Neutron diffraction for studying the influence of the relative humidity on the carbonation process of cement pastes

I Galan\textsuperscript{1}, C Andrade\textsuperscript{1}, M Castellote\textsuperscript{1}, N Rebolledo\textsuperscript{1}, J Sanchez\textsuperscript{1}, L Toro\textsuperscript{1}, I Puente\textsuperscript{2,3}, J Campo\textsuperscript{2,3} and O Fabelo\textsuperscript{2,3}

\textsuperscript{1}Eduardo Torroja Institute IETcc-CSIC, Serrano Galvache 4, 28033 Madrid, Spain
\textsuperscript{2}Institut Laue Langevin, 6, rue Jules Horowitz, 38042, Grenoble, France
\textsuperscript{3}Instituto de Ciencia de Materiales de Aragón ICMA, Pedro Cerbuna 12, 59000 Zaragoza, Spain

isabelgalan@ietcc.csic.es

\textbf{Abstract.} The effect of humidity on hydrated cement carbonation has been studied by means of in-situ neutron diffraction measurements. The evolution of the main crystalline phases in the bulk of the sample, portlandite and calcite, has been monitored during the process. Data obtained from neutron diffraction allow the quantification of the phases involved. The results highlight the great influence of humidity on carbonation. At very low humidity there are almost no changes. Between 53 and 75\% relative humidity, portlandite decrease and calcite increase data can be fitted to exponential decay functions. At very high humidity portlandite remains nearly constant while calcite increases slightly with time, almost linearly.

1. \textbf{Introduction}

Carbonation of hydrated cement is one of the most important processes that condition the durability of reinforced concrete. The reaction between atmospheric CO\textsubscript{2} and basic components of the cement paste leads to a lowering of the very alkaline pH that characterizes hydrated cement. This pH fall may move the steel from passivity to corrosion zone, which in turn can cause important damages in the concrete structure. The carbonation phenomenon is influenced by many factors, being the water content in the material and the environmental relative humidity (RH) some of the most determinant [1-4].

The neutron diffraction instrument D1B, at Institut Laue Langevin (ILL), allows in-situ measurements of the carbonation process of cement paste specimens at constant RH. A previous experiment with a similar set-up was performed at D20, ILL [5]. The phase’s changes due to carbonation in three types of cement pastes at 65\% RH were measured. The present work attempts to compare the phase’s evolution at five different RH.

2. \textbf{Experimental}

Cylindrical cement paste specimens, 1x4 cm, were fabricated using CEM I 42.5R and deuterated water, with a water/cement ratio in weight of 0.5. The specimens were then cured for 28 days in their molds in a saturated humid chamber. After demoulding the specimens were placed in constant RH chambers, where the humidity was achieved and maintained by means of saturated salt solutions (Table 1); they were kept there for 90 days. After this pre-treatment the specimens were subjected to 100\% CO\textsubscript{2} fluxes for 8-12 hours, also in constant humidity conditions.
The carbonation experiments were performed at D1B instrument at ILL. Neutron diffraction spectra were collected every fifteen minutes all through the experiments.

**Table 1.** Saturated salt solutions for constant RH chambers.

| Saturated solution | MgCl₂ | Mg(NO₃)₂ | NaNO₂ | NaCl | BaCl₂ |
|--------------------|-------|----------|-------|------|-------|
| RH % (at 25°C)     | 33    | 53       | 65    | 75   | 90    |

The experimental set-up used for the in-situ carbonation experiments (Figures 1 and 2) is quite similar to the one described in [5]. The saturated solution is located inside the lower part of the device. The CO₂ is introduced in this part through a tube, and the specimen is positioned, standing on a fixed basis. This part is closed by a vanadium cylindrical body. The upper part of the body is closed by a cap connected to a tube for CO₂ releasing. The set-up is placed between the neutron beam and the detector.

Three of the carbonation experiments, at 33, 53 and 65% RH, were measured with 1.28 Å neutrons, while for the ones at 75 and 90% RH 2.52 Å neutrons were used. 1.28 and 2.52 Å are the two wavelengths available at the instrument D1B.

3. Results and discussion

Intensity-angle-time diffractograms were obtained for the five experiments. The spectra obtained at 53% (1.28 Å) and 75% RH (2.52 Å) are shown in figures 3 and 4. Two phases, portlandite (P) and calcite (C), were identified in all diffractograms. In the spectra obtained with 1.28 Å neutrons the main diffraction peaks of portlandite appear at 2θ angles of 28.5 and 41.9, and the ones of calcite at 19.5; 24.6; 26.2; 32.8 and 39.0. In the spectra obtained with 2.52 Å neutrons the peaks of portlandite are at 58.1, and the ones of calcite at 38.9; 49.7; 53.3; 67.7 and 83.0.

At 33% RH almost no changes were observed during the process. At 90% RH, while the portlandite main peak remained constant, a slightly increase in the calcite peaks was observed. For the rest of the RH, the portlandite decrease and the calcite increase could be clearly seen.

**Figure 1.** Paste specimen on the lower part of the device. **Figure 2.** Experimental set-up between neutron beam and detector.

**Figure 3.** Diffraction spectra for 53% RH. **Figure 4.** Diffraction spectra for 75% RH.
Rietveld refinement of the powder diffraction patterns has been carried out using the Fullprof program [6] and considering just two crystalline phases, portlandite and calcite. The pseudo-Voigt profile function of Thomson et al. [7] was used to fit the peak shapes. The refinements of portlandite and calcite were performed considering the P-3M1 and R-3C space group, respectively. A NaCaIF sample was used to refine lambda and zero point and to determine the instrument Cagliotti parameters. Scale factor of both phases, preferential orientation parameters for portlandite and grain size parameter ‘y’ were refined and the phases’ relative proportion before and after carbonation was calculated (Figures 5 and 6). Bragg-R factor varies between 3.7 and 45 for portlandite and between 2.5 and 63 for calcite.

The portlandite initial quantities in specimens pre-treated at 33, 53 and 65% RH are close to 100%, as expected. Specimens pre-treated at 75 and 90% HR present lower quantities, 63 and 80%, respectively; this fact could be attributed to a light pre-carbonation of the cement or the specimens. The portlandite amount diminishes with time in all cases, being this decrease almost insignificant for the 33% specimen and very important for the rest. From 53% RH on, increasing humidity implies diminishing the calcite/portlandite proportion. A decrease in the proportion does not mean necessarily portlandite consuming; other amorphous phases may be suffering carbonation.

Fitting the curves of the main diffraction peaks to Pseudo-Voigt functions, the corresponding areas have been calculated. Figures 7 and 8 represent the evolution of the main peak areas in 53 and 75% RH atmospheres. At 33% RH both phases maintain their main peak area almost constant throughout the time; at 90% RH, although portlandite remains practically constant, calcite increases slightly with time, almost linearly, which may be attributed to other phases’ carbonation. Data from 53, 65 and 75% RH have been fitted to exponential decay functions with the form

\[ y = y_0 + A \cdot \exp\left(-\frac{x}{\tau}\right) \]  

(1)

The R² values obtained by fitting calcite data are: 0.750; 0.825 and 0.922 for 53, 65 and 75% RH, respectively, much higher than the ones of portlandite data: 0.584; 0.313 and 0.856.
The decay constant $\tau$ is in these three cases higher for calcite than for portlandite; this means that the calcite needs more time to reach its maximum value than the portlandite to reach its minimum. $A$, the difference between initial and maximum values, is considerably higher in the calcite than in the portlandite for the three specimens considered; at a certain time, more calcite is being produced than portlandite is disappearing. Comparing $y_0$ with the values reached by both phases at the end of the experiment a completion degree can be calculated. In the 53% RH experiment calcite has almost reached its maximum and portlandite its minimum. In the 65% RH specimen the minimum value of portlandite is nearly reached while calcite has only reached 80% of the maximum. The specimen carbonated at 75% RH is the one with the lowest completion degree, 75% calcite and 90% portlandite.

Using the instrument Cagliotti parameters and considering no strains, the grain sizes of both phases were estimated with Fullprof in some initial and final states with the formula given by [8]. Table 2 shows the values obtained. Initially portlandite grain size increases with RH, probably because higher humidity leads to longer hydration and consequently to bigger crystals. In the final state the sizes at 53 and 75% RH are very similar but still much smaller than at 90% RH. Microscopy techniques should be used in order to better understand portlandite crystals growth during carbonation. Calcite crystals sizes are bigger at 75 than at 53 % RH. This may be due to the earlier completion of the process at 53% where maximum values are almost reached after 400 minutes, while at 75% the crystals growth is still on process.

| Grain size (Å) | Calcite 53% RH | Portlandite 53% RH | Calcite 75% RH | Portlandite 75% RH | Calcite 90% RH | Portlandite 90% RH |
|---------------|-----------------|---------------------|---------------|---------------------|-----------------|---------------------|
| Initial       | -               | 1620                | -             | 4252                | -               | 6302                |
| Final         | 400             | 7724                | 3022          | 7045                | 2018            | 10282               |

4. Conclusions

The neutron diffraction experiments performed have allowed the in-situ monitoring of the carbonation process at different RH. This technique, besides making possible quite complicated experimental set-up, gives unique information about crystalline phases of big volumes of the sample bulk.

Humidity determines the evolution of phases during carbonation. At very low RH no changes occur. Between 53 and 90% RH portlandite/calcite proportion decreases, being this reduction more important for the lowest RH. Diminishing the proportion portlandite/calcite does not mean that portlandite is consumed; other phases may be suffering carbonation.

Considering exponential decay behavior for 53, 65 and 75% RH, calcite needs more time to reach the maximum than portlandite its minimum, and only the 53% process is complete after 500 minutes.

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