Non Destructive Characterisation of Cement Mortar during Carbonation

Son Tung Pham and William Prince

Abstract—The objective of this work was to examine the changes in non destructive properties caused by carbonation of CEM II mortar. Samples of CEM II mortar were prepared and subjected to accelerated carbonation at 20°C, 65% relative humidity and 20% CO_2 concentration. We examined the evolutions of the gas permeability, the thermal conductivity, the thermal diffusivity, the volume of the solid phase by helium pycnometry, the longitudinal and transverse ultrasonic velocities. The principal contribution of this work is that, apart of the gas permeability, changes in other non destructive properties have never been studied during the carbonation of cement materials. These properties are important in predicting/measuring the durability of reinforced concrete in CO_2 environment. The carbonation depth and the porosity accessible to water were also reported in order to explain comprehensively the changes in non destructive parameters.

Keywords—Carbonation, cement mortar, longitudinal and transverse ultrasonic velocities, non destructive tests.
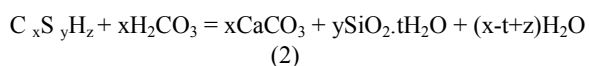
I. INTRODUCTION

NON destructive techniques (NDT) have been applied for quality assessment and monitoring the internal integrity (voids, cracks, degradation, etc.) of cement-based materials [1]. The comparison of the physical properties determined by NDT can provide an indirect approach to their performances. Although much research has been devoted to the development of NDT or of data processing for a better assessment of building materials, the use of these techniques is not yet addressed in the study of carbonation.

With the presence of water in the pores, the carbon dioxide from the air reacts with several constituents of the cement material to form calcium carbonate. The principle reactions of the carbonation process are:

The carbonation of portlandite:

$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O \qquad (1)$$

The carbonation of calcium silicate hydrate C-S-H:

$$C_xS_yH_z + xH_2CO_3 = xCaCO_3 + ySiO_2.tH_2O + (x-t+z)H_2O \qquad (2)$$

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The progress of these carbonation reactions causes a change in the pH of the internal environment, which induces the depassivation and corrosion of the steel rebar. The duration for CO_2 to reach the rebar is often regarded as the service time of the reinforced concrete structure. The onset of the corrosion can be predicted by the assessment of durable indicators [2]. While NDT are popular to assess the state of health of structures in reality, only some of the properties which can be determined by NDT are considered as durable indicators, for example, the gas permeability and the electrical resistivity. Other properties still need more research to be taken into account in assessing the durability of structures.

In this study, we propose to investigate the evolution of the non destructive properties caused by the carbonation in a cementitious matrix using different characterisation techniques. We will report the change in the following areas: the gas permeability, the thermal conductivity and thermal diffusivity, the solid phase's volume, the longitudinal and transverse ultrasonic velocities. The porosity accessible to water and the carbonation depth will also be examined in order to draw comprehensive explanations for the changes in non destructive properties during carbonation.

II. MATERIALS AND METHODS

A. Mortar CEM II

We used a normalised mortar prepared with French cement CEM II / BM (V-LL) 32.5 R and standard sand certified in accordance with EN 196-1. The water/cement and sand/cement ratios were respectively 0.5 and 3. At the end of the mixing, the mortar was placed in cylindrical moulds (Ø = 40 mm, h = 60 mm). The samples were demoulded after 24 hours and then cured for 90 days in a humid chamber (20°C, 100% relative humidity).

B. Accelerated Carbonation Test

To implement the test, the samples were subjected to axial diffusion of CO_2 in an environmentally controlled chamber at 20°C, 65% relative humidity and 20% CO_2 concentration for 7 days, 14 days and 32 days. After removing the samples from the chamber, the phenolphthalein test was used to distinguish the well carbonated and non carbonated zones.

C. Gas Permeability

The test was performed in a helium permeameter under variable pressures: 1 bar, 2 bars, 3 bars, and 5 bars. For each pressure, we waited for the gas flow to become constant. The

intrinsic permeability K was then calculated in accordance with CEMBUREAU method [3].

D. Thermal Properties

The thermal properties were performed at 20°C using a Hot Disk Thermal Constants analyser. A plane Hot Disk sensor was fitted between two pieces of the sample – each one with a plane surface facing the sensor. By passing an electrical current, high enough to increase the temperature of the sensor between a fraction of a degree up to several degrees, and at the same time recording the resistance (temperature) increase as a function of time, the Hot Disk sensor was used both as a heat source and as a dynamic temperature sensor.

E. Helium Pycnometry

Micromeritics helium pycnometry AccuPyc II 1340 was used to determine the actual volume of the solid phase. This method consists of injecting a gas at a given pressure in a container of known internal volume containing the sample and then relaxing it in a second chamber of known volume. The measure of the new equilibrium pressure is used to calculate the actual volume of the sample using the ideal gas law.

F. Longitudinal and Transverse Ultrasonic Velocities

The ultrasonic setup is composed of a pulse generator and receiver SOFRANEL model 5800 PR, two piezoelectric transducers of longitudinal waves and two piezoelectric transducers of transverse waves, a computer for data acquisition and data processing with a card oscilloscope/digitizer of 20 MHz sampling frequency, and a program of acquisition and signal processing developed under LabView environment.
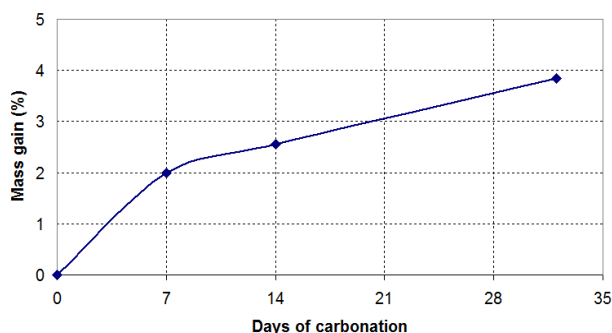
III. RESULTS AND DISCUSSION

A. Mass Gain

Fig. 1 Mass gain during carbonation of cement mortar

The carbonation reactions (1), (2) shows that a quantity of CO_2 was captured to give $CaCO_3$ as a product of carbonation. Also, water released by calcium hydroxide and C-S-H on carbonation may aid the hydration of the unhydrated cement. For this reason, all the mass were measured at dry state to reflect only the gain in mass of the solid phase. An electronic scale was used to measure the mass increase of the specimens due to CO_2 uptake. CO_2 uptake was determined by the initial mass and the final carbonated mass as shown in (3).

$$\Delta m = \frac{m_{after\ carbonation} - m_{initial}}{m_{initial}} . 100\% \qquad (3)$$

The results of the change in mass during carbonation are presented in Fig. 1. We observe that the mass increases in a continuous manner. On the other hand, the apparent volume of the specimens remains constant during carbonation. Therefore, we deduce an increase in the density of the mortar after carbonation. These changes are beneficial and result in improved strength, increased surface hardness, reduced moisture movement which reduces the potential of efflorescence.

B. Carbonation Depth

In Fig. 2, we observe that the carbonation propagation is a linear function with the square root of the duration of carbonation. This result is coherent with the prediction of carbonation depth in literature: $x = A.\sqrt{t}$ [11], where A is a constant taking into account both the composition of the cement material (water/cement ratio, type of binder,…) and the environmental conditions (relative humidity, temperature, pressure,…). The results can be used as a calibration while developing a model of carbonation.
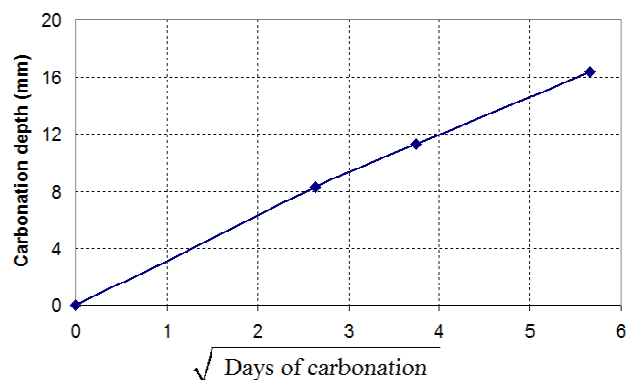

Fig. 2 Evolution of the carbonation depth

C. Porosity Accessible to Water

The porosity accessible to water was determined by the classical method using hydrostatic weighing [4]. The results in Fig. 3 show that the more the sample is carbonated, the more the porosity accessible to water decreases. When the CO_2 reaches deeper in the cement matrix (Fig. 2), the quantity of products of carbonation ($CaCO_3$) becomes greater and therefore the porosity decreases. This observation confirms the increase in the mass.
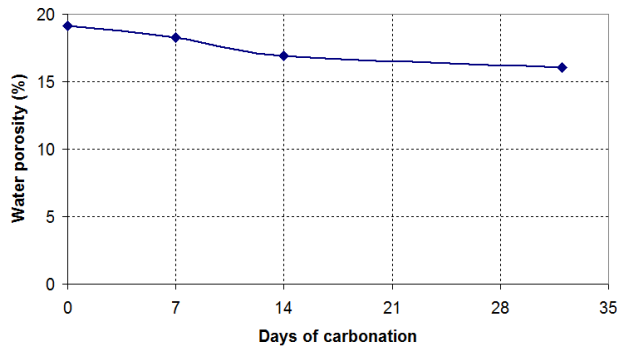
Fig. 3 Evolution of the porosity accessible to water during carbonation

D. Gas Intrinsic Permeability

Fig. 4 presents the evolution of the gas intrinsic permeability during carbonation. Contrary to what we expected, an increase in the gas intrinsic permeability was observed. The results seem to be in conflict with the decrease of the porosity. However, the water porosity decreases after carbonation means that the totality of pores decreases, but we have no specific information about the meso and macro pores, the porous domains which influence the gas permeability. According to Walid Jaafar [5], an increase in the volume of macropores after carbonation, which was observed by mercury intrusion porosimetry, might be the caused of the increase in the gas intrinsic permeability. Why the volume of macropores increases after carbonation is still discussed. According to Eitel [6], the increase in mesopore volume is caused by the porous structure of the silica gels that are formed during the carbonation. Swenson and Sereda [7] reported that the increase in mesopores is caused by cracks in the $CaCO_3$ gangue that surrounds the portlandite crystals. Other authors have attributed the increase in mesopores to carbonation shrinkage.
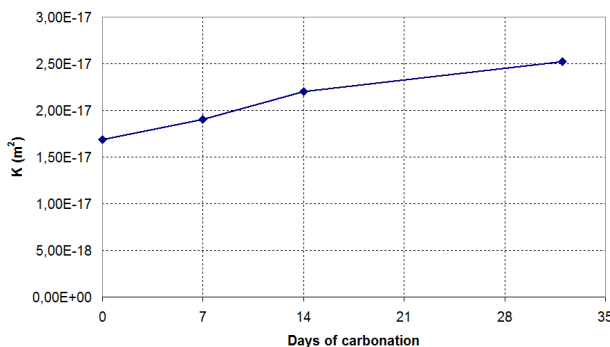

Fig. 4 Evolution of the intrinsic permeability to helium during carbonation

E. Thermal Conductivity and Thermal Diffusivity

Fig. 5 presents the thermal conductivity during carbonation. One measure was taken at 65% of relative humidity; another was taken when the specimens were dried. We observe an increase in the thermal conductivity as a function of the carbonation duration. Due to the low thermal conductivity of

the air, the thermal conductivity varies with the density [8]. Hence, the increase in the thermal conductivity during carbonation is coherent with the decrease of the total porosity.

The results show that the thermal conductivity at dry state is smaller than that obtained at 65% relative humidity. For building materials, it is common to use the following equation to show influence of the relative humidity on the thermal conductivity:

$$\lambda = k.\lambda_0 e^{0,08H} \tag{4}$$

where k is a coefficient of dimension, λ_0 is the thermal conductivity of dry material, and H is the relative humidity in percentage. The values of k were calculated and presented in Table I. We observe that k increases and remains stable after carbonation.

TABLE I
COEFFICIENT OF DIMENSION k DURING CARBONATION

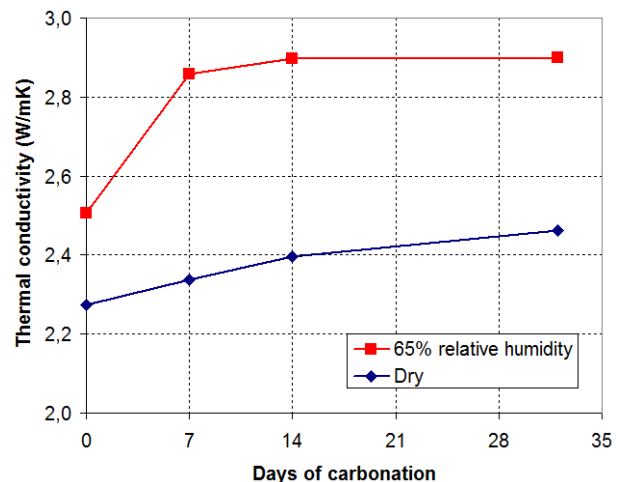| Days of carbonation	k
0	0,0061
7	0,0067
14	0,0067
32	0,0068

Fig. 5 Evolution of the thermal conductivity during carbonation

As in the case of the thermal conductivity, we observe also an increase in the thermal diffusivity. These results of the thermal conductivity and thermal diffusivity show that the carbonated cement mortar is more sensible to heat transfer than the non carbonated one. This finding is important for the study of fire resistance and energy conservation.
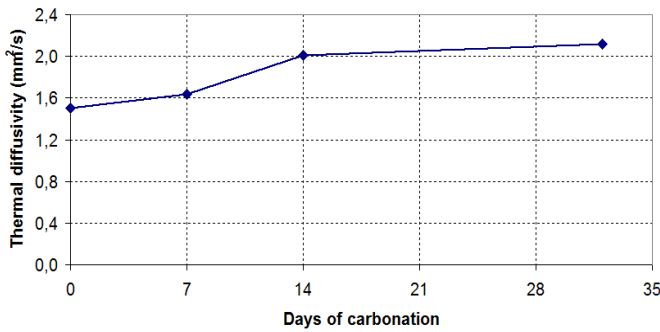
Fig. 6 Evolution of the thermal diffusivity during carbonation

Fig. 7 Evolution of the longitudinal ultrasonic velocity (V_L) during carbonation

F. Ultrasonic Velocities

We present the evolutions of longitudinal and transverse ultrasonic velocity in Fig. 7 and 8, respectively. These velocities increase continuously when carbonation occurs. Because the ultrasonic velocity in the air is smaller than in the dense material, the observations show an increase in the density, which is coherent with the results observed in mass gain. The characteristics of ultrasonic wave propagation in a material can provide valuable information on material properties, microstructure and damage state. These methods have many advantages: ease of implementation, ability to work with one side of the material, can pass through large thicknesses, obtaining immediate results of measurements. Furthermore, we can calculate the Poisson's ratio and dynamic modulus of elasticity from ultrasonic velocities as follow.

Poisson's ratio:

$$\upsilon = \frac{V_L^2 - 2V_T^2}{2V_L^2 - 2V_T^2} \qquad (5)$$

Dynamic modulus of elasticity:

$$E = 2\rho V_T^2(1+\upsilon) \qquad (6)$$

Fig. 9 shows that the Poisson's ration remains constant before and after carbonation. In contrast, the dynamic modulus of elasticity increases after carbonation (Fig. 10). This results in a stiffer cement mortar. These observations show a positive influence of the carbonation on the cement based material.
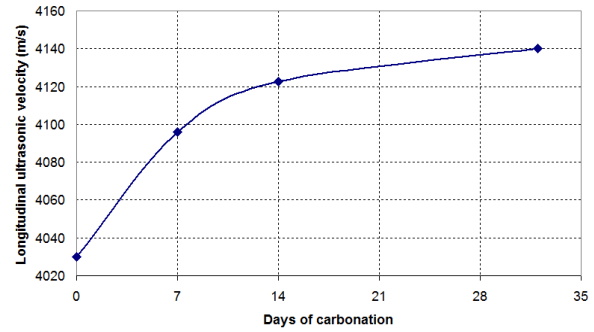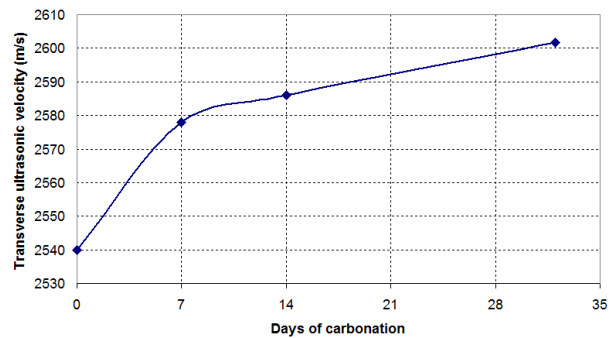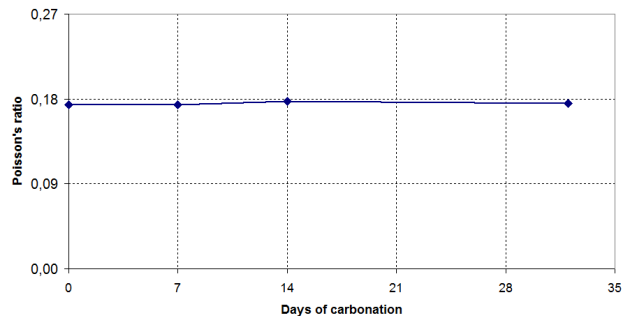

Fig. 8 Evolution of the transverse ultrasonic velocity (V_T) during carbonation

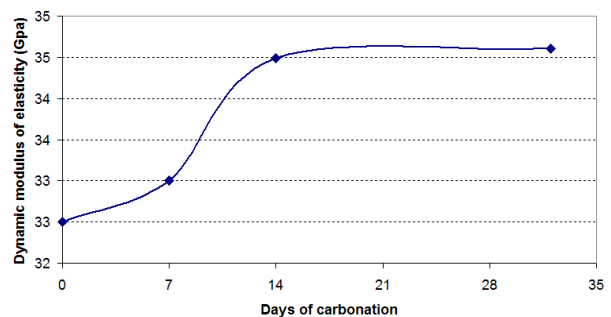Fig. 9 Evolution of the Poisson's ratio during carbonation

Fig. 10 Evolution of the dynamic modulus of elasticity during carbonation

G. Ultrasonic Velocities

The actual volumes of the solid phases were determined using helium pycnometry on two groups of samples before and after the period of carbonation. The results are presented in Fig. 11. We can see clearly that the accelerated carbonation resulted in a significant increase in the actual volume in comparison with the natural carbonated sample, which was maintained at 20°C and 65% relative humidity without additional CO_2. The increase in the volume of the solid phase can be explained by the formation of $CaCO_3$ during carbonation, because the carbonation of one mole of portlandite leads to an increase in volume of 4 cm^3 [9, 10], and the carbonation of one mole of C-S-H leads to an increase in volume of 12 cm^3 [11] or 39 cm^3/mol [12]. Due to differences in the volume, the carbonation product ($CaCO_3$) clogs the pores, thereby decreasing the porosity.
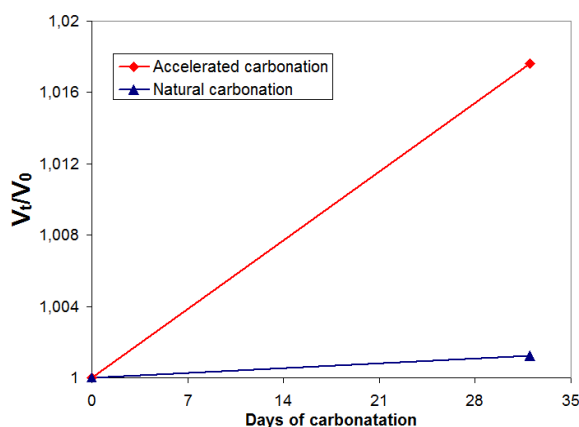

Fig. 11 Evolution of the solid phase volume during accelerated carbonation and natural carbonation

IV. CONCLUSION

The results of this study show significant changes in physical properties of cement mortar during carbonation. The capture of CO_2 results in a mass gain and an increase in the density. The $CaCO_3$ produced by the carbonation of $Ca(OH)_2$ and C-S-H clogs the pores and therefore decreases the porosity. As consequence, the thermal properties and the ultrasonic velocities increase after carbonation, as well as the dynamic modulus of elasticity. Contrary to the decrease in porosity, the intrinsic gas permeability increases due to the carbonation shrinkage. These observations indicate a positive consequence of carbonation on cement based materials in term of strength at the expense of the thermal and sonic insulation.

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