The longer the better? The impact of XRD measurement time on Portland clinker quantitative phase analysis results

Quanto mais longo, melhor? O impacto do tempo de medição de DRX nos resultados da análise quantitativa de fase de clínquer Portland

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ABSTRACT

This work assessed the role of the XRD measurement time (0.5 to 40 h) and step sizes (0.010 and 0.020°) on the quantitative phase analysis of a Portland clinker. Synchrotron XRD was used as benchmarking. Rietveld quantitative phase analysis revealed that while the total C_3S and C_2S contents were not significantly affected by the measurement condition (among the laboratory XRD data), longer measurements (4 and 40 h) yielded higher C_3S M3 contents, approaching the synchrotron data. Furthermore, measurement times of 0.5 and 1 h yielded higher orthorhombic C_3A (double) and lower C_4AF (2 wt%) than the 40 h measurement, related to the high signal overlapping of the aluminate phases. Increasing the measurement time reduced the R_{wp} value from 6.6 to 4.3. Overall, measurements longer than 2 h did not affect the total silicates contents nor the aluminates quantification (total and polymorphs), while C_3S polymorphism quantification was not affected for measurements longer than 4 h.

Keywords: X-ray diffraction; XRD; RQPA; Rietveld refinement; Portland clinker.

Resumo

Este trabalho avaliou o papel do tempo de medição por DRX (0,5 a 40 h) e dos tamanhos de passo (0,010 e 0,020°) na análise quantitativa de fases de um clínquer Portland. O DRX por luz síncrotron foi utilizado como comparativo. A análise quantitativa de fases pelo método de Rietveld revelou que, enquanto os teores totais de C_3S e C_2S não foram significativamente afetados pelas condições de medição (entre os dados de DRX de laboratório), medições mais longas (4 e 40 h) apresentaram maiores teores de C_3S M3, aproximando-se dos dados de síncrotron. Além disso, tempos de medição de 0,5 e 1 h resultaram em maiores teores de C_3A ortorrômbico (o dobro) e menores teores de C_4AF (2% em massa) em comparação com a medição de 40 h, devido à alta sobreposição de sinal das fases aluminatos. O aumento do tempo de medição reduziu o valor de R_{wp} de 6,6 para 4,3. De forma geral, medições superiores a 2 h não afetaram os teores totais de silicatos nem a quantificação dos aluminatos (totais e polimorfos), enquanto a quantificação dos polimorfos de C_3S não foi afetada para medições superiores a 4 h.

Palavras-chave: Difração de raios X; DRX; AQFR; Refinamento Rietveld; Clínquer Portland.

1 INTRODUCTION

X-ray diffraction (XRD) is a technique that has been increasingly growing to assess Portland clinker/cement mineralogical composition, both for quality control in the industry and for academic research. Intuitively, “data quality” may impact the quantitative phase analysis (QPA) results [1]. Factors related to the instrumental/measurement setup can affect such quality in terms of signal-to-noise relation, radiation, and the so-called peak profile aberrations (*e.g.*, axial divergence, tube tails, *etc.*). Measurement parameters such as

step size and scanning speed also affect statistics and peak resolution [2], potentially affecting the QPA results. However, extensive scans may evidence the above-mentioned aberrations, as pointed out by Toby [3]. In this scenario, the measurement parameters choice should consider the data quality required and obviously the time available, especially in the context of routine, quality control measurements.

This work assessed the effect of the measurement time (from 0.5 to 40 h) and step size (0.010 and 0.020°) in the quantitative phase analysis results of a grey Portland clinker. The results were compared with synchrotron XRD data.

2 EXPERIMENTAL PROCEDURES AND DATA ANALYSIS

A grey Portland clinker (PC) was used, with a media particle size of 12.9 µm, density of 3.24 g/cm³, and the following chemical composition: SiO_2 = 20.4%, Al_2O_3 = 5.2%, Fe_2O_3 = 3.6%, CaO = 64.8%, MgO = 1.6%, SO_3 = 1.2%, K_2O = 1.0%, Na_2O = 0.5%, and loss on ignition (950°C) = 0.6%. Laboratory XRD (LXRD) measurements in flat samples were conducted using a D6 Phaser (Bruker) diffractometer operating with CuK$\alpha_{1,2}$ radiation (λ = 1.54 Å) at 40 kV and 15 mA, equipped with an SSD160-2 detector with a 4.15° angular window. A fixed 0.5° divergence slit was set in the incident beam, a 2.5° Soller slit and a Ni filter was set in the diffracted beam, and a beam knife was placed 3.0 mm above the sample to reduce air scattering. Scans were collected in the 10-70° 2θ range. The two step sizes (0.010 and 0.020°) and five total measuring times (40, 4, 2, 1, and 0.5 hours) were used, yielding maximum intensities from 9.6 to 398k counts. A PC sample was backloaded into the sample holder to minimize preferred orientation, and the very same sample was used for all LXRD measurements to avoid introducing additional variability related to sampling and preparation. In addition, synchrotron XRD (SXRD) measurements were conducted in capillary samples (1.0 mm Kapton sample holder) at the EMA beamline of Sirius/LNLS with λ = 0.62 Å and a 0.003° step size. More details on the SXRD measurements can be found elsewhere [4]. Rietveld quantitative phase analysis (RQPA) was conducted using TOPAS v7 software (Bruker) and ICSD database. The refinement procedures followed Ref. [5]. The presence of the C_3A polymorphs and alkali sulfate(s) were confirmed in SAM-treated samples. In summary, the background (6th order Chebyshev), lattice parameters (constrained to ±1% from the original value), and the (Lorentzian) crystallite size were refined, besides preferred orientation for C_3S and portlandite.

3 RESULTS AND DISCUSSION

Table 1 shows the RQPA results of PC. The total contents of C_3S and C_2S were not significantly affected by the measurement condition (considering the estimated error), even when comparing LXRD with SXRD. In turn, the measurement conditions affected the polymorphs contents – especially for C_3S. SXRD yielded higher C_3S M3 than LXRD (except for the 0.5 h measurement) and this can be partially associated with preferred orientation (6 0 -6 for C_3S M3 and 1 0 1 for C_3S M1), minimized using capillary sample holder in SXRD as discussed in Ref. [4]. When comparing the LXRD data with the 0.01° step size, one can see that increasing the measurement time increased the C_3S M3 content, approaching the SXRD results. This may be associated with better statistics due to longer data collection, which may also minimize preferred orientation issues. Regarding aluminates, the C_3A and C_4AF contents were affected by the measurement condition. The measurement times from 2 to 40 hours yielded equivalent contents of the C_3A polymorphs, total C_3A, and C_4AF, while the shorter measurement times (1 and 0.5 h) led to overestimations of C_3A, especially for the orthorhombic polymorph, to the point that the shortest measurement yielded the double of C_3A than the longest measurement (4.8 wt% *vs.* 2.4 wt%). In addition, these two shorter measurement times yielded lower C_4AF contents, especially for 0.5h_0.02°. This can be associated with the signal overlapping of the aluminate phases, as demonstrated in Figure 1: the longer measurement time and shorter step size allowed for a better pattern fit within the 33.0-34.2° 2θ range. Besides, the LXRD measurements at longer times and shorter step size led to aluminates contents closer to the SXRD data, although not equal.

Different agreement indices are used to assess the "fitting quality", *i.e.*, the closeness between the experimental/measured data and the proposed model. The weighted profile R-factor (R_{wp}) of the refinements is shown in Table 1. Increasing the measurement time generally reduced the R_{wp}, indicating a fit quality improvement. This can be explained by the fact that longer measurement times (up to a certain limit) yield better statistics [1]. This was more evident for the 1h_0.01°and 0.5h_0.02° measurements which had a significantly higher R_{wp} than the longer measurements. Figure 2(a) shows that the 40h-long measurement led to a better signal-to-noise ratio than the 1h measurement, reducing the difference between the measured data and the proposed model, and consequently reducing the R_{wp}. This occurred even though longer measurement

times may evidence some features related to the experimental setup and/or sample impurities [3], as exemplified in Figure 2(b,c) where the longer measurements underlined the presence of impurities – pointed out as (i), and absorption edge (due to the Ni filter use) – pointed out as (ii). Nonetheless, these features can be appropriately modeled by including these eventual impurities in the refinement and using a physically-based profile fit such as the FPA (used here) [6]. Despite that, all the LXRD measurements yielded lower R_{wp} than SXRD. Although the synchrotron X-ray emission is "cleaner" (fully monochromatic), two factors may have led to this trend: (a) the convolution-based approach used to model the line profile of SXRD is not entirely based on physically meaning convolutions such as the full axial model of FPA, and (b) although SXRD measurement was conducted with a high-speed detector, it took 25 minutes (reaching ~15k counts) which is significantly shorter than most of the LXRD measurements conducted here (reaching up to ~400k counts).

Table 1: RQPA results for the different measurement times (in wt%). Values in parentheses correspond to the estimated error.

Phase/measurement	SXRD*		40h_0.01°		4h_0.01°		2h_0.01°		1h_0.01°		0.5h_0.02°	
C_3S M1	24.1	(0.4)	32.6	(0.5)	33.8	(0.5)	36.3	(0.5)	37.8	(0.7)	35.8	(1.1)
C_3S M3	52.9	(0.4)	43.4	(0.5)	43.1	(0.6)	40.5	(0.6)	38.9	(0.8)	41.4	(1.1)
Total C_3S	**77.1**	**(0.6)**	**76.0**	**(0.7)**	**76.9**	**(0.8)**	**76.8**	**(0.8)**	**76.7**	**(1.1)**	**77.1**	**(1.5)**
α'_H C_2S	1.3	(0.2)	0.5	(0.2)	0.5	(0.2)	0.6	(0.2)	0.2	(0.3)	0.2	(0.5)
β-C_2S	1.7	(0.2)	2.5	(0.3)	1.6	(0.2)	2.2	(0.2)	2.4	(0.3)	2.8	(0.5)
Total C_2S	**3.0**	**(0.2)**	**3.0**	**(0.3)**	**2.2**	**(0.3)**	**2.8**	**(0.3)**	**2.6**	**(0.5)**	**3.0**	**(0.7)**
C_3A cubic	2.7	(0.2)	3.8	(0.3)	3.5	(0.3)	3.2	(0.3)	3.2	(0.5)	3.5	(0.7)
C_3A orthorhombic	2.5	(0.2)	2.4	(0.3)	3.0	(0.3)	3.3	(0.3)	4.9	(0.5)	4.8	(0.7)
Total C_3A	**5.2**	**(0.3)**	**6.2**	**(0.4)**	**6.4**	**(0.5)**	**6.6**	**(0.5)**	**8.0**	**(0.7)**	**8.3**	**(0.9)**
C_4AF	12.3	(0.3)	11.3	(0.3)	11.5	(0.3)	11.1	(0.4)	10.5	(0.5)	9.3	(0.6)
Aphthitalite	1.7	(0.0)	2.3	(0.1)	2.1	(0.1)	2.1	(0.1)	1.2	(0.1)	1.2	(0.1)
Periclase	0.4	(0.0)	0.4	(0.0)	0.5	(0.0)	0.4	(0.0)	0.6	(0.1)	0.6	(0.1)
Portlandite	0.1	(0.1)	0.7	(0.1)	0.2	(0.1)	0.1	(0.1)	0.1	(0.2)	0.1	(0.3)
Quartz	0.2	(0.0)	0.2	(0.0)	0.2	(0.0)	0.2	(0.0)	0.2	(0.1)	0.3	(0.1)
Rwp	10.4		4.3		4.6		5.1		6.6		6.5	

*SXRD: Synchrotron XRD data.

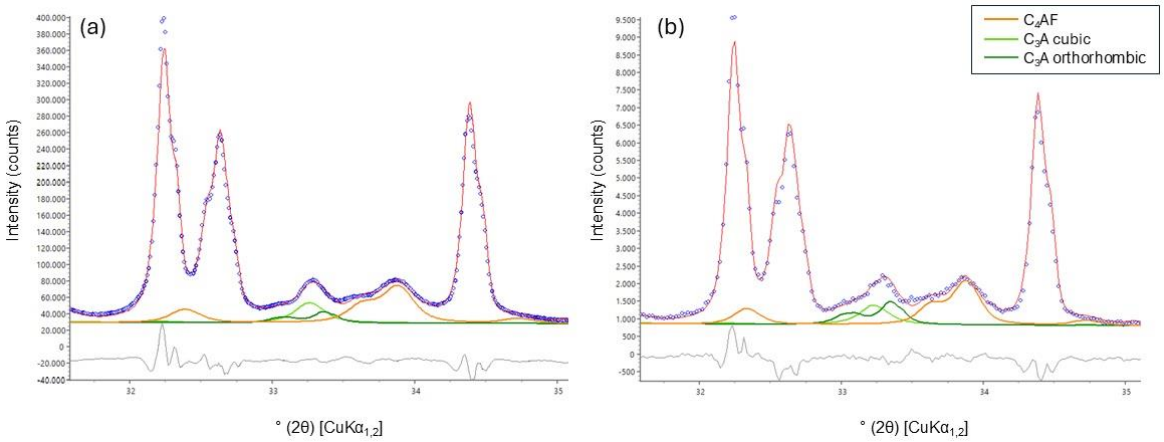

Figure 1: Selected range of the patterns of PC, with the refined contribution of C_3A and C_4AF. (a) 40 hours with step size = 0.01°; (b) 0.5 hours with step size = 0.02°. Note: blue dots = measured data; red line = fit; grey line = difference.

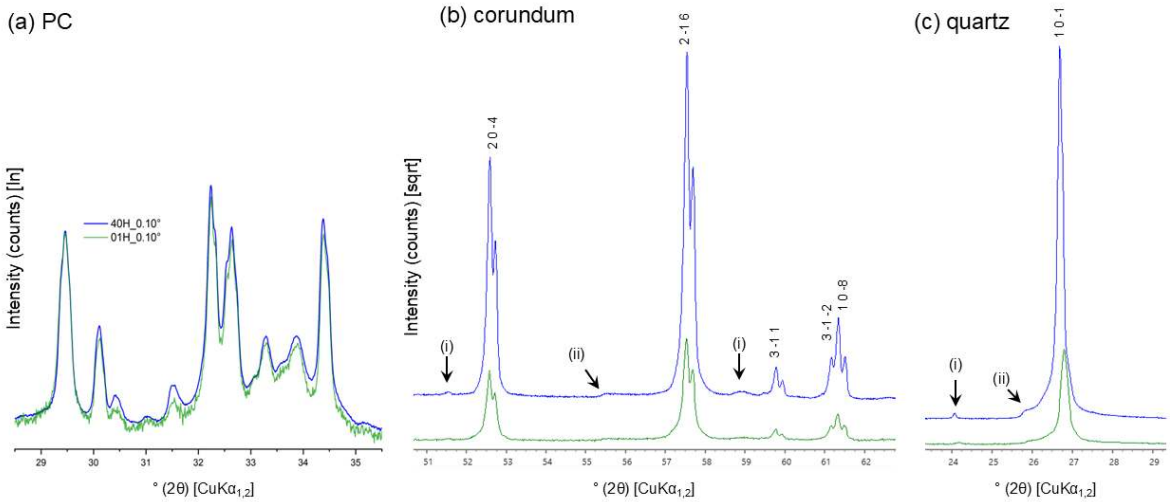

Figure 2: Selected ranges of the XRD patterns of: (a) PC measured for 40 and 1 hour (step size = 0.01°) – the Y-axes were rescaled to match the intensity of both patterns; (b) corundum and (c) quartz standard samples, measured for 20 hours and step size = 0.01° (top/blue) and 35 minutes with a step size = 0.015° (bottom/green). Note: (i) correspond to impurities; (ii) absorption edge (Ni filter).

4 CONCLUSION

This work assessed the role of the XRD measurement time (0.5 to 40h) and step sizes (0.010 and 0.020°) on the quantitative phase analysis of a Portland clinker. Synchrotron XRD was used as benchmarking. The total C_3S and C_2S contents were not affected by the measurement time or step size, while the C_3S polymorphs were significantly affected by it when comparing the 40 and 4-h measurements with the other measurements, reaching differences of up to 5.2 wt% for a given polymorph. Regarding aluminates, both the total and polymorphs C_3A, and the C_4AF contents were affected by the measuring conditions. Shorter measurement times (0.5 and 1h) led to orthorhombic C_3A overestimation (by 100%) and C_4AF underestimation (up 2 wt% lower) when compared with the 40h measurement. Increasing the measurement time progressively yielded a better fit in terms of R_{wp}, reducing it from 6.5-6.6 for the two quickest measurements to 4.3 for the 40h-long scan, associated with better statistics. Overall, for the experimental setup used here, XRD measurements longer than 4 h did not result in significant differences between the phase contents – polymorphs and total contents – nor terms of R_{wp}, while shorter measurements (with either step size used) did.

5 AGRADECIMENTOS

[omitir durante a submissão, blind review].

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