

Thermogravimetric analysis for monitoring carbonation of cementitious materials

Uptake of CO₂ and deepening in C–S–H knowledge

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Abstract Cement paste carbonation, i.e., the reaction between CO₂ and the hydrated cement phases, mainly calcium hydroxide or portlandite, can lead to a pH decrease, which in turn can give rise to steel corrosion in reinforced concrete. At the same time, the carbonation reaction contributes to combine CO₂ and fix it as calcium carbonate. It is a crucial phenomenon from the point of view of structure durability and also for cement-based materials sustainability. Cement paste specimens with two w/c ratios and eight types of cements were submitted to different environmental conditions for 4 years and the evolution of calcium carbonate formed or carbon dioxide bound was followed by TG performed in inert atmosphere. The amounts of calcium hydroxide, evaporable and C–S–H gel water were also measured. The CO₂ bound follows the same trend in all samples and environments: at the beginning there is a sharp increase followed by a very slow stretch and reaching a maximum after less than 2 years in most cases. The calcium hydroxide amounts evolve very differently in each environment. While outside it is almost consumed after 1 year, inside there is a decrease in the first year, but an increase in the next 3 years. The behavior of the C–S–H water in both environments is similar to that of the portlandite inside. The evaporable water diminishes in all cases to 1 %. From the data obtained by TG, the quantification of the C–S–H gel as well as the calculation of the Ca/Si ratio and the hydration of the gel formed by different type of binders has been possible.

Keywords Carbonation · Thermal analysis · Cement · CO₂ uptake quantification · Hydration water in C–S–H gel · Different binders

Introduction

Cement paste carbonation, i.e., the reaction between CO₂ and the hydrated cement phases, mainly calcium hydroxide or portlandite and calcium–silicate–hydrate (C–S–H) gel, can lead to a pH decrease, which in turn can give rise to steel corrosion in reinforced concrete. In safe conditions, the steel inside the concrete is protected by a passive layer formed at pH values between 12.5 and 13.6. When the pH in the concrete pores solution lowers below 8, the passive layer becomes unstable leading to a generalized corrosion on the steel surface [1–4]. At the same time, the carbonation reaction in concrete contributes to combine CO₂ and fix it as calcium carbonate, stable at temperatures higher than 600 °C. In other words, carbonation is a crucial phenomenon from the point of view of structure durability and also for cement-based materials sustainability.

The most used technique for evaluating carbonation effects in concrete is the phenolphthalein indicator, which gives information about the pH, changing color at pH 8–9. This method has proved its utility for preventing steel corrosion, but it does not give information about the phases that are being consumed and formed. Thermogravimetric analysis (TG) is a powerful tool for quantifying the carbonation reaction in cement-based materials as it allows for the calculations of the amounts of the main phases involved in the process [5–12].

From the point of view of the CO₂ uptake in cement-based materials, there have been some publications [13–17], but in these studies no exhaustive experimental

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work about the temporal evolution of the process has been found. In order to evaluate the real CO₂ sink effect of these materials, it is necessary to measure the progress in time, i.e., the rate and the maximum values that can be reached, and also their relationship with the variables involved, such as type of cement, exposure, and water/cement (w/c) ratio.

In this study, data about CO₂ combination along the time in cement pastes exposed to natural carbonation are presented, and the variables that determine the process are discussed.

Experimental

Cement paste specimens with two w/c ratios, 0.45 and 0.6, were prepared. Eight types of cement were selected: one without additions, three with 6–20 % additions (pozzolan, fly ash, and fly ash/limestone), and four with 21–35 % additions (pozzolan, fly ash, ground-granulated blast-furnace slag (GGBS)/fly ash, and limestone). The names and compositions of the cements are given in Table 1.

The 1 × 1 × 6 cm prisms prepared were cured for 48 h in a 95 % relative humidity (RH) chamber and then they were dried in air in the laboratory for 26 days. After this period, half of the specimens were kept in the laboratory, with 22 °C average temperature and 38 % average RH (Fig. 1). The other half of the specimens were placed outside, sheltered from the rain, with 16 °C average temperature and 57 % average RH (Fig. 2). These specimens placed outside do not have any contact with the rain, the soil, or any acids.

The specimens were submitted to natural carbonation in both environments for 4 years, during which TG measurements were performed. The analyses were done in a STA 449F3 equipment of Netzsch using 50 mg of ground powder of less than 100 μm. The samples were heated from room temperature to 1,000 °C at 5 K min⁻¹ in N₂ atmosphere. This technique allows to measure the amounts of CO₂ bound as calcium carbonate, H₂O forming



Fig. 1 Prismatic specimens exposed inside



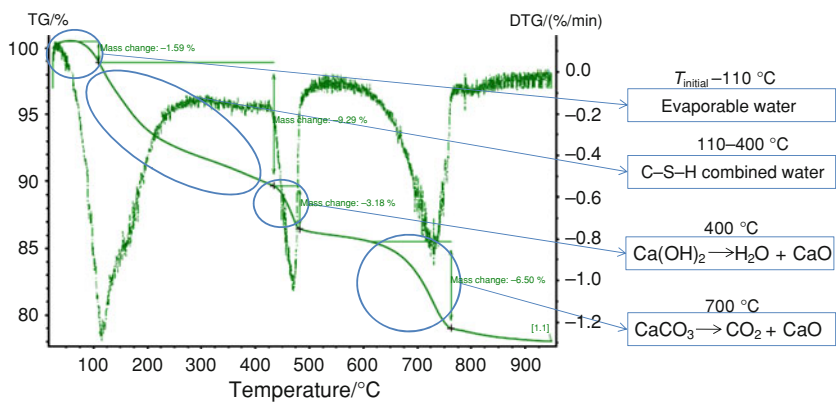
Fig. 2 Prismatic specimens placed outside sheltered from the rain

Table 1 Cements used for the tests

Nr.	Cement	Clinker/ %	Additions	CaO/ %
1	CEM I 42.5R	95–100	–	63.83
2	CEM II/A-P 42.5R	80–94	Pozzolan	52.64
3	CEM II/A-V 42.5R	80–94	Fly ash	56.31
4	CEM II/A-M 42.5R	80–94	Limestone, fly ash	57.15
5	CEM II/B-P 32.5N	65–79	Pozzolan	49.23
6	CEM II/B-V 32.5R	65–79	Fly ash	48.58
7	CEM II/B-M 42.5N	65–79	GGBS, fly ash	54.20
8	CEM II/B-LL 32.5N	65–79	Limestone	55.96

portlandite, evaporable and C–S–H gel water present in the samples (Fig. 3). There are several methods to calculate these quantities based on the thermal analysis data; some authors consider fixed temperature ranges [7, 18], while others base their calculations on the slopes of the graphs in the regions of interest [19]. In the present case, the evaporable water is taken as the water lost up to 110 °C. Although C–S–H gel decompose from 110 to 1,000 °C, the most significant weight loss occurs between 110 and the beginning of portlandite decomposition. For the sake of simplicity and standardization of results, in this article, only the water lost from 110 to the beginning of portlandite decomposition, around 400 °C, is calculated and named “C–S–H combined water”. Nevertheless, it is important to emphasize that this water does not comprise the total amount of C–S–H water: the authors consider that the differences are within the range of the TG technique accuracy. The same explanation applies for the calculation of the amounts of portlandite and calcium carbonate. As these quantities may be over-estimated by the amount of C–S–H water decomposing in the corresponding

Fig. 3 TG and DTG graphs of a cement paste with the main decompositions depicted: evaporable water, C–S–H gel water, portlandite, and calcium carbonate



temperature intervals, the differences between the “correct” values and the overestimated ones are also within the range of the technique’s accuracy.

To normalize values, the results of this technique are expressed per grams of ignited mass, i.e., calcined cement at 1,000 °C.

Results and discussion

Evolution of combined CO₂ in the samples

Graphs in Fig. 4 represent the CO₂ values measured in the specimens fabricated with cements numbered from 1 to 4, respectively, with both w/c ratios and exposed outside sheltered from the rain and inside for 4 years. In addition to the values measured at the times of test, 28 and 90 days, 1 and 4 years, the initial CO₂ in the cements is included, i.e., at time zero. All the percentages are referred to ignited

cement weight. The CO₂ data as a function of time can be fitted in all the cases studied to exponential functions like equation (1).

$$y = y_0 + A \cdot e^{-x/\tau} \tag{1}$$

where y_0 is the maximum value, A is the amplitude, i.e., the difference between the initial value and the maximum, and τ is the time constant equal to the time needed to reach 63.2 % of the maximum value. The fittings to exponential functions are also depicted in the figures. The values obtained for each fitting are in Table 2.

The maximum values of CO₂ combination reached by the specimens, i.e., A absolute values, vary inside between 18 and 21 % and outside sheltered from the rain between 28 and 30 %, these values being very similar in all four groups of specimens. Outside the specimens with higher w/c combine slightly more CO₂; inside, on the contrary, the specimens with the lowest w/c are the ones that combine more. This behavior is followed in all cases except in the

Fig. 4 CO₂ in specimens fabricated with cements numbered 1–4 in Table 1

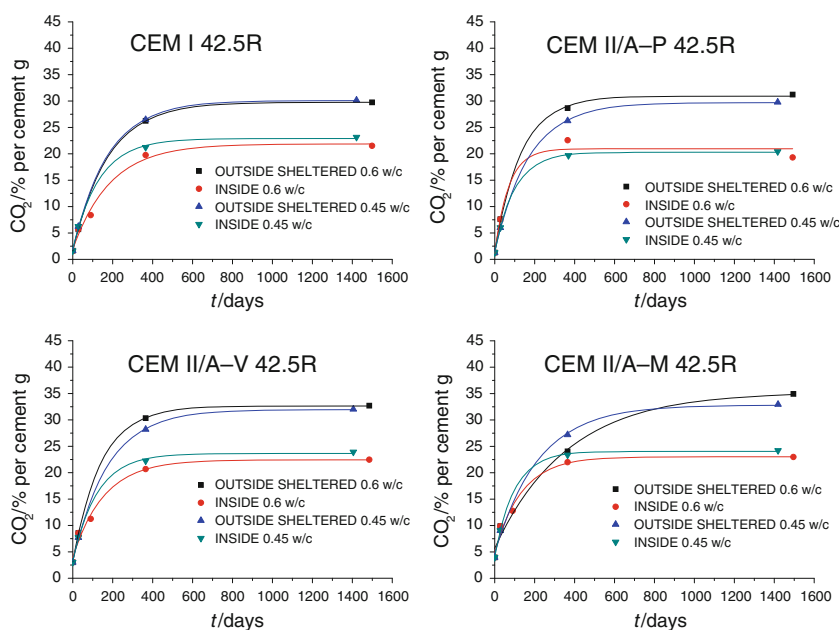


Table 2 Coefficients of the exponential fittings cements 1–4

	$y_0/\%CO_2$	$A/\%CO_2$	τ/days	R^2
CEM I 42.5R				
w/c 0.6				
Outside	30	-28	176	1.0000
Inside	22	-20	188	0.9901
w/c 0.45				
Outside	30	-28	175	0.9998
Inside	23	-21	132	0.9990
CEM II/A-P 42.5R				
w/c 0.6				
Outside	31	-29	132	0.9992
Inside	21	-20	69	0.9808
w/c 0.45				
Outside	30	-28	170	0.9998
Inside	20	-19	100	0.9998
CEM II/A-V 42.5R				
w/c 0.6				
Outside	33	-30	141	1.0000
Inside	22	-19	156	0.9853
w/c 0.45				
Outside	32	-29	176	0.9998
Inside	24	-20	122	0.9989
CEM II/A-M 42.5R				
w/c 0.6				
Outside	35	-30	363	0.9878
Inside	23	-18	135	0.9837
w/c 0.45				
Outside	33	-28	218	0.9973
Inside	24	-20	99	0.9998

specimens fabricated with pozzolan cement exposed inside. The explanation for this fact resides on the porosity of the samples, which is influenced among others by the w/c, and which plays a key role in the carbonation phenomenon. On one hand, the higher porosity due to the higher w/c favors diffusion and gives rise to greater specific surface for the reaction, but on the other hand it produces less amount of carbonatable material per volume.

In the specimens considered, the porosity, measured by Mercury Intrusion Porosimetry at the age of 28 days, varied in the 0.45 w/c samples between 25 and 37 % (in volume) and in the 0.6 w/c ones between 32 and 42 %, being in most cases higher in the specimens with higher w/c.

According to the results, although the porosity is lower in specimens with lower w/c, inside, with RH lower than 40 %, the higher amount of carbonatable material gives rise to higher CO₂ combination. At RH around 60 %, higher porosity leads to higher CO₂ binding.

The values of τ , related to the combination rate, are in most cases close to the range 100–200 days. In the 16 cases studied, there are only 3 exceptions: specimens with composite additions exposed outside (219 and 363 days for the 0.45 and 0.6 w/c specimens, respectively) and the 0.6 w/c pozzolan specimen exposed inside (69 days). In the 0.45 w/c specimens, the rate is higher inside than outside, i.e., $\tau_{\text{out}} > \tau_{\text{in}}$, which does not mean that there is more CO₂ combined inside, but that the maximum is reached before in this environment. In specimens with 0.6 w/c, this behavior is only followed in half of the cases.

According to the data obtained after 2 years most specimens would have reached their maximum.

In Fig. 5, the corresponding data of specimens fabricated with cements numbered from 5 to 8 are represented, as well as the fittings to the exponential function (1). The fitting parameters are given in Table 3.

The maximum combination in specimens with 21–35 % additions varies considerably depending on the type of cement, the results are not as homogeneous as in the specimens with less than 20 % additions. The cement with 21–35 % additions that gives higher percentages of CO₂ bound is the one fabricated with a mixture of GGBS and limestone, CEM II/B-M 42.5N. In this specimen, the values obtained are similar to the ones in the specimens with 6–20 % additions: between 26 and 30 % outside and around 18 % inside. In specimens fabricated with 21–35 % limestone and fly ash, the maximum values reached are very similar: 25–26 % outside and 16–19 % inside. Finally, the specimens with pozzolan are the ones that combine less in both environments: 13–16 % inside and 23 % outside.

Regarding τ values, they are between 50 and 231, in most cases lower than in the specimens with 6–20 % additions. Like in these latter specimens, in the ones with 21–35 % additions and 0.45 w/c, $\tau_{\text{out}} > \tau_{\text{in}}$, indicating higher rates of combination inside. In the 0.6 w/c specimens, the opposite happens, with the rates being higher outside.

The amounts of CO₂ bound and the rates of binding depend clearly on the environment. The exposure conditions determine the humidity inside the concrete pores, which is a crucial parameter in diffusion, dissolution and reaction of CO₂ and the hydrated phases of cement. Outside, with 58 % average RH the reaction is favored, while the lower humidity inside, 38 %, makes the process more difficult.

As has been shown, the influence of the w/c ratio is also related to the environment. The same explanation given for specimens with 0–20 % additions applies for the ones with 21–35 %: outside the specimens with higher w/c combine more CO₂, and inside the behavior is opposite. This behavior does not apply to pozzolan specimens, which may

Fig. 5 CO₂ in specimens fabricated with cements numbered 5–8 in Table 1

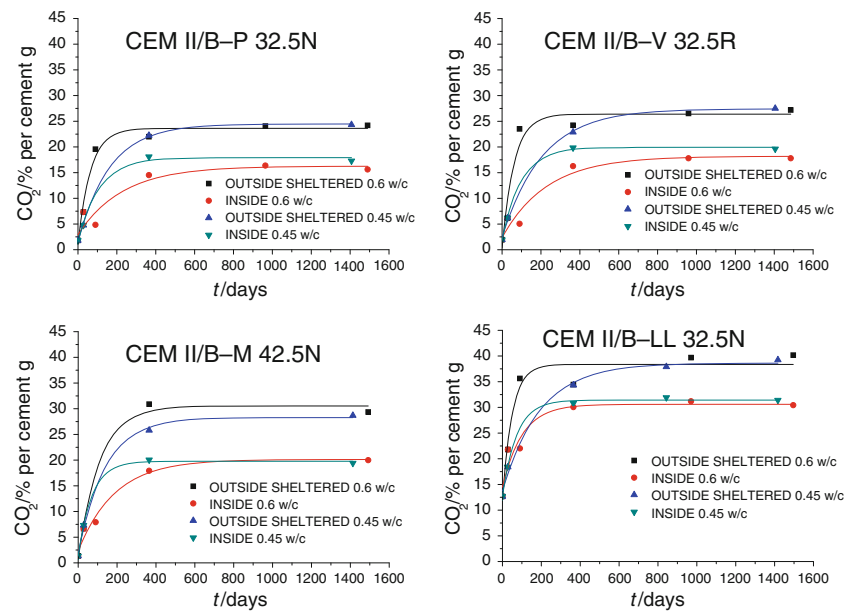


Table 3 Coefficients of the exponential fittings cements 5–8

	$y_0/\%CO_2$	$A/\%CO_2$	τ/days	R^2
CEM II/B-P 32.5N				
w/c 0.6				
Outside	24	-23	64	0.9810
Inside	16	-13	230	0.9137
w/c 0.45				
Outside	24	-23	163	0.9993
Inside	18	-16	109	0.9940
CEM II/B-V 32.5R				
w/c 0.6				
Outside	26	-26	62	0.9498
Inside	18	-16	231	0.9544
w/c 0.45				
Outside	27	-25	207	0.9986
Inside	20	-18	98	0.9990
CEM II/B-M 42.5N				
w/c 0.6				
Outside	31	-30	109	0.9937
Inside	20	-18	188	0.9759
w/c 0.45				
Outside	28	-26	139	0.9979
Inside	20	-18	71	0.9989
CEM II/B-LL 32.5N				
w/c 0.6				
Outside	38	-26	50	0.9582
Inside	31	-16	101	0.8787
w/c 0.45				
Outside	39	-25	194	0.9938
Inside	31	-19	79	0.9972

be related to the formation of the carbonatable material, as shown in next section.

The exponential function (1) and its parameters describe the combination of CO₂ as a finite process, i.e., after a certain time, the maximum is reached. As the carbonatable material is finite, this equation suits better than the “square root of time equation” used often for describing the evolution of the pH change front as an infinite process. In [20], finite functions were also proposed for in situ-accelerated carbonation monitored by neutron diffraction: exponential decay functions for the carbonating phases and Boltzmann function, sigmoidal shape, for the calcite formation.

Portlandite, evaporable and C–S–H gel water at 28 days

In Figs. 6, 7, 8, the amounts of portlandite, evaporable and C–S–H gel water in the samples at 28 days are represented. The amounts of portlandite (Fig. 6) formed in the specimens without additions, around 13 %, are slightly higher than in the ones with 6–20 % additions, between 10 and 12 %. The lowest amounts correspond to the specimens with 21–35 % additions, between 8 and 11 %. Within this group, the specimens with less portlandite are the ones with pozzolan, not reaching 9 %, and the ones with fly ash, between 9 and 10 %. The specimens with mixed additions, both the ones with 6–20 % (A–M) and the ones with 21–35 % (B–M) form almost the same amount of portlandite; it is important to note that although both contain fly ash, the amounts may vary as the ones with 6–20 % additions contain limestone and the ones with 21–35 %, GGBS.

With regard to the w/c ratio, in almost all cases, the specimens with 0.45 w/c form more portlandite than the

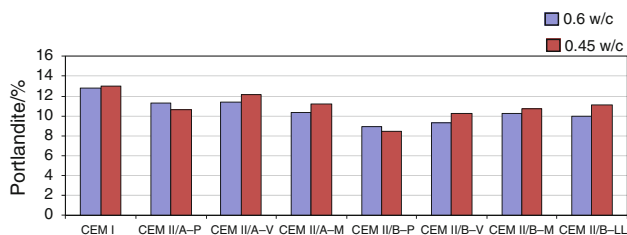


Fig. 6 Portlandite amounts at 28 days

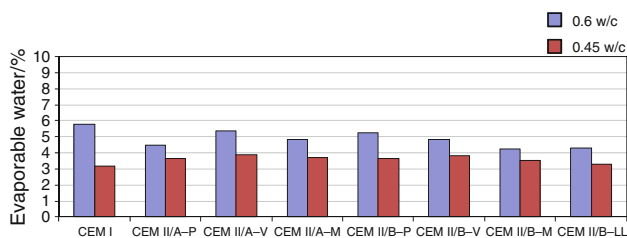


Fig. 7 Evaporable water amounts at 28 days

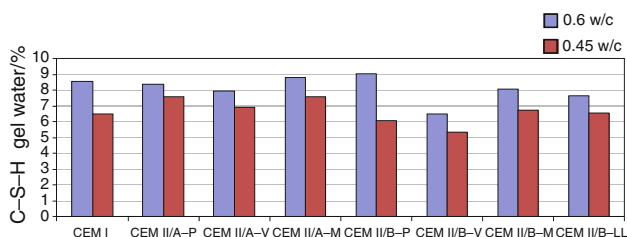


Fig. 8 C-S-H gel water amounts at 28 days

ones with 0.6, occurring the opposite in specimens with pozzolan; the amount of portlandite appears to be more important than the w/c with regard to the CO₂ combination in the two environmental conditions considered.

Both the evaporable (Fig. 7) and the C-S-H gel water (Fig. 8) are higher in the specimens with higher w/c. In the 0.6 w/c specimens, the evaporable water varies between 4 and 6 % and the gel water between 7 and 9 % in most cases. In the 0.45 w/c, specimens the amounts are 3–4 and 6–8 %, respectively. Only the specimens with 21–35 % fly ash present lower amounts of gel water.

It is important to notice that the amounts of evaporable water measured by TG are not as accurate as the amounts of the other compounds measured at higher temperatures. As the analyses are performed with powder, there is a direct effect of the environmental humidity on this “evaporable” or not bound water in the samples. Nevertheless its measurement allows the comparison between different samples and gives an approximate idea of the amounts and their evolution.

From the data in Figs. 6, 7, 8, it can be concluded that higher w/c gives rise to higher hydration of the gel and

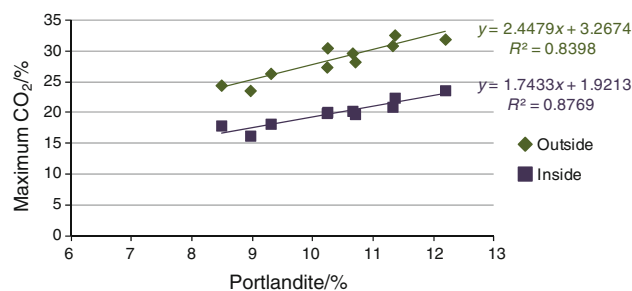


Fig. 9 Maximum CO₂ versus portlandite at 28 days in specimens type II cement without limestone

higher evaporable water, but in general to lower formation of portlandite.

With regard to the relationship between CO₂ combination and portlandite formation, Fig. 9 represents the values of the maximum CO₂, i.e., y₀, and the portlandite amounts at 28 days in specimens fabricated with cement type II without limestone addition.

As can be seen, there is a clear linear relationship between both quantities: as the amount of portlandite formed during hydration increases, so does the amount of CO₂ that can be combined during carbonation. The specimens with percentages of limestone higher than 5 % do not follow this trend because the maximum CO₂ in these cases also includes the corresponding to the additions. The specimens without additions do not follow it either, presenting higher amounts of portlandite than the rest, but similar amounts of maximum CO₂ as the II/A type cements.

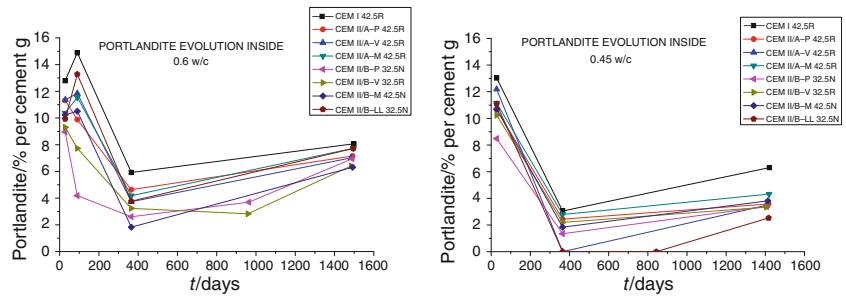
Although the C-S-H gel also carbonates decalcifying [21], there is no apparent relationship between the gel water at 28 days and the CO₂ combination. The evaporable water at 28 days does not give any information either about the maximum amounts of CO₂ that can be combined.

Evolution of portlandite, evaporable and C-S-H gel water in the samples

After 1 year of exposure, the specimens placed outside do not have anymore portlandite, all has been consumed to form calcium carbonate. In the following years, no new portlandite is formed in these specimens. In the ones placed inside, however, although it diminishes with respect to the initial amount, in all cases there is portlandite left after 4 years. In Fig. 10, the evolution of portlandite in the specimens with 0.6 and 0.45 w/c, respectively, is represented.

In some 0.6 w/c specimens, a little increase between 28 and 90 days is observed, followed by a considerable decrease at 1 year. From that time until the fourth year, the amounts increase in all cases. In the 0.45 specimens, there is a similar behavior, reaching zero in some cases after

Fig. 10 Portlandite in 0.6 and 0.45 w/c specimens inside



1 year and increasing after in the period between 1 and 4 years.

Relating these results with the ones of CO₂ combined in the specimens placed inside it can be concluded that while the CO₂ increases, the amounts of portlandite decreases. Once the CO₂ is stabilized and stops the combination, the amounts of portlandite increase again. This new formation of portlandite in the inner specimens could give rise in the future, if the humidity conditions are optimal, to new calcium carbonate formation. Outside no portlandite is formed after 28 days which may indicate it will not form in the future.

The evolution of the C–S–H gel water in both environments (Fig. 11) is similar to the one of portlandite inside. It shows a decrease in the first year and an ulterior increase in the following 3 years. For the formation of hydrated phases, apart from an adequate humidity, it is necessary that there is some anhydrous or “hydratable” material left. As the specimens were cured for only 2 days, it is reasonable to expect that there is still non-hydrated material in them. The environmental conditions do not

seem to affect this process of re-hydration as the behaviors inside and outside are very similar.

As for the evolution of the evaporable water (Fig. 12), it decreases in all samples to almost the same value, around 1 %, i.e., neither the cement type nor the environment or the w/c ratio have a deep effect in its reduction with time. As noted before, the values of evaporable water measured by TG should be taken carefully because the samples are ground to powder before testing which may interfere with the evaporable water equilibrium with the atmosphere.

Mass balance

The mean calcium/silicon (Ca/Si) ratio of the C–S–H gel in plain Portland cement pastes is about 1.7–1.8 [21–23]. In composite cement pastes, this ratio decreases as a function of the type and amount of mineral additions present in the cement mix. For the following calculations, and based on the values published in the literature [21–23], 1.8 will be considered for cement without additions (Nr. 1) and with limestone addition (Nr. 8); 1.7 for cements with 6–20 %

Fig. 11 Gel water in 0.6 and 0.45 w/c specimens outside and inside

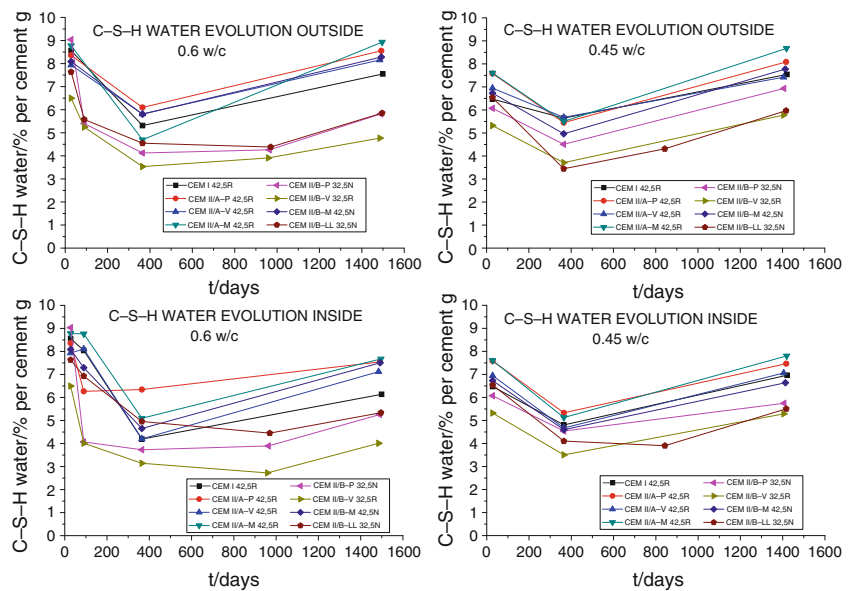
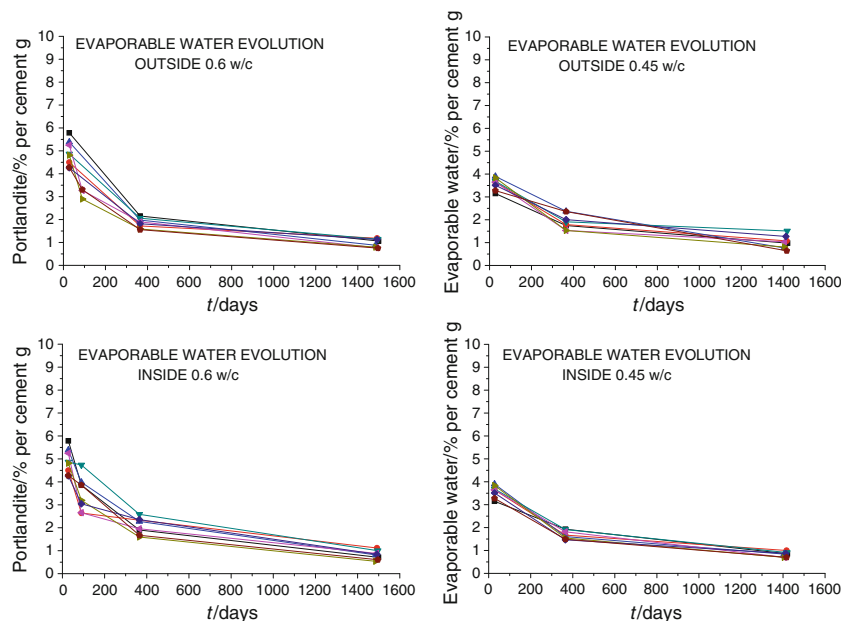
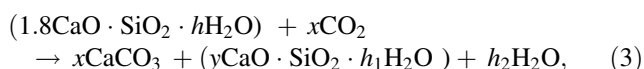
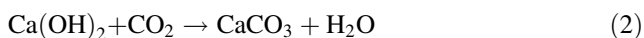


Fig. 12 Evaporable water in 0.6 and 0.45 w/c specimens outside and inside



additions (Nr. 2–4); and 1.6 for cements with 21–35 % additions (Nr. 5–7). Limestone additions, although partly reactive [21, 24], do not have pozzolanic or hydraulic properties, which means they do not form C–S–H gel with lower Ca/Si ratio than portland cement as the other additions do. This is the reason why 1.8 was also chosen for cement Nr. 8.

Using the obtained values of CaCO_3 , $\text{Ca}(\text{OH})_2$, and C–S–H water, and considering the carbonation reactions of portlandite (2) and C–S–H (3)



it is possible to estimate the Ca/Si ratio in the C–S–H after 1 year of exposure (y) and also the water molar proportion in the gel (h and h_1).

First of all, subtracting the amounts of CaO corresponding to initial CaCO_3 and $\text{Ca}(\text{OH})_2$ from the total CaO content in the cement, the amounts of CaO corresponding to the initial C–S–H gel are obtained. Subtracting then the amount of CaO of the CaCO_3 formed after 1 year and of the $\text{Ca}(\text{OH})_2$ left, the corresponding CaO of the final C–S–H gel is calculated. With these amounts and the initial molar relation, the final Ca/Si can be deduced.

For these calculations, only the main phases involved are taken into account, i.e., minor phases, such as hydrated aluminates and sulfo-aluminates, which decompose in the same temperature range as the C–S–H gel water and which interact as well with the CO_2 , are not considered.

Figure 13 represents the values of the CaO stoichiometric coefficient in the C–S–H after 1 year, y . The numbers

correspond to the cements indicated in Table 1. The value of the CO_2 and CaCO_3 stoichiometric coefficient, x , is equal to the initial CaO stoichiometric coefficient, between 1.8 and 1.6, and the final one, y . As can be observed, the Ca/Si lowering is more important in the specimens placed outside, reaching values between 0.6 and 1.2, than in the ones exposed inside, between 1.0 and 1.4. This fact seems logical considering the differences in the CO_2 combination in the two atmospheres, i.e., the carbonation of the gel inside is less severe than outside. Comparing the w/c ratios, the Ca/Si values are very similar the only difference being the greater homogeneity in the data of 0.45 w/c specimens.

The values obtained for Ca/Si ratios for specimens prepared with cement Nr. 1, around 1.2, agree with the ones published by Castellote et al. [25] for paste specimens fabricated with cement without additions, 0.5 w/c, and exposed inside for 8 months. In this case, the Ca/Si ratio was calculated using the results obtained by ^{29}Si magic angle spinning-nuclear magnetic resonance (M.A.S.-

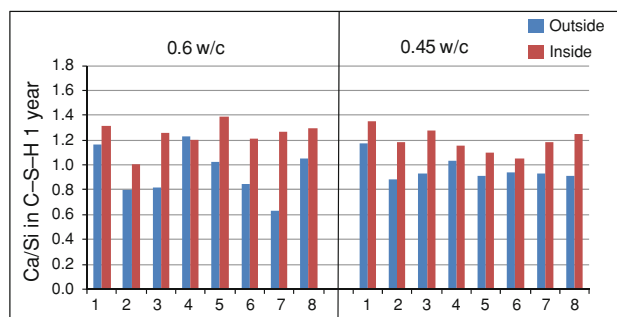


Fig. 13 Ca/Si molar relationship in C–S–H after 1 year

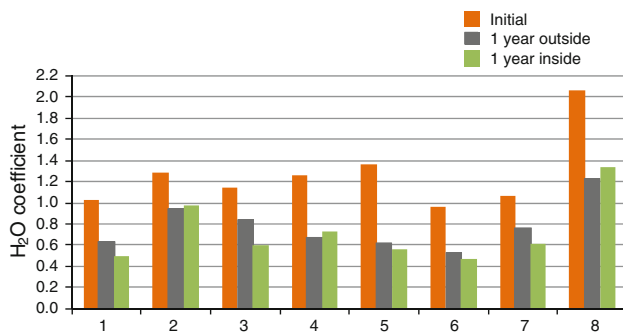


Fig. 14 Stoichiometric coefficients of the C–S–H water in 0.6 w/c specimens

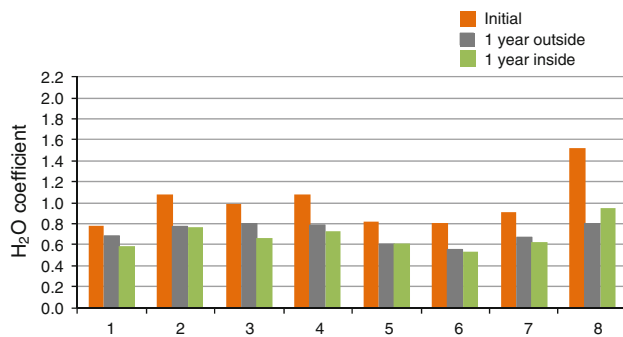


Fig. 15 Stoichiometric coefficients of the C–S–H water in 0.45 w/c specimens

N.M.R.). This fact may be a proof of validation of the mass balance and the calculation procedure presented here.

From the initial amounts of CaO and H₂O in the gel, the h coefficient for the water can be calculated. h_1 and h_2 are obtained using the initial amounts of C–S–H water and the ones after 1 year. In Figs. 14 and 15, the stoichiometric coefficients of the C–S–H water in the samples with 0.6 and 0.45 w/c respectively, are represented. The initial value corresponds to h and the final to h_1 . As can be deduced from the general reaction, h_2 is equal to h minus h_1 .

First of all, it can be noticed that the initial molar proportion CaO/H₂O is much higher in the samples with 0.45 w/c than in the ones with 0.6. As was deduced from Fig. 8, higher w/c leads to greater hydration of the gel. The H₂O coefficients after 1 year are similar for both w/c, which means the differences between initial and final values are more pronounced in 0.6 w/c specimens. There is not a clear relationship between the H₂O molar reduction and the environment. Comparing the cements, it can be observed that the gel formed from cement with limestone, Nr. 8, is the one that reached the greatest hydration of the gel.

The values obtained for the initial C–S–H water stoichiometric coefficient are lower than the ones published in [23], measured by small angle X-ray and neutron scattering, around 1.8. This may be attributed to the different time

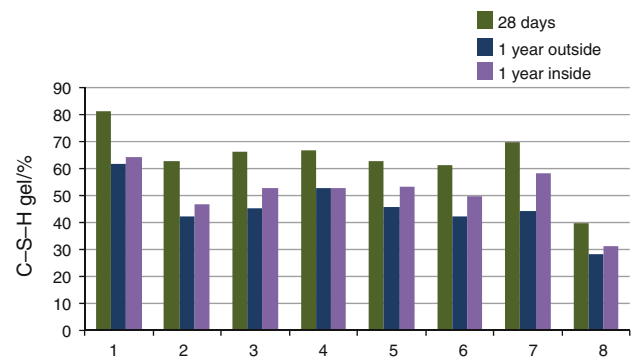


Fig. 16 C–S–H gel amounts in 0.6 w/c specimens

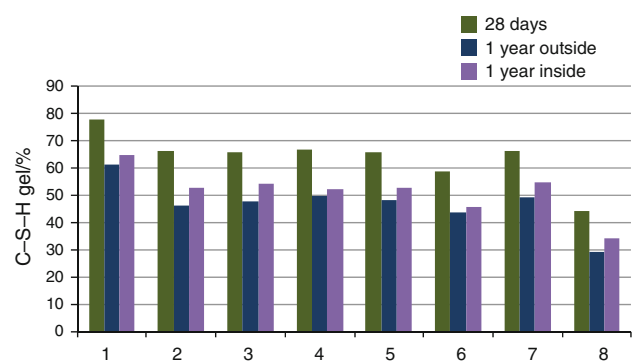


Fig. 17 C–S–H gel amounts in 0.45 w/c specimens

of curing: 2 days for our specimens and 28 days for the ones used in [23].

Relating the values in these graphs (Figs. 14, 15) with the ones in Fig. 13, it can be deduced that the CaO/H₂O in the C–S–H gel is not maintained after 1 year of carbonation: in samples exposed outside, the molar relationship decreases in most cases, while in the ones inside, it increases. This result is related to the higher carbonation degree and subsequent decalcification of the gel in the samples exposed outside compared to the ones inside.

Finally, from the amounts of CaO and H₂O obtained and the stoichiometric coefficients, the total amount of C–S–H gel in the specimens can be calculated (Figs. 16, 17).

Relating the values in Figs. 16 and 17 with the ones in Fig. 8, it can be noticed that, although the specimens with higher w/c ratio combine more water in the gel, the amounts of gel formed are not always greater in these specimens. In fact, in specimens fabricated with cements with pozzolan (Nr. 2 and 5) and limestone (Nr. 8), the opposite occurs: 0.45 w/c specimens form more gel than the ones with 0.6 w/c. In all the cases, the water/gel ratio is lower in specimens with 0.45 w/c.

The amounts of gel left after 1 year are in most cases between 40 and 50 %. As was said before, the carbonation inside is less severe than outside; as a consequence of this,

the amounts of gel left inside are in all cases greater than outside. The two exceptions are cements Nr. 1 and 8. The first one form 80 % gel. This can be explained as this cement does not contain additions. Pure portland cement forms more hydrated phases than any pozzolanic or hydraulic additions, hydration of which is controlled by their reactivity and pozzolanic activity, among others. The second case, cement with limestone addition, form 40 % gel. As was said before, limestone additions do not have pozzolanic or hydraulic properties, i.e., it does not form C–S–H gel. As was shown in Figs. 14 and 15, this cement is the one that leads to the highest stoichiometric coefficient for the water in the gel. This cement, with the lowest percentage of hydratable material, is the one that less gel formed, but the one that hydrated it most.

Conclusions

The conclusions drawn from the investigation are as follows:

- The evolution of the CO₂ binding in cement pastes exposed to natural carbonation can be fitted to exponential functions $y = y_0 + A \cdot \exp(-x/\tau)$. The maximum values reached and the rates vary depending on the exposure atmosphere, which determines the humidity inside the material: outside, sheltered from the rain, 30 % of CO₂ per grams of ignited cement can be combined; inside, the maximum absorption is 20 %.
- The influence of the w/c ratio in the combination of CO₂ is conditioned by the environmental humidity: in atmospheres with average RH <40 %, the specimens with lower w/c combine more CO₂; in atmospheres with average RH near 60 %, higher w/c ratio leads to higher absorption.
- In specimens fabricated with type II cements without limestone additions, the maximum CO₂ bound is linearly related to the amounts of portlandite formed at 28 days. No relationship has been found between evaporable and C–S–H water at 28 days and the CO₂ combination.
- Outside sheltered from the rain, all portlandite is consumed after 1 year of exposure. In the specimens exposed inside, there is a decrease in the portlandite amounts during the first year, followed by an increase in next 3 years. After 4 years, the specimens exposed inside combine less CO₂ and do not consume all portlandite.
- The values obtained for the Ca/Si ratio in the gel after 1 year in specimens fabricated with cement without additions, around 1.2, agree with the ones in [25] measured by N.M.R., validating the mass balance calculation. The more pronounced decreases in the Ca/Si ratio of the gel and the reduction of the CaO/H₂O ratio evidence the higher severity of the gel carbonation in the samples exposed outside.
- Higher w/c ratio leads to greater hydration of the gel, but not always to greater amount of gel. The ratio between water in the gel and total amount of gel is in all cases lower in specimens with 0.45 w/c. After 1 year, the amounts of gel lower from 60–70 to 40–50 % in most cases.
- The cement with limestone addition, with the lowest amount of hydratable material, is the one that forms less gel but the one having the highest molar ratio of H₂O/CaO in the gel.

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