Variation in Phase Quantification of White Portland Cement by XRD

J. A. Canul-Polanco(✉) and O. M. Jensen

Technical University of Denmark, Lyngby, Denmark
janpo@byg.dtu.dk

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1 Introduction

X-ray diffraction has been used for at least a century in the cement industry to identify the crystalline phases of Portland cement [1]. More recently, the quantification of phases by X-ray diffraction (QRXD) together with other microstructural techniques have been successfully applied to Portland cement [2].

To improve the QXRD analysis, different pretreatments procedures have been considered, such as grinding to a particle size below 5 μm and chemical selective dissolution [3]. For example, an aqueous solution of KOH and sucrose is used to produce a residue rich in alite and belite, whereas salicylic acid and methanol results in a residue containing aluminate, ferrite, sulfate, and other minor phases. However, those methods can be time-consuming, and in the cement industry, it is preferred to use fast but still reliable methods.

In this project, QXRD was used for phase quantification of white Portland cement (WPC) without any selective chemical dissolution or physical grinding before the measurements. This paper also describes the challenges presented during the measuring and refinement to quantify the crystalline phases of the WPC. All samples were analyzed through the software High Score Plus (HSP) and the external method for quantification of the amorphous phase.

2 Experimental Details

The samples were measured under the following conditions (Table 1):

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Table 1. Conditions of the XRD measurements.

Data collection properties and settings		
Model	Type	PANalytical, X'Pert3 powder
X-ray source	X-ray radiation	CuK$\alpha_{1,2}$ (λ = 1.5406 Å), line focus
	Generator operation	45 kV, 40 mA
Diffractometer optics	Incident divergence slit	0.5° fixed
	Incident anti-scatter slit	1° fixed
	Incident beam mask	10 mm
	Incident Soller slits	0.04 rad
	Receiving anti-scatter slit	1° fixed
	Receiving Soller slits	0.04 rad
	Scanning mode	Continuous
	Detector type	X'celerator
	Detector length	2.122° 2θ linear position-sensitive X-ray det.
	Spinning speed	4 rpm
	Sample	Back loaded in powder
Scan parameters	Angular range	5–70° 2θ
	Step size	0.02° 2θ
	Time per step	30 s
	Total measurement	30 min

For the XRD pattern deconvolution, the Rietveld refinement method was used with the HSP software. The refinement was done under the following considerations:

- The background was refined using a flat background, a polynomial function with 4–5 coefficients, the 1/x term, and the correction for specimen displacement was applied.
- The zone between 5 and 7° 2θ was left out of the analysis.
- The scale factor, unit cell, and profile (w Cagliotti parameter) were refined for each crystalline phase. The variation for the unit cell was constrained to one percent, and the w parameter had a limit between 0.0001 to 0.2.
- Preferred orientation correction factors were applied for some phases constraining the factor between 0.7 and 1 with March-Dollase correction. In the particular case of gypsum, two different approaches were performed, the spherical harmonics with an order of 8, and the March-Dollase correction with a factor constrained between 0.4 and 1.
- The external standard used was α-Al_2O_3 corundum, with a known crystallinity of 99.5%. The same conditions of measurement and refinement were applied. In addition to this, the refinement included an asymmetry function "split width and shape".

3 Results

Figure 1 (left) shows an XRD measurement of WPC under the conditions given in Table 1. The main crystalline phases found were: Alite M3 (A-M3), Alite M1 (A-M1), β-Belite (β-B), γ-Belite (γ-B), tricalcium aluminate cubic (C3A), basanite (BA), gypsum (G), portlandite and calcite (the last two not indicated in Fig. 1). However, the gypsum peak in plane 020 (position °2θ: 11.68) shows a high degree of preferred orientation (PO). Therefore, the measurement was performed in a total of four times on the same WPC: two different samples were measured at two different instruments (with repacking between measurements). The gypsum peak (020) remained with a similar high intensity. Figure 1 (right) shows a measurement performed with different conditions, but the gypsum peak (020) remained the same, and other phases showed less intensity.

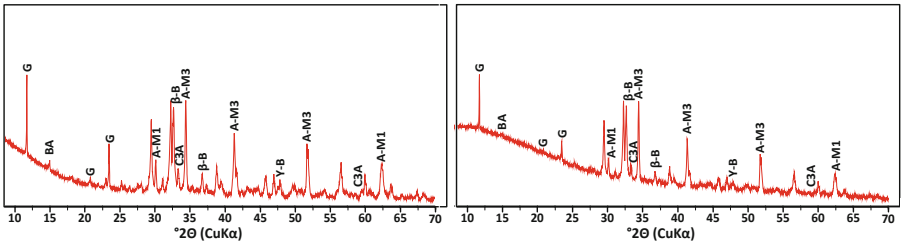

Fig. 1. Crystalline phases found in the WPC. Left: XRD measurement, as described in Table 1. Right: XRD measurement under an incident anti-scatter slit of 2°, receiving anti-scatter slit of 2°, and a higher spinning speed of 16 rpm. Both measurements are done on instrument 1.

Among the different approaches to minimize PO [4, 5], it was chosen to mix the cement with an amorphous filler material. In this case, silica fume (SF) was used. Therefore, a mixture of anhydrous WPC with 5% SF was measured (Fig. 2 left and right). Also, these measurements were done like for the WPC samples above; two different samples were measured at two different instruments and different instrument settings. It is seen that the addition of a second powder offset the gypsum peak (position °2θ: 11.68).

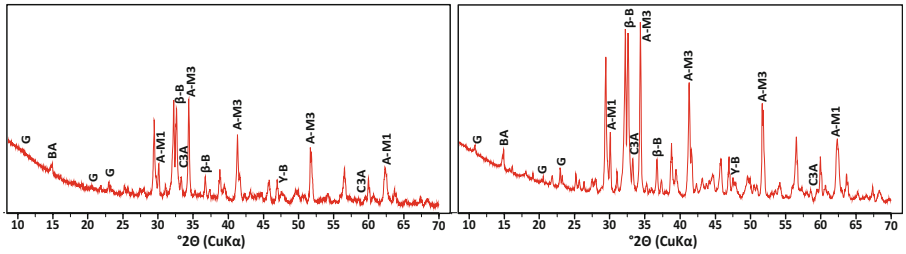

Fig. 2. XRD measurements of WPC with 5% SF with two different diffractometers (Left: Instrument 1 and Right: Instrument 2). Left: XRD measurement conditions, as given in Table 1. Right: XRD measurement conditions such as incident anti-scatter slit of 2°, receiving anti-scatter slit of 7.5 mm, and spinning speed of 4 rpm. Instrument 2 was a PANalytical, Empyrean model.

The Rietveld refinement was applied to all measurements, as described in the section of experimental details. One of the challenges during refinement was to identify the PO of phases besides gypsum: calcite (104), alite (606), and portlandite (002). Another important parameter during the refinement was the background. The phase content could change as a function of the choice of background [6]. In HSP, a manual or automatic background can be chosen. All refinements were performed on automatic with a bending factor of 0 and granularity of 6.

The phase quantification of the cement is shown in Table 2. Results were normalized to 100%, excluding amorphous content (in particular SF). Some significant differences can be observed. There are three possible reasons for these variations: instrument type, measurement configuration, or the SF addition. The dry mixture of a crystalline material with the amorphous filler material gives rise to scattering in the diffraction pattern, increasing the background (not seen in Fig. 2 due to scaling), plus contamination [5]. Even if it is not noticeable in Fig. 2, the statistical improvement (R_{wp} and GOF) in the WPC-SF and WPC-SF-2 results is partly a consequence of increasing the background by adding SF (see Table 2).

Table 2. Phases quantification results of samples with and without SF addition. R_{wp}: weighted R profile, GOF: goodness of fit. NC: No correction for preferred orientation during refinement, Total $CaSO_4$: refers to the sum of the percentage contents of gypsum and basanite.

Phases	Instrument 1			Instrument 2		
	XRD Rietveld WPC^{NC} (wt%)	XRD Rietveld WPC (wt%)	XRD Rietveld WPC-SF (wt%)	XRD Rietveld $WPC\text{-}2^{NC}$ (wt%)	XRD Rietveld WPC-2 (wt%)	XRD Rietveld WPC-SF-2 (wt%)
Alite M3	39,0	43,6	43,5	41,3	42,1	43,0
Alite M1	26,7	21,9	24,1	25,3	24,1	25,0
B-belite	22,3	22,3	22,2	22,2	23,2	23,4
γ-belite	1,9	2,5	2,1	1,9	1,8	1,8
C_3A	2,8	3,2	1,7	2,7	3,0	1,8
Portlandite	1,0	1,1	0,4	1,7	1,4	1,0
Calcite	0,8	0,5	0,6	0,6	0,8	1,1
Gypsum	3,6	2,3	1,3	3,1	2,4	0,0
Basanite	1,9	2,6	4,0	1,3	1,2	2,9
Total alite	**65,7**	**65,5**	**67,6**	**66,6**	**66,2**	**68,0**
Total belite	**24,2**	**24,8**	**24,3**	**24,1**	**25**	**25,2**
Total $CaSO_4$	**5,5**	**4,9**	**5,3**	**4,4**	**3,6**	**2,9**
R_{wp}	*11,2*	*6,8*	*6,5*	*7,8*	*6,5*	*6,1*
GOF	*4,6*	2,9	*2,7*	*5,5*	*4,6*	*4,3*

The Rietveld refinement was performed with and without the PO models (March Dollase and Spherical Harmonics). The use of PO models resulted in a better refinement considering only R_{wp} and GOF factors (Table 2). However, the use of these

models might reduce the accuracy of the quantification of other phases without any PO. The two alite polymorphs M3 and M1 are difficult to quantify individually by XRD due to their close similarities in XRD spectra. However, their quantified sum seems to be fairly constant independently of the analysis, method, and instrumentation. Since the reactivity and other properties of the alite polymorphs are almost identical, the uncertainty of their individual quantification has no practical relevance.

The followed methodology in this project can lead to 2% or less variation in phases content. It is shown in Table 2 how the SF addition increases the variation of quantification of minor phases for the same WPC refined with the same software and method. On the other hand, using a different instrument and configuration leads to a variation of no more than 1.5%.

The preferred orientation of phases should be analyzed carefully. For this particular applied method, the total $CaSO_4$ content did not vary more than 1% between the refinements with and without SF. However, it was mentioned that for a specific phase determination, other methods might be applied to have more precise results.

4 Conclusions

The following conclusions can be drawn for the specific WPC evaluated in this study:

1. The high intensity of gypsum in the plane 020 due to preferred orientation was confirmed by using a dry mix of 5% silica fume and 95% white Portland cement.
2. The SF addition method can significantly reduce the intensity and PO of some phases.
3. Statistically, the use of PO models improves refinement.
4. The refinement method used in this project gives an approximately 2% variation (max.) in the quantification of samples measured in different instruments and measurement configurations.

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