

X-Ray Diffraction and SEM of the Concrete Before and After Carbonation

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Abstract : *With the increase in the number of reinforced concrete structures (buildings and engineering structures), we are witnessing a worldwide increase in the deterioration of these structures. Reinforcement corrosion is the main cause of disorder in the building industry. Reinforcement corrosion can be caused by carbonation of the concrete covering.*

This carbonation results in a slow modification of the structure of the material and a change in its behaviour. Carbonation has 2 main effects, which are antagonistic :

-it is beneficial by improving mechanical strength and resistance to aggressive water.

-it is harmful by reducing the chemical protection of the reinforcement.

Two microscopic methods of investigating carbonation were used in our study:

-X-ray diffraction (DRX), the aim of which is to compare the crystalline phases of our concretes before and after carbonation by testing the distribution of Ca(OH)₂ and CaCO₃ and also to monitor the evolution of carbonation as a function of time.

-The kinetics of the carbonation of our concretes can be illustrated comparatively by images obtained by scanning electron microscope (SEM) using BSE (Back Scattered Electron) techniques on polished surfaces.

We can conclude that in XRD, carbonation results in the disappearance of portlandite and that SEM observations reveal carbonation, even at very low thicknesses.

Key words: *Carbonation, SEM, XRD, Concrete, Corrosion*

1. Introduction

Carbonation is a crucial factor in ensuring the durability of reinforced concrete structures. It involves the gradual conversion of one of the primary components of hardened concrete, portlandite, into calcite on exposure to carbon dioxide in the air and humidity.

The process of carbonation proceeds at a significantly slow pace. To better evaluate the long-term consequences, accelerated tests are conducted in the laboratory by installing a station for accelerated carbonation [1]. The aim of this study is to evaluate various techniques for the microscopic investigation of carbonation, such as the scanning electron microscope (SEM). This method enables visualization of the sample's morphology, grain size, and mineral composition, allowing differentiation between carbonated and non-carbonated zones. Additionally, X-ray diffraction (XRD) is utilized to test the intensity distribution of Ca(OH)₂ and CaCO₃.

The experimental study investigated the concrete performance of three levels using two types of cement, CEM I and CEM II, a superplasticizer Medaflow 30, and three water-to-cement ratios. These concretes underwent pre-treatment in a climate-controlled chamber at a temperature of 20 degrees Celsius and relative humidity of 66% for several months before being placed in an accelerated carbonation chamber.

2. Experimental Program

2.1. Materials Characterization

Cement: The investigation revolves around two types of cement. Table 1 provides a summary of the mineralogical compositions of various cements.

TABLE I : mineralogical composition of cements.

Cement	C1 (CEM I)	C2 (CEM II)
Mineralogical Composition [%]		
C ₃ S	63,2	15,0
C ₂ S	14,8	49,4
C ₃ A	0,8	10,0
C ₄ AF	14,4	7,3
gypsum	3,9	4,1
limestone	-	15

Aggregates : The aggregates used in this study were obtained from the El Khroub quarry owned by the National Company of Aggregates, identified by a rock with a high calcium carbonate content ($\text{CaCO}_3 \approx 98\%$). The concrete was composed of three granular classes ; 0/5 (s), 3/8 (g1), and 8/16 (g2).

Superplasticizer: The used superplasticizer is based on polycarboxylate (Medaflow 30).

2.2. Composition, Conservation and Characteristics of Concretes

We made concretes from 6 different formulations with W/C ratios ranging from 0.35 to 0.67, covering the strength range from 12 to 55 MPa at 28 days (Fig1) and having the same slump at the Abrams cone (plastic concretes). We used two types of cement (CEM I and CEM II), limestone aggregates and a Medaflow 30 superplasticizer. The concrete compositions were established using the Dreux Gorisse method [2].

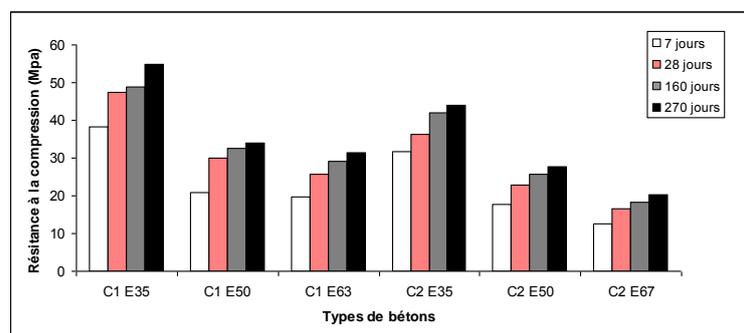


Fig.1 : Evaluation of compressive strength as a function of time

2.3 Sample Pre-Treatment

To speed up the equilibration of the specimens, we used a ventilated climatic chamber to control humidity and temperature. The cycle chosen was based on 7 days: 5 days at 50°C and 40% relative

humidity[3][4], followed by a day of ramping to 20°C and 66% relative humidity, and storage for 24 hours (Figure 2). [1]

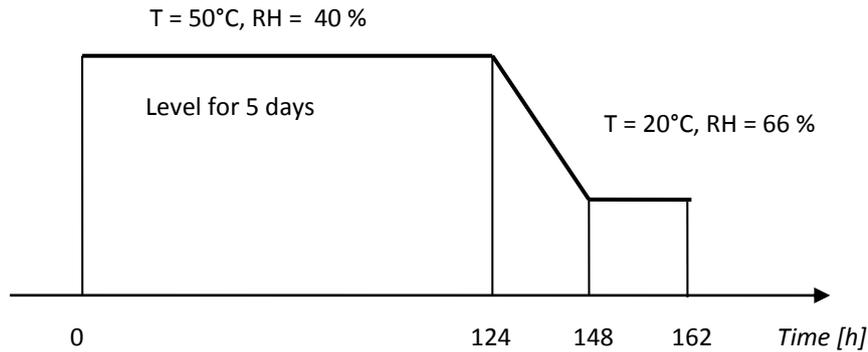


Fig. 2 : Diagram of the drying cycle in a programmable T and RH environmental chamber [1]

2.4. Accelerated Carbonation Test

Carbonation was carried out in a carbonation chamber that we set up during this study in our CRMD laboratory, with a capacity of 95 litres [1]. The CO₂ was supplied from a pressurised 50% air and 50% CO₂ mixture bottle, the flow rate of which was regulated using a pressure gauge [3]. Relative humidity of 66% is achieved using a saline solution saturated with sodium nitrite (NaNO₂) [5][6][7]. The temperature is 20°C. A fan ensures the homogeneity of the unit (Fig.3).



Fig. 3 : General view of the CRMD accelerated carbonation unit [1]

2.5. X-Ray Diffraction (XRD)

The aim of this qualitative method is to compare the crystalline phases of our materials, before and after carbonation, and also to follow the evolution of carbonation as a function of time. The experimental device used is a "Philips" powder diffractometer with a curved counter. It works with the $k\alpha_1$ line of copper: $\lambda = 1.54056 \text{ \AA}$.

Identification is carried out by comparing the diffractogram obtained with an international database (JCPDS) containing reference diffractograms of more than 80,000 phases. This method enables the different crystalline phases making up the material to be identified [8].

- Evolution of Concrete Carbonation with Time

The appearance of the diffractograms over time is shown in Figure 4, Figure 5 and Figure 6 for the different concretes studied. The main mineralogical phases are calcite CaCO₃ (main peak at 29.4°), which comes from the aggregates, the limestone filler of CEM II and carbonation, and portlandite (main peaks at 18.01° and 34.11°).

We can also observe the presence of some minor phases such as silica SiO₂ in the form of quartz (main peak at 26.6°) which comes from the CEM II cement [9] and also ettringite.

As our concretes contain a large fraction of aggregates (73%) by mass compared with the cement fraction, which is equal to 19%, we mainly observe calcite peaks originating from the aggregates.

The most interesting observation concerns the persistence of portlandite peaks for high-performance concretes, even after 28 days of accelerated carbonation. On the other hand, for concretes with a W/C = 0.50 (C1 W50 and C2 W50), we observe the disappearance of the portlandite peaks from 7 days of accelerated carbonation. A new peak at 21.18° associated with vaterite was detected in C2 W50 concrete from 28 days of carbonation. The intensity of the peak associated with this new form of calcite increases after 3 months of carbonation.

In the high W/C concretes (C1 W63 and C2 W67), the portlandite peaks disappeared after 7 days of carbonation. We also observe the appearance of the new peak corresponding to vaterite [10].

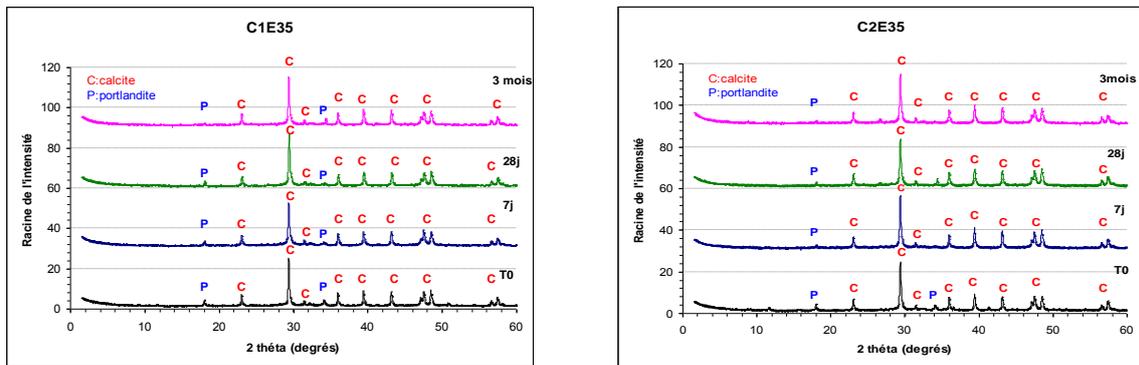


Fig. 4 : Changes in diffractograms of C1 W 35, C2W 35 as a function of carbonation time

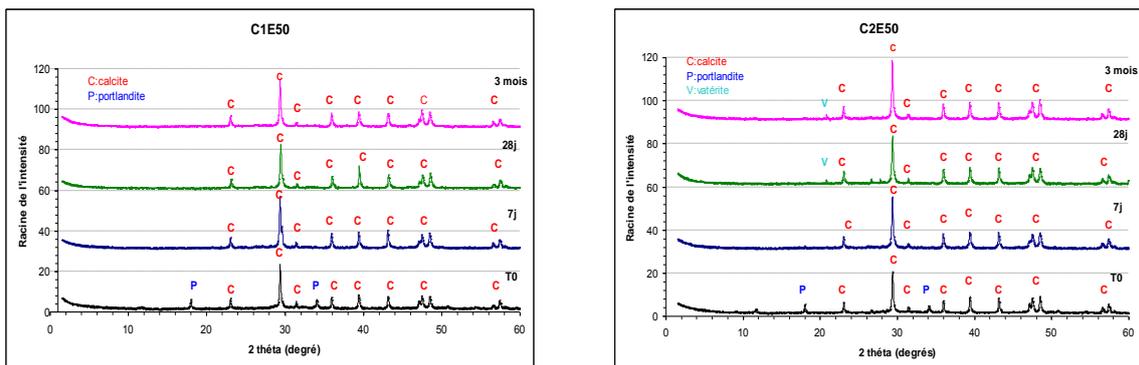


Fig. 5 : Changes in diffractograms of C1 W50 and C2W50 as a function of carbonation time

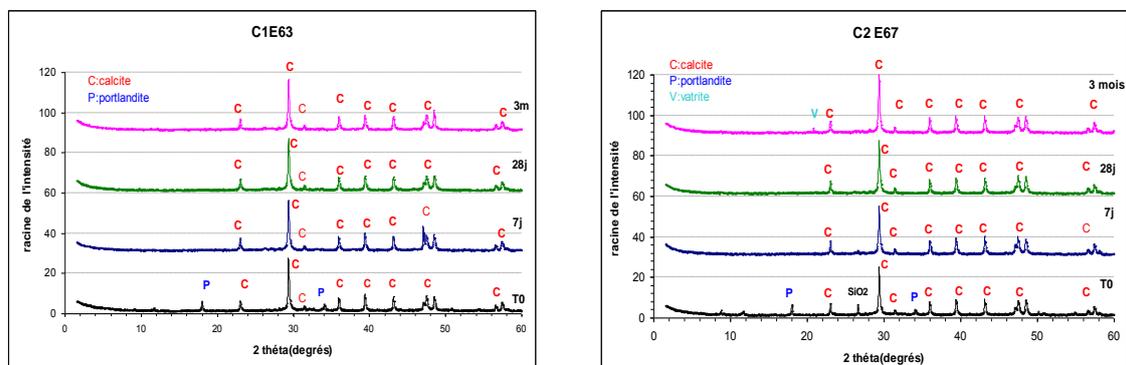


Fig. 6 : Changes in diffractograms of C1 W63 and C2W 67 as a function of carbonation time

2.6. Scanning Electron Microscope (SEM) Analysis

The scanning electron microscope used for this work is a Hitachi S.4500 field effect microscope. The backscattered electron detector is of the Multi-channel Plate type, allowing work at low voltage (1 kV) and high voltage (36 kV), with a resolution of a few nanometres [2].

Figure 7 shows the microstructure of the sound state of C1W63 concrete before being subjected to accelerated carbonation, where we can see the presence of the various anhydrous.

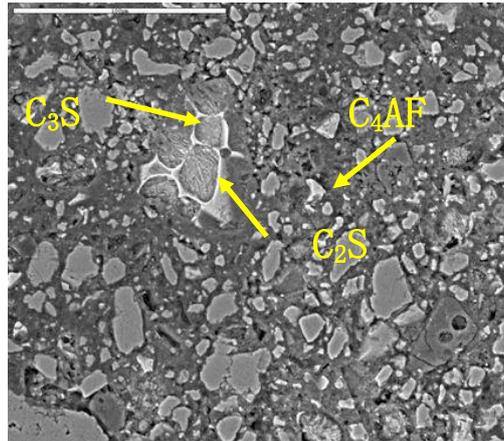


Fig 7 : BSE micrograph of C1 W 63 concrete - healthy part (before carbonation) (x500)

Figure 8 shows C1 W63 concrete after accelerated carbonation for 28 days. We note the existence of two zones.

Figure 9 and Figure10 allow us to compare the (1)-degraded and (2)-densified zones of fully carbonated C1 W63.

In the degraded part, where there are almost no residual anhydrous elements left apart from C₄AF, capillary porosity appears to be greater than elsewhere. calcite is not visible. the carbonated zone is very compact due to the presence of calcite, particularly in the cement/aggregate transition zone and in capillary porosity. Carbonation does not affect the pores closed by dense C-S-H, which are the Hadley grains.

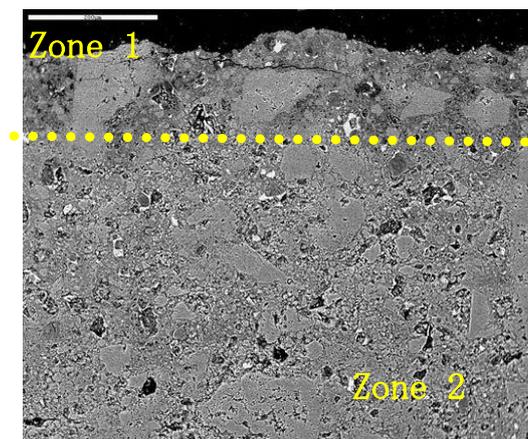


Fig. 8 : BSE micrograph (x 1000) of C1 W63 concrete - carbonated for 28d

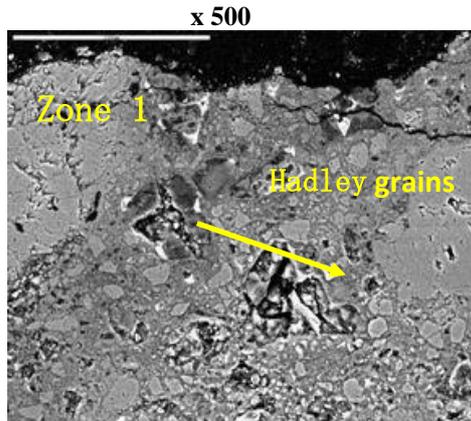


Fig. 9 : BSE micrograph of fully carbonated C1W63 concrete (28 days) - degraded part

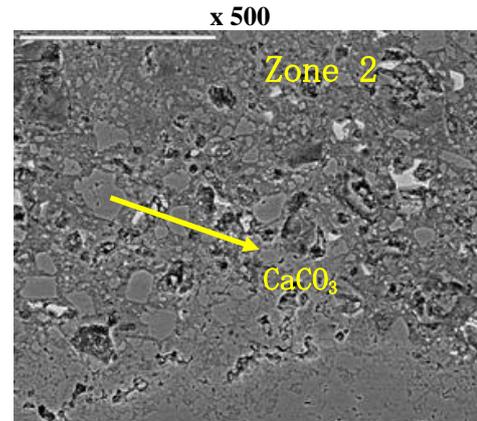


Fig. 10 : BSE micrograph of fully carbonated C1 W63 concrete (28 days) - densified part

Figure 11 shows the sound part of C2 W50 concrete carbonated at 3 days. The bands of portlandite in light grey preferentially fill the transition interface between the aggregate and the paste as well as part of the capillary porosity. In Figure 12, this is the carbonated part of the same concrete. The portlandite bands are no longer visible and the whole paste is densified by calcite. It is also possible to note the total disappearance of the anhydrous.

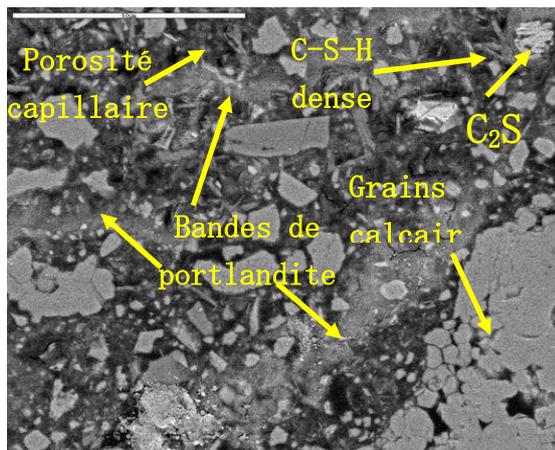


Fig. 11 : BSE micrograph (x1000) of C2 W50 concrete carbonated for 3 days -healthy part

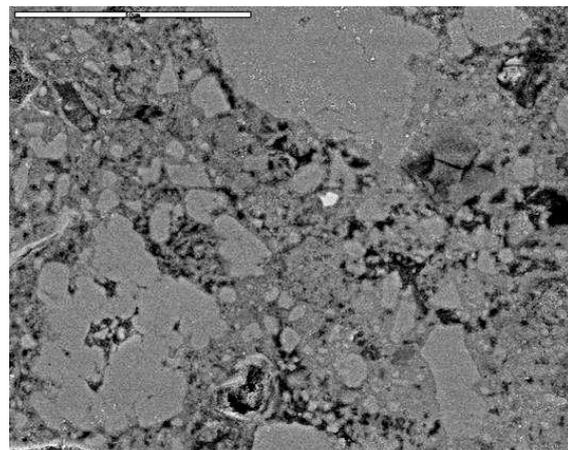


Fig. 12 : BSE micrograph (x1000) of C2 W50 concrete carbonated for 3 days -carbonated part

3. Conclusion

In XRD we observe that carbonation results in the disappearance of portlandite. The presence of portlandite detected in XRD is therefore a good tracer for monitoring the progress of carbonation. This of course applies to the carbonation of portlandite, which is the first stage of carbonation.

The subsequent stages of carbonation cannot be detected in the same way, since the reactive hydrates (C-S-H) are mainly amorphous and therefore cannot be detected by XRD.

For CEM II-based concretes, accelerated carbonation results in the appearance of diffraction peaks associated with the formation of vaterite. This isomorph of calcite is perhaps the result of a more advanced stage of carbonation.

The SEM identified two degraded but different zones: a porous zone with low levels of calcification and a denser zone with carbonation.

SEM observations reveal carbonation, even at very low thicknesses (from 10 μm).

4. References

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