CO$_2$ Sink Effect of Concrete Carbonation

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ABSTRACT

Although carbonation of cement phases is well known, the amount of carbon dioxide combined during the process has been much less investigated. Related to the greenhouse effect much more attention is being paid to the sinks for CO$_2$ in order to correctly compute the gases emission during production of materials. In the case of cement a strict calculation should discount the CO$_2$ emitted from that fixed by the concrete. This is the aim of present work which is a study of the cement based materials ability to combine CO$_2$. Using Thermogravimetry and Differential Thermal Analysis as well as phenolphthalein indicator, quantities of CO$_2$ combined and carbonation depth in several cement pastes and concretes exposed to different environments have been measured. A calculation to estimate the contribution of cement based materials carbonation to the partial re-absorption of the CO2 emitted in cement production is proposed.

INTRODUCTION

One of the main problems related to climate change is the greenhouse effect produced by the partial absorption of infrared radiation emitted by the Earth from the so called 'greenhouse gases', including carbon dioxide. The work proposed here is part of the initiatives undertaken by the cement industry to help to reduce the greenhouse effect and the studies conducted to estimate the contribution of cement based materials in the fighting against climate change. For this purpose, the extent of the CO$_2$ sink effect of concrete carbonation is studied. The United Nations Framework Convention on Climate Change defines sink as "any process, activity or mechanism which removes a greenhouse gas, an aerosol or a precursor of a greenhouse gas from the atmosphere".

Carbonation of concrete occurs when the CO_2 from the atmosphere reacts with alkaline components of the concrete, resulting in the formation of $CaCO_3$. This reaction leads to a decrease in pH of the aqueous phase of the concrete pores, from very alkaline values greater than 12 to values below 8. If the reaction reaches the steel reinforcement, its passive layer may disappear, exposing the steel surface to corrosion.

Considering corrosion and pH lowering, the Spanish Instruction for Structural Concrete, EHE, establishes minimum requirements for cover thicknesses of reinforcement based on the aggressiveness of the environment where the element will be placed, on the cement type, on the concrete characteristic strength and on the service life of the element, ensuring that if it is strictly fulfilled, the reinforcement will not be reached by the carbonation front within the service life time of the element considered.

The main objective of this study is to estimate the quantity of CO_2 that is reabsorbed into the cementitious materials due to the carbonation phenomenon, taking into account the composition of the cements, the environments in which the materials are exposed, the type of concrete and the time.

EXPERIMENTAL

The work developed for this study consisted on experiments and calculations to determine the quantity of CO_2 absorbed per gram of cement in specimens fabricated for the study, as well as in old samples. In order to supplement the data of the study, an exhaustive review of published work related to the measure of the amount of CO_2 combined or $CaCO_3$ formed in materials made of cement has been conducted.

Specimens. Cements. Exposure environments

For the manufacture of the specimens 15 types of cement produced in Spain have been used. Their names, additions, producer and geographical origin are given in Table 1. With each type of cement 10mmx10mmx60mm prismatic paste specimens and 75mmx150mm cylindrical concrete specimens were produced.

Table 1. Cements Selected for the Tests

Ref.	Cement	Clinker %	Additions	Producer	Origin
1	CEM I 42,5R	95-100	No additions	Lafarge-Asland	Toledo
2	I 42,5R/ SR	95-100	No additions	Uniland	Barcelona
14	CEM II/A-L 42,5R	80-94	Limestone	Cosmos	Huelva
3	CEM II/B-LL 32,5N	65-79	Limestone	Cemex	Alicante
4	CEM II/A-M (V-L) 42,5R	80-94	Fly ash, Limestone	Portland-Valderrivas	Madrid
5	CEM II/B-M (S-V) 42,5N	65-79	GBFS, Fly ash	Holcim	Almería
6	CEM II/A-P 42,5R	80-94	Pozzolan	CEISA	Las Palmas
7	CEM II/B-P 32,5N	65-79	Pozzolan	Cemex	Toledo
9	CEM II/A-V 42,5R	80-94	Fly ash	Lemona	Vizcaya
10	CEM II/B-V 32,5R	65-79	Fly ash	Cosmos	Córdoba
13	CEM IV/B (V) 32,5N	45-64	Fly ash	Alfa	Santander

8	CEM II/A-S 52,5N	80-94	GBFS	Tudela Veguín	León
15	III/A 42,5N/SR	35-64	GBFS	Tudela Veguín	Oviedo
11	III/B 32,5N/SR	20-34	GBFS	Alfa	Santander
12	III/C 32,5N/SR/BC	5-19	GBFS	Cemex	Tarragona

Two water/cement (w/c) ratios were used for the mixtures: 0.6 and 0.45. For the specimens with w/c 0.6 cements numbered 1-12 were used, for the ones with w/c 0.45 all 15 were used. The mix proportions for the concretes are in Table 2.

Table 2. Concrete Mixes

Mix A: building works		Mix B: civil works	
Cement	300 kg	Cement	400 kg
Gravel 6-12 mm	1144 kg	Gravel 6-16 mm	949 kg
Sand 0-2 mm	820 kg	Sand 0-2,5 mm	297 kg
Water	180 kg	Sand 0-5 mm	614 kg
w/c	0,6	Water	180 kg
		w/c	0,45

Mix A is considered representative of concrete used for building works, and mix B for civil works. In the mixing of B concretes a fluidifying additive was used in order to obtain acceptable consistencies.

In order to reproduce the most possible real conditions, the curing period of the specimens was set at 48 hours, 24 before demolding and 24 once demolded. Paste and concrete specimens were subjected to three different environmental conditions: outside not sheltered from rain, outside sheltered from rain, and inside. The three environmental conditions were located in Madrid.

In addition to the specimens manufactured specifically for the study, samples from old structures and specimens were taken and analyzed in order to evaluate if time affects the amount of CO_2 reacted. As for the old specimens, three types of concrete specimens manufactured in 1991, 1999 and 2001 respectively, were selected. The specimens from 1991 were 7cmx7cmx28cm prisms fabricated with 395 cement kg per concrete m^3 and six different experimental mixes: two without additions, two with fly ash, one with silica fume, and one with both fly ash and silica fume. For all mixes plasticizers and superplasticizers were used. The specimens were kept outside sheltered from rain. The specimens from 1999 were 7,5cmx15cm cylinders fabricated with 400 cement kg per concrete m^3 and microsilica and fly ash additions as well as superfluidifier. These specimens were kept inside. The specimens from 2001 were made from a concrete used to build a house. A standard mix for building works was supposed for making the calculations, that is, 300kg/m^3 and 0,5 w/c ratio. The specimens were kept the first four years outside not sheltered from rain and the rest of the time sheltered from rain.

Two emblematic reinforced concrete structures designed by Eduardo Torroja were chosen for taking old samples: the roof of the Zarzuela Hippodrome, built in 1935, and a 'rib' built in 1951 in the gardens of the Eduardo Torroja Institute. To perform the calculations it was assumed in both cases a 0.5 w/c ratio and 300 kg of cement without additions per m^3 of concrete.

Characterization techniques

Samples of the fabricated specimens as well as samples taken from old specimens and structures were characterized by Thermogravimetry, TG, and Differential Thermal Analysis, DTA, tests. At the age of the test the depth of carbonation was measured by phenolphthalein coloration in all specimens. The characteristic parameters of environmental conditions, i.e. temperature, relative humidity, precipitation and CO_2 concentration were measured regularly both inside and outside.

RESULTS OF THE STUDY

Environmental conditions

The data of relative humidity (RH), temperature, precipitation and environmental CO_2 concentration measured in the test period of the specimens fabricated for the study are in the following ranges (Table 3):

Table 3. Environmental Conditions during Test Period

|	**Inside**	**Outside**
Temperature (ºC)	13-25	0-31
RH (%)	24-68	27-97
[CO_2] (ppm)	500-850	500
Daily precipitation (mm)		0-39.6

Carbonation depths and rates

In the paste specimens made for the study it was found a similar behaviour in the carbonation depth with respect to the exposure environment. In general, specimens that were outside sheltered from rain presented maximum depth after 1 year, appearing colourless all the area tested. Specimens inside also presented fully carbonated the cross section, but in this case with very soft pink colour, i.e., indicating that they have been carbonated, and that the pH has dropped below 12, but not below 8. Finally, in the specimens outside not sheltered from rain about half of them presented maximum depth colourless and the other half partial depth. These results were found in all paste specimens with 0.6 w/c ratio. For the ones with 0.45 w/c ratio there were a few exceptions: specimens with maximum carbonation depth in the three environments and specimens with partial penetration depth in the three environments.

In figures 1 and 2 the rates of carbonation for the concrete specimens with 0.6 and 0.45 w/c in the three exposure environments are represented. The carbonation rate was calculated with the formula $x = k \cdot t^{1/2}$. The specimens are grouped according to type of additions, with the reference numbers shown in Table 1.

These graphs clearly show a higher rate of carbonation in the concretes made with the mixes considered representative for building works than in the ones made with the mixes representative for civil works. In some cases the carbonation depth is double in the building type specimens than in the civil work ones.

In general, the specimens that were kept outside sheltered from rain are the ones with the highest carbonation rates, while the ones that were kept inside present the lowest rate. In this sense the 0.45 w/c specimens present a more homogenous behaviour than those with 0.6 w/c. It's interesting to emphasize the increase in depth with the percentage of addition within some of the groups of cement types; this effect is indicated by arrows in figures 1 and 2.

Concrete specimens 1 and 2 made with cement without additions show a very similar behaviour in the rate of carbonation in each of the environments, with both the 0.6 w/c and the 0.45. The fact that one cement is resistant to sulphate and the other is not, does not appear to have an effect on the rate of carbonation.
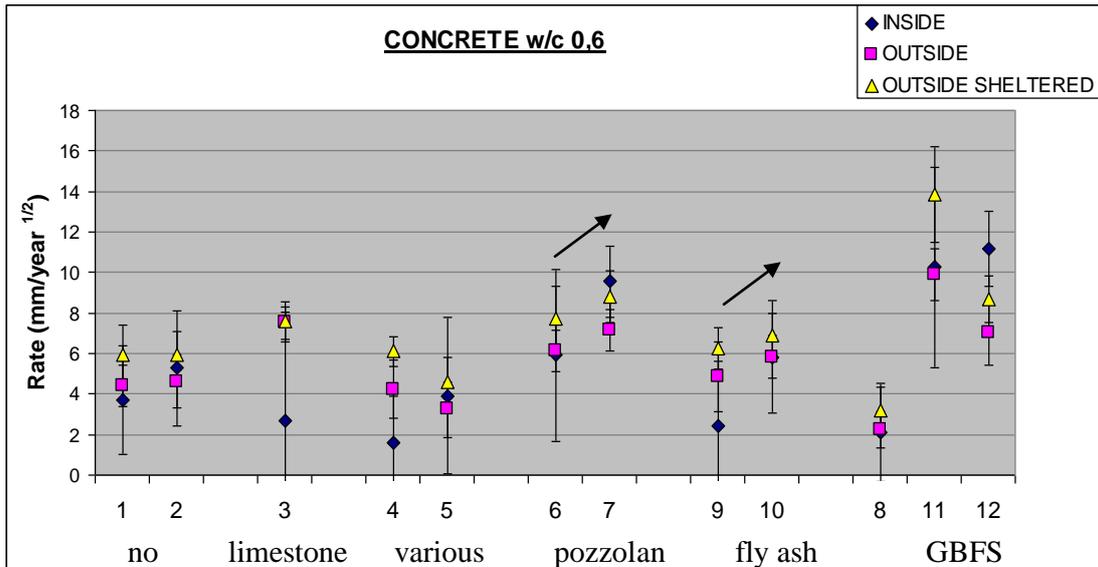

Fig. 1. Carbonation Rates of Concrete Specimens 0.6 w/c
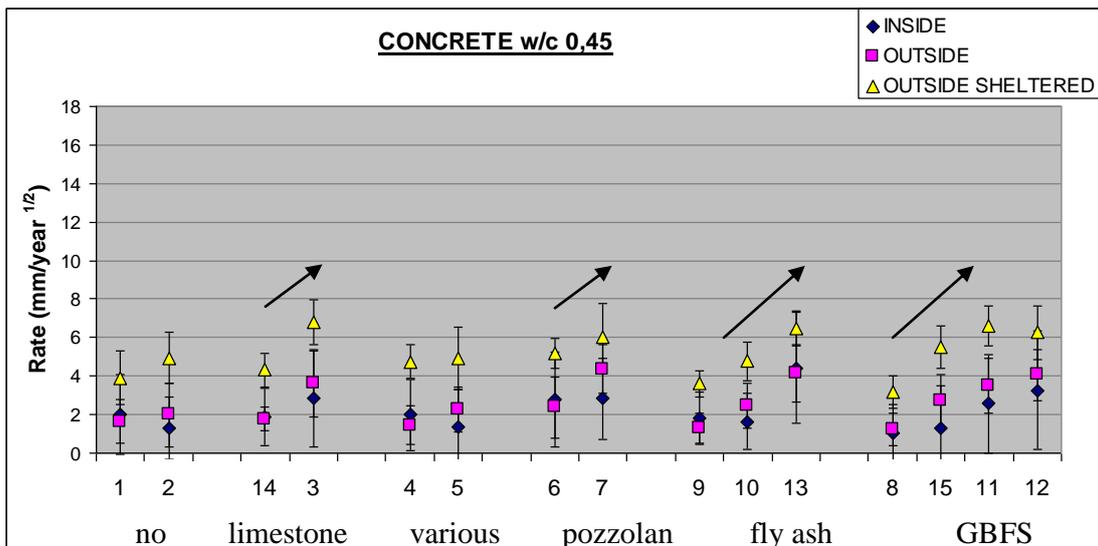
Fig. 2. Carbonation Rates of Concrete Specimens 0.45 w/c

The graph in figure 3 represents the carbonation rate of the old specimens. Most of them present a rate lower than 3 mm/year$^{1/2}$, not reaching four of the specimens made in 1991 the rate of 1 mm/year$^{1/2}$. The specimen fabricated in 1999 is the one which presents the higher rate, close to 5 mm/year$^{1/2}$.
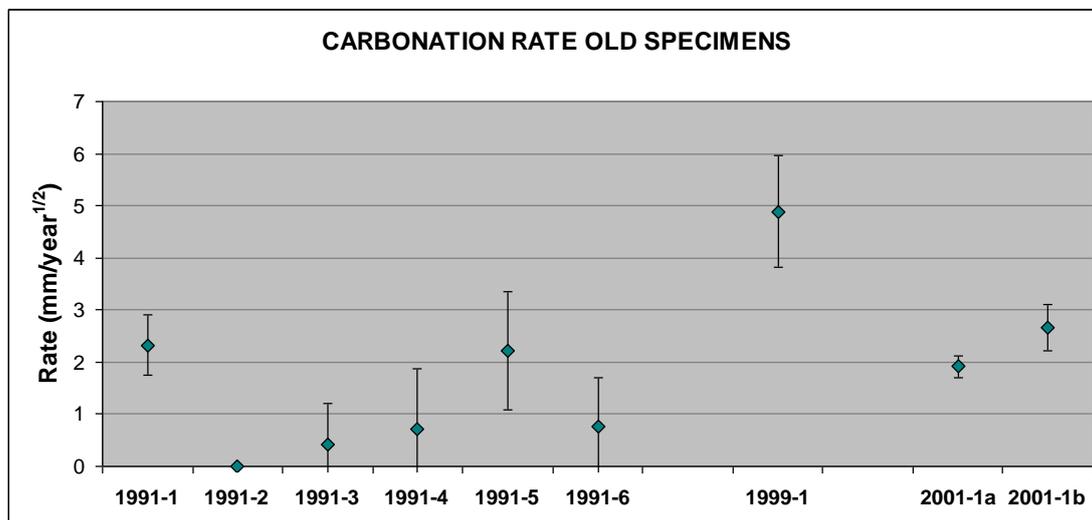

Fig. 3. Carbonation Rates of Old Specimens

Some of the authors that have studied the natural carbonation phenomenon from the point of view of calcium carbonate formation are Parrott, L. J. (1989), Parrott L. J. (1991/92) and Houst Y. F. (2002). These authors have also published the corresponding data of carbonation rates. As the environmental conditions and type of specimens are very different these data are not easily comparable but, in any case, it should be noticed that none of the rates published by theses authors exceeds 6.5 mm/year$^{1/2}$.

Quantities of combined CO_2

In graphs of figures 4 and 5 the percentages of CO_2 absorbed (per gram of cement) in 1 year in the pastes made with 0.6 and 0.45 w/c ratio respectively are represented.
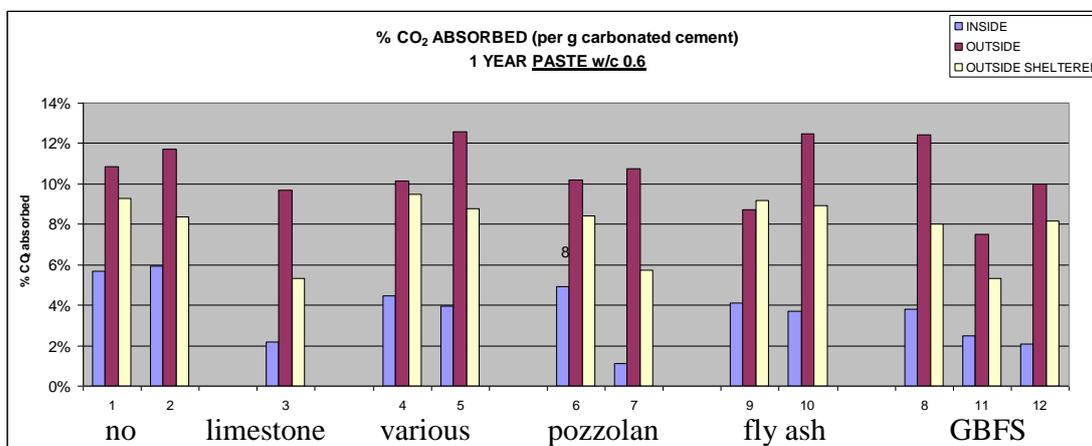
Fig. 4. CO$_2$ Quantities Absorbed in Paste Specimens 0.6 w/c

The behaviour of the 0.6 w/c specimens (Fig. 4) is very homogeneous with regard to the influence of the environment on the absorption capacity. It can be clearly observed that the specimens that absorb less CO$_2$ are those who remained in the laboratory, not reaching values higher than 6%. On the contrary, the ones that absorbed more are the ones that were outside not sheltered from the rain which reach values of absorption of 12 g of CO$_2$ per 100 grams of cement in the carbonated zone. The specimens that stayed the outside sheltered from rain absorb between 5 and 10% of CO$_2$ per gram of carbonated cement.
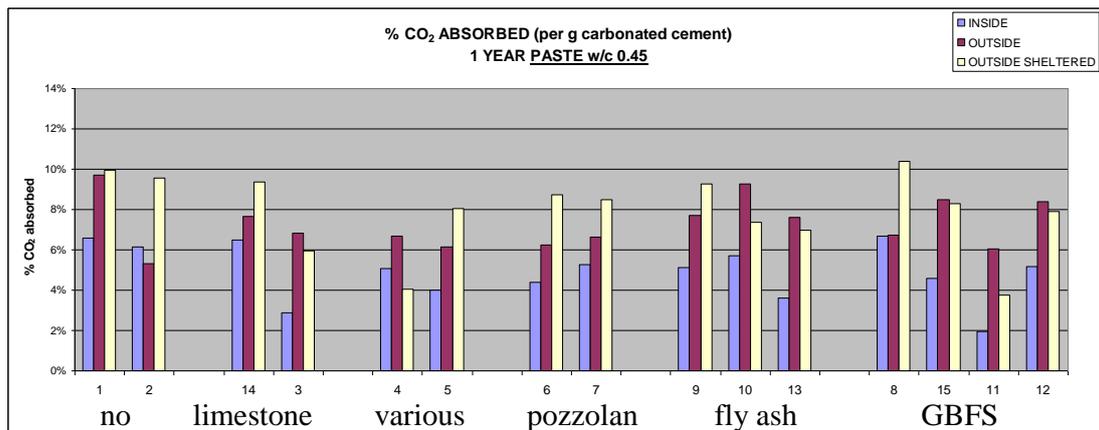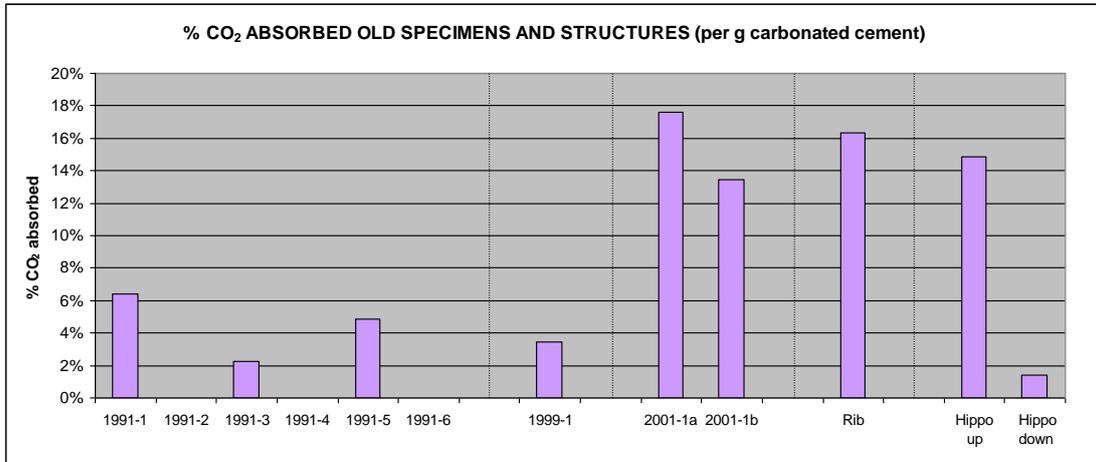

Fig. 5. CO$_2$ Quantities Absorbed in Paste Specimens 0.45 w/c

In the w/c 0.45 specimens (Fig. 5) also the specimens held inside are the ones which absorb less CO$_2$, with the exception of specimen 2 without additions and specimen 4 with fly ash and limestone. Now, however, the specimens that absorbed more are in half of the cases those sheltered from rain and in the other half the ones not sheltered.

The behaviour of the two groups of concrete specimens, w/c 0.6 and 0.45, is similar to the paste specimens with 0.6 w/c with regard to the environments. In almost all cases the specimens that absorb less are the ones inside and the ones that absorb more are the ones outside not sheltered from rain. In general, with few exceptions, the specimens of concrete made with w/c 0.45 absorb less CO$_2$ than the specimens made with w/c 0.6, being the percentages of absorption quite similar to those found in the paste specimens.

In Figure 6 the amounts of CO$_2$ absorbed in the carbonated part of the old specimens and structures are represented. In the first group of specimens produced in 1991 three of the six have not practically absorbed CO$_2$ during the exposure time. The other three 17 years old specimens do absorb CO$_2$ but do not reach 7% in weight of absorption, being the specimens made with fly ash the ones that more CO$_2$ absorb. The specimen made in 1999 has absorbed less than 4% of CO$_2$ per gram of carbonated cement in nine years. The specimens made in 2001 with a building type concrete have absorbed between 13% and 18% CO$_2$ in seven years. In the 'Rib' sample tested, a quantity of 16.3% CO$_2$ absorbed over about 57 years was measured. The two samples from the Hippodrome present amounts of CO$_2$ absorbed very different, in the upper part about 15%, and in the lower part less than 2%. The difference

cannot be explained because of the difficulty of knowing exactly the repairs, alterations and paintings which have suffered the old structures throughout their life.


Fig. 6. CO$_2$ Quantities Absorbed in Old Specimens and Structures

Finally, figures 7 and 8 represent all the data collected in this study of CO$_2$ absorbed as a function of time, both for specimens made for the study and the old ones, as well as for the data collected from the literature.

Figure 7 represents data from 0 to 10 years and figure 8 from 10 to 80 years. The two horizontal lines represent the maximum possible absorption calculated according to the formula of Steinour, H. H. (1959) and Pade, C. (2007), respectively, who believe that up to 78.5% and 75%, respectively, of the CaO present in the cement can be carbonated. Since these are different samples and different conditions the values can not be compared directly, however, it can be said that in most cases absorptions above 20% are not reached.
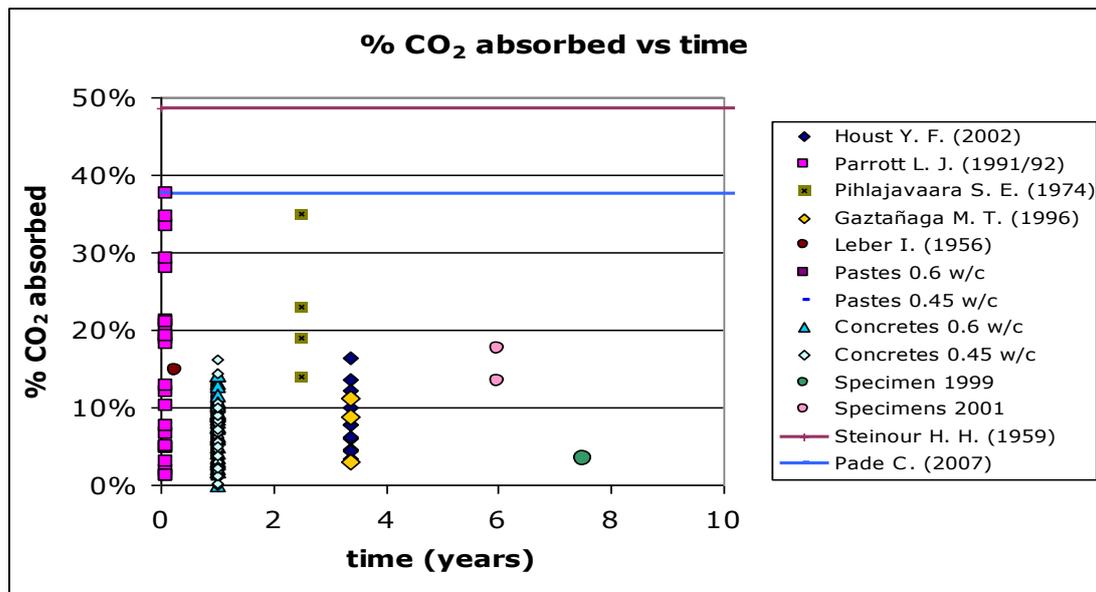
Fig. 7. Quantities of CO$_2$ Absorbed as a Function of Time 0-10 Years
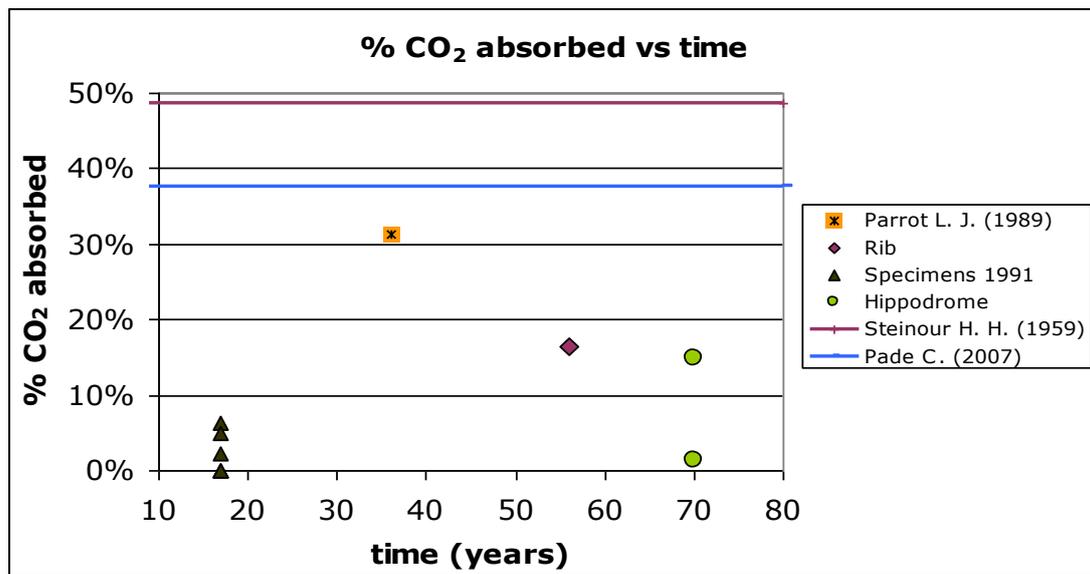
Fig. 8. Quantities of CO$_2$ Absorbed as a Function of Time 10-80 Years

DISCUSSION OF RESULTS

Indicator parameters and characterization techniques in carbonation

The depth of carbonation x, measured by the technique of phenolphthalein coloration, and the carbonation rate k calculated from the formula $x=k \cdot t^{1/2}$, are parameters of interest in studying the corrosion of steel reinforced concrete, identifying the change in pH, however, these parameters do not provide any information on the amount of calcium carbonate formed in the concrete, since no direct relationship has been found between the depths of carbonation, measured by the technique of phenolphthalein, and the quantities of calcium carbonate formed, measured by Thermogravimetry and Differential Thermal Analysis,

The amount of CO$_2$ absorbed or combined per gram of carbonated cement is a key parameter not only to calculate the ability of cement based materials to re-absorb carbon dioxide, but also to model the progress of carbonation.

Influence of the different variables on the carbonation

Exposure environments

Humidity is one of the most influential factors in the advancement of the carbonation front and in the amount of CO$_2$ combined by carbonation. In general terms, specimens fabricated for the study that stayed outside sheltered from rain present higher carbonation depth after one year than those that were outside not sheltered. In contrast, the amounts of CO$_2$ absorbed in this 'carbonated' zone are greater in the specimens that were outside not sheltered than the ones outside sheltered. These differences are related to saturation degree of the pores due to rain and moisture changes that occur inside the concrete as a consequence of the rain-drying cycles.

In the internal environment, with temperatures ranging 13-25 ° C, RH 24-68% and [CO_2] of 500-850 ppm, the amount of carbon dioxide combined in the specimens and the carbonation depth during the first year of exposure are considerably lower than in the external environment, with temperatures ranging 0-31 ° C, RH 27-97% and [CO_2] of 500 ppm, both sheltered and not sheltered from rain. This result indicates that the higher concentration of CO_2 in the interior does not imply a greater absorption of CO_2 in the range of CO_2 concentrations considered.

Type of cement

The influence of type of cement is also very important in the process of carbonation. There are significant differences in the resistance to carbonation (amount combined and carbonated depth) on the different specimens depending on the type of cement used, related both to the type of additions and to the amount of clinker per m^3 of concrete. In general, with increasing amount of clinker, the amount of CaO increases, i.e. material subject to carbonate. When introducing additions to the cement it is important to take into account that the water/clinker ratio will increase, but it is also very important to know the contribution of the additions to the CaO content.

By increasing the amount of CaO generally increases the amount of CO_2 absorbed and decreases the depth of carbonation, being the relationship with depth much more clear than the relationship with the combined CO_2. Both relationships become more evident when considering the groups of additions separately, and also by dividing them by environments. In any case, it is important to note the presence of exceptions.
Until now it can be stated that there is a combined dependence of the type of cement and the environmental conditions on the carbonation.

Life time

There are several models to predict the progress of the carbonation front, mostly based on the solution of Fick's law. The effectiveness of these models has been tested experimentally on numerous occasions; however, it is important to be cautious when using them as the constants of proportionality depend on many factors.
Regarding CO_2 combined there are very few models or proposals. The evolution of CO_2 combination with time is not evident. Young samples may have greater absorption than older ones. In general, the ones studied here do not exceed 20% of the cement amount of CO_2 absorption in the carbonated zone.

Composition of concrete

About the composition of the concrete it can be said that by increasing the amount of cement in the concrete, both the carbonation depth and the amount of CO_2 absorbed decrease, being the main cause for that the porosity decreasing. The fact that the amount of CO_2 decreases with cement content increasing indicates that, despite the higher amount of carbonatable material, the decrease of porosity makes this reason weak and does not permit a greater absorption of CO_2.

Calculation of CO_2 absorption in structures

Once the carbonation depth and the CO_2 absorbed in the carbonated zone are measured for each type of concrete and exposure, it is possible to relate these data with real structures in order to calculate the CO_2 that will be re-absorbed during their service life. The third variable needed for this calculation is the exposed surface of the concrete structure, that is, the area susceptible to carbonate in each type of exposure. Multiplying the three terms by the quantity of cement in the concrete, the amount of CO_2 absorbed per concrete volume unit is obtained. Considering the relationship between cement production and CO_2 emissions, the quantity of CO_2 absorbed in cement based materials can be related to the CO_2 emitted during cement production.

CONCLUSIONS

Cement based materials recombine CO_2 due to their alkaline character.
The combination of CO_2 by carbonation is influenced by the environmental exposure, mainly by the humidity. It is also influenced by the type of cement, amount of CaO and type and percentage of additions. Also the type of concrete affects the absorption of CO_2 primarily by the variation of porosity. Finally the dependence of the absorption of CO_2 over time is unclear and should be studied in depth in the future.
From the available data it can be said that the CO_2 absorption in the carbonated zone is below 20% per gram of cement both in young as in old samples.
Knowing the exposed surface susceptible to carbonate it is possible to calculate and estimate the amount of CO_2 that real structures will absorb during service life.

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