Third International Conference on Sustainable Construction Materials and Technologies http://www.claisse.info/Proceedings.htm

Long-term Study of Reinforcement Corrosion in Concrete Structures in Marine Atmosphere Zone

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ABSTRACT

This work analyses the behaviour of marine aerosol salinity in marine atmosphere zone in a Brazilian coast region and its interaction with concrete structures. Marine aerosol salinity was monitored by the wet candle method and chloride concentrations in concrete were periodically monitored as well. Six different concrete mixtures were used for this purpose. Powdered concrete samples were extracted from the concrete specimens at five different exposure periods to obtain chloride profiles. Results show a strong decrease in airborne salinity with the distance from the sea as well as in chloride penetration into concrete structures. However, this does not take place at the same rate. A non-linear relationship represents this behaviour. Numerical extrapolations of chloride profiles over time were performed, which show that chloride deposition rate on the wet candle can be used as an environmental indicator, helping to set different marine aggressiveness subzones.

Keywords. Chloride deposition, concrete durability; marine atmosphere zone, wet candle

INTRODUCTION

Reinforced concrete structures in marine atmosphere zone are subjected to the influence marine aerosol salinity, which is generated either in the open sea or in the surf zone (Gong *et al.*, 1997). However, it is in the last one where the marine aerosol incorporates more and heavy salt particles under a generation process strongly influenced by wind characteristics (Fitzgerald, 1991). After being generated, marine aerosol is transported inland by wind. During this transport, salt particles that compose marine aerosol settle after having covered a certain distance from the sea, depending on their weight, wind characteristics and obstacles present in aerosol trajectory (Lovett, 1978, Fitzgerald, 1991, Morcillo *et al.*, 2000). This leads to a strong decrease tendency of salt concentrations in atmosphere in the first meters away from the sea (Meira *et al.*, 2008).

Concerning the interaction of chloride ions from marine aerosol and reinforced concrete structures, chlorides from marine aerosol deposit on concrete surface and from that penetrate into bulk concrete. In time, chloride concentrations in concrete tend to increase and reinforcement corrosion only starts when a certain level of chloride content is exceeded at the rebar surface (Glass and Buenfeld, 1997).

It was previously observed that, similarly to marine aerosol salinity decrease inland, there is also a decrease tendency for the total amount of chloride that penetrate into concrete structures built in marine atmosphere zone (Mustafa and Yusof, 1994, Meira *et al.,* 2007). These studies, which were carried out under field exposure, observed decreases up to 70% in chloride penetration into concrete in the first hundred meters from the sea. Furthermore, a non-linear relationship between chloride content in marine atmosphere zone and total chloride content in concrete was also observed (Meira *et al.,* 2007). However, long-term studies on this topic are still needed to help on analysing this kind of relationship.

The aim of this paper is to analyse the relationship between chloride deposition rate on the wet candle device, as an indirect measurement of chloride presence in marine aerosol, and chloride accumulation into concrete. This analysis was used as a basis to propose different chloride aggressiveness subzones in marine atmosphere zone and took into account long-term data, the chloride threshold advance in concrete and service life analysis.

Modelling of chloride penetration into concrete has been traditionally done by the use of Fick's second law, assuming as constants the surface chloride concentration and the diffusion coefficient (Crank, 1975). Advances have been obtained on this modelling considering the effect of variables like time (Mangat and Molloy, 1994), temperature (Saetta *et al.,* 1993), saturation degree of concrete (Almenar, 2000), etc, on chloride transport. Taking into account the multiple influence of variables on chloride transport into concrete, numeric models have been proposed to represent these phenomena. This way, finite difference method has been used in some approaches (Tang and Nilsson, 1996, Nielsen and Geiker, 2003) and finite element method has been used in more sophisticated models (Pérez, 1999). This work used the finite difference method with some simplifications described in section 4.

EXPERIMENTAL WORK

An environmental characterization was carried out considering climatic and sea-salt data. Climatic data were collected by a Brazilian Government weather station located in the region where the research took place and it was done on temperature, relative humidity, and wind speed and wind direction. The UTC (coordinated universal time) references were followed on these measurements.

Sea-salt data was measured by the wet candle device, according to the specifications established in the ASTM standard G140 (2002). These devices were placed at sites located at 10, 100, 200 and 500 meters from the sea. Samples from the wet candle device were collected monthly and analysed by potentiometric titration throughout the research period.

Prismatic concrete specimens of 0.15 x 0.15 x 1.40 m were cast using a Brazilian cement CPIIF (Filler-modified Portland). Water to cement ratios were set at 0.50, 0.57 and 0.65, representing materials with a large range of porosity characteristics and comprising the mixtures C1 – C3 (Table 1). Compressive strength, concrete slump and mercury intrusion porosimetry were also measured to characterize the concretes (Table 1).

Table 1. Concrete mixtures and properties.

Concrete	C1	C2	C3
Cement (kg/m^3)	406	356	320
Sand (kg/m^3)	769	812	840
Aggregate (kg/m^3)	947	947	947
Plasticiser (kg/m^3)	1,22	1.06	-
w/c ratio	0.50	0.57	0.65
Slump (mm)	8 ± 1	8 ± 1	8 ± 1
Compressive strength (MPa) – 28 days	31.0	27.0	20.3
Total porosity (mercury intrusion porosimetry –180 days) – (%vol.)	13.0	13.7	15.7

The specimens were cured in a wet chamber for 7 days before being placed at locations 10, 100, 200 and 500 m away from the sea, at the same monitoring stations used for measuring chloride deposition. The specimen faces not perpendicular to the predominant winds were waterproofed with a polyurethane coating to simulate the unidirectional transport of chlorides into concrete.

After six, ten, fourteen, eighteen and forty-six months of exposure, samples were extracted from the specimens to obtain chloride profiles in concrete. The first step in obtaining the samples was to remove (by drilling), from the prismatic specimens, 7 cm diameter cores. 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 or 35 mm, depending on the exposure time. For each sample, the total chloride content was determined by potentiometric titration, following the procedures of the International Union of Laboratories and Experts in Construction Materials, Systems and Structures - RILEM (2002).

Measurements of the saturation degree of concrete porous network were also done along the observation period using a methodology based on mass measurements of concrete specimens over time and comparisons with saturated mass of these specimens (Guimarães and Helene, 2005). This methodology is not discussed here, but the behaviour of this variable for the concretes studied in this paper is incorporated to the numeric approach used in section 4. Detailed data of this variable and methodology can be seen in Meira (2004).

RESULTS

The local temperature in the region chosen for the experimental work shows little variation, ranging roughly from 20 to 30 degrees Celsius. The relative humidity stays usually between 60 and 80 %, with higher values during longer rain periods. Winds are usually from S-SE-E directions and their speeds are typically low and stay in the range between 1 and 4 m/s daily average.

The results of chloride deposition on the wet candle device show a clear reduction of airborne salinity in the first 200 m (Figure 1). This reduction demonstrates that chloride aggressiveness is stronger in the first land zones. After this distance from the sea, there are also differences on measured data, but they are less accentuated.

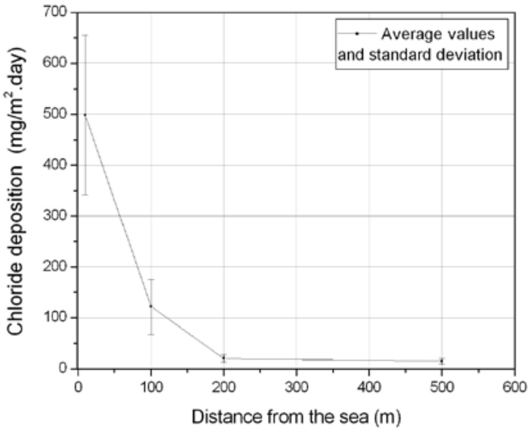
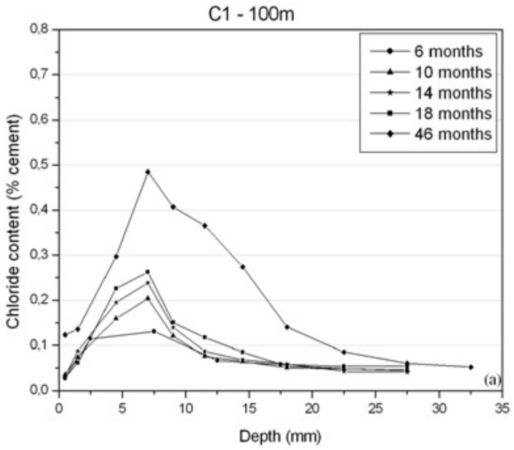


Figure 1. Chloride deposition on the wet candle device.

During the experimental study, dozens of chloride profiles were obtained. Profiles show that there is a clear increase in chloride content over time, as a consequence of a continuous exposure to marine aerosol (Figure 2a). Chloride profiles also show lower chloride penetration into concrete with the distance from the sea, as a consequence of the availability of chlorides in atmosphere at each exposure site (Figure 2b). A typical decrease in chloride content with w/c decrease is also presented, which is related to materials porosity (Figure 2c). Profiles behaviour is the basis for the analysis done in the next section, where simulations for 50 years of field exposure are incorporated.



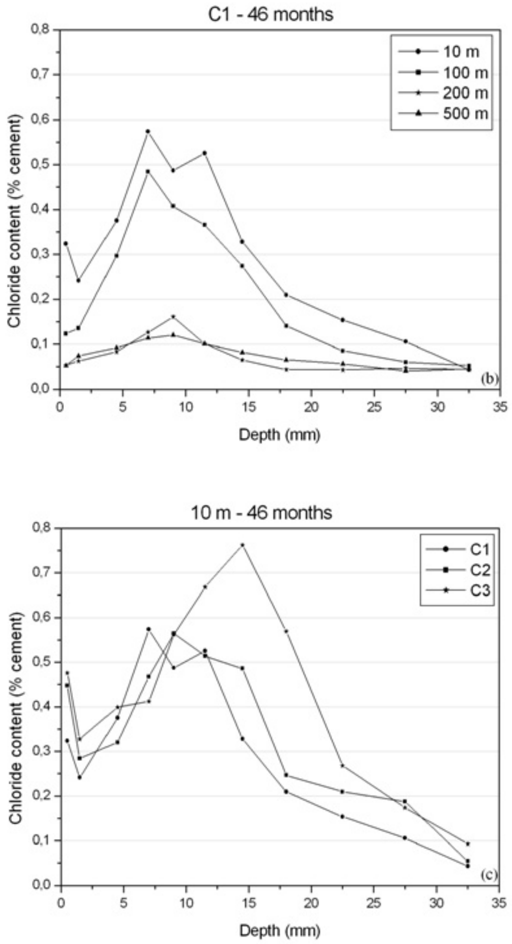


Figure 2. Chloride profiles in concrete – influence of exposure time (a), distance from the seashore (b) and concrete characteristics (c).

SERVICE LIFE ANALISYS AND PROPOSAL OF AGGRESSIVENESS SUBZONES

One way to set relationships between chloride deposition rate on the wet candle and concrete structures performance is through service life analysis. This was done here by numeric extrapolations over 50 years of exposure, considering chloride profiles during the first 46 months of exposure, environmental and concrete characteristics influence on chloride transport, 0.4 % of cement mass as total chlorides threshold (Glass and Buenfeld, 1997) and service life as the time for chloride threshold to be reached at the rebar surface (initiation period of reinforcement corrosion). The procedures adopted are resumed below in three steps, which consider the rescaling of chloride profiles, the numerical obtaining of transport parameters and numerical extrapolations and proposal of aggressiveness subzones.

Rescaling of chloride profiles

When concrete structures are subjected to wetting and drying cycles, which is the case of concrete structures in marine atmosphere zone, chloride profiles tend to be two-zone profiles, with a maximum chloride concentration a few millimetres inside (Tuutti, 1993, Pérez, 1999). In accordance with this behaviour, chloride profiles obtained in this study are two-zone profiles with an external zone, where wetting and drying cycles take place and favour to capillary sorption and an inner zone, where the humidity remain at higher levels and the transport of chlorides can be attributed mainly to diffusion (Pérez, 1999, Castro *et al.*, 2001, Meira *et al.*, 2007).

In this study, only the diffusion zone was considered. A rescaling of chloride profiles starting from the end of convection zone was used (Nilsson *et al.*, 2000). The maximum chloride concentration in the interface between convective and diffusion zones ($C_{máx}$), which means the surface chloride content of the rescaled profile, was represented by Equation 1, where, C_0 is the initial chloride content in concrete, $k_{cmáx}$ is a material and environmental dependant coefficient and D_{ac} is the accumulated deposition of chlorides on the wet candle.

$$C_{máx} = C_0 + k_{cmáx}\sqrt{D_{ac}} \quad (1)$$

Numerical obtaining of transport parameters

Using the finite difference method, least-squares fitting (Hornbeck, 1982) and computational routines, a numerical simultaneous fitting was done to each set of chloride profiles representative of each concrete and exposure station to obtain the parameters of the model: D_0 and m, which are detailed along this section. Equation 2 corresponds to the finite difference representation of Fick's second law of diffusion and it is complemented by Equation 3 that represents the dependence of diffusion coefficient on some variables. In these equations, $C_{i,j}$ is the chloride concentration at the depth *i* and time *j*, Δx is the depth variation, Δt is the time variation, D_{ap} is the apparent diffusion coefficient, D_0 is a referential diffusion coefficient and *f(t), f(T)* and *f(SD)* represent, respectively, the influence of time, temperature and water saturation degree of concrete on apparent diffusion coefficient (Mangat and Molloy, 1994, Almenar, 2000, Nielsen and Geiker, 2003, Boddy *et al.*, 1999).

$$C_{i,j+1} = \frac{(C_{i+1,j} - 2C_{i,j} + C_{i-1,j})}{\Delta x^2}.\Delta t.D_{ap} + C_{i,j} \quad (2)$$

$$D_{ap} = D_0.f(t).f(T).f(SD) \quad (3)$$

The influence of temperature was not considered in this study, due to its low influence on the apparent diffusion coefficient in this specific case. As a result, Equation 3 was rewritten as Equation 4, where t_0 is a reference time (1 s), *t* is the variable time, *m* is a time dependant coefficient and *SD* is the water saturation degree of concrete porous network. The structure of *f(t)* and *f(SD)* terms was based on previous works that consider the concrete hydration over time (Mangat and Molloy, 1994, Boddy *et al.*, 1999) and the influence of water content in concrete porous network in chloride transport (Almenar, 2000). The behaviour of water saturation degree of concrete over time was represented by Equation 5, where SD_{max} and SD_{min} are, respectively, the maximum and the minimum saturation degree observed.

$$D_{ap} = D_0.f(t).f(SD) \Rightarrow D_{ap} = D_0.\left({}^{t_0}\!/_{t} \right)^m.e^{4.6(SD-1)} \quad (4)$$

$$SD = \frac{SD_{\max} + SD_{mim}}{2} + \frac{SD_{\max} - SD_{mim}}{2}\sin\left(2\pi\frac{(t-t_0)}{365}\right) \quad (5)$$

Numerical extrapolations and proposal of aggressiveness subzones

Simulations of $C_{máx}$ were done, considering average chloride depositions on the wet candle of 500, 120 and 15 mg/m^2.day, which are close to average values for the studied region. Numeric extrapolations of chloride profiles were done for 50 years also using finite difference method. From these profile extrapolations, the advance of chloride threshold was obtained and represented in Figure 3.

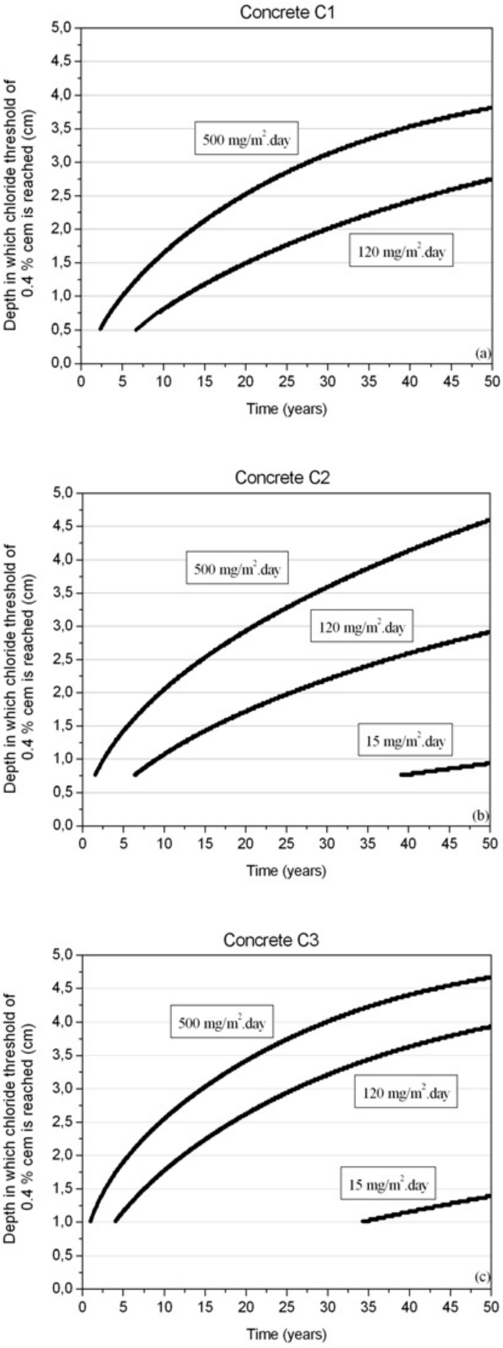


Figure 3. Simulations of chloride threshold advance in concretes C1 (a), C2 (b) and C3 (c).

Simulations done in Figure 3 show that, considering service life as the time for chloride threshold to be reached at the rebar surface, it is possible to observe different situations about service life, depending on chloride deposition rate. For example, after 50 years, concrete structures with w/c of 0.5 – C1 (Figure 3a) and located at sites with 15 mg/m^2.day average chloride deposition rate did not present 0.4 % of cement mass at any depth. For sites with 120 mg/m^2.day chloride threshold takes place at 27.5 mm depth and for sites with 500 mg/m^2.day it takes place at 38.0 mm depth, indicating that if reinforcement was placed at 30 mm depth, structures subjected to 500 mg/m^2.day had already reached their service life. For concretes with w/c of 0.57 – C2 (Figure 3b), these depths after 50 years were 9, 29 and 46 mm, respectively, which indicates that more than 45 mm of reinforcement cover are necessary for concrete C2 to reach a service life close to 50 years at sites with 500 mg/m^2.day. A similar analysis can also be done for concrete C3 (Figure 3c).

Chloride penetration into concrete in marine atmosphere zone is closely related to the availability of chlorides in atmosphere. Simulations done here show that chloride deposition rate on the wet candle device can be used as an environmental indicator for concrete durability study in marine atmosphere zone, helping to set minimum durability requirements for concrete structures depending on the deposition level expected. For the studied region, the reference of distinct chloride deposition levels on the wet candle lead to different combinations of w/c ratios and concrete cover requirements, considering 50-year service life, which can be represented in different aggressiveness subzones and concrete requirements, as presented in Table 2. To comprise the presented ranges in Table 2, chloride penetration into concrete was assumed as the main reason for reinforcement depassivation. This was supported by the low rates of concrete carbonation observed in this experiment. Furthermore, some interpolations were done using curves from Figure 3, as well as a minimum concrete cover of 30 mm was adopted.

Table 2. Proposal of aggressiveness subzones

Aggressiveness subzones		**Maximum water to binder ratio**	**Minimum concrete cover (mm)**	**Distance from the sea for the studied region (m)**
Aggressiveness level	**Chloride deposition rate (mg/m^2.day)**			
High	Higher than 100	0.50	40	Less than 100
Moderate	Between 100 and 10	0.55	35	Between 100 and 750
Depreciable	Less than 10	0.60	30	More than 750

CONCLUSIONS

The use of chloride deposition on the wet candle as an environmental indicator for service life analysis can be done thorough simulated curves of chloride threshold advance for each level of chloride deposition on the wet candle. From an expected chloride deposition level for a given environment and the characteristic curves of chloride threshold advance for each concrete it is possible to preview the expectancy of service life for different concrete structures, considering different concrete covers or, in another way, to suggest a minimum concrete cover depth for a required time of service life.

Taking into account that marine atmosphere zone can assume different extensions depending on aerosol characteristics, wind regime, land surface, etc., the proposal of aggressiveness subzones for marine atmosphere zone considering ranges of chloride deposition rates seems to be suitable. As a consequence, concrete structures in marine atmosphere zone should have different durability requirements depending on the chloride deposition level expected.

ACKNOWLEDGMENTS

The authors thank the Brazilian Government Agency for the Improvement of Graduated Professionals and Eduardo Torroja Construction Research Institute for partially supporting this research. The authors also thank the Bazilian National Institute of Meteorology for providing climatic data.

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