Cement and Concrete Research 67 (2015) 226–236

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

# Impact of accelerated carbonation on OPC cement paste blended with fly ash

A. Morandeau [a,b,c,d], M. Thiéry [c,e], P. Dangla [d,*]

[a] Department of Civil and Environmental Engineering, Princeton University, Princeton, NJ, USA
[b] Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ, USA
[c] Université Paris-Est, IFSTTAR, MAT, F-75732 Paris, France
[d] Université Paris-Est, Laboratoire Navier, Ecole des Ponts ParisTech, IFSTTAR, CNRS, F-77455 Marne-la-Vallée, France
[e] DGAC/STAC, F-94485 Bonneuil-sur-Marne, France

ARTICLE INFO

*Article history:*
Received 12 February 2014
Accepted 3 October 2014
Available online 23 October 2014

*Keywords:*
Carbonation (C)
Calcium-silicate-hydrate (C-S-H) (B)
Fly ash (D)
Microstructure (B)
Portland cement (D)

ABSTRACT

Cement is a huge carbon dioxide producer. Supplementary cementitious materials can help reduce this outcome. However, carbonation of these blended cements remains an active subject of research. Accelerated carbonation tests (10% $CO_2$, 25 °C and 62% RH) are performed on fly ash blended cement pastes. Experiments are performed at varying ages of carbonation (1 to 16 weeks) to measure the evolution of the carbonation depth over time and to quantify key parameters: thermogravimetric analysis (TGA), mercury intrusion porosimetry (MIP) and gamma ray attenuation method (GRAM). The total porosity decreases with a rearrangement of the microstructure due to carbonation and the creation of big capillary pores for the paste with the highest contents of fly ash (60 vol.%). The C-S-H molar volume evolution during fly ash-blended cement carbonation is calculated using a method combining MIP, TGA and GRAM formerly successfully applied to OPC paste in a paper published in the same journal.

## 1. Introduction

The worldwide cement industry accounts for at least 5 to 7% of the anthropogenic $CO_2$ emissions [1], hence solutions that reduce ordinary Portland cement (OPC) content in concrete are needed in order to decrease its environmental impact. Blended cements using supplementary cementitious materials (SCM) (such as fly ash, slag, limestone, metakaolin, silica fume) are increasingly being used in industry to reduce the OPC content, but it is necessary to understand the long term performance and durability of these materials in order to optimize the whole life cycle. For this purpose, an evaluation of the durability of the reinforced concrete structure including the effect of $CO_2$ (carbonation) is necessary.

Carbonation is the reaction of gaseous atmospheric $CO_2$ with the calcium-bearing phases of concrete and is known to cause a lowering of alkalinity leading to the corrosion of the re-bars. The hydration products which are concerned by carbonation are mainly calcium hydroxide (CH[1]) and calcium silicate hydrates (C-S-H). In this work, the influence of the substitution of fly ash in clinker has been studied in order to evaluate the resistance to carbonation of blended cement-based materials with fly ash.

For OPC, CH is the main buffering compound. In blended cement, the contribution of C-S-H will be a key point to investigate since the pozzolanic reaction that takes place between portlandite and reactive silica from fly ash decreases the CH content and increases the C-S-H amount [2]. Mechanically, this reaction is considered as beneficial by clogging the bigger capillary pores and refining the microstructure [3], or filling cracks [4]. Nevertheless, such concretes blended with fly ash may become more sensitive to the presence of carbon dioxide due to a lower ability of the matrix to bind $CO_2$ in CH. Hence their chemical resistance against carbonation is decreased. Many studies have been carried out on OPC systems blended with fly ash [5–11]; however it is still uncertain how carbonation influences the pore size distribution (rearrangement of the microstructure) in the case of fly ash-blended cements.

The current literature concerning the microstructure of materials made of fly ash-blended OPC cements and the impact of carbonation don't show a real consensus. Moreover, the observations seem to be highly dependent on the conditions of carbonation ($CO_2$ concentration, relative humidity (RH) and temperature). In the case of OPC cement pastes (w/c ranging from 0.3 to 0.6), Pihlajavaara [12,13] was the first to point out that carbonation affects the capillary pores with diameters between 10 and 100 nm by globally reducing their volume. Matsusato et al. [14] observed the same trend on OPC mortars where the porosity in the range of 20 nm–300 nm was reduced by carbonation. Despite a

---

* Corresponding author.
*E-mail addresses:* antoinem@princeton.edu (A. Morandeau), mickael.thiery@aviation-civile.gouv.fr (M. Thiéry), patrick.dangla@ifsttar.fr (P. Dangla).

[1] It is recalled that according to the cement notations: $C = CaO$, $H = H_2O$, $S = SiO_2$, $\overline{C} = CO_2$, $A = Al_2O_3$ and $F = Fe_2O_3$.

http://dx.doi.org/10.1016/j.cemconres.2014.10.003
0008-8846/© 2014 Elsevier Ltd. All rights reserved.

systematic reduction in total bulk porosity, Houst [15] observed using mercury intrusion porosimetry on OPC cement paste of high water cement ratio (w/c = 0.8) that there was a shift in the porosity towards greater pore radii during carbonation. Recently, Miragliotta [16] and Thiery et al. [17] came to the same conclusion for low grade OPC concretes. Bier et al. [18] investigated the effect of carbonation on the pore size distribution of cementitious materials which were manufactured with different types of cement. It was found that for OPC cement, accelerated carbonation led to a considerable reduction in the capillary pore volume, whereas, for cement blended with blast furnace slag, a coarser capillary porosity was formed during carbonation. Moreover, it is worth noting the investigations of carbonation of air lime mortars [19,20]. These studies showed an increase in pore volume at around a pore diameter of 100 nm which was attributed to the transformation of $\mathtt{CH}$ macrocrystals to $C\overline{C}$ microcrystals. Furthermore, the authors observed a monotonic increase in the volumes of pores with diameters below 30 nm which was attributed to the attachment of $C\overline{C}$ crystals at the surface of aggregate particles and/or at the surface of $\mathtt{CH}$ macrocrystals.

Thus the development of blended cements with supplementary cementitious materials (such as fly ash, slag, limestone, metakaolin and silica fume) is a large area of research and innovation in the field of cement sciences [21]. In this work, destructive methods including phenolphthalein spray test, thermogravimetric analysis, and mercury intrusion porosimetry are combined to gamma ray attenuation (non-destructive) in order to investigate the evolution of porosity and pore size distribution according to the carbonation level and the amount of fly ash incorporated in the cementitious system. This work follows a recent study provided by the same authors [22] where a method was presented to determine the molar volume evolution of C-S-H during its carbonation. The same method will be applied in the current study: OPC cement paste blended with fly ash is submitted to accelerated conditions of carbonation (10% $CO_2$).

## 2. Materials

### 2.1. Formulation and fabrication

The cement used in this study is an ordinary Portland cement CEM I (CEM I 52,5 N CE PM-ES CP2 NF). The Bogue composition is 59% $C_3S$, 19% $C_2S$, 2% $C_3A$, 14% $C_4AF$ and 5% gypsum. Class F fly ash (Silicoline) is used as a supplementary cementitious material (chemical composition given by the manufacturer: 50 wt.% $SiO_2$, 29 wt.% $Al_2O_3$, 8.5 wt.% $Fe_2O_3$). Five formulations were studied with a fly ash volume substitution fixed at 0%, 30% or 60% (cf. Table 1). The highest substitution ratio is out of standards according to EN 206. CN and CP are two well-known formulation compositions previously studied in the literatures [23,24] in terms of moisture (ad- and desorption) and transport properties and more recently [22] in terms of microstructural and chemical changes due to accelerated carbonation (10% $CO_2$). This last article detailed all the experimental protocols we used in the present work; hence this article will present the experimental methods only briefly.

In order to avoid early drying, sealed plastic bottles were used as moulds for the preparation of the cement pastes. The plastic bottles were: (i) filled in 3 steps and air was removed by vibrating the samples between each step, (ii) sealed using a cork and parafilm, and (iii) put in an anti-segregation rotating system for 24 h. They were then left for at least 6 months at 20 °C before being subjected to carbonation. The fly ash-blended cement pastes were left for at least 11 months so that the pozzolanic reaction had time to stabilize [25].

### 2.2. Pretreatment

After the sealed curing period (between 6 and 11 months, depending on the formulation), plastic bottles were cut in two pieces in order to obtain two cylinders (height $\simeq 60$ mm, $\phi = 70$ mm). The samples were preconditioned prior to carbonation by covering each sample with a self-adhesive aluminium foil over the lateral face and bottom faces, so that all transport phenomena occurred unidimensionally. The specimens were placed in a temperature-controlled oven at 45 °C for 56 days. Finally, the specimens were stored for 56 days at 20 °C and 62 ± 5% RH over a saturated $NH_4NO_3$ solution. This last pretreatment was used to accelerate the carbonation mechanism by controlling the moisture content of the specimens as close as possible to the optimum RH in the range of 40%–70% [8,26–29]. Note that the pretreatment duration was too short to obtain homogeneous RH in the samples, but these heterogeneous moisture profiles were quantified by gamma-ray attenuation measurement as reported in Section 3.2 and in [22].

### 2.3. Accelerated carbonation test

Accelerated carbonation was performed using an incubator (Sanyo MCO5-AC) which controlled the temperature ($T = 25 \pm 0.5$ °C) and $CO_2$ concentration. The relative humidity was fixed using a saturated salt solution of $NH_4NO_3$ (RH = 63 ± 5%). Temperature, relative humidity and $[CO_2]$, were monitored using HM70 and GM70 probes (Vaisala). A 10% $CO_2$ concentration was chosen in order to be consistent with our previous investigation [22] where we showed that X-ray diffraction patterns were similar compared with natural carbonation and 10% $CO_2$ accelerated carbonation on mortars made of the same cement. This choice was also made to accelerate the carbonation test in a reasonable time limit and thus avoid strong drying during the experiment, but without leading to a dramatically different microstructure than the one observed in tests conducted at a lower $CO_2$ concentration. Obviously, this may be questioned when adding fly ash since these materials bring aluminium in the system.

**Table 1**
Formulations used in this work and water-to-binder ratio (cement and fly ash), water-to-cement ratio, and volumic and mass fraction of fly ash. The highest substitution ratio is out of standards (cf. EN 206). The hydration degree is calculated using $\mathtt{CH}$ content (TGA). Porosity is measured either by MIP or by GRAM.

| Characteristics | Units | CN | CN30 | CN60 | CP | CP30 |
|---|---|---|---|---|---|---|
| Fly ash (fa) | vol.% | 0 | 30 | 60 | 0 | 30 |
| Fly ash (fa) | wt.% | 0 | 23 | 51 | 0 | 23 |
| $w/(c + \text{fa})$ | – | 0.45 | 0.45 | 0.45 | 0.6 | 0.6 |
| $w/c$ | – | 0.45 | 0.64 | 1.13 | 0.6 | 0.86 |
| *Noncarbonated* | | | | | | |
| Porosity (MIP) | % | 19.2 ± 0.7 | 29.2 ± 1.1 | 37.8 ± 1.0 | 31.0 ± 2.1 | 42.7 |
| Porosity (GRAM) | % | 37.9 ± 0.7 | 47.4 ± 1.2 | 52.9 ± 1.7 | 47.1 ± 0.6 | 54.9 ± 1.0 |
| Hydration degree (TGA) | – | 0.86 ± 0.02 | 0.83 ± 0.01 | 0.98 ± 0.01 | 0.84 ± 0.04 | 0.93 ± 0.01 |
| *Carbonated* | | | | | | |
| Porosity (MIP) | % | 12.3 ± 1.1 | 23.4 ± 2.7 | 36.4 ± 1.2 | 23.1 ± 3.1 | 34.2 ± 2.1 |
| Porosity (GRAM) | % | 30.2 ± 1.1 | 36.0 ± 0.8 | 46.5 ± 0.9 | 36.5 ± 1.3 | 48.8 ± 0.8 |