Cement and Concrete Research 109 (2018) 64–80

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: www.elsevier.com/locate/cemconres

Comparison between natural and accelerated carbonation (3% CO_2): Impact on mineralogy, microstructure, water retention and cracking

Martin Auroy[a], Stéphane Poyet[a,*], Patrick Le Bescop[a], Jean-Michel Torrenti[b], Thibault Charpentier[c], Mélanie Moskura[c], Xavier Bourbon[d]

[a] Den-Service d'Etude du Comportement des Radionucléides (SECR), CEA, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France
[b] Université Paris-Est, IFSTTAR, Département Matériaux & Structures, 14-52 Boulevard Newton, F-77447 Marne la Vallée Cedex 2, France
[c] NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, F-91191 Gif-sur-Yvette Cedex, France
[d] Andra, Parc de la Croix Blanche, 1-7 rue Jean Monnet, 92298 Chatenay-Malabry Cedex, France

ARTICLE INFO

Keywords:
Carbonation (C)
Acceleration (A)
Characterization (B)
Microstructure (B)

ABSTRACT

The consequences of accelerated carbonation at 3% CO_2 were compared with those of natural carbonation (0.04%). Cement pastes (CEM I and CEM V/A) as well as the three major constitutive phases (C-S-H of different C/S ratios, portlandite and ettringite) were used and changes in the mineralogy, microstructure, water retention and cracking were investigated. The main conclusion was that accelerated carbonation at 3% CO_2 was representative of natural carbonation although it promoted the precipitation of metastable calcium carbonate (aragonite and vaterite) in place of calcite. The results also showed that the presence of aragonite and vaterite were characteristic of the carbonation of ettringite and C-S-H respectively.

1. Introduction

Atmospheric carbonation refers to the reaction between atmospheric carbon dioxide (CO_2) and the calcium bearing phases of hydrated cement leading to calcium carbonate precipitation ($CaCO_3$) [1]. $CaCO_3$ exists under several allotropic forms: although calcite is the thermodynamically stable phase [2], aragonite and vaterite are commonly detected [3–12]. The main consequence of carbonation is the drop in the pH induced by portlandite dissolution that induces steel depassivation and can trigger active corrosion under adequate conditions (moisture and oxygen availability) [13]. Carbonation modifies the microstructure of cementitious materials [14–18] and subsequently their transport properties [11,16,19–23]. It was also shown that accelerated carbonation could generate shrinkage [24–27] and eventually cracking in the carbonated zone [11,23,28,29].

Carbonation is partly driven by the gaseous diffusion of CO_2 within the concrete porosity. It is therefore a very slow process: it generally takes decades for the carbonation front to reach the rebars (depending on the concrete properties and cover) [30–36]. In the laboratory, carbonation is commonly accelerated in two ways: (*i*) by exposing the samples to be carbonated to relative humidity (RH) ranging from 50 to 70% for which the carbonation rate was found to be maximal [24,30,37,38], and (*ii*) by increasing the CO_2 content [37,39–44]. The carbonation rate was found to increase with the square root of CO_2 content [37,43,45,46]. For this reason, it was proposed to assess the carbonation rate in natural conditions using the results of accelerated tests [39,42,44–47]. Different CO_2 contents up to 100% have been used so far [48] although no significant acceleration has been remarked for CO_2 contents exceeding 20% [43,49]. National standards in Europe differ in CO_2 contents: 1% in Belgium, 2% in Germany, 4% in the UK, 20% in the Nordic countries and 50% in France and Italy. It should also be noted that there is no European standard, which highlights the lack of consensus in the community [50].

Accelerated carbonation was not always found to be representative of natural carbonation. Bernal et al. [51–53] showed that tests on geopolymers with CO_2 contents greater than 1% led to unduly aggressive conditions that did not replicate the mechanisms at work under natural exposure. Sanjuán et al. [42] tested concrete resistance to carbonation. They noted that the relative ranking of the considered concretes was modified in accelerated conditions (5% CO_2) compared with natural carbonation. Note that this was not the case for lower CO_2 contents (1%) [44]. Cui et al. [49] performed accelerated carbonation tests with various CO_2 contents (from 2% to 100%) and they noted that high CO_2 concentrations led to a denser microstructure that was no longer representative of that existing with lower CO_2 concentrations. They also suggested that a limit of 20% CO_2 not be exceeded to allow for comparison with natural carbonation. This is consistent with the results of Groves et al. [54,55] who observed strong differences in the

---

[*] Corresponding author at: CEA Paris-Saclay, DEN/DANS/DPC/SECR/LECBA, B158 PC25, F-91191 Gif-sur-Yvette cedex, France.
E-mail address: stephane.poyet@cea.fr (S. Poyet).

https://doi.org/10.1016/j.cemconres.2018.04.012
Received 18 September 2017; Received in revised form 15 February 2018; Accepted 6 April 2018

decalcification and polymerization of the C-S-H in C_3S pastes exposed to the atmosphere and pure CO_2. Similarly, Castellote et al. [56] showed that using 3% CO_2 did provoke changes in the mineralogy and microstructure that were very similar to those observed in natural carbonation. Beyond 3%, the C-S-H appeared to be strongly decalcified and polymerized (silica gel). Goñi et al. [5] compared the mineralogical composition of concretes carbonated in the laboratory atmosphere and in pure CO_2. Under natural carbonation, aragonite and vaterite were the two main calcium carbonate phases that were detected, whereas calcite was the only phase under pure CO_2. This is supported by the results of Šauman [57] who studied the carbonation of tobermorite and concluded that vaterite was the main product but that vaterite formation was inversely proportional to the CO_2 content: at high CO_2 contents, calcite was predominant. Anstice et al. [58] also observed significant amounts aragonite and vaterite in addition to calcite in natural conditions, whereas calcite was the predominant form of calcium carbonate in accelerated conditions. Anstice et al. also noted strong differences in the composition of the pore solution and in residual portlandite contents between natural and accelerated carbonation.

Accelerated carbonation tests are commonly used in the laboratory to test the resistance of cement-based materials to carbonation or to investigate its consequences. For instance, Auroy et al. [23] recently characterized the impact of carbonation on water transport in unsaturated conditions. To this end, specimens of cement pastes were carbonated at 3% CO_2 and then tested. Unlike CEM I, a strong permeability increase was obtained for blended cements that was associated with cracking induced by C-S-H decalcification. The essential question that remained was: to what extent can we expect these results to be impacted by the acceleration of carbonation? And more generally, are there significant differences between natural and accelerated carbonation using low CO_2 contents? The objective of this study was to provide some answers to these questions. Accordingly, the changes in the mineralogy, microstructure, water retention and cracking of elementary phases (namely ettringite, portlandite and C-S-H) and cement pastes induced by natural and accelerated carbonation (at 3% CO_2) were compared.

2. Materials

2.1. Cement pastes

Four different hardened cement pastes made with CEM I (OPC) and CEM V (OPC with slag and fly ash) were used (Table 1). Two of them were carbonated at 3% CO_2 (i.e. accelerated carbonation) while the two others were carbonated in the laboratory atmosphere (i.e. natural carbonation).

The two pastes for accelerated carbonation were prepared using CEM I - denoted ‘PI(acc)’ using CEM I 52.5 Lafarge Val d'Azergues - and CEM V - denoted ‘PV(acc)’ using CEM V/A 52.5 Calcia Airvault - with constant water–to-binder ratio (w/b) equal to 0.40. The pastes were cast in polypropylene cylindrical molds (Ø50 × 100 mm) and vibrated to remove entrapped air bubbles. The specimens were kept two weeks after casting in their sealed molds before unmolding. The specimens were then cured for 4 months in sealed containers immersed in a specific curing solution, the composition of which was designed to prevent calcium and alkalis leaching. Then 6 mm-thick disks were cut from the central part of the cylinders and carbonated for one year (at 25 °C, 55% RH and 3% CO_2). The use of TGA and XRD allowed us to check that carbonation had reached a stabilized and uniform state within the disks [23]. The properties of the non-carbonated pastes PI(acc) and PV(acc) were obtained using discs that were not carbonated (just after the cure) whereas the properties of the carbonated pastes PI(acc) and PV(acc) were measured using discs that were carbonated.

Table 1
Composition, water-to-binder ratio and carbonation time of the cement pastes.

	Accelerated carbonation (3% CO_2)		Natural carbonation (0.04% CO_2)	
	PI(acc)	PV(acc)	PI(nat)	PV(nat)
OPC	100%	56%	100%	55%
Slag		22%		22%
Fly ash		22%		23%
w/b	0.40	0.40	0.50	0.45
Carbonation time	1 year	1 year	3 years	18 years

The two other pastes were naturally carbonated in the laboratory (around 0.04% CO_2). The first paste - denoted ‘PI(nat)’ - was provided by the Lafarge Research Center. The paste was prepared using an undisclosed CEM I 52.5 with w/b = 0.50 and poured into Ø25 × 25 mm molds. After unmolding, the specimens were cured during five months at 100% RH and ambient temperature. They were then dried at 45 °C for two months before being carbonated (3 years at ambient temperature and 65% RH). The resulting carbonated area was around 2–3 mm thick and showed significant cracks. The second paste - denoted ‘PV (nat)’ using CEM V/A Ciments d'Origny Lumbres - was prepared in 1994 with w/b = 0.45 [59]. The paste was poured into Ø30 × 60 mm molds, cured for 14 months in portlandite saturated water and kept for an additional 20 months in sealed bags (20 °C) before exposure to the laboratory atmosphere. After 18 years of exposure, the carbonated area was 10 mm thick. The properties of the non-carbonated pastes PI(nat) and PV(nat) were obtained using samples taken in the non-carbonated parts of the specimens. In the same way, the properties of the carbonated pastes PI(nat) and PV(nat) were measured using samples taken in the carbonated parts.

It is plain to see that the pastes considered in this study differ in cements, water-to-cement ratios and ages. This was because the pastes PI(nat) and PV(nat) were found and supplied after the PI(acc) and PV (acc) pastes were prepared in the laboratory. Although different, they were nonetheless used to compare qualitatively the respective consequences of natural and accelerated carbonation to verify whether accelerated carbonation at 3% CO_2 was representative of natural carbonation (0.04% CO_2).

2.2. Elementary phases

The three major phases of hydrated cement were studied: C-S-H, portlandite and ettringite. Portlandite powder was provided by VWR (RECTAPUR); it is known to potentially include calcium carbonate up to 3% (mass%).

Ettringite was synthesized following the protocol used by Renaudin et al. [60]. First a solution of $CaCl_2$ (0.66 M) and $AlCl_3$ (0.33 M) was prepared in a CO_2-free glovebox. It was then introduced into a vessel containing 250 mL of Na_2SO_4 (0.08 M). NaOH (2 M) was added so the pH would reach 11.5 ± 0.1. Twenty-four hours later, the solution was filtered and the resulting product was thoroughly rinsed using deionized water to remove any remaining NaCl crystals. The solid residue was dried in the glovebox to remove any excess water in order to obtain a fine powder (with grains smaller than 200 μm).

The C-S-H samples were prepared according to the protocol used by many other authors [61–65]. Four C-S-H with different CaO/SiO_2 ratios (C/S = 0.8, 1.2, 1.5 and 1.7) were prepared in a CO_2-free glovebox by mixing stoichiometric amounts of CaO (Prolabo, pure at 99.5%) with dry colloidal silica (Aerosil 200) in a big volume of deionized water (water-to-solid ratio of 50/1 by mass). The solution was then stirred 15 min every hour until pH stabilization. The synthesis was thus considered to be finished, which generally took at least 30 days. Thereafter, the solution was filtered using a büchner funnel together with a 0.22 μm filter paper. The resulting solid residue was dried under vacuum to obtain a dry powder with grains smaller than 200 μm. The reader should keep in mind that this protocol generally leads to C/S ratio of the solid that is lower than that the initial one [66–69]. The C/S ratio of