Chloride Penetration into Carbonated Concrete

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ABSTRACT

To ensure the durability of concrete structures it is necessary to understand its behaviour in the presence of aggressive agents. Carbonation and chloride action are the two leading causes of degradation in reinforced concrete structures. Despite the combined action of these two mechanisms being a reality, there is little research on the effect of CO_2 presence on the chloride behaviour in concrete.

This work studies the total chlorides ingress into carbonated concrete. For this, samples with CEM I 42.5R were cast with 0.6 of water/binder ratio. After 90 days of the curing period, half of the samples were subjected to accelerated carbonation (20ºC, 55%Relative Humidity and 4%CO_2) for 1 month. The other half was protected with a plastic film during the same period. Chloride immersion test, based on LNEC E390 (Portuguese specification), were performed with samples subjected to both experimental conditions. Afterwards, the depth of chlorides and CO_2 penetration was evaluated.

The results show that, for these conditions, the CO_2 presence has a direct influence on chloride behaviour. The non-carbonated samples showed a profile with a higher amount of chloride than carbonated ones.

Introduction

A significant number of concrete structures around the world was early damaged. In the USA, for example, it is estimated that only about 30% of existing bridges have exceeded 50 years old [1]. Among the factors that contribute to this kind of damage is the aggressiveness of chloride ions, one of the main reasons for damage of reinforced concrete structures due to steel rebars corrosion [2]. According to Tilly and Jacobs [3] simultaneous chloride ingress and concrete carbonation account for over 50% percent of the degradation of concrete structures. However, previous studies were mostly confined to the deterioration of concrete structures under a single deteriorating phenomenon, such as chloride ingress or carbonation individually, although the real environment may be a combination of such factors [4].

Concerning the influence of concrete carbonation on the chloride penetration there is a supposed "opposite effect". It is known that the carbonation changes the concrete microstructure and the pH of the concrete. Thus, the carbonation may directly influence the chloride diffusion into concrete. First, because microstructural change decreases the penetrated amount of chlorides. Second, on the other hand, because the pH decrease can act releasing the chemically bound chlorides and increasing the amount of free chlorides that can penetrate into the concrete.

Recently research has begun to look into the effect of combined degradation mechanisms [5; 6; 7]. Chloride ingress and carbonation are among the most studied. However, there is no consensus on the effect of the combined action of chlorides and carbonation on the durability of concrete. In their experimental research, Chengfang *et al.* [8] studied the effect of carbonation on chloride transport. They submitted OPC concrete samples to carbonation chamber (20% CO_2, 20ºC and 70% Relative Humidity, RH) for 14 and 28 days and after to immersion in 5% NaCl solution following by drying in laboratory environment cycles. They concluded that after carbonation, chloride diffusivity coefficient increased with the carbonation time. On the other hand, Malheiro *et al.* [9] immersed mortar samples for a day in a 3.5% NaCl solution and then placed these samples for six days in a carbonation chamber (4%CO_2, 20ºC and 55%RH). The researchers repeated this cycle during 56 days and conclude that carbonation has a direct influence on chloride penetration, decreasing it. In the same way, but studying concrete, Backus *et al.* [10] submitted the samples to wetting and drying exposure regime during a 12 month period and say that the combination of carbonation with the entrance of chloride can act reducing the penetration of chlorides in concrete. However, the lack of standardisation about the various parameters involved in the tests such as the type of test, temperature, humidity and concentration of NaCl and CO_2 makes it difficult to compare results.

To contribute to this important and ongoing discussion, this experimental work studies the penetration of chlorides in carbonated concrete by accelerated tests.

Materials and methods

Material and mixtures. In this work one has used Ordinary Portland Cement (OPC), CEM I 42.5R, which chemical composition is presented in Table 1. Fine aggregate with a fineness modulus of 5.04 and coarse aggregate with maximum size 12.70 mm were used. Tape water was used for all the produced mixtures.

Table 1: Chemical composition of OPC (CEM I 42.5R)

SiO_2 [%]	Al_2O_3 [%]	Fe_2O_3 [%]	CaO [%]	MgO [%]	SO_3 [%]	K_2O [%]	Na_2O [%]	Cl^- [%]	Loss on ignition [%]	Insoluble residue [%]	Remaining elements [%]
20.33	4.59	3.06	62.30	2.12	3.10	0.76	0.19	0.07	1.78	1.21	0.49

One mixture was tested in this study, which composition and main properties are presented in Table 2. Cylindrical concrete samples with ϕ100x200 mm were cast. After casting, the samples were

covered with a plastic sheet and were stored in a humidity chamber (21 ºC and 98% RH) for one day. Then, they were removed from the moulds and were cured immersed in water for 90 days.

Table 2: Materials and main properties of the studied concrete

Materials	
Proportions	
Cement [kg]	380
Water [l]	228
Sand 0/4 [kg]	855.76
Coarse aggregate 4/8 [kg]	282.22
Coarse aggregate 6/12 [kg]	508.95
Property	
Slump [mm]	20.5
Compressive strength [MPa]:	
28 days	32.84
90 days	35.09
365 days	39.59
Capillary water absorption [$kg/m^2/min^{1/2}$]	0.281
Open porosity [%]	13.50

Sample Preparation. After curing, the samples were cut in order to obtain two slices. The top and bottom of the samples were discarded. Then, the lateral and bottom faces of the samples were covered with an epoxy resin. The top face of samples was not covered in order to simulate a unidirectional flux during the immersion period.

The new samples (ϕ100x75 mm) were divided in two groups, A and B. The group A was subjected to accelerated carbonation while the group B (reference group) remained in laboratory environment for the same period.

Carbonation. Before accelerated carbonation, the samples of group A were subjected to preconditioning procedures to achieve the equilibrium with environmental humidity near 60% and accelerate the carbonation process. This preconditioning had two stages. In the first stage, the samples remained in a chamber with controlled temperature and humidity (20 ºC and 60% RH) until reaching a constant mass. Second, they were protected with several layers of plastic film and put in an oven (40 ºC), for 20 days, to distribute the humidity inside the specimen. After this, the plastic film was removed and the group A was subjected to accelerated carbonation in carbonation chamber (4% CO_2, by volume, 20 ºC and 55% RH), following the recommendations of the European Standard [11], for 1 month (Fig. 1). It is important to note that the samples were not split at the end of the carbonation period as usual.

Chloride penetration. When the carbonation tests were finished, the immersion test, based on Portuguese specification [12] were performed with samples previously subjected to accelerated carbonation, group A, and with reference samples, group B. During this test, the samples were immersed in a saturated solution of calcium hydroxide until reaching a constant mass. After, they remained four months immersed in 15% sodium chloride solution (Fig. 1).

Figure 1: Combined action: Carbonation test (left) and Immersion test set-up (right).

When the exposure period was over, the samples were marked according to each sample depth and were continuously powdered at each 5 mm from the surface to bulk until 30mm. After this extraction, total chloride content in each powered sample was measured according to RILEM recommendation [13]. These results were used for drawing chloride profiles.

Determination of carbonation depth and chloride penetration depth. After finishing the powder extraction process, the samples were split perpendicularly to the aggressive agents penetration direction. After, the carbonation depth and the chloride penetration depth were determined. The colorimetric technique was used. For group A, the half samples were used in different ways: the first one was sprayed with a 1% phenolphthalein solution in 70% ethyl alcohol in order to determine the advance of the carbonation front. The other one was sprayed with 0.1 M $AgNO_3$ solution in order to determine the penetration depth of chlorides. For group B, the half samples were only sprayed with 0.1 M $AgNO_3$ solution.

Complementary test. The porosimetry testing was performed with an Auto Pore IV scanning mercury porosimeter having a pressure range from 0.10 to 33000 psi. The contact angle and the mercury surface tension considered were 130° and 0.485 N/m, respectively.

The pressures were converted to equivalent pore diameter using the Washburn equation [14], as expressed in Eq. 1; where d is the pore diameter (μm), γ is the surface tension (mN/m), θ is the contact angle between mercury and the pore wall (°), and P is the net pressure across the mercury meniscus at the time of the cumulative intrusion measurement (MPa).

$$d = \frac{-4\gamma\cos\theta}{P} \tag{1}$$

For this test, the samples were removed from regions close to the surface regardless chloride presence and carbonation. MIP requires complete removal of water from the sample prior to intrusion of the mercury. Thus, prior to the test, samples were oven-dried at 60°C for 24 hours.

Results
There were three samples for each experimental condition. Thus, each result represents the average of these three samples.

Chloride profile. Fig. 2 shows the chloride profiles obtained for group A and B after four months in immersion.
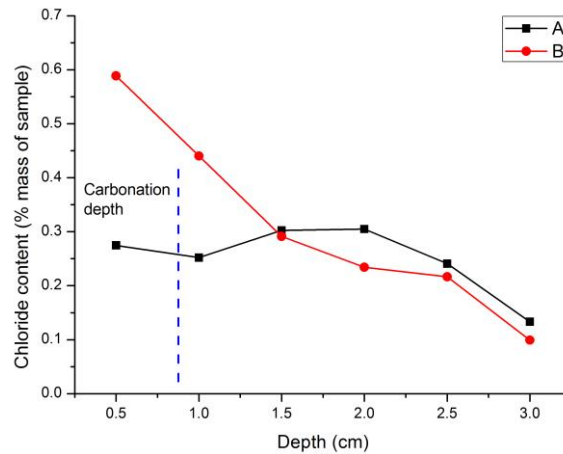
Figure 2: Chloride profile for group A, carbonated concrete, and group B, non-carbonated concrete, after four months in chloride immersion.

It is possible to note in Fig. 2 that the chloride penetration happens in a differet way in CO_2 presence. In carbonated concrete, group A, the chloride profile has similar values throughout the profile while in non-carbonated concrete, group B, the surface has values higher than bulk and it is possible to see a sharply drop in this profile. Furthermore, in group A, in carbonated area and surroundings, chloride profiles present lower chloride contents for the test specimen than those subjected to group B. Furthermore, there is a chloride peak after carbonated zone (1.5cm). After this peak there is a reduction in total chloride content.

Carbonation and chloride depth. The depth of carbonation front reached for the samples studied in group A was equal to *7.62mm*. The depth of chloride penetration reached for the samples studied in group A and B was *53.02mm* and *33.71mm*, respectively. Fig. 3 shows one of analysed samples in group A.

Figure 3: Chloride depth (left) and Carbonation depth (right) reached in group A.

According this data is possible to note that in carbonated concrete, group A, the chloride penetration was deeper than in non-carbonated concrete, group B.

Complementary test. The mercury intrusion porosimetry (MIP) results are plotted in Fig. 4. They show the relationship between cumulative intrusion, in mL/g, and pore size diameters. We used the following classification: large capillary pores, 10–0.05 μm, medium capillary pores, 0.05–0.01 μm, and gel pores, <0.01 μm [15].
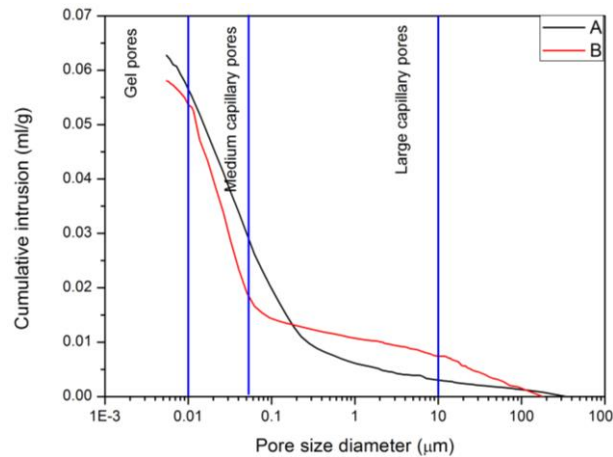
Figure 4: Cumulative intrusion versus pore size for cycles A, carbonated concrete, and B, non-carbonated concrete.

It can be observed in Fig. 4 that, for samples subjected to the combined action of chlorides and carbon dioxide (cycle A), the large capillary pores are decreased while the medium capillary pores and gel pores are increased concerning samples subjected only to chloride penetration (cycle B).

Discussion

Carbonation can reduce the permeability and, thus, result in decrease in the amount of chloride ions that penetrates in concrete . The chloride profiles presented in Fig. 2 clearly show the influence of carbonation on chloride penetration for the studied mixtures. In this case, the carbonation acts by reducing the amount of total chlorides present in carbonated area and surroundings.

This fact can be related to the refinement of the pores of the concrete caused by carbonation. There is a consensus that carbonation promotes microstructural changes that culminate in the densification of pores. The carbonation reaction gives rise to calcium carbonate which solubility is limited and, therefore, tends to precipitate during the carbonation process [16]. This precipitation, at an initial phase, results in the pore mentioned above densification and consequent reduction of permeability. For conditions studied, the refinement of the pores seems to play a important role.

The MIP results can confirm the decrease in the permeability of the carbonated concrete showed in Fig. 4. These results show an increase in medium capillary pores and gel pores and a decrease in large capillary pores for carbonated samples. That is, under these conditions, the chlorides penetrate with difficulty.

On the other hand, the carbonation can reduce the capacity of chloride binding [17] and, consequently, lead to an increase in the rate of chloride ion ingress. The results reached from sprayed with $AgNO_3$ solution corroborate this statement. In carbonated concrete the chloride penetration is deeper than in non-carbonated one. Furthermore, as we can see in Fig. 2, the superficial concentration of chloride is dramatically reduced in carbonated concrete. Probably, it happens because in carbonated areas and surroundings there is a reduction in chloride binding. In Fig. 2 we can observe that the amount of chloride in carbonated zone is almost constant. Consequently, in the end of carbonated area, still there is a lot of chloride to penetrate in concrete. After the carbonated zone there is a reduction in chloride content (Fig. 2). This is expectable because in this area the chloride binding happens normally.

Conclusions

Based on these results, it is possible to point to the following conclusions:

- The behaviour of chlorides is affected by the action of carbonation;
- For the conditions studied, the carbonation reduces the surface concentration of chlorides and total chlorides content in carbonated areas and surroundings;

- The changes in the permeability of the concrete caused by carbonation can be the primary reason for the decrease in the amount of chloride ions that penetrates in concrete. In samples subjected to combined action, the large capillary pores are reduced while the medium capillary pores and gel pores are increased concerning samples subjected only to chloride penetration.

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