Available online at www.sciencedirect.com

ScienceDirect

Cement and Concrete Research 37 (2007) 1182 – 1192

Cement and Concrete Research

Measurement methods of carbonation profiles in concrete: Thermogravimetry, chemical analysis and gammadensimetry

Géraldine Villain*, Mickaël Thiery, Gérard Platret

Laboratoire Central des Ponts et Chaussées, 58, boulevard Lefèbvre, 75 732 Paris cedex, France, Route de Bouaye, BP 4129, 44 341 Bouguenais cedex, France

Received 3 February 2006; accepted 25 April 2007

Abstract

This paper deals with two experimental methods to determine carbonation profiles in concrete. Gammadensimetry is a non-destructive test method able to measure the total penetrated CO_2 and to monitor the carbonation process during laboratory accelerated tests. The second method is thermogravimetric analysis (TGA) supplemented with chemical analysis (CA): as TGA is performed on a small mortar sample not representative of the whole tested concrete, CA is needed to proportion the sample cement content, the sand content and to correct the TGA results becoming thus representative of the concrete mix. Consequently, TGA-CA gives accurate quantitative profiles in carbonated cementitious materials. Results are reported for an ordinary Portland cement paste, and three concrete mixes, containing siliceous or calcareous aggregates. The CO_2 mass loss due to carbonation occurs from 530 to 950 °C, which overlaps the temperature range of the calcareous aggregate dissociation. To solve the problem, the origin of $CaCO_3$ is carefully analyzed. Calcium carbonate ensuing from C–S–H carbonation dissociates in a lower temperature range than the more stable one ensuing from portlandite carbonation and from limestone, which enables C–S–H carbonation to be distinguished from calcareous aggregates. Therefore, TGA-CA allows the $CaCO_3$ ensuing from C–S–H carbonation to be measured and to calculate the portlandite degraded by carbonation. Thus, the total calcium carbonates profiles can be deduced even when calcareous aggregates is present in the concrete mix.

Keywords: Carbonation (C); $Ca(OH)_2$ (D); Calcium–silicate–hydrate (C–S–H) (B); Thermal analysis (B); Gammadensimetry

1. Introduction

In reinforced concrete, the steel reinforcement is physically and chemically protected from corrosion by the surrounding concrete. The pore interstitial solution constitutes a very alkaline environment (pH close to 13.5), in which the rebars are passivated. When carbon dioxide (CO_2) from the atmosphere penetrates into the concrete pores, it dissolves in the interstitial solution and thereby modifies the chemical balances between the solution and the hydrates. This leads to the precipitation of calcium carbonates ($CaCO_3$) in ordinary Portland cementitious materials; the densification of the microstructure and the decrease of the pH the interstitial solution. Consequently, the reinforcement is not protected anymore and is likely to corrode. The carbonation process thus leads to the degradation of the reinforced concrete structures [1–3].

The usual, simple method to monitor the concrete carbonation is a colorimetric method based on phenolphthalein spraying. It assesses a carbonation depth (P_c) corresponding to a pH value roughly equal to 9 and is applied either on cores of real structures or on specimens carbonated in laboratory conditions. This colorimetric test is commonly linked with CO_2 carbonation models, which are based on the diffusion process in the porous material [4,5] and which imply a steep carbonation front. Meanwhile, different studies show that the carbonation front is not sharp but gradual [6–9]. Hence, more sophisticated models, which take into account not only the diffusion process but also the non-instantaneous chemical reactions [10–13], have been developed. In order to better understand the carbonation process, to better describe this phenomenon and to validate models, it is necessary to measure quantitative carbonation profiles to monitor the carbonation progress over time. The methods presented here have allowed

---

* Corresponding author. Tel.: +33 2 40 84 57 22; fax: +33 2 40 84 59 97.
E-mail address: geraldine.villain@lcpc.fr (G. Villain).

0008-8846/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2007.04.015

the validation of an analytical model developed by Thiéry [13], which shows that the kinetics of the carbonation reactions are rate-controlling, rather than CO_2 diffusion, which explains the gradual carbonation front [14].

The aim of this study is to develop measurement methods for carbonation profiles in cementitious materials, whatever their mix design, in particular with or without limestone aggregates. We focus here on the TGA method and its comparison with the gamma-ray absorption method. The parallel use of the gamma-densimetric method shows that it is necessary to supplement thermogravimetric analysis (TGA) by chemical analysis (CA) to obtain more precise carbonation profiles, on the one hand, and to enable more detailed analysis of the TGA results, on the other hand. It is shown that it is possible to identify portlandite and discriminate carbonates from aggregates, from carbonation of portlandite or from carbonation of C–S–H by TGA.

After a short review of the literature and description of the experimental program, the non-destructive method of gamma-ray absorption by carbonated specimens, used in this study, is described. This method measures, during the carbonation process, the density evolution, from which the total fixed CO_2 content is inferred. Gammadensimetry has shown the necessity to supplement TGA with a chemical analysis (CA) able to determine the cement content. Subsequently, the TGA method coupled with CA is presented with emphasis on the sample preparation. Then, the results obtained on several concretes by the two methods are discussed in order to define the accuracy and limitations of the method and to better understand the reaction mechanism of the hydrates with CO_2 during the carbonation process.

2. Review of existing experimental methods

To determine the extent of carbonation or to investigate the microstructure of carbonated cementitious materials, different methods have been proposed, but most of them are qualitative.

Observations of fresh-broken surface of carbonated specimens under optical or scanning electron microscopes reveal different forms of calcium carbonates and carbonated hydrated calcium silicate (C–S–H) [15–18]. Sauman [15] and Slegers and Rouxhet [19] have shown that X-ray diffraction can detect portlandite $Ca(OH)_2$ and amorphous cementitious products and can moreover distinguish various calcium carbonates (calcite, vaterite and aragonite) in crushed samples of hydrated cement paste. Slegers and Rouxhet [19], as weel as Lo and Lee [20], have reported that it is also possible to identify the different forms of calcium carbonated by infrared (IR) spectrometry. Thanks to IR spectroscopy, Slegers and Rouxhet [19] concluded that the carbonation of C–S–H leads to the formation of an amorphous silica gel, in agreement with trimethylsilylation used by Dunster [21].

There also exist quantitative methods. Rafaï et al. [18,22] have measured the proportions of carbon and oxygen isotopes by extracting the CO_2 from a small sample of hydrated cement pastes and proportioning the gaseous isotopes in a mass spectrometer in order to quantify the calcium carbonate formed during carbonation. Thermogravimetric analysis (TGA) is the easiest, and so the most widely used method. It is possible to quantify portlandite and calcium carbonate ensuing from carbonation by TGA. It is generally applied to hydrated cement pastes [7,17,18,23] and sometimes to concrete [6,9]. Unfortunately, researchers do not agree on the temperature ranges of decomposition of calcium carbonates, which is clarified latter in this paper. Houst and Wittman [8] have developed another method, combining thermal decomposition of carbonates and infrared analysis of the emitted gas (CO_2). This enabled the determination of the CO_2 content in ground mortar samples that contain siliceous aggregates.

3. Experimental program

3.1. Materials studied and sample pretreatment

Table 1 gives the mixture proportion of the materials studied. After a 3-month water curing, three 110 mm × 220 mm specimens were sawn into 100-mm-high samples and then water saturated under vacuum. They were then oven dried for 1 month at 45 °C, then for 1 month at 20 °C in a chamber at a controlled relative humidity (RH) of 53%. The aim of this pretreatment was first to obtain an internal relative humidity as uniform as possible and secondly, to achieve the best conditions for carbonation, which lie between 40% and 70% RH in the atmosphere [24]. During the drying and carbonation phases, the circumference of the specimens is protected by two layers of adhesive aluminium to ensure unidirectional gas exchange with the atmosphere. Hence, both sawn faces are submitted to drying, and then to carbonation. For the most porous material (called B25, see Table 1), one of the sawn faces was also protected after drying, at the beginning of carbonation (i.e., at the moment t_0), in order to preserve an uncarbonated area.

For each concrete, three cylindrical specimens were prepared: one to monitor the drying process by gammadensimetry (at t_0), one to monitor the carbonation progress over time also by gammadensimetry and the last one for TGA.

A further set of six prismatic specimens ($70 \times 70 \times 140$ mm^3) were prepared in the same way as the cylindrical specimens, for

Table 1
Features of the studied concrete mixes with calcareous and siliceous aggregates

		B25	B35EAS	B40
Silico-calcareous sand (0/5) and gravel (4/20)	(kg/m^3)	1906	0	1898
Siliceous sand and gravel (0/20)	(kg/m^3)	0	1890.8	0
Cement CEM I 52.5 PM ES (Lafarge Saint-Vigor)	(kg/m^3)	230	340	300
Air entraining agent		0	0.32	0
Water	(kg/m^3)	193	181.1	187.4
Total water/cement ratio	(–)	0.84	0.53	0.62
Cement content	(%)	9.88	14.10	12.58
Compressive strength. Average at 28 days Rc28	(MPa)	26.9	36.3	40.7
Bulk porosity measured by water saturation at 90 days	(%±0.5%)	14.8	13.8	14.5
Calculated portlandite content at 28 days	(%)	2.40	3.43	3.06

the phenolphthalein spraying test. Due to the use of aluminium protection, only the upper leveled face was submitted to drying and carbonation.

A special cylinder is used to monitor regularly the drying process by gammadensimetry, from saturation to the moment t_0. Afterwards, this cylinder is completely dried in an oven at 105 °C and is tested once more by gammadensimetry in order to determine the dry density and so the profile of saturation degree at t_0.

3.2. Accelerated carbonation test

The accelerated carbonation took place in a chamber at $T=20\pm2$ °C, $HR=53\pm5\%$ and CO_2 content close to 45±5%. Samples were removed from the chamber at 7, 14 and 28 days and a gammadensimetric test made each time on two cylinders. The carbonation depth was measured by phenolphthalein spraying on a fresh split surface of one of the prismatic $70\times70\times140$ mm^3 specimens. At 14 days, a cylinder was tested by gammadensimetry, then sawn under alcohol to obtain a carbonation profile by TGA-CA according to the method described below (see paragraph 5).

4. Non-destructive method by gammadensimetry

The gammadensimetry method is summarized here. More details are given in [25]. The non-destructive tests by gammadensimetry do not require a specific preparation in addition to the specimen preconditioning.

4.1. Measurement principle and procedure

Gammadensimetry is based on the absorption of gamma-rays emitted by a radioactive source of Cesium Cs^{137}, which follows Lambert's law (Eq. (1)). Measuring N_0 the number of incidental photons in the air, N the number of photons through concrete and the thickness across the sample l (m), and knowing μ (m^2/kg) the mass absorption coefficient of the material under investigation, it is possible to calculate the concrete density ρ (kg/m^3):

$$\rho=\frac{-1}{\mu\cdot l}\ln\left(\frac{N}{N_0}\right) \tag{1}$$

The set-up used in this study allows a cylindrical sample to be tested at different heights. During the measurement at a given height, the sample is placed in the centre of a plate rotating around its axis. The measurement then corresponds to the average density of a concrete slice, whose height is equal to the beam diameter, namely 6 mm.

4.2. Calculation of the carbonation profile

The authors showed in [9,25] that no drying occurs during the accelerated carbonation test and, as a consequence, that the density variation is only due to the CO_2 ingress. The carbonation profile is thus obtained by difference between the non-carbonated concrete density ρ_0 at the moment t_0 and the density ρ of the carbonated concrete, at the moment t, according to the Eq. (2)

$$\frac{\Delta\rho}{\rho}=\frac{\rho(t)-\rho_0(t_0)}{\rho_0} \tag{2}$$

The uncertainty of measurement of the relative density variation $\frac{\Delta\rho}{\rho}$ is equal to 0.12% for each depth.

The quantity of penetrated CO_2 can also be expressed as a concentration C_{CO_2} in mol/L of non-carbonated concrete (see Eq. (3)).

$$C_{CO_2}=\frac{\rho(t)-\rho_0(t_0)}{M_{CO_2}} \tag{3}$$

with M_{CO_2} the molar mass of carbon dioxide. The uncertainty of measurement is then equal to $u_c=7\times10^{-2}$ mol/L.

Given the measurement principle of gammadensimetry, all the CO_2 molecules, which have penetrated in the porous material, are taken into account: the molecules present in the gas phase, those dissolved in the interstitial solution, those fixed by adsorption on solid components or those precipitated as calcium carbonate ($CaCO_3$). However, it is not possible to distinguish the various phases of CO_2 by this method. As detailed in [14], the total CO_2 content in the gaseous and liquid phases is roughly equal to 4×10^{-3} mol/L, in the accelerated testing conditions and in the totally carbonated area. It is much lower than the uncertainty of measurement and, consequently, the CO_2 gaseous and dissolved is not significant in the gammadensimetry measurements.

On the other hand, this non-destructive test makes it possible to monitor the evolution of the carbonation process as a function of time on the same specimen, as illustrated by Fig. 1.

5. Method by thermogravimetric analysis coupled with chemical analysis (TGA-CA)

Thermogravimetry continuously measures the mass of a sample subjected to a steady increase of temperature in order to quantify reactions involving gaseous emissions. Thermogravimetric analysis (TGA) is thus a convenient method to determine concrete carbonation, because it quantifies the calcium carbonates

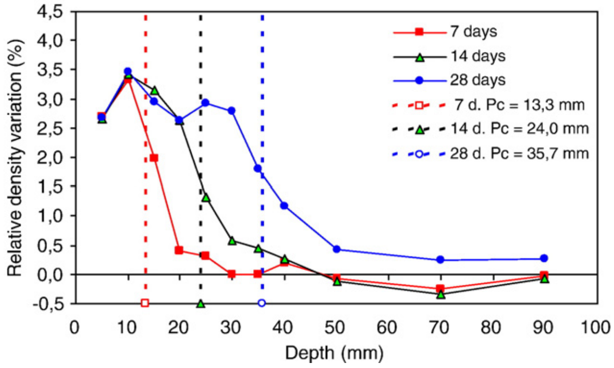

Fig. 1. Carbonation profiles and depth P_c in B25 concrete sample submitted to the accelerated test at 7, 14 and 28 days.

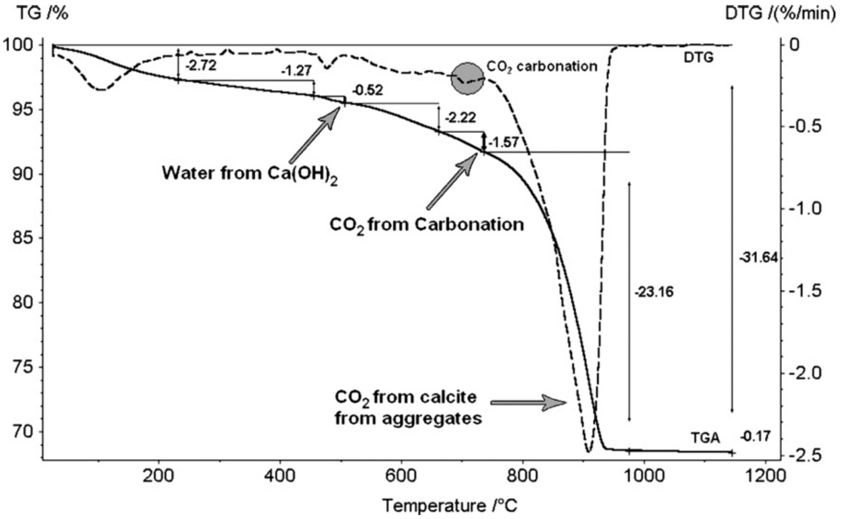

Fig. 2. Dissociation of a carbonated sample of crushed concrete mortar during a TGA test: concrete containing limestone aggregates.

and portlandite contents in a sample of mortar extracted from concrete ("concrete mortar") and reduced into powder [6,26].

The proposed method based on TGA aims to measure an accurate quantitative profile expressed as the amounts of the chemical phases in the concrete specimen, at different depths. But, firstly, TGA is performed on a powder sample of "concrete mortar" without coarse aggregates which is not representative of the whole tested concrete. Secondly, calcite of limestone sand could disturb the measurement of calcite ensuing from carbonation. As a consequence, TGA has to be combined with the chemical analysis (CA) of a part from the same powder sample in order to know exactly its cement content and its sand content, to correct TGA results becoming thus representative of the studied concrete mix. This accurate method is called TGA-CA. In addition, TGA-CA can be useful for non-homogeneous cementitious materials: cement pastes or concrete showing sedimentation phenomena, as well as skin regions of real concrete structures.

5.1. Preparation of the powder samples

To obtain a carbonation profile by TGA-CA, it was necessary to saw small slices from the specimens. The position of the slices was decided according to the carbonation depth (P_c) in order to analyze several areas in the region of the carbonation front and at least one area in the non-carbonated region. Sawing was carried out under alcohol to cool the blade and to prevent leaching by water.

The pieces of concrete mortar were selected to avoid the edges and thus skin effects (due to the mould) and by avoiding coarse aggregates, which "dilute" the hydrates and the reaction products, to be measured. The pieces of "concrete mortar" were preserved in airtight bottles, while waiting to carry out the tests. Before TGA, they were crushed in an agate mortar and the coarser sand grains are eliminated.

The powder obtained was divided into three parts. The first one of 0.225 g was used for the TGA. The second one of 1 g was used for the chemical analysis. The third part was preserved in

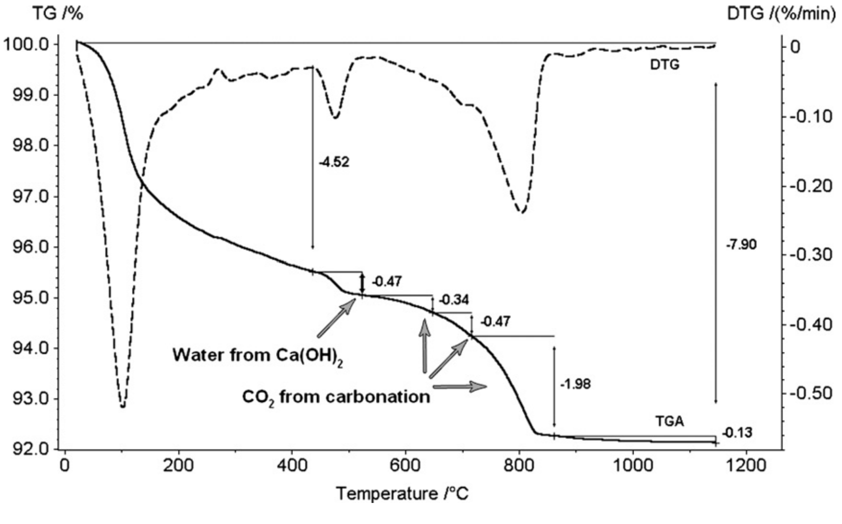

Fig. 3. Dissociation of a carbonated sample of crushed concrete mortar during a TGA test: concrete containing siliceous aggregates.

Table 2
Chemical analysis of cement CEM I 52.5 PM ES from Saint-Vigor (Lafarge)

		%
Soluble silica	SiO_2	21.39
Aluminium oxide	Al_2O_3	3.49
Titanium oxide	TiO_2	0.18
Ferric oxide	Fe_2O_3	4.16
Calcium oxide	CaO	65.12
Magnesium oxide	MgO	0.82
Sodium oxide	Na_2O	0.12
Potassium oxide	K_2O	0.3
Sulfuric anhydrite	SO_3	2.86
Manganese oxide	MnO	0.09
Insoluble Residue	RI	0.31
Total loss on ignition at 1000 °C	LI	1.1
Total of dosed elements		99.94

an airtight bottle, to be used for X-ray diffraction (DRX) or infra-red spectroscopy (IR) tests.

5.2. Thermogravimetric analysis (TGA)

The thermal analyser NETZSCH STA 409 E used in this study, enables the thermogravimetric curve (TGA), the derived thermogravimetric curve (DTG) and the curve from differential thermal analysis (DTA) to be obtained simultaneously on each sample. The 0.225 g part of the powder sample was heated from 25 to 1150 °C with a 10 °C per minute heating rate.

Each phase (including the hydrates) is characterized by its own temperature range of decomposition and by a specific mass loss; for example, for portlandite, it is a loss of water, and for calcite, it is a loss of CO_2. The lowest temperature of the dissociation range is determined by the characteristics of the equipment and the heating rate. The maximum temperature of the dissociation range is a function of the quantity of the studied phase. The temperature ranges are clearly defined by the edges of the characteristic peak of the DTG curve.

In addition, the thermal dissociation of calcium carbonate is influenced by the grain size. Thus, calcite resulting from carbonation (of finer granulometry) dissociates before the calcite which is contained in the limestone aggregates [26]. A typical TGA curve is presented in Fig. 2, which highlights the temperature ranges corresponding to the loss of H_2O from portlandite ($Ca(OH)_2$) and the loss of CO_2 ensuing from the carbonation products and from calcareous aggregates, according to the temperature ranges defined by [26]. Fig. 3 illustrates the thermal dissociation of a carbonated concrete powder sample, whose mix contains siliceous aggregates (B35EAS). The temperature range corresponding to the loss of CO_2 ensuing from carbonation is clearer and more extended. This point is considered further in Section 6.1.

Table 3
Chemical analysis of B40 concrete powder samples taken at different depths

Depth (mm)	SiO_2 (%)	CaO (%)	Fe_2O_3 (%)	Al_2O_3 (%)	RI (%)
3	0.56	32.45	0.78	0.55	31.91
11	0.56	32.44	0.71	0.49	32.83
19	3.01	36.30	0.75	0.54	23.33
27	3.22	40.68	0.68	0.45	21.62
35	*4.50*	*33.97*	*1.00*	*0.70*	*32.06*
43	3.06	36.88	0.64	0.43	19.31
51	3.57	36.08	0.75	0.52	29.11

Table 4
Cement content of B40 concrete powder samples taken at different depths

Depth (mm)	SiO_2 (%)	CaO (%)	Fe_2O_3 (%)	Al_2O_3 (%)	
3	2.6	8.6	18.7	15.8	Carbonated area
11	2.6	9.6	17.1	14.0	
19	14.1	12.0	18.0	15.5	
27	15.0	11.4	16.3	12.1	Non-carbonated area
43	14.3	10.9	15.4	12.3	
51	16.7	17.3	18.0	14.9	

5.3. Chemical analysis (CA)

Chemical analysis (CA) makes it possible to proportion the mineralogical phases of carbonated or uncarbonated concrete areas and thus to inform about the degradation state of the material under investigation.

The second part of the powder sample was crushed and sieved at 315 μm. Then 1 g was diluted in a nitric acid solution (diluted at 1/50). The solution obtained was then filtered and analyzed:

- the soluble cationic oxides (SiO_2, Al_2O_3, TiO_2, Fe_2O_3, CaO, MgO and MnO) were proportioned by atomic emission spectrometry; and
- the alkaline ones (Na_2O and K_2O) were proportioned by atomic absorption spectrometry.

In addition, the filter content was incinerated at 1000 °C to obtain the insoluble residue [27]. Table 2 gives the CA results of cement CEM I 52.5 from Saint-Vigor (Lafarge) which is present in the concrete mixes.

5.4. Choice of a tracer of cement

CA was carried out in order to determine the cement content of the crushed sample coming from the specimen slices. In a

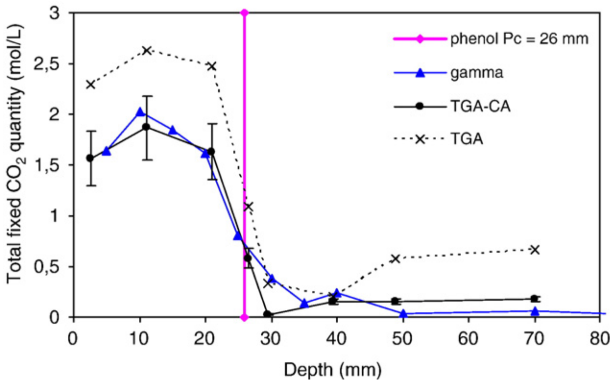

Fig. 4. Improvement of the determination of the total fixed CO_2 quantity by correction TGA results by the cement content measured by CA (B25 concrete specimen).

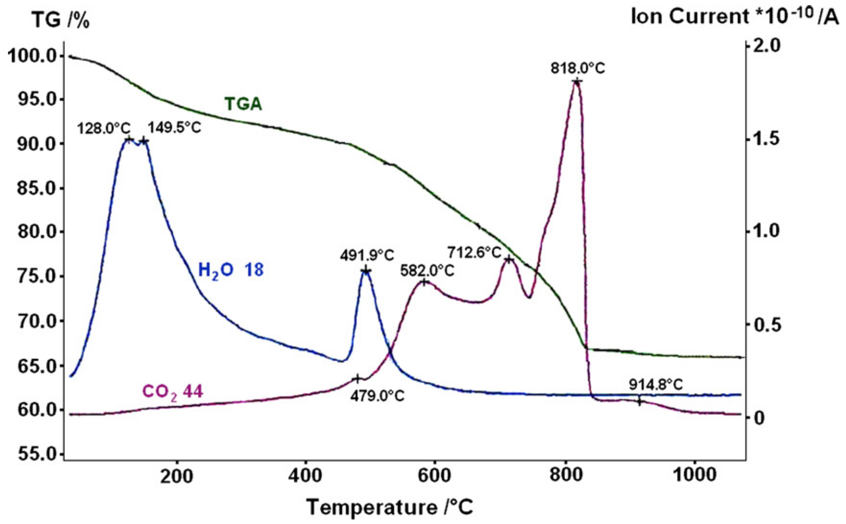

Fig. 5. Plots of the mass change (TG Analysis) and of mass spectroscopy (ion currents for H_2O mass number 18 and CO_2 mass number 44) in the cement paste sample.

non-carbonated material, the following main tracers of cement (SiO_2, CaO, Fe_2O_3 and Al_2O_3) can be used. Table 3 is an example of CA results obtained for a B40 concrete specimen. These results are used to calculate the cement content in the concrete powder samples taken at different depths (except at 35 mm) in this specimen (see Table 4).

- Soluble silica (SiO_2) is present in large quantity in cement; thus, it is suitable to obtain the cement content in the non-carbonated material. But it cannot be used to determine the cement content of the powder samples in the carbonated area. Indeed, insoluble products are formed [21,28,9], such as amorphous silica gels, produced by the C–S–H carbonation [15,19]. Indeed, it is observed in Table 3 that the soluble silica content significantly decreases, while the insoluble residue increases in the first two slices corresponding to the carbonated area.
- Lime (CaO) is also present in great quantity in cement. However, it is sometimes necessary to take into account the calcium carbonates of aggregates in the calculations, for concrete containing limestone aggregates. Lime from calcareous aggregates is measured by TGA between 760 and 1000 °C but, in the carbonated area, carbonated products of cement hydrates can dissociate in the same temperature range (as shown further). Thus, CaO is a possible tracer of cement in the non-carbonated area but not as convenient as SiO_2. It is not possible to use CaO as a tracer of cement in the carbonated concrete, what is illustrated in Table 4. In cement pastes, TGA could determined the carbon dioxide content and thus enables the calculation of the cement content by CA, and also TGA could assess alone the cement content in the cement paste reduced into powder. But, the studied samples are submitted simultaneously to segregation, drying and carbonation processes, which prevent a correct evaluation of the cement content only by means of TGA.
- Platret and Deloye [26] advise against using Fe_2O_3 as a tracer of cement because Fe is present in several forms (metal and different oxides), which impairs the accuracy of the proportioning. Hence, it can be observed in Table 4 that the use of Fe_2O_3 overestimates the cement content in comparison with the cement content calculated by using the SiO_2

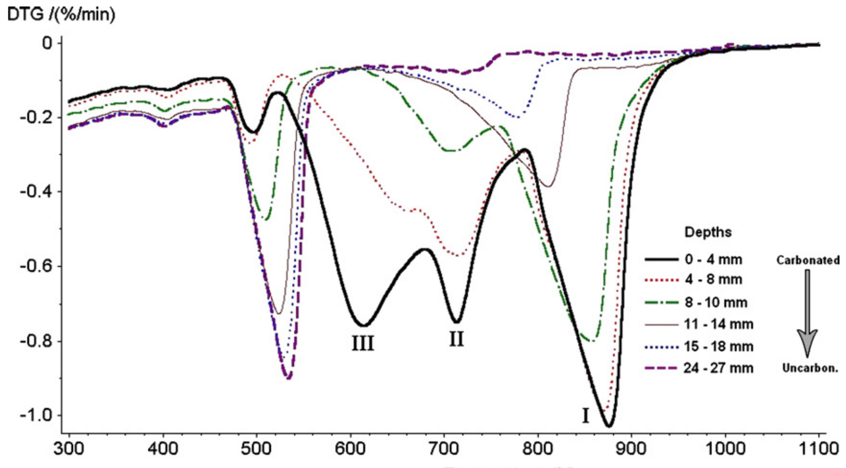

Fig. 6. TGA results (DTG) of paste samples sawn at different depths: cement paste P45 carbonated for 14 days.

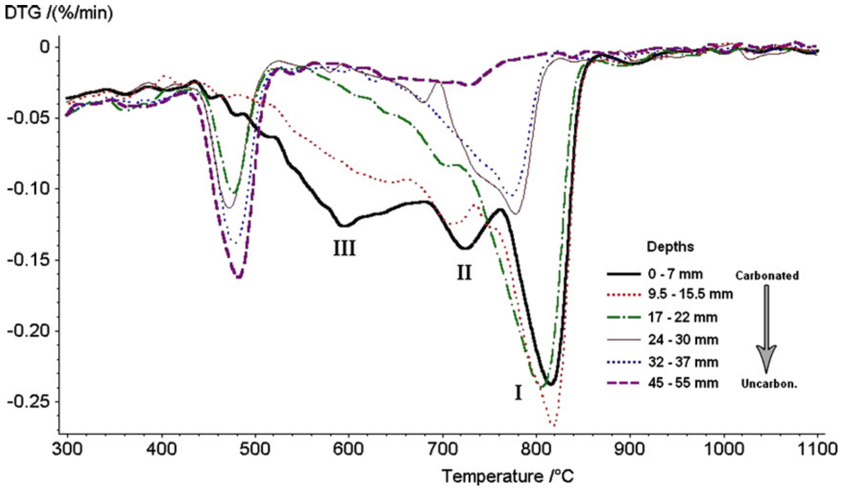

Fig. 7. TGA results (DTG) of concrete mortar samples sawn at different depths: B35EAS concrete carbonated for 14 days.

or CaO content in the non-carbonated area, where the use of CaO or SiO_2 is convenient.

- Aluminium (Al_2O_3) is present in relatively small quantity in cements. No other product containing Al_2O_3 is present in the studied concrete mixes. Moreover, carbonation does not decrease the solubility of Al_2O_3 (see Tables 3 and 4). Thus, the aluminium content is recommended to calculate the cement content in the powder samples, either carbonated or not.

In addition, for all the powder samples taken in the non-carbonated studied materials (B25, B35EAS and B40), the cement content has been assessed by using SiO_2, CaO and Al_2O_3 contents. The resulting average cement content obtained by the Al_2O_3 content is roughly 0.9% higher than the one obtained by CaO and 1.6% lower than the one obtained by SiO_2.

As a consequence, the cement content in each powder samples is determined by using the aluminium content with a maximal uncertainty of 1.6%.

5.5. Calculation of the various profiles

The TGA measurement is expressed in mass of lost gas for 100 g of tested powder sample and is noted here Δm_p. The cement content of the concrete powder (Q_p^{cem}) is determined by chemical analysis. Moreover, the concrete mix gives the cement content in the studied material (Q_c^{cem}). In these conditions, it is possible to calculate all TGA results for 100 g of concrete (Δm_c) according to Eq. (4).

$$\Delta m_c = \Delta m_p \frac{Q_c^{cem}}{Q_p^{cem}} \tag{4}$$

It is then possible to compare this result with the relative density variation obtained by gammadensimetry because the volume variations are negligible [29]. The carbon dioxide content (C_{CO_2}), which corresponds to a mass loss by TGA, is calculated according to Eq. (5):

$$C_{CO_2} = \frac{\Delta m_c \cdot \rho_0}{M_{CO_2}} \tag{5}$$

where M_{CO_2} is the CO_2 molar mass and ρ_0 the concrete density at t_0. The average value of ρ_0 can be used, if the water content is homogeneous in the specimen after the drying process. In the opposite case, the water content profiles obtained by gammadensimetry are used [13] in order to enhance the profile accuracy.

Finally, by TGA-CA, the profiles of portlandite and calcium carbonates from various origins can be determined.

5.6. Uncertainty of measurement

The tested powder samples are not representative of the concrete specimen they are taken from. For this reason, CA is

Table 5
Analysis of TF-IR results obtained on P45 powder samples taken at different depths

Depth (mm)	Non-carbonated hydrates		Carbonation products			
	Portlandite	C–S–H	Calcite	Vaterite+aragonite	Aragonite	Amorphous silica gel
Peak	$3644\ cm^{-1}+1653\ cm^{-1}$	$972\ cm^{-1}$	$1456\ cm^{-1}$	$875\ cm^{-1}$	$713\ cm^{-1}$	$1080\ cm^{-1}+1200\ cm^{-1}$
2	+	0	+++	+++	++	+++
6	+	+	+++	+++	+	+
9	+	++	+++	+++	+	+
12.5	++	+++	+++	++	0	0
16.5	+++	+++	+	+	0	0
20	+++	+++	+	0	0	0
25.5	++++	+++	0	0	0	0

Table 6
Analysis of TF-IR results obtained on B35EAS powder samples taken at different depths

Depth (mm)	Non-carbonated hydrates		Carbonation products	
	Portlandite	C–S–H	Calcite	Vaterite+aragonite
Peak	$3644\ cm^{-1}+1653\ cm^{-1}$	$972\ cm^{-1}$	$1456\ cm^{-1}$	$875\ cm^{-1}$
3.5	+	0	+++	+++
12.5	+	0	+++	+++
19.5	++	0	++	++
27	++	++	++	+
34.5	+++	++	+	+
50	+++	+++	0	0

used to determine the actual cement content and to correct the TGA results. Fig. 4 shows the comparison between the carbonation profiles obtained by TGA only, by TGA-CA and by gammadensimetry. The indicated uncertainty of TGA-CA measurement has been assessed by combining:

- the typical features of the various apparatus (TGA and CA);
- the error due to the overlap of the peaks (TGA), which are characteristic of certain dissociation (see Section 6.1);
- the error due to the cement content evaluation by Al_2O_3 content (instead of SiO_2 or CaO) in the uncarbonated area (CA); and
- the uncertainty of the cement content of the global concrete mix.

The cement content measurement by CA is the main error cause, in particular in concrete mixes with low cement content. Thus, the maximal uncertainty of TGA-CA measurement depends on the concrete mix and on the maximal CO_2 value C_{max} (for instance the uncertainties are roughly equal to $0.1 \cdot C_{max}$ mol/L for P45, M50 and B35EAS, $0.14 \cdot C_{max}$ for B40 and $0.17 \cdot C_{max}$ for M25). Though the uncertainty is important for the M25 concrete, Fig. 4 shows the improvement in the carbonation profile determination by using TGA-CA instead of TGA only.

6. Discussion about the results of TGA-CA and gammadensimetry

6.1. Temperature of decomposition of the carbonated products

In the literature, opinions diverge about the interpretation of the mass loss between 520 and 650 °C. This one can be due to a water loss from hydrates, in particular in the non-carbonated concretes. It can also come from the decomposition of carbonated products. In order to know the nature of this mass loss between 520 and 650 °C and assure the dissociation temperature ranges of the various forms of $CaCO_3$, a TGA coupled with a mass spectrometry was carried out on a slice of completely carbonated cement paste sample (see Fig. 5), which contains water and the cement corresponding to the concrete mixes studied here, with $E/C = 0.45$ (cement paste called P45). Furthermore, TGA-CA was carried out according to the protocol described in this paper. The results show that the loss of mass between 520 and 650 °C corresponds mainly to a CO_2 emission.

Moreover, it can be noted that the dissociation of the phases containing CO_2 comprises three peaks, which begin approximately from 520 °C, 680 °C and 780 °C. It can be deduced that they correspond to more or less thermally stable calcium carbonates. Moreover, it confirms that the calcium carbonates breaking up between 780 and 900 °C can be confused with calcium carbonates from the calcareous aggregates (dissociation temperature range from 720 to 980 °C). These given temperatures are only indicative because they depend on the extension of the precedent peak and on the matter quantity: the peaks overlap. The peak shape also depends on the carbonate stability, and thus on the progress of the carbonation process.

6.2. Origin of the various calcium carbonates determined by TGA-CA

In order to determine the origin of calcium carbonates measured by TGA-CA, several tools are available:

- On the P45 cement paste samples, TGA-CA tests and Fourier transform infrared spectroscopy (FT-IR) were carried out.

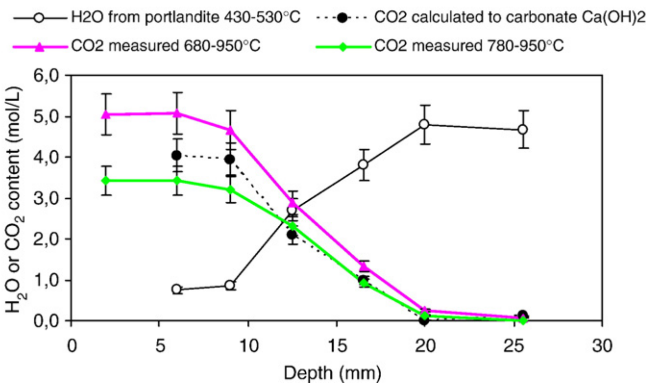

Fig. 8. Profiles obtained by TGA-CA in the cement paste P45 carbonated for 14 days.

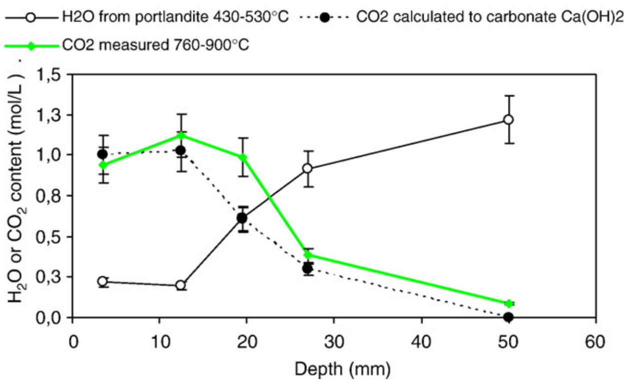

Fig. 9. Profiles obtained by TGA-CA in the B35EAS concrete carbonated for 14 days.

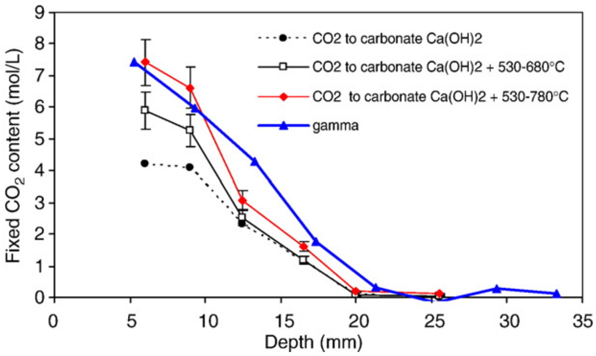

Fig. 10. Profiles obtained by TGA-CA and by gammadensimetry in the cement paste P45 carbonated for 14 days.

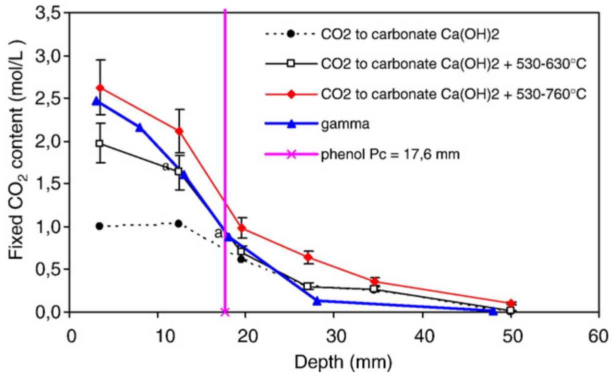

Fig. 11. Profiles obtained by TGA-CA and by gammadensimetry in the B35EAS concrete carbonated for 14 days.

- In the same way, on B35EAS concrete containing siliceous aggregates, results from TGA-CA and FT-IR spectroscopy were obtained.

6.2.1. Portlandite $Ca(OH)_2$ carbonation

For all the materials, the known decrease of the peak characteristic of portlandite (≈430–530 °C), while carbonation progresses, is confirmed. In parallel a peak (I) develops (Figs. 6 and 7) and begins at roughly 750 °C in the least carbonated layers (more deeply taken). Then it shifts gradually towards the highest temperatures (≈780–950 °C). In the slices closest to the surface, showing therefore a more advanced carbonation, two peaks difficult to distinguish (II and III) appear gradually between approximately 550 and 780 °C. Moreover, even in the very carbonated slices, the presence of residual portlandite determined by TGA-CA or by FT-IR, which is presented further (see Tables 5 and 6), is noticed. Indeed, the large crystals of $Ca(OH)_2$ are covered, during the carbonation process, by a rather tight layer of $CaCO_3$, which prevents a total carbonation of the crystal core [21,16,7,14]. But this residual portlandite is released by the crushing of the studied samples.

The profiles, deduced from the TGA-CA results (Fig. 8 for P45 and Fig. 9 for B35EAS), show:

- H_2O from the residual portlandite (≈430–530 °C);
- CO_2 from $CaCO_3$ measured from 760 to 950 °C (peak I);
- CO_2 from $CaCO_3$ measured from 650 to 950 °C (peaks I and II); as well as
- CO_2 estimated and necessary to carbonate the disappeared portlandite, by supposing that the portlandite distribution is homogeneous in the slices.

The observation of these profiles makes it possible to deduce that $CaCO_3$ ensuing from portlandite carbonation dissociate mainly at high temperature and may correspond to calcite, which is a well-crystallized form of $CaCO_3$ [15,14]. The temperature range of the corresponding dissociation is difficult to assert because the peaks overlap. As a consequence, both decomposition are given in order to obtain lower and upper bounds of $CaCO_3$ ensuing from $Ca(OH)_2$ carbonation (760–950 °C, respectively, 650–950 °C). However, it is not possible to determine them directly by TGA-CA in the concrete mixes, which contain limestone aggregates, which break up at a similar range of temperature. Consequently, since the $Ca(OH)_2$ peak is very clear, the carbonates ensuing from the portlandite carbonation are calculated by means of $Ca(OH)_2$ measurements in the continuation of this paper.

6.2.2. C–S–H carbonation

Moreover, it can be deduced from the profiles Figs. 10 and 11 that the calcium carbonates measured between 530 and 760 °C (respectively 530–650 °C) result from the degradation of other hydrates, C–S–H in particular, in agreement with other literature results [15,16,19,21]. According to Sauman [15], carbonation of C–S–H leads to the formation of vaterite, which seems to be an unstable type of calcium carbonate, imperfectly crystallized or having finer crystals, which dissociate between 500 and 700 °C, at a lower temperature than calcite. Grandet [23] also observes by X-ray diffraction the formation of vaterite during the carbonation of C–S–H. On the basis of precedent work for non-carbonated cementitious materials [30] and for carbonated materials [19], a qualitative analysis of the FT-IR results obtained on the P45 paste (see Table 5) and the B35EAS concrete (see Table 6) was carried out.

In conclusion, the qualitative FT-IR results seem to corroborate the TGA-CA results, i.e., C–S–H disappear in the most carbonated slices closest to the surface at the same time as amorphous silica gels and less stable forms of $CaCO_3$, like vaterite and aragonite, appear. For a more detailed analysis of the kinetics of the portlandite and C–S–H carbonation, it is necessary to refer to Thiery et al. [14]. As previously, good bounds of the total CO_2 content are provided by both profiles:

- CO_2 calculated to carbonate portlandite plus CO_2 measured within 530–760 °C, and
- CO_2 calculated to carbonate portlandite plus CO_2 measured within 530–650 °C.

6.3. Comparison of CO_2 profiles measured by gammadensimetry with those determined by TGA-CA

For all the studied materials (P45, B25, B40 and B35EAS), the profiles of total CO_2 content determined by the two methods

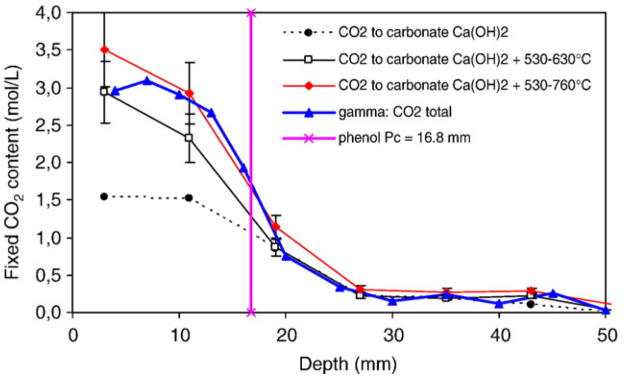

Fig. 12. Profiles obtained by TGA-CA and by gammadensimetry in the B40 concrete carbonated for 14 days.

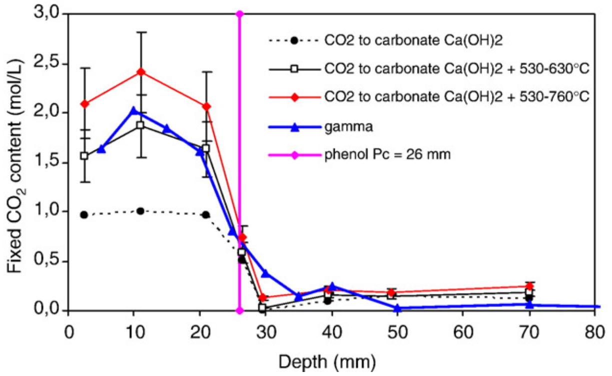

Fig. 13. Profiles obtained by TGA-CA and by gammadensimetry in the B25 concrete carbonated for 14 days.

are in a good agreement (see Figs. 10–13). Meanwhile, the cement paste specimens (Fig. 8) are different for TGA-CA and gammadensimetry, on the contrary to the concrete specimens (only one specimen for the two tests). But the profiles match.

On the Figs. 12 and 13, a decrease of the CO_2 content is observed in the superficial slice. It can be assumed that a slight leaching occurred, when the 220-mm-high specimens were initially sawn under water to obtain the 100-mm high ones. Houst and Wittmann [8] also observed a superficial similar phenomenon, which they attribute to ion migration during wetting and drying cycles.

Besides, taking into account, that TGA-CA makes it possible to determine accurately the portlandite profile and thereby the profile of CO_2 necessary to carbonate the portlandite, the comparison with gammadensimetric results (Figs. 11–13) confirms that the CO_2 loss between 530 and 650 or 760 °C is related to the carbonation of other hydrates, C–S–H in particular. But it is not yet possible to give the maximal limit of the temperature range: for the B40 concrete the profile of the total CO_2 content (gamma) indicates rather 760 °C whereas for the B25 concrete it is rather 630 °C.

7. Conclusions

Two experimental methods to determine carbonation profiles in concrete are presented here. They contribute to better describe the carbonation process in order to predict the carbonation progression in concrete and thus to be able to assess the service lifespan of reinforced concrete structure.

Gammadensimetry makes it possible to measure very accurately the total penetrated CO_2, without a specific preparation of the specimens. Moreover, it is a non-destructive test method able to monitor the carbonation process over time. However, a reference uncarbonated auscultation before degradation (at t_0) is required. That is the reason why gammadensimetry cannot easily and accurately quantify the CO_2 content in a core of an aged concrete structure. Gammadensimetry is recommended to monitor laboratory accelerated tests.

It is shown in this paper that TGA has to be supplemented with CA to give accurate quantitative profiles. Chemical analysis allows us to obtain the cement content in a part of the powder sample taken in concrete specimens and tested also by TGA. The oxide used to determine the cement content has to be aluminium oxide Al_2O_3 because it is (i) more precise than Fe_2O_3, (ii) not disturbed by the calcareous aggregates like CaO and (iii) because its solubility is not reduced by hydrate carbonation like SiO_2. Then, TGA-CA is able to supply accurate portlandite profile in all materials, as well as calcium carbonate profile directly in concrete containing siliceous aggregates. A CO_2 mass loss due to carbonation from 530 to 950 °C is measured. As a consequence, when calcareous aggregates are present in the concrete mix, the direct evaluation of carbonates by TGA-CA is not possible anymore. The origin of the CO_2 mass loss has first to be known. Thanks to the comparison with gammadensitometric profiles, FT-IR spectroscopy results and previous works of literature, it was highlighted that the stable $CaCO_3$ (calcite), probably ensuing from portlandite carbonation, dissociate between roughly 760 and 950 °C (or 650–950 °C) and unstable vaterite and aragonite, probably ensuing from C–S–H carbonation, dissociate between roughly 530 and 760 °C (or 530–650 °C). It is not yet possible to give a precise temperature, which limits the temperature range of the C–S–H and portlandite dissociation, and a further study should be performed. Therefore, TGA-CA makes it possible to assess upper and lower bounds of the $CaCO_3$, ensuing from C–S–H carbonation, and to calculate the portlandite degraded by carbonation and thus to deduce good bounds of the total calcium carbonates profiles. Then, profiles obtained by gammadensimetry and TGA-CA really agree.

It has finally to be noticed, that TGA-CA can be used to determine carbonation profile either in structure cores or in laboratory carbonated specimens.

Acknowledgments

The authors are grateful to the company NETZSCH, which supported the gas analysis in this study. They sincerely thank P. Roussel and E. Massieu for their technical contribution and P. Belin for his attentive reading of this paper.

References

[1] L.J. Parrott, A Review of Carbonation of Concrete, Cement and Concrete Association, 1987 42 pp.

[2] T. Chaussadent, Etat des lieux et réflexions sur la carbonatation du béton armé, Etudes et Recherches des LPC, série Ouvrages d'Art OA29, Ed. by LCPC Paris, (1999) 80 p.

[3] V.G. Papadakis, C.G. Vayenas, M.N. Fardis, Physical and chemical characteristics affecting the durability of concrete, ACI Mater. J. 8 (2) (1991) 186–196.

[4] V.G. Papadakis, C.G. Vayenas, M.N. Fardis, Fundamental modeling and experimental investigation of concrete carbonation, ACI Mater. J. 88 (4) (1991) 363–373.

[5] Y.F. Houst, F.H. Wittmann, Influence of porosity and water content on the diffusivity of CO_2 and O_2 through hydrated cement paste, Cem. Concr. Res. 24 (6) (1994) 1165–1176.

[6] L.J. Parrott, D.C. Killoh, Carbonation in a 36 year old in-situ concrete, Cem. Concr. Res. 19 (1989) 649–656.

[7] A.A. Rahman, F.P. Glasser, Comparative studies of the carbonation of hydrated cements, Adv. Cem. Res. 2 (6) (1989) 49–54.

[8] Y.F. Houst, F.H. Wittmann, Depth profiles of carbonates forming during natural carbonation, Cem. Concr. Res. 32 (2002) 1923–1930.

[9] G. Villain, G. Platret, Comparison of two experimental methods to determine carbonation profiles in concrete, in: V.M. Malhotra (Ed.), Proceedings Supplementary Papers of the 6th CANMET/ACI Int. Conf. on Durability of Concrete, Thessaloniki, Greece, 2003, pp. 179–194.

[10] A.V. Saetta, R.V. Vitaliani, Experimental investigation and numerical modeling of carbonation process in reinforced concrete structures: Part I: Theoretical formulation, Cem. Concr. Res. 34 (4) (2004) 571–579.

[11] A. Steffens, D. Dinkler, H. Ahrens, Modeling carbonation for corrosion risk prediction of concrete structures, Cem. Concr. Res. 32 (2002) 935–941.

[12] M. Thiery, P. Dangla, G. Villain, G. Platret, Modelling of coupled CO_2–H_2O-ions transports and chemical reactions of carbonation in concrete, Proceedings of the Conference Poromechanics-Biot Centennial (1905–2005), Oklahoma City, USA, 2005, pp. 807–812.

[13] M. Thiery, Modélisation de la carbonatation atmosphérique des matériaux cimentaires—Prise en compte des effets cinétiques et des modifications microstructurales et hydriques, PhD thesis (in French), LCPC Paris (2005) 333p.

[14] M. Thiery, G. Villain, P. Dangla, G. Platret, Investigation of the carbonation front shape on cementitious materials: Analysis of the effects of the chemical kinetics, Cem. Concr. Res. (in press), doi:10.1016/j.cemconres.2007.04.002.

[15] Z. Sauman, Carbonization of porous concrete and its main binding components, Cem. Concr. Res. 1 (1971) 645–662.

[16] G.W. Groves, D.I. Rodway, I.G. Richardson, The carbonation of hardened cement pastes, Adv. Cem. Res. 3 (11) (1990) 117–125.

[17] G.W. Groves, A. Brough, I.G. Richardson, C.M. Dobson, Progressive changes in the structure of hardened C_3S cement pastes due to carbonation, J. Am. Ceram. Soc. 74 (11) (1991) 2891–2896.

[18] N. Rafaï, H. Hornain, G. Villain, V. Baroghel-Bouny, G. Platret, T. Chaussadent, Comparison and validity of carbonation measurement methods (in French), Rev. Fr. Génie Civ. 6 (2) (2002) 251–274.

[19] P.A. Slegers, P.G. Rouxhet, Carbonation of the hydration products of tricalcium silicate, Cem. Concr. Res. 6 (1976) 381–386.

[20] Y. Lo, H.M. Lee, Curing effects on carbonation of concrete using a phenolphthalein indicator and Fourier-transform infrared spectroscopy, Build. Environ. 37 (5) (2002) 507–514.

[21] A.M. Dunster, An investigation of the carbonation of cement paste using trimethylsilylation, Adv. Cem. Res. 2 (7) (1989) 99–106.

[22] N. Rafaï, R. Letolle, P. Blanc, P. Gegout, E. Revertegat, Carbonation-decarbonation of concretes studied by the way of carbon and oxygen stable isotopes, Cem. Concr. Res. 22 (1992) 882–890.

[23] J. Grandet, Contribution à l'étude de la prise et de la carbonatation des mortiers au contact des matériaux poreux, PhD thesis (in French), Université Paul Sabatier, Toulouse, (1975) 287 p.

[24] H. Wierig, Longtime studies on the carbonation of concrete under normal outdoor exposure, RILEM. Seminar, Hannover, Germany, 1984, pp. 239–249.

[25] G. Villain, M. Thiery, Gammadensimetry: a method to determine drying and carbonation profiles in concrete, ND&E Int. 39 (4) (2006) 328–337.

[26] G. Platret, F.-X. Deloye, Thermogravimetry and carbonation of cements and concretes, Actes des Journées des Sciences de l'Ingénieur du réseau des Laboratoires des Ponts et Chaussées, Publication LCPC, Paris, 1994, pp. 237–243, (in French).

[27] Test method: solubilization by acid attack, determination of insoluble residue (in French), In: Recueil des modes opératoires pour l'analyse des ciments, bétons, sols et roches, Publication LCPC, Paris, (1996).

[28] H. Matsusato, K. Ogawa, M. Funato, T. Sato, Studies on the carbonation of hydrated cement and its effect on microstructure and strength, Proceedings of the 9th Int. Congress on the Chemistry of Cement, Performance and durability of concrete and cement systems, New Dehli, India, vol. 5, 1992, pp. 363–369.

[29] G. Villain, M. Thiery, Uncertainty of gammadensimetry measurements in concrete specimens, Bull. Lab. Ponts Chaussées 260 (2006) 69–82 (http://www.lcpc.fr/en/sources/blpc).

[30] F. Farcas, P. Touzé, Infrared Fourier Transform (IRFT) spectrometry: a valuable technique for characterizing cement, Bull. Lab. Ponts Chaussées 230 (2001) 77–88 (http://www.lcpc.fr/fr/sources/blpc) (in french).