THE EXISTENCE OF NON-CRYSTALLINE PHASES IN ANHYDROUS PORTLAND CLINKER: AN X-RAY DIFFRACTION INVESTIGATION

A existência de fases não-cristalinas no clínquer Portland anidro: Uma investigação por difração de raios X

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ABSTRACT

Portland clinker (PC) may contain an amorphous or non-crystalline (ACn) fraction most likely coming from poor phase crystallization, although there is not a consensus on that. This work assessed the presence of ACn in eight commercial PC, using CuKα$_{1,2}$ and strictly monochromatic CuKα$_1$ radiation and the external standard method. The results showed that CuKα$_{1,2}$ radiation generally yielded equivalent or higher ACn contents than CuKα$_1$ measurements. Four clinkers showed ACn contents of 8.6-12.2 wt% and 4.5-8.3 wt% respectively for CuKα$_{1,2}$ and CuKα$_1$ measurements, above the precision threshold. Thus, anhydrous Portland clinker may present an important ACn content.

Keywords: XRD; Portland clinker; ACn; Amorphous; Rietveld refinement.

RESUMO

O clínquer Portland (CP) pode conter uma fração amorfa ou não cristalina (ACn) provavelmente proveniente da má cristalização de fases, embora não haja um consenso sobre isso. Este trabalho avaliou a presença de ACn em oito CP comerciais, utilizando radiações CuKα$_{1,2}$ e monocromática CuKα$_1$, e o método do padrão externo. Os resultados mostraram que a radiação de CuKα$_{1,2}$ geralmente levou à teores de ACn equivalentes ou maiores do que as medições em CuK$_{α1}$. Quatro clínquer apresentaram teores de ACn de 8,6-12,2% em peso e 4,5-8,3% em peso, respectivamente para medições em CuKα$_{1,2}$ e CuK$_{α1}$, acima do limite de precisão. Assim, o clínquer Portland anidro pode apresentar um importante teor de ACn.

Palavras-chave: DRX; Clínquer Portland, ACn; Amorfo; Refinamento Rietveld.

1 INTRODUCTION

Although Portland cement has been used for about 200 years, some questions remain. One of these questions is if there are amorphous or non-crystalline (ACn) phases in anhydrous clinker. The non-crystalline fraction in anhydrous cement can rise from the melt residue that has failed to crystallize (SUHERMAN *et al.*, 2002), most likely composed of aluminate-rich phase (DE LA TORRE *et al.*, 2017). X-ray diffraction (XRD) coupled with Rietveld quantitative phase analysis (RQPA) has been successfully used over the past decades to evaluate the mineralogical composition of anhydrous and hydrated PC samples.

Snellings *et al.* (2014) attributed the possible presence of such non-crystalline phases to the poor comminution of the material for XRD analysis, reporting no significant ACn content for a CEMI PC micronized with a McCrone mill for 20 min in isopropanol compared to around 6 wt% ACn for the as-received PC. However, De la Torre *et al.* (2017) used the same device to mix quartz as internal standard in the same type of PC, reporting 17 wt% ACn for the sample milled for 15 min vs 19 wt% for the sample homogenized in agate mortar. Furthermore, De la Torre *et al.* (2001) reported an average ACn content of 19 wt% (determined through the internal standard method) for monoclinic C_3S synthesized in the laboratory with median particle size of 3 µm. Jansen *et al.* (2011) attributed it to parameters refined in the RQPA such as the atomic displacement in the structure of the external standard material and the microstrain of alite.

However, many recent works from highly respected research groups using rigorous experimental and data analysis procedures reported the presence of significant contents of amorphous or crystalline non-quantified (ACn) in anhydrous PC (6-20 wt%). Ma *et al.* (2021) reported ACn values of 16.6 wt% and 18.1 wt% for two Portland clinkers, using laboratory XRD (LXRD) and the external standard method. Mejdi *et al.* (2020) reported an ACn content of 12.8 wt% in OPC, determined by LXRD and the external standard method. Shirani *et al.* (2021) reported an ACn content of 23.5 wt% for anhydrous PC using LXRD and the internal standard method. Morales-Cantero *et al.* (2022) found ACn of 8.8 wt% and 18.9 wt% for anhydrous PC, and 12 wt% for anhydrous white PC using synchrotron XRD (SXRD) and the internal standard method. De Matos *et al.* (2022) reported an ACn of 20.60 wt% in anhydrous OPC, determined by both internal and external standard methods using LXRD. Suherman *et al.* (2002) assess two commercial clinkers and three NIST standard clinkers (RM8486, RM8487, and RM8488) through LXRD and SXRD using the internal and external standard methods. The authors reported ACn values of 7.2-15.9 wt% for the commercial clinkers, and 6.1-14.0 wt% for the standard clinkers. Besides, ACn was observed even after silicate dissolution.

The presence of ACn in anhydrous PC brings some critical uncertainties: *(i)* QPA results for anhydrous cement may not be accurate, and consequently, input information (*e.g.*, for thermodynamic modelling) is not reliable; *(ii)* the ACn fraction in hydrated samples, which contain non-crystalline phases deriving from cement hydration (*e.g.*, C-S-H), may be partially composed of ACn from anhydrous cement, making it difficult to determine the phase assemblage accurately; and *(iii)* the effect of ACn fractions on the hydration and final properties of cement is unknown. In this context, the current work assessed the existence of ACn in eight anhydrous Portland clinkers measured with two XRD setups.

2 MATERIALS AND METHODS

2.1 MATERIALS

Eight Portland clinkers were assessed, being seven grey (PC-A/G) and one white (WPC). The clinkers were received in the pallet form and milled in the laboratory with a jar mill until reaching a particle size distribution compatible with a commercial PC, reaching D_{v10}, D_{v50} and D_{v90} respectively within 2-3, 11-15, and 23-31 µm (measured through laser diffraction). Table 1 shows the chemical composition of the clinkers obtained through X-ray fluorescence, and their respective mass absorption coefficient (MAC) values for CuKα radiation.

Table 1: Chemical composition of the clinkers (wt%).

Property	PC-A	PC-B	PC-C	PC-D	PC-E	PC-F	PC-G	WPC
SiO_2	20.37	19.42	20.04	20.91	19.53	20.78	19.44	24.54
Al_2O_3	5.23	4.20	3.98	4.50	4.55	4.92	4.51	4.29
Fe_2O_3	3.56	3.74	3.12	2.63	2.27	4.13	3.22	0.24
CaO	64.83	60.24	60.49	65.72	62.35	63.99	62.26	69.70
MgO	1.61	6.59	7.54	1.06	3.20	0.51	6.98	0.39
SO_3	1.19	1.58	1.19	0.82	1.70	1.38	1.48	0.13
K_2O	1.01	0.24	1.36	0.35	1.24	0.68	0.85	0.04
Na_2O	0.49	0.09	0.19	0.14	0.47	0.13	0.24	0.00
P_2O_5	0.14	0.81	0.09	0.14	0.13	0.17	0.07	0.05

TiO_2	0.27	0.52	0.21	0.29	0.22	0.27	0.31	0.10
Mn_2O_3	0.06	0.20	0.15	0.08	0.08	0.16	0.07	0.01
SrO	0.61	0.79	0.03	0.32	0.11	0.25	0.16	0.04
ZrO_2	0.03	0.25	0.02	0.10	0.04	0.10	0.05	0.02
LoI*	0.59	1.26	1.54	2.92	4.07	2.46	0.28	0.42
MAC** (cm^2/g)	100.90	96.38	95.31	98.47	94.99	100.15	97.13	97.67

*LoI: loss on ignition at 950°C; **MAC: mass absorption coefficient.

2.1 EXPERIMENTAL PROCEDURES AND DATA ANALYSIS

Laboratory XRD experiments were conducted in two different experimental setups: *(i)* $CuK\alpha_1$: recorded using an Empyrean (PANalytical) diffractometer equipped with a PIXcel^{2D} detector in Bragg-Brentano reflection mode, operating at 40 kV and 40 mA, using strictly monochromatic $CuK\alpha_1$ radiation (λ = 1.5406 Å). The optics consisted of a hybrid monochromator (composed of a parabolic X-ray mirror and a 2-crystal Ge (220)) and 1/4° fixed divergence slit in the incident beam; a 2.3° Soller slit in the diffracted beam. The step size was 0.0131° and the total counting time was 600 min; *(ii)* $CuK\alpha_{1,2}$: recorded using an X`Pert Pro (PANalytical) diffractometer equipped with an X´Celerator detector in Bragg-Brentano reflection mode, operating at 45 kV and 40 mA, using $CuK\alpha_{1,2}$ radiation (λ = 1.5418 Å). The optics consisted of a 2.3° Soller slit, a 1° fixed anti-scatter slit, a 1/2° fixed divergence slit, and a 10 mm beam mask in the incident beam; a 2.3° rad Soller slit, a 5.0 mm fixed anti-scatter slit, and a 0.020 mm Ni filter in the diffracted beam. The step size was 0.0167° and the total counting time was 120 min. Knife edge were used in both experiments to prevent near-sample-surface air scattering to be detected.

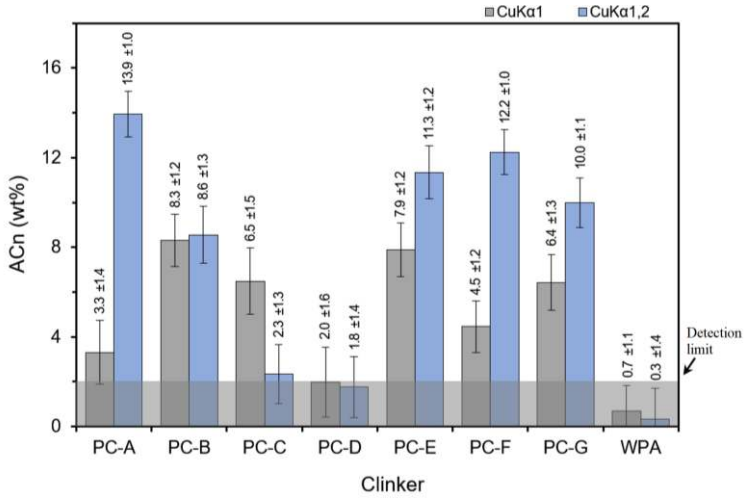
TOPAS v5 (Bruker) software was used for RQPA, with the following ICSD structures: C_3S M3 (94742); C_3S M1[1]; C_3S T3 (162744); β-C_2S (81096); α'_H C_2S (81097); C_3A cubic (1841); C_3A orthorhombic (1880); C_4AF (98839); periclase (9863); portlandita (202220); aphthitalite (26018); goergeyite (30790); syngenite (157072); kotoite (94630); and arcanite (79777). It is stressed that these models accommodate foreign elements such as MgO (in C_3S M3 and periclase) and alkalis (in C_3A orthorrombic and alkali sulfates) found in Table 1. The fundamental parameters approach with the full axial model (CHEARY; COELHO, 1992) was used for line profile fitting. For the Rietveld analysis, the global parameters refined were the background (2nd order Chebyshev polynomial) and the sample displacement. The same phases were included in all the refinements: C_3S M1 and M3 (for PC)/T3 (for WPC), β and α'_H C_2S, cubic and orthorrombic C_3A, C_4AF, lime, portlandite, periclase, aphthitalite, syngenite, goergeyite, and quartz. Phases with less than 0.1 wt% and/or with no evident peaks were removed from the analysis. For the individual phases, the scale factor, lattice parameters (allowing for ±1% variation from the original values), and Lorentzian crystallite size were refined, besides the Gaussian strain for C_4AF. The preferred orientation of C_3S M3 (6 0 -6) and C_3S M1 (1 0 -1) were refined using the March-Dollase (DOLLASE, 1986) approach constrained within 0.7-1.0. The ACn content was determined by the external standard method and G-factor approach (JANSEN *et al.*, 2011) using a corundum (α-Al_2O_3) as the external standard, measured under the conditions *(i)* and *(ii)* detailed above.

3 RESULTS AND DISCUSSION

Figure 1 shows the ACn content of the clinkers for both $CuK\alpha_1$ and $CuK\alpha_{1,2}$ measurements. The detection limit was considered as 2 wt% based on previous literature reports for RQPA of PC (DE MATOS *et al.*, 2022; LEÓN-REINA *et al.*, 2009; SNELLINGS *et al.*, 2014).

[1]Not on ICSD; superstructure from: M.N. De Noirfontaine, M. Courtial, F. Dunstetter, G. Gasecki, M. Signes-Frehel, Tricalcium silicate Ca_3SiO_5 superstructure analysis: A route towards the structure of the M1 polymorph, Zeitschrift Fur Krist. 227 (2012) 102–112.

Figure 1: Amorphous or crystalline non-quantified (ACn) fraction of the clinkers. Note: (i) error bars correspond to the estimated error; (ii) the detection limit was estimated as 2 wt% based on previous literature reports (DE MATOS *et al.*, 2022; LEÓN-REINA *et al.*, 2009; SNELLINGS *et al.*, 2014).



In general, CuK$\alpha_{1,2}$ radiation yielded equivalent or higher ACn contents than monochromatic CuKα_1 radiation – except for PC-C. This may be associated with the higher difficulty in properly distinguishing the clinker phases with highly overlapped peaks in CuK$\alpha_{1,2}$ measurements even though the instrumental contribution was well described by the fundamental parameters approach (checked with a NIST LaB_6 sample, not shown), in addition to the fact that using duochromatic radiation increases the correlation in data analysis (CUESTA *et al.*, 2015). Nonetheless, the clinkers CP-B, -E, -F and -G yielded ACn had ACn contents within 8.6-12.2 wt% for CuK$\alpha_{1,2}$ measurements, and 4.5-8.3 wt% for CuKα_1 measurements. These values are beyond the detection limit assumed for both measuring setups, even considering the estimated error (up to 1.3 wt% for these clinkers). Thus, the results suggest that the presence of ACn in Portland clinker should not be discharged.

4 CONCLUSION

XRD measurements with CuK$\alpha_{1,2}$ and monochromatic CuKα_1 radiation were conducted in eight anhydrous Portland clinkers, and the external standard method was employed to determine their amorphous or non-crystalline (ACn) content. The results showed that CuK$\alpha_{1,2}$ radiation yielded equivalent or higher ACn contents than monochromatic CuKα_1 radiation. Despite that, using either radiation did not lead different conclusions regarding the presence of ACn. Four clinkers presented ACn contents of 8.6-12.2 wt% for CuK$\alpha_{1,2}$ measurements and 4.5-8.3 wt% for CuKα_1 measurements, beyond the detection limit threshold (2 wt%) even considering the estimated error (≤1.3 wt%). Thus, anhydrous Portland clinker may present an important ACn content, in line with recent literature reports.

5 ACKNOWLEDGMENTS

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