Carbonation profiles in cement paste analyzed by neutron diffraction

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Abstract. The present work deals with the carbonation process in cement based materials such as concrete. In order to clarify the evolution of the two main phases involved in the process, portlandite and calcium carbonate as a function of depth, spatially resolved neutron diffraction experiments have been performed at SALSA diffractometer at ILL in carbonated cement paste samples. Specimens submitted to different carbonation processes, both natural and accelerated, have been analyzed with this non destructive technique. The evolution of the main diffraction peaks of portlandite and calcite has been followed by means of neutron diffraction patterns measured at different depths. The results indicate that, in specimens subjected to CO₂ atmospheres for 24 and 48 hours, the amount of calcite increases from the centre of the specimen to the surface. In both type of specimens calcite is formed at all depths analyzed, with higher quantities for the ones submitted to the longest carbonation period. Regarding the evolution of portlandite in these specimens, it almost completely disappeared, with only a low amount of the phase constant throughout the sample. In specimens subjected to air in a closed chamber for 21 months, higher amounts of portlandite were observed throughout the sample and little increase of calcite in the outer part, pointing out a much less severe reaction. The absorption effects are characterized by measuring in perpendicular directions and an absorption coefficient is calculated for portlandite.

1. Introduction

The term ‘carbonation’ in cement based materials applies to the reaction between acid components from the atmosphere, mainly carbon dioxide, and basic components from the hydrated cement, mainly portlandite (calcium hydroxide), to form calcium carbonate. The reaction begins at the exposed surface of the cement structure, continuing towards the inner part of the material. The diffusion rate and the amount of calcium carbonate formed in the pores depend on many variables: type of cement, water/cement ratio, environmental conditions, setting and curing, among others [1-5].

Considering steel reinforced concrete structures, carbonation may become a problem if the reaction front reaches the steel. The reason for this danger is the lowering of the pH that takes place in the concrete pores solution due to the calcium hydroxide carbonation. In safe conditions the steel inside the concrete is protected by a passive layer formed at pH values between 12.5 and 13.6. When the pH lowers below 8 the passive layer becomes unstable leading to a generalized corrosion on the steel surface [6-9].

The main technique used for preventing steel corrosion caused by concrete carbonation is the phenolphthalein indicator, which changes color at pH 8-9. Although this indicator shows two distinct
zones separated in most cases by a sharp front, it has been already proved that between the carbonated and the non-carbonated zone there is a transitional region. In that region the portlandite decrease and the calcium carbonate increase are not abrupt, but gradual [10-14]. Most of these studies use Thermogravimetrical Analysis (TGA) for computing the amounts of portlandite and calcium carbonate present at different depths in the samples. For using this destructive technique the samples must be cut or sawn at the required depth and then milled, analyzing only some milligrams of the powder; the main disadvantages of the TGA are the unavoidable contact of the CO$_2$ with the cement paste powder and the difficulty to obtain representative samples. Other techniques used for studying carbonation, such as X-ray diffraction, Infrared spectroscopy and pH measurements, also work with little amounts of powder, having the same disadvantages as TGA. A more sophisticated technique used is the gammadensitometry, which is non-destructive, but requires uncarbonated references for interpreting results and does not give information about portlandite.

Neutron diffraction (ND), a non-destructive technique, has already been used for studying in-situ carbonation processes at constant relative humidity [15-16]. ND has been very useful for obtaining information about the crystalline phases involved in the process, mainly portlandite and calcite, in the bulk of the samples.

In the present work spatially resolved ND is used for analyzing carbonation profiles, that is, for following the evolution of the main phases with the depth.

2. Experimental

Cylindrical cement paste specimens, 1x4 cm, were fabricated using cement without additions (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 at 65% by means of NaNO$_2$ saturated salt solutions. Some samples were kept there for 2 months and, after that, they were subjected to 100% CO$_2$ atmospheres for 24 or 48 hours, also in 65% RH atmospheres. Other samples were kept in the chambers with 65% RH and air, that is, 0.04% CO$_2$, for 21 months. During the time of exposure the chambers were opened three times, after 6, 12 and 18 months for few minutes, renewing the air.

The ND measurements were performed at SALSA instrument at Institut Laue Langevin (ILL). 2D diffraction patterns were collected every cubic millimeter from the sample center to the edge, that is, in five steps the whole radius was covered. As shown in Figures 1 and 2 the samples were placed vertically between the neutron source and the detector. The neutron wavelength used was 1.648 Å. With this lambda the main diffraction peak of portlandite appears at 36.5º and the one of calcite at 31.4º. The two phases were measured in the samples along the ‘x’ radial direction, which coincides with the bisection of the incident and diffracted beams. Each measurement took 1 hour, that is, 5 hours per phase and sample.

Measurements in the ‘x’ radial direction were performed in the 3 types of samples (carbonated at 100% CO$_2$ for 24 hours, at 100% CO$_2$ for 48 hours and at 0.04% CO$_2$ for 21 months).

In order to evaluate neutron absorption effects, measurements along the ‘y’ radial direction, perpendicular to ‘x’, were also performed in the samples carbonated in 0.04% CO$_2$. The main difference between the two directions is the distance the neutrons have to traverse inside the samples. In the ‘x’ direction this distance decreases with depth, while in the ‘y’ direction it is maintained almost constant in the five measurement volumes. The comparison of the patterns obtained in both perpendicular directions has allowed for the analysis of the absorption.
3. Results and discussion

Figures 3 and 4 show the evolution with depth of the calcite main diffraction peak from the center of the specimen to the surface (from the left to the right), measured in the ‘x’ direction.

**Figure 3.** 2D diffraction patterns of the main calcite diffraction peak scanning in position along the ‘x’ direction in the sample exposed to 100% CO$_2$ for 24 hours. The horizontal axis is the diffraction angle two theta and the vertical is the over 5° around the diffraction ring.

**Figure 4.** 2D diffraction patterns of the main calcite diffraction peak scanning in position along the ‘x’ direction in the sample exposed to 100% CO$_2$ for 48 hours.

Figure 3 corresponds to the sample exposed to 100% CO$_2$ for 24 hours and Figure 4 to the one carbonated in the same atmosphere for 48 hours. The images were obtained from the Lamp data analysis program [17]. As it can be seen, in the samples submitted to accelerated carbonation, the
evolution with depth is clear: calcite increases from the inside to the surface. In the samples exposed to air in a closed chamber for 21 months the calcite main diffraction peak is not very well defined, both in the ‘x’ direction as in the ‘y’.

Considering portlandite evolution, in the samples exposed to accelerated carbonation the diffraction peaks are very weak and exhibit intensities almost half that of those corresponding to samples exposed to air.

Figures 5 and 6 represent the integration of the diffraction peak over the height of the 2D detector as a function of radial position in samples exposed to 0.04\% CO$_2$ for 21 months measured in the ‘x’ and ‘y’ direction, respectively. The images were also obtained from Lamp. The lower part of the image (scan 66 in Figure 5) corresponds to the inner part of the sample and the top to the surface (scan 70). In Figure 5 it seems that portlandite increases from the inner part of the sample to the surface. In Figure 6 the evolution of the peak is very different: the intensity is almost maintained throughout the sample, decreasing slightly at the surface (scan -4.5). This fact may be due to the different paths covered by the neutrons inside the samples and the subsequent absorption. In order to analyze this effect, in Figure 7 a scheme of the neutron diffraction paths inside the samples is represented for the measurements in both directions.

**Figure 5.** Portlandite main diffraction peak ‘x’ direction sample exposed to 0.04\% CO$_2$ 21 months. The centre of the sample is at the bottom on the Y axis (scan 66) and the surface at the top (scan 70).

**Figure 6.** Portlandite main diffraction peak ‘y’ direction sample exposed to 0.04\% CO$_2$ 21 months. The centre of the sample is at the bottom on the Y axis (scan -0.5) and the surface at the top (scan -4.5).
The distances covered by the neutrons in the ‘x’ direction differ considerably for each measurement point, decreasing while ‘going out’; in the ‘y’ direction the paths are all quite similar and almost independent from the measurement depth. The distance depends also slightly on the diffraction angle, that is, on the phase considered. For the calculations, the Lambert-Beer law is used:

\[ I = I_0 \cdot \exp\left(-\alpha \cdot L \cdot C\right) \]  

(1)

where \( I_0 \) is the incident intensity, \( I \) is the attenuated intensity when passing through a material, \( \alpha \) is the absorption coefficient, \( L \) is the path covered and \( C \) is the concentration of ‘absorbers’ in the material. Relating the attenuated intensities with the paths in both directions, the value of \( A = \alpha \cdot C \) can be calculated.

**Figure 7.** Neutron diffraction paths in ‘x’ direction, differing for each measuring point, and ‘y’ direction, being very similar for all measuring depths.

In this case, the intensities are the peaks’ areas, calculated between \( 2\theta = 35.7^\circ \) and \( 2\theta = 37.5^\circ \) for the portlandite phase. Dividing the Lambert-Beer expression for ‘y’ by the corresponding for ‘x’ and taking logarithms, the following expression is obtained:

\[ \ln\left(\frac{I_y}{I_x}\right) = A \cdot (L_x - L_y) \]  

(2)

Figure 8 represents \( \ln\left(\frac{I_y}{I_x}\right) \) versus \( (L_x - L_y) \) and the corresponding linear fitting.

**Figure 8.** \( \ln(I_y/I_x) \) versus \( (L_x-L_y) \), being the slope of the line the absorption parameter \( A = \alpha \cdot C \).
The calculated value of the parameter $A = \alpha \cdot C$ is 0.085 mm$^{-1}$. This factor allows the conversion of the peak areas in the perpendicular directions.

Applying the A value to the samples submitted to accelerated carbonation, the portlandite peak areas obtained in the 'y' direction do not change throughout the sample and are approximately half of those in the natural carbonated sample.

Regarding the calcite peak in the sample submitted to air, the differences of intensity in both directions are not significant. As the amount of this phase in this sample is quite low and the peaks are not sharp, the corresponding absorption coefficient cannot be calculated from this set of data.

4. Conclusions
Neutron diffraction has allowed to measure carbonation profiles in cement paste samples. In the specimens subjected to CO$_2$ atmospheres for 24 and 48 hours the amount of calcite increases from the centre of the specimen to the surface. In both type of specimens calcite is formed at all depths analyzed, with higher quantities for the ones submitted to the longest carbonation period. Regarding the evolution of portlandite in these specimens, it almost completely disappeared, with only a low amount of the phase constant throughout the sample. In specimens subjected to air in a closed chamber for 21 months, higher amounts of portlandite are observed throughout the sample and little increase of calcite in the outer part, pointing out a much less severe reaction. The neutron absorption effects in this type of materials have been characterized by measuring in perpendicular directions and comparing the portlandite main peak areas.

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