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# Evaluation of the aggressive potential of marine chloride and sulfate salts on mortars applied as renders in the Metropolitan Region of Salvador – Bahia, Brazil

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# ABSTRACT

In recent years, growing interest has focused on determining the performance of materials and evaluating the service life of structures exposed to various environmental forces. In this context, the determination of the aggressive potential of marine salts on mortars used as external renders is critical. The present study aimed to evaluate the spatial distribution of marine salts relative to distance from the sea. This was done by monitoring the deposition rate of chlorides and sulfates in wet candle sensors, located at nine stations scattered around the Metropolitan Region of Salvador, state of Bahia, Brazil. The study also determined the effectiveness of water-soluble salts at penetrating three different types of mortars of varying cement content via deposition and diffusion. The methodology employed enabled an evaluation of the efficiency of the monitoring sensors' measurement of the aggressiveness potential of local marine aerosol, and determination of the comparative performance of the three mortars tested, from the standpoint of resistance to salt penetration. The type and amount of salts captured both in solution and in powder samples extracted from the mortars were determined by ion chromatography. The analysis of the various types of mortars tested indicated which types are more resistant to the aggressive potential of the region's marine aerosol and the distance from the shore where local buildings are liable to be most strongly affected.

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# 1. Introduction

The atmosphere surrounding buildings is dynamic and undergoes changes due to anthropogenic and natural activities, which may alter the characteristics of the materials composing the structures. Many studies have been performed concerning the mechanisms and results of interaction between atmospheric substances and those in construction materials. Among these studies, some stand out for better clarifying the chemical deterioration processes in monuments or structures exposed to atmospheric aerosol and/or acid deposition (Leysen et al., 1989, 1990; Zappia et al., 1992, 1993, 1998; Fobe et al., 1993; O'Brien et al., 1995; Perry and Duffy, 1997; Sabbioni et al., 1998, 2001, 2003; Gobbi et al., 1998; Martinez-Ramirez, 2000; Okochi et al., 2000). Few studies refer to the action of marine aerosol on construction materials or historical monuments.

In coastal regions, the atmosphere is enriched with particles that are naturally generated by the action of wind on the water surface. These particles compose the sea spray, which introduces ionic species into the atmosphere, principally chlorides and sulfates (Warneck, 1988; Seinfeld and Pandis, 1998; Campos, 1995; Pitts and Pitts, 2000).

The masses of air enriched with sea spray particles, composed primarily of seawater, can cause accumulative deposition of ions on the external renders. These ions are able to penetrate into the interior of the material through ionic diffusion, thus hastening its degeneration. Soroka and Carmel (1987) consider environments charged with salts extremely dangerous to construction materials, since they penetrate and crystallize inside the material, causing degeneration of the physical structure. According to these authors, this is primarily true with regards to mortars. The accumulation of ions on mortars has prejudicial effects. This occurs principally because of salt crystallization inside of the mortar pores, which causes a volume increase, resulting in high internal pressure that destroys the porous structure of the material. Most building materials of mineral origin commonly used as external renders do not resist this pressure. Besides salt crystallization within the pores of the external renders, chemical attacks can occur, for example, by sulfates, and pressure can be provoked by the penetration of

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humidity (Soroka and Carmel, 1987). Sabbioni et al. (2001) refer to chemical reactions occurring on mortars, which were collected from archaeological, historic, and modern buildings in various European locations, by quantification of sulfur anions ( $SO_3^{2-}$  and  $SO_4^{2-}$ ) in the collected samples.

Brazil is the country with the longest coastline in South America (approximately 8000 km) and Bahia is the state with the largest portion of this coast (1188 km). The vector of development of its principal cities is located in coastal regions where the action of sea spray is propitious for the creation of an aggressive atmosphere toward construction materials and products. The evaluation of this aggressiveness potential of the environment due to deposition of marine salts on rendering materials of local structures was the objective of this study. This may help in the planning of more economical building projects, in terms of cost–benefit, by using renders more compatible with local environmental conditions.

In the city of Salvador, capital of the state of Bahia, an intense presence of sea spray can be detected along the entire 45 km of beach that borders the city. This continues along the greater metropolitan area for another 120 km of ocean line. The resulting atmosphere of this region has a strong presence of marine aerosol and was characterized by Campos (1995) as having very high levels of chloride ions when compared with marine atmospheres in other regions of the world (Warneck, 1988; Sievering et al., 1990; Harrison and Pio, 1983). The lack of studies on how the regional environment can affect construction techniques and materials may be responsible for the use of construction materials that are incompatible with local conditions, causing or increasing problems with building conservation.

For this reason, the evaluation of the salt content of marine aerosol in the region and its effect on mortars in exposed local structures deserves special attention.

# 2. Materials and methods

#### 2.1. Mortar types used

In order to simulate the deposition of atmospheric aerosol on buildings, we created test specimens. These were formed of three mortar types frequently used for external render on buildings in this region. They are differentiated by the proportions of cement, sand, sandy clay and water used in each type, according to Table 1. The type of cement utilized was Portland, specifications C II F-32, in line with the Brazilian NBR 7211 standard (ABNT, 1983). The maximum diameter of the sand grains was 1.2 mm, with a fineness modulus of 1.55 and swelling coefficient of 1.39%, which were determined according to the standard Brazilian methodology.

Sandy clay consists of clay material used as an additive to the construction materials, aiming to reduce the quantity of lime (CaO). The sandy clay utilized had a maximum dimension of 2.4 mm, fineness modulus of 1.65, and contained, on average, 80% sand, 15% clay, and 3-5% silt.

The mortars were produced on the laboratory scale with the composition indicated in Table 1, using Pavitest mortar-mixers, model SD71B, and were submitted, while fresh, to tests for consistency level, incorporated air content, water retention, and mass density, according to the recommendations of the Brazilian Association of Technical Norms (ABNT, 1994a). The results of these tests are also presented in Table 1.

# 2.2. Production of mortar test specimens

The test specimens were formed in cylindrical shapes (50 × 100 mm) using the technical standards (ABNT, 1995). They were then treated in a chamber with controlled temperature and relative humidity ( $T = 22 \pm 2$  °C; RH > 90%) for 28 days. After that

#### Table 1

Composition and characteristics of the mortar types used

Materials	Type of	mortar		ABNT <sup>a</sup> norm that
	A	В	С	indicates the test methodology
	Proporti	ions in ma	ass (kg)	
Cement	1.0	1.0	1.0	
Sand	7.1	3.7	2.6	
Sandy clay	5.8	3.0	2.1	
Water	3.7	1.8	1.3	
Tests with fresh mortars				
Consistency level, mm	252	252	250	NBR 13276
Water retention, %	95.0	95.4	95.0	NBR 13277
Mass density, kg m <sup>-3</sup>	1.95	1.99	2.02	NBR 13278
Incorporated air content, %	2.6	1.8	1.3	NBR 13278
Tests with mortars as test specim	nens			
Resistance to axial compression, MPa	1.0	4.0	7.7	NBR 13279
Resistance to diametrical	0.17	0.65	1.4	NBR 5739
compression, MPa				
Water absorption by	20.0	19.1	17.6	NBR 9778
immersion, %				
Water absorption by	1.3	0.91	0.61	NBR 9779
capillarity, kg m <sup>-2</sup> min <sup>-1/2</sup>				
Specific mass, kg dm <sup>-3</sup>	1.64	1.69	1.72	NBR 9778
Cement consumption, kg m <sup>-3</sup>	108	207	287	

<sup>a</sup> Brazilian Association of Technical Standards.

they were numbered and identified according to mortar type, and marked on top. Then, they were tested for the following characteristics: resistance to pressure (axial and diametrical), water absorption by immersion, water absorption by capillary action, and specific mass (ABNT, 1994b).

# 2.3. Sampling

#### 2.3.1. Sampling stations

Nine sampling stations were chosen in areas with high growth rates in the city of Salvador and its Metropolitan Region. The sampling stations were geographically referenced and identified by their distance from the coast, varying from 70 m to approximately 5 km. The final choice of the location of each sampling station depended on the availability of an open but covered area, free of interference from walls, trees or other obstructions, thus permitting wind circulation. In addition to this, it was necessary to provide safety for the exposed material. In Fig. 1, a regional map is included, showing the locations of the sampling stations.

# 2.3.2. Sampling of the atmospheric aerosol and exposure of the test specimens

In order to sample the atmospheric aerosol and determine their main ions and aggressiveness potential, we relied on the device proposed by the standard G140 of the American Society for Testing and Materials (ASTM, 1996), which uses the Wet Candle Method. The sampling device (see diagram in Fig. 2) consisted basically of a 500-mL Erlenmeyer flask containing deionized water, which was adapted externally with a perforated rubber stopper with a test tube wrapped in gauze passing through it, with the lower end of the gauze immersed in the water.

Through capillary action, the gauze lining the tube remains permanently moistened. The ionic components of the atmospheric aerosol are deposited onto the gauze. By diffusion, these ions move toward the aqueous solution where they remain until removed for analysis.

A wet candle sensor was installed in the nine sampling stations in a covered balcony, protected against rain, at a distance from the soil of 1.5 m, and far away from walls that could hinder the free

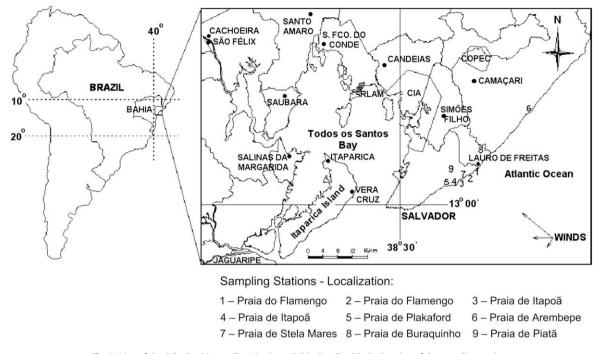
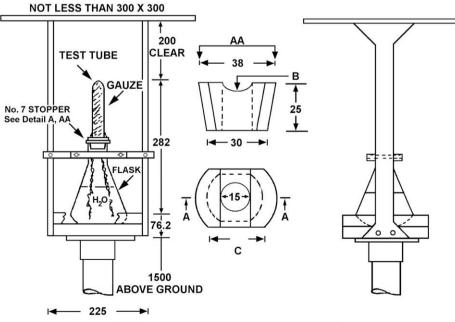


Fig. 1. Map of the Salvador Metropolitan Region – Bahia, Brazil, with the location of the sampling stations.

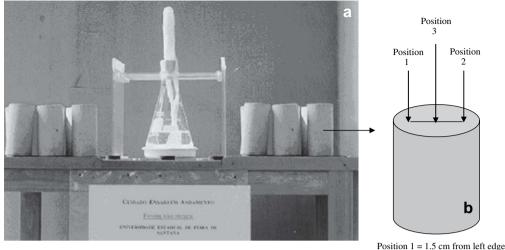
circulation of air. Simultaneously, test specimens of the three different types of mortar were installed in the stations. Fig. 3a shows the arrangement of the wet candle sensor with the mortar test specimens for exposure to the atmospheric aerosol. The mortar specimens remained exposed for five months. During this time, the wet candle sensor was replaced several times to give exposures as follows: four 1-week periods, then one 2-week period, then two 3-week periods, and finally two 4-week periods. The purpose of shorter time intervals at the beginning of the study was to define the minimum quantities of ions that would be sampled on the wet candle, thereby ensuring suitable samples for the analytical method employed, in terms of the concentration of the ions of interest. In addition, it was necessary to ascertain the performance of the sampling device and to select sampling periods that would maintain the integrity of the samples, while more easily correlating the deposition of the ions on the wet candle and the quantity of ions found in mortar test specimens exposed simultaneously for the entire period. The relation between the marine aerosol deposited on the wet candle during the periods of its exposure and on the mortar samples tested will be shown later herein.

Periodically, before the end of the wet candle sensor's exposition time, the level of the deionized aqueous solution was refilled to



Note 1 - Dimensions are in millimeters (mm).

Fig. 2. Sketch of the sampling device used in the Wet Candle Method (ASTM, 1996).



Position 2 = 1.5 cm from right edge Position 2 = 1.5 cm from right edge Position 3 = Central position

Fig. 3. Wet candle sensor with the mortar test specimens for exposure to the atmospheric aerosol (a) and test specimen drawing showing the positions where the samples were removed for analysis (b).

compensate for losses by evaporation, therefore maintaining the conditions at a reasonably constant level for diffusion of the ions.

The exposure of mortar test specimens at the sampling stations was also executed during these five months. This was done in order to make possible the identification of the effects incurred by local atmosphere on the external render, represented by the test specimens used. The positioning of the set of test specimens and the wet candle sensor was maintained constant in relation to the prevailing direction of the local wind. The relation between the deposited marine aerosol on the wet candle and that deposited on the mortar samples will be discussed below.

# 2.4. Analytical procedure

At the end of each wet candle sensor exposure period, the solution level in the Erlenmeyer was raised to the original with deionized water, the gauze component of the wet candle sensor was incorporated into the solution, and the device was substituted with a new one. The solutions containing the ionic components of atmospheric aerosol were then stored in 20 mL polyethylene flasks, centrifuged for 5 min (13,500 rpm) to separate any insoluble particles that were detached from the gauze, and immediately analyzed for chlorides, nitrates and sulfates by ion chromatography, with micro membrane suppression (H<sub>2</sub>SO<sub>4</sub>, 20–25 mMol L<sup>-1</sup>). The separation of anions was done by using a Sykan LCA A14 column measuring 250 mm in length by 3 mm in internal diameter, and using a solution of 3 mMol L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub>/0.5 mMol L<sup>-1</sup> NaHCO<sub>3</sub> as eluent.

The samples for determining the salt content deposited in the test specimens of the various mortar samples were removed from the cylindrical test specimens at three different points, i.e., at two diametrically opposite points 1.5 cm from the left and right edges of the test specimens, corresponding to the ions originating from atmospheric aerosol deposited on the surface of the mortar test specimens and diffused up to that distance inside it, and from the center, at a distance of 2.5 cm from the above points. The diagram of a mortar test specimen in Fig. 3b indicates the location of the holes from which material was removed for analysis.

The removal of the material for analysis was done using an electric drill with a vídia center bit. At each of the points a 4-cm hole was drilled, collecting all the powder for analysis (an average of 3 g of material). This material was stored in small polyethylene

flasks. The ions were extracted in water by means of an ultrasound bath and analyzed by the chromatographic method previously cited.

Sodium was also analyzed in the samples by flame photometry to be used as a marine tracer, allowing us to distinguish the fraction of sulfate ions from sea spray and that from other sources using the following equation:

$$[SO_4^{2-}]_{nss} = [SO_4^{2-}]_T - 0.06024 \times [Na^+]_T$$

where: nss = "non-sea salt";  $[SO_4^{2-}]_{nss}$  = the molar concentration of sulfate deposition in the sample not originating from the sea spray;  $[Na^+]$  = the molar concentration of sodium deposition in the sample; and 0.06024 = the molar ratio between concentrations of  $SO_4^{2-}$  and Na<sup>+</sup> in the seawater (Campos, 1995).

Quality control of the analytical data was through simultaneous analyses of ion chromatography (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) and flame photometry (Na) of reference rain samples of Environment Canada – National Water Research Institute/National Laboratory for Environmental Testing, and an artificial rain prepared in our laboratory.

# 3. Results and discussion

# 3.1. Dry deposition of chlorides, nitrates and sulfates from the atmospheric aerosol

Although the nitrate present in the atmospheric aerosol is a common tracer of urban and industrial emissions (such as  $SO_{4-nss}^{2-}$ ), it is not an original component of sea spray. The detection of its presence in the local atmosphere through ion chromatographic analysis of the deposition samples, using the Wet Candle Method, as well as test specimens of exposed mortar, justifies the presentation of its results in this work.

The aggressiveness potential of the local marine atmosphere on the various types of mortars used in regional construction was taken as the time-weighted mean of the dry deposition shown in the wet candle sensor, as a function of the number of days corresponding to each sampling period (Table 2), and in the test specimens of mortar exposed in the monitoring stations as a function of the distance from the sea (Table 3).

Many factors influence the mechanism of dry deposition of atmospheric components, involving the transport of material through the air, which is controlled mainly by diffusion processes. These factors are especially affected by meteorological variables, which control the transfer of chemical species to surfaces at different levels of efficiency. Variables include wind velocity, relative humidity, which can contribute to increase the particle descent velocity by increasing its mass and density, and other variables such as wind direction and air temperature. Marine atmospheres are richer in salts at higher wind velocity, a condition that favors the generation and emission of sea spray into the atmosphere. Thus, meteorological data were recorded during the entire monitoring period, observing that the weekly measurements were very stable (for example, wind velocity was between 2.6 and  $3.4 \text{ m s}^{-1}$ ). Individual hourly readings had the following variations during the period of monitoring (between the months of August 2002 and January 2003): wind velocity between 0.6 and 8.1 m s<sup>-1</sup>, temperature between 18 and 31 °C, and relative humidity between 67 and 100%. Throughout the 10 periods of exposure of the wet candles at the nine sampling stations (a minimum of one week and maximum of a month), the meteorological conditions varied very little; hence, no correlation was observed between the deposition of atmospheric salts and the meteorological parameters.

The tendency of the dry deposition of atmospheric salts originating from marine spray (chlorides and part of the sulfates) or other sources (nitrates and other sulfates) that deposited onto the wet candle sensor during the five months of sampling is presented in Fig. 4 relative to distance from the sea. The black lines, which indicate the best graphic trend at those points, represent the tendency of the dry deposition of those ions to be correlated with the distance between the sampling site and the seashore. The values of *R* (correlation coefficient) indicate that only the deposition of ions originating from sea spray, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup><sub>ss</sub>, shows a strong correlation. The others, incorporated into the atmospheric aerosol via traffic exhaust, do not correlate deposition with distance from the seashore.

The chloride deposition rates (Fig. 4a) show a tendency to decrease with the distance from the sea. Considering the data of Table 2, more significance was seen up to about 150 m (sampling station 3). The reason is that a large part of the sea spray is in the form of coarse particles (larger than  $2 \,\mu$ m), which are deposited in the proximity of the emission source. In this study, it was estimated that 81% of the Cl<sup>-</sup>, which represents the sea spray in the atmosphere of this region, is deposited within a distance of about 150 m (see Table 2). This was calculated in relation to the total deposition that occurs along the sampling network up to the last station, about 5 km from the seashore.

# Table 2

Time-weighted mean dry deposition of chloride, nitrate, total sulfate  $(SO_4^{2-}{}_{Total})$ , sulfate from sea spray  $(SO_4^{2-}{}_{ss})$  and sulfate from other sources  $(SO_4^{2-}{}_{nss})$  at different distances from the sea

Sampling station/	Dry de	position	$[mg m^{-2} d^{-1}]$		
(distance from the sea, m)	Cl-	$NO_3^-$	$SO_4^{2-}$ <sub>Total</sub>	$SO_4^{2-}s^{a}$	SO <sub>4</sub> <sup>2-</sup> nss <sup>b</sup>
1/(72)	43	1.1	8.1	6.1	2.0 (25)
2/(138)	7.7	0.93	2.8	1.5	1.3 (46)
3/(143)	14	1.2	6.0	1.7	4.3 (72)
4/(532)	3.6	1.2	4.0	0.84	3.2 (80)
5/(788)	2.5	1.3	3.5	0.70	2.8 (80)
6/(1165)	2.2	1.2	2.5	0.70	1.8 (72)
7/(2226)	4.1	0.88	5.5	0.90	4.6 (84)
8/(2645)	1.5	1.0	4.7	0.52	4.2 (89)
9/(4705)	1.5	0.92	3.6	0.64	3.0 (83)
Deposition percent up to ≈150 m [%]	81	-	-	68	-

Values in parentheses indicate the percentage related to the SO<sub>4</sub><sup>2-</sup><sub>Total</sub>.

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	mpling station/	Position i	Position in the test specimen	specime	u,														
Mottar type     A     B     C     C     A     B     C     C     A     B     C     C     A      1314     12	istance from the sea, m)	1			2			3			1			2			т		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		Mortar ty	pe																
$ \begin{bmatrix} [CT], \ \mu gg^{-1} \end{bmatrix} \\ \begin{bmatrix} [$		A	В	C	A	В	J	A	В	U	A	В	C	A	В	U	A	В	U
318     258     177     271     286     243     210 (26)     291 (35)     135 (24)     362     1016     727     266     997     784       219     230     121     214     244     158     205 (32)     159 (25)     73 (21)     127     2401     1919     1246     2093     2015       134     84     78     59     73 (24)     17 (40) $40$ (22) $400$ 757     938     207     565       15     12     6     8     14     6     22 (49)     17 (40) $46$ (16) $400$ 757     938     227     584     709     755       15     24     21     13     132 (24)     12 (26) $430$ 757     938     755     765     755       15     24     21     18     11     13 (24)     122 (25)     41 (43)     535     765     755       36     68     22     31 (24)     122 (24)     535     949 </td <td></td> <td>[Cl<sup>-</sup>], µg {</td> <td>1-1</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>[SO<sup>2</sup>-], µg §</td> <td>а<sup>-1</sup></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>		[Cl <sup>-</sup> ], µg {	1-1								[SO <sup>2</sup> -], µg §	а <sup>-1</sup>							
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	138)	219	230	121	214	244		205 (32)	159 (25)	73 (21)	1227	2401	1919	1246	2093	2015	958 (28)	1651 (27)	1611 (29)
	143)	134	84	78	92	88	59	73 (24)	117 (40)	40 (22)	400	843	477	342	785	765	708 (49)	824 (34)	496 (27)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	532)	15	12	9	∞	14	9	22 (49)	17 (40)	<4.6 (16)	400	757	938	227	584	707	285 (31)	920(41)	611 (27)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	788)	15	24	42	18	45	37	13 (28)	17 (20)	28 (26)	439	747	1073	544	709	755	554(36)	776 (35)	698 (28)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1165)	22	21	39	18	28	11	13 (24)	12 (20)	<4.6 (4.4)	535	949	1130	612	930	957	381 (25)	612 (24)	602 (22)
18 17 21 18 19 51 41 (53) 19 (34) 6 (7.6) 342 651 1044 458 862 1313 13 24 21 10 26 35 13 (36) 33 (40) <4.6 (3.9) 352 949 1025 525 997 1034 13-318 12-258 6-177 8-271 14-286 6-243 13-210 12-291 <4.6-135 342-1227 651-2401 477-1919 227-1246 584-2093 707-2015 35±11 31±8 15±8	2226)	36	35	68	22	35	61	39 (40)	28 (28)	21 (14)	727	1132	1323	487	1026	1380	717 (37)	987 (31)	1323 (33)
13 24 21 10 26 35 13(36) 33(40) <4.6(3.9) 352 949 1025 525 997 1034 13-318 12-258 6-177 8-271 14-286 6-243 13-210 12-291 <4.6-135 342-1227 651-2401 477-1919 227-1246 584-2093 707-2015 35±11 31±8 15±8	2645)	18	17	21	18	19	51	41 (53)	19 (34)	6 (7.6)	342	651	1044	458	862	1313	458 (36)	882 (37)	1159 (33)
13-318 12-258 6-177 8-271 14-286 6-243 13-210 12-291 <4.6-135 342-1227 651-2401 477-1919 227-1246 584-2093 707-2015 35±11 31±8 15±8	4705)	13	24	21	10	26	35	13 (36)		<4.6 (3.9)	352	949	1025	525	266	1034	535 (38)	1045 (35)	573 (22)
	nge, $\mu g g^{-1}$									<4.6-135	342-1227	651-2401	477-1919	227-1246	584-2093	707-2015	285-958	612-1651	496-1611
	erage diffusion to the central position, %	I	I	I	I	I	1			$15\pm 8$	I	I	I	1	I	1	35 ± 7	$33 \pm 5$	$28 \pm 4$

1/(7) 3/(1-2)/(7) 5/(7) 5/(7) 5/(7) 5/(7) 9/(4) /alues in parentheses indicate the percentage of ion diffusion to the central position of the test specimen

<sup>&</sup>lt;sup>a</sup> ss = sea spray. <sup>b</sup> nss = non-sea salt.

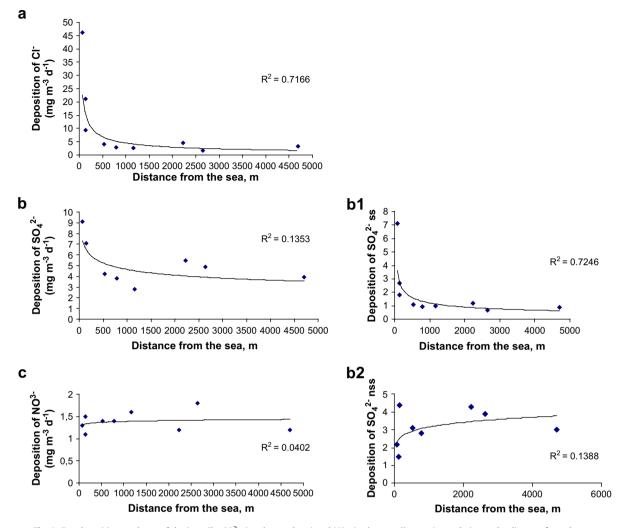


Fig. 4. Dry deposition tendency of the ions Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> (total, ss and nss) and NO<sub>3</sub><sup>-</sup> in the sampling stations relative to the distance from the sea.

For sulfate, this tendency is less accentuated, since a very small portion of this ion that is incorporated into the local atmospheric aerosol has its origin in sea spray. Fig. 4b1 and b2 show, by graphic representation, the behavior of sulfate  $SO_4^{2-}$ <sub>ss</sub> (originating from sea spray) and  $SO_{4-nss}^{2-}$  (non-sea salt) vs. distance from the sea. The concentration of the former diminishes in the atmosphere with the distance from the sea. This reflects the deposition of coarse particles in the proximity of the local emissions. In addition, during transport those particles may be intercepted by building surfaces, causing a gradually lessened concentration of those ions in the atmosphere. Similar to the percentage of Cl<sup>-</sup> deposited within about 150 m (Table 2), it was calculated that 68% of the  $SO_4^{2-}$  s deposition occurred within this distance. The concentration of SO<sub>4</sub><sup>2-</sup><sub>nss</sub> particles in the atmosphere doesn't show an increase trend with the distance from the sea (Fig. 4b2). In a similar way, it is observed in Fig. 4c that there is no significant trend of  $NO_3^-$  deposition in relation to distance from the sea. Beyond the NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup><sub>nss</sub> not having a sea spray origin, the fact of none of them decrease with distance from the sea can be explained by the homogeneity of traffic density along the sampling network, as traffic is the main local source of  $NO_3^-$  and  $SO_4^{2-}$  nss through oxidation processes of NOx and SO<sub>2</sub>. The deposition of NO<sub>3</sub> varied in the narrow range between 0.88 and 1.3 mg  $m^{-2}\,d^{-1}$ throughout the 5 km of extension of the network. The contribution of both types of sulfates, calculated for each sampling station, can be seen in Table 2. The variation in  $SO_{4-nss}^{2-}$  deposition along the network is greater than that found for  $NO_3^-$ , but its percentage in relation to the total  $SO_4^{2-}$  at distances greater than 138 m from the sea (station 2) also varies very little: between 72 and 89%, or a variation of 17% (Table 2).

# 3.2. Deposition rate of the salts in the exposed test specimens at the sampling stations

The data collected through atmospheric aerosol deposition using the wet candle sensor permitted a spatial evaluation of the aggressiveness potential of the atmosphere. In order to observe how this potential acts upon regional structures, three types of mortar commonly used in the region were utilized as test specimens. These were exposed in sampling stations as described above to allow a natural interaction between the renders and the local atmosphere. Mortar blanks of the different types, that is, test specimens that were not exposed to the atmospheric aerosols, were sampled and measured in the same way and at the same positions as the exposed specimens, as described above (Fig. 3b). The concentrations of chloride and sulfate in the blanks were deducted from the measurements made up of the exposed samples.

Table 3 presents the concentrations of  $Cl^-$  and total  $SO_4^{2-}$  determined in the removed material of the test specimens of the different types of mortars, after exposure to the atmospheric aerosol during five months. The data of Table 3 show that the chloride

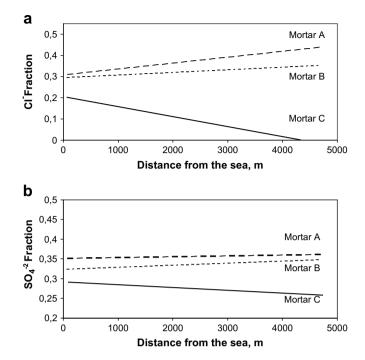
enrichment is higher in the test specimens of the three types of mortars at sampling sites closer to the sea, within about 150 m (sampling station 3). Through the ion concentrations determined in the material taken from the central position (position 3, Table 3) in the test specimens and the total amount of each ion in the three positions, that is, at 1.5 cm from each edge and at the central position, the amount of  $Cl^-$  and  $SO_4^{2-}$  that diffused into the central part of the test specimens was calculated. The subtraction of the blanks, that is, the concentrations of the ions in the test specimens not exposed to the atmospheric aerosol, was included in these calculations.

Considering the total quantity of  $Cl^-$  found in the material removed from the three points in the mortar test specimens (Fig. 3b and Table 3), and calculating the percentage of  $Cl^-$  deposited on them when exposed at the sampling stations up to 150 m from the seashore, a good correlation can be observed between the deposition of sampled  $Cl^-$  on the wet candle during 10 different periods and on the mortar test specimens exposed during five months. In other words, the deposition of  $Cl^-$  was similar to that found when sampling with the wet candle (Section 3.1): 83% on the type A and B mortar test specimens and 70% on the type C mortar test specimens. This difference can be explained by the fact that the type C mortar is more resistant to the aggressive action of atmospheric aerosol, making it more difficult for the ions deposited upon its surface to diffuse inward.

Fig. 5(a) and (b) show the chloride and total sulfate fractions, respectively, that were determined in the material removed from the central position of the different types of test specimen, exposed in the sampling stations. As the amount of atmospheric aerosol deposition on the mortar test specimens varies with the exposure location, the concentrations of ions determined in different points of the test specimens have been transformed into "fractions" to normalize the amount of ion accumulated in the central position as a result of diffusion. That is, the fractions of  $Cl^{-}$  or  $SO_{4}^{2-}$  quantify the percentage of the ions in the central position of the test specimens relative to the total found for each ion in the three analyzed positions: 1.5 cm from the left and right edges and in the central position. They were calculated by dividing the concentration of the ion in the central position ( $\mu g g^{-1}$ ) by the sum of the concentrations in the three positions. Fig. 5 shows that the diffusion of both chloride and sulfate ions occurred more easily in the type A mortar test specimens, i.e., on average, 35% for both  $Cl^-$  and  $SO_4^{2-}$ . This diffusion percentage was followed by type B and C mortars, which is expected due to the increase in the amount of cement used per cubic meter in these types of mortar. The greater cement content decreased their porosity and hence, their permeability, increasing their resistance to the penetration and transport of ions into the material. On the other hand, the tests carried out with the three different types of fresh mortars and as test specimens (Table 1) indicated that the type C mortar absorbed less water by immersion and by capillarity. This characteristic renders this material more resistant to the penetration of ions via atmospheric water vapor and to the subsequent hydration/crystallization of salts inside it, reducing the aforementioned harmful effects. In addition, the tests also incorporate little air into this type of mortar, resulting in lower porosity, another important aspect in terms of the durability of these materials.

In the test specimens of mortar type B, the percentage of  $Cl^-$  and  $SO_4^{2-}$  that had been diffused for the central position fell, respectively, to 31 and 33%, and to 15 and 28% for mortar type C.

The wet candle and the exposed mortars test specimens were also submitted to the deposition of gases as NOx and SO<sub>2</sub>, that would be contributing for the deposition of NO<sub>3</sub> and SO<sub>4</sub><sup>2</sup> <sub>nss</sub>. The data of Table 3 also show that dry deposition of SO<sub>2</sub> is not only the major source of sulfate in the mortars but is also much more efficient in total salt enrichment than deposition of sea salt



**Fig. 5.** Fractions of chloride (a) and total sulfate (b) salts determined in the central position of the exposed test specimens composed of different type of mortars.

particles. Even at the sites very close to the sea there is much more enrichment sulfate in the test specimens than chloride. Thus, in this work, the aggressiveness potential of marine salts on mortars used in local construction can be considered just in relation to chloride salts. However, even though sea spray is not the main source of the  $SO_4^{2-}$ , which is incorporated in the atmospheric aerosol of the region, its behavior in the different types of mortars is shown. Direct comparisons cannot be made between the results obtained from the wet candle (ion deposition in  $mg m^{-2} d^{-1}$ ) and those obtained from the material removed from the different points in the test specimens (ion concentration in those positions,  $mgg^{-1}$ ). The wet candle device was changed at the end of each period of exposure (10 periods throughout five months), while the mortar test specimens remained exposed throughout that time. This enabled the measurement of migrating salts deposited on the surface of the test specimens, simulating the action of aerosol deposited upon the local buildings. Nevertheless, a correlation can be drawn between the wet candle and mortar test specimen results. Fig. 6 shows a strong correlation between these data with respect to chloride. In the case of sulfate, however, these data cannot be correlated because of the distinct sources of this ion in the local aerosol. These sources greatly enriched the test specimens with sulfate during their five months of exposure.

Although chemical reactions are known to occur inside building overlay materials, producing insoluble salts that cause part of the damage encountered in mortars, as in the case of sulfatation processes, this work considered only the deposition/ formation of soluble salts of the ions under study, which are considered aggressive to the overlay materials of the buildings in the region. However, as mentioned in Section 3.2, the quantity of those ions in the spaces of the mortars was subtracted from the quantity deposited by atmospheric aerosol on the exposed test specimens. Therefore, the water-soluble salts taken into account to evaluate the aggressiveness potential of the local aerosols on the buildings' overlay materials should be representative of the

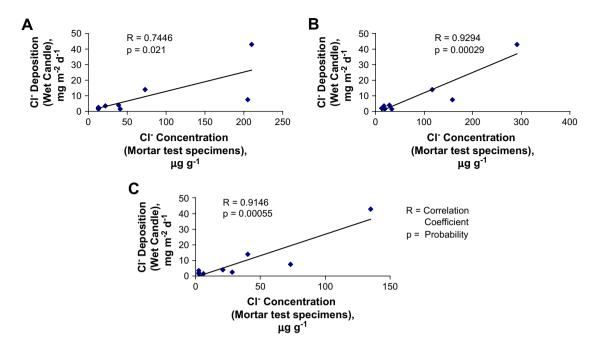


Fig. 6. Correlation between the Cl<sup>-</sup> concentration at the central position of the mortar test specimen types A, B and C and the average deposition at the wet candle, in nine sampling stations.

process, an assumption that is confirmed by the correlations shown in Fig. 6.

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#### 4. Conclusions

Considering the deposition of chloride at varying distances from the sea and the incorporation of this ion into the atmospheric aerosol, we can conclude that 81% of the average aggressiveness potential to exposed construction materials, in the region of study, is found to be within a 150-m distance from the sea.

Regarding the  $SO_4^{2-}$ , the action of the sea spray is only significant at a very short distance from the sea, about 140 m, where 64% of this ion incorporated in the aerosol has its origin in the sea spray. The nitrate salts present in the atmosphere of the studied region varied in average about 32% over a distance of 5 km probably due to the homogeneity of the vehicles traffic along the sampling network.

The mortar showing the strongest resistance to the penetration of salts was type C, whose cement content exceeded 200 kg m<sup>-3</sup>, although it had lower mass proportions of sand and water. It had lower water absorption capacity and lower porosity than types A and B.

The results shown in this work may help in planning better costbenefit building projects, since the use of more suitable materials can give improved resistance and durability to the construction.

It is important that the ideal quantity of cement used in mortars be evaluated when seeking to minimize the aggressiveness of marine atmospheres, while taking care to avoid the formation of rigid external renderings, which tend to crack and thereby favor even more the infiltration of aggressive agents.

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