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Depth profiles of carbonates formed during natural carbonation

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Abstract

The depth profiling of carbonates formed during a natural carbonation of mortars with one face exposed directly to rain and the opposite face sheltered have been measured. The amount of carbonates formed on mortars sheltered from rain is generally higher. The depth of carbonation evaluated by the phenolphthalein test cannot be directly correlated with the carbonate profile. The CO_2 diffusion coefficients calculated on the basis of the distribution of carbonates are of the same order of magnitude as those measured by a direct method. A threshold value of diffusivity appears when the sand concentration increases. This point is discussed and compared with other characteristics of mortars and concretes that exhibit similar behavior.

Keywords: Microstructure; Carbonation; Diffusion; Durability; Portland cement

1. Introduction

The importance and the consequences of the carbonation of the concrete cover on reinforcing steel are well known. The depth of carbonation is usually measured after spraying of a pH indicator, which changes its color in a certain pH interval [1]. In fact, the propagation of the carbonation is more complex than generally assumed and cannot be fully described by such a simple method. More sophisticated techniques like X-ray diffraction, thermogravimetry, infrared and Raman spectroscopy, and traditional chemical analyses have all been used to evaluate quantitatively the ingress of carbon dioxide into mortar and concrete. These methods have been discussed among others by Parrott [2].

The possibility to carry out precise and reproducible sampling, as well as having high performance analytical facilities available, have allowed us to measure the depth profile of carbonates in mortars previously exposed outdoors. From such measurements, it is possible to evaluate the diffusion coefficients of CO_2 and O_2 and to compare these values with those obtained from direct measurements [3].

It is generally admitted that concrete exposed outdoors, but sheltered from rain, carbonates more quickly than concrete which is not sheltered. This is due to the pore blocking by periodic rain water. With the aim of verifying previous observations and of evaluating carbonation kinetics quantitatively, carbonate content was measured as a function of depth on mortar specimens exposed outdoors, one face being directly exposed to rain and the other face sheltered from rain. The carbonation depth was also measured after spraying a solution of phenolphthalein on a freshly fractured surface. Six different mortars with water to cement ratio (w/c) ranging from 0.4 to 0.9 were exposed and analyzed.

2. The carbonation process

From the chemical point of view, the carbonation of cementitious materials is a neutralization reaction of the basic compounds of hydrated cement (essentially $Ca(OH)_2$ and C–S–H) by carbonic acid. CO_2, present in nonpolluted air at 0.035% by volume, is dissolved in the aqueous pore solution and forms carbonic acid.

The pore solution of hardened cementitious materials like mortar or concrete contains essentially sodium and potassium hydroxides. Indeed, the solubility of $Ca(OH)_2$ strongly decreases when the concentration of hydroxyl ions

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increases. For a hydroxyl ion concentration of 0.5 mol/l, Longuet [4] has calculated that the concentration in Ca^{2+} ions is about $1 \cdot 10^{-5}$ mol/l.

Carbonation reactions can be written as follows:

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O \tag{1}$$

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + 2NaOH \tag{2}$$

$$3Na_2CO_3 + 3CaO \cdot 2SiO_2 \cdot 4H_2O \rightarrow$$

$$3CaCO_3 \downarrow + 2SiO_2 + 6NaOH + H_2O \tag{3}$$

In reality, the reaction takes place in aqueous solution where $Ca(OH)_2$ must dissolve after precipitation of $CaCO_3$. C–S–H, the calcium silicate hydrate, is a xerogel that reacts with carbonate ions. Both reactions (2) and (3) release hydroxyl ions, which can react again with CO_2 according to Eq. (1) and the process continues as long as $Ca(OH)_2$ and C–S–H are present. Reaction (1) induces a decrease in pH of the pore solution. The same reactions may be written for potassium hydroxide.

Numerous factors influence the rate of carbonation. The following factors are among the most important ones:

- water to cement ratio
- curing conditions, i.e., the degree of hydration
- cement content
- type of cement
- CO_2 concentration of the surrounding air
- water content
- temperature
- alkali content
- presence of damaged zones and cracks

The carbonation kinetics can be described, as a first approximation, to be a diffusion process of a gas (CO_2) through a porous material with a given moisture content. This means that it is assumed that the reaction of dissolved CO_2 is much faster than the diffusion process. By applying Fick's first law, the following equation can be found after integration [5]:

$$x = \sqrt{\frac{2Dc}{a}}\sqrt{t} \tag{4}$$

Where x is the carbonated depth at time t, D the effective diffusivity of CO_2, c its concentration in the atmosphere and a the concentration of the reactive compounds.

Table 1
Chemical composition of the Portland cement (CEM I) used in this study (all values are in mass %)

Insol.	LOI	CaO	MgO	Al_2O_3	Fe_2O_3	SiO_2	Na_2O	K_2O	SO_3
0.4	3.0	63.0	1.95	4.7	2.95	19.9	0.4	0.9	2.5

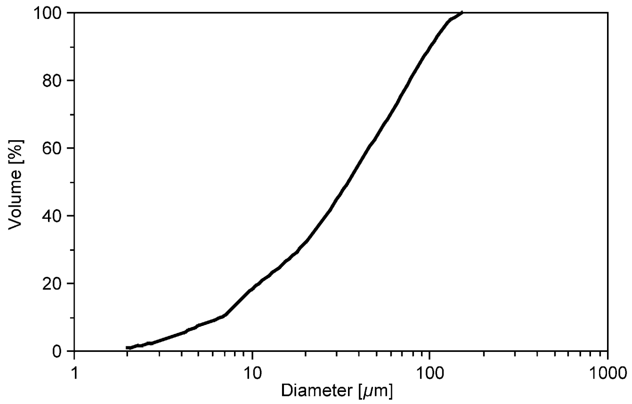

Fig. 1. Grading curve of the Portland cement used.

This equation can be written under the well-known form:

$$x = A\sqrt{t} \tag{5}$$

with:

$$A = \sqrt{\frac{2Dc}{a}} \tag{6}$$

By applying Fick's first law, several simplifying assumptions have been made. D is not constant, it is a function of numerous parameters. It may depend on time (degree of hydration), on location (curing effect, wall effect) and on the moisture content. The temperature has two effects on the diffusivity. The CO_2 diffusion is enhanced by an increase in temperature, whereas the moisture content is reduced, providing more space for gas diffusion which further increases diffusivity. After a certain time, the carbonation reaches a depth where the microstructure is relatively homogeneous. Neither wall effect, nor large variations of the degree of hydration have then to be taken into consideration.

In reality, after a certain period of time, carbonation does not reach a precise depth defined by a single number as indicated by Eq. (5). After a sufficiently long period of

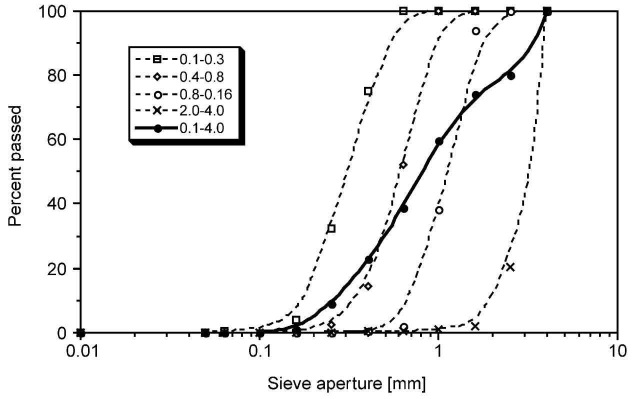

Fig. 2. Grading curve of the sand fractions and the compared grain size distribution used for the preparation of mortars.

Table 2
Composition of the fresh mortars. All values are given in kg/m^3, except the air content which is in l/m^3

w/c	0.4	0.5	0.6	0.7	0.8	0.9
Cement	405	400	398	396	393	391
Aggregate[a]	1853	1726	1611	1498	1383	1271
Water	162	200	239	277	314	352
Air	9	20	25	30	37	43
Bulk density	2420	2326	2248	2171	2090	2014

[a] The aggregate contains 25% of each fraction of sand shown in Fig. 2.

time, three zones can be distinguished. The first zone close to the surface exposed to air is fully carbonated or rather its carbonate content is constant. Then a transition zone, often called *carbonation front*, can be observed, where the degree of carbonation decreases gradually to zero. The third zone is not carbonated at all. In fact, carbonation is never complete and the depth and the shape of the carbonation front vary as a function of numerous factors, like the exposure type and the composition of the material. Another parameter, which has to be taken into consideration in this context, is the local variability of the material properties such as porosity and pore-size distribution. Measurements with pH indicators allow us to define a line which is generally difficult to situate precisely within the carbonation front.

3. Experimental

3.1. Materials

The cement used is a normal Swiss Portland cement (CEM I) from the plant at Eclépens. Its chemical composition is given in Table 1 and the results of its particle size analysis, measured with a laser diffraction granulometer (Malvern Mastersizer), in Fig. 1.

Quartz sand in four granulometric fractions (0.1–0.3, 0.4–0.8, 0.8–1.8 and 2.0–4.0 mm) was used. Results of the grain size distribution determined by sieving are given in Fig. 2.

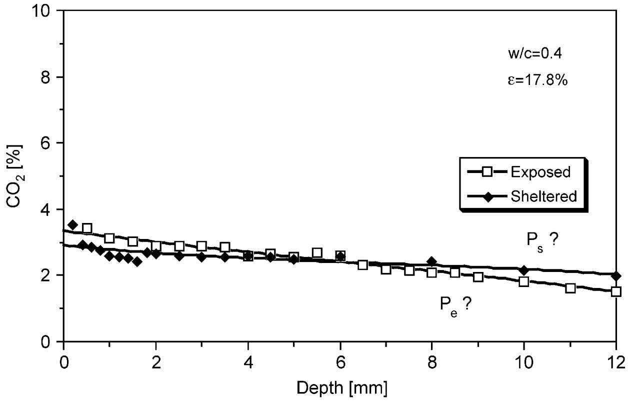

Fig. 3. Depth of carbonate profile after 40.5 months of outdoor exposition of a mortar with w/c = 0.4. The carbonation depths P_e and P_s could not be measured.

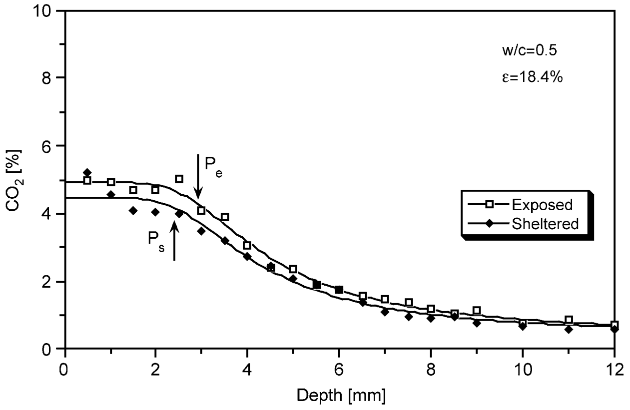

Fig. 4. Depth of carbonate profile after 40.5 months of outdoor exposition of a mortar with w/c = 0.5.

The compositions of the mortars are given in Table 2. Six slabs 400/400/70 mm with a cement content of approximately 400 kg/m^3 were prepared, cured for 28 days in water and then kept for 14 months in the atmosphere of the laboratory (20–25 °C, RH < 50%). After this period of storage, slices (100/400/70 mm) were cut from the slabs. The fresh cut surfaces of these specimens were exposed outdoors with an inclination of 45° facing West. In this way, one face of the specimens was directly exposed to rain and the opposite face was sheltered.

3.2. Characterization and analysis of the mortars

The classical method based on buoyancy was used to determine the bulk density. Specimens were saturated with water under vacuum, weighed in water, in air and after drying at 105 °C. The porosity was calculated from the water absorption under vacuum.

Samples were taken with an apparatus especially developed at the Stone Conservation Laboratory (LCP) of

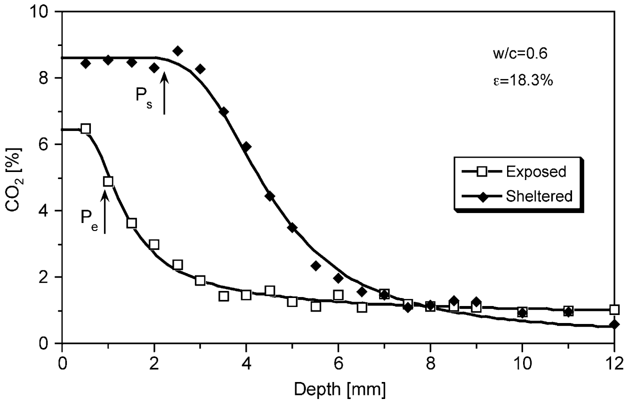

Fig. 5. Depth of carbonate profile after 40.5 months of outdoor exposition of a mortar with w/c = 0.6.

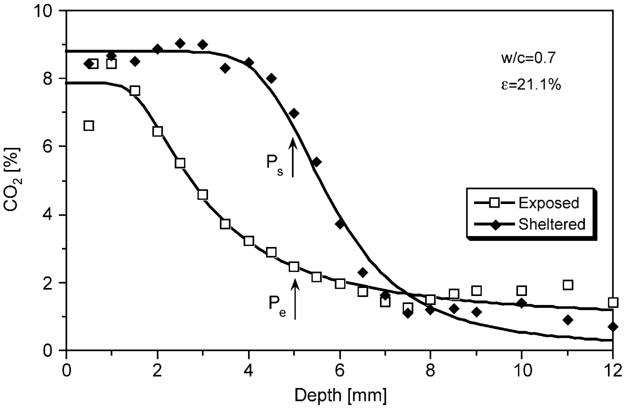

Fig. 6. Depth of carbonate profile after 40.5 months of outdoor exposition of a mortar with w/c = 0.7.

the Swiss Federal Institute of Technology in Lausanne (EPFL), initially developed for the analysis of sulfates in stone monuments [6]. A milling machine with a special tool comprised of four cutters was used to take samples. The cutting head was moved automatically in steps of 0.2–0.5 mm with a precision of 0.03 mm. The sampling diameter was 36 mm. After each milling step, the resulting powder was collected and directly analyzed. This method allows us to determine the profile of CO_2 concentration as a function of depth. All carbonate analyses were carried out with a special analyzer (Leybold CSA 2003). This apparatus comprises an induction oven allowing the thermal decomposition of carbonates and an infrared analyser for CO_2. The thermal decomposition takes place in an O_2 atmosphere leading to oxidation of all carbon containing compounds. This method is very sensitive and can be used either for trace analysis or major contents.

After sampling, a solution of phenophtalein was sprayed on fresh fractured surfaces of mortar. The uncarbonated mortar turns to red, whilst the carbonated mortar remains unchanged [1]. The mean carbonation depth of the exposed face is marked P_e and the one of the sheltered face P_s in Figs. 3–8. The fractured surfaces have also been optically analyzed by means of a microscope. The noncarbonated zones appear clearly darker.

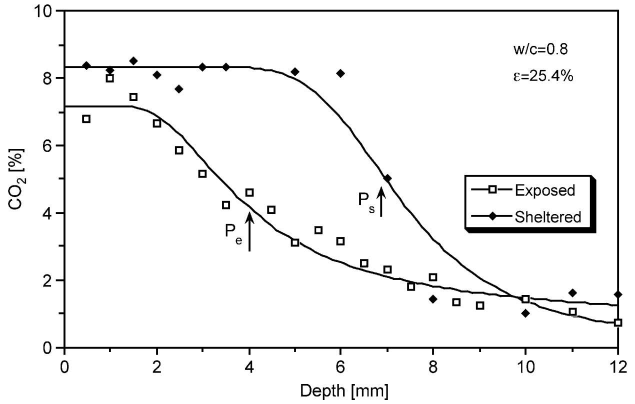

Fig. 7. Depth of carbonate profile after 40.5 months of outdoor exposition of a mortar with w/c = 0.8.

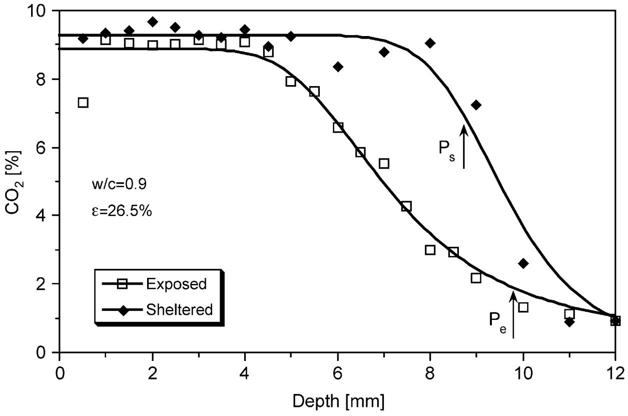

Fig. 8. Depth of carbonate profile after 40.5 months of outdoor exposition of a mortar with w/c = 0.9.

4. Results

The specimens were analyzed after 40.5 months of outdoor exposure. The results of carbonation measurements for the two types of exposure are graphically given in Figs. 3–8. Total porosity (ε), measured before carbonation is indicated in the same figures. The solid curves were obtained by fitting the following function to experimental points:

$$y = \frac{a_1}{1 + \exp\left(a_2 - \frac{a_3}{x}\right)} \tag{7}$$

a_1, a_2 and a_3 are parameters.

The visual inspection of samples with high w/c treated with phenolphthalein shows two clearly separated zones, one totally carbonated and the other not at all. At w/c = 0.4, noncarbonated islands can be observed in an otherwise carbonated environment.

5. Discussion

It can be seen that higher w/c ratios lead to higher carbonate contents and increased depth of carbonation. The carbonate content depends on the content of hydration products, which depends itself on w/c. Observations of the fresh surfaces, on which phenolphthalein was sprayed, show a clear border line between red and unchanged surfaces for the mortars with w/c $\geq$ 0.6. The mortar with w/c = 0.4 exhibits, on the two faces, an area of approximately 30 mm depth containing red islands. This observation, although less clear, can also be made on the mortar with w/c = 0.5. In these samples, carbonation does not follow a well-defined front, as in other specimens, but carbonation is incomplete and deep. A visual examination shows that the mortar contains numerous air pores between 0.5 and 2 mm, which are formed due to the difficulty to compact such a dry mortar completely. Thus, CO_2 can diffuse quickly into the mortar, thanks to a system of large connected pores and carbonates the mortar locally. A biporous system has already been proposed to describe hardened cement paste [3] and mortar [7]. The same schematic representation (Fig. 9) can be used to illustrate such a porous system. There is another possible origin for the peculiar behavior of the mortars with $w/c = 0.4$. At this low value of w/c, mortar undergoes autogeneous drying. This means that CO_2 can penetrate microcracks induced into the porous structure by autogeneous shrinkage without being captured in the reaction front. This effect is to be studied further in order to be able to predict the durability of modern high strength concretes.

The mortars with higher w/c (≥ 0.6) have a more homogeneous and finer porosity and do not exhibit this type of carbonation. The carbonate content of mortars with $w/c = 0.4$ and 0.5 weakly decreases from the surface. The carbonation depths P_e and P_s measured after spraying of the phenolphthalein solution are also given in Figs. 3–8. The structure of the cut surfaces of the mortars with $w/c = 0.5$ and 0.7 is shown in Fig. 10, as well as the rough border line of the carbonated zone revealed by the phenolphthalein test. The shape of the profiles of carbonate in the mortar with a $w/c \geq 0.6$ corresponds approximately to those measured by Tuuti [8] and Kashino [9]. The maximum of carbonated products varies between 8% and 10% CO_2 close to the exposed surface and 1% inside the mortar. This last value is due to the residual CO_2 content of the mortar components. The amount of carbonate decreases as w/c becomes lower. This is certainly due to a lower degree of hydration.

The carbonate content measured on the faces of the mortars directly exposed to rain is generally lower and the profile less steep than that measured on the sheltered face. CO_2 diffusion is lower on the exposed face, because pores are being blocked by absorption of periodic rainwater. The carbonation process on the faces directly exposed to rain is generally more complex: water-containing CO_2 can penetrate by capillarity and this also carbonates the mortar. In this case, gas diffusion is no longer the only transport mechanism. The carbonate content of the superficial layer of these mortars varies. This is certainly due to the transport of dissolved hydroxyl ions during cycles of wetting and drying.

There is no simple correlation between measurements of carbonation depth as determined after phenolphthalein spraying and the depth profiles of carbonate content. In fact, no coloration can be observed in certain areas that are not fully carbonated (see, for instance, Figs. 5 and 6). It is more surprising that, on the same mortars, measured carbonation depth corresponds to rather different carbonate contents (see, for instance, Figs. 6 and 8). However, part of these differences could be due to the variability of the carbonation front measured after phenolphthalein spraying and which should be indicated with a standard deviation. The sampling of powder creates new fresh reactive surfaces of cement compounds and CH, which give red color with

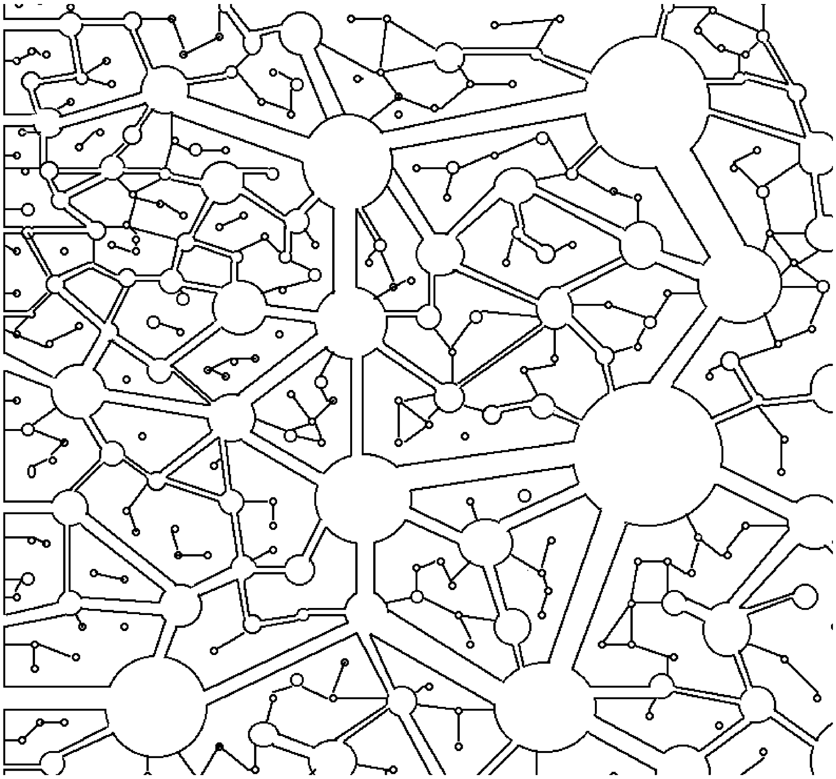

Fig. 9. Schematic representation of a biporous system [7].

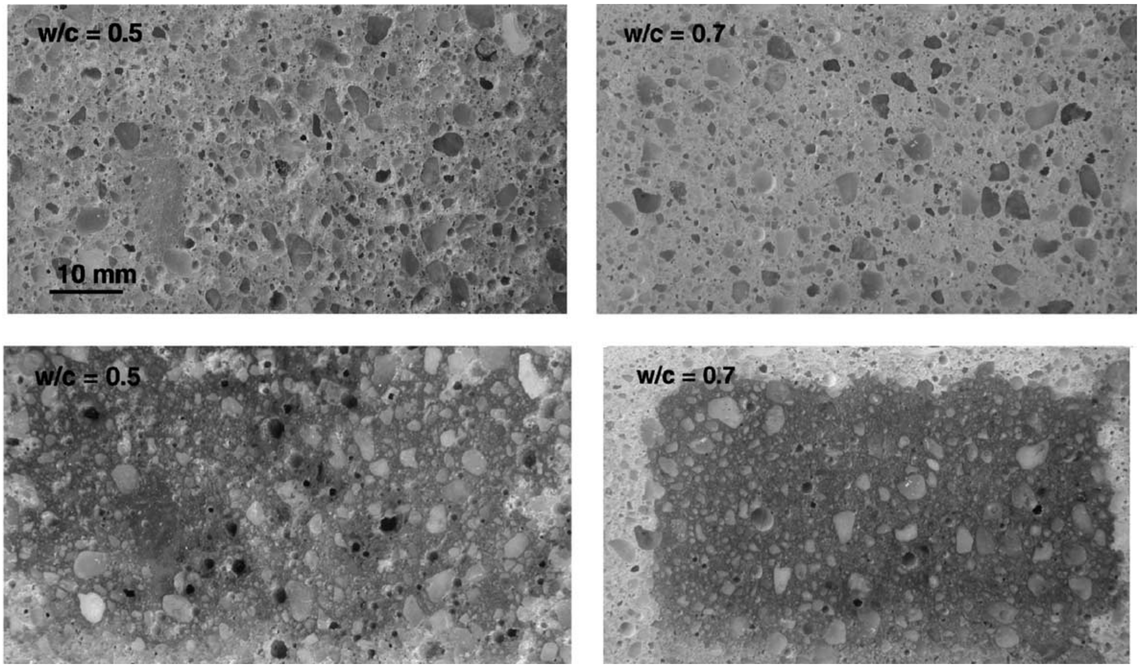

Fig. 10. Photographs of partially carbonated surfaces of two mortars (up) and of the same mortars after phenolpthtaleine spraying (down). The darker zones are noncarbonated.

phenolphthalein. The chemical analyses of carbonate give a mean value corresponding to the volume of the sample. This volume, which is 200 mm^3 for a sampling corresponding to a step of 0.2 mm, is not always representative. This can be explained by sudden variations in composition.

The carbonate content of each mortar has been calculated. It was assumed that beyond a depth of 10–12 mm, the carbonate content was constant and due to the residual carbonate content of the mortar components. The amount of carbonate formed is proportional to the surface between the curve of the carbonate content and a straight line parallel to the abscissa defined by the residual carbonate content. The carbonate profile has been approximated by a step function. The results are represented graphically in Fig. 11. At high w/c, the CO_2 content increases nearly linearly with w/c, but at low w/c a minimum is reached and, at very low values, CO_2 content increases again.

On the other hand, a carbonation depth was calculated with the same approximation as the carbonate content. These apparent carbonation depths are shown in Fig. 12. The points corresponding to the exposed face of mortars with w/c = 0.6 and higher are on an increasing branch as can be anticipated from Fig. 11. This is because these mortars have an excess of large pores due to high w/c. Such a linear relationship between carbonation depth and w/c has been already proposed by Vénuat [10]. The carbonation depth at low w/c also increases because of incomplete compaction and damage induced by autogeneous shrinkage.

If the amount of carbonation compounds formed after time *t* is equated with the amount of reactive compounds *a*

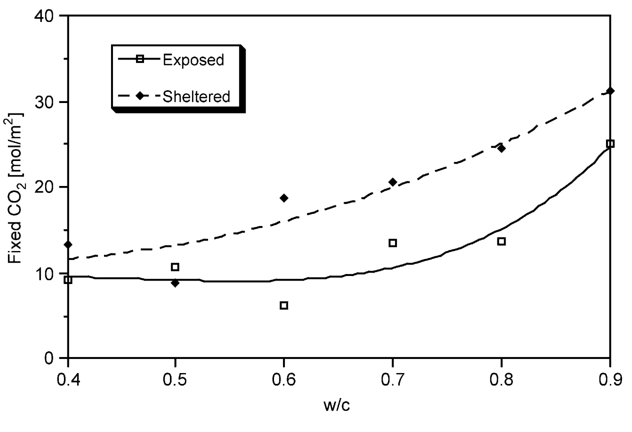

Fig. 11. Carbonates formed during 40.5 months of outdoor carbonation.

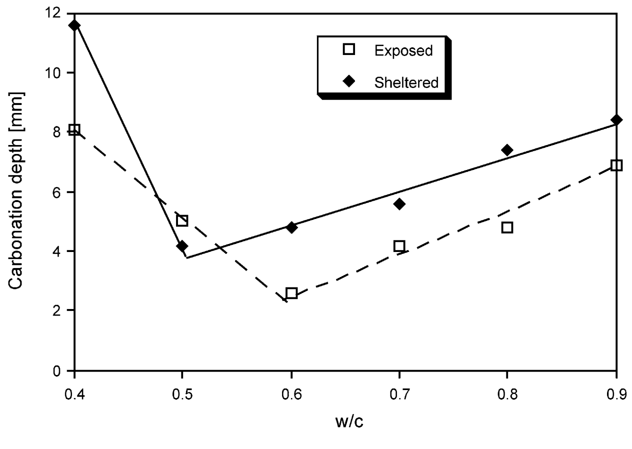

Fig. 12. Apparent carbonation depths calculated from carbonation profiles.

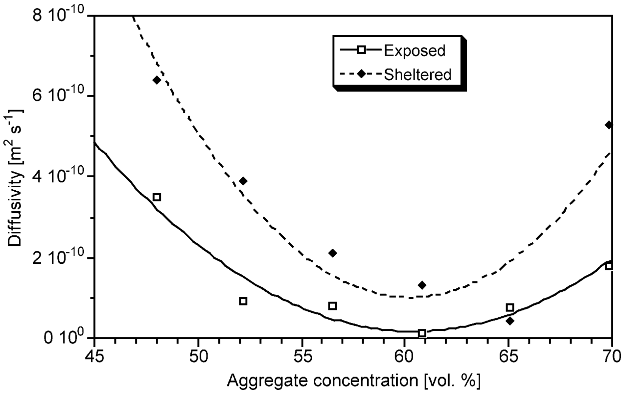

Fig. 13. Calculated effective diffusivity of CO_2 for the different mortars.

in Eq. (4) and, if the depth of carbonation x as calculated is used, the coefficient of diffusion D of CO_2 can be calculated. The results of these calculations with a CO_2 concentration of 0.035% (0.016 mol/m^3) are graphically represented in Fig. 13.

The coefficients of diffusion as computed according to Eq. (4) are of the same order of magnitude as those measured on mortars of comparable porosity [11], but with a different cement content and a finer sand (0.1–0.6 mm). A minimum in the coefficients of diffusion for a sand concentration of approximately 60% can be observed. Similar experimental results were found earlier, with a sand concentration of about 50% [11].

Other characteristics related to transfer of water vapor and CO_2 [12,13] and also Young's modulus [13] exhibit a similar behavior. A threshold is observed when the concentration of nonporous aggregates increases. Various explanations have been given. The percolation of interfacial transition zones (ITZ) around aggregates was proposed by many authors [11–18]. At a given concentration of aggregates, different interfacial transition zones, which have a higher porosity than the bulk cement paste become interconnected and thus may create easy paths for mass transfer. Since the thickness of the ITZ and the mean layer of hardened cement paste between the grains become of the same order of magnitude, this observation can also be interpreted to be due to an overall modified matrix [19]. Wittmann et al. [13] explained the sudden decrease in Young's modulus of mortars when the sand concentration increases above 50% by the fact that the thickness of the film of cement paste between the sand grains becomes too low, e.g., of the same size as the maximum cement grains. The latter can no longer fill the space between sand grains completely and thus the porosity increases suddenly. In this case, sand grains act as a kind of sieve for cement particles. When the cement content is too low, the hydration products cannot fill the space between sand grains any more and a supplementary porosity appears. The percolation of these pores could also explain the appearance of a threshold. It is likely that all the above mechanisms act simultaneously. The samples of mortar were cut just before the outdoor exposure in order to suppress all wall effects. It is likely that the superficial composition of mould mortars exposed to the same environment is slightly different. Indeed, the skin of the mortars is richer in cement and more porous. This should lead to higher superficial carbonate contents.

6. Conclusion

The amount of carbonates and the depth of carbonation are higher if the surfaces of mortars exposed outdoors are sheltered from rain. This is due to added resistance to CO_2 diffusion by capillary absorbed and condensed water which blocks the porous system temporarily. At high w/c, the amount of carbonate and the carbonation depth increase linearly with w/c.

No simple relationship could be found between the depth of carbonation as measured after phenolphthalein spraying and with the carbonation depth profile measurements. This can be due to the method of sampling, which breaks noncarbonated hydrated and anhydrous cement grains. The color change observed after spraying with phenolphthalein may be due to reactions on the newly created surfaces. Mortars with a $w/c = 0.4$ and 0.5, do not have a well defined carbonation front, but a large zone of decreasing carbonate content, with islands of noncarbonated material. This is linked to incomplete compaction and the presence of well-dispersed air pores, due to the dry consistency of the fresh mortar. These pores allow CO_2 to diffuse deep into the mortar before it carbonates fully the cement paste between the pores. A biporous model can explain these results. Autogeneous drying, which reduces the RH in the mortar and induces damage, may also be at the origin of the observed behavior.

The mortars with $w/c \geq 0.6$ have a well-defined carbonation front. The more porous, the larger its width. The coefficient of diffusion of CO_2 through mortars was calculated on the basis of the profile of carbonate formed during 40.5 months of exposure. The calculated diffusion coefficients are of the same order of magnitude as those measured by direct methods [3].

A threshold in the coefficient of diffusion of CO_2 as the sand concentration increases was found. Such a threshold of the coefficient of diffusion was already observed from previous direct measurements [11]. This behavior can be explained by the percolation of interfacial transition zones of large pores or by an insufficient local cement content between sand grains which leads to more porous hardened cement matrix between aggregates.

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