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# Chloride penetration into concrete structures in the marine atmosphere zone – Relationship between deposition of chlorides on the wet candle and chlorides accumulated into concrete

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#### **Abstract**

The relationship between chlorides from marine aerosol and chlorides accumulated into concrete is discussed in this paper. The experimental programme comprised an environmental characterisation, with climatic and chloride deposition data, and a study of chloride penetration into concrete based on natural exposure of specimens in a marine atmosphere zone. Results show that salt concentration in marine aerosol strongly decreases in the first meters from the sea. Chlorides present in the atmosphere can be studied using the wet candle method and correlated with chlorides accumulated into concrete. This relationship can be represented by the equation  $C_{\text{tot}} = C_0 + k_{\text{d}} \cdot \sqrt{D_{\text{ac}}}$ , where  $k_{\text{d}}$  is a coefficient which depends on concrete and environmental characteristics,  $C_{\text{tot}}$  is the average total amount of chlorides accumulated into concrete,  $C_0$  is the chloride content in concrete before exposure and  $D_{\text{ac}}$  is the accumulated dry deposition of chlorides.

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#### 1. Introduction

The degradation of concrete structures in marine environments is a world-wide problem with potentially large impacts on a country's economy. The influence of the environment and concrete characteristics on chloride transport into concrete has been studied by the scientific community for several years. The effect of variables like cement composition, pozzolanic additions, temperature and saturation degree of concrete pores on chloride transport has been analysed [1–6]. Mathematical modelling of chloride penetration into concrete represents another group of works

that addressed this matter, where either analytical or numerical models are proposed [7–10].

Most publications on this subject have laboratory studies as references. However, in general, laboratory conditions did not accurately represent real conditions, where influencing parameters act simultaneously. There are few works developed under real conditions and many of them consider either the underwater structures or structures in tidal zones [11–13]. The interaction of chlorides from marine aerosol with real structures built inland has been studied even less [14–16].

Marine aerosol is mainly generated along the seashore by breaking waves movement and is carried inland by wind [17]. When wind speed increases, there is an increase in both the number of marine particles generated and the percentage of larger drops in the aerosol spectrum [17,18]. As a consequence, salt concentrations exponentially increase with wind speed [17,19,20].

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When transporting marine aerosol inland, wind also plays an important role. Stronger winds enable larger particles to cover longer distances before settling [20,21]. Thus, higher salt concentrations can be observed at the same distance from the sea when wind speed increases [20,22]. This effect weakens at distances farther from the sea, where larger particles are less numerous, due to the gravimetric effect. As a consequence, it remains a strong tendency for sea salt concentrations to decrease inland [20,23–25]. This can be observed in Fig. 1, which shows the relationship between chloride deposition measurements and distance from the sea in different countries [25–27].

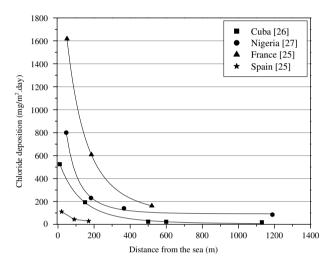


Fig. 1. Relationship between chloride deposition from marine aerosol and distance from the sea.

Deposition measurements are a common way to analyse salt presence in marine atmosphere zone. The wet candle device is usually used for this purpose, as part of standardized procedures to measure the amount of chloride salts which is captured from the atmosphere on a prescribed exposed area of the apparatus [28].

A similar decrease tendency for the total amount of chlorides that penetrate into concrete structures built in marine atmosphere zone was also observed in previous studies carried out under natural exposures [15,16]. Decreases of near 70% on chloride penetration into concrete were observed in the first hundred meters from the sea [15]. However, these findings still represent few data about this phenomenon and did not make significant advances to establish direct relationships between chlorides from marine aerosol and their interaction with concrete structures.

This paper focuses on this gap in knowledge and discusses the relationship between chlorides from marine aerosol and those accumulated into concrete structures located at different sites in a marine atmosphere zone in a tropical region in the northeast of Brazil. An empirical model to represent the relationship between chloride deposition on the wet candle device and the average total amount of chlorides accumulated into concrete is proposed.

# 2. Experimental work

The experimental work was divided in two parts. The first one focused on the environmental characterisation and the second concentrated on studying chloride concentrations

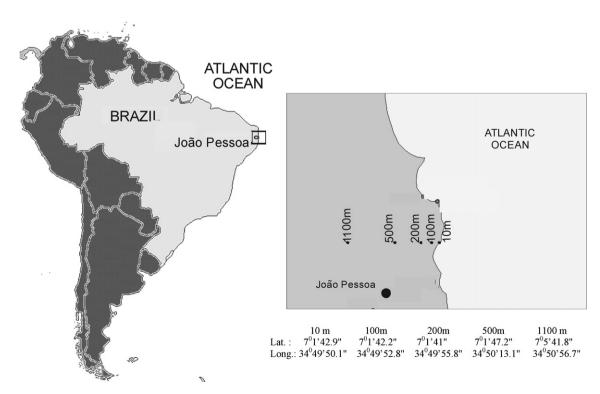


Fig. 2. Region where the experimental work took place and geographical coordinates of monitoring stations.

in concrete. This stage was performed in João Pessoa city, which is located in the northeast of Brazil (Fig. 2).

#### 2.1. Environmental characterisation

The environmental characterisation comprised climatic and chloride deposition data. The climatic data were collected by a weather station, which belongs to the Brazilian Government and which is located 1.1 km from the sea, at the same place as one of the monitoring stations. Temperature, relative humidity and rainfall data were collected by using a psychrometer and a pluviometer, respectively. Wind direction and wind speed data were obtained using a universal anemograph. The UTC references were followed.

The chloride dry deposition rate is a parameter which has been used to study the presence of salts in marine environment and has supported some studies about atmospheric corrosion [25–27,29]. In this work, the chloride dry deposition rate was measured at five monitoring stations placed at sites 10, 100, 200, 500 and 1100 m from the sea (Fig. 2) in order to characterise inland transportation of marine aerosol. In this case, it is important to elucidate that chloride deposition means the chlorides deposited on a retaining device while marine aerosol is transported inland.

The area chosen for the experimental work was as flat as possible, to avoid significant variations in height, and free of obstacles to reduce the effect of ground roughness in the measured data. At each station, a wet candle device was installed according to the specifications established by the American Society for Testing Materials (ASTM) G140 [28]. Liquid samples from each wet candle device were collected monthly and analysed by potentiometric titration with silver nitrate solution 0.05 M. This procedure was repeated throughout the research period.

### 2.2. Study of chloride concentration in concrete

Prismatic concrete specimens of  $0.15 \times 0.15 \times 1.40$  m were cast using Brazilian cements CPIV (Portland pozzola-

Table 1 Chemical composition and physical properties of cements

Composition/property	Cement I	Cement II	
SO <sub>3</sub> (%)	2.96	3.21	
SiO <sub>2</sub> (%)	29.34	18.11	
Al <sub>2</sub> O <sub>3</sub> (%)	5.72	4.31	
Fe <sub>2</sub> O <sub>3</sub> (%)	2.40	2.27	
CaO (%)	48.40	59.87	
MgO (%)	3.44	3.61	
Na <sub>2</sub> O (%)	0.37	0.21	
K <sub>2</sub> O (%)	2.17	1.51	
Insoluble residue – IR (%)	22.67	1.45	
Loss on ignition – LI (%)	4.18	5.50	
C <sub>3</sub> A content (%)	5.40	6.80	
Natural pozzolan content (%)	25.4	_	
Blaine (cm <sup>2</sup> /g)	4820	3650	
Specific density (g/cm <sup>3</sup> )	2.98	3.06	

nic) and CPIIF (Filler-modified Portland), with chemical composition presented in Table 1, and specified as cement I and cement II, respectively. Water to cement ratios (w/c) were set at 0.65, 0.57 and 0.50, composing the concrete mixtures C1–C6 presented in Table 2. This range of w/c was adopted to permit significant measurements in a shorter exposure time. Compressive strength and concrete slump were measured, following the specifications established by the Brazilian Association of Technical Standards [30,31]. Concrete porosity was measured by mercury intrusion porosimetry. Samples taken from the concrete specimens after 180 days of exposure time were used for this purpose. These properties are also presented in Table 2.

The specimens were cured in a wet chamber for 7 days and, afterwards, their first 40 cm, which constitute the underground part, were covered with an impermeable asphalt membrane to prevent the possibility of wicking effect from the ground. Then, they were placed at sites 10, 100, 200 and 500 m from the sea (Fig. 2), at the same monitoring stations used for measuring chloride deposition, and the non-waterproofed part of the specimens (1 m) was exposed to the marine environment. The monitoring station at 1100 m from the sea was not used to study chloride concentration in concrete. After 6, 10, 14 and 18 months of exposure, cylindrical samples were extracted from the specimens to obtain chloride profiles in concrete.

The cylindrical samples had a 7.0 cm diameter and were obtained by drilling from the prismatic specimens at levels between 0.35 and 0.85 m from the ground. The direction of coring was parallel to the historically established predominant wind direction. Care was taken to avoid washing effect on specimen surfaces, protecting them with a waterproof tape during drilling. The first millimetre of each core was powdered and was used as a surface sample. Additional samples, also powdered, were taken up to the depth of 30 mm from six layers of 5 mm in the first extraction and nine layers of 3, 3, 2, 2, 3, 3, 4, 5 and 5 mm thickness, in the last three sample extractions. For each sample, the total chloride content was determined by potentiometric titrations, following the procedures of the International Union of Laboratories and Experts in Construction Materials, Systems and Structures (RILEM) [32].

Table 2 Concrete mixtures and properties

concrete mixtures una proj	oci ties					
Concrete:	C1	C2	C3	C4	C5	C6
Cement type:	I	I	I	II	II	II
Cement (kg/m <sup>3</sup> )	320	356	406	320	356	406
Sand (kg/m <sup>3</sup> )	840	812	769	840	812	769
Aggregate (kg/m <sup>3</sup> )	947	947	947	947	947	947
Plasticiser (kg/m <sup>3</sup> )	_	1.06	1.22	_	1.06	1,22
w/c ratio	0.65	0.57	0.50	0.65	0.57	0.50
Slump (cm)	$9\pm1$	$8\pm1$	$8\pm1$	$8\pm1$	$8\pm1$	$8 \pm 1$
Compressive strength (MPa) – 28 days	21.0	26.9	32.0	20.3	27.0	31.0
Total porosity (mercury intrusion porosimetry – 180 days) – γ (vol.%)	15.5	13.8	12.8	15.7	13.7	13.0

#### 3. Results

The results are presented in two sections. The first one focuses on the environmental characteristics and the second on chloride profiles. During this experimental study, several chloride profiles were obtained, which are fully described in another document [23]. Here, only representative profiles of each analysed case are presented.

#### 3.1. Environmental characteristics

The region chosen for the experimental work is representative of a typical tropical climate. The local temperature shows little variation, roughly ranging from 20 to 30 °C. The relative humidity usually stays between 60% and 80%, with higher values during longer periods of rainfall. Periods of heavy rainfall occur from March to June, with a significant increase in June. Mild winds characterise the region where the research took place. Monthly average values of wind speed remained between 2.3 and 3.6 m/s and predominant winds were from the quadrant S-E. More detailed climatic data can be accessed in a previous published paper [24].

The results of chloride deposition on the wet candle (D) are shown in Fig. 3. The data show a clear fall off of airborne salinity in the first meters from the sea, which agrees with previous published data that show decrease rates roughly ranging between 85% and 95% in the first 500 m [26,27]. In the present case, the decrease of D values is stronger in the first two hundred meters from the sea. After this region, there are also differences in chloride presence, but they are less accentuated. Another aspect to be emphasised is that increase and decrease tendencies occur simultaneously for all monitored distances. It indicates that, in the range of the studied distances, the wet candle device fairly

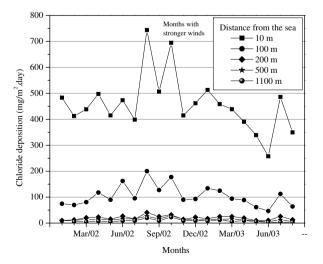


Fig. 3. Chloride deposition on the wet candle device at 10, 100, 200, 500 and 1100 m from the sea.

reproduces the marine aerosol behaviour, independently of the distance from the sea.

Fig. 3 also shows that there are not great month-to-month differences in chloride data within each group of distances considered during the study period, which can be explained by the low intensity of wind in most of months. August–October/2002 data represent the few months in which there is a slight increase in salt measurements, as a consequence of the influence of wind speeds above 3 m/s [21,24]. Furthermore, less important influences on this behaviour can be pointed out: a slight relative humidity decrease in this period, which contributes to a more concentrated aerosol [33] and the absence of the washout effect due to rainfall during the referred period, which contributes to higher measurements [34].

## 3.2. Chloride profiles

Chloride profiles show a typical influence of concrete characteristics on chloride transport into concrete [11–14], as a consequence of the materials porosity and the chloride binding capacity of the mixtures, which have different cements and cement contents per volume of concrete. Typical chloride profiles for representing these situations are shown in Fig. 4.

The influence of concrete porosity can be seen in Fig. 4a, for specimens at 10 m from the sea. It shows that w/c plays an important role on chloride penetration into concrete, due to its influence on the materials porosity, which is one of the most important parameters that affect chloride transport.

Fig. 4b shows a typical case of chloride content increase over time and Fig. 4c shows the influence of the distance from the sea on chloride profiles. Concretes closer to the shoreline are subjected to higher chloride concentrations in the atmosphere and, thus, chloride profiles embody this situation, as a consequence of the chloride availability in the surrounding environment.

When comparing cement influences, a slight delay in chloride content increase over time can be seen for concretes made with cement II. Taking into consideration that no significant differences on porosity were observed for the same w/c concretes (Table 2), probably due to a short curing period, the profile differences can be mainly credited to a higher chloride binding capacity of concretes made with cement II [23], due to its higher  $C_3A$  content. Fig. 4d shows a typical case of these differences in chloride profiles.

A clear increase in chloride content over time is observed for all concrete types and exposure conditions. This takes place at different rates, depending on concrete characteristics and the location of the specimens. The lowest rate of chloride penetration into concrete was observed for concrete C6 placed at 500 m from the sea. In the opposite way, concrete C1, placed at 10 m from the sea, presented the highest rate of chloride ingress into concrete.

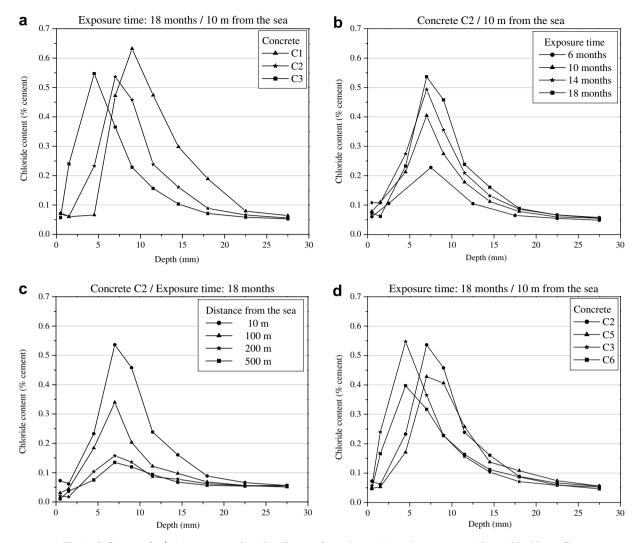


Fig. 4. Influence of w/c (a), exposure time (b), distance from the sea (c) and cement type (d) on chloride profiles.

## 4. Discussion

# 4.1. Chloride penetration into concrete as a function of time

Regarding that concrete specimens were exposed in a region with high levels of relative humidity [24], high humidity contents in concrete porous network are also expected, which can vary in a larger scale in surface layers and generate a growth gradient of humidity content from surface to inner layers, due to environmental interaction [23,35]. As a consequence, it may be also expected that chloride salts are transported into concrete by a combination of capillary sorption and diffusion, with a preponderance of capillary sorption in surface layers, where wetting and drying cycles play an important role, and diffusion in inner layers [8,36,37]. This results in two-zone profiles [8,37], which are similar to those presented in Fig. 4. Thus, considering a sharp increase in humidity content from surface to bulk concrete [23] and the

form of chloride profiles in this study, a predominance of diffusion in the "average" process was accepted, as an approximation to real conditions. As a consequence, the total amount of chlorides that penetrate into concrete must be proportional to the square root of time [38].

Fig. 5 presents the relationship between the average total amount of chlorides accumulated into concrete ( $C_{\rm tot}$ ), which is considered up to 30 mm depth in the present case, and the square root of time for all concretes. This relationship follows Eq. (1), where  $C_0$  is the chloride content in concrete before exposure,  $k_t$  is a coefficient that represents the rate of  $C_{\rm tot}$  increase as a function of time and t is the exposure time. A typical  $C_{\rm tot}$  increase with the square root of time can be seen. This increase tendency takes place more intensively for concretes at 10 and 100 m from the sea, which agrees with the chloride availability at each monitoring station. This behaviour can also be observed by  $k_t$  values, which represent the angular coefficient of fitted lines and show lowest values for concretes at 200 and 500 m from the sea (Fig. 5):

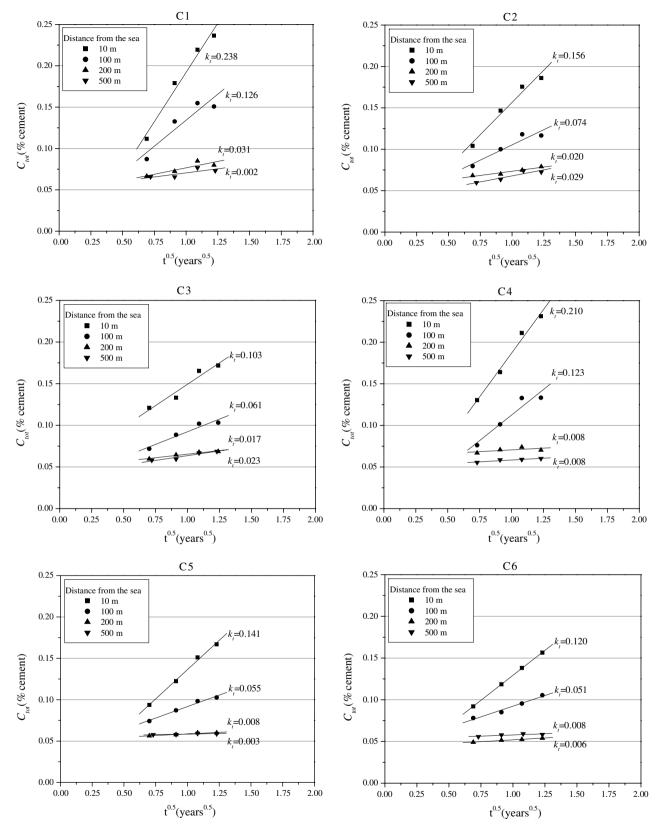
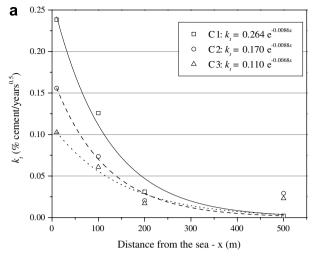


Fig. 5. Relationship between  $C_{\text{tot}}$  and square root of time for concretes C1–C6.

$$C_{\text{tot}} = C_0 + k_t \sqrt{t} \tag{1}$$

Regarding  $k_t$  decrease tendency as a function of the distance from the sea, exponential decay functions can be

fitted within each group of concrete following Eq. (2), where x represents the distance from the sea and a and b are constants derived from the empirical fitting (Fig. 6).  $k_t$  values account for the environmental influence on the



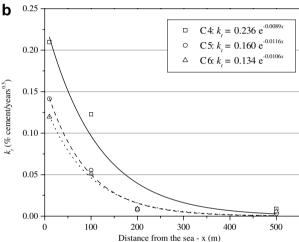


Fig. 6. Relationship between  $k_t$  and distance from the sea for concretes made with cement I (a) and cement II (b).

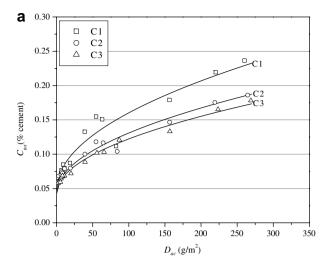
chloride penetration rate into concrete structures, which comprises the availability of chlorides from marine aerosol in the marine atmosphere zone:

$$k_t = a \cdot e^{-b \cdot x} \tag{2}$$

Fig. 6 represents  $k_t$  decrease tendency curves for all studied concretes and also shows the material influence on  $k_t$  behaviour. The influence of concrete porosity is clear. Lower rates of chloride accumulation into concretes with lower w/c are observed. On the other hand, concretes made with cement II (C4–C6) presented, in most cases, lower  $C_{\rm tot}$  increase rates, as a consequence of their higher chloride binding capacity.

# 4.2. Chloride penetration into concrete as a function of chloride deposition

The relationship between chlorides from marine aerosol and those which penetrate into concrete can be seen in Fig. 7. It presents data of  $C_{\text{tot}}$  (average total amount of chlorides accumulated into concrete) and the accumulated



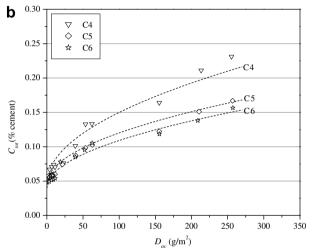


Fig. 7. Relationship between  $C_{\text{tot}}$  and  $D_{\text{ac}}$  for concretes made with cement I (C1–C3) and cement II (C4–C6).

deposition of chlorides on the wet candle device  $(D_{\rm ac})$ , which is the sum of the month-to-month deposition values.

Chloride penetration into concrete, despite its relation of dependence on other environment and material parameters, is closely related to surface chloride concentrations. By chloride profiles in concrete and chloride deposition data, a non-linear relationship between surface chloride concentration ( $C_s$ ) and  $D_{ac}$  was observed [23], showing that the increase of  $C_s$  tends to be attenuated for higher values of  $D_{ac}$ . It can be justified by the fact that a significant amount of chlorides present in marine aerosols does not deposit on concrete surface and, thus, does not penetrate into concrete [16].

In this way, the relation of dependence between surface chloride concentration and chloride transport into concrete may help to explain the behaviour observed between  $C_{\rm tot}$  and  $D_{\rm ac}$  (Fig. 7). Furthermore, aspects like the porosity reduction due to the formation of chloro-aluminates complexes [39] and the fact that there is a non-linear relationship between ion concentration in solutions and its transport velocity [40–42] can be mentioned, contributing to explain the non-linear relationship between  $C_{\rm tot}$  and  $D_{\rm ac}$ .

Table 3 Representative functions for  $C_{\text{tot}}$ – $D_{\text{ac}}$  relationship

Concrete	C <sub>0</sub> (% cement)	$k_{\rm d} \left(\% \text{ cement}/\sqrt{\text{g/m}^2}\right)$	Function	$r^2$	Number of points
C1	0.0480	0.01123	$C_{\text{tot}} = 0.0480 + 0.01123 \cdot D_{\text{ac}}^{0.5}$	0.941	16
C2	0.0429	0.00880	$C_{\text{tot}} = 0.0429 + 0.00880 \cdot D_{\text{ac}}^{0.5}$	0.964	16
C3	0.0428	0.00795	$C_{\text{tot}} = 0.0428 + 0.00795 \cdot D_{\text{ac}}^{0.5}$	0.988	16
C4	0.0465	0.01034	$C_{\text{tot}} = 0.0465 + 0.01034 \cdot D_{\text{ac}}^{0.5}$	0.950	16
C5	0.0456	0.00745	$C_{\text{tot}} = 0.0456 + 0.00745 \cdot D_{\text{ac}}^{0.5}$	0.970	16
C6	0.0401	0.00690	$C_{\rm tot} = 0.0401 + 0.00690 \cdot D_{\rm ac}^{0.5}$	0.963	16

Fig. 7 shows that the growth tendency of  $C_{\text{tot}}$  weakens for higher values of Dac, which indicates that chloride penetration into concrete takes place at relatively small rates, when  $D_{\rm ac}$  increases. The functions used to represent the  $C_{\text{tot}}$ – $D_{\text{ac}}$  relationship follow Eq. (3), where  $k_{\text{d}}$  is a coefficient that shows the influence of concrete characteristics on chloride accumulation into concrete and account for the environmental characteristics of the studied region.  $k_d$ represents the rate of Ctot increase and, thus, changes in variables that affect chloride transport into concrete influence on  $k_d$  values. The decrease in concrete porosity means lower  $k_{\rm d}$  values, as well as in concretes with higher chloride binding capacity. This can be clearly seen in Table 3, which shows that  $k_d$  values decrease from concrete C1 to C3 and from C4 to C6, due to the porosity effect. In the same way, k<sub>d</sub> values are slightly higher for concretes made with cement I (C1-C3) than those derived from concretes made with cement II (C4-C6), due to a higher C<sub>3</sub>A content of cement II:

$$C_{\text{tot}} = C_0 + k_{\text{d}} \cdot \sqrt{D_{\text{ac}}}$$
 (3)

Fitting curves indicate a satisfactory correlation between experimental data, with coefficients of determination higher than 0.94 (Table 3). This behaviour can be explained by the fact that chloride deposition on the wet candle, in some way, represents the chloride availability in surrounding microenvironments and these chloride ions are the ones able to deposit on the concrete surface and penetrate into concrete.

The functions presented in Table 3 are empirical expressions and, thus, are applicable to concretes and environments similar to those studied in this paper. Furthermore, they take into consideration that there are not significant differences among climatic characteristics at monitoring stations. However, these expressions represent an alternative to describe the relationship between chlorides from marine aerosol and those accumulated into concrete in the marine atmosphere zone.

Eq. (3) was not tested for high levels of chloride deposition, like those observed in Sweden [20], which represent more than 5000 mg/m² day at seashore when wind speed reaches 15 m/s. Nevertheless, the present study covers a large range of deposition rates below the level of 1000 mg/m² day, which are usual in many places and suitable for the marine atmosphere zone.

The total porosity of concrete  $(\gamma)$ , which is presented in Table 2, is a variable that influences chloride transport.

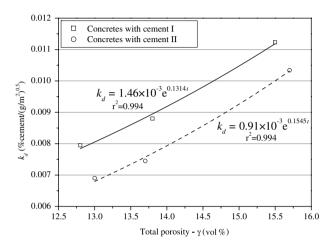


Fig. 8. Relationship between  $k_{\rm d}$  and total porosity of concrete ( $\gamma$ ) for concretes made with cements I and II.

Thus, it is possible to set expressions to represent the relationship between  $k_d$  and  $\gamma$ , regarding each cement type, which does not invalidate other relationships with other variables concerned with chloride transport into concrete. Eq. (4) represents the  $k_d$  increase tendency with the total porosity of concrete, where a and b are coefficients derived from the empirical fittings (Fig. 8):

$$k_{\rm d} = a \cdot e^{b \cdot \gamma} \tag{4}$$

The proposed functions in Table 3, which are derived from Eq. (3), represent the strong relationship between  $C_{\rm tot}$  and  $D_{\rm ac}$ . On the other hand, taking into account the influence of  $\gamma$  on chloride transport into concrete and, consequently, on  $k_{\rm d}$  and  $C_{\rm tot}$  values,  $\gamma$  can be used as a factor that affects the first relationship. The influence of cement type on chloride transport is also present, generating different curves to represent the  $k_{\rm d}$ - $\gamma$  relationship (Fig. 8), which ratifies comments made before about the chloride binding capacity of concretes made with cements I and II.

# 5. Conclusions

Chlorides present in the atmosphere, which represent the availability of chlorides to deposit on the concrete surface and penetrate into concrete, can be studied using the wet candle method and be correlated with chlorides accumulated into concrete, which does not invalidate other relationships, like the one of square root of time. In this way, far from the sea,  $D_{\rm ac}$  decreases and, consequently,  $C_{\rm tot}$  also decreases. The  $C_{\rm tot}$  decrease takes place at a lower rate than the observed in chloride deposition measurements, following a non-linear relationship.

The  $C_{\rm tot}$ – $D_{\rm ac}$  relationship is well represented by the equation  $C_{\rm tot} = C_0 + k_{\rm d} \cdot \sqrt{D_{\rm ac}}$ , where  $C_{\rm tot}$  is the average total amount of chlorides accumulated into concrete,  $C_0$  is the chloride content in concrete before exposure,  $D_{\rm ac}$  is the accumulated deposition of chlorides on the wet candle device and  $k_{\rm d}$  is a coefficient which depends on concrete and environmental characteristics. For the environment where this research took place,  $k_{\rm d}$  remained in the range  $7 \times 10^{-3}$  and  $11 \times 10^{-3}$  (% cement/(g/m²)<sup>0.5</sup>) and shows that there are slight and consistent differences among concrete mixtures, as a consequence of their porosity characteristics and their ability to bind chlorides.

Other aspects that may influence on  $k_{\rm d}$  behaviour and, consequently, on  $C_{\rm tot}$ – $D_{\rm ac}$  relationship, like the saturation degree of concrete porous network, changes in concrete microstructure over time and environments with chloride deposition levels significantly higher than those observed in this work, were not analysed in this paper and, certainly, should integrate future work to improve the proposed empirical model.

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