Effects of Carbonation on the Microstructure and Macro Physical Properties of Cement Mortar

Son Tung Pham and William Prince

Abstract—The objective of this work was to examine the changes in the microstructure and macro physical properties caused by the carbonation of normalised CEM II mortar. Samples were prepared and subjected to accelerated carbonation at 20°C, 65% relative humidity and 20% CO_2 concentration. On the microstructure scale, the evolutions of the cumulative pore volume, pore size distribution, and specific surface area during carbonation were calculated from the adsorption desorption isotherms of nitrogen. We also examined the evolution of macro physical properties such as the porosity accessible to water, the gas permeability, and thermal conductivity. The conflict between the results of nitrogen porosity and water porosity indicated that the porous domains explored using these two techniques are different and help to complementarily evaluate the effects of carbonation. This is a multi-scale study where results on microstructural changes can help to explain the evolution of macro physical properties.

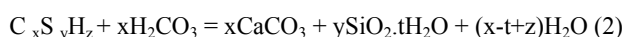*Keywords*—Carbonation, cement mortar, microstructure, physical properties.

I. INTRODUCTION

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:

$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O \qquad (1)$$
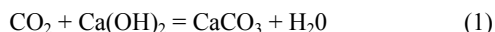
The carbonation of calcium silicate hydrate C-S-H:

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

The progress of these carbonation reactions causes a change in the microstructure, which is highlighted by various parameters such as variations in porosity, specific surface area and pore size distribution. These microstructural evolutions during carbonation lead obviously to changes in macro physical properties such as the gas permeability and the thermal conductivity.

Son Tung Pham is a Ph.D. student at the Department of Civil Engineering, National Institute of Applied Sciences in Rennes, 20 Avenue des Buttes de Coësmes, CS 70839, 35708 Rennes Cedex 7, France (phone +33 (0) 667059404, e-mail: spham@insa-rennes.fr).

William Prince is a professor at the Department of Civil Engineering, National Institute of Applied Sciences in Rennes, 20 Avenue des Buttes de Coësmes, CS 70839, 35708 Rennes Cedex 7, France.

The coherence between the observations on micro and macro scales is still discussed. While most authors have observed a decrease in the porosity accessible to water [1], [2], this result cannot explain the increase in the gas permeability observed by some authors [1], [3]. Some investigators believe that the water molecule, because of its small radius of 0.1nm [4], can penetrate not only into meso and macro pores (radius larger than 2nm) but also into nano and micro pores [5]. Hence, the water porosity decreases after carbonation means that the totality of pores decreases, but no specific information about the meso and macro pores, the porous domains which influence the gas permeability, can be drawn.

Although the mercury porosimetry method is suitable for meso and macro pores with radii of 2nm to 60µm, the high pressure which is needed to intrude the mercury into the pores might lead to the micro damage during the test and influence the results [6]. For this reason, we propose to investigate the evolution of the microstructure caused by the carbonation in a cementitious matrix using nitrogen adsorption, which is suitable for meso pores with radii of 2nm to 32nm. We will report the change in the following areas: the cumulative pore volume, the BET specific surface area [7], and the pore size distribution. The observations on microstructural changes will help to discuss the evolutions of macro properties that we propose to measure, such as the gas permeability and the thermal conductivity. Although the thermal conductivity is important for fire resistance and energy conservation, its evolution during carbonation of cement materials has never been studied.

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 =40mm, h =60mm). 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. Nitrogen Adsorption

The sheets and packets of C-S-H constitute respectively the microscopic and mesoscopic scales of the cementitious matrix. Nitrogen adsorption-desorption isotherms were performed on grinding powders extracted from the samples. This test can provide information about the mesoscopic scale because the nitrogen molecules are adsorbed to the surface of C-S-H packets but they do not enter inter foliar spaces. We used the specific surface area analyser Micromeritics Gemini VII for this test. From adsorption desorption isotherm curves, the BET specific surface area [7] and the BJH pore size distribution [8] were calculated.

D. 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 [9].

E. Thermal Conductivity

The thermal conductivity was 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.

III. RESULTS AND DISCUSSION
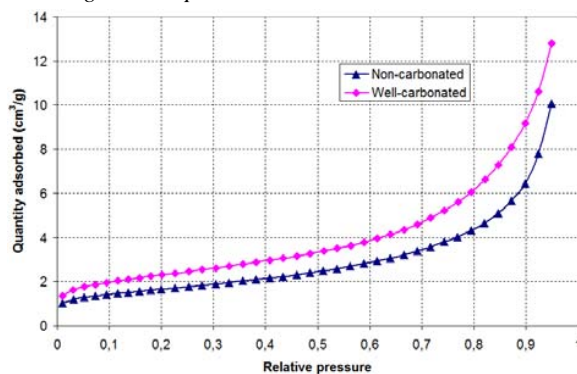
A. Nitrogen Adsorption

Fig. 1 Nitrogen adsorption isotherms of cement mortar

In Fig. 1, we present the nitrogen adsorption isotherms for the two types of samples (carbonated and non-carbonated). The experiment was performed three times on each sample, and we obtained the same curves, which indicated a good repeatability of the results. When comparing the isotherms of the carbonated sample with those of the non-carbonated sample, we observe that nitrogen adsorption on the carbonated sample is more significant.

Regarding the pore distribution curves (Fig. 2), we observe that the carbonation results in a slight decrease in the micropore volume and an increase in the mesopore volume. The carbonation of portlandite is manifested by the crystallisation of numerous calcite crystals on the portlandite plates. Thus, it is understandable that the carbonation results in an increase in the specific surface area (Table I) and a modification of the pore network.

TABLE I
EVALUATION OF SPECIFIC SURFACE AREA

Material	BET Nitrogen (m^2/g)
Non-carbonated	5,9
Well-carbonated	8,3

TABLE II
WATER ACCESSIBLE POROSITY

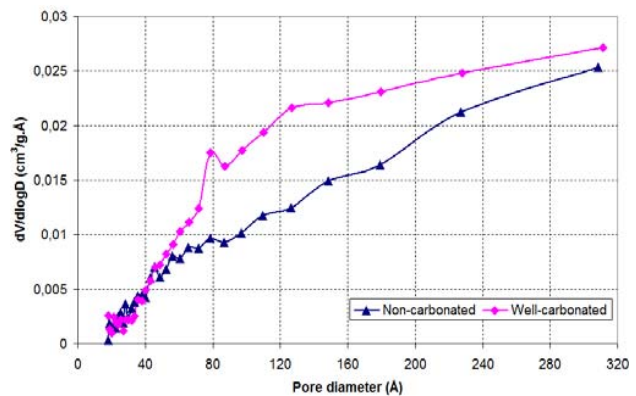| Material	Porosity (%)
Non-carbonated	18,7
Well-carbonated	16,1

Fig. 2 Pore size distribution for well-carbonated and non-carbonated cement mortar
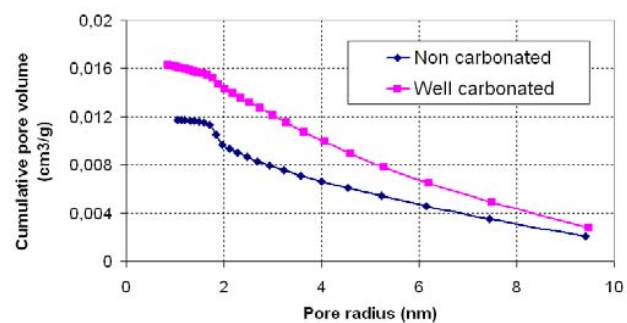
B. Total Porosity

Fig. 3 Cumulative pore volume determined by nitrogen adsorption

We present in Table II the porosity accessible to water determined by the classical method using hydrostatic weighing [10]. The results reveal a clear decrease in the total

porosity. Similar results have already been reported in the literature [1], [2]. This result is therefore opposite in comparison with the result obtained by the nitrogen adsorption (Fig. 3). Both techniques seem to cover different porous domains. According to Baroghel-Bouny [5], the size of nitrogen molecules does not allow them to access the microporosity, whereas the water molecules can enter these micropores. Hence, the nitrogen adsorption test provides information mainly about the mesoporous domain.

In the domain of nano and micro pores, the calcium carbonate formed during carbonation obstructs the pores, by consequence, the water accessible porosity decreases. This decrease in the volume of micropores was confirmed in Fig. 2 where we presented the pore size distribution calculated from nitrogen adsorption desorption isotherms.

C. Carbonation Depth

In Fig. 4, 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,…).
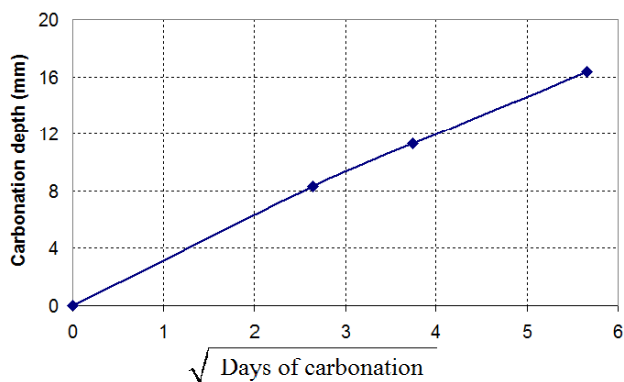

Fig. 4 Evolution of the carbonation depth during carbonation

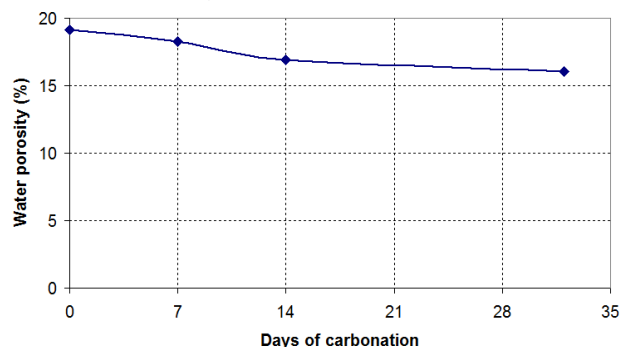### D. Porosity Accessible to Water- Gas Permeability – Thermal Conductivity

Fig. 5 Evolution of the porosity accessible to water during carbonation

The results in Fig. 5 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. 4), the quantity of products of carbonation ($CaCO_3$) becomes greater and therefore the porosity decreases. In combination with the results determined by nitrogen adsorption, it seems that the decrease in the total porosity is mostly because of the decrease in the volume of micro pores. In contrast, the volume of mesopores increases with the carbonation. We also observed an increase in the intrinsic permeability to helium as presented in Fig. 6. The results showed that the evolution of the gas permeability during carbonation is largely influenced by the changes in the mesoporous domain.
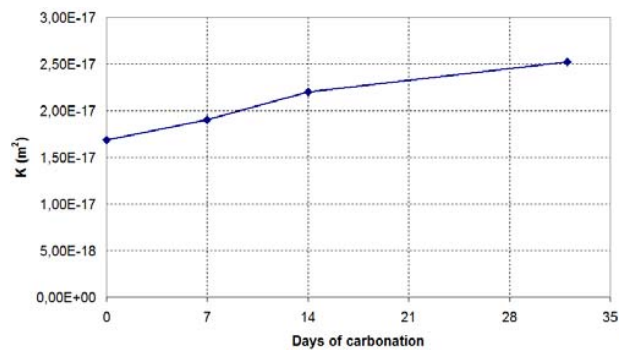

Fig. 6 Evolution of the intrinsic permeability to helium during carbonation

Fig. 7 presents the thermal conductivity during carbonation. 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 [12]. Hence, the increase in the thermal conductivity during carbonation is coherent with the decrease of the total porosity.
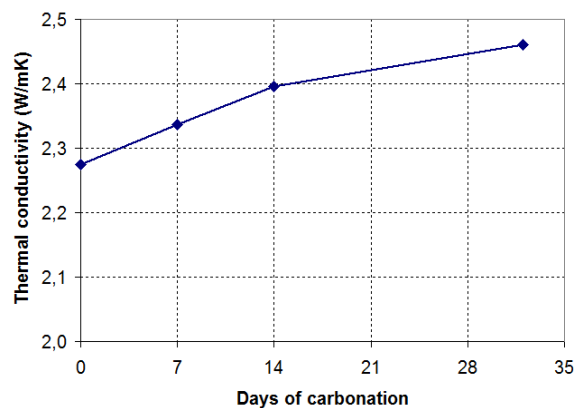

Fig. 7 Evolution of the thermal conductivity during carbonation

IV. CONCLUSION

The results of this study indicate that nitrogen and water

molecules do not get access into the same porous domains. Investigation using nitrogen adsorption gives information about meso pores, while the one using water-accessible porosity covers all three domains: macro, meso and micropores.

Thus, the porosity and specific surface area determined by nitrogen adsorption increase when carbonation occurs. At a given relative pressure, the well-carbonated cement mortar adsorbs more nitrogen than the non-carbonated sample. Furthermore, the adsorption occurs mainly in the mesoporous domain with pore sizes larger than 2nm.

In constrast, the porosity accessible to water decreases after carbonation. The combination of the two techniques allows drawing a conclusion that, after carbonation, the volume of meso pores increases at the expense of the volume of micropores.

The decrease in the volume of micro pores is explained by the formation of $CaCO_3$ during carbonation that obstructs the pores. This results in the increase of the thermal conductivity after carbonation.

It appears that the gas intrinsic permeability is mostly influenced by the meso pores. The results shows that the increase in volume of meso pores after carbonation might be the cause of the increase in the intrinsic permeability to helium.

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