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Consequences of carbonation on microstructure and drying shrinkage of a mortar with cellulose ether

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ABSTRACT

This paper presents the consequences of the carbonation phenomenon in the case of a mortar with cellulose ether as admixture on its mechanical properties, microstructure and length variations. Carbonation was found to improve mechanical strengths and decrease the global porosity with modifying the pore size distribution. The latter is beneficial regarding durability. However, carbonation also led to an increase of shrinkage, and thus to a probable increase of cracking. Carbonation and shrinkage kinetics could be slowed down by sheltering the material from carbonation during hardening.

1. Introduction

Factory made mortars are complex materials resulting from the mixing of mineral constituents (sand, mineral binder, water) and often organic admixtures such as cellulose ether (CE) and latex. Such mortars have plenty of uses in building fields: frontage coating, tile fixing, concrete repair, etc. Industrial mortars are little studied in literature in comparison with concrete; especially their behaviour with respect to durability. It remains that the understanding of the durability potential is of the highest importance for materials which are often the first barrier of constructions against environmental aggressions, particularly in the case of coatings and repairs.

The consequence of chemical attack is usually a significant reduction of the service life of the mortar and the concrete structure [1–3]. The most wide environmental aggression of cement-based materials such as coating mortars is carbonation. It is accompanied by a decrease of pore solution pH. This attack of the calcium phase by carbon dioxide of the air occurs from placing. Thus, carbonation is strongly coupled with other processes such as cement hydration and drying at the early ages of the material [3,4]. These coupled phenomena affect the dimensional stability, the bond properties and more generally, the durability of the material.

Several authors have studied the carbonation consequences in the case of concrete structures [5–8]. They concluded that carbonation results not only in the increase of strengths, particularly when the water/cement ratio (w/c) is low [6], but also in the increase of shrinkage.

Increase of strengths is the consequence of the reduction of the porosity due to the formation of $CaCO_3$ crystals in the pores of the material [6]. The reduction of porosity is coupled with changes in the pore size distribution. Indeed, Mercury Intrusion Porosimetry (MIP) tests show that the reduction of porosity affects in most cases pores lower than 100 μm of diameter, while pores with diameter higher than 100 μm remain not affected by this reduction [7].

Shrinkage due to carbonation can be measured in laboratory using natural or accelerated carbonation tests. This shrinkage is often explained by the dissolution of portlandite and its reaction with the dissolved carbon dioxide [8]. However, there is no scientific consensus on the origin of carbonation shrinkage.

In the present paper, we studied the consequences of carbonation on mechanical properties, microstructure and dimensional variations of a mortar with cellulose ether. We also studied the influence of curing duration on these parameters aiming the investigation of the impact of hydration degree on the carbonation kinetics. Note that curing means here the conservation in an environment without CO_2 after the material manufacturing.

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2. Experimental program

2.1. Materials and conservation

The main composition studied here was designed in order to be representative of typical industrial compositions of factory made mortars, especially those used for coatings in buildings. This composition was the result of different preliminary studies performed in the framework of the Consortium for Research on industrial Mortars (CEReM) [9,10]. Thus, this composition was also studied in these different researches performed in the framework of this consortium. However, a second proportion of 0.5% CE is included hereafter. It is only given as a variant for some tests, mainly accelerated carbonation test.

The mortars was made of a CEM I 52.5 R Portland cement (according to European standards EN 197-1), 0.15–0.35 mm siliceous sand (2.65 density and 15.2 $m^2\ kg^{-1}$ specific area) and siliceous filler (with SiO_2 >99%, 6.5 μm diameter and 2.7 density). The chemical composition of cement and sand are given in Tables 1 and 2. These various compositions were verified by X-ray spectrometer method (XRS). In this study, the siliceous sand and filler were chosen in order to not influence the rate of calcite produced by carbonation especially in the case of TGA analysis. The organic admixture is cellulose ether (methyl hydroxyl propyl cellulose, denoted MHPC), commonly used in factory made mortars to improve their water retention and consistency [9]. Two proportions were used as shown in Table 3, which gives the mass proportions of each solid constituent. The water–cement ratio (w/c) was equal to 1.

The solid constituents were mixed finely before a progressive addition of water. The high w/c ratio allows obtaining a fluid mix, which was placed without vibration in prismatic moulds which dimensions were $16 \times 4 \times 1\ cm^3$. This geometry is used in order to obtain specimens of 1 cm thick, simulating a layer coating.

In the present study, the term "curing" refers to a conservation of the mortar in a laboratory ambiance without CO_2. Specimens were put in a chamber maintained at the same atmospheric conditions (temperature and relative humidity (RH)) than that of the carbonation chamber, i.e. 20 ± 2 °C and 65 ± 5% RH (see Section 2.2.1 below). The CO_2 in this chamber was absorbed by a lime saturated solution. In the followings, the "reference mortar" refers to a mortar conserved in the chamber free from CO_2, denoted "curing chamber".

24 h After manufacturing, specimens intended to accelerated carbonation tests were partially wrapped with an aluminium adhesive tape (0.2 mm thick). Five sides of the $16 \times 4 \times 1\ cm^3$ specimens were covered. The sixth side ($16 \times 4\ cm^2$) was not covered and was let in contact with the ambiance in the test chamber. The CO_2 diffusion within the specimen is then unidirectional through the sample thickness.

2.2. Tests and protocols

2.2.1. Accelerated carbonation tests

Accelerated carbonation tests were performed under atmospheric pressure at 20 ± 2 °C and 65 ± 5% RH in a chamber containing a fixed CO_2 concentration. In the case of concrete mixtures, the CO_2 concentration usually taken in French laboratory tests is equal to 50% according to French recommendations (AFPC-AFREM procedure [10]). However, such a high concentration would result in very short test duration since the studied mortar is much more porous than concrete. In addition, this high concentration would be so far from the natural carbonation of such material. In order to obtain reasonable test duration in laboratory, the CO_2 concentration was thus fixed equal to 5%, after a preliminary experimental campaign with various CO_2 concentrations [4,11].

The relative humidity in the carbonation chamber (65%) is obtained with an ammonium nitrate saturated solution. This value is known as an optimum for the acceleration of CO_2 diffusion through the material [4].

Specimens were submitted to carbonation just after manufacturing in their moulds. After 24 h, they were partially wrapped with an aluminium adhesive tape, as explained in Section 2.1.

The carbonation kinetics was characterised by the time evolution of a carbonation depth. The phenolphthalein solution was sprayed on a fragment of samples cut from the specimen. The carbonation depth was then determined by the coloured turning of the phenolphthalein pH-indicator. As shown in Fig. 1, the carbonation front is the frontier between a sane zone coloured in pink (pH > 9) and a carbonated zone not-coloured (pH < 9). Nine measures were performed at each date for obtaining the average carbonation depth and its standard deviation (Fig. 1).

2.2.2. Mercury Intrusion Porosimetry (MIP)

MIP measurements were used to characterise the mortars microstructure: porosity and pore size distribution. The apparatus used was a Micromiretics Autopore III, whose pressure reaches more than 400 MPa, which corresponds reaching pores of 3 nm of diameter. These tests were carried out after 5 days on two kinds of samples: reference mortar and carbonated mortar.

Table 2
Chemical composition of the sand used.

	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	K_2O
% Mass	98.4	0.048	0.860	0.020	0.017	0.400

Table 3
Mass proportions of studied mortars.

Constituent	Proportions (% of the dried mass)
Cement CEM I 52.5 R	30
Siliceous sand	65
Siliceous filler	5
MHPC cellulose ether	0.27 and 0.5

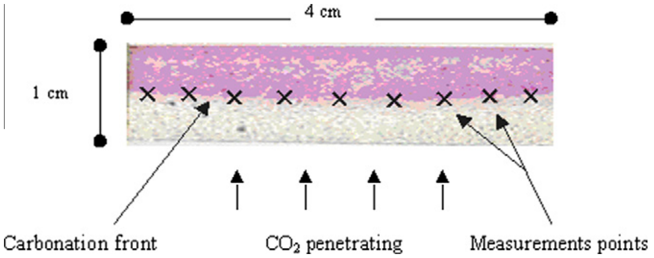

Fig. 1. Position of the nine measured depth used to calculate the average carbonation depth (in pink: non-carbonated zone). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2.3. Mechanical properties

The mechanical behaviour was characterised by three points bending tests on $16 \times 4 \times 1\ cm^3$ specimens and compression tests on $8 \times 4 \times 1\ cm^3$ specimens after 5 days from manufacturing for carbonated specimens and their references (not carbonated).

2.2.4. Monitoring dimensional and mass variations

The dimensional variations due to carbonation were measured by monitoring the evolution in time of the $16 \times 4 \times 1\ cm^3$ specimens' length by using a dial indicator with ±10 μm precision. In parallel, the evolution in time of the specimens mass was also recorded (scales with ±0.01 g precision) on the same samples. Three samples were used for obtaining the average values of the dimensional and mass variations and its standard deviations.

3. Results and discussion

3.1. Study of carbonation without curing

In this section, the reference mortar is compared to a mortar submitted to accelerated carbonation tests just after manufacturing.

The turning of the phenolphthalein indicator is quite clean highlighting a regular carbonation front of all the samples (Fig. 2). The average carbonation depths are plotted as a function of exposure time, as shown in Fig. 3. This figure shows that the total carbonation is reached after approximately 116 h (less than 5 days). It returns that the carbonation kinetic remains quite high despite the relatively low CO_2 concentration used (5%). Carbonation depths are lower during the first 56 h in case of mortar with 0.27% of cellulose ether.

Table 1
Chemical composition of the cement used.

	SiO_2	CaO	Fe_2O_3	Al_2O_3	SO_3	MgO	K_2O	Na_2O	TiO_2	MnO	SrO	P_2O_3
% Mass	19.81	64.02	2.38	5.19	3.50	0.90	1.11	0.06	0.28	0.05	0.15	2.23