Effect of Carbonation on the Microstructure and Moisture Properties of Cement-Based Materials

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ABSTRACT

We provide a comprehensive understanding of the effects of carbonation on the microstructure, and the moisture properties of cement-based materials made of ordinary Portland cement (OPC) and fly ash (FA). The bulk porosity is measured on a large panel of non-carbonated or fully carbonated cement pastes and concrete specimens by hydrostatic weighing and by mercury intrusion porosimetry (MIP). The carbonatable amount of CH and C-S-H (corresponding to the maximum degree of carbonation that is reached for these hydration compounds) is assessed when the carbonation mechanism is considered stabilised. The induced reduction in porosity is correlated with the calcium carbonate (CC) content quantified by thermogravimetric analysis (TGA) and associated both with CH and C-S-H carbonation. The identified variation of molar volume occurring during the C-S-H carbonation is dependent on the CO\textsubscript{2} concentration and is different if pozzolanic C-S-H are considered since for this latter a negative difference of solid volume can be observed. The effect exerted by carbonation on the pore size distribution (PSD) is also elucidated by means of MIP and by analysing the diagrams of the spin-lattice relaxation time ($T_1$) determined by Nuclear Magnetic Resonance of proton H (NMR). The proportion of coarse capillary pores (radius>100 nm) increases with the degree of carbonation for materials of a high water/cement (w/c) ratio although a systematic reduction in total porosity for OPC systems is still measured. Moreover, this paper discusses the influence of carbonation on the water vapor desorption isotherms (WVDIs). An analysis of the $T_1$-diagrams and the WVDIs of carbonated and non-carbonated materials made of OPC shows that the same fine-textured morphology of the C-S-H seems remains in spite of a partial decalcification and polymerisation.

KEYWORDS

Carbonation, C-S-H, Mercury intrusion porosimetry, NMR, Water vapor sorption isotherm.

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1 INTRODUCTION

Carbonation of cement-based materials is based on a complex reactive-transport mechanism governed by CO$_2$-diffusion within the porous network and the chemical reactions between CO$_2$ and the hydration compounds (generally CH and C-S-H). It is well established that carbonation is generally responsible for significant microstructural changes [Ngala & Page 1997]. For ordinary Portland cement (OPC) systems, carbonation leads to a reduction in porosity which is generally ascribed to the positive difference of molar volume between CH and the precipitated C$_4$C (4 cm$^3$ mol$^{-1}$ if calcite is forming). But it is obvious that the observed decrease in porosity cannot only be related to CH carbonation and consequently that the carbonation of C-S-H may also significantly contribute to this evolution. It is for this reason that a determination of the variation of molar volume of the solid phase occurring during the C-S-H carbonation should be investigated. Furthermore, it is also known that the carbonation of materials made of fly ash (FA) can lead to a coarser microstructure and a possible increase in porosity. Nevertheless, since the reasons for such behaviour are still not well understood, a comprehensive analysis of the evolution of the pore size distribution (PSD) caused by carbonation is necessary.

2 MATERIALS AND EXPERIMENTAL PROCEDURES

An grey OPC ($C_3S$ 59%, $C_2S$ 19%, $C_3A$ 2%, $C_4AF$ 14%, gypsum 5%), a white OPC ($C_3S$ 54%, $C_2S$ 28%, $C_3A$ 11%, $C_4AF$ 1%, gypsum 5%) and a class F fly ash (S 50%, A 23%, F 9%) were used in this study. Cement pastes were fabricated with a water-to-cement ratio (w/c) ranging from 0.25 to 0.60. Cement pastes of w/b=0.3/0.4/0.5 with two levels of cement replacement by FA (20% and 40%) were also fabricated. Cement paste specimens were prepared in plastic bottles tightly sealed to avoid water evaporation and rotated to keep an homogeneous material. The cement pastes were removed from their mould at 18 months. A concrete (M25) was also prepared with the same grey OPC cement (w/c=0.84, s/(s+g)=0.47) and was water-cured during 90 days. The cement paste specimens were crushed in small pieces (1 mm$^3$) which were dried in a desiccator where a NH$_4$NO$_3$ salt solution controls a relative humidity (RH) of 53% until mass loss stabilisation (i.e. at least 14 days). Cylindrical concrete specimens (2 geometries: diameter=11 cm and height=5 cm or 0.2 cm) were dried at 45°C during 28 days. After this pre-treatment, the crushed samples of cement paste and the concrete specimens were then exposed in a carbonation chamber where the CO$_2$ concentration is maintained constant (10% or 50%) and the RH is controlled by a NH$_4$NO$_3$ salt solution. The samples were held in this CO$_2$-incubator until the mass increase due to the CO$_2$ fixation onto the cementitious matrix is stabilised. This criterion is considered to represent a full carbonation state. Obviously, the carbonation duration depends of the CO$_2$ concentration and the size of the samples: a few days for the crushed cement paste samples, a few weeks for the 0.5-diameter concrete specimens and at least two months for the 5-cm diameter concrete specimens. Moreover, some cement paste samples were exposed to natural carbonation (CO$_2$=0.04%) in a laboratory room where the RH is maintained around 50%. Examples of mass increase kinetics during the exposure period to CO$_2$ are shown in Fig. 1 in the case of the cement paste samples made of OPC. It is worthwhile noting that the slight decrease in the sample mass towards the end of the test illustrates that the carbonation mechanism becomes stabilised and indicates that the free water released from the hydration products (CH and C-S-H) due to carbonation is starting to dissipate from the samples upon drying.

In order to investigate the influence of carbonation on the properties of the materials (chemical composition, microstructure changes and moisture properties), different techniques were performed on non- and fully-carbonated materials: thermogravimetric analysis (TGA), mercury intrusion porosimetry (MIP), assessment of the accessible-to-water porosity ($P_w$), spin-lattice relaxation ($T_1$) Nuclear Magnetic Resonance (NMR) measurements [Faure et al. 2005] and assessment of the water vapour desorption isotherms (WVDIs) [Baroghel-Bounty 2007].
3 INVESTIGATION OF THE POROSITY CHANGES DUE TO CARBONATION

3.1 Evaluation of the amount of carbonatable amount of CH and C-S-H

In order to correlate the evolution of the porosity with the amount of CC related to CH and C-S-H carbonation, it is first necessary to dispose of an accurate assessment of the maximum carbonation degree of CH and C-S-H when the carbonation mechanism is stabilised, i.e. when the material is considered as fully carbonated. The initial amount of CH and CC are measured by TGA during the heating, respectively in the temperature range 450°C-550°C and 550°C-950°C (see two examples of TGA results in Fig. 2 for carbonated and non-carbonated cement pastes made of or without FA). Of interest is the fact that the temperature range corresponding to the decomposition of CC during the heating is very broad which makes the determination of the CC content formed by carbonation difficult if a limestone aggregate is used (in mortar or concrete). Figure 3 illustrates the initial CH content \( n_{0}^{CH} \) for the studied cement pastes only made with OPC (determined by TGA on non-carbonated materials), as well as the initial C-S-H content assessed by means of a semi-analytical model [Bernard et al. 2003] (the chosen stoichiometry for the C-S-H is \( C_{2}S_{1.7}H_{x} \)). Figure 3 also shows the amounts of CC produced by the carbonation reactions of CH (\( n_{CC}^{CH} \)) and C-S-H (\( n_{CC}^{C-S-H} \)). These values are determined according to the characteristics of the non-carbonated specimens (\( n_{0}^{CH} \) and initial amount of CC \( n_{0}^{CC} \) indicating a possible slight air-carbonation during the fabrication or the pre-treatment of the samples) and to the total amount of CC (\( n_{CC}^{T} \)) within the carbonated samples, i.e.

\[
\begin{align*}
\Delta n_{CC}^{CH} &= n_{0}^{CH} - n_{CH}^{T} \\
\Delta n_{CC}^{CSH} &= n_{CC}^{T} - n_{CC}^{CH} - n_{0}^{CC}
\end{align*}
\]

Figure 1. Kinetics of mass increase during the carbonation of cement paste samples (crushed) of \( w/c=0.35/0.45/0.55 \).

Figure 2. Examples of thermoanalytical curves (first derivative of the relative mass loss, TGD) for cement pastes (non-carbonated and fully-carbonated with \( CO_2=50\% \)).

Figure 4 illustrates the degree of carbonation of CH (\( n_{CC}^{CH}/n_{0}^{CH} \)) and C-S-H (\( n_{CC}^{C-S-H}/[3n_{0}^{C-S-H}] \)) of the materials under study. It seems that CH cannot be fully carbonated and that a maximum carbonation level of 0.8 (for \( w/c=0.45 \) and accelerated conditions \( CO_2=50\% \)) is observed. This behaviour is classically related to the formation of a CC coating around the CH hexagonal crystals that drastically hinders ion transfers and the carbonation kinetics of CH. Moreover, an optimum carbonation for CH can be noticed for \( w/c=0.45 \). Actually, when the \( w/c \) is high, massive clusters of CH crystals are observed [Gallucci & Scrivener 2007] and thus the reduction in accessibility and passivation effects are enhanced. On the other hand, when the \( w/c \) is low, CH crystals are certainly smaller but they are surrounded by a denser matrix of C-S-H that also makes them less accessible. Note that the maximum degree of CH carbonation depends on the \( CO_2 \) concentration. It is observed that the amount of carbonatable CH is higher when the \( CO_2 \) concentration is above 10%. Figure 4 also illustrates the equivalent behaviour between results at \( CO_2=10\% \) and natural carbonation as regards the carbonatable amount of CH. Concerning C-S-H, the influence of reduction in accessibility occurring during the formation of CC is less pronounced thanks to a much higher exposed surface area to \( CO_2 \).
than CH crystals. Consequently, for C-S-H a maximum degree of carbonation (close to 1) can be reached if the CO₂ concentration is high (50%) leading to an almost total decalcification.

3.2 Evaluation of the changes in porosity related to the carbonation level of CH and C-S-H

The amount of CC₃ produced by CH carbonation makes possible the calculation of the drop in porosity due to the only carbonation of CH given that carbonation of CH is mainly responsible for the formation of calcite (polymorph of CC₃) [Groves et al. 1991] and that the corresponding variation in molar volume is well known (Dv(CH)=3.8 cm³.mol⁻¹). The accessible-to-mercury porosity (applied Hg pressure from 0.01 kPa to 400 MPa) has been determined on the non-carbonated and fully-carbonated samples. Figures 5 and 6 illustrate the variation in porosity which is only related to the other hydration compounds than CH, in fact mainly C-S-H (i.e., Δϕ₃=Δϕ₃ₐₜ₉₅ CH xDv(CH) Δϕ₃ₐₜ₉₅ is plotted as a function of the C₃C amount produced by the carbonation of the other hydration compounds than CH (n₃₊₅₉₅₋₅₉₅ CH₉₅₋₅₉₅ and measured by TGA. Since the cement used in this study to prepare the cement pastes has a very low C₃A content (in order to ensure a high resistance to the sulphate attack), the predominant hydrated compounds other than CH are mainly composed ,in this instance, of C-S-H.

In the case of pastes made of OPC, Fig. 5 shows, for each CO₂ concentration, a satisfactory linear relation between the C₃C content (per unit volume of porous material) thus related to the C-S-H carbonation and the corresponding variation in porosity. The slope reflects the change in volume Dv(CH) if a mole of C₃C is formed from C-S-H. It is found that Dv(CH)=17.5 cm³.mol⁻¹ for CO₂=50%, Dv(CH)=21.6 cm³.mol⁻¹ for CO₂=10% and Dv(CH)=28.5 cm³.mol⁻¹ for natural conditions of exposure. It is possible to demonstrate that Dv(CH)=v₃(CH) x(1/x)v₃(SH₃) where x and y are the stoichiometric parameters defining the chemical composition of the C-S-H (C₃SₓH₉₋₅ₓ) and v₃(CH) and v₃ are the molar volumes of the C-S-H and the formed amorphous silica gel, respectively. Whether the value of Dv(CH) is positive or negative is governed by the molar volume of silica gel (SH₃) which depends on the amount of chemically-bound water molecules silica gel contains. Actually, a great variability of v₃ is reported in the literature: from 12 to 34 cm³.mol⁻¹ according to Wolery [1992]. The positive value for Dv(CH) observed for the OPC systems under study shows that the formed silica gel has certainly a high degree of hydration (t close to 2). The lower observed values for Dv(CH) when the CO₂ concentration is higher may be understood if one considers that high CO₂ concentration preferentially leads the production of aragonite of lower molar volume than vaterite and calcite.

Figure 6 illustrates the evolution of porosity as a function of the concentration of C₃C produced by the C-S-H carbonation in the case of cementitious systems containing FA. Therefore, the amount of C₃C assessed by TGA also includes the C₃C formed by carbonation of the pozzolanic C-S-H. For a moderate degree of the C-S-H conversion (n₃₋₅₉₅ CH<3000 mol.m⁻³) and in the case of the cement pastes containing FA with a replacement ratio of 20%, the change in porosity as a function n₃₋₅₉₅ CH evolves similarly (with the same upward trend) than the OPC pastes without FA. For a higher carbonation degree of the C-S-H (n₃₋₅₉₅ CH>3000 mol.m⁻³), Fig. 6 reveals that a decrease in porosity as a function n₃₋₅₉₅ CH is observed giving evidence that the C-S-H carbonation causes a drop of the volume of the solid phase. Undeniably, this effect is due to the carbonation of the pozzolanic C-S-H which may produce a poorly-hydrated silica gel of a low molar volume (v₃) due certainly to a release during carbonation of a great amount of free water initially chemically-bound within the C-S-H. Note that this peculiar behaviour observed for the pozzolanic C-S-H is more evident with a higher FA replacement ratio of 40% since given that it is observed in Fig. 6 that carbonation can then significantly contribute to an increase in porosity. This phenomenon is in agreement with other results taken from literature which show an increased porosity and a loss of strength for concrete made with a high FA (or slag) content (see for instance Thaulow et al., 2000). It is generally proposed to interpret this deleterious consequence of carbonation on the global porosity as an effect of the decalcification of the C-S-H which is more pronounced if pozzolanic C-S-H of lower initial C/S ratio (1.2-1.4) than ordinary C-S-H are concerned and if the CH content in the system is limited because for instance of the pozzolanic activity of FA [Thomas et al. 2003].
Effect of carbonation on the microstructure and the moisture properties of cement-based materials

Figure 3. Initial CH and C-S-H contents for different cement pastes (w/c=0.25 to 0.55). CC produced by reaction of CH and C-S-H.

Figure 4. Carbonation levels of CH and C-S-H vs. W/C of different cement pastes and carbonation conditions.

Figure 5. Variation in porosity related to the CC produced by C-S-H carbonation (case of OPC pastes).

Figure 6. Variation in porosity related to the CC produced by C-S-H carbonation (case of pastes prepared with OPC and FA).

Figure 7. PSD of hardened OPC pastes (non-carbonated and carbonated with CO₂=50%) of different w/c (0.60, 0.50, 0.35 and 0.25). Determination by mercury intrusion porosimetry (MIP).
Figure 8. PSD determined by MIP of different slices sawn from the surface to the core of a specimen of OPC paste (w/c=0.45) exposed to CO₂ (50%) during 14 days.

Figure 9. WVSIs of concrete M25 (non-carbonated and carbonated with CO₂=50%). Water content (w) and liquid water saturation (S) vs. RH.

Figure 10. Distribution of T₁ relaxation time in the case of non-carbonated and carbonated (CO₂=50%) white cement pastes.

4 MICROSTRUCTURE CHANGES (INFLUENCE ON PORE-SIZE DISTRIBUTION)

Figure 7 illustrates the PSDs for non-carbonated and carbonated OPC pastes of w/c ranging from 0.6 to 0.25. These PSDs are determined by MIP performed on freeze-dried samples (lyophilisation). The analysis of the PSDs shows that, although carbonation is responsible for an apparent clogging of the microstructure between 10-100 nm (corresponding to capillary mesopores attributed to the voids among outer C-S-H clusters according to the general classification proposed by Mindess, 2002), carbonation is also capable of producing larger capillary macropores of 100-200 nm size if w/c is high enough (i.e. >0.45). To understand this feature a descriptive model can be used, such as the one proposed to interpret the evolution of the microstructure which takes place during the carbonation of non-hydraulic lime mortars [Lawrence et al. 2002]. Although the porosity in the range 10-100 nm is filled by CCₐ of higher volume than the parent hydrated compounds CH and C-S-H, a new porosity may also appear between CCₐ microcrystals which are packed within the pore space previously occupied by CH macrocrystals. This size of the created pores is of the same order of magnitude as the size of the CCₐ crystals (calcite), i.e. around 100 nm. The creation of these macrocapillary pores seem reinforced if carbonation is occurring with a high CO₂ concentration and if the water content within the material is low given that these carbonation conditions prevent the diffusion of ions through the pore solution and thus contribute to a localised formation of CCₐ crystals around the CH clusters. On one hand, the carbonation at high CO₂ (at least 50%) is so accelerated that the formation of CCₐ crystals takes place directly at the surface of CH crystals where Ca²⁺ and CO₃²⁻ ions meet and form calcite. On the other hand, if the cement-based material is too dry, the water film covering the pore surface is too thin to facilitate the diffusion of ions. Note that for the studied cement pastes of high
w/c (0.5 and 0.6), the appearance of a coarser microstructure when the material is carbonated is more pronounced. This might be attributed to the formation of larger CH crystals embedded in a highly porous matrix which enables the expansion of calcite crystals and makes the cluster of C\textsubscript{C} crystals less dense.

Figure 9 represents the WVDIs (at 20°C) of concrete M25 (carbonated and non-carbonated) determined by the desiccator method. Concrete disks (2 mm-thickness) were submitted to decreasing RH steps from 100% (deionised water) to 3% (dry silica gel) by using saturated salt solutions for intermediate RH values and by waiting for weight loss equilibrium for each step (at least 2 months). The water content (w) and liquid water saturation (S) are plotted vs. RH. The significant reduction in porosity due to carbonation of this concrete made of OPC thus allows an explanation for the water content of the carbonated disks being clearly lower than the water content of the healthy samples. By choosing S instead of w to plot the WVSIs, the impact of the clogging effect of the porosity is side-stepped. It is thus possible to isolate the sole influence of the changes affecting the PSD caused by carbonation. Therefore, since carbonation does not significantly affect the WSI if S is chosen to quantify liquid water inside the porous material, it seems that carbonation does not change the PSD in the range of the pore size accessible by this technique, i.e. mainly the intrinsic porosity of the C-S-H. This feature is observed even if carbonation results in a decalcification/polymerisation of the C-S-H which is thus likely to stay moderate in the case of OPC systems. A higher degree of decalcification (drop of C/S) may be observed if pozzolanic C-S-H with low C/S ratio are carbonated leading therefore to a serious modification of the microstructure of the C-S-H and a creation of a microporosity not observed in raw materials. The highly cross-linked formed silica gel has actually an open nature compared to non-carbonated C-S-H slits.

In Figure 9, the fact that the WVDIs of the carbonated and non-carbonated OPC concrete have relatively the same shape, illustrating thus the slight modifications of the microstructure of the C-S-H, is in agreement with the experimental observations dealing on the weak difference about the porosity variations, assessed either by MIP and by the determination of the accessible-to-water porosity, between carbonated and non carbonated samples. It confirms that the whole modifications of the microstructure caused by carbonation of OPC systems are entirely detectable by MIP.

Inverse Laplace processing of the spin-lattice relaxation data enables the determination of the $T_1$ distribution (distribution of the longitudinal relaxation time) which is known method to characterise the mobility of water molecules within cement-based materials. Since this mobility depends on the size of the pores, the analysis of $T_1$-diagrams gives information on the pore size distribution of hardened cement pastes by probing their water mobility. The $T_1$ distribution of hardened cement-based materials exhibits at least three modes as illustrated in Fig. 10 for a non-carbonated and a carbonated paste fabricated with a white cement (w/c=0.4). These materials are tested after saturation by liquid water. The diagrams are normalised by the water content of the tested specimens to get rid of the influence of the clogging effect on the porosity by the formation of C\textsubscript{C} and to highlight the changes in PSD. In Fig. 10, the three observed $T_1$ peaks are attributed to the chemically-bound water (very short $T_1$ values: 0.1-1 ms), to the gel pores ($T_1>$10 ms) and to capillary pores ($T_1=1-10$ ms). The gel and capillary porosities correspond to two distinct pore sizes: <10 nm and >10 nm, respectively [Faure et al. 2005]. The fact that the $T_1$ peak characterising the intrinsic porosity of the C-S-H remains unchanged proves that carbonation poorly affects the microstructure of the C-S-H confirming the previously observed WVSIs results. Nevertheless, carbonation seems to modify the capillary microstructure by filling one part of the capillary pores and by creating a new porosity as has been shown by MIP.

**CONCLUSION**

A comprehensive study of the consequences of carbonation on the microstructure of cement-based materials has been performed. Firstly, the changes of porosity have been quantified and correlated to the amount of C\textsubscript{C} formed due to the carbonation of CH and C-S-H. In this manner, the variation of
molar volume \(D_{v_{\text{CSH}}}\) related to the C-S-H carbonation has been determined. Hence it has been shown that \(D_{v_{\text{CSH}}}\) depends on the \(\text{CO}_2\) concentration and if the C-S-H are pozzolanic or not given that decalcification of pozzolanic C-S-H by carbonation can lead to a significant reduction in the volume of the solid phase. These results help confirm the practical experience obtained from feedback about in field data showing that carbonation of concrete made of fly ash can provoke an increase in porosity. The impact of carbonation on the microstructure of cement-based materials has also been studied by complementary techniques (MIP, NMR, WVTI) making possible a thorough investigation of the changes of the PSD. Resulting from a rearrangement of the microstructure, it seems can the carbonation of OPC systems mainly affects the capillary pores, both by the reduction of the porosity among the outer C-S-H and the increase of macro capillaries corresponding to the disappearance of the clusters of CH crystals replaced by a packing of CC crystals leaving new voids. Furthermore, it has been shown that the intrinsic PSD of C-S-H is not really affected by carbonation.

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