Experimental Contribution Concerning the Effect of Carbonation Reaction on the Oxygen Permeability of Concrete

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Abstract
Reinforced concrete (RC) structures are prone to steel corrosion that affects their service life. The two main processes, involved in the destruction of the steel-concrete self-protection are the carbonation and the penetration of chlorides. Understanding the behavior of these degrading phenomena is of paramount importance to enhance the field of predicting the service life of RC structures. In this investigation, a total number of 54 cylindrical specimens (150×100 mm²) and 54 cubic specimens (100×100 mm²) from six different concrete mixtures covering a range of water-to-cement ratio (w/c) between 0.76 and 0.36 was tested.
The effect of the carbonation reaction on the concrete oxygen permeability (assessed by a recent method), compressive strength, and weight has been investigated. The obtained data were analyzed to establish correlations to predict the oxygen permeability of non-carbonated concrete with concrete characteristics such as w/c ratio and compressive strength. Test results show good correlations. The results of the accelerated carbonation test showed that compressive strength increases with carbonation.
Concerning the effect of carbonation reaction on concrete oxygen permeability which is the main goal of this paper, test results showed that carbonation considerably affects the concrete permeability. This result was observed for all concrete mixtures. Moreover, the relationship between carbonation depth and concrete oxygen permeability in ordinary concrete differed than high performance concrete. Furthermore, the increase of the oxygen permeability observed after the carbonation has been justified by the analysis of the Scanning Electron Microscopy images that show the formation of larger pores in comparison with non-carbonated concrete.

Keywords
carbonation, compressive strength, oxygen permeability

1 Introduction
Reinforced concrete (RC) is a composite material in which concrete low tensile strength and ductility are counter reacted by the inclusion of reinforcement bars having tensile strength and ductility. The durability of RC structures will be determined by the ability of these materials to resist the different types of degradations during their service life [1]. In many countries, in the purpose of achieving the required service life, repairing and strengthening RC structures requests a huge annual budget [2, 3].
The most common deterioration mechanism that causes the reduction of the durability of the RC structures is the corrosion of the reinforcement bars [4, 5].

Over recent years, researchers have carried out several experimental studies aiming at understanding the corrosion patterns.
Carbonation and chloride penetration are the major factors that cause the corrosion of the reinforcement bars in RC elements [1, 6]. Steel corrosion induced by carbonation reaction may lead to concrete cover cracking and spalling due to the larger volume that the rust of the corroded steel bars occupies, while chloride ions attack punctually the steel bars (pitting) in which it causes the loss of the mechanical strength of steel bars [1, 4, 7]. In recent decades, global warming has dramatically
increased the atmospheric carbon dioxide concentration to which the RC structures are exposed. As a consequence, the concrete carbonation has become one of the most critical issues related to the durability of the RC structures in urban environment [8].

The concrete carbonation reaction is a physical-chemical process that starts when the CO₂ diffuses into the pore system [4, 9, 10] and ends with the formation of calcite [11–13] along with the decrease of the pH which leads to steel corrosion onset [1, 8]. In natural conditions, it takes several years for a carbonation front progress of few centimeters, in regular concrete. To anticipate concrete behavior concerning carbonation, accelerated tests are carried out. In these tests, optimal temperature and relative humidity conditions are provided, together with high CO₂ concentration. According to Fick’s diffusion law, the carbonation rate varies with the square root of CO₂ concentration. Besides this, other sources of discrepancy shall be considered when extrapolating from accelerated testing to behavior under natural conditions. The temperature and, especially, the relative humidity and the possibility of contact with water (concrete saturation) must be considered. Then, the presence of correction factors in models to predict natural carbonation, based on accelerated carbonation results, is quite common [14–16], ensuring a proper transposition from accelerated testing to natural conditions.

Although the different steps of carbonation process are discussed in detail by the scientific community, investigating the effect of the carbonation reaction on the permeability properties, as well as the assessment of the carbonation via other indicators of performance or durability such as compressive strength, permeability, porosity/capillarity, require further researches within the aim of providing more data.

The effect of carbonation on the concrete permeability has been studied by several researchers. Test results showed that water permeability of fully carbonated cement grout decreased by 3 to 6 orders of magnitude in comparison with non-carbonated cement grout specimens [17]. These results were later validated by Song and Kwon [18]. On the other hand, Thiery [19] has found trends, water permeability increases with carbonation, while for the specimens where the oxygen permeability test was assessed, the results of permeability were not uniform with an increasing in some mixtures whilst decreased in others. The same observation has been stated by Russel et al. [20] in different concrete mixtures where, gas was used to measure concrete permeability with a general trend of increasing of the permeability results. Russel also concluded that the permeability can be related to the carbonation rate.

Furthermore, the development of non-destructive test method to assess in-situ concrete permeability such as Torrent method for air permeability [21] allows researchers to have the possibility to indirect assess the concrete carbonation [6]. In the same direction, the literature reported that a relationship exists between carbonation depth and oxygen permeability results measured at 28 days [22]. Hence, it can be seen that permeability of concrete is an important indicator to foresee concrete durability and based on the aforementioned research findings studying it can be seen that the effect of carbonation on the concrete permeability is not a settled subject which needs more investigation, firstly, in order to clarify the controversy that exists and secondly, to enhance the field of assessing the durability of the RC structures through other indicators which has gained momentum in the recent years.

However, it is worth to mention that the real durability of the RC structures is influenced by load effect that play a key role in the penetration of the aggressive agent as CO₂ and this is due to the increase of the tensile micro-cracking in concrete matrix [23, 24]. According to [24] the rate of carbonation under tensile stress increases with increasing applied load therefore, in order to predict carbonation rate of concrete while exposed to an external load a correction factor can be adopted when the rate of carbonation has been measured as function of time on concrete samples without load. Castel et al. [23] proposed a relationship that allowed the prediction of the increase of carbonation depth using a tensile steel stress criterion (Ϭ). In the same context, den Heede et al. [25] considering as deterioration threshold the steel depassivation found that service life for the uncracked concrete is greatly higher than concrete with a crack 0.3 mm wide and with a depth of 25 mm from the 50 mm cover depth. The loss of service life was over 90 %.

The strategy adopted in this paper is to present first the relationship between the oxygen permeability and concrete characteristics, such as w/c ratio and compressive strength, for several concrete mixtures with a varying w/c ratio. The same tests were also carried out in carbonated specimens. Therefore, the effect of carbonation reaction on the oxygen permeability of concrete has been also investigated.
2 Experimental program

2.1 Materials

Three classes of aggregates were used 0/4, 4/8 and 8/16 with Portland cement CEMII 52.5. Fine sand 0/1 class was used to correct the fineness modulus of sand 0/4 class. Various tests were carried out for the identification of the characteristics of these materials. The test results have showed that these materials are acceptable for manufacturing hydraulic concrete.

In this case study six concrete mixtures were designed. These mixtures correspond to different compressive strength classes determined on standard cylindrical specimens 150 × 300 mm² at 28 days. These specimens were conserved and tested in accordance to well-regulated specifications and procedures [26, 27]. The different results of the concrete mixtures proportions and basic properties are given in Table 1. The mixtures design followed the Goerge-Dreux method [28].

In this investigation, two types of specimens were prepared for the tests, cubic specimens 100 × 100 mm² and cylindrical specimens 150 × 100 mm² sawn from 150× 300 mm² specimens. The cube specimens are for assessing the concrete compressive strength while cylindrical specimens are for evaluating the concrete oxygen permeability and weight variation.

2.2 Testing procedures

The oxygen permeability was assessed using a test method developed by Talah and Kharchi [29]. In particular, the proposed device differs from other devices by the cell (see Fig. 1), which is the main element of the experimental procedure as well as by the elimination of the confining pressure and air cylinder. The test measurement of this method is based on the determination of the apparent permeability coefficient ka in (m²) calculated using Eq. (1).

\[
k_a = \frac{2 \pi P Q A_{atm} (R_2^2 - R_1^2) x \mu}{(P^2 - P_{atm}^2)} x h x (R_2 - R_1).
\]

Where \( h \) is the specimen's thickness (m), \( Q \) is the gas debit (m³/s), \( P \) and \( P_{atm} \) are the inlet and outlet (atmospheric) pressure respectively (N/m²), \( R_1 \) and \( R_2 \) are the inner and outer radius, respectively, of the concrete specimen (m), \( \mu \) is the gas dynamic viscosity (Ns/m²), for the oxygen which was the gas used in this test \( \mu = 20.2 \times 10^{-6} \) Ns/m² at 20°C.

<table>
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<tr>
<th>Table 1 Proportions and basic properties of concrete mixtures</th>
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<td>Mixtures</td>
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<tr>
<td>Constituents (kg/m³)</td>
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<tr>
<td>CEM II 52.5</td>
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<tr>
<td>Fine Sand 0/1</td>
</tr>
<tr>
<td>Sand 0/4</td>
</tr>
<tr>
<td>Gravel 4/8</td>
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<tr>
<td>Gravel 8/16</td>
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<td>Silica Fume</td>
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<td>Superplasticizer (l/m³)</td>
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<td>w/c</td>
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<td>Slump (mm)</td>
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<td>Compressive strength (Rc) (MPa)</td>
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<td>Standard deviation (MPa)</td>
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As mentioned before the specimens that have been used to determine the oxygen permeability were cylindrical \(150 \times 100 \text{ mm}^2\). The originality of this method resides in the assessment of the oxygen permeability through hollow cylindrical specimens which reflects the actual construction practices [29]. The holes were realized by using a plastic pipe of 30 mm diameter in order to have an accurate thickness of 60 mm to be crossed by the oxygen. The different specimens prepared for testing are shown in Fig. 2.

All the specimens were kept 28 days in the laboratory condition and packaged with impermeable film to avoid natural carbonation. Subsequently, they were stored for a period of 8 months along with the cubic specimens under the laboratory conditions (i.e., at 20 °C ± 5 and RH between 65 and 75 %).

Before starting the accelerated carbonation test, the compressive strength and oxygen permeability were first assessed through respectively non-carbonated cubic and cylindrical specimens. The cylindrical and cubic specimens were prepared to the carbonation test according to the French Standard XP P18-458 [30] and covered with double layer of adhesive aluminum to allow unidirectional carbonation penetration. It is worth to note that the direction of the oxygen flux during the permeability test is the same as for accelerated carbonation which is perpendicular to the casting direction.

An accelerated carbonation chamber with volume of 700 L (Fig. 3) was manufactured for this study at the National Center of Studies and Integrated Research on Building Engineering (CNERIB), Algiers, Algeria. As suggested in [30, 31] the specimens were placed in the accelerated carbonation chamber at 20 °C and 65 ± 5 % RH with a CO\(_2\) content of 50 ± 5 %. The RH was kept constant using a saturated saline solution of sodium nitrate. The CO\(_2\) percentage during the experiment was determined using a detector of CO\(_2\), type CTX 300 with a range of detection varying between 0 and 100 %. Regular verification has been made in order to maintain 50 % of CO\(_2\) so that the specimens stay under the same conditions during the testing.

In two different stages, and for each concrete mixture, 3 cubes and 3 cylinders were taken from the chamber to testing rig. Before measuring the carbonation depth through spraying phenolphthalein solution on fresh broken concrete specimens [30], oxygen permeability and weight have been assessed on the same cylindrical specimens.

3 Results and discussion
3.1 Determination of the intrinsic permeability

In this paper, the permeability of concrete is expressed through the intrinsic permeability coefficient (k\(_{\text{int}}\)). The calculation of the intrinsic permeability coefficient is done by applying the Klinkenberg method [32]. The relationship between apparent and intrinsic permeability is given by the formula below, Eq. (2).

\[
k_a = k_{\text{int}} \left( 1 + \frac{\beta}{P_m} \right)
\]

Where, \(\beta\) is the Klinkenberg coefficient; \(P_m\) is the mean pressure, calculated via using Eq. (3).

\[
P_m = \frac{P + P_{\text{atm}}}{2}
\]

Where \(P\) is the inlet (absolute) pressure of gas and \(P_{\text{atm}}\) is the outlet (atmospheric) pressure.
The method used for determining the intrinsic permeability coefficient, consists of measuring \( k_a \) via Eq. (1) at different pressures three different pressures at least, and plotting it against the inverse of the mean pressure. Therefore, the intrinsic permeability coefficient is defined as the y-intercept of the line connecting the permeability and the inverse of the mean pressure \( P_m \) (see Fig. 4).

According to [33] the intrinsic permeability value can be a better parameter for characterization of a concrete for durability compared to the traditional Darcy’s coefficient of permeability, as it is independent of the fluid properties and the applied pressure gradient.

### 3.2 Some of the oxygen permeability correlations with concrete characteristics

Test results depicted in Fig. 5 show the oxygen intrinsic permeability results determined at 28 days on non-carbonated concrete for the different concrete mixtures versus \( w/c \) ratio. Besides, the relationship between \( w/c \) ratio and oxygen intrinsic permeability is also highlighted.

Through the results depicted in Fig 5, it can be seen that \( w/c \) ratio is inversely proportional to the oxygen intrinsic permeability of concrete. According to [1, 19, 34, 35] concrete with low \( w/c \) ratio result a denser cement matrix with low total porosity and less continued pore in concrete.

![Fig. 4](image-url) Some result obtained from experimental measurement of the oxygen permeability for non-carbonated concrete F1 mixture (left) and carbonated specimens F4 mixtures (right)

![Fig. 5](image-url) Oxygen intrinsic permeability of concrete vs. \( w/c \) ratio

The relationship between \( w/c \) ratio and the concrete oxygen intrinsic permeability was obtained by regression analysis. According to [36] power regression analysis was used for the three different cement types to express the relationships between permeability coefficient and \( w/c \) ratio. The coefficients of determination \( R^2 \) found by the authors were over 0.9. In this case, and following [36], power regression analysis is adopted also to express the relationship. The regression analysis result shows that good relationship exists between \( k_{int} \) and \( w/c \) ratio with a coefficient of determination \( R^2 \) equal to 0.89 (see Fig. 5).
In order to further characterize the concrete mixtures prior to the accelerated carbonation test the relationship between the compressive strength ($R_c$) and the oxygen intrinsic permeability determined at 28 days has been derived. Following [37] a general relationship between the oxygen permeability coefficient and $R_c$ has been found. The shape of the regression function is as follows: $Y = aX^b$ where $Y$ and $X$ are the permeability coefficient and the compressive strength, respectively; $a$ and $b$ are constants. After that, for the same relationship, the same power function has been used by Bondar et al. [38]. In this case, power regression analysis has been selected to express the relationship. The function obtained through the regression analysis is presented in Fig. 6. The coefficient of determination $R^2$ found equal to 0.94, which indicates that good relationship exists between $k_{int}$ and $R_c$.

3.3 The effect of carbonation reaction on the concrete compressive strength

The evolution of the compressive strength values measured on cubic specimens ($100 \times 100$ mm$^2$) as a function of carbonation depth is depicted in Fig. 7.

As shown by the figure, the carbonation reaction considerably affects the concrete compressive strength. As the carbonation depth increases the concrete compressive strength increases. This result is in accordance with the findings reported in [39]. The percentage of the strength increase is generally related to the rate of carbonation where the concrete mixture F3 has reached an 88% increase of its compressive strength which corresponds to the highest carbonation depth.

The increase of compressive strength observed in this study following Thiery [19] is due to the carbonation reaction that causes the reduction of the porosity and formation of new crystals with high strength which in turn leads to an improvement in the mechanical performance of the material. The formed mineral CaCO$_3$ consolidates the microstructure since calcium carbonate is recognized as an excellent binder. This result can also be explained by assessing the weight changes before and after carbonation. In this case, the results of weight variation with respect to the carbonation depth of all concrete mixtures are shown in Fig. 8.

Test results presented in Fig. 8 show that all concrete mixtures have weight gain and the weight of the concretes mixtures proportionally increase with the carbonation depth. The highest value of the weight gain corresponds to the highest carbonation depth. The high-performance concrete mixtures F5 and F6 show a larger weight gains with carbonation when compared with the other ordinary concrete mixtures.

According to Chabil [34] the process of carbonation leads to the formation of above mentioned compound (i.e, CaCO$_3$) having high molar volume (36.9 cm$^3$/mol) compared with Ca(OH)$_2$ which has a molar volume equal to 33.1 cm$^3$/mol. The increases of the specimen’s weight after carbonation substantiate the increase of the concrete compressive strength.
Furthermore, exponential regression analysis of the results depicted in Fig. 8 showed that the weight gain can be an approximate indication for the carbonation depth with a coefficient of determination $R^2$ equal to 0.74.

### 3.4 The effect of carbonation reaction on the concrete oxygen permeability

For the different concrete mixtures, the evolution of the relative intrinsic permeability expressed as function of the carbonation depth is given in Fig. 9.

Two different behaviors were observed that conduct to two different relationships. The regression analysis shown in red line is for concrete mixtures F5 and F6 results while, the blue line concerns the regression analysis of the concrete mixtures F1, F2, F3 and F4 results. Test results show that the carbonation reaction considerably affects the concrete permeability as carbonation increases the permeability of concrete increases. These results are observed in all concrete mixtures. This increase in permeability due to carbonation is also obtained by Russel [20] and in some mixtures by Thiery [19]. Furthermore, it can be seen that the effect of carbonation on the permeability depend of the compressive strength. High performance concrete is more influenced by carbonation in comparison with ordinary concrete. This has been observed also where the influence of carbonation on the compressive strength was analyzed (Fig. 7). Linear regressions of the ordinary concrete mixtures and high performance concrete mixtures were also performed. The regression analysis showed existence of good correlation with coefficient of determination CoD ($R^2$) equal to 0.75 and 0.97.

Thiery has observed in some mixtures this trend and explained that carbonation reaction caused the reduction of porosity but in the same way this reaction creates larger pores with a new and high intercommunication pore structure after the formation of the CaCO$_3$ which can be the reason of the oxygen intrinsic permeability increase. Also, the mercury intrusion test results have been done by Thiery supports this finding.

On the concrete mixture F1 where a carbonation depth equal to 25 mm, the carbonated zone and non-carbonated zone have been analyzed via SEM images. Test results show that carbonation reaction affects the porosity system which leads to the creation of macro porosity that can probably affect the interconnectivity of the concrete pore system. This phenomenon is clear in the SEM images shown in Fig. 10. This result supports the increase of the concrete oxygen permeability that has been observed herein for the carbonated concrete. The arrows presented on the SEM image (b) indicate the CaCO$_3$ formation after consummation of the Ca(OH)$_2$.

The porosity of the SEM images presented in Fig. 10 was determined. The used program is Image-J, an open source software. This program is also used by several researchers to determine the porosity and the ratio between the

![Fig. 9 Oxygen intrinsic permeability versus carbonation depth](image1)

![Fig. 10 SEM images of concrete mixture F1 with w/c ratio equal to 0.76 and d equal to 25 mm for a) non-carbonated and b) carbonated zones](image2)
aggregate and the binder of the historical mortars [40, 41].
A threshold of the grey levels allowed isolating the holes as shown in Fig. 11. Therefore, the software made the automatic count of the holes (black) and sums their total area.

The porosity of carbonated and non-carbonated zones is respectively, 6.24 % and 1.62 %. The obtained values explain that carbonation reaction affects the permeability of concrete with the creation of larger pores due to the consummation of \( \text{Ca(OH)}_2 \) and formation of calcite which in turn lead to the increase of permeability.

For the same carbonated zone where MEB analysis has been carried out, X-ray diffraction (XRD) analysis has also been performed. The results depicted in Fig. 12 shows the total consummation of \( \text{Ca(OH)}_2 \). The highest pick is at 27° 2θ corresponds to the calcite (C), precisely vaterite (PDF 24-003D) with percentage of 74.3 %. The other picks correspond to other minerals such as calcium silicate hydrate (CSH) (PDF 29-0373) and calcium silicate (CS) (PDF 18-0.306).

4 Conclusions
The main goal of this paper is to clarify the controversy that exists of the effect of carbonation reaction on the permeability of concrete. For several concrete mixtures with w/c ratio ranging between 0.76 and 0.36 the influence of the carbonation reaction on the concrete oxygen permeability, compressive strength and concrete porosity has been experimentally studied. The conclusions that can be drawn from this investigation are as follows:

For the non-carbonated concrete the assessment of the oxygen permeability through the \( \frac{w}{c} \) ratio and compressive strength shows the existence of good correlations with coefficients of determinations equal to 0.88 and 0.92, respectively.

The carbonation reaction has a positive effect on the concrete compressive strength where the fully carbonated concrete has the highest gain in compressive strength. Furthermore, it was observed that high performance concrete is more influenced by carbonation in comparison with ordinary concrete.

The concrete carbonation reaction led to the formation of new elements that induce the compressive strength and the concrete weight to increase. These results are observed for all concrete mixtures.

The results obtained showed that permeability increases as carbonation progresses. Furthermore, this increase depends on the compressive strength of concrete and the effect of carbonation of the oxygen permeability is more significance in high performance concrete rather in ordinary concrete.

SEM images justify the increase of the oxygen permeability via the observation of the creation of larger porosity that influences the interconnectivity of the pore system.

The results reported herein provided valuable insights on the effect of carbonation on the permeability of concrete mixtures using one type of cement. The differences
between the effect of carbonation in high performance and ordinary concretes should to be considered when developing a model for service life prediction. Further research studies adopting other type of cement are needed for further generalization and understanding.

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References


[15] LNEC "LNEC E 465 Concrete. Methodology for estimating the concrete performance properties allowing to comply with the design working life of the reinforced or prestressed concrete structures under the environmental exposures XC and XS", National Laboratory for Civil Engineering, Lisbon, Portugal, 2005.


[34] Chabil, F.-Z. D. "Carbonatation des betons adjuvantes a base de resources locales Algeriennes" (Carbonation of concrete admixtures at the base of Algerian local resources), PhD Thesis, Université d’Orléans, Université de Constantine, 2009. [online] Available at: https://tel.archives-ouvertes.fr/tel-00797822/document (in French)


