High-resolution synchrotron powder diffraction analysis of ordinary Portland cements: Phase coexistence of alite

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Abstract

The mineralogical composition of four commercial and NIST RM-8488 Portland clinkers have been analysed by Rietveld methodology using high-resolution synchrotron X-ray powder diffraction data. Alite phase coexistence has been observed in four patterns. White Portland clinkers show a single alite or a very small amount of a second alite with smaller volume due to higher magnesium content. Grey Portland clinkers show a much pronounced alite phase coexistence which has been related to higher magnesium contents. Details about these analyses are given. Furthermore, the full mineralogical composition (including the non-diffracting content) has been determined from the overestimation of the added standard, $\alpha$-Al$_2$O$_3$, in the Rietveld analyses. White clinkers contain $\sim$15 wt.% of non-diffracting content while this fraction is much smaller in grey clinkers, $\sim$7 wt.%.

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1. Introduction

There is a great interest in the Quantitative Phase Analysis (QPA) of Ordinary Portland Cements (OPC) as their final performances depend on the mineralogical composition (and texture).

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Rietveld analysis [1] via Laboratory X-ray Powder Diffraction (LXRPD) is the most powerful as well as available technique for obtaining QPA. However, LXRPD data may contain systematic errors such as strong preferred orientation, optical aberrations which change with $2\theta$, microabsorption and strong peak overlapping of the different phases. Furthermore, the small mean penetration depth ($\sim$25 μm for Cu Kα) may lead to poor particle statistics if the sample is not rotated, especially
for the large alite crystals. Hence, in order to validate the QPA obtained by LXRPD, it is desirable to compare the obtained results with an analytical technique that has not such drawbacks.

High-Resolution Synchrotron X-ray Powder Diffraction (HRSXRPD) overcomes most of the drawbacks described above. Rotating capillary geometry (transmission) avoids preferred orientation. High energy X-rays minimize microabsorption and a large amount of sample is tested leading to good particle statistics. High-resolution data minimize the overlapping and parallel synchrotron X-rays geometry, with an analyser crystal, do not show optical aberrations. Hence, we have previously reported HRSXRPD data for Portland cement to achieve good QPA of commercial OPC [2] and to show that accurate Rietveld QPA for cements can be obtained [3]. Other authors have also used synchrotron radiation for the quantitative phase analysis of cements [4,5].

QPA using the Rietveld method is standardless but the crystal structures of all phases must be known as the process comprises the comparison of the measured and calculated patterns. This methodology has been applied to grey and white Portland clinkers and cements of different complexities [6–9] including the quantification of the non-diffracting contents [4,10]. It is also being adapted to carry out the on-line mineralogical analyses in cement factories [11,12]. The four main phases in OPC are alite (C₃S or Ca₃SiO₅), belite (C₂S or Ca₂SiO₄), aluminate (C₃A or Ca₃Al₂O₆) and ferrite (C₄AF or Ca₄Al₂Fe₂O₁₀).

In this work, we present results of QPA of commercial OPC (grey and white) by using HRSXRPD including the quantification of the non-diffracting contents. We have also analysed a NIST RM-8488 clinker.

2. Experimental section

2.1. Samples

Two commercial white Portland clinkers (W1, W2), two commercial grey Portland clinkers (G1, G2) [all from different factories] and a NIST RM-8488 clinker have been analysed by HRSXRPD. The five samples were mixed with α-Al₂O₃ standard.

2.2. X-ray data collection

HRSXRPD patterns were collected on ID31 powder diffractometer of ESRF, European Synchrotron Radiation Facility, (Grenoble, France) using a short penetrating wavelength $\lambda = 0.40027 \text{ Å} (30.97 \text{ keV})$ selected with a double-crystal Si(111) monochromator and calibrated with Si NIST ($a = 5.43094 \text{ Å}$). The Debye–Scherrer configuration was used with the samples loaded in borosilicate glass capillaries, diameter of 2 mm, and rotating during data collection. The overall measuring time was $\approx 100 \text{ min}$ to have very good statistics over the wide angular range $2.5–30^\circ$ (in 2h) ($9.15–0.77 \text{ Å}$). The data from the multi-analyser Si(111) stage were normalised and summed into 0.003° step size. Powder data for one sample, G1, was collected with a slightly different wavelength, $\lambda = 0.42970 \text{ Å}$.

2.3. Synchrotron X-ray data analysis

The powder patterns were refined by the Rietveld method with GSAS suite of programs [13] by using a Lorentzian peak shape function. The references of the crystal structures for the cement phases were reported in [3] including that of the corundum standard. The refined overall parameters were: background coefficients, cell parameters, zero-shift error, peak shape parameters and phase fractions. Brindley correction was not necessary. The peak shape parameter LY was refined freely for each phase and the anisotropic peak shape parameter (STEC in GSAS program) was refined when necessary.

3. Results and discussion

3.1. Phase coexistence of alite

Fig. 1 displays a selected region of W1, W2, G2 and RM-8488 HRSXRPD patterns. Alite is the high temperature monoclinic (MIII) polymorph of Ca₃SiO₅ [14] present in OPC since it is stabilised.
at room temperature by the presence of foreign ions. W1 does not show alite phase coexistence, see Fig. 1, whereas, W2, G1, G2 and RM 8488 display this coexistence. Fig. 2 shows a selected region of the Rietveld plot for G1 with peaks from the different phases labelled, as an example of the quality of the fits. Two alites computed with the same structural description [14] but with different unit cells volumes were introduced to perform the refinements/quantifications. Rietveld results for all samples are given in Table 1. Table 2 gives the elemental compositions measured by X-ray Fluorescence for all clinkers.

Alite MIII (monoclinic) is stabilised mainly by the substitution of Ca$^{2+}$ by Mg$^{2+}$. White Portland clinkers contain very small amounts of Mg$^{2+}$ and...
consequently the volumes of C₃S of these samples are larger, see Table 1. Furthermore, alite phase coexistence, if present, is very small (W2 clinker contains 2.0 (1)% of the C₃S phase with the smallest volume). Grey clinkers (G1 and G2) have higher contents of Mg²⁺ and they display overall smaller volumes, see Table 1. The amount of the alite phase with the smallest volume (119.9 Å³ per formula unit) is higher for the analysed grey clinkers, see Table 1. Additionally, they have a small amount of MgO as free periclase. RM-8488 clinker also shows two alites with different volumes and it contains less Mg²⁺, see Table 2, and no periclase is present in the pattern. These results indicate that both alite phases contain magnesium cations. However, the Mg²⁺-content in the smallest volume phase is higher. The superstructures of these two coexisting alites should be different but we are using the same structural description in the analyses since there are no alternative structures available. More synthetic and structural studies are needed to properly understand and describe the structural role of the impurities (Mg²⁺, Al³⁺, etc.) in the alite(s).

### 3.2. HR-SXRPD and LR-XRPD studies

The Rietveld analytical results given in Table 1 (and those shown in Fig. 1) indicates that the alite phase coexistence is very pronounced in grey clinkers which contain a high amount of magnesium. This is the first direct evidence of alite phase coexistence in commercial OPC which has been possible due to the extreme high resolution of the ID31 synchrotron powder diffraction data. The influence of the alite phase coexistence in the Rietveld analysis of LXRPD data remains to be fully studied. Preliminary results indicate that laboratory data with Cu Kα₁,₂ radiation do not show any signs of phase coexistence. The analyses are good when using a unique structural description for alite. However, when strictly monochromatic
Cu K\(_{\alpha1}\) radiation is used, some signs of phase coexistence are evident in the patterns that need to be taken into account. A full comparison of accurate HRSXRPD analytical results and the mineralogical contents from LXRPD data will be reported elsewhere.

3.3. Non-diffracting content analysis

All clinkers were mixed with \(\alpha\)-Al\(_2\)O\(_3\) in order to indirectly obtain the amorphous contents [15]. This quantification is obtained from the small overestimation of the standard in the Rietveld analyses, see Table 1. Hence, the particle statistics must be very good and HRSXRPD is much better at providing that than LXRPD. Although more analyses are needed, the studied samples indicate that white Portland clinkers contain approximately 15–20 wt.% of non-diffracting/amorphous content. These values for grey OPC clinkers are much smaller and closer to 7–8 wt.% These results are in agreement with the manufacturing processes and other reports [2,4]. The amount of liquid phase in grey-OPC kilns is larger and the particles are better crystallised (low non-diffracting contents), whereas the amount of liquid phase in white-clinker kilns is smaller and so particles grow containing more defects which leads to an increase of the non-diffracting content.

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References