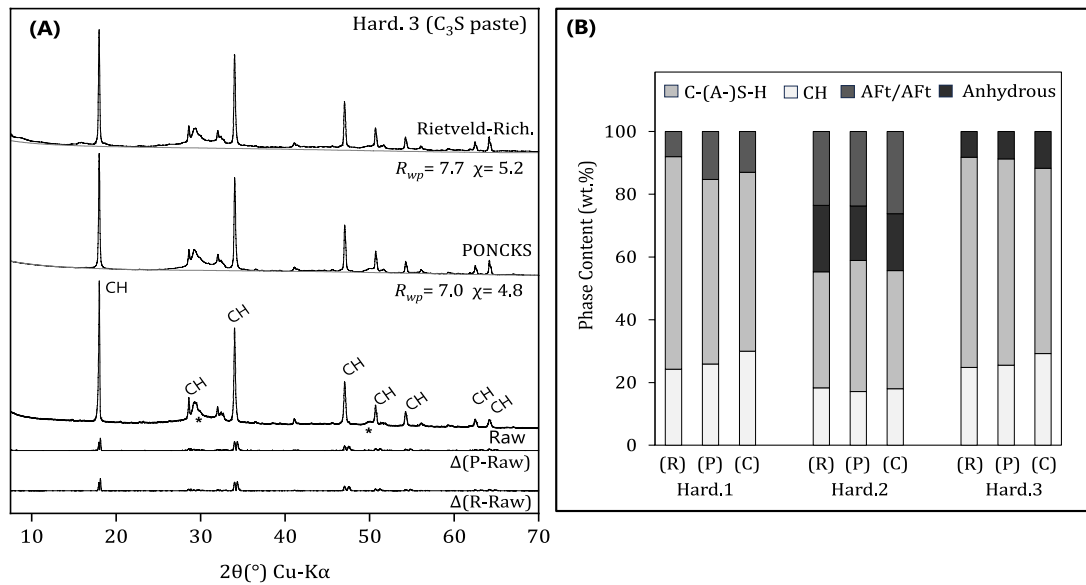
However, portlandite contributions are consistently underestimated across all samples, regardless of the QPA approach. This discrepancy is particularly noticeable at the (001) reflection around 2θ = 18° 2nd and contributes to the observed high residuals and agreement indices. This underestimation is likely due to insufficient grinding fineness, which can

result in poor particle statistics and induce orientation effects. This limitation—related to the deliberately simplified sample preparation—is one of the trade-offs of the proposed method.

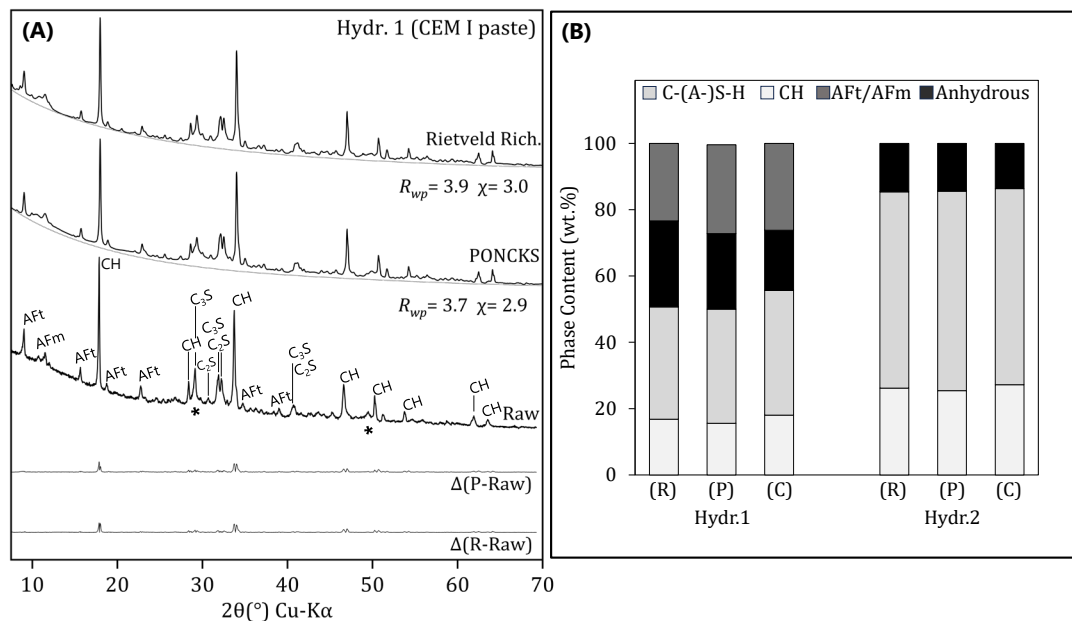
Quantitatively, the QPA determined for all hardened samples, as shown in Fig. 3(B), is close to the values obtained from the hydration model, with an uncertainty within the range of ± 5 wt.%. This level of uncertainty is comparable to that obtained for the model mixtures, suggesting that it more likely originates from the QPA procedure itself — as applied here — rather than from the C-S-H phase contribution.

### 3.4 Application to hydration monitoring

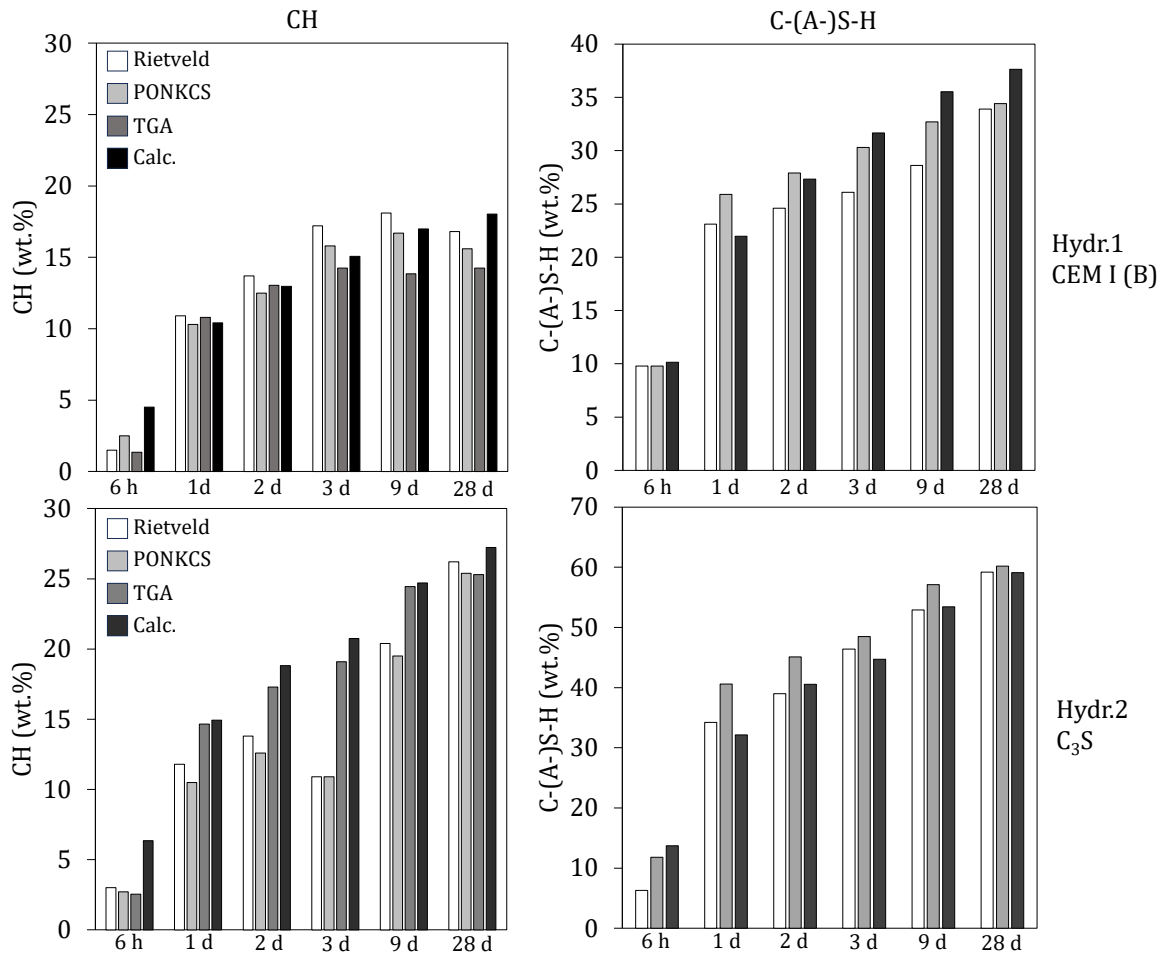
Similar results were obtained with the hydration monitoring of the Hydr. 1 and Hydr. 2 pastes (Table 1). Diffractograms acquired after 28 days of hydration using the Hydr. 1 sample (CEM I Befes paste) are shown in Fig. 4(A). Both approaches (Rietveld-Richardson and PONKCS) can accurately describe the experimental diffractograms



**Fig. 3** (A) Calculated and observed XRD patterns gathered on Hard. 3 (C<sub>3</sub>S paste), with the asterisk (\*) indicating C-S-H. (B) Associated Rietveld-QPA (R) PONKCS-QPA (P) and modeling results (C) acquired on considered hardened pastes.



**Fig. 4** (A) Calculated and observed XRD pattern gathered on 28 days Hydr. 1 paste (CEM I), with the asterisk (\*) indicating C-S-H. (B) Associated Rietveld-QPA (R), PONKCS-QPA (P) and modeling results (C) acquired on considered hydrating pastes at 28 days.



**Fig. 5** Rietveld and PONKCS-QPA, TGA and modelling results acquired on hydrating pastes (CEM I and C<sub>3</sub>S) for portlandite (CH) on the left and C-S-H on the right.

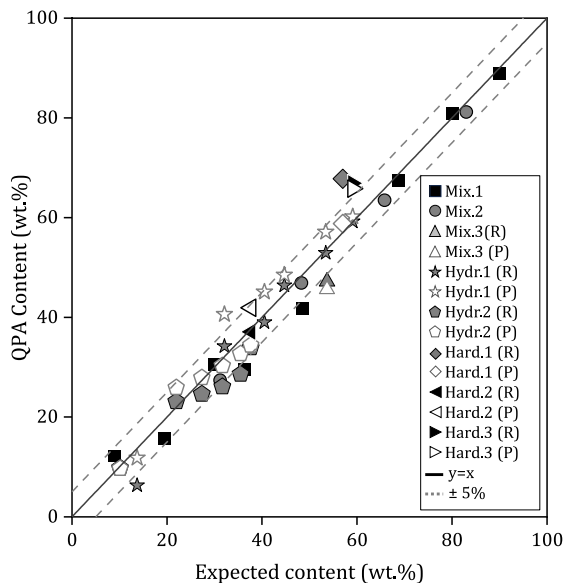
together with the C-S-H contribution. Portlandite content is again systematically underestimated, due to the QPA procedure as applied in this study (e.g., limited grinding, preferred orientation, or uncertainties in TGA reference values).

The contribution of the AFm phases around  $2\theta = 8^\circ$  is also not well reproduced, regardless of the QPA approach or hydration time.

However, these are minor phases with limited impact on the overall diffractogram, and little effort was made to refine their contribution further. Ultimately, the associated QPA results, **Fig. 4(B)**, remain within  $\pm 5$  wt.% of the hydration model, consistent with the uncertainty observed for the model mixtures, and valid for both major and minor phases.

**Figure 5** shows the QPA results for all the Hydr. 1 and Hydr. 2 samples for C-S-H and portlandite. The quantifications are compared to the results obtained by TGA (for portlandite) and the hydration model. No significant amounts of calcite were detected by either XRD or TGA in either sample set, suggesting no carbonation occurred during sample preparation or conditioning. The two approaches yielded equivalent C-S-H mass fractions close to the given values obtained by TGA and the hydration model, irrespective of the paste and the timescale under consideration. More defined differences, however, are on occasion measured regarding the mass fractions of the portlandite found by QPA on the complete Hydr. 1 and Hydr. 2 sets, in keeping with previous observations. These poor estimates are apparent on the Hydr. 2 samples at early ages, although they remain close in overall terms to the values determined by numerical modeling and TGA.

In the study, the QPA provided by the Rietveld-Richardson and PONKCS methods are similar and in agreement with the theoretical values, as shown in **Fig. 6**. The quantitative results on Hard. 2 and Hard. 3 samples yielded less or equal to 5% uncertainty than the expected values. This value is indicative, for instance, of the Hard.1 paste (mature paste from CEM I, Val d’Azergues cement plant, **Table 1**), the QPA only differs by 2% compared to the values predicted by the hydration model in the case of PONKCS. However, the deviation is nearly 10% for the Rietveld-Richardson approach. The C-S-H mass



**Fig. 6** Composition of all considered sample of the study determined by Rietveld-QPA (R) and PONKCS-QPA (P) versus the expected values.

fractions obtained for the hydration monitoring of the Hydr. 1 and Hydr. 2 pastes all have an uncertainty of the order of  $\pm 5$  wt.% compared to the values predicted by the hydration model, a value comparable to the uncertainty range obtained from the model mixtures shown in Fig. 1.

## 4. Discussion

The two approaches selected to describe the C-S-H phase in the QPA analysis by Rietveld deliver similar results. While both methods can be used to quantitatively study the mineralogy of a cementitious material, they have different specificities. For the PONKCS approach, acquiring the diffractogram of a pure C-S-H paste was needed to calibrate the model. This step aims to calibrate a crystallographic structure. The virtual density, or pseudo-formula mass, is then determined using a known mix, which makes it possible to assess the contribution of the amorphous phase to the diffractogram. The result of this simulation may depend on the amorphous synthesis method (Battocchio et al., 2012; Grangeon et al., 2013; Renaudin et al., 2009; Wang et al., 2019), and it also allows the introduction of bias while the samples are being prepared. These steps restrict the accessibility of this approach. At the same time, it is possible to keep the contribution calibrated so that it can be reused to post-process other experimental diffractograms (provided the acquisition conditions are the same). Lastly, it should be noted that this approach implies that all the diffractograms must be acquired using a similar experimental setup.

The Rietveld-Richardson approach is straightforward because it draws on several crystal structures suggested by Richardson (2014). This method, therefore, does not require calibration since the crystallographic data is clearly defined, and the mineral structure imposes the crystal density. It follows that additional diffractogram acquisition is not required. This method does not impose a unique defect-tobermorite structure (Battocchio et al., 2012; Geng et al., 2017; Grangeon et al., 2013) as has been the case until now, but a mineralogical combination of different structures. In this study, four structures were enough to describe the C-S-H phase: T5\_14sc, T5\_11SC, T3\_14sc, and T11\_14sc. Owing to the higher number of crystal phases introduced during the Rietveld calculation, calculation times may be significantly longer than the PONKCS approach. However, in common with the PONKCS method, the calculated contributions may be stored so they can be reused with other diffractograms acquired independently of the experimental setup. Therefore, these two methods appear more or less interchangeable, and the choice of using one or the other will depend on the user. It is necessary to obtain a synthetic C-S-H for calibrating the PONKCS approach and it should be kept in mind that once calibrated, this phase is not adjusted during the QPA. Only the scale factor is adjusted in the analysis (i.e., the mass fraction), and all other parameters are fixed (in particular, the crystal lattice parameters or the C/S ratio). The quality of the fit between the experimental diffractogram and the QPA therefore depends on the match between the pure synthetic C-S-H (C/S = 1.4 in our case) and the C-S-H present in the actual material (which may have different C/S ratios and incorporate aluminum and impurities, for example). In the authors' mind, this is a major limitation of the PONKCS approach. In contrast, the classical Rietveld approach offers much greater freedom – without prior calibration – and allows for a much better description of the contribution of C-S-H to the experimental diffractogram, which is the whole point of using the structural models proposed by Richardson.

The uncertainties obtained on the quantification may seem high ( $\pm 5$  wt.%) compared to other studies using the Rietveld method. Nonetheless, these uncertainties could be minimized, as has been suggested in other studies (León-Reina et al., 2009, 2016; Snellings et al., 2014), by optimizing the refinement strategy (Aranda et al., 2012; Mejd

et al., 2020) and factoring in the polymorphism when choosing the input data. In addition, determining and employing coefficients  $K_p$  and  $\mu_s$  using an internal or external standard could improve the accuracy of the QPAs performed in this study. Despite the more considerable quantification uncertainties ( $> 5$  wt.%) obtained on some diffractograms, the two QPA approaches yield similar results, suggesting a decreased quality on those diffractograms and allegedly a sample preparation effect (Scrivener et al., 2017). Nevertheless, based on these QPA results, this strategy is not sensitive to the instrumentation used while acquiring the results or to the type of material analyzed.

The input data used in this study can be further extended to describe the C-(A-)S-H phase, as XRD profiles display minimal variations with different Ca/Si and Al/Si ratios (Cuesta et al., 2021; Poyet et al., 2025; Renaudin et al., 2009). It is worth emphasizing that quantitative phase analyses using Richardson's structural models for C-S-H are now routinely carried out in the laboratory (Kangni-Foli et al., 2021; Poyet et al., 2025). Likewise, the PONKCS approach relies on a pure C-S-H phase with a known Ca/Si ratio; its suitability for describing additional C-(A-)S-H phases in the samples examined here must also be considered. Although the Ca/Si ratios of CEM I pastes were not measured in this study, the PONKCS method successfully reproduced the observed XRD patterns, suggesting that the contribution of the C-(A-)S-H phase was accurately represented in the calculated pattern, despite uncertainties about the phase actual stoichiometry. This approach is then relevant to describe C-(A-)S-H contributions in the XRD observed pattern acquired on CEM I pastes. Furthermore, Richardson (2014) proposed different C-S-H structural models with a wide range of Ca/Si and H<sub>2</sub>O/Si ratios, supporting the approach's applicability to other cementitious systems. Thus, despite potential differences in C-(A-)S-H structure in the cement pastes studied here, both the QPA-Rietveld and QPA-PONKCS approaches appear accurate enough to quantify C<sub>3</sub>S and CEM I pastes mineralogical content using XRD data.

The relative uncertainty regarding the quantification is logically more significant in the minor phases; this phenomenon is also observed elsewhere (De la Torre & Aranda, 2003). This complexity was mainly found in the AFt/AFm phases, where their calculated contribution does not match the expected data. A similar observation was made with portlandite; although this is a major phase, deviations over 5 wt.% were obtained. These erroneous quantifications could be related to the input data. These data were established on pure synthetic phases under acquisition conditions that were very different from those used in this study, i.e., synchrotron radiation and a capillary sample holder, where the preferential orientation phenomena are negligible. Further crystallographic data could then be considered.

The sizeable uncertainties in the QPA found on samples undergoing hydration are found again primarily on early-age samples. In addition, it was noted that a sample's mineralogical variety could be a source of complexity for the QPA due to the many different parameters that need to be refined and the increased number of minor phases in the mineralogical system. Lastly, although this study was performed on the HighScorePlus software, the strategy put forward here can be transposed (with adaptations) to conduct a Rietveld QPA on another XRD post-processing software such as Siroquant<sup>3</sup>, FullProf<sup>4</sup> and MAUD<sup>5</sup> (see Notations). The observations and remarks made in this work are general.

## 5. Conclusion

In this study, the PONKCS approach was employed to describe the contribution of the C-(A-)S-H amorphous phase to the diffractogram of a cement paste and to quantify it with an accuracy of  $\pm 5$  wt.% compared to the hydration model from Parrott & Killoh and cross-analyses by TGA. The study highlighted that it is possible to describe the C-(A-)S-H phase using the structural models Richardson

suggested and obtain similar results. Irrespective of the samples studied among the mixes (Mix) and hydrated pastes (Hard) or in the process of hydration (Hydr.), the QPA is systematically close to the comparative experimental TGA and numerical values, with a confidence interval of approximately 5% for these two quantification methods. The findings validate the relative accuracy of the approach, despite some deliberate simplifications, such as limited control over grain size, introduced to maintain ease of application. It follows that the structural models suggested by Richardson provide a more accessible alternative than the PONKCS approach for describing C-(A)-S-H within the Rietveld method. The methodology put forward in this study could be implemented on mineralogical assemblies with one or more other amorphous phases, provided a theoretical crystallographic structure is available. This Rietveld QPA strategy could be improved per the user's requirements and the specific characteristics of the materials under study. However, it is a simple, accessible preliminary approach for quantifying cementitious materials.

## Notations

- 1 Provided by Septodont Company: <https://www.septodont.fr/>
- 2 Cambridge Crystallographic Data Centre (CCDC) : <https://www.ccdc.cam.ac.uk/>
- 3 Siroquant: <https://www.siroquant.com/siroquant-v4>
- 4 Fullprof: <https://www.ill.eu/sites/fullprof/>
- 5 MAUD: <https://luttero.github.io/maud/>

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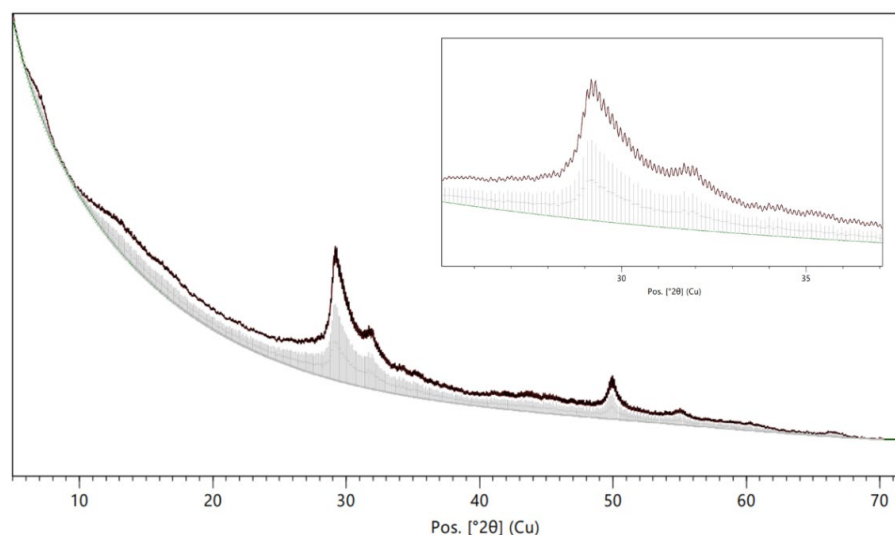
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## Appendix: PONKCS method for C-(A)-S-H

The C-(A)-S-H phase is described based on the diffractogram of a C-S-H paste ( $C/S = 1.4$ ) using an hkl phase with the Pawley method (Pawley, 1981). The phase consists of a set of peaks reproducing the contribution of the amorphous phase measured experimentally, as illustrated in **Fig. A1**. A tetragonal space group (space group  $n^{\circ}75$ ) was assigned to “fit” the amorphous contribution (Mejdi et al., 2020). A diffractogram of single-crystal silica (no diffraction), acquired with a similar experimental device, was used to determine the background. It is important to note that, although several authors have employed

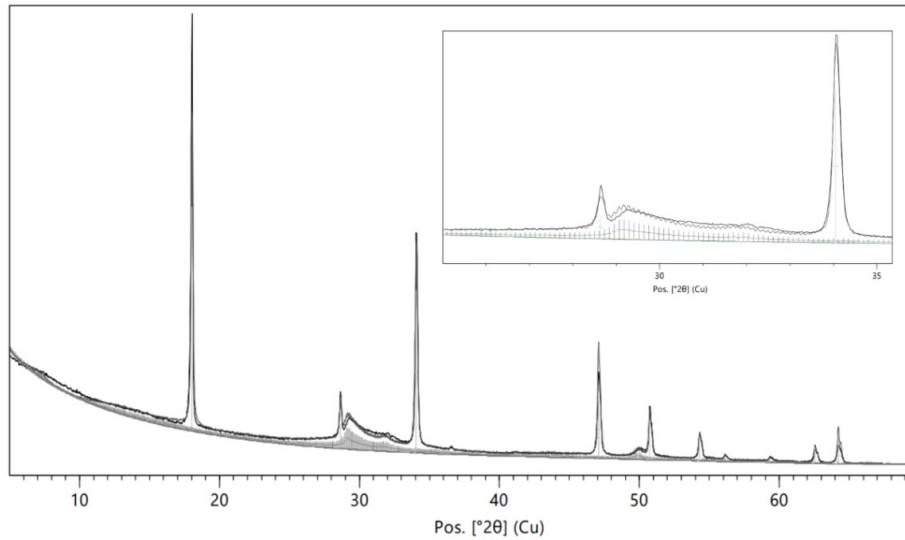
different methods for adjusting the background, there has been no agreement to date regarding the most relevant approach (Madsen et al., 2011b; Snellings et al., 2014; Stetsko et al., 2017).

The ZMV parameter, was determined on a fully hydrated  $C_3S$  paste whose portlandite proportion was determined by TGA and supported using the hydration model detailed earlier in this study. A Rietveld refinement was then performed, and the parameter ZMV adjusted until the consecutive portlandite weight content was obtained. The calibration outcome is shown in **Fig. A2**. The resulting hkl file was then used unchanged in further QPA calculations.



**Fig. A1**

Pure C-S-H ( $C/S = 1.4$ ) pattern (black line) and associated hkl fitting (grey vertical line).



**Fig. A2**  
C<sub>3</sub>S paste pattern (black), the calculated pattern using PONKCS approach (grey wavy-line) and peak contribution (grey vertical-line).

### Author contributions

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Stéphane Esnouf : Methodology, Supervision, Validation, Writing – Revising Draft.

Alexandre Dauzères : Project administration, Funding acquisition, Writing – Revising Draft.

Thibault Charpentier : Supervision, Validation, Formal analysis, Formal analysis, Writing – Revising Draft.

Loïc Mazé : Validation, Writing – Revising Draft.

### Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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