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Interpretation of chloride profiles from concrete exposed to tropical marine environments

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Abstract

The chlorides from the sea and marine breeze are the main source for corrosion in marine environments, and their profiles in concrete are commonly modeled and used for prediction purposes. However, no reliable results may be obtained if the action of environmental agents, such as the relative humidity (RH), temperature, winds, rains and drying periods, on such profiles are not well known through several periods of time. Although these limitations are recognized in several works, there are very few field and isolated data in the literature to explain and support, according to different exposure conditions and periods of time, the shape and meaning of the chloride profiles. Any prediction model could acquire more reliability only after knowing and incorporating such information. This work presents concentration profiles, which were obtained from concretes exposed to different microclimates, and discusses their behavior and meaning according to the environmental parameters, concrete quality and several periods of time.

Keywords: Chloride; Concentration profile; Concrete; Corrosion; Tropical marine environment

1. Introduction

The chlorides coming from the marine breeze are the main source of aggressivity for reinforced concrete and the main cause for its deterioration. They can penetrate the concrete in different forms that depend, fundamentally, on the concrete quality conditions, as well as on the surrounding atmosphere.

The chlorides can penetrate the concrete through capillary suction when it is dry, by convection when a fluid (water) transports them [1], or also by a concentration gradient (diffusion) when the material is dampened. A combination of all of these mechanisms is present in the most of the cases due to the environment influence.

The environment, which surrounds the concrete in tropical marine climates, can have strong variations of humidity (Fig. 1), temperature (Fig. 2), winds direction (Fig. 3) and chlorides that could be deposited on the structures. Therefore, a monitoring of these variables from the atmosphere allows understanding of the chloride penetration mechanisms, and can help to make decisions in order to protect the concrete from deterioration.

In general, the chloride concentration profiles obtained under different climates are used in mathematical models for obtaining diffusion coefficients and/or predicting remaining service life and corrosion thresholds [2–4]. However, any effort to model the behavior of the chloride profile must be accompanied by an analysis and inclusion of the environmental parameters that originated it. Otherwise, the model would have a limited validity.

Several authors [5–8] have obtained chloride profiles and related them with the environment that surrounds the concrete. The form of the profile is attributed in some of them to the environmental conditions, but more data are needed, in some cases, to justify that. Other important works [9] start to show multimechanistic chloride transport when modeling, but they are still limited and a lack of a significant quantity of field data avoid their perfectioning.

The aim of this work is to present concentration profiles, which were obtained from concretes exposed to different

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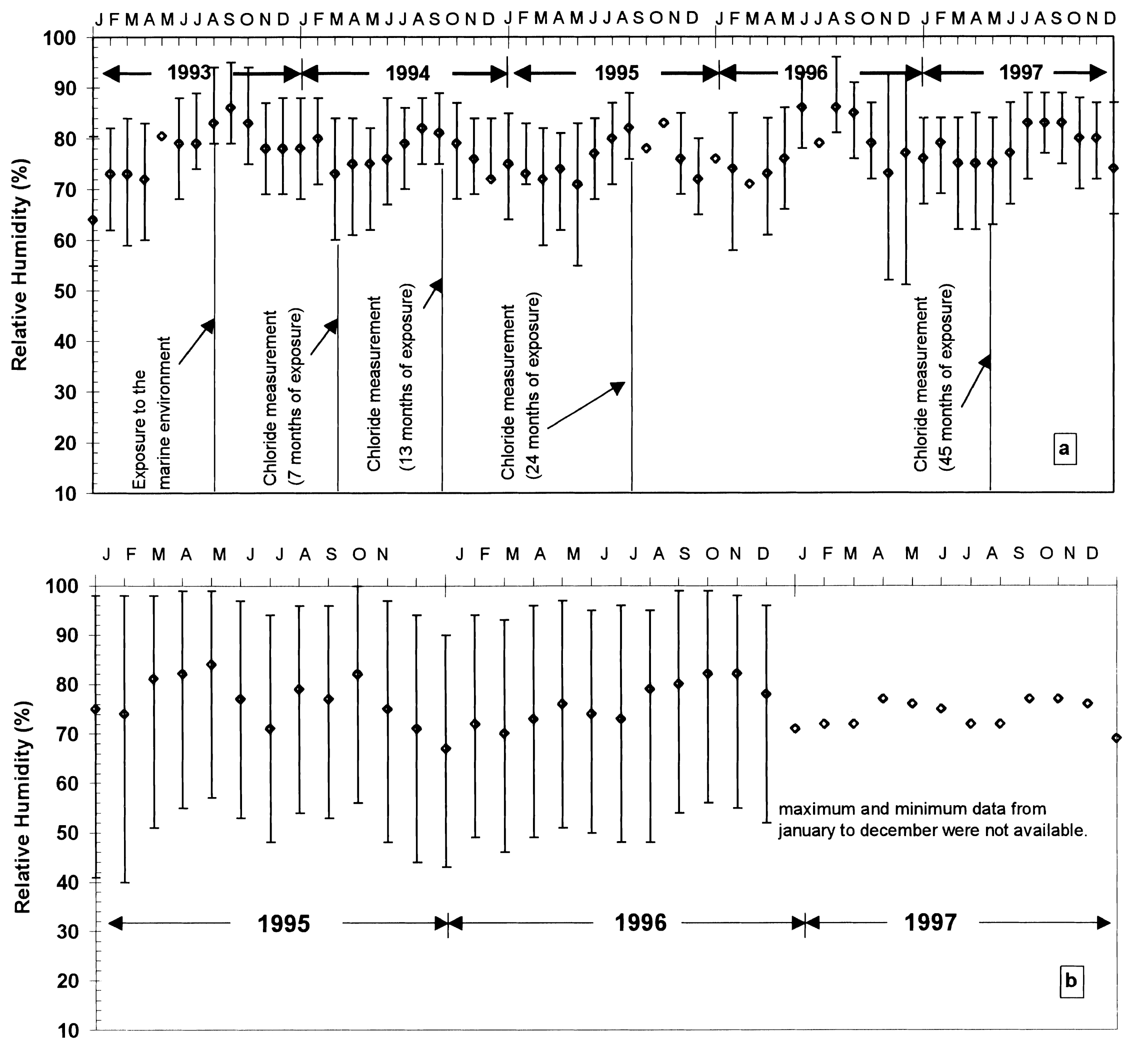

Fig. 1. Yearly average RH variation in (a) the Port of Progreso, Yucatán, México and (b) the Maracaibo Lake. Maximum and minimum values correspond to the monthly averages of the maximum and minimum RH.

microclimates, and discuss their behavior and meaning according to the environmental parameters, concrete quality and several periods of time.

2. Experimental

The chloride profiles, which will be discussed in this work, come from ongoing investigations about cylindrical probes exposed to the marine environment of Yucatán in México, a bridge above the Maracaibo Lake in Venezuela and buildings in front of the beach of Recife in Brazil.

The concrete cylinders had 7.5 ± 0.3 cm diameter $\times$ 15 cm length with times of curing (tc) of 1, 3 and 7 days, as well as water–cement (W/C) ratios of 0.76, 0.70, 0.53, 0.50 and 0.46. They were prepared using Portland cement (ASTM Type I) and crushing aggregates [10,11]. Each W/C ratio and tc combination was represented by two cylinders, and the average of their measurements is represented in all the following figures and tables. The concrete cylinders have been exposed for about 4 years to the tropical marine climate of Yucatán at distances of 50, 100 and 780 m from the seaside.

The data from the bridge above the Maracaibo Lake correspond to cores of the same dimensions (300–400 kg/m^3, W/C = 0.40) that were taken at different locations after 33 years of construction. The bridge is supported by cables in the longest spans and is 8678 m long.

The data from the beach of Recife correspond to cores of the same dimensions that were taken at different locations in several buildings of the coast, which were 10 years old by then. The average compressive strength of the buildings was between 15 and 25 MPa, the annual range of temperature is between 25°C and 40°C, and the annual RH is around 75%. The only rain period in Recife is from March to July.

The chloride amount was determined with the ion selective electrode for the specimens exposed in Mexico and the Mohr method for those of the Venezuelan bridge. The

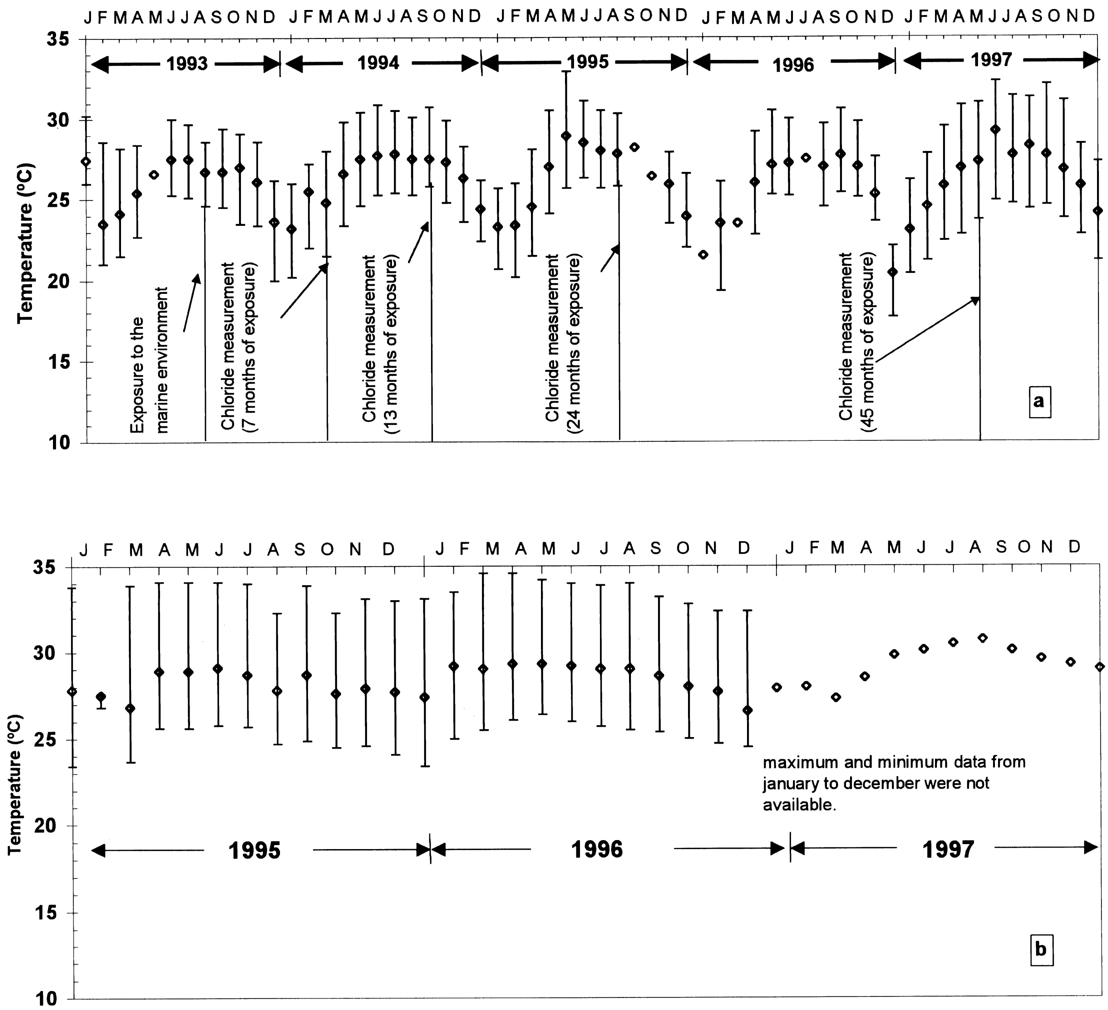

Fig. 2. Yearly average temperature variation in (a) the Port of Progreso, Yucatán, México and (b) the Maracaibo Lake. Maximum and minimum values correspond to the monthly averages of the maximum and minimum temperature.

chloride amount was determined through the method of ASTM C1152 in the case of Recife's samples.

3. Results and discussion

3.1. Two-zone profile

In general and depending on the concrete quality, it is accepted that a continuous dampened zone exists close to the concrete nucleus and a wet and dry one at the surface [12]. However, the consulted literature does not demonstrate under which conditions such a hypothesis is valid. Experimental trials in tropical climates have also shown no existence of these two zones in the absence of chlorides, where the denser concrete wets and dries completely during the day [13,14]. However, things are different in tropical marine climates.

Fig. 4 corresponds to cylinders exposed at 100 m from the seaside in Mexico, and shows chloride profiles with an intermediate maximum, which could be the interface between the two mentioned zones. The two-zone profile could be due, among others, to some of the following reasons: the skin effect of concrete [15], the interface between carbonated and noncarbonated layers, chloride washing by rain [16] or the interface between the zones of dampening and continuous wetting and drying (absorption–desorption) [12]. The concrete skin has a different composition than the bulk due to the wall effect during casting or the precipitation of brucite during contact with seawater [17]. The skin effect has a limited depth, which coincides most of the times with the interface between mortar and concrete. There are some works [18] that show profiles, which could be attributed to this effect. The maxima observed in this paper are not related with this effect because of the depth at which they take place. On the other hand, carbonation of the specimens was checked [19,20], and the carbonation front did not coincide with the maximum of our profiles as can be observed in Table 1. It is necessary to recognize that

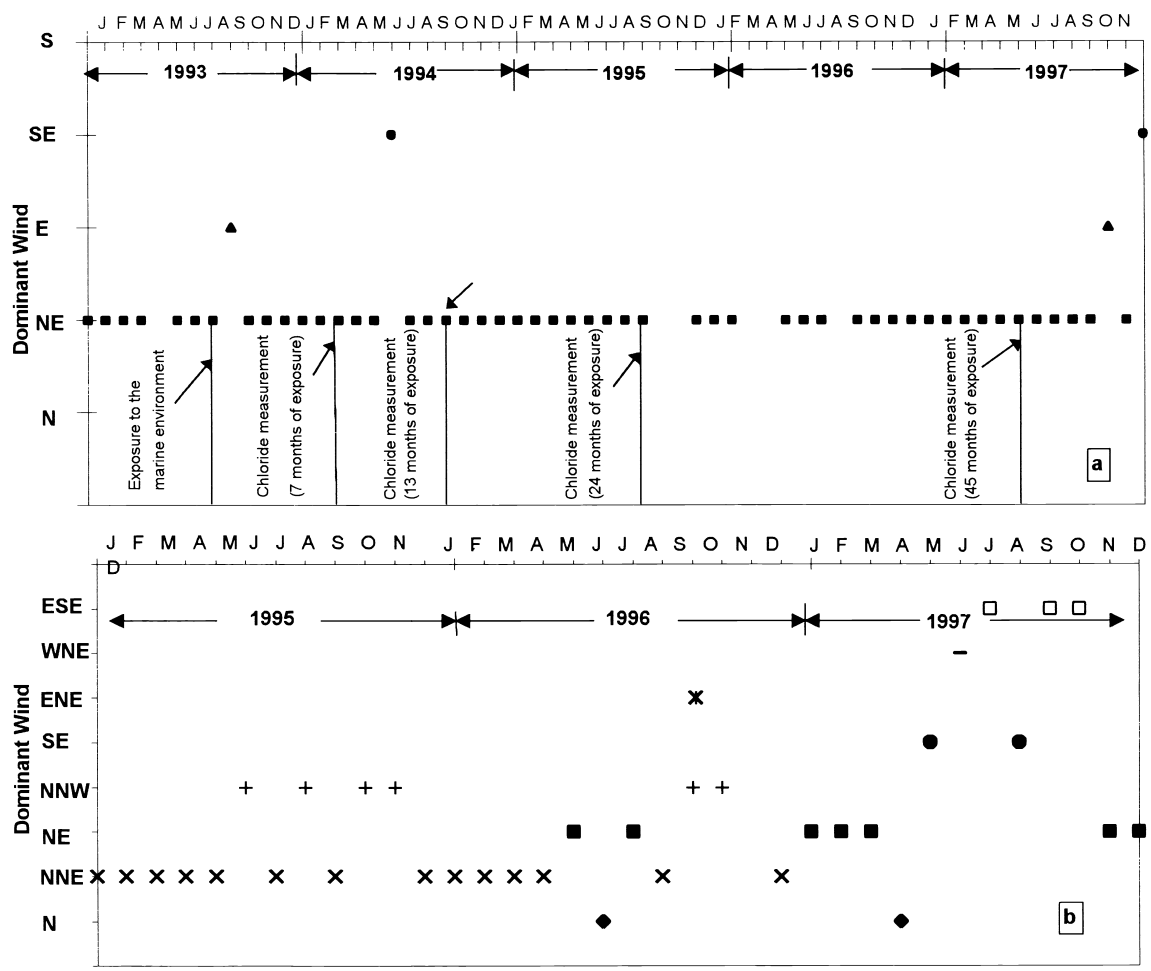

Fig. 3. Yearly winds variation in (a) the Port of Progreso, Yucatán, México and (b) the Maracaibo Lake.

carbonation was checked with phenolpthalein instead of timolpthalein. The two-zone profile of our study is affected by the atmospheric drying and wetting effect, as well as by the chloride washing when raining.

The profiles of Fig. 4 show that the denser the concrete, the widest internal zone confirming that, while denser the concrete, the dry periods will affect less the internal layers in the presence of chlorides. This means that the internal and continuing dampened zone is thicker in the denser concretes [21]. The data from Fig. 4 were taken after an exposure longer than 24 months to the tropical marine environment and during the rain period (Fig. 5a). This means that the obtained profiles are reflected in the surface concentration, the effect of the rain washing, as well as the changes of RH and temperature from the whole period (Figs. 1a and 2a). There were RH ranges between 55% and 95%, as well as temperature ranges from 20°C to 33°C during this long period as illustrated in Figs. 1a and 2a, where the average of the maximum and minimum monthly values are represented. These RH and temperature changes promoted periods of wetting and drying, which favored the chloride penetration and the formation of the concentration gradients as shown in Fig. 4. This situation was equivalent to that observed in piles from docks exposed to total saturation in

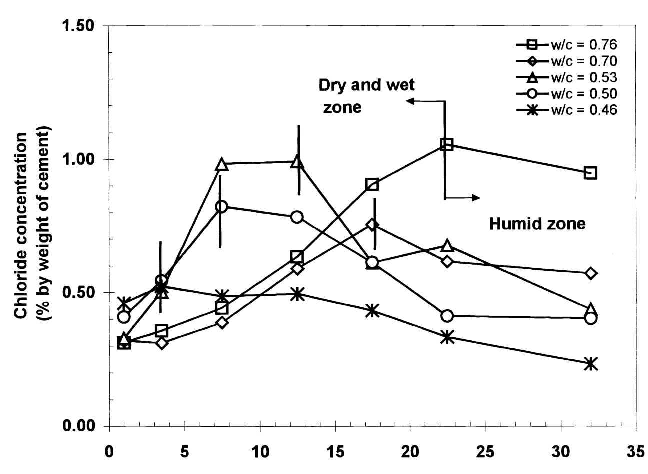

Fig. 4. Concentration profiles identifying the two zones inside concrete for different W/C ratios. Data from specimens exposed for 24 months at 100 m from the seaside and with 7 days of curing in Progreso, Yucatán, México.

Table 1
Carbonation depth, distance from the concrete surface to the highest value of the chloride profile and highest value of the profile of concrete cylinders exposed to the tropical marine environment of Progreso, Yucatán, México for 24 months, 7 days of curing and at three distances from the seaside

Distance to the sea (m)		W/C ratio 0.76	0.70	0.53	0.50	0.46
50	A	11.50	9.50	5.50	3.50	2.50
	B	22.50	17.50	17.50	12.50	12.50
	C	3.82	3.32	1.78	1.70	1.20
100	A	17.50	14.00	10.00	9.50	3.00
	B	22.50	17.50	12.50	7.50	3.50
	C	1.05	0.75	0.98	0.82	0.52
780	A	20.00	13.00	6.00	6.50	3.00
	B	22.50	17.50	7.50	12.50	17.50
	C	0.66	0.61	0.61	0.60	0.42

(A) Carbonation depth (mm), (B) distance from the concrete surface to the highest value of the chloride profile (mm), (C) highest value of the chloride profile (percent by weight of cement).

the immersion zone and wetting and drying cycles in the tidal zone [22]. The existence of two zones was evident not only through the change in the chloride concentration profile, but on the concrete ohmic drop (directly related to resistivity) that showed a higher value close to the surface than close to the rebar as observed in Table 2.

Table 2
Ohmic drop of concrete cylinders exposed to the tropical marine environment of Progreso, Yucatán, México for 24 months, 7 days of curing and at three distances from the seaside

Distance to the sea (m)		W/C ratio 0.76	0.70	0.53	0.50	0.46
50	A	0.70	1.65	3.95	1.75	3.35
	B	0.60	1.45	2.42	1.60	3.00
	C	0.07	0.14	1.10	0.18	0.30
100	A	10.60	3.30	49.50	19.50	7.75
	B	9.90	2.80	21.50	19.00	7.60
	C	0.66	0.47	N.A.	0.34	0.38
780	A	78.50	65.50	74.00	41.46	48.45
	B	77.00	64.50	73.50	41.00	48.00
	C	1.33	0.82	0.50	0.46	58.00

(A) Ohmic drop of concrete (0–35 mm), kΩ; (B) ohmic drop of croncrete (0–17 mm), kΩ; (C) ohmic drop of concrete (17–35 mm), kΩ. N.A. = not available.

The above discussion makes the observer believe that the concrete internal layers do remain humid in the presence of chlorides due to their hygroscopic character and despite the strong dry periods. Therefore, under these circumstances, the interface between the two zones could be established by a change in the direction of the chloride concentration gradient.

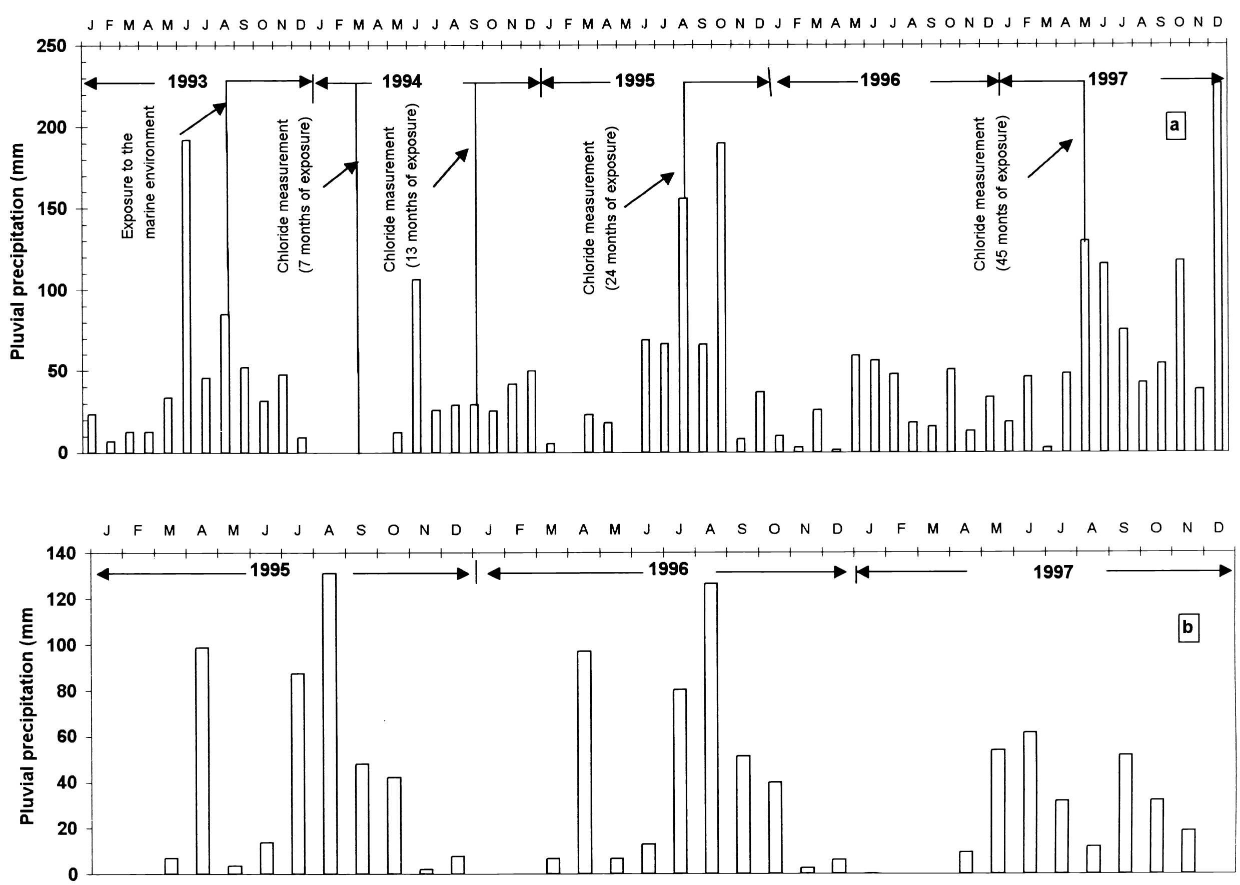

Fig. 5. Pluvial precipitation during the tested period in (a) the Port of Progreso, Yucatán, México and (b) the area close to the Maracaibo Bridge.

On the other hand, when a concrete is of good quality and positioned in environments with high chloride contamination, it is more probable that only one zone exists, which remains always dampened, even when exposed in the tidal zone and despite the temperature gradients. Fig. 6 shows a chloride profile of the bridge over the Maracaibo Lake that exemplifies this case and, therefore, exhibits an apparent pure diffusion behavior. This behavior is understood due to the fluctuations of RH, temperature and winds observed in Figs. 1b, 2b and 3b. These fluctuations are around an average that allows the continuous dampening and chloride availability as to maintain the form of the concentration profile. In Fig. 4, the W/C ratio of 0.46 shows a similar situation, but it is not exposed in a tidal zone so it is susceptible to the rain washing as observed in the surface concentration. The case of Recife is similar to that of Maracaibo, and some buildings present a similar profile as deduced from Table 3. This was due mainly to the concrete quality.

The above information confirms that the form of the chloride concentration profile depends on the environmental conditions, and that it can change a lot depending also upon the concrete quality. Therefore, when doing mathematical modeling, it is necessary not only to take into account a large universe of profiles during several years in order to validate the predictions but also knowing the environmental parameters that promoted their form. The chloride concentration profile did not show significant influence of carbonation or the skin effect under our experimental trials.

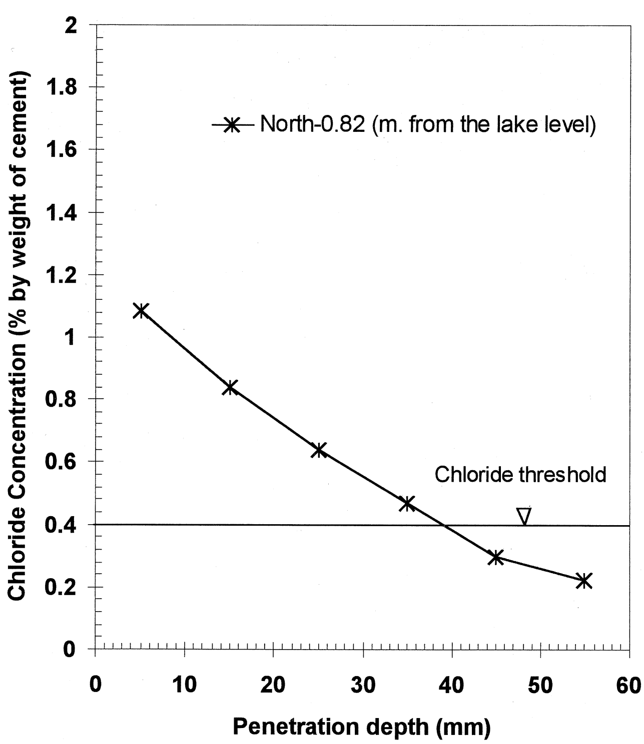

Fig. 6. Chloride concentration profile of the north face of the brace beam "A" in the Maracaibo Bridge.

Table 3
Chloride values at different depths of a concrete building in Recife, Brazil

Sample	Sample depth (mm)	% total chloride
A	10	1.27
B	20	0.79
C	30	0.41

3.2. Effect of the microclimates on the form of the concentration profile

On the other hand, a microclimate can take place inside the concrete when it is exposed to different aggressives [7] or when buildings of the same type are positioned in the same piece of land but under different environments. Fig. 7 shows a 24-month-old concrete, which was exposed to the marine environment of Progreso. The form of the concentration profiles is similar even at different distances from the seaside (50, 100 and 780 m). The same situation took place for all the other kinds of concretes exposed to the same environment, and it demonstrates that under the conditions of this work the mechanism of chloride penetration does not change with the distance to the sea. However, the data in Table 4 show that for 24 months of exposure the surface concentration of specimens cured for 7 days having different W/C ratios, in general, increased with the sea proximity for any kind of concrete. This means that, despite all the rain periods, the surface concentration shows a well-defined trend with the distance to the sea. It also shows that, at short distances from the sea, the differences in the environment reflect on the chloride contamination grade. The behavior of the surface concentration regarding the W/C ratio will not be discussed here. On the other hand, Table 5 shows in general a higher chloride concentration in the nucleus with the sea proximity, higher W/C ratio at 24 months of exposure and 7 days of curing. The analysis of the data in different microclimates, as described in this paper, could allow the design of

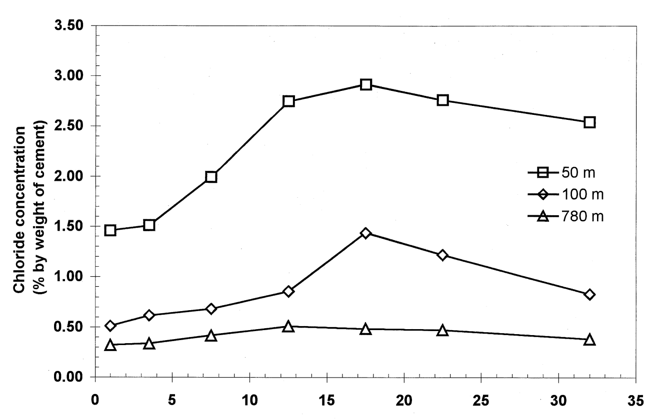

Fig. 7. Chloride concentration profiles of concretes with W/C ratio of 0.53 and 3 days of curing exposed during 24 months at 50, 100 and 780 m from the seaside.

Table 4
Chloride concentration (percent by weight of cement) on the concrete surface from cylinders exposed to the tropical marine environment of Progreso, Yucatán, México for 24 months, 7 days of curing and at three distances from the seaside

W/C ratio	Surface chloride concentration, percent by weight of cement (7 days of curing)		
	50 m	100 m	780 m
0.46	0.41	0.46	0.43
0.50	0.73	0.41	0.16
0.53	0.77	0.33	0.27
0.70	1.39	0.32	0.24
0.76	1.43	0.31	0.21

structural elements not only based on the concrete quality but on the distance to the sea.

On the other hand, the chloride penetration also changes with the height, as observed in the Maracaibo Bridge. Fig. 8 illustrates this showing four profiles taken at different depths but all at the same time. As in the case of Progreso, the microclimates in the Maracaibo Lake are playing an important role in the chloride accumulation, so these data could allow the design of structural elements based on the height from the sea. Other recommendations regarding structural design in microclimates but in cold weather and applied to bridges have been done also by Sandberg [22], who found a change in the form of penetration with the height. In this case, the combination of the atmospheric parameters allowed a two-zone profile.

3.3. Effect of the time and the climatic conditions in the form of the concentration profile

During a structure service life, the chloride can penetrate the concrete in different manners and the profile changes its form continuously. Each case is different depending on the predominant climatic conditions. Fig. 9 shows the changes in the form of the chloride concentration profile with time. It exemplified the case of a concrete with W/C ratio of 0.50 and 1 day of curing noting that a similar situation happened in the other concretes with low W/C ratios. The chloride profile was flat before the exposure to the environment as expected. The amount of chloride measured was due to some contamination in the materials of this region [11].

The profile showed a diffusional form after about 7 months of exposure due to, among other reasons, the chloride ingress that was constant, the fluctuation of RH between 67% and 95% (Fig. 1a) and the lack of rain as observed in Fig. 5a. The same behavior was observed in the cores taken from the Maracaibo Bridge (Fig. 8), where the element was not exposed to the rain and the environmental conditions fluctuated less than those in Progreso (Figs. 1b, 2b and 3b).

The profile obtained at about 13 months of exposure in Progreso showed the influence of the rain period of that year as observed in Fig. 5a. The surface concentration decreased regarding that of the interior as a consequence of the rains,

Table 5
Chloride concentration (percent by weight of cement) on the concrete nucleus, where the reinforcement is usually placed, from cylinders exposed to the tropical marine environment for 24 months, 7 days of curing and at three distances from the seaside

W/C ratio	Chloride concentration in the concrete nucleus, percent by weight of cement (3.2 cm depth, 7 days of curing)		
	50 m	100 m	780 m
0.46	0.35	0.23	0.32
0.50	1.37	0.40	0.22
0.53	1.68	0.44	0.33
0.70	3.07	0.57	0.46
0.76	4.13	0.45	0.71

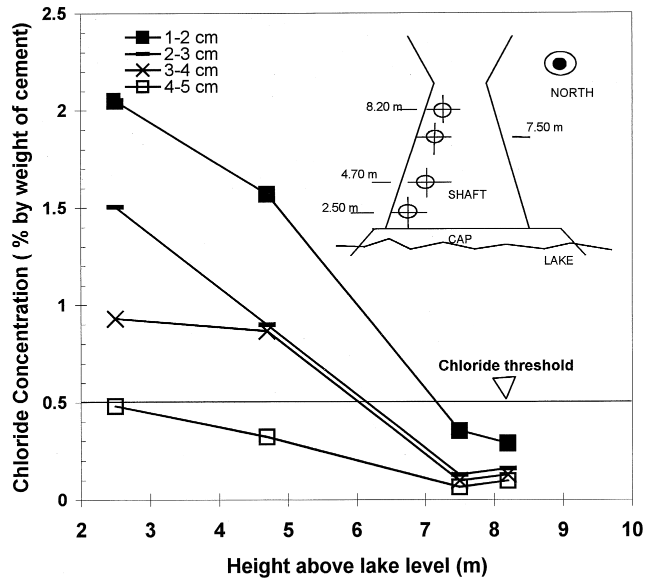

Fig. 8. Chloride concentration profiles at different heights and depths of a shaft from the Maracaibo Bridge.

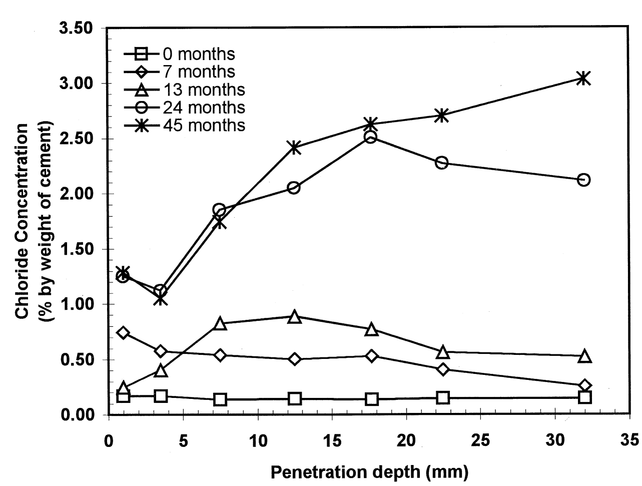

Fig. 9. Effect of aging in the form of the concentration profile for a concrete with W/C ratio of 0.50 and 7 days of curing and exposed during 0, 7, 13, 24 and 45 months at 50 m from the seaside in Progreso, Yucatán, México.

the RH variations ranges between 67% and 95%, and the temperature is between 20°C and 31°C (Figs. 1a and 5a). In this period, the two-zone profile started to appear clearly.

The same form of profile appeared at 24 months of exposure, but with an increase in the internal concentration. The interface between the two zones had a displacement, where the dampened zone was thinner than at 13 months of exposure. This may be due to the higher temperature and RH gradients observed in this period (Figs. 1a and 2a).

After 45 months of exposure, several rain periods and a greater chloride supply from the atmosphere affected the concrete. The profile was then reversed, possibly due to the chloride saturation in the nucleus and the continuous rain periods that caused, in this stage, a gradient to the external part.

Because of the above observations, the form of the chloride profiles at different times and types of exposure in the same place makes it necessary to take into account that the concentration profile of a structural element can depend strongly from the environment and not to be reproduced with time. This situation suggests the use of mathematical models to make predictions only after having several field profiles, as well as the environmental parameters to explain the observed behavior [23,24]. Otherwise, any assumption will be valid only for the time scale at which it was obtained.

4. Conclusions

(1) The environmental conditions of the tropical marine climate in cylindrical concrete specimens promoted the formation of two zones: one internal that is always dampened and one external that is always wetting and drying. The thickness of these zones is a function of the concrete quality (W/C ratio) and the media aggressiveness. The two-zone profile does not exist in the absence of chlorides (concrete wets and dries completely during the day), or when the chloride concentration is high with stable environmental conditions and concrete is of very good quality (like in the Maracaibo Lake or Recife Beach).

(2) Under the conditions of this study, the mechanism of chloride penetration does not change with the microclimates. However, the chloride concentration in the concrete nucleus (where the rebars use to be) decreases when the distance to the sea and the W/C ratio increases. Several recommendations to the designers can be deduced from this study in order to take into account not only the concrete quality but also the distance and the height regarding the seashore in the structural design.

(3) The form of the concentration profile changes with time as a result of the environmental agents interaction so that the mathematical modeling must take into account quite a few profiles with time in order to obtain reliable results and predictions. Otherwise, the obtained results will be valid only for the scale of time at which were obtained.

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