

Effect of Last Generation Additives on the Concrete Durability

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1. Introduction

The influence of carbonation on corrosion of reinforcement depends on the degree of ease of diffusion of CO₂ through the concrete from its surface, also on environmental conditions, on the pore structure of concrete (cement, aggregates, and water (without additives)) and on the W / C, where a high ratio generates porous and permeable mortar and concrete (Duran C., 2003; Troconis O. et al., 2006).

Permeability is not necessarily related to porosity, but depends on the geometry of the pores and the distribution of pore sizes: two porous bodies can have similar porosities but different permeability, so it is important to consider the penetration of CO₂ into the concrete. If the concrete is not permeable, the attack will be relatively superficial and limited to the surface. The attack in concrete is governed by molecular diffusion, which is much slower than convection processes. The use of concrete with low permeability is the primary means to prevent or minimize the effects of external attack (Morin et al., 2001; Papadakis et al., 1992). A well-proportioned mix of aggregate, which follows a continuous grading curve will produce concrete of good workability, high cohesion and a reduced tendency to segregation. At the same time it will be slightly porous and therefore possess a prolonged durability. Superplasticizer additives added to the mix, filling the interstitial space between large particles, which can cause a high density, high strength and resilient material, with a smaller amount of mixing water (Erdogdu S., 2000; Morin et al., 2001).

The main mechanism for CO₂ transport in concrete is diffusion, and with moisture, carbonation leads, a phenomenon to be considered from the viewpoint of durability of reinforced concrete (Carvajal et al., 2006).

There are expressions that relate the diffusion coefficient of concrete with compressive strength, where increase of resistance, decrease of diffusion coefficient. Because the phenomenon of diffusion of gases is of long-term, resistance in ancient age must to be taken into account and not the resistance usually specified at 28 days.

1.1 Carbon dioxide

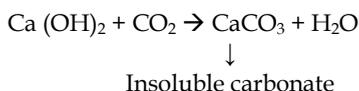
The CO₂ could form carbonic acid with water. The entry of CO₂ inside the concrete is produced through the pores and capillaries of the cement paste. As a result, the pH of carbonated concrete decreases and once the carbonation front reaches the armor begins to dissolve the passive film that protects steel from corrosion.

1.2 Carbonation of concrete

The importance of considering the carbonation in reinforced concrete structures, increases in holding that causes a chemical imbalance and a decrease in pH of water in the pores of the concrete from 12.6 to 13.5 to values around 9, causing depassivation strengthening reinforcements adverse reactions of chlorides and sulfides, and exposing them to corrosion.

Without the passive layer, the steel is corroded as if it were exposed to the environment without any protection, and, the carbonation depends on many factors, but those with a higher incidence are: type of cement, concrete permeability, W/C ratio, concrete curing, relative humidity and CO₂ concentration in the environment (Barrera et al., 2003; Carvajal et al., 2003; da Silva et al., 2002).

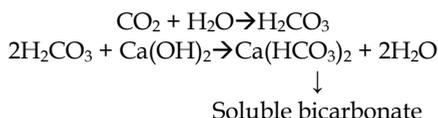
Carbonation is the process by which atmospheric CO₂ is combined with calcium hydroxide [Ca (OH)₂] to form calcium carbonate, losing its alkalinity by decreased pH.



In a mass of plain concrete, the carbonation can be beneficial, improving some of its properties, such as breaking loads between 22% to 78% higher, to obtain a denser concrete generated by an open porosity that is closed (5 to 12%).

On the other hand, the attack produced by carbonic acid, which reacts with calcium hydroxide released from the hydration process of concrete which promotes its alkalinity, will form acid carbonates or bicarbonates (more soluble than carbonates) that has lower pH. Due to this decrease in alkalinity of the concrete, it loses the passivity of the reinforcement, leaving them prone to corrosion.

The CO₂ present in polluted environments produces carbonic acid that diffuses into the concrete mixing with pore water (Knopf et al., 1999).



The water in the atmosphere, rain or fog, contains a slight amount of carbonic acid by absorption of atmospheric CO₂ and are exceptions the industrial areas and cities, where the fumes, especially heating, mixed with steam and the fog for a longer period of time, it depositing on all surfaces.

A depth that CO₂ has penetrated and reactions have occurred that has changed the pH, usually it's called "carbonation front" (Thiery et al., 2007).

The alkalinity of concrete is mainly due to calcium hydroxide (Ca(OH)₂, pH 13 approx.) formed during hydration of cement silicates and alkalis that may be part of the cement. These substances place the pH of the aqueous phase contained in the pores between 12 and 14, most alkaline of pH range.

Corrosion will occur in concrete that has a permeability such that allow the carbonation to reach the concrete in contact with steel or soluble chlorides can penetrate to the steel. If the concrete is in a dry atmosphere (below 40% RH) or submerged in water (without air intake), the risk of corrosion to the reinforcement decreases. An optimum for the corrosion process is 50 to 70% RH (Troconis O. & Duracon Collaboration, 2006).

Considering the effect of carbonation, the pH decreases to values close to 9, which causes the passive iron oxide layer is destroyed (Duran C., 2003).

1.3 Accelerated carbonation chamber

As the carbonation is a long-term process, it was implemented a test system of accelerated carbonation, to attack the concrete more quickly and effectively, obtaining experimental results with more speed than the real time. The accelerated carbonation chamber was designed in many countries for this purpose and in general is to expose the concrete samples and continuous ideal environment for the development of carbonation, where four variables can be controlled: temperature, CO₂ concentration, relative humidity and pressure (Carvajal et al., 2003, 2006; Duran C., 2003). The conditions of T ° and RH ranges are 20 and 25°C and 50-70% respectively, due to these are the environmental conditions of higher penetration rate of CO₂.

To generate a constant environment in the system, the CO₂ pressure has not changes. Respect to the concentration of CO₂, the atmosphere of the chamber is saturated with 100% CO₂ (Carvajal et al., 2003, 2006).

The carbonation chamber, is in acrylic, 6 mm thickness and dimensions 1.00 x 0.50 x 0.50 m. The addition of pure CO₂ through pipes made of PVC previously adapted.

1.4 Rate of carbonation

A simple model to predict the rate of carbonation of concrete is that which relates the depth of carbonation with the square root of exposure time.

$$X_{CO_2} = K_{CO_2} \sqrt{t}$$

Where:

X_{CO_2} = depth of carbonation, mm

K_{CO_2} = carbonation constant : mm * year^{-0.5}

t = time: years

The information obtained can provide the time that is associated with a certain depth of carbonation. Likewise, it can gets the time associated to generate a greater damage, that is, reaching the reinforcement of the structure (CYTED, 1998; Carvajal et al., 2006).

1.5 Additives

The additives are chemicals added to concrete. Additives are defined as "a material other than water, aggregates and hydraulic cement used as a component of concrete or mortar and added to the mixture immediately before or during mixing" (American Concrete Institute, 1991).

1.5.1 Additives used in the study

The additives tested are classified as water-reducing admixtures of high rank. According to ASTM C494 classification are type A and F.

Higher Reducing Water- admixtures (HRWR) reduce the water content of concrete between 12 and 25%, which is why they are used to increase strength and reduce permeability of concrete by reducing water content in the mixture, or to greatly increase the settlement and produce a fluid concrete without adding water. Its use is essential for high-strength concrete with high contents of cementitious materials and silica fume mixtures.

1.5.1.1 Polycarboxylate-based additive

The polycarboxylate based additive is an additive high water reducing capacity, based on synthetic polymers allows maximum flow, high cohesion and maintain the workability of the mixture for long periods.

1.5.1.2 Nanosilica based additive

Nanosilica is a nano additive in liquid silica-based nano-sized particles. It is recommended as much water reducer, high activity. Belongs to a last generation additives, where chemical reactions in the concrete make nanoparticles of silica nanoparticles cement.

1.6 Capillary absorption

Capillary absorption is a reaction that has a concrete (porous solid) from having contact with a liquid, which penetrates and goes into their pores as well as the relationship between their section and the surface tension permits.

According CYTED (1998), the Manual Inspection Evaluation and Diagnosis of Corrosion in Reinforced Concrete Structures, is defined as follows: "capillary absorption is the mass of water per unit area that can be absorbed into the capillaries when the concrete is in contact with liquid water. Represents the effective porosity or accessible to water and therefore to an aggressive environment.

To measure the absorption of concrete, tests performed on samples previously conditioned or witnesses to this effect, to measure the mass absorbed for different times, since it comes in contact with the liquid

This test is simple to implement and to determine the absorption coefficient of the material according to the amount of water absorbed per unit area at a given time (root of time).

2. Experimental procedure

2.1 Materials

Pozzolanic cement, potable water and crushed gravels were used for the manufacture of concrete with and without additives.

The gravels with size range of 6-40 mm were used. The fine aggregate was river sand with a maximum size of 4 mm.

Additives: nanosilica and polycarboxylate.

The chemical composition of the Pozzolanic cement is shown in Table 1.

Com	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃
%	29.7	4.6	3.3	56.6	1.5	0.2	0.4	2.2

Table 1. Composition of Pozzolanic Cement

2.2 Specimens preparation

2.2.1 Specimens cure

Specimens were demounted 2 days after casting, and then they were cured in humid chamber for 28-days, with a 95 + 3 % R H and 20 + 2°C temperature range.

2.2.2 Grade of concretes

The concrete without additives was H25 with w/c 0.60 and a slump cone of 19 cm.

The concrete with polycarboxylate was H25 with w/c 0.48 and a slump cone of 19 cm.

The concrete with nanosilica was H25 with W/C 0.55 and a slump cone of 10 cm. The different W/C ratios are the result of the search for a particular settlement for each concrete, due to the properties of the additives used.

2.3 Experimental method

2.3.1 Compressive strength

Compressive strength test of the concrete was made according to NCh 1037 (ASTM C-39)

2.3.2 Accelerated carbonation test

The specimens that enter to accelerated carbonation chamber, must be conditioned to favour the entrance of CO₂ to their inside through drying in oven at 60°C, temperature that does not damage the capillarity of the concrete, for 24 hours and/ or to invariable weight. The process of carbonation was accelerated using a controlled environment in a special apparatus: temperature (25+ 2 °C), Relative Humidity (50 - 70 %) and CO₂ concentration (100%), to expose the specimens for 5, 7, 9 and 11 days.

The method used to determine the carbonation depth was the application of a phenolphthalein solution in alcohol/water (50/50). For the measure of the carbonation depth, the methodology recommended by RILEM (1988) was used.

2.3.3 Capillary absorption

The test was made according to the standard DIN 18550-Part 1, drying four quarters of the specimens for a period of 48 hours at 50°C ± 10°C, until obtaining a constant weight. The dry specimens were isolated with a plastic film to avoid the humidity absorption from the environment. The time of the test was 48 hours.

The test was applied to the internal faces as well as the external ones with the purpose of discuss the possible differences in capillary absorption between both faces.

It was determined the coefficient of water adsorption (C_i), from the curve of water absorption accumulated in function of the root of time.

3. Results

For the specimens with nanosilica and polycarboxylate, without accelerated carbonation, it has a minimum evolution of strength between the ages of 28 and 58 days which are considered negligible. When they were carbonated presented an increment in the strength. For the specimens without additives and no carbonated, they get strength to late ages (26,5% of difference) while the carbonated specimens presented a decrease of the strength (Table 2).

The specimens manufactured with polycarboxylate additive show lesser carbonation depth and consequently lesser carbonation coefficient than the others. The results are in Table 3.

Abbreviations: P: polycarboxylate

N1: nanosilica

N2: without additives

Numbers: 5, 7, 9 and 11 are days of carbonation

The concrete with nanosilica presents an intermediate carbonation; higher than the concrete with polycarboxylate and lesser than the concrete without additive thus it shows coefficients of carbonation.

Type of concrete	28	56	58	Age of concretes (days)
Carbonated Polycarboxilate	58.3	61.9	61.8	Compressive Strength (MPa)
No Carbonated Polycarboxilate	58.3	58.3	58.3	
Carbonated Nanosilica	37.8	44.1	44.9	
No Carbonated Nanosilica	37.8	37.8	37.9	
Carbonated, without additives.	30.3	30.9	30.5	
No Carbonated without additives	25.3	32.0	32.0	

Table 2. Compressive strength with age of carbonated and no carbonated concretes

Type of concrete	Carbonation coefficient
5P	0.85
7P	3.30
9P	4.43
11P	4.92
5N1	7.19
7N1	9.69
9N1	9.55
11N1	10.32
5N2	12.74
7N2	11.79
9N2	11.12
11N2	12.72

Table 3. Accelerated carbonation coefficient for concretes with different days of carbonation

Days of carbonation	Polycarboxylate (P)	Nanosilica (N1)	Without additive (N2)
0	0,32	0,91	0,80
5	0,29	0,95	0,75
7	0,36	0,88	0,97
9	0,61	0,79	1,19
11	0,50	0,53	1,60

Table 4. Average capillary absorption coefficient for different type of concrete and time of carbonation

The concrete without additive presents the highest carbonation, thus it shows the highest carbonation coefficients.

The specimens with polycarboxylate additive had better response in capillary absorption, in all the times of carbonation. The results are in Table 4.

The concrete with nanosilica is the one that shows a higher coefficient in the initial days of the carbonation, decreasing as time passes, that indicates a higher absorption of water at the beginning than any of the other two.

The concrete without additive shows a higher absorption coefficient in the last days of the carbonation.

It was demonstrated that the specimens with high density show less carbonation. (Figure 1) The highest strength shows the least capillary absorption and carbonation depth, and the highest densities, as it is possible to deduce with the results obtained summarized in the figures 2 to 6.

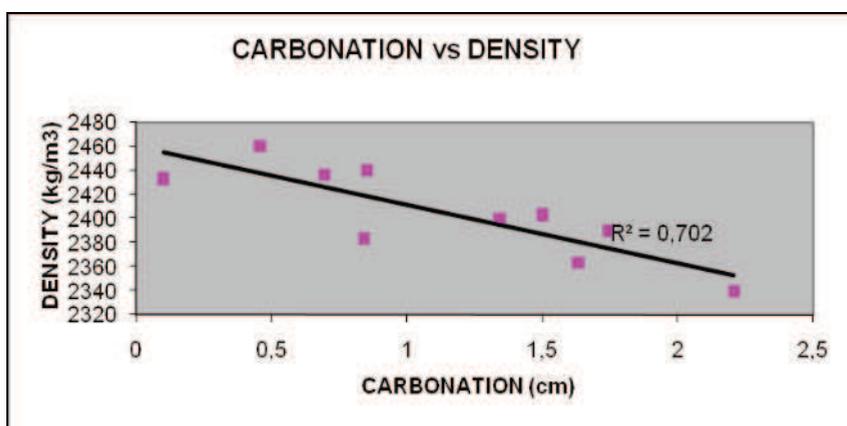


Fig. 1. To higher density, lesser carbonation is produced

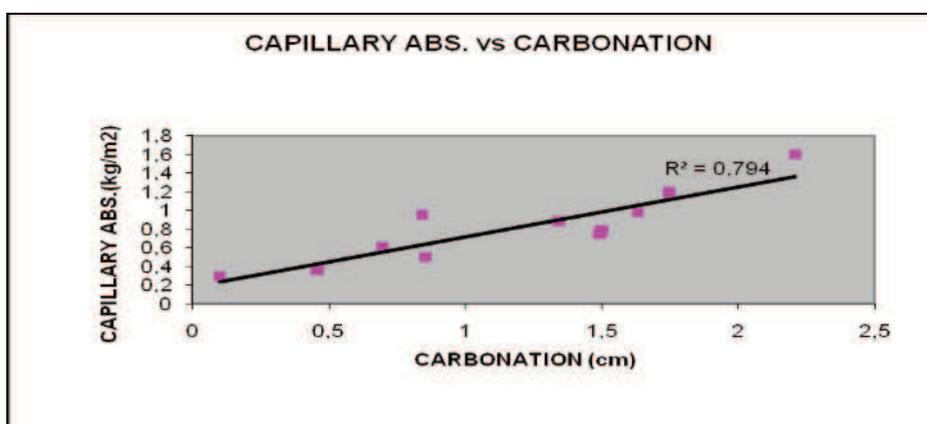


Fig. 2. Relation between capillary absorption and carbonation depth

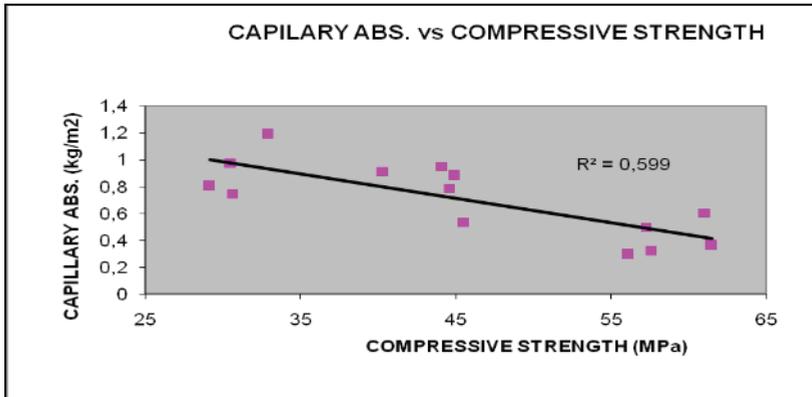


Fig. 3. Relation between capillary absorption and compressive strength

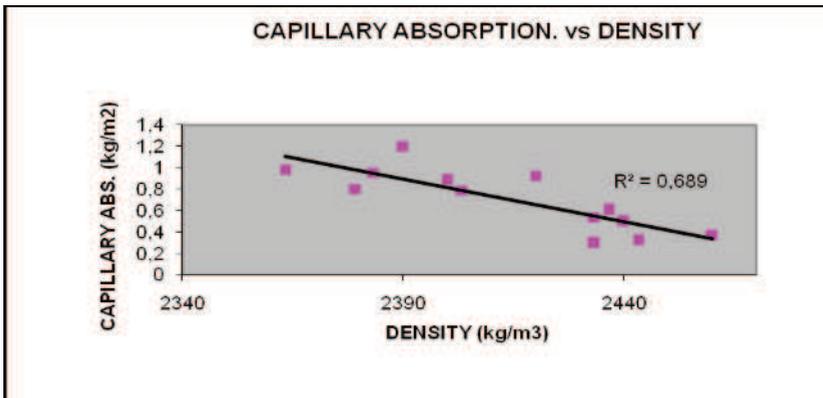


Fig. 4. Relation between capillary absorption and density

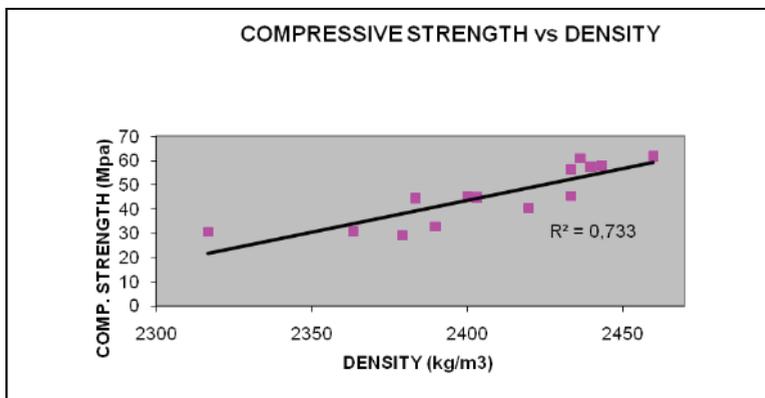


Fig. 5. Relation between compressive strength and density

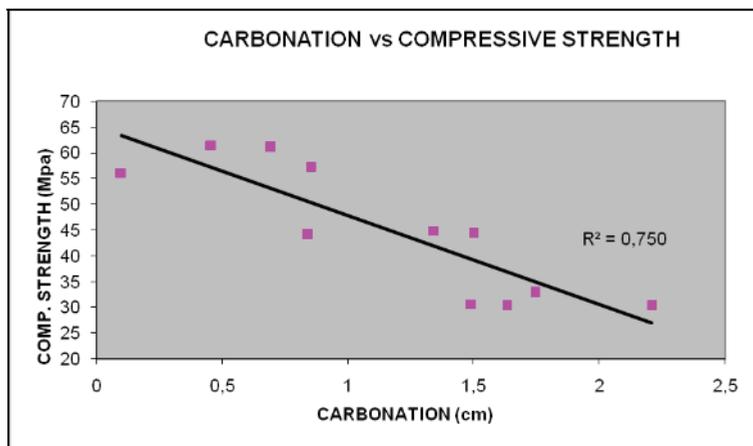


Fig. 6. Relation between carbonation and compressive strength

4. Conclusions

From the results obtained it was possible to conclude that the specimens of higher density correspond to the ones of higher strength which show lesser depth of carbonation and lesser capillary adsorption.

It is worth to mention the importance of the composition of concrete where include the parameter of density to know its behaviour before the results of compressive strength, it could be possible in the future.

In the specimens without additives it is seen that accelerated carbonation tends to produce higher water absorption. This is explained chemically, because the acid carbonates produced by excess of CO_2 have higher water solubility than the carbonates formed in not contaminated environments, where they are insoluble and help to seal the pores of the concrete.

The specimens which have additives present a carbonation coefficient lesser than the ones composed by concrete without additives, may suggest a higher durability in the long term for the specimens with additives.

The specimens with additives, although they were carbonated, show a better behaviour; the penetration tends to stop in time, giving protection to the concrete mass and indirectly to the reinforcing steel.

Regarding the compressive strength, the concrete with polycarboxylate got the highest values of compressive strength and resisted in a better way the accelerated carbonation process. As to the concrete with nanosilica in spite of not having a lesser settlement, it shows lesser strength. At the same time the concrete without aggregate, for the same age shows the least strength.

The concrete with nanosilica presents a higher absorption in spite of having a settlement much lesser than the concrete with polycarboxylate.

However the decrease of the absorption coefficient for higher time of carbonation that matches with a lesser speed of the advance facing the carbonation depth can be explained if it is accepted that the capillaries can have lesser diameter in the concrete mass, and therefore the capacity of forming carbonates to the inside may be seen as decreased although to be

able to explain convincingly this behaviour more exhausting studies in future projects should be carried out.

Regarding the capillary absorption, the specimens with additive absorb lesser quantity of water resulting in a concrete less attainable to water and/or to the aggressive agents, being the absorption in the concrete with nanosilica much higher than in the concrete with polycarboxylate for initial ages of carbonation.

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Quality control is a standard which certainly has become a style of living. With the improvement of technology every day, we meet new and complicated devices and methods in different fields. Quality control explains the directed use of testing to measure the achievement of a specific standard. It is the process, procedures and authority used to accept or reject all components, drug product containers, closures, in-process materials, packaging material, labeling and drug products, and the authority to review production records to assure that no errors have occurred. The quality which is supposed to be achieved is not a concept which can be controlled by easy, numerical or other means, but it is the control over the intrinsic quality of a test facility and its studies. The aim of this book is to share useful and practical knowledge about quality control in several fields with the people who want to improve their knowledge.

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