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Chloride penetration resistance in sound and micro-cracked concretes through different experimental techniques

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Abstract

Concrete resistance to chloride penetration is one of the main design parameters for the assessment of reinforced concrete structures durability in chloride-contaminated environments, and it is usually determined through one of the accredited accelerated tests in uncracked configuration. In this study, the resistance to chloride penetration was evaluated on six different concrete types, in uncracked and load-induced micro-cracked configurations, subject to pure diffusion and considering two different analysis techniques, colorimetric and potentiometric titration. Results showed that in uncracked conditions, good correlation subsisted between the diffusion coefficients evaluated through the two techniques. In cracked configuration (micro-cracks 10-75 μm wide and 5-45 mm deep) with both techniques a significant increase in chloride diffusion coefficient was detected for concretes with lower w/c ratio, suggesting that the effect of cracks may be more pronounced for more impervious concretes.

Keywords

Reinforced concrete; durability; cracked concrete; load-induced micro-cracks; chloride diffusion coefficient; blended cements.

1. Introduction

Chloride-induced corrosion of steel rebar is one of the main durability issues concerning reinforced concrete (RC) structures worldwide [1]. The durability design for structures located in chloride bearing environments is performed as a function of several design parameters concerning both the exposure conditions and the characteristics of the material. Among the latter, chloride penetration resistance of concrete is of major concern. According to the most recent durability design codes, this

parameter can be experimentally measured under accelerated laboratory conditions. Several testing procedures and analysis techniques have been designed in the recent years to this purpose, out of which some are cheaper and less time consuming, such as the accelerated migration tests followed by a colorimetric technique to highlight the chloride penetration profile, while others require longer exposure times and more complex laboratory analyses, such as the diffusion tests followed by powder sampling and potentiometric titration to measure chloride concentration profiles. The obtained results, in terms of chloride migration or diffusion coefficient, are strictly related to the adopted testing procedure, and are associated to some "conversion" coefficients, used to predict the long-term behavior of concrete in a durability design. This is considered to be one of the most critical aspects in the current durability design models. Furthermore, another critical aspect is related to the fact that the effects of cracks are not taken into account [2]. Cracks are in fact inevitable in real RC structures and represent a preferential path for the penetration of aggressive substances such as chlorides. The literature agrees that the presence of cracks may shorten the corrosion initiation time of steel rebar and current regulations for structural design in severe environments recommend some maximum allowable crack widths in order to guarantee the durability. Anyway, although many studies have been performed on the subject, there is still not enough experimental data available to implement the effect of cracks in current durability design codes. This is also due to the multitude of experimental methods used to investigate the topic, that makes it difficult to summarize and compare the results obtained from different studies.

Firstly, this is a consequence of the multitude of different cracking methods that have been proposed in literature. Basically, cracks can be simulated on small unreinforced concrete specimens by notching with plastic or metal sheets inserted during casting and removed after a few hours. These simulated cracks have the advantage of being more replicable, and with known crack width and depth. Their morphology is, anyway, very different from real cracks, and their width is typically not lower than 50 μm [3-6]. As an alternative, load-induced cracks may be reproduced, with a variety of different methods that strictly depends on the geometry of the concrete specimens. Cracks can be generated by tensile stresses in small unreinforced specimens through the Brazilian splitting test [7-9] or the expansive core method [10], reproducing parallel-walled cracks that cross the entire thickness of the specimen. V-shaped cracks, more representative of cracks occurring in RC elements subject to bending, can be reproduced on beam-shaped concrete specimens subject to 3- or 4-point bending procedure [11, 12], obtaining cracks widths even in the order of magnitude of thousands of microns. To do this, the beam-shaped specimen must be reinforced with steel rebar in order to avoid brittle failure. On the other hand, V-shaped micro-cracks on unreinforced specimens of limited dimensions can be reproduced through very specific methods, such as the wedge splitting method [13], or through the pulling of metallic plates glued on the specimen's surface [14].

The investigation of chloride penetration resistance on small unreinforced specimens in uncracked and cracked conditions is often performed through accelerated testing methods that involve the application of an external electrical voltage to force the migration of chloride ions. One of the advantages of this technique is that it is associated to a colorimetric analysis, that allows to highlight how the chloride penetration front is altered by the presence of a crack, and from that to calculate the chloride migration coefficient in correspondence of the crack [14-15]. The penetration of chlorides in concrete through migration, anyway, is not representative of what occurs on field. Furthermore, in the case of cracked concrete, the effect of crack on chloride penetration could be altered by a redistribution of current inside the specimen [15]. The medium-long term tests for chloride pure diffusion are more representative for chloride penetration in completely immersed concrete. The analysis that is typically associated to these tests is the sampling of concrete powders at different

depths followed by potentiometric titration, while rarely the colorimetric technique is performed. With powder sampling and titration, it is possible to evaluate the chloride content profile as a function of depth [5, 11, 12]. With this technique, however, it is more difficult to analyze cracked specimens, since it is difficult to take powder samples exactly in correspondence of the crack.

Finally, the difficulty in approaching this topic relies also in the quantification of the effects of cracks on the durability design parameters such as the chloride diffusion coefficient of concrete. In those cases where colorimetric analysis is performed after a pure diffusion exposure test, the authors mainly report the variation in the chloride penetration profile in correspondence of the crack [14], without determining the chloride diffusion coefficient. When dealing with powder collection and titration, a chloride diffusion coefficient can be evaluated, through the interpolation of chloride concentration profiles with Fick's second law. In this case, a huge variability of data has been reported in literature, depending also on the procedure adopted to collect powder samples. For instance, Mu *et al.* [5] performed a study on the effects of crack density on chloride penetration, simulating cracks through artificial notches (about 400 μm wide and 16 mm deep) in unreinforced concrete specimens, and, after chloride diffusion, a unique powder collection was performed on the whole surface of cracked concrete specimens. With this procedure, a significant influence of crack number on chloride diffusion was reported, with diffusion coefficient values more than doubled for single cracked concrete with respect to uncracked one, and more than ten times higher for crack number equal to 5. In other cases, concrete powders were collected in correspondence of the crack in order to evaluate a chloride diffusion coefficient as much as possible in correspondence of the crack [11, 12]. In these cases, reinforced mortar beams were subject to 3-point bending procedure in order to study the effects of a single load-induced crack on chloride penetration under loading. In [11], crack width of 300 μm was considered, leading to an increase in chloride diffusion coefficient of about 20% in correspondence of the crack with respect to the control (uncracked and unloaded) concrete. In [12], different crack widths were considered, and a constant increase of chloride diffusion coefficient was detected until a value of crack width equal to 135 μm, corresponding to a more than doubled diffusion coefficient with respect to uncracked conditions, and a more marked increase rate (more than ten-folded values) for wider crack widths. These results suggested that the durability of RC elements could be affected also by micro-cracks, characterized by crack widths lower than 100 μm, far below the threshold values reported in design codes and regulations for structural design. However, studies on this subject are very limited and do not allow to quantify the impact of cracks on the resistance to chloride penetration.

Further research is then needed in order to evaluate the effects of cracks on chloride penetration in concrete, and on design parameters such as the chloride diffusion coefficient, in particular investigating the possible effect of the testing procedure on results in correspondence of the crack. This work is part of a wider research program aimed at evaluating the effects of cracks on reinforced concrete durability. In this study, chloride penetration resistance of concrete was evaluated in uncracked and micro-cracked configurations, considering three different cement types and two w/c ratios. A specific cracking procedure, a sort of three-point bending procedure, was performed to obtain V-shaped, bending-induced micro-cracks on unreinforced specimens. Concrete specimens were subject to unidirectional pure diffusion of chlorides by immersion, for two different exposure times, and then were analyzed with two different analysis techniques, colorimetric and potentiometric titration, and subsequently chloride diffusion coefficients (by colorimetric and by titration) were derived. The results in correspondence of the crack were then analyzed as a function of crack geometrical parameters, *i.e.* crack width and crack depth.

2. Materials and methods

Specimens were realized with six different concrete mixes, considering three different cement types and two w/c ratios. The three cement types considered were an Ordinary Portland Cement (OPC), type CEM I 42.5R according to EN 197-1, a Portland-Limestone Cement (PLC), type CEM II/A-LL42.5R, and a Pozzolanic Cement (PC), type CEM IV/A(V) 42.5R-SR, containing an amount between 11 and 35% of pozzolanic materials, in prevalence siliceous Fly Ash. Three mixes were obtained with 422 kg/m^3 of cement, 1731 kg/m^3 of aggregates and 190 kg/m^3 of water (w/c ratio 0.45), while other three mixes were realized with 422 kg/m^3 of cement, 1619 kg/m^3 of aggregates and 232 kg/m^3 of water (w/c ratio 0.55). The aggregates were crushed and calcareous type, with maximum dimeter of 9 mm and subdivided into 5 grain size fractions. An acrylic-based superplasticizer was added to the 0.45 w/c mixes in order to improve workability. Details on mixing proportions and properties at fresh and hardened state for the different concrete types are reported in Table 1.

For each concrete mix, six cubic specimens, 100 mm side dimension, were realized in order to assess compressive strength, and six prismatic specimens, dimensions 120×90×50 mm in order to assess chloride penetration resistance. Of the six prismatic specimens, four were provided with a V-shaped notch, around 3 mm deep along the longitudinal direction on the casting surface, designed to promote the formation of a load-induced crack in the same position (Section 2.1). After casting, the specimens were covered with a plastic film, were demolded about 18 hours later, and placed in a curing chamber (temperature about 20°C and RH higher than 90%).

Compressive strength test was performed according to EN 12390-3 on two replicate cubic specimens after 7, 28 and 120 days of moist curing. The average compressive strength values are reported in Table 1, with Ordinary Portland always showing the highest compressive strength after 28 days of moist curing, followed by Pozzolanic and Portland-Limestone concrete types. A considerable increase of compressive strength was detected at 120 days of moist curing, above all for Pozzolanic concrete types, more pronounced for w/c ratio of 0.45.

All the prismatic specimens were cured for 28 days, and subsequently exposed to chlorides by immersion test, for two different exposure times.

2.1 Load-induced micro-cracking

A specifically developed loading procedure was applied to the specimens presenting the V-shaped notch, in order to obtain bending-induced micro-cracks in the longitudinal direction. The cracking procedure was performed within 24 hours after casting, by encasing the specimens in a confinement system and applying a load in a sort of three-point bending procedure. The specimens were in fact placed in a universal testing machine, with the notch facing downwards. Two rubber strips were used as lateral supports, parallel to the notch, and a further rubber strip was placed on the opposite face in correspondence of the notch. The load was applied with a displacement-controlled procedure, at constant rate of 0.5 mm/min, and was released when it reached a value 20% higher than the load corresponding to the first appearance of the crack on both sides of the specimen. At the end of the cracking procedure, the samples were then placed in the curing chamber.

In a previous study, this same procedure was proved to be effective in creating a V-shaped bending micro-crack, with a single crack opening in correspondence of the notch, and a single crack development, with crack depth smaller than the width of the specimen. More details on the cracking procedure and the characterization of cracks can be found in [15]. For this study, cracks were characterized on a concrete slice after the exposure to chlorides just close to the split surface, on the portion of specimen used for colorimetric technique (see next paragraph).

2.2 Chloride penetration resistance and crack characterization

After curing, all the prismatic specimens in uncracked and cracked configurations, were pre-conditioned and prepared for the immersion test according to EN 12390-11. Specimens were vacuum saturated with demineralized water and left immersed for 24 hours. Subsequently, all the surfaces, except the casting surface, were sealed with epoxy resin and, once the resin was set, immersed in a saturated calcium hydroxide solution for 18 hours. The specimens were then immersed in a 3% by mass sodium chloride solution, for two different exposure times, 32 and 90 days. For each concrete type, chloride penetration resistance was assessed on two replicate cracked specimens for each exposure time, and on two replicate specimens in uncracked configuration, that after being analyzed at 32 days of exposure were sealed again with epoxy resin and immersed for other 58 days.

At the end of the exposure time, each specimen was split with a hydraulic press, in order to assess the chloride penetration resistance through two different techniques (Figure 1). One piece was exploited to perform the *colorimetric technique*, by spraying a silver nitrate solution (0.1 M) on the freshly split surface, to highlight the chloride penetration profile. Chloride penetration depth was then measured with a caliper in seven different points, in correspondence of the central position and at a distance of 10, 20 and 30 mm on each side. In the case of cracked specimens, the central measurement was executed considering the maximum penetration depth in correspondence of the crack, starting from the tip of the notch. From the measurements of chloride penetration depth, the chloride diffusion coefficient evaluated through colorimetric technique, D_{col}, was estimated from the correlation proposed by Collepardi *et al.* [16], that considers the chloride penetration depth, *x*, proportional to the square root of time, *t*:

$$x = 4\sqrt{D_{col} \cdot t} \tag{1}$$

For *x,* the average value of chloride penetration depth for uncracked specimens and the maximum penetration depth in correspondence of the crack in cracked configuration, were considered.

The other piece of concrete specimen was used to collect powder samples and evaluate chloride concentration through *potentiometric titration*. Powder samples were collected by dry-drilling the specimens at five different depths, 0-5 mm, 5-10 mm, 10-15 mm, 15-20 mm, 20-25 mm (for concretes with *w/c* equal to 0.55 after 90 days of exposure also at 25-30 mm and 30-35 mm). In order to collect powders as much as possible in correspondence of the crack, a drill bit of 8 mm in diameter was used, and to collect enough powder for potentiometric titration (at least 3 grams) 5 different holes were performed for each depth, in correspondence of the notch (and therefore the crack). For uncracked specimens, the same procedure was kept, collecting powder samples as much as possible in the central part of the specimen, just enough away from the corners to avoid edge effects (the specimens were large enough to perform both the analyses, *i.e.* colorimetric and collection of powder samples, after two different exposure times). The powders were then dried in an oven at 105°C for at least 24 hours, to obtain the dry mass, dissolved in nitric acid and finally titrated using an automatic potentiometric titrator, model Mettler Toledo EasyPlus Titration. In order to evaluate the chloride diffusion coefficient through titration technique, D_{titr}, and the exposed surface chloride concentration, C_s, the profiles with chloride concentration at different depths were then interpolated (excluding the first point) according to Fick's second law for chloride diffusion [17]:

$$C(x,t) = C_S \left[1 - erf \left(\frac{x}{2 \sqrt{D_{titr} \cdot t}} \right) \right]$$ (2)

Where $C(x,t)$ is chloride concentration at depth x and time t, and erf is the error function.

The same piece of concrete specimen used for the colorimetric test was subsequently prepared for crack characterization, in order to derive the two main crack parameters, *i.e.* crack width and crack depth. To this purpose, the split surface was impregnated, at atmospheric pressure and room temperature, with a two-component epoxy resin characterized by low viscosity and mixed with a powdered dye. This procedure was performed in order to both highlight crack path and avoid as much as possible crack modifications during the cutting. After 24 hours a thin concrete slice, 2-3 mm from the split surface, was cut with a water-cooled cutting saw and polished with abrasive papers. The polished surface was then observed with a Wild M8 stereo microscope, equipped with a Leica DFC290 RGB digital camera. Images were acquired with Leica Application Suite software (LAS v4.9) and crack opening was evaluated as an average of 5-6 measurements, within the first millimeter from the exposed surface (estimated uncertainty ±1 μm). Crack depth was measured with a caliper from the exposed surface to the tip of the crack (estimated uncertainty ±0.5 mm).

3. Results and discussion

3.1 Crack geometrical parameters

In Figure 2 are reported the results in terms of crack width and crack depth for each concrete type and exposure time. Cracks were characterized by a crack width included in the range 10-75 μm, and a crack depth included in the range 5-45 mm. Substantially, an increasing trend of crack depth as a function of crack width was detected, even if the dispersion of data was high and no clear correlation could be found. Furthermore, no clear influence of concrete type and exposure time could be detected. These results are in line with those obtained in a previous study [15] where the same cracking procedure was adopted and an accelerated testing procedure was performed to evaluate chloride penetration resistance after 7 and 28 days of curing. In that case no consideration could have been made of the self-healing process of cracks, but the fact that in this study similar crack openings and crack depth were obtained in concrete specimens cured for 28 days and exposed for 32 and 90 days by immersion suggested that in both cases no significant self-healing occurred in cracks.

Cracks characterized by such narrow widths are in the range of micro-cracks (crack width < 0.1 mm), that can be comparable to those originated by drying-induced micro-cracking [18,19], with the difference that here just a single micro-crack is produced and analyzed, instead of a pattern of multiple, interconnected and randomly oriented micro-cracks.

3.2 Chloride penetration resistance

In Figure 3*a* and *b* are reported, as an example, the data obtained on OPC concrete with *w/c* ratio of 0.45 with the two analysis techniques, colorimetric and potentiometric titration, respectively. The data were obtained, for each exposure time, on two replicate specimens, both analyzed through the two analysis techniques.

Figure 3*a* shows the chloride penetration depth obtained at different exposure time as a function of the square root of time. Solid and dashed lines represent the mathematical interpolations used to

derive the chloride diffusion coefficients, D_{col}, according to Equation 1, whose values are reported in the legend. It can be noticed that for the uncracked specimen, a decrease in chloride penetration rate, and therefore of D_{col}, occurred over time, from 3.0 to $1.2 \cdot 10^{-12}$ m^2/s.

This effect was already detected [20] and is typically referred to as the so called *ageing effect*. However, data obtained after 32 and 90 days of exposure are not sufficient to quantify this effect, and further long-term tests are still underway to investigate this issue. In the cracked specimens, in general, the maximum chloride penetration depth, measured at a given exposure time, and the relative diffusion coefficient, D_{col}, exceeded the values measured on the uncracked specimens. The results were more difficult to be interpreted as a function of time, since different specimens with different crack parameters were used for different exposure times. Therefore, often, the chloride penetration depth in correspondence of the crack resulted lower in specimen analyzed after 90 days of exposure with respect to the one analyzed after 32 days of exposure, if the cracks had very different width and depth. For this reason, the effect of the crack on chloride penetration resistance will be further analyzed as a function of crack geometrical parameters in Paragraph 3.3.

Figure 3*b* shows the chloride concentration, expressed as percentage by mass of cement, obtained with potentiometric titration at different depth from the exposed surface. Solid and dashed lines represent the mathematical interpolations used to derive the chloride diffusion coefficients, D_{titr}, and chloride surface concentrations, C_s, according to Equation 2, whose values are reported in the legend. Considering both the uncracked and cracked specimens, the chloride concentration was higher for higher exposure time. However, with this technique the evaluation of the effect of the crack was more difficult. In general, for each exposure time, the chloride concentration in the cracked specimen exceeded, almost at every depth, the concentration in the uncracked one. However, the same was not valid for the trend of D_{titr}, that in cracked condition sometimes resulted lower than in uncracked one, as in the example reported in Figure 3*b*, at both the exposure times. This is due to the fact that the same interpolation was performed to evaluate at the same time both C_s ad D_{titr}, and in the case of cracked specimens often the significantly higher value of C_s led to a lower value of D_{titr} with respect to the uncracked specimens.

All the results obtained with colorimetric technique (D_{col}) and potentiometric titration (D_{titr} and C_s) are reported in Figure 4a and 4b, respectively, as average values of the two replicate specimens, error bars representing maximum and minimum values. Moreover, with colorimetric technique on cracked specimens it was also possible to evaluate a diffusion coefficient in the uncracked part, far from the crack (dotted bars in Figure 4a).

The results in sound configuration considering both the techniques and the exposure times showed that, at a constant w/c ratio, concretes made with pozzolanic cement (PC) offered highest resistance to chloride penetration, followed by concretes made with Portland cement (OPC) and finally Portland-limestone cement (PLC). This was expected, since pozzolanic concretes are known to provide a better pore refinement in the cement paste due to the pozzolanic reaction that is mainly responsible for the higher resistance to chloride penetration, and since they also have higher bounding capacity with respect to OPC concrete [21]. This effect was more marked for lower w/c ratio, and above all for higher exposure times. In fact, in Pozzolanic concrete occurred the highest reduction of D when going from 32 to 90 days of exposure, about 65% and 45% for w/c of 0.45 and 0.55 with colorimetric technique, and about 70% for both w/c ratios by titration.

For all the concrete types, an increase in the w/c ratio led always to an increase of D_{col} and D_{titr}, in general more marked for lower exposure time, and among the cement types, more marked for Portland-limestone cement. Finally, it can be noticed that with colorimetric technique the

reproducibility of data obtained on different uncracked specimens was higher, while D_{titr} obtained through potentiometric titration suffered of a higher dispersion.

The effect of micro-crack on chloride diffusion coefficient resulted more marked when considering D_{col} obtained through colorimetric technique. In this case, in fact, the average values in cracked conditions are 2 to 5 times higher than in sound conditions for concretes with w/c of 0.45, while a smaller increase of about 5-50% was recorded for concretes with w/c of 0.55. From the analyses with titration technique, as previously observed, the effect of the crack on the diffusion coefficient resulted less marked or even not significant. As it concerns colorimetric technique, results in uncracked and sound conditions were often very similar, and in those cases some differences were detected, these could only be attributed to the heterogeneity of concrete. To avoid high noise in further analyses of results when discussing the effect of cracks and crack geometrical parameters (Paragraph 3.4), the coefficient in uncracked conditions will be considered rather than that in sound conditions. A first overview on how the presence of a crack affects the diffusivity of chlorides in concrete can be derived analyzing the ratio between the diffusion coefficient in cracked condition and uncracked condition (D_{cr} / D_{uncr}), as a function of the diffusion coefficient in uncracked conditions, for each exposure time (Figure 5a and 5b). Despite at 32 days of exposure the noise in results is higher, for both the exposure times an increase in D_{cr} / D_{uncr} can be detected for decreasing values of D_{uncr}, above all for concretes with w/c ratio of 0.45. This may imply that the effect of the crack is more marked in more impervious concretes, that are typically designed to oppose a higher resistance to the penetration of aggressive substances such as chlorides

3.3 Comparison $D_{col} - D_{titr}$

In investigating the effect of cracks on the resistance to chloride penetration it was observed that the two analytic techniques presented advantages and disadvantages. The colorimetric technique is an easy, fast, and cheap technique, usually performed at the end of accelerated migration test (*e.g.* NT BUILD 492 [22]). It was proved in previous studies to be very powerful in highlighting how the chloride penetration front was locally altered by the presence of a crack, even if the crack was in the range of micro-cracks (width lower than 100 μm) [14, 15]. However, while in concrete subject to chloride migration the change in color in correspondence of the chloride penetration front appears very clear, the application of this technique to specimens subject to pure diffusion, as those analyzed in this study, gives as a result less clear distinction between the chloride penetrated and unpenetrated areas, as reported also by other authors [14]. Moreover, the $AgNO_3$ solution sprayed on the split surface leads to a change in color only when chlorides are higher than a certain threshold concentration (c_d), and this value was reported in previous studies in literature to be characterized by a high variability, depending on several factors such as the cement type and mix composition, the sprayed volume and concentration of $AgNO_3$ solution, the pore solution volume, and the techniques employed to collect powders and the chloride concentration in concrete for comparison [23]. Considering OPC concrete, for instance, $AgNO_3$ change in colour was reported to occur for amounts of total (acid soluble) chlorides included in the range 0.2–1% by mass of cement in [21, 24], while 0.4–0.5% by cement in [25]. Regarding the other types of concrete, in this study a Portland-limestone cement and a Pozzolanic cement (with mostly siliceous Fly ash) were employed. In Portland-limestone cement, the amount of clinker is replaced by unreactive limestone, even if no studies were found reporting c_d values for this type of cement, it could be assumed to be similar to that of OPC. Fly Ash concretes are typically considered to have a higher bounding capacity with respect to OPC concretes, due to a higher content of active aluminate in the binder, leading to the production of a higher amount of Friedel's salt, and a higher content of C–S–H gel [21]. Anyway, by comparing the

total chloride content corresponding to the change in colour of $AgNO_3$ for different cement types, in [26] a considerably lower value was found for the Fly Ash type, about 0.03-0.04% by mass of concrete, with respect to OPC type, which was about 0.17-0.18% by mass of concrete. It was reported, therefore, that $AgNO_3$ colorimetric technique was even more accurate for Fly Ash mixtures in detecting the chloride penetration depth, and consequently, also the diffusion coefficient (in that case migration coefficient from Rapid chloride migration test - D_{RCM}) was calculated for the accurate chloride penetration front, which was not affected by chloride bounding.

Finally, another critical aspect is the interpolation of data in order to derive a value of chloride diffusion coefficient. Since this parameter decreases in time, Collepardi proposed to interpolate together data coming from different exposure times, while in this work, each single exposure time has been considered independently. On the other hand, potentiometric titration is among the most accredited techniques to evaluate the chloride concentration at different depths in concrete and to derive a chloride diffusion coefficient through the interpolation according to Fick's second law of diffusion. The disadvantage related to this technique relies on the fact that a sufficient amount of powder needs to be sampled, as previously explained, and therefore in the case of micro-cracks could be not sensible enough to assess the increase in chloride penetration with respect to uncracked concrete. As it concerns interpolation with Fick's second law, the fact that the two parameters, C_s and D_{titr}, are derived from the same interpolation could also affect the results concerning the evaluation of the chloride diffusion coefficient. Finally, with this technique it is possible to evaluate just the diffusion coefficient related to a single exposure time. Based on these observations, it may reasonably be assumed that the colorimetric technique is more appropriate when attempting to quantify the effect of cracks on the resistance to chloride penetration in concrete.

In order to see if a correlation exists between the diffusion coefficient evaluated with the two techniques, Figure 6 reports D_{col} and D_{titr} for all the concrete types and exposure times considered, and for sound and cracked configurations. The values of D_{titr} showed systematically higher values than D_{col} values, about 3 to 10 times higher. One reason for this could be related to the fact that with titration acid-soluble (and therefore total) chlorides are evaluated, while with colorimetric technique the free-chlorides are considered. A good correlation was anyway found between D_{col} and D_{titr}. In Figure 6 data were interpolated with a power function and in the legend the values of R^2 are reported. A quite good correlation ($R^2=0.85$) was found for uncracked concretes considering a single interpolation for all the cement types, w/c ratios and exposure times. On the other hand, since the two different techniques gave very different results for cracked concretes with w/c of 0.45, the cracked concretes were individually interpolated for each w/c ratio. For w/c of 0.55 cracked concretes the interpolation was still quite good ($R^2=0.70$), but this could be due to the fact that for this w/c ratio the effect of micro-crack on chloride penetration was less pronounced (see later). For cracked concretes with w/c of 0.45, the effect of micro-crack was marked, but the correlation between the chloride diffusion coefficient evaluated with the two technique was less accurate ($R^2=0.16$).

Therefore, at least for uncracked configuration, and when the effects of cracks on chloride penetration are almost negligible, a good correlation between the diffusion coefficient evaluated through the two techniques subsists, and this could be useful to take better advantage of the colorimetric technique, also on field, since it is a much simpler, quicker, and cheaper with respect to powder sampling and potentiometric titration. It is worth mentioning, however, that even if colorimetric technique could allow to estimate a chloride diffusion coefficient, it is not possible with this technique to evaluate the concentration of chlorides in correspondence of rebar depth, to compare it with the critical chloride threshold and evaluate whether the reinforcement is still in passive conditions. Moreover, despite the

data in cracked configuration presented higher variability and therefore a lower R^2, the obtained correlations in the cases of cracked and sound concretes resulted rather comparable.

3.4 Effect of crack width and depth on chloride penetration resistance

Results obtained with the two techniques were further analysed to assess the effect of cracks on the chloride penetration resistance with respect to the crack geometrical parameters, crack width and crack depth.

The results in terms of maximum penetration depth evaluated through colorimetric technique were compared to the measurements of crack depth (Figure 7). It can be noticed that in many cases the maximum penetration depth of chlorides (X_{max}) was lower than crack depth (d_{cr}). In those cases, the chloride diffusion coefficient in cracked condition could be roughly considered as the diffusion coefficient evaluated in the crack (D_{crack}), while in the other cases the coefficient evaluated in cracked conditions was a combination of diffusion coefficient in the crack and in sound concrete after crack apex.

This was taken into account while evaluating the effects of cracks on chloride penetration resistance. In particular, Figure 8a and 8b show the increment of chloride diffusion coefficient in cracked conditions with respect to uncracked conditions ($D_{col,cr}$ / $D_{col,uncr}$), as a function of the two crack geometrical parameters, crack width and crack depth, respectively, and highlighted in red are those cases in which D_{crack} was evaluated.

From the results, it can be noted that most of the cases in which the crack was less deep than 15 mm and less wide than 30 micron the coefficient in cracked condition was a combination of the coefficient in the crack and beyond crack apex, while over those limits the chloride penetration did not reach crack apex. Considering all data, for cracks with crack opening included in the range 20−75 μm and crack depth around 10−45 mm, $D_{col,cr}$ / $D_{col,uncr}$ resulted around 1−2 for concretes with w/c of 0.55 (data included in dark grey area), while the increase in chloride diffusion coefficient resulted in general significantly higher for comparable cracks in concretes with w/c ratio of 0.45 (data in light gray area). More in detail, diffusion coefficients about 3 times higher were recorded for cracks about 10 to 50 μm wide and 10 to 30 mm deep, and up to 5−9 times higher for cracks 30-50 μm wide, and deeper than 30 mm. These results seem to imply that cracks, even with small width and shallow depth, can have a significant impact in concretes that are more impervious in uncracked conditions. This is in accordance with a previous study where an accelerated testing procedure was applied [15], and similar results have been also reported in other experimental [13] and numerical [27] studies on this topic. Furthermore, for concretes with w/c ratio of 0.45, independently from the cement type, the increase in the chloride diffusion coefficient in the crack seemed to have an increasing trend increasing crack width and crack depth, even if a clear correlation was not found.

Similarly, an attempt in quantifying the effect of cracks was also made considering the increase in the chloride diffusion coefficient in the crack with respect to sound conditions, evaluated through titration technique ($D_{titr,cr}$ / $D_{titr,s}$), and showed as a function of crack width and crack depth in Figure 9a and 9b, respectively. The values referred to D_{crack} in cracked conditions are those in which the last powder sampling was included in the depth of the crack and are shown in Figure 9a and 9b with light and dark blue symbols. In accordance with colorimetric results, also with this technique the increment in the chloride diffusion coefficient in cracked concretes with w/c of 0.55 resulted very limited, between 1 and 1.5 times higher than in sound conditions, while the effects resulted more significant for concretes with w/c of 0.45, where values up to 5 times higher were recorded.

The increase in diffusion coefficient evaluated through titration was anyway more limited with respect to the colorimetric technique. This could be due to the fact that the crack was always very

narrow, while to perform potentiometric titration a sufficient amount of concrete powder is needed (for this study a drill bit with Ø 8 mm was employed). The amount of chlorides found was therefore referred also in the uncracked concrete surrounding the crack, underestimating the amount of chlorides strictly present in the crack, and therefore the value of diffusion coefficient in correspondence of the crack. Moreover, when evaluating the chloride diffusion coefficient through potentiometric titration, two different but interrelated parameters are evaluated, *i.e.* C_s and D_{titr}. Titration technique resulted therefore less appropriate to define the effect of cracks on chloride penetration resistance of concrete.

In the attempt of decoupling the penetration of chlorides inside the crack and beyond crack apex, further analyses were carried out considering the additional penetration depth beyond crack apex (ΔX_{cr} in Figure 7a). ΔX_{cr} was evaluated as the difference between the maximum penetration depth (X_{max}) and crack depth (d_{cr}) and was compared to the average chloride penetration depth in the uncracked part of the specimen (X). Figure 10a and 10b show the difference $\Delta X_{cr}-X$ as a function of crack width and crack depth. In analogy with Figure 8, the cases in which the maximum penetration depth resulted lower than crack depth ($\Delta X_{cr}<0$) are shown in red colors. When considering $\Delta X_{cr}-X$, three cases may occur:

- If it is equal to zero the same penetration depth from crack apex than in the uncracked part beyond crack apex occurred, as if chlorides almost immediately arrived at crack apex, and the diffusion after crack apex was comparable to that in sound conditions.
- If it is higher than zero chlorides penetrated more from crack apex than in uncracked concrete, as if the presence of a crack promoted the chloride penetration with respect to uncracked conditions.
- If it is lower than zero then the penetration depth beyond crack apex was lower than in uncracked concrete. This could be explained considering the geometrical layout of the problem, since the micro-crack has a narrow opening, several orders of magnitude smaller than crack depth, and when chlorides penetrate inside the crack the diffusion occurs towards the apex but also in direction perpendicular to crack walls. The diffusion, therefore, is no more unidirectional in correspondence of the crack, and after crack apex, where chlorides do not diffuse in one direction as a quite homogeneous front such as in uncracked concrete, but in all directions in the area surrounding the tip of the crack.

From Figure 10a and 10b it can be observed that all the results are related to this last condition (lower penetration depths after crack apex than in uncracked concrete), and also in many cases a $\Delta X_{cr}<0$ was found. This effect seemed to be above all correlated to crack depth and to concrete w/c ratio. In fact, from Figure 10b, it seems that the more the crack is deep, the more the additional penetration depth is lower than the penetration depth in uncracked concrete, independently from the cement type and the exposure time also for those cases where the increment in the chloride diffusion coefficient was high. On the other hand, concretes with w/c ratio of 0.45 showed less negative values of $\Delta X_{cr}-X$ for comparable crack depth, meaning that the values of additional penetration depth were more similar to the penetration depth in the uncracked concrete. This was probably due to the fact that the diffusion in direction perpendicular to crack walls was lower (more impervious concrete), while diffusion towards crack apex was promoted. These results go in the same direction of what has been stated before, *i.e.* that cracks may have more pronounced effects on chloride penetration in more impervious concretes. A similar result was obtained under accelerated exposure conditions [15], being therefore independent from testing procedure. In that study, anyway, the penetration of chlorides was forced,

in the direction of the crack, through the application of an external electrical voltage, and almost in all cases a penetration depth further crack apex was found. In this study, natural diffusion occurred in all the directions, including perpendicularly to crack walls, and for the deepest crack the chloride penetration profile was almost always less deep than crack apex (red symbols). It is worth noting, anyway, that this does not necessarily mean that no chlorides were present after crack apex, since the change in color of silver nitrate used for the colorimetric technique is visible only when chlorides are in an amount higher than a certain threshold.

With the same aim, a similar analysis was also performed processing data in terms of chloride concentration from potentiometric titration technique, which is more suitable to detect the effect of the crack rather than the evaluation of the diffusion coefficient. In this case, the difference in chloride concentration between the chloride concentration in correspondence of crack apex and the chloride concentration in the outermost layer in uncracked conditions (ΔCl^-) was evaluated. This was possible only when the measured crack depth resulted lower than the depth of powder sampling, hence those specimens where this condition was not satisfied were not taken into consideration. Figure 11a and 11b show the results obtained, as a function of crack width and crack depth, respectively. Also in this case, most of the results are below zero, indicating that a lower concentration of chlorides was detected beyond crack apex than in uncracked concrete. This difference seemed to be more correlated to crack depth than crack width, and concretes with 0.45 w/c ratio showed, for comparable crack parameters, less negative ΔCl^- values, meaning that after crack apex a more similar amount of chlorides was found with respect to sound conditions. It could be derived, in accordance with the results found through colorimetric technique, that a higher effect of the crack occurs in more impervious concretes. Anyway, this was also a consequence of the fact that independently from the concentration of chlorides in correspondence of crack apex, the amount of chlorides in the outermost layer in sound conditions for concretes with higher w/c ratio were significantly higher than those in lower w/c concretes.

4. Conclusions

In this study, the chloride penetration resistance was investigated in six different types of concrete, made with Portland, Portland-limestone and Pozzolanic cement and two different w/c ratios, 0.45 and 0.55. Specimens were analyzed under uncracked conditions and in presence of a micro-crack, obtained with a specific loading procedure. They were then subject to chloride pure diffusion for two exposure times, 32 and 90 days, and subsequently analyzed through two different techniques, colorimetric and potentiometric titration. The following results can be outlined.

1. Considering both techniques applied to uncracked configuration, at a constant w/c ratio concretes made with pozzolanic cement showed higher resistance to chloride penetration, followed by concretes made with Portland cement and Portland-limestone cement. A good correlation was found between the chloride diffusion coefficients evaluated through colorimetric technique and potentiometric titration in the case of uncracked concrete, independent from cement type, w/c ratio and exposure time. This could be useful to take better advantage of the colorimetric technique, also on field, as an easiest, less time consuming and cheaper technique to estimate a chloride diffusion coefficient.

2. Micro-cracks were characterized by 10-75 μm crack width and 5-45 mm crack depth. An increase in chloride diffusion coefficient in correspondence of the crack was always detected, above all for concretes with 0.45 of w/c ratio, and in particular with colorimetric technique. Due to some technical aspects related to the powder sampling and potentiometric titration, probably

with this technique the effects of micro-cracks were underestimated. In cracked configuration a higher dispersion of data was detected but the correlation between results obtained through the two techniques gave a similar trend with respect to the uncracked configuration.

3. With colorimetric technique, the chloride diffusion coefficient evaluated in correspondence of the crack resulted just 1-2 times higher than in uncracked conditions for concretes with 0.55 w/c ratio, while, for comparable crack width and crack depth, an increase up to 3 and even 9 times was recorded for w/c 0.45 concretes. With titration technique similar results were obtained for concretes with w/c of 0.55, while an increase up to 5 times was detected for concretes with w/c of 0.45. In none of the cases, anyway, a clear correlation was found between the increase in diffusion coefficient in cracked configuration and crack geometrical parameters (*i.e.* crack width and crack depth), not even in those cases where the chloride diffusion coefficient in cracked condition could be roughly considered as the diffusion coefficient evaluated in the crack.

4. An attempt was made in order to decouple the penetration of chlorides inside the crack and beyond crack apex. With colorimetric technique this was done by comparing the additional penetration depth from crack apex with respect to the penetration depth in uncracked condition, while with titration technique, comparing the chloride concentration after crack apex with chloride concentration on the outermost layers. From both the analyses, the effect of a micro-crack on chloride diffusion seemed to be higher for more impervious concretes, and more correlated to crack depth than crack width.

References

[1] L. Bertolini, B. Elsener, P. Pedeferri, E. Redaelli, R. Polder, Corrosion of steel in concrete – Prevention, diagnosis, repair. Second ed., Weinheim: Wiley VCH, 2013.

[2] ACI Committee 201 (2016) ACI 201.2R-16 guide to durable concrete. American Concrete Institute, Indianapolis

[3] K. Audenaert, G. De Schutter, L. Marsavina, The influence of cracks on chloride penetration in concrete structures - Part I: Experimental evaluation, in: K. Audenaert, L. Marsavina, G. De Schutter (Eds.), Transport mechanisms in cracked concrete, Acco, 2007, pp. 35-43.

[4] L. Marsavina, K. Audenaert, G. De Schutter, N. Faur, D. Marsavina, Experimental and numerical determination of the chloride penetration in cracked concrete, Constr Build Mater. 23, No. 1 (2009) 264-274.
https://doi.org/10.1016/j.conbuildmat.2007.12.015

[5] S. Mu, G. De Schutter, B.G. Ma Non-steady state chloride diffusion in concrete with different crack densities. Mater. Struct. 46(1–2) (2013) 123–133.
https://doi.org/10.1617/s11527-012-9888-0

[6] Y. Li, X. Chen, L. Jin, R. Zhang, Experimental and numerical study on chloride transmission in cracked concrete, Constr Build Mater. 127 (2016) 425-435.
https://doi.org/10.1016/j.conbuildmat.2016.10.044

[7] A. Djerbi, S. Bonnet, A. Khelidj, V. Baroghel-bouny, Influence of traversing crack on chloride diffusion into concrete, Cem. Concr. Res. 38 (2008) 877-883.
https://doi.org/10. 1016/j.cemconres.2007.10.007

[8] S.Y. Jang, B.S. Kim, B.H. Oh, Effect of crack width on chloride diffusion coefficients of concrete by steady-state migration tests, Cem. Concr. Res. 41 (2011) 9-19.
https://doi.org/10.1016/j.cemconres.2010.08.018

[9] S.S. Park, S.J. Kwon, S.H Jung, Analysis technique for chloride penetration in cracked concrete using equivalent diffusion and permeation, Constr Build Mater. 29 (2012) 183-192.
https://doi.org/10.1016/j.conbuildmat.2011.09.019

[10] M. Ismail, A. Toumi, R. Francois, R. Gagne, Effect of crack opening on the local diffusion of chloride in cracked mortar samples, Cem. Concr. Res. 38 (2008) 1106–1111.
https://doi.org/10.1016/j.cemconres.2008.03.009

[11] N. Gowripalan, V. Sirivivatnanon, C.C. Lim Chloride diffusivity of concrete cracked in flexure. Cem. Concr. Res. 30(5) (2000) 725–730.
https://doi.org/10.1016/S0008-8846(00)00216-7

[12] M. Şahmaran, Effect of flexure induced transverse crack and self-healing on chloride diffusivity of reinforced mortar, J. Mater. Sci. 42 (2007) 9131–9136.
https://doi.org/10.1007/ s10853-007-1932-z

[13] J. Weiss, J. Couch, B. Pease, P. Laugesen, M. Geiker, Influence of Mechanically Induced Cracking on Chloride Ingress in Concrete, J. Mater. Civ. Eng. 29(9) (2017) 04017128.
https://doi.org/10.1061/(ASCE)MT.1943-5533.0001922

[14] I.S. Yoon, E. Schlangen, Experimental examination on chloride penetration through micro-crack in concrete. KSCE J. Civ. Eng. 18, No.1 (2014) 188-198.
https://doi.org/10.1007/ s12205-014-0196-9

[15] N. Russo, M. Gastaldi, P. Marras, L. Schiavi, A. Strini, F. Lollini, Effects of load-induced micro-cracks on chloride penetration resistance in different types of concrete, Mater. Struct. 53 (2020) 143.

https://doi.org/10.1617/s11527-020-01580-y

[16] M. Collepardi, A. Marcialis, and R. Turriziani, La cinetica di penetrazione degli ioni cloruro nel calcestruzzo. Il Cemento, 67 (1970) 157-164.

[17] M. Collepardi, A. Marcialis, R. Turriziani, Penetration of chloride ions into cement pastes and concretes, J. Am. Ceram. Soc. 55 (1972) 534. https://doi.org/10.1111/j.1151-2916.1972.tb13424.x

[18] H.S. Wong, M. Zobel, N.R. Buenfeld, R.W. Zimmerman, Influence of the interfacial transition zone and microcracking on the diffusivity, permeability and sorptivity of cement-based materials after drying. Mag. Concr. Res. 61(8) (2009) 571–589.

[19] Z. Wu, H.S. Wong, N.R. Buenfeld, Influence of drying-induced microcracking and related size effects on mass transport properties of concrete. Cem. Concr. Res. 68 (2015) 35–48. https://doi.org/10.1680/macr.2008.61.8.571

[20] M. Collepardi and S. Biagini, Effect of water/cement ratio, pozzolanic addition and curing time on chloride penetration, in: Proceedings of the ERMCO '89, Stavanger, Norway, 1989, pp. 606-615.

[21] Baroghel-Bouny, V., Belin, P., Maultzsch, M., & Henry, D. (2007). AgNO$_3$ spray tests: advantages, weaknesses, and various applications to quantify chloride ingress into concrete. Part 1: Non-steady-state diffusion tests and exposure to natural conditions. Mater. Struct., 40(8), 759-781.

[22] NT BUILD 492, Concrete, mortar and cement-based repair materials: chloride migration coefficient from non-steady state migration experiments. Nordtest, Espoo (Finland), 1999.

[23] He, F., Shi, C., Yuan, Q., Chen, C., & Zheng, K. (2012). AgNO$_3$-based colorimetric methods for measurement of chloride penetration in concrete. Constr Build Mater., 26(1), 1-8.

[24] Baroghel-Bouny, V., Belin, P., Maultzsch, M., & Henry, D. (2007). AgNO$_3$ spray tests: advantages, weaknesses, and various applications to quantify chloride ingress into concrete. Part 2: Non-steady-state migration tests and chloride diffusion coefficients. Mater. Struct., 40(8), 783-799.

[25] Otsuki, N., Nagataki, S., & Nakashita, K. (1992). Evaluation of AgNO$_3$ solution spray method for measurement of chloride penetration into hardened cementitious matrix materials. Materials Journal, 89(6), 587-592.

[26] V.Elfmarkova, P. Spiesz, H.J.H. Brouwers, Determination of the chloride diffusion coefficient in blended cement mortars. Cem. Concr. Res. 78 (2015) 190-199.

[27] S.D. Abyaneh, H.S. Wong, N.R. Buenfeld, Simulating the effect of microcracks on the diffusivity and permeability of concrete using a three-dimensional model. Comput. Mater. Sci. 119 (2016) 130–143.

	OPC45	PLC45	PC45	OPC55	PLC55	PC55
Cement (kg/m^3)	422	422	422	422	422	422
Water (kg/m^3)	190	190	190	232	232	232
Aggregate (kg/m^3)	1731	1731	1731	1619	1619	1619
w/c ratio	0.45	0.45	0.45	0.55	0.55	0.55
Superplasticizer (% wt. vs cem)	0.47	0.30	0.36	-	-	-
Slump (mm)	130	170	165	150	165	150
Density (kg/m^3)	2496	2526	2477	2466	2413	2399
$f_{c,cube,7days}$ (MPa)	54.0	56.9	54.6	46.5	38.3	38.8
$f_{c,cube,28days}$ (MPa)	76.9	60.8	67.4	53.9	44.8	50.4
$f_{c,cube,120days}$ (MPa)	86.9	76.8	81.4	60.2	52.4	59.6

Table 1. Mixing proportions and properties for different concrete types.
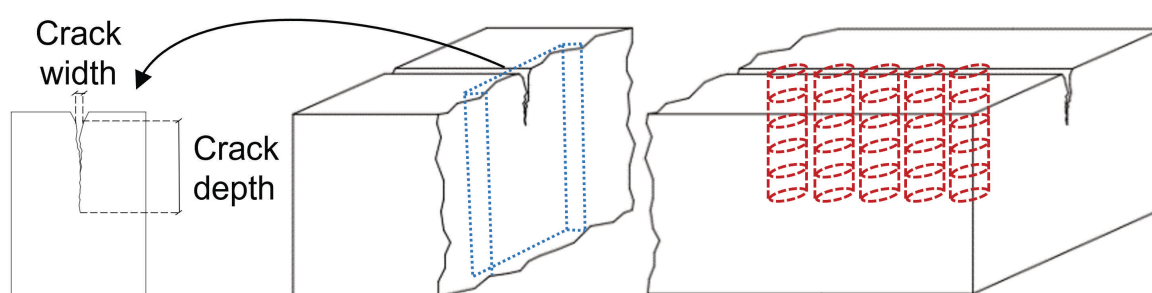
Figure 1 – Cracked concrete specimen analyzed after the exposure to chlorides, with colorimetric technique (left piece) and potentiometric titration (right piece), dashed lines representing drilling holes for powder sampling, dotted lines indicating saw cutting for crack characterization.
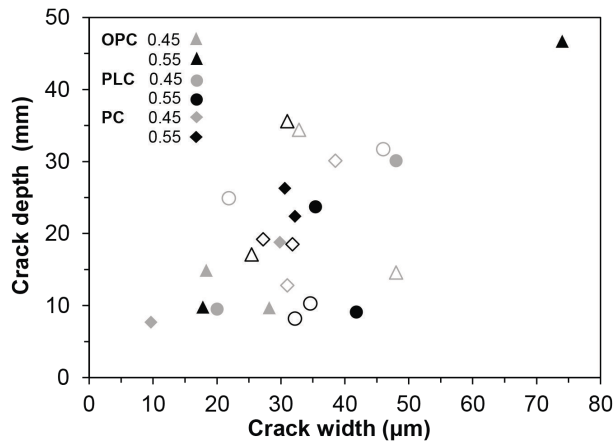
Figure 2 – Crack parameters, width and depth, for the different cement types, grey and black symbols representing *w/c* ratio of 0.45 and 0.55, respectively, filled and empty symbols representing 32 and 90 days of exposure, respectively (identical symbols indicate replicate specimens).
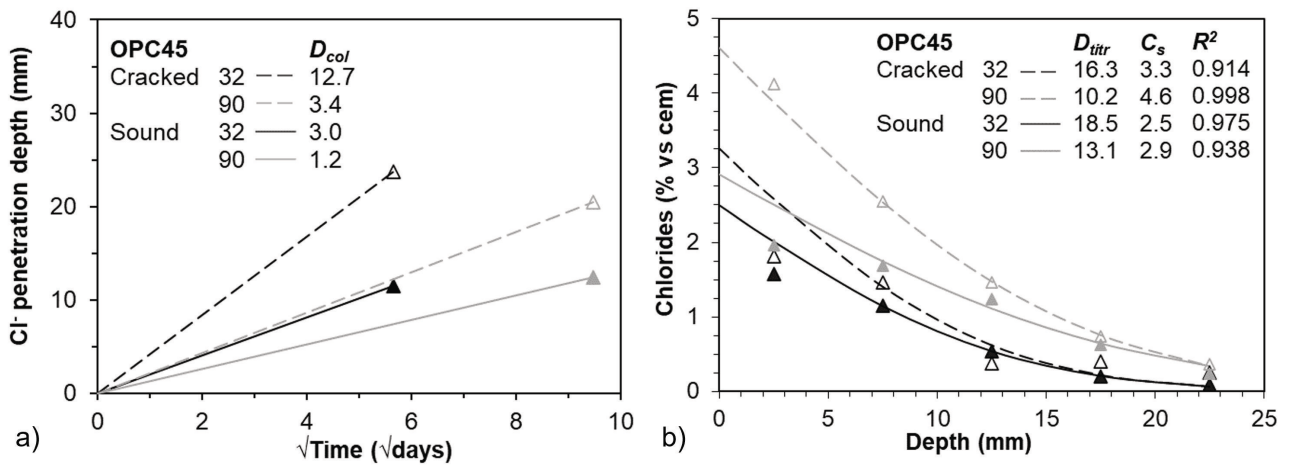
Figure 3 – Example of interpolation of data obtained with (a) colorimetric technique and (b) potentiometric titration, for some specimens in OPC, w/c 0.45; D_{col} and D_{titr} expressed in ($\cdot 10^{-12}$ m^2/s), C_s in (% vs cem).
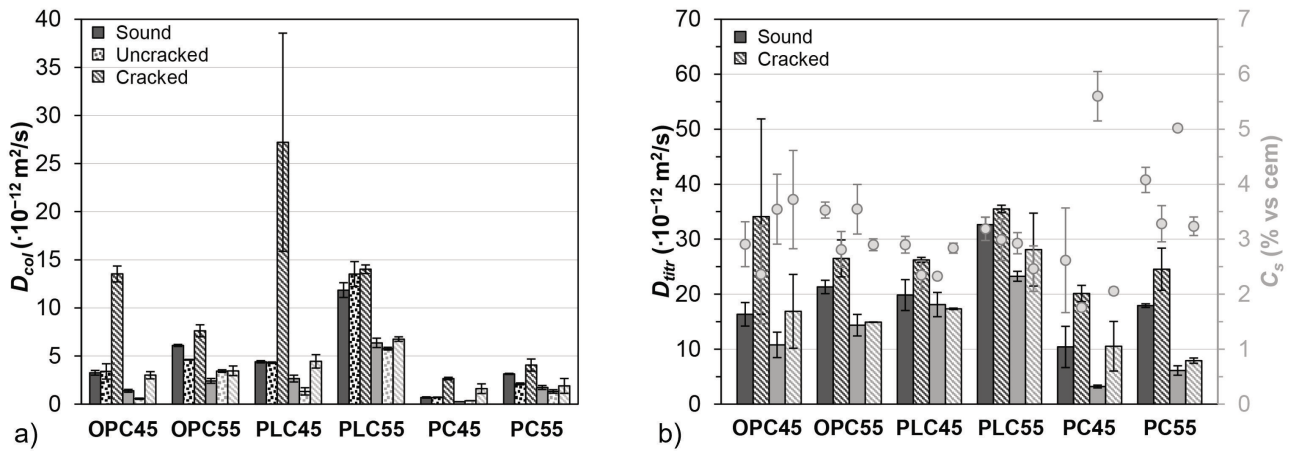
Figure 4 – (a) Diffusion coefficient evaluated through colorimetric technique (D_{col}) for the different concrete types, in sound (solid), uncracked (dotted) and cracked (hatched) configurations and (b) diffusion coefficient (D_{titr}, *bars*) and superficial chloride concentration (C_s, *dots*) evaluated through titration technique for the different concrete types, in sound (solid) and cracked (hatched) configurations; exposure time 32 days (darker) and 90 days (lighter).
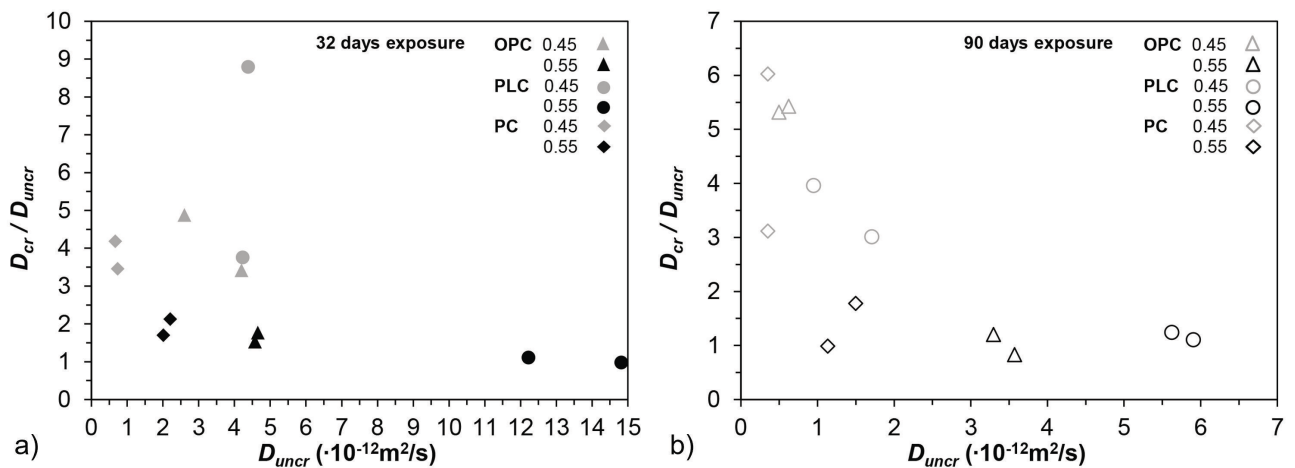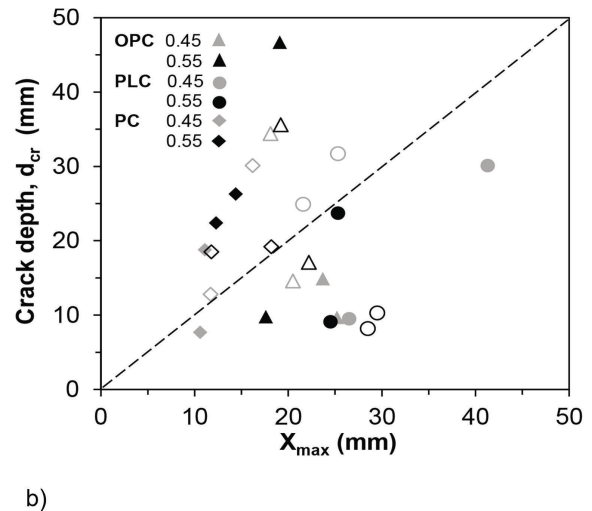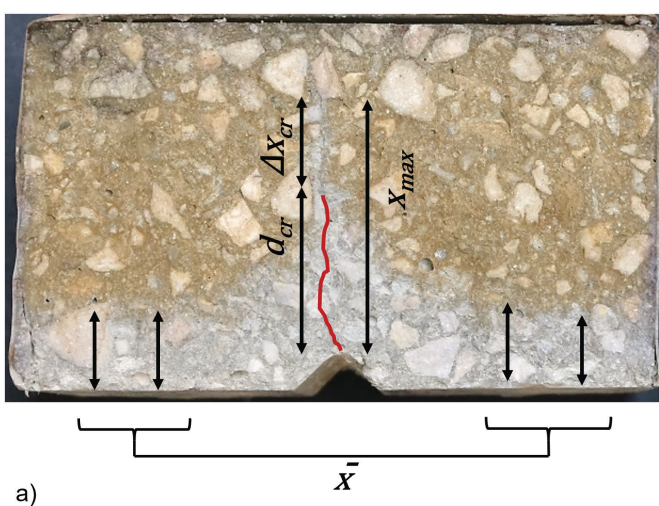

Figure 5 – Increment of diffusion coefficient evaluated through colorimetric technique in cracked conditions with respect to uncracked conditions (D_{cr}/D_{uncr}) as a function of diffusion coefficient in uncracked condition, after (*a*) 32 and (*b*) 90 days of exposure.
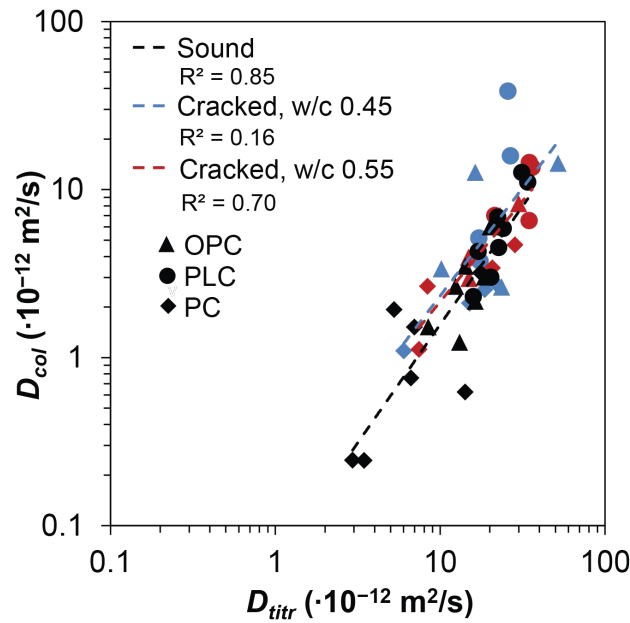
Figure 6 – Relationship between diffusion coefficient evaluated through colorimetric technique (D_{col}) and titration technique (D_{titr}) for the different concrete types; black symbols representing sound configuration for both w/c ratios, for cracked configuration blue symbols representing concretes with w/c of 0.45 and red symbols concretes with w/c of 0.55.


a)

b)

Figure 7 – (a) Result of colorimetric procedure on a PLC45 specimen after 32 days of exposure and parameters considered for the evaluation of the additional chloride penetration in the crack; (b) Comparison between maximum penetration depth (X_{max}) and crack depth for all cracked specimens, filled and empty symbols representing 32 and 90 days of exposure, respectively.
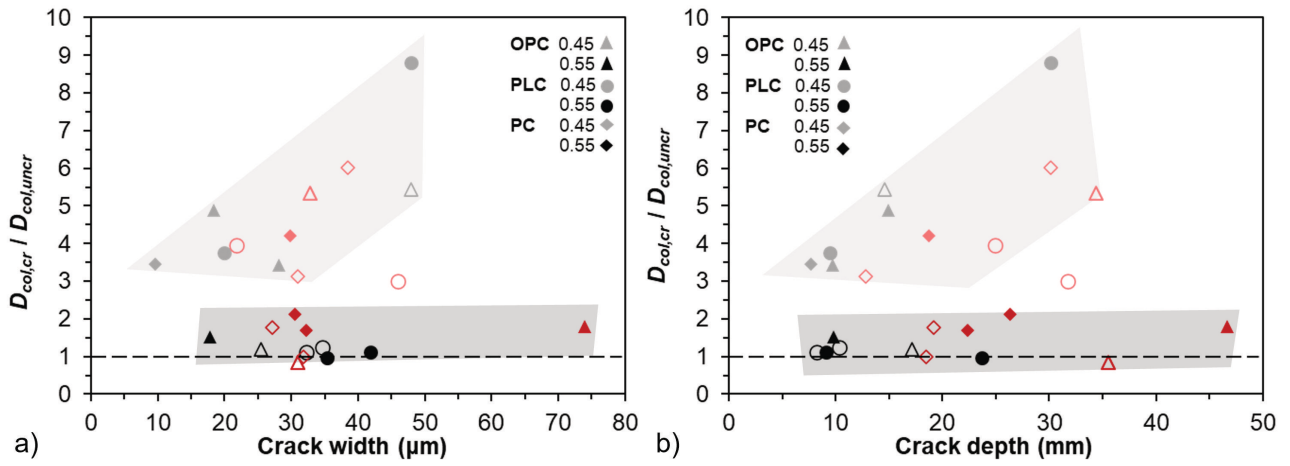
Figure 8 – Increment of diffusion coefficient evaluated through colorimetric technique in cracked conditions with respect to uncracked conditions ($D_{col,cr}/D_{col,uncr}$) as a function of (*a*) crack width and (*b*) crack depth; filled and empty symbols representing 32 and 90 days of exposure, and light and dark red symbols referred to D_{crack} for 0.45 and 0.55 specimens, respectively.
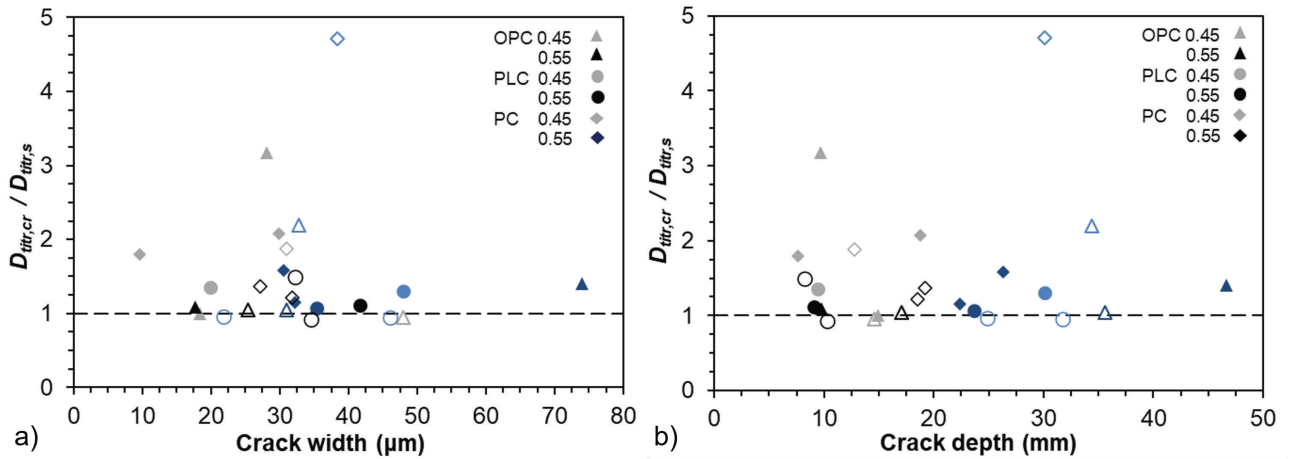
Figure 9 – Increment of diffusion coefficient evaluated through titration technique in the crack with respect to sound conditions ($D_{titr,cr}/D_{titr,s}$) as a function of (*a*) crack width and (*b*) crack depth; filled and empty symbols representing 32 and 90 days of exposure, and light and dark blue symbols referred to D_{crack} for 0.45 and 0.55 specimens, respectively.
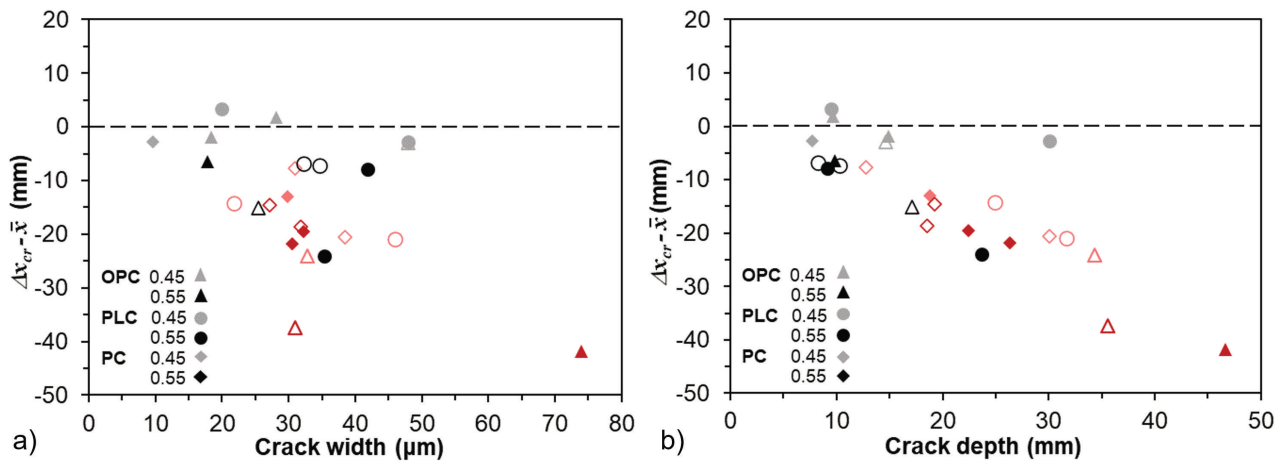
Figure 10 − Difference between the additional penetration depth in the crack and the average penetration depth in uncracked part (Δx_{cr}-$\bar{x}$) as a function of (*a*) crack width and (*b*) crack depth; filled and empty symbols representing 32 and 90 days of exposure, and light and dark red symbols referred to the cases $\Delta x_{cr} < 0$ for 0.45 and 0.55 specimens, respectively.
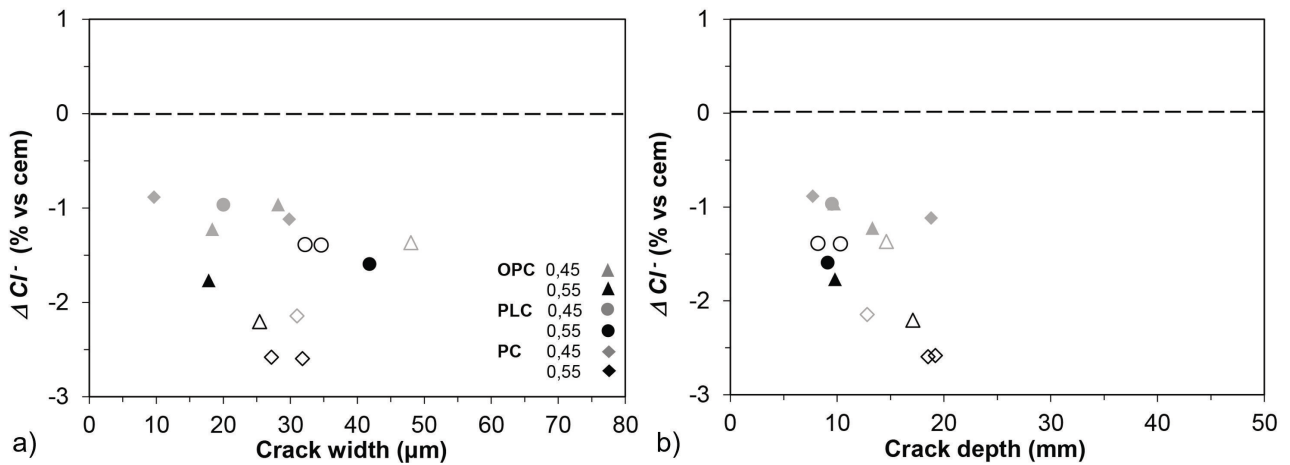
Figure 11 − Difference between the chloride concentration at crack apex and near the exposed surface in uncracked condition (ΔCl^-) as a function of (*a*) crack width and (*b*) crack depth; filled and empty symbols representing 32 and 90 days of exposure, respectively.