CIÊNCIA e NATURA

ISSN 2179-460X
OPEN ACCESS

Ci. e Nat., Santa Maria, v. 46, e75364, 2024 • https://doi.org/10.5902/2179460X75364
Submitted: 18/04/2023 • Approved: 31/10/2024 • Published: 29/11/2024

Chemistry

Evaluation of chloride deposition using the wet candle method: a study in the city of Cabo Frio, RJ

Avaliação da deposição de cloretos através do método da vela úmida: um estudo na cidade de Cabo Frio, RJ

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ABSTRACT

In a context of durability design of reinforced concrete structures, it is necessary to establish the divisions of the aggressiveness classes of the different maritime and coastal environments in order to contribute to the study of the classification of environmental aggressiveness. In this paper, the deposition of aggressive ions and the general climatic aspects of the coastal region of the city of Cabo Frio, RJ, are evaluated. For the analysis, the wet candle method (Brazilian NBR 6211, 2001) was adopted. The exhibitions were held at five different points throughout the city, each with three wet candles. To quantify the chloride content, the conductimetry method was used, which is done by measuring the electrical conductivity of an electrolyte solution due to ion migration. The results point to a high level of chlorides in the initial range of distance from the sea and a considerable decrease from approximately 900 meters from the seashore. In this way, it was possible to verify that the city, in its interior, is under moderate to minimal aggressiveness. In the initial distances of the seashore, there is high aggressiveness. These results show the importance of considering micro exposure environments during the design phase of reinforced concrete structures.

Keywords: Durability; Reinforced concrete; Ambiental aggressiveness; Chloride

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RESUMO

Em um contexto de projeto de durabilidade de estruturas de concreto armado, há necessidade de estabelecer as divisões das classes de agressividade das diferentes regiões marítimas e costeiras, a fim de contribuir para o estudo da classificação de agressividade ambiental. Neste trabalho são avaliados a deposição de íons agressivos e os aspectos climáticos gerais da região litorânea da cidade de Cabo Frio, RJ. Para a análise, foi adotado o método da Vela Úmida (NBR 6211:2001). As exposições foram realizadas em cinco pontos distintos ao longo da cidade, contando cada um com três velas úmidas. Para quantificar o teor de cloretos utilizou-se o método de condutimetria, o qual se baseia na variação da condutividade elétrica de uma solução eletrolítica devido à migração de íons. Os resultados parciais apontam teor elevado de cloretos na faixa inicial de distanciamento do mar e diminuição considerável a partir de aproximadamente 900 metros da orla marítima. Dessa forma, foi possível verificar que nas distâncias iniciais da orla marinha, a cidade encontra-se sob elevada agressividade e, em seu interior, sob agressividade de moderada a mínima. Esses resultados evidenciam a importância da consideração de microambientes de exposição durante a fase de projeto de estruturas de concreto armado.

Palavras-chave: Durabilidade; Concreto armado; Agressividade ambiental; Cloretos

1 INTRODUCTION

Historically, the population distribution was from the coast, reaching today the largest urban affluence to the next coastal regions. According to the Brazilian demographic census of 2010, the highest concentration of population is in the coastal zone, corresponding to 54.8% of the population (IBGE, 2022). By looking at the history of civilizations, it is possible to observe, together, the evolution of constructions and construction materials.

Since the 20th century, reinforced concrete has played an important role in civil construction, being among the most widely used materials since then. Despite being a resistant material, when exposed to coastal regions, it is subject to significant weather interference. Consindering this reality and taking into account the urban and simultaneously marine aspect region, this characteristic presents the challenge of determining parameters and the need for caution, as the action of the environment is directly linked to the performance and safety of the structure. This reality brings the challenge of determining construction parameters and the need for caution, since the performance of a structure is directly linked to environmental factors (Sell Junior, 2020).

Meira et al. (2017) highlight the importance of studying micro-regions of aggressiveness. The authors propose that the marine atmospheric zone be divided into different levels of aggressiveness, taking into account the microclimates within an environment. This is because marine interferences can vary in intensity; a marine atmospheric zone has particular and interdependent physical and chemical aspects. Therefore, it is necessary to carefully analyze the overall conditions of the region, which poses the challenge of understanding the characteristic aspects of aggressiveness in order to achieve adequate parameters for structural performance, durability, and safety.

In addition to mechanical stresses, it should be noted that the chemical and physical actions of the environment are directly related to the good performance of a structure. Thus, risk assessment must safely and consciously include defining the environmental aggressiveness class to be adopted for the design and execution of reinforced concrete structures. In this regard, the way Brazilian design codes consider aggressiveness classes is pointed out by researchers and professionals in the field as insufficient to ensure the service life of structures in diverse environments (Medeiros et al., 2019).

The prescriptive approach traditionally used in specifying concrete for durability is limited to setting limit values for parameters such as nominal cover of reinforcement, water/cement ratio, compressive strength, and cement consumption depending on the class of aggressiveness to which the concrete will be subjected (Wally, 2019). However, Beushausen et al. (2021) emphasize that aggressiveness classes cannot be generalized nor indiscriminately applied to different regions, requiring a more rigorous and detailed characterization of the exposure environment. The main international regulations classify the exposure environment based on different degradation mechanisms. The exposure classes adopted in different international standards are commonly divided into categories defining the environment in question, and subclasses related to the intensity of aggressiveness.

Meira (2004) highlights the relevance of studying microregions of aggressiveness. For example, the author proposes that the marine atmosphere zone be divided into three different levels of aggressiveness depending on its distance from the sea and chloride deposition rate. Table 1 shows the proposed limit values.

Table 1– Levels of aggressiveness in marine atmosphere zone

Aggressiveness	**Chloride deposition mg.(m^2.day)$^{-1}$**	**Distance from sea [m]**
Elevated	> 100	< 100
Moderate	Between 10 and 100	Between 100 and 750
Minimum	< 10	> 750

Source: Meira (2004)

For regions with higher wind intensities, up to 18 m.s^{-1}, Morcillo et al. (2000) considered that chloride deposition values below 100 mg.(m^2.day)$^{-1}$ characterize a low aggressiveness region, while zones of high aggressiveness are those where depositions higher than 400 mg.(m^2.day)$^{-1}$ are observed, emphasizing the relevance of the aggression characteristics specific to microregions.

The adoption of classification mechanisms in microenvironments, however, presents great challenges since several characterization campaigns in different points are necessary to obtain reliable results. As a way of expanding the volume of data regarding the aggressiveness of marine atmosphere zones, this paper presents the environmental characterization in microenvironments of the Cabo Frio region, located in the Lakes region, north coast of the state of Rio de Janeiro.

2 METHODOLOGY

2.1 Preparation of candles and collection of samples

The investigation primarily targeted the city of Cabo Frio, a Brazilian municipality located in the state of Rio de Janeiro, approximately 155 km from the state capital, Rio de Janeiro. It is situated at a latitude of 22° 52′ 46″ south and a longitude of 42° 01′ 07″ west, at an altitude of 4 meters above sea level (Figure 1).

Figure 1 – Local do Estudo, região de monitoramento

Source: Author/Private collection of the authors (September, 2022)

The determination of chloride content in the atmosphere was carried out according to the wet candle method as established by NBR 6211:2001. The Brazilian standard was based on the American ASTM D512 – 89 (ASTM, 2004). The equipment used consists of an Erlenmeyer flask containing 200 ml of glycerinated water, to which is attached a tube with a diameter of 25 mm and a height of 150 mm wrapped in gauze, and two test tubes with a diameter of 15 mm inside the flask, through which the gauze descends until it comes into contact with the bottom of the flask.

Figure 2 – Location of the monitoring points

Source: Author/Private collection of the authors (September, 2022)

Figure 3 – Wet candle exposure station

Source: Author/Private collection of the authors (September, 2022)

Through the process of capillarity, the gauze becomes moistened and captures the ions present in the atmosphere, which move into the solution contained in the flask. The equipment was exposed for 45 consecutive days in summer, autumn, winter, and spring. The partial results presented in this work refer to the first two seasons of the year and are compared to other studies previously carried out in different regions. Each of the exposures had five monitoring points, as shown in Figure 2, in triplicate, as illustrated in Figure 3. The analysis points P1, P2, P3, P4, and P5 are located at distances of 35, 55, 710, 1045, and 1400 m, respectively, from the seaside. Subsequently, the candles were collected and the gauzes were washed. The wash water was added to the content of the original wet candle, and the final volumes of all samples were determined.

2.2 Determination of total ion content

The chloride content in each of the samples was determined through the conductometry method. Souza et al. (2018) highlight the effectiveness of this method in measuring the salt content in solution, obtaining values related to electrical conductivity, as also proposed by ASTM D4308 - Standard Test Method for Electrical Conductivity of Liquid Hydrocarbons by Precision Meter. According to the authors, by measuring electrical conductivity, it is possible to quickly determine the amount of salts that a solution can contain, based on a standard saline solution. This allows for a safe correlation between the electrical conductivity of a solution and its salinity.

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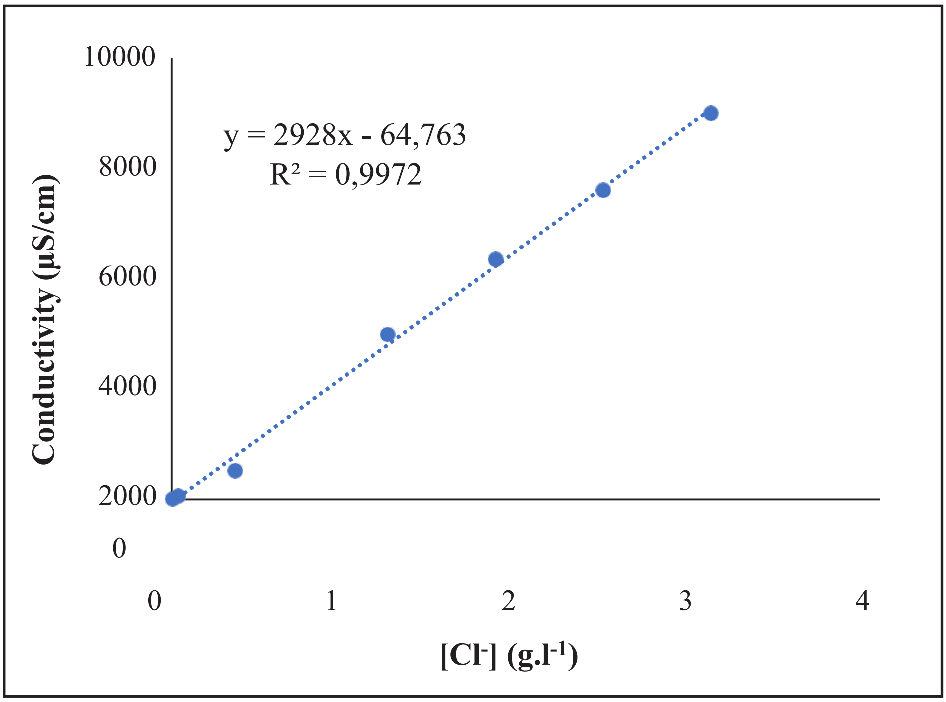
The determination of electrical conductivity was carried out using a microprocessed conductivity meter from the Quimis brand calibrated with a standard solution of potassium chloride (KCl) 0.01 Mol.L-1, which corresponds to 1408.3 mS/

cm at 25 ºC. the standard curve of conductivity as a function of the variation in the concentration of chloride ions used in this study can be seen in Figure 4.

Initially, the conductivity meter was turned on and allowed to stabilize for approximately 30 minutes before taking readings. During this interval, the conductivity measuring probe was washed with deionized water and dried with soft absorbent paper. Subsequently, the equipment was calibrated with a standard solution of 0.01 M KCl. Deionized water used for the construction of the wet candles was used as a blank, followed by the reading of the samples. After each reading, the probe was washed and dried before taking the next sample reading, as established by the manufacturer.

Figure 4 – Standard conductivity curve as a function of chloride ion concentration



Source: Organized by authors (2022)

3 RESULTS AND DISCUSSIONS

The local climatology during the study period, monitored by the Admiral Paulo Moreira Sea Studies Institute, was characterized by average maximum temperatures of 32°C in summer and 27°C in autumn. As for average minimum temperatures, 24°C was observed in summer and 19°C in autumn. The predominant wind directions in the region were from NE and ENE (northeast and east-northeast), accounting for approximately 70% of the wind frequency in the region. The average wind speed varied between 4.3 m/s and 5.4 m/s in summer and 3.8 m/s and 4.5 m/s in autumn. The average monthly precipitation during the study period was 115 mm in summer and 50 mm in autumn.

The monitoring points were determined based on the distance from the sea, obtained from the coastline, and the safety of the location. The partial results of chloride deposition obtained during the first two seasons of the year (summer and autumn), corresponding to 45 days of exposure in each, and the corresponding averages are presented in Tables 2 and 3.

Table 2 – Chloride deposition during summer

Sample	Distance [m]	Volume [l]	Conductivity [μS/cm]	Chloride [g/l]	Chloride deposition mg.(m² .day)$^{-1}$
P1.1	35	0,254	2650	0,927	523,34
P1.2	35	0,308	3840	1,334	912,77
P1.3	35	0,4	1048	0,38	506,72
P2.1	55	0,315	211	0,094	65,93
P2.2	55	0,385	135,5	0,068	58,52
P2.3	55	0,367	145,3	0,072	58,51
P3.1	710	0,218	262	0,112	54,06
P3.2	710	0,32	165,1	0,079	55,83
P3.3	710	0,23	169,2	0,08	40,84
P4.1	1045	0,354	131,1	0,067	52,62
P4.2	1045	0,275	114,3	0,061	37,37
P4.3	1045	0,345	134,8	0,068	52,25
P5.1	1400	0,245	153,3	0,074	40,55
P5.2	1400	0,25	142,5	0,071	39,33
P5.3	1400	0,305	153,6	0,075	50,55

Source: Compiled by the authors (2022)

Table 3 – Chloride deposition during autumn

Sample	Distance [m]	Volume [l]	Conductivity [µS/cm]	Chloride [g/l]	Chloride deposition mg.(m2 .day)-1
P1.1	35	0,295	1740	0,616	404,07
P1.2	35	0,43	1642	0,583	557,00
P1.3	35	0,365	1075	0,389	315,74
P2.1	55	0,345	147,2	0,072	55,50
P2.2	55	0,36	154,7	0,075	59,96
P2.3	55	0,335	187,2	0,086	64,06
P3.1	710	0,319	725	0,270	191,21
P3.2	710	0,305	657	0,247	167,07
P3.3	710	0,355	662	0,248	195,81
P4.1	1045	0,365	112,3	0,060	49,05
P4.2	1045	0,345	85,1	0,051	39,24
P4.3	1045	0,267	124,8	0,065	38,41
P5.1	1400	0,357	143,3	0,071	56,37
P5.2	1400	0,35	128,4	0,066	51,31
P5.3	1400	0,371	116	0,062	50,90

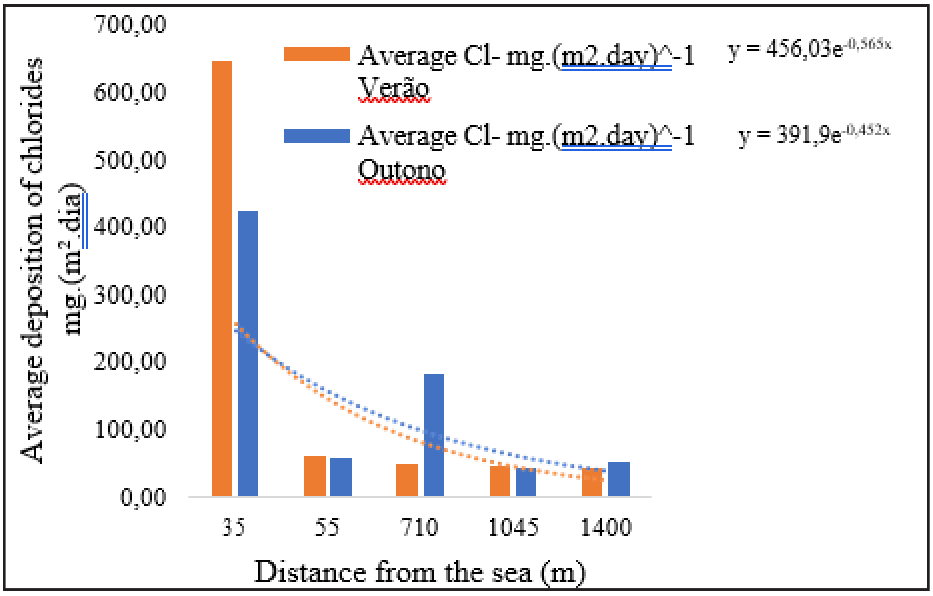
Source: Organized by the authors (2022)

Additionally, the averages obtained at each analysis point are presented in Figure 5.

It can be observed that the deposition of chlorides in the first 35 m from the sea exceeded the average of 600 mg.(m².day)$^{-1}$, reaching a maximum value of 912.77 mg.(m².day)$^{-1}$ and a minimum of 506.72 mg.(m².day)$^{-1}$ during the summer period. In the autumn, the average deposition was 425 mg.(m².day)$^{-1}$, with a maximum value of 557 mg.(m².day)$^{-1}$ and a minimum of 315.74 mg.(m².day)$^{-1}$.

It is possible to observe a disparity between the results obtained at distances of 35 and 55 meters from the sea. Both points were allocated in the first houses facing Praiado Foguete in the city of Cabo Frio. However, station P2 was sheltered due to the circulation of vehicles in the area. Therefore, the importance of considering microenvironments within the same (in this case, marine) environment is reiterated. Although the difference between stations P1 and P2 (= 20 m) is small in the context of the marine environment, the difference between the mean chloride deposition values is quite significant (= 476 mg.(m².day)$^{-1}$) and may be a consequence of the protection provided to station P2. Additionally, it is noted that between the range of 1 km and 1.4 km, the results find equilibrium at an average of approximately 50 mg.(m².day)-1. This fact may result from the contribution of characteristic factors such as, mainly, the predominance and intensity of the sea breeze. Another contributing factor is the geographical configuration of the region, which is surrounded by different maritime sources and is a flat area free of major elevations in its topography. This significantly contributes to the advancement of the maritime air mass into the interior of the continent.

Figure 5 – Chloride deposition at different distances and seasons of the year



Source: Organized by the authors (2022)

Finally, Table 4 presents a comparison of the results obtained in this study with other studies conducted on the Brazilian coast.

Table 4 – Chloride deposition in different Brazilian states

Cabo Frio, RJ (Presentstudy)		João Pessoa, PB (Meira et al., 2006)		Florianópolis, SC (Garcia et al., 2007)		Vitória, ES (Borba Jr., 2011)	
Dist [m]	**Cl^- mg.(m².day)$^{-1}$**	**Dist [m]**	**Cl^- mg.(m².day)$^{-1}$**	**Dist [m]**	**Cl^- mg.(m².day)$^{-1}$**	**Dist [m]**	**Cl^- mg.(m².day)$^{-1}$**
35	536,6	10	480,3	10	1095	10	502,08
55	60,4	100	117,6	100	11,5	65	62,16
710	117,4	200	19	200	21,1	120	116,65
1045	44,8	500	13,8	400	15	240	32,6
1400	48,2	-	-	600	6,5	520	9,4
-	-	-	-	1000	23,7	-	-

Fonte: Autoria (2022) / Indication: Organized by the authors (2022)

In this way, when comparing the data shown in the Table 4, it can be observed that there is similarity and some relationship in the behavior of salinity at certain distances. However, it is also possible to observe a variation in concentration values in the area closest to the sea depending on the region. While in the Northeast, the initial concentration reaches approximately 500 mg.(m².day)$^{-1}$, in the South region this value is around 1,000 mg.(m².day)$^{-1}$. Despite the high variability inherent in environmental parameters, these averages can provide a good understanding of how these values may differ according to the environment.

4 CONCLUSIONS

The results obtained from the first two exposures indicate a region of high concentrations of aggressive ions in the first 1045 meters from the beach, with a balance found in regions of lower concentrations, that is, from 1045 m away from the sea. There is also a greater difference in the decrease of chloride deposition from summer to autumn, which may be related to weather conditions and, mainly, wind predominance. These differences may become more evident with the contribution of the next exposures throughout the year.

In addition to the differences attributed to the chloride concentration due to the weather conditions of each season, it was also possible to observe the influence of micro-regions, a fact evidenced by the differences in the results obtained among the monitoring points.

Therefore, when observing the trend between the average depositions based on the model proposed by Meira (2004) initially highlighted, the preliminary results suggest a classification by micro-exposure environments. This classification indicates high aggressiveness within the first 35 m, extending to distances of approximately 900 m; moderate aggressiveness between 900 and 1300 m, and minimal aggressiveness at distances greater than 1300 m. Thus, the importance of building a data framework on the aggressiveness of marine environments is reiterated, contributing to the understanding of the mechanisms to which concrete will be subjected during its service life and enabling improvements in normative texts that deal with the durability design of reinforced concrete structures.

ACKNOWLEDGEMENTS

The authors thank FAPERGS (Research Support Foundation of Rio Grande do Sul) for the financial support (PqG 07/2021). R.C.F. Barbosa thanks CNPq (Brazilian National Council for Scientific and Technological Development) for the Master scholarship grant. To the Chemistry Department of the Federal Rural University of Rio de Janeiro(UFRRJ) for developing the chemical analyses.

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How to quote this article

Barbosa, R. C. F., Barbosa, R. C. F., Barbosa, R. C. F., Strunkis, C. de M., Casartelli, E. A., Wally, G. B., & Magalhães, F. C. (2024). Evaluation of chloride deposition using the wet candle method: a study in the city of Cabo Frio, RJ. *Ciência e Natura*, 46, e75364. https://doi.org/10.5902/2179460X75364