Combined use of laboratory X-ray diffraction and microtomography in early age cement hydration

A. Cuesta, S. Shirani, A.G. De la Torre, I. Santacruz, A. Morales-Cantero, I. Koufany, C. Redondo-Soto, I.R. Salcedo, L. León-Reina and M.A.G. Aranda*

Universidad de Málaga, Málaga, Spain

Email: g_aranda@uma.es, a_cuesta@uma.es, shiva_shirani@uma.es, mgd@uma.es, isantacruz@uma.es, alejandrom@uma.es, imane.k@uma.es, cinthyars@uma.es, inesrs@uma.es, lauralr@uma.es

ABSTRACT

In situ laboratory X-ray powder diffraction (LXRPD) is widely used for studying cement hydration at early ages. However, this approach has limitations due to the intrinsic characteristics of the main methodologies (flat sample and capillary) and their blindness to the amorphous phases and microstructures. In addition, laboratory X-ray microtomography (µ-CT) is being used for several applications but the accuracy of the obtained results is not established. Here, we present an innovative approach where LXRPD and µ-CT data are taken in the same volume of the same hydrating paste within a thick capillary with time. The results from both techniques should agree, resulting in more reliable information. The methodology developed here is based on capillaries of 2 mm of diameter to minimize self-drying and to have very good powder averaging. In this proof-of-principle investigation, µ-CT data have been collected for a PC-42.5R paste, w/c=0.50, at 12 hours and 1, 3 and 7 days, and for LXRPD at 1, 3 and 7 days. Powder diffraction data have been analysed by the Rietveld method and the results have been verified by mass balance calculations. µ-CT data have been segmented. The results indicate that the developed methodology is accurate. The long-term aim of this research is to be able to monitor the reaction of the amorphous components of widely-used supplementary cementitious materials (SCMs) like the amorphous silica in fly/volcanic ashes or the metakaolin in calcined clays.

1. Introduction

The quantitative phase analysis of crystalline phases in hydrating cements by LXRPD is well established (Aranda et al., 2012). Furthermore, the overall amorphous content can be determined by using internal (De la Torre et al., 2001) or external (Jansen et al., 2011) standard approaches. Conversely, the quantitative analysis of the hydrating components and microstructures by µ-CT (Withers et al., 2021) is still challenging (Brisard et al., 2020; Kong et al., 2020). Interested readers are addressed to these two reviews to have better insights about the features that can be studied and eventually quantified by µ-CT. One of the applications of µ-CT is to follow in situ 4D (3D + time) the hydration of cements (Gallucci et al., 2007; Gastaldi et al., 2012). These early works reported the component evolution qualitatively but quantitative data, for instance segmentations, were not reported. Synchrotron µ-CT is being used for in situ characterization of cement hydration (Parisatto et al., 2015; Moradian et al., 2019; Poirier et al., 2022; Vigor et al., 2022), but their limited availability often prevents investigations lasting more than 1-2 days. Moreover, the accuracy of the obtained results was not investigated. Here, we report an investigation for a standard PC-42.5R cement where the evolution of the crystalline phases has been quantitatively determined by the Rietveld method. Moreover, the µ-CT data have been quantitatively analysed and the results agree relatively well with those obtained from the diffraction study.

2. Materials and Methods

2.1 Materials

The employed commercial PC conforms to CEM I 42.5R according to EN 197-1. Pastes were prepared with a water-to-cement (w/c) mass ratio of 0.50, at 25±2 °C and without admixture(s). The paste was loaded in a glass capillary, φ=2 mm, for the X-ray powder diffraction and microtomographic studies.
2.2 Methods

LXRPD measurements for the paste within a capillary of 2 mm of diameter were collected on a D8 ADVANCE (Bruker AXS) diffractometer using strictly monochromatic MoKα₁ radiation (λ=0.7093 Å). The acquisition time per full pattern was 3 h 08 min. Data collection and analysis details are the same than those previously reported (Salcedo et al., 2021) unless the overall acquisition time that it was 1 h longer. Laboratory µ-CT data, for the same paste loaded within the same capillary, were acquired on a SKYSCAN 2214 (Bruker) scanner. Each scan time took 3 h 45 min. Data acquisition and reconstruction protocols are similar to those already reported (Salcedo et al., 2021). The voxel size here is 1.1 µm. For early age in situ studies, the timing is important. Data from both techniques are not taken simultaneously but sequentially. For instance, the 1 d µ-CT dataset started ~22 h after water mixing and finished ~26 h. The powder patterns were collected just after the µ-CT data. Hence, the degree of reactions from LXRPD should be slightly larger than those obtained from µ-CT.

3. Results and discussion

The three powder patterns collected at 1, 3 and 7 days of hydration have been analysed by the Rietveld method. The plots for the patterns taken at 1 and 7 days are shown in Figure 1, as examples. The quantitative results are given in Table 1 together with the Rietveld quantitative phase analysis (RQPA) of the initial cement. The results are obtained in weight percentages and referred to 100 g of paste for a direct comparison. This is done by calculating the mass amount of C-S-H gel, assumed stoichiometry (CaO)₁₈(SiO₂)₄H₂O, knowing the mass ratio between portlandite and the gel, 2.62 (Cuesta et al, 2018). Moreover, the free water, i.e. H₂O in Table 1, is reduced by the amount incorporated in the hydrated phases. These values can also be expressed in vol% considering the mass densities. This will allow us to make a comparison with the results from the µ-CT analyses, see next.

<table>
<thead>
<tr>
<th>time</th>
<th>C₃S</th>
<th>C₃A</th>
<th>C₄AF</th>
<th>Cc</th>
<th>minors$</th>
<th>H₂O²</th>
<th>AFt</th>
<th>CH</th>
<th>C-S-H⁴</th>
<th>He⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>t₀</td>
<td>38.9</td>
<td>8.6</td>
<td>4.5</td>
<td>6.9</td>
<td>3.5</td>
<td>4.3</td>
<td>33.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1 d</td>
<td>15.5</td>
<td>8.3</td>
<td>2.2</td>
<td>6.3</td>
<td>4.8</td>
<td>0.5</td>
<td>19.0</td>
<td>9.1</td>
<td>9.1</td>
<td>25.2</td>
</tr>
<tr>
<td>3 d</td>
<td>7.9</td>
<td>8.9</td>
<td>1.0</td>
<td>4.8</td>
<td>5.3</td>
<td>0.3</td>
<td>14.5</td>
<td>10.7</td>
<td>12.3</td>
<td>34.1</td>
</tr>
<tr>
<td>7 d</td>
<td>6.6</td>
<td>8.6</td>
<td>0.5</td>
<td>4.6</td>
<td>5.0</td>
<td>0.4</td>
<td>13.4</td>
<td>11.3</td>
<td>13.2</td>
<td>36.2</td>
</tr>
</tbody>
</table>

²Cc stands for calcite. Hc stands for hemicarbonate. $Minors are the summary of the remaining crystalline phases including gypsum, bassanite and quartz (from the addition in the cement). ⁴The amounts of H₂O and C-S-H gel are obtained from the known hydration reactions.

We consider that the renormalization to 100 g of paste is correct because three independent verifications. Firstly, belite content should remain constant, within the variability of the analyses, as this phase does not hydrate during the first week. This is indeed the case, see Table 1. Secondly, the theoretical portlandite content can be determined from the degree of reaction of C₃S, (Cuesta et al, 2018). The expected values are 8.9, 11.9 and 12.4 wt% at 1, 3 and 7 days. The values reported in Table 1 are 9.1, 12.3 and 13.2 wt%, respectively; the agreement is remarkable. Moreover, this cement had 3.9 wt% of SO₃ and hence, the maximum amount of ettringite that can be formed would be 13.6 wt%. This value agrees relatively well with the measured AFt content at 7 days, 11.3 wt%, which is still slightly growing. Therefore, the LXRPD study is accurate, and now we focus on the µ-CT study for the same hydrating specimen.
Mounting the capillary for μ-CT study must ensure that the same volume is being scanned in the different measurements. This is indeed the case as it is evident from Figure 2, which shows selected orthoslices displaying the evolution of cement hydration. Clearly and as expected, small whitish particles (anhydrous cement particles) react much faster than the bigger ones. This is highlighted in the enlarged views also shown in the bottom row of Figure 2.

![Figure 2](image)

**Figure 2.** Top row: Selected orthoslices of the studied capillary, φ=2.0 mm, showing the cement hydration evolution with time. The whitish particles are the anhydrous Cement Particles (CP) and the grey regions are the Hydrated Products (HP). Porosity develops as blackish regions. Bottom row: enlarged views to highlight the observed densification and the preferential hydration of the smallest CP, see red circles.

A first qualitative study can be carried out by inspecting the evolution of the resulting grey-value histograms for the same hydrating volume, see Figure 3. Three main features can be observed in Figure 3. (1) The number of voxels corresponding to the CP decreases with time as expected. (2) The area of the peak corresponding to the HP increases with time and it densifies (it moves to higher grey level values). This densification is due to the reaction of free water and CP to give further HP, including portlandite. It is worth noting that due to the spatial resolution of the measurements, the water capillary porosities at 12 h cannot be disentangled from the HP main peak. HP mainly contains C-S-H gel, portlandite and ettringite. (3) After 1 day, shrinkage and air porosity development is evident as the tiny increase of the amount of low grey level voxels. However, the spatial resolution of these measurements, 3-4 μm, is not sufficient to accurately quantify this developing microporosity.

![Figure 3](image)

**Figure 3.** Grey level histograms showing the overall evolution of the different components with time. For the description of the labels, see the text.

The quantitative μ-CT study was carried out by global thresholding segmentation. The threshold for the HP/CP boundary was found constant, i.e. 19850 grey level, see Figure 3. The thresholds for porosity/HP boundary were variable, close to 9000 grey level. The segmentations were carried out with the Dragonfly software and the results are given in Table 2. This table also displays the values obtained from LXRPD, but expressed as vol% taken into account the mass densities of the different components. The agreement between both sets of data is noteworthy, keeping in mind that there is a time delay of about three hours.

Segmentations by Machine Learning methodology is being carried out and the results will be reported elsewhere. This second approach could lead to adequate segmentations of amorphous SCMs in low-carbon blends. This is not possible with the global thresholding approach used here, because of the similarities in the attenuation coefficients. The redundancy in the in situ data will also help. The SCMs particles can only decrease in volume, meanwhile the volume of the hydration products should increase.
Table 2. Segmentation results for the in situ µ-CT study for the hydrating PC 42.5 paste with w/c=0.50 at RT. These values are compared to the ones obtained in the LXRPD study.³

<table>
<thead>
<tr>
<th>Components</th>
<th>12h/vol%</th>
<th>1d/vol%</th>
<th>1d/vol% LXRPD</th>
<th>3d/vol%</th>
<th>3d/vol% LXRPD</th>
<th>7d/vol%</th>
<th>7d/vol% LXRPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>0.5</td>
<td>1.4</td>
<td>-</td>
<td>2.5</td>
<td>-</td>
<td>2.6</td>
<td>-</td>
</tr>
<tr>
<td>HP</td>
<td>78.2</td>
<td>81.0-82.2</td>
<td>81.3</td>
<td>82.0-84.1</td>
<td>87.1</td>
<td>82.1-84.3</td>
<td>88.3</td>
</tr>
<tr>
<td>CP</td>
<td>21.3</td>
<td>17.6-19.8</td>
<td>18.7</td>
<td>15.5-15.9</td>
<td>12.9</td>
<td>15.3-15.7</td>
<td>11.7</td>
</tr>
</tbody>
</table>

³The amounts of the components from the µ-CT study are renormalized to exclude porosity (italics) for direct comparison to LXRPD. ¹Calcite in LXRPD data is computed within HP because of its attenuation coefficient.

4. Conclusions

An accurate experimental protocol for in situ cement hydration studies has been established for pastes sealed in thick capillaries, i.e. 2 mm of diameter to have excellent powder averaging. Rietveld quantitative phases analyses have been obtained by using MoKα₁ strictly monochromatic radiation. The results agree very well with the expected values from mass balance calculations. Moreover, microtomographic data have also been collected for the same volume of the studied specimen. The quantitative results from segmentations have been compared to those calculated from the diffraction study. This is a first step in our long-term research intended to quantitatively analyse the pozzolanic reactions of SCMs by combining diffraction and tomographic techniques which are highly complementary.

Acknowledgements

Financial support from PID2020-114650RB-I00 research grant, co-funded by FEDER, is acknowledged.

References