BEHAVIOUR OF CONCRETE UNDER SEVERE ENVIRONMENT - EFFECT OF CARBONATION ON THE CHLORIDE DIFFUSION COEFFICIENT FROM NON-STEADY-STATE MIGRATION TEST

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To ensure the durability of concrete structures it is necessary to understand its behaviour in the presence of aggressive agents. Carbonation and chloride ingress are the two main causes of degradation in reinforced concrete. The combination of these factors can create a very harsh environment for concrete structures. Given the importance of chloride migration coefficient for areas such as service life prediction, this work intends to study the influence of carbonation on the chloride migration coefficient of ordinary Portland cement (OPC) concrete. Concrete specimens were cast with different water-cement ratios: 0.4, 0.5 and 0.6. After 90 days of curing, half of samples were subjected to carbonation chamber (4% CO_2, 20 °C and 55% RH) for 6 months. The other half was protected with plastic sheet during the same period. Non-steady-state migration test was performed in specimens with and without exposure to carbon dioxide environment. The results show that, for these conditions, the carbonation has a direct influence on chloride diffusion coefficient, increasing it. The carbonated samples studied showed a chloride migration coefficient up to 130% higher than noncarbonated ones. This fact can be related to the reduce in chloride binding capacity caused by carbonation front.

1. Introduction

A significant number of concrete structures around the world have deteriorated prematurely [1]. In the USA, for example, about 9.1% of the nation's bridges were classified as structurally deficient in 2016. The most recent estimate puts the nation's backlog of bridge rehabilitation needs at $123 billion [2]. Usually reinforcement corrosion is the main cause of the reduction of service life of concrete structures. Among the factors that contribute to this kind of damage is the aggressiveness of chloride ions, one of the main reasons for damage to ordinary concrete structures [3].

The ions chloride penetrate into concrete mainly by capillary absorption and diffusion [4]. But, in order to quantify the chloride ingress speed in concrete, the chloride diffusion coefficient is normally used because the diffusion controls the ingress of chlorides at a certain depth in concrete, while the capillary is only significant in the surface layers [5,6]. The rapid chloride migration test is a commonly used accelerated test for the determination of this coefficient in concrete. Service life prediction models, such as FIB and LNEC [7, 8], use results from chloride migration test in their

formulation because it is considered a fast and efficient test.

The migration test is carried out on concrete moulded for this purpose, or on specimens that have been in real environments but without considering any other type of aggression that this specimen may have suffered. However, in fact, the deterioration of concrete structures in real environments is a consequence of a combination of deterioration phenomenon. For instance, structures exposed to marine environments (atmospheric, splash and tidal zone) or de-icing salts (Figure 1) are also exposed to the action of carbonation [9]. The combination of these factors, chloride and carbon dioxide, can create a very harsh environment for concrete structures.

Recently research has begun to look into the effect of combined degradation mechanisms. 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. The service life of concrete structures is directly affected by its durability. Thus it is necessary to expand the study of the combined degradation mechanisms.

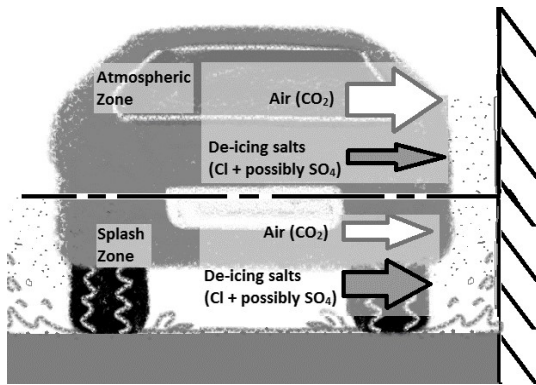* Autor corespondent/*Corresponding author*,
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Fig. 1 - Road structure exposed to de-icing salts and water [9].

On the one hand, in their experimental research, Chindaprasirt et al. [10], for example, used mortars with a constant water/cement ratio of 0.5 and similar flow to combine carbonation (accelerated testing environment with 5% CO_2 during 60 days), and chloride (rapid chloride penetration test, modified rapid migration test and chloride penetration depth after 30 days of immersion in 3% NaCl solution) to determine the effects of carbon dioxide on chloride penetration and chloride diffusion coefficient. The authors concluded that, for Ordinary Portland Cement (OPC) mortar, the exposure to carbon dioxide environment does not lower the chloride penetration resistance of mortar regardless the accelerate chloride test used. On the other hand, Kuosa et al. [11], also used mortars with water/cement ratio equal 0.5 to combine carbonation (accelerated testing environment with 4% CO_2 during 157 days) and chloride (chloride migration test) to determine the effects of carbon dioxide on chloride migration test and concluded that the carbonated surface layer increases the

chloride migration depth. The authors do not show the results from carbonation depth achieved nevertheless the difference in these results can be the key for the detected difference in the final result.

Researches using others accelerated tests to study the combined action also present opposite results [12 - 15]. However, the lack of standardization about the various parameters involved such as type of test, temperature, humidity and concentration of NaCl and CO_2 makes it difficult to compare results. In order to contribute to this important and ongoing scientific discussion, this experimental work studies the influence of carbonation on the chloride diffusion coefficient.

2. Experimental Program

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 4.03 and two coarse aggregate, one with fineness modulus of 6.3 and the other with 7.0 were used. Tap water was used for all the produced mixtures.

Three mixtures, with different water/cement ratio, were tested in this study, which are presented in Table 2. Cylindrical concrete specimens with ϕ100x200 mm were casted. After casting, the specimens 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 1

Chemical composition of OPC (CEM I 42.5R).

SiO$_2$ [%]	Al$_2$O$_3$ [%]	Fe$_2$O$_3$ [%]	CaO [%]	MgO [%]	SO$_3$ [%]	K$_2$O [%]	Na$_2$O [%]	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

Table 2

Mixtures and main properties of the studied concrete

Materials	Water/cement ratio		
	0.4	0.5	0.6
Proportions			
Cement [kg]	380	380	380
Water [l]	152	190	228
Superplasticizer [%]	1.97	0.45	-
Sand 0/4 [kg]	1052.17	989.83	855.76
Coarse aggregate 4/8 [kg]	263.88	261.30	282.22
Coarse aggregate 6/12 [kg]	515.28	492.64	508.95
Property			
Slump [mm]	5.5	9.5	20.5
Compressive strength [MPa]:			
28 days	66.05	47.02	32.84
90 days	74.73	51.64	35.09
365 days	75.87	53.45	39.59
Capillary water absorption [kg/m^2/min$^{1/2}$]	0.088	0.173	0.281
Open porosity [%]	6.97	10.75	13.50

Sample Preparation. After the curing period, all samples were cut in order to obtain three slices. The top and bottom of the samples were discarded. The new samples (ϕ100x50 mm) were divided in two groups, A (carbonation plus chloride penetration) and B (only chloride penetration).

2.1. Accelerated Tests

Carbonation. Before accelerated carbonation the specimens of group A were subjected to preconditioning procedures in order to achieve the equilibrium with environmental humidity near 60% and accelerate the carbonation process. This preconditioning had three stages. In the first stage, the specimens remained in a chamber with controlled temperature and humidity (20 ºC and 60% RH) until reaching constant mass. Second, they had the lateral and the bottom face covered with paraffin in order to guarantee the one-dimensional attack of aggressive agents through the top of the specimen. Third, in order to distribute the humidity inside the concrete specimens, they were protected with several layers of plastic film and put in a ventilated oven (40 ºC), for 20 days. The specimens were weighed before and after being in oven and one has verified that the water loss was not bigger than 0.1%. After preconditioning procedures, the plastic film was removed and the samples were subjected to accelerated carbonation in carbonation chamber (4% CO_2, 20 ºC and 55% RH), following the recommendations of the European Standard [16], for 6 months

The group B (reference group) remained in laboratory environment (20ºC and 60%RH), protected with plastic sheet, during the preconditioning procedures and carbonation period. The main goal to protect the samples in group B was to prevent the carbonation and maintain the temperature used for group A.

Chloride penetration. When the carbonation tests were finished, Non-Steady-State Migration Tests (MT) were performed [17] on specimens previously subjected to accelerated carbonation, group A, and with reference specimens, group B.

For specimens of group A, the paraffin was removed and then all the specimens were subjected to MT. These specimens were previously saturated with limewater under vacuum conditions

and stored in the solution for 18 ± 2 h. Afterwards, the samples were placed in rubber sleeves. The catholyte was filled with a 10% NaCl solution and the anolyte with a 0.3M NaOH solution. The test duration and applied voltages were determined based on the initial current measured at 30 V according to LNEC E463 [17]. It is important to note that, because of preconditioning (group A), probably, the samples of group A and B have an internal humidity different before start the MT.

However, after saturation in limewater, this difference disappear.

At the end of the test, the samples were split perpendicularly to the aggressive agents' penetration direction. The penetration depth of chloride was used to determine a chloride ion diffusion coefficient and the following equation derived from the Nernst–Plank equation [18] (Equation 1) where D is chloride ion diffusion coefficient (cm^2/s), R is gas constant (8.314 J/K mol), T is temperature (K), L is the thickness of specimens (cm), z is the ion valence, F is Faraday constant (9.65 x 10^4 C/mol), E is values of potential (V), x_f is the chloride penetration depth indicated by the colorimetric indicator $AgNO_3$, and t is the time of test duration (s).

$$D = \frac{RTL}{zFE} \times \frac{x_f}{t} \qquad (1)$$

Determination of carbonation depth and chloride penetration depth. When finished the MT, the carbonation depth and the chloride penetration depth were determined. The colorimetric technique was used.

In order to determine the advance of the carbonation front, the fractured surfaces were sprayed with a 1% phenolphthalein solution in 70% ethyl alcohol. Twenty-four hours after spraying the solution, when the margin between carbonated and non-carbonated concrete is often more clearly, the carbonation depth was measured in 5 different points, according to RILEM CPC-18 [19].

In order to determine the penetration depth of chlorides, the fractured surfaces were sprayed with 0.1 N $AgNO_3$ immediately after the fracture. Fifteen minutes after spraying the solution, when the white precipitate of the silver chloride is clearly visible in the fracture surface, the chloride penetration depth was measured, according to LNEC E463 [17].
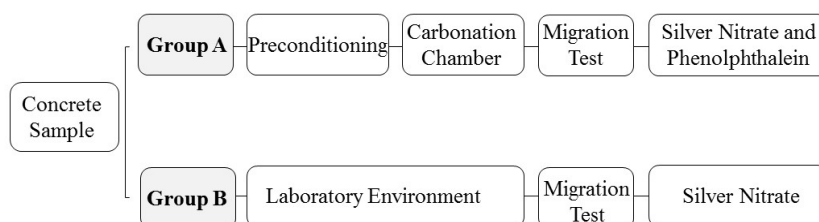

Fig. 2 - Schematic diagram of accelerated test.

For group A, the half specimens were used in different ways: the first one was used to determine the carbonation depth and the other one was used to determine the penetration depth of chlorides (x_f) and, consequently, the chloride ion diffusion coefficient (Equation 1). For group B, the half specimens were used only to determine the penetration depth of chlorides.

The schematic diagram of accelerated tests is shown in Figure 2.

Complementary test. The water absorption by immersion was carried out based on Portuguese Specification [20]. This complementary test was chosen to better understand the specimens' porosity with and without carbonation. First, the specimens were dried in a ventilated oven at a temperature of 105 ± 5 ºC until the difference in mass during 24 h was less than 0.1%. The dry mass was called M_d. Afterwards, the specimens were immersed in water until the change in mass during 24 h was less than 0.1%. The obtained saturated mass was called M_S. M_h is the hydrostatic mass of the specimen immersed in water. The water absorption by immersion (W_i) was calculated according Equation 2.

$$W_i = \frac{(M_S - M_d)}{(M_d - M_h)} \quad (2)$$

3. Results

Carbonation. The Figure 3 shows the depth of carbonation front obtained for the specimens studied in group A. Each point represents an average of three specimens' results.
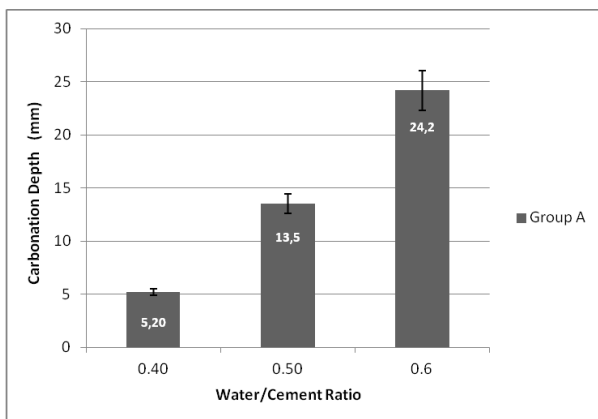

Fig. 3 - Carbonation depth for six months test time.

As expected, the carbonation depth increases with the increasing water/cement (w/c) ratio. Concrete with w/c ratio equal to 0.6 presented the biggest carbonation depth. It is 1.89 times bigger than concrete with w/c ratio equal to 0.5 and almost 5 times bigger than concrete with w/c ratio equal to 0.4.

Chlorides. The Figures 4 and 5 show, respectively, the chloride penetration depth and the chloride ion diffusion coefficients obtained from MT. The figures show the results for group A, carbonation and chlorides, and group B, reference group, only chlorides. Each point represents an average of three specimens' results.
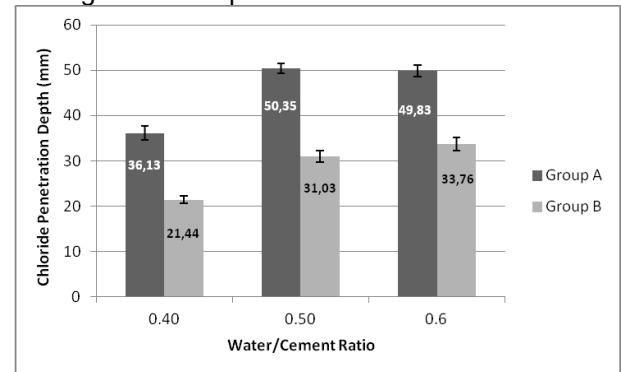

Fig. 4 - Chloride penetration depth for group A, chloride and carbonation, and group B, only chloride.
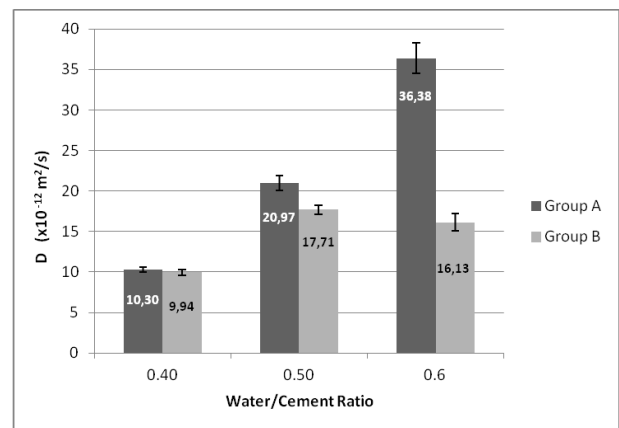

Fig. 5 - Chloride coefficient for group A, chloride and carbonation, and group B, only chloride.
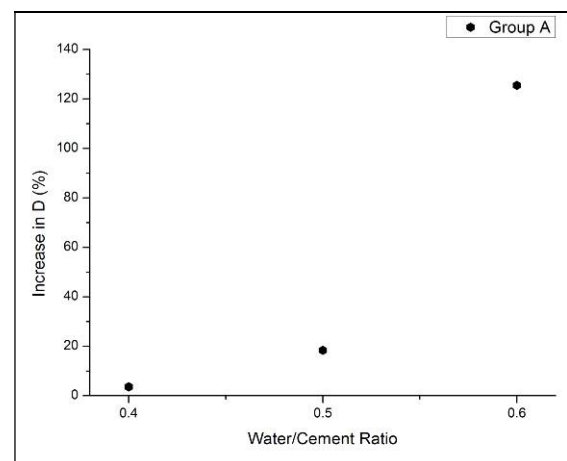

Fig. 6 - Increase in the chloride diffusion coefficient, after combined action of carbonation and chlorides, according water/binder ratio.

It is possible to note in Figures 4 and 5 that there is an increase in chloride penetration depth and chloride diffusion coefficient, when the samples were subjected to combined action of carbonation and chloride ion. Chloride penetration

depth was maximum, x_f= 50mm, for specimens with water/cement ratio equal to 0.5 and 0.6 but in all specimens, regardless water/cemente ratio, the carbonation depth was completely penetreted by chlorides. The carbonation concrete seems to works as a "privileged way" for chlorides penetration, increasing significantly the chloride penetration depth.

For chloride diffusion coefficient, the increase is more pronounced in concrete with w/c ratio equal to 0.6. Under conditions studied, the difference between the chloride diffusion coefficient achieved in carbonated concrete, group A, and the one achieved in non-carbonated concrete, group B, increases with the increasing w/c ratio (Figure 6).

Water Absorption by Immersion. The Figure 7 shows immersion water absorption results obtained for group A, carbonation and chlorides, and group B, only chlorides. These results represents the average value obtained from three specimens.
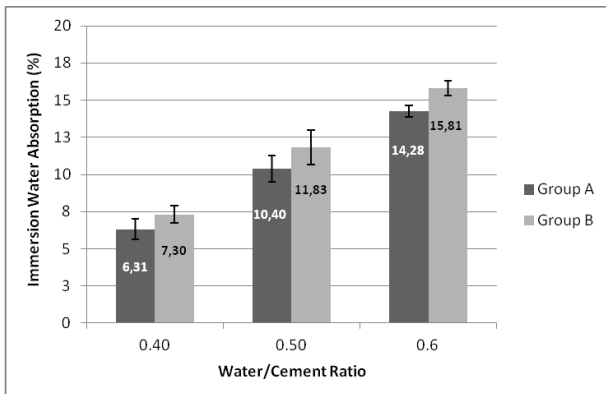

Fig. 7 - Immersion water absorption values for concrete under different aggressive conditions.

It can be seen that the water absorption by immersion increases with the increasing w/c ratio regardless carbonation presence. In addition, there is an influence in immersion absorption values caused by carbonation. Although this influence do not be very significant, it is observed that carbonation decreases the immersion values regardless w/c ratio. Since the water absorption by immersion is related to the open porosity, it is possible to say that carbonation changes the porosity of concrete, decreasing it.

Discussion: Carbonation and chloride diffusion. Concrete specimens were cast with different w/c ratios: 0.4, 0.5 and 0.6 and cement CEM I 42.5 R. After 90 days of curing, half of samples were subjected to carbonation for 6 months and the other half was protected with plastic sheet during the same period. Thus, non-steady-state migration test was performed. For the adopted conditions, combined action of exposure to chloride ions and carbonation has influence on

the chloride penetration depth and the chloride diffusion coefficient, increasing them.

Considering that the carbonation changes the concrete microstructure and its pH [1], it may directly influence the chloride penetration into concrete through diffusion. About the concrete microstructure, Ngala and Page [21] studied the effect of carbonation on pore structure and found that, after carbonation, there is a reduction in total porosity for the OPC specimens. For the conditions studied in this work it is possible to observe this phenomenon too (Figure 7).

The pH changes of the pore solution are due to interaction of carbon dioxide with the cement hydrates. This aspect also may directly influence the chloride diffusion into concrete because the pH decrease caused by carbonation [22] can contribute towards releasing chemically fixed chlorides and increasing free chlorides content, which may actively ingress into concrete [23]. One possible source of chloride ions within concrete are in Friedel´s salt form $(3CaO.Al_2O_3.CaCl_2.10H_2O)$. This salt is a result of the combination of chlorides and tricalcium aluminate and, in this context, plays a significant role due to their ability to fix chlorides [24]. However, studies point to an increase of the solubility of the Friedel´s salt when increasing the degree of carbonation [25] because its stability is related to the pH of the pore solution [24, 25].

According to the discussion above, these two phenomena, microstructure and pH change, may play roles in opposite way when cementitious material suffers carbonation: porosity reduction and chloride release (or binding difficulty). The porosity reduction can lead to a decreased in chloride penetration. On the other hand, the binding difficulty can lead to an increase in chloride penetration because there are more free chloride to penetrate into the material. Thus, the prevalence of one effect over the other may result in different consequences to chloride transport into cement-based materials.

Considering that the chloride penetration depth and the chloride diffusion coefficient increased in group A, that is, in carbonation presence, it is possible that the binding difficulty effect was more pronounced than porosity reduction. This effect is more evident for bigger w/c ratios because, in these cases, the carbonation depth is also bigger.

These results are in the same way to Kuosa *et al.* [11] despite these authors had investigated mortar instead of concrete. This fact reinforces the thesis that carbonation increases the diffusion coefficient of chlorides in OPC specimens. However, it is also important to evaluate the results obtained in research involving other types of accelerated tests, such as ones containing immersion and drying cycles, carbonation chamber with an atmosphere con-

taining NaCl and others. Thus, it will be possible moving toward a consensus on the impact of combined action, chlorides and carbonation, on the durability of reinforced concrete structures.

Furthermore, it is necessary to think about the use of migration test to quantify the chloride ingress speed in partial or complete carbonated concrete. The partial carbonated specimens (the case of the present study and, probably, [10, 11]) cannot be homogeneous. They have double layers, carbonated and non-carbonated one, with different characteristics. The complete carbonated specimens and non-carbonated specimens have different characteristics and, consequently, different chloride diffusion coefficients. It is important to take this in mind so that we can move towards results that are closer to reality.

4.Conclusions

Based on the results achieved it is possible to conclude, for the studied conditions, that the carbonation has a direct influence on chloride migration coefficient, increasing it. This fact can be related to the prevalence of chloride binding capacity reduction , which means that there are more free chlorides, over the porosity reduction. Furthermore, it is possible to say that , there is an influence in immersion absorption values caused by carbonation.

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