Northeastern Brazilian marine atmospheric corrosion performances of galvanized steel and copper specimens

[1]K. J. C. Brambilla, [2]P. A. M. Pereira, [3]K. F. Portella, [4]M. S. Cabussú, [5]D. P. Cerqueira, [6]R. N. Salles; [7]P. C. Inone, [8]G. C. da Silva, [9]F. Piazza, [10]J. M. da Silva, [11]S. L. Henke
[1]LACTEC - PoBox 19067, 81531-980; Curitiba, PR, +554133616200, +554133616056, kelly.campos@lactec.org.br
[2]LACTEC - PoBox 19067, 81531-980; Curitiba, PR, +554133616766, +554133616056, princia@lactec.org.br
[3]LACTEC - PoBox 19067, 81531-980; Curitiba, PR, +554133616220, +554133616056, portella@lactec.org.br
[4]COELBA - Granjas Rurais Pres. Vargas s/n, 41290-000, Salvador, BA, +557133705250, mcabussu@coelba.com.br
[5]COELBA - Granjas Rurais Pres. Vargas s/n, 41290-000, Salvador, BA, +557133705250, dcerqueira@coelba.com.br
[6]COELBA - Granjas Rurais Pres. Vargas s/n, 41290-000, Salvador, BA, +557133705250, rsalles@coelba.com.br
[7]LACTEC - PoBox 19067, 81531-980; Curitiba, PR, +554133616288, +554133616056, inone@lactec.org.br
[8]LACTEC - PoBox 19067, 81531-980; Curitiba, PR, +554133616288, +554133616056, piazza@lactec.org.br
[9]LACTEC - PoBox 19067, 81531-980; Curitiba, PR, +554133616288, +554133616056, cunha@lactec.org.br
[10]LACTEC - PoBox 19067, 81531-980; Curitiba, PR, +554133616288, +554133616056, maurilio@lactec.org.br
[11]LACTEC - PoBox 19067, 81531-980; Curitiba, PR, +554133616288, +554133616056, henke@lactec.org.br

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Abstract

Copper, in turn, is the most used material in the field of electricity, especially in electrical contacts. Already, the zinc is the metal most used in atmospheric exposure conditions, used in sheet form as in castings, but its most important application is as a coating for corrosion protection of steel structures. Salvador, it has disadvantages as an environment conducive to corrosion, by setting up a wet surface time t4, high corrosive environment (C4). In this work was proposed to study the performance of these metals compared to the effects of air pollution of an industrial site. For both atmospheric corrosion sites (ACS) were implanted natural weathering standard in order to assess the aggressiveness of atmospheric contaminants on the performance of metal specimens (galvanized steel and copper). In determining their corrosion rates were analyzed for sulfate and chloride ions, atmospheric, given the proximity of this ACS to the seafront, due to these propitiate the acceleration of corrosion. The results allowed observing that the average local concentration of sulfate was higher than the chloride, because of the proximity of the pollutant source, and that the corrosion rate of galvanized steel was more significant than 61,5% of copper.

Keywords: atmospheric corrosion, copper, galvanized steel, performance

Introduction

The city of Camaçari in Bahia, Northeastern Brazilian city (shown in Fig. 1) is the largest integrated industrial complex in the Southern hemisphere. The local has more than 90 chemical companies, petrochemical and other industries as automotive, pulp copper metallurgy, textile, beverages and services [1]. Thus, Camaçari-BA is classified as an industrial environment, with high sulfur compounds concentration [2-3].

According to Köppen, Camaçari-BA has a climate classified as warm and humid, which is typical of the tropical region near the coast, with irregular distribution of rainfall, extending almost throughout the year. It is a city with about 2,466 h annual sunshine, wind speed annual average of 2.2 m/s, average annual temperature of 25 ºC and average annual humidity of about 81%. These weather conditions coupled with industrial pollution are extremely harmful to engineering materials, providing corrosion or degradation of metallic materials, by having a time of wet surface (t) high (4,000 h/year), in this case, sorted by NBR 14643/01 [4] and t4, i.e., high corrosive environment (C4) [4-5].

A large part of the materials present in everyday life is susceptible to degradation, as well as most of the metals of distribution, transmission and data communication lines, such as cables, towers, telephone lines, accessories network, among others. Based on this information, in this research is proposed a comparative analysis of the performance of galvanized steel and copper by determining the rate of corrosion and deterioration of the metals of overhead electrical power distribution (RD) in the city of Camaçari-BA. For this purpose, a methodology was developed based on the deployment of an atmospheric corrosion station (ECA) in Camaçari-BA which was monitored monthly meteorological parameters, rates of chloride and sulfate, in order to obtain data for the classification of atmospheric corrosivity and, have been installed, galvanized steel plates and copper.

Figure 1. Photo of the industrial plant of Camaçari-BA [1].

Classification of atmospheric corrosivity

The atmospheric corrosion is a very common process, because the vast majority of structures exposed to the atmosphere are metallic. It occurs when it forms a thin film of electrolyte on the metal surface, allowing the attack of the electrochemical type. The film is formed due to the presence of moisture in the atmosphere. Even for the low relative humidity as 60% may develop that film [6]. The rate of corrosion depends strongly on relative humidity and the constituents of the atmosphere [7].

The Brazilian normalization NBR 14643 [8], provides standards for the classification of corrosivity of atmosphere compared to metallic materials such as carbon steel, aluminum, copper and zinc. This reflects, then, the current knowledge about this type of classification and describes the atmosphere in five categories of corrosivity, ranging from C1 (very low) to C5 (very high), as shown in Table 1.

The degree of corrosive atmosphere on zinc and copper can be made from the corrosion rates obtained in the first year of exposure, as shown in Table 2.

Atmospheric corrosion of galvanized steel

Usually, the life time of zinc coatings depends on their thickness, being more or less independent of the application method (hot immersion, metallic coating or plating). Tests conducted in the United States have shown that a thin layer of 0.025 mm of galvanic coating in suburban or rural areas have an average lifetime of about 11 years, eight years in the marine areas and nearly three years on the coast [9-10]. Zinc acts as a sacrificial anode on the steel, giving it effective galvanic protection, thus avoiding a direct impact corrosive attack on steel.

Approximately 1 nm of the outer surface is rich in zinc corroded surface contaminants such as chloride and sulfate ions, and the composition of the corrosion layer is not constant with depth [11]. Moreover, experimental measurements of zeta potential and isoelectric point as a function of pH 6-8 indicates that the probability of owning corrosion products of zinc with a negatively charged surface decreases in the order: zinc hydroxycarbonate>> zinc hydroxysulfate> zinc hydroxide> zinc hydroxychloride> zinc oxide [12-13]. Thus, the negative charge of the zinc corrosion products is able to assist in the repulsion of chloride ions and thereby preventing the attack on zinc [12]. This protection method has been used for many years, mainly in the automotive industry, which contributed to the development of these coatings [14].

According to Gemelli (2001) the atmospheric corrosion of zinc results from the reaction:

$$Zn + \frac{1}{2}O_2 + H_2O \rightarrow Zn(OH)_2 \qquad (1)$$

The formation of basic salts occurs by the reaction of zinc hydroxide with pollutants from the atmosphere.

In an atmosphere so polluted, the pH of the electrolyte on the surface of zinc can lower the point of dissolving the basic sulfates.

In marine atmosphere the reaction of $Zn(OH)_2$ with the chlorides form the basic chlorides of the type $Zn(OH)_xCl_{2-x}$. The corrosion rate of zinc is lower than the speed measured in a heavily polluted industrial atmosphere.

Table 1. Categories of atmospheric corrosivity [8].

Category of Corrosive	Aggression
C_1	Very Low
C_2	Low
C_3	Average
C_4	High
C_5	Very High

Table 2. Categories of atmospheric corrosivity according to data obtained in the first year of exposure [8].

Category of corrosive	Units	Zinc	Copper
C_1	g/m^2/year	≤ 0,7	≤ 0,9
	µm/ year	≤ 0,1	≤ 0,1
C_2	g/m^2/ year	0,7-5	0,9-5
	µm/ year	0,1-0,7	0,1-0,6
C_3	g/m^2/ year	5-15	5-12
	µm/ year	0,7-2,1	0,6-1,3
C_4	g/m^2/ year	15-30	12-25
	µm/ year	2,1-4,2	1,3-2,8
C_5	g/m^2/ year	30-60	25-50
	µm/ year	4,2-8,4	2,8-5,6

Atmospheric corrosion of copper

The corrosion of copper in the atmosphere has been studied extensively since copper is a material typically used in electronics [15-16].

The great resistance to atmospheric corrosion of copper is mainly determined by the protective role of the layer of corrosion products that remain attached to its surface, particularly the inner layer of cuprite which behaves as a physical barrier preventing the oxidation of the metal. It seems that within the cuprite also serves as an intermediary in the patina formation that involves the oxidation of copper ions to form salts based on copper. For instance, the transformation of cuprite in paratacamite has been reported in coastal patinas [17]. Basic salts formed are insoluble species that remain adhered to the inner layer of cuprite to provide some protection to the metal. It is known that the chloride is a hygroscopic salt which helps to keep moisture from the surface of the metal layer and its corrosion products. The sodium chloride, for example, in an atmosphere with relative humidity above 75% becomes hygroscopic [18-19] and in an environment with relative humidity above 90%, facilitates the formation of a permanent layer of water in surface where it is deposited. Jesus *et al.* [20] concluded that the corrosion rate increased and the corrosion potential decreased with increasing chloride content in the middle, showing that the chloride concentration influences the corrosion resistance of copper tubing.

The layer of surface water is suitable for the adsorption and oxidation of sulfur dioxide (SO_2) to form a surface layer rich in acidic sulfates [21]. Besides knowing that from the composition of corrosion products, it is clear that the sulfur dioxide and nitrogen oxides play a central role in the formation of patina. It was found that in their presence, corrosion begins to be significant, once the relative humidity is above 50-63% [22-23].

In a dry copper oxidizes forming a protective layer of Cu_2O, but without formation of patina [24]. It is formed when the surface of copper and its oxide layer remains wet, Nassau *et al.* [25] showed that copper patinas formed as displayed on a billboard consisted of cuprite Cu_2O, brochantite $CuSO_4(OH)_6$, antlerite $Cu_3SO_4(OH)_4$, posnkakite $Cu_4SO_4(OH)_6.H_2O$ and atacamite $Cu_2Cl(OH)_3$.

Experimental

Climatic Classification Camaçari-BA.

High temperatures and humidity are factors that contribute to the increased degradation of materials in the atmosphere [26]. Based on this concept, Brooks apud Morcillo *et al.* [27]

presented an index of the potential corrosion from meteorological data. The numerical value called the decay index of Brooks (Id), may represent an important index of the potential corrosion from meteorological data, and is calculated from the saturation pressure of water vapor (this value can be obtained experimentally or by using standard tables) [28] the temperature and relative humidity averages in the region. According to the Id value of the corrosion rate has a direct correlation with the atmospheric corrosivity as illustrated in Table 3.

Table 3. Index of Brooks' deterioration [28].

Id	**DEGREE OF DETERIORATION**	**Id**	**AGGRESSION**
Id < 1	Very Low	0 -1	Not aggressive
1 < Id < 2	Low	1 - 2	Very low aggressive
2 < Id < 5	Moderate	2 - 4	Low aggressive
Id > 5	High	4 - 5	Aggressive
		5 -10	Very aggressive

Determination of chloride (Cl^-) in the atmosphere

The determination of chlorides in the atmosphere (Figure 2) was performed according to ABNT NBR 6211 [29], which prescribe the method of wet sail for determination of inorganic chloride (Cl^-) through volumetric analysis.

Figure 2. Sailing collector chlorides and candle holder.

Determination of total sulfating rate in the atmosphere

The total sulfating rate in the atmosphere was determined according to ABNT NBR 6921 [30]. It was obtained by oxidation or fixation on a surface reactive sulfur compounds such as SO2, SO3, H2S and SO42-. The sulfating rate collector is shown in Figure 3.

Figure 3. Sailing collector sulfates and candle holder.

Natural Weathering Stations

The deployment of the natural weathering station was designed to evaluate the aggressiveness of airborne contaminants, coupled to the local climate on the performance of metal samples similar to metal structures used in the region. This station was located in an area capable of representing the best possible assessment of the region in order to consider the environmental factors involved, since that according to the nature and concentration of contaminants an environment can be characterized as very aggressive for a particular metal and not aggressive to others.

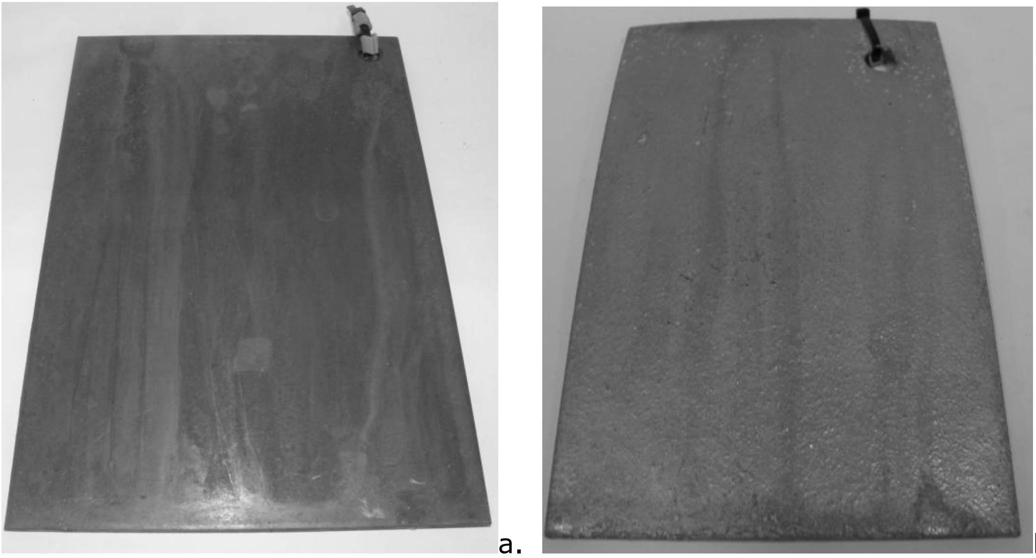
The samples were installed according to ABNT NBR 6209 [31].

In Figure 4 is shown the panel's natural weathering substation (NWS) installed at Camaçari-BA.

Figure 5 shows a photograph of a copper thin plate (Figure 5a) and a galvanized steel thin plate (Figure 5b) after almost 1 ½ years of exposure to atmospheric corrosion Camaçari-BA.

The thin plate were properly cut, degreased with solvent (acetone), prepared by chemical cleaning, were weighed and their area determined according to ABNT NBR 6210 [32]. After preparation of the plates, they were coded rings containing letters and numbers.

Figure 4. Panel NWS Camaçari-BA.



a. b.

Figure 5. Copper (a.) and galvanized steel (b), samples.

Samples have been taken quarterly. After each exposure of samples and have gone through a preliminary visual inspection and photographic recording was carried out proper cleaning of corrosion products in accordance with the kind of standard material. This work was adopted, first, light mechanical cleaning of corrosion products adhering weakly, using soft bristle brushes, and then proceeded to the chemical cleaning involving the removal of products generated by dissolving the reagents in chemicals for each type of material as ABNT NBR 6210 and ASTM G1-90 [33].

Because of this mass loss is influenced by the exposed area and exposure time, these variables were combined and expressed in a formula (Eq. 2) that determines the corrosion rate as standard [35].

$$\text{Corrosion rate} = \frac{K.M}{S.t.\rho} \tag{2}$$

Where (K) is a constant that determines the unity of the corrosion rate (according to Table 7), (M) is the loss of weight in g to the nearest 1 mg, (S) is the area of sample in cm^2, with approximation of 0.01 cm^2, (t) is the exposure time in hours and (ρ) is the density in g/cm^3.

Results and Discussion

Meteorological data

During the analysis period, Camaçari showed higher levels of rainfall to the latest annual average [36-37]. Thus, the deterioration rate of the atmosphere (ID), obtained from the expression Brooks was 5.1. It was classified as very aggressive.

The rain while leaches pollutants, can also decrease the concentration of electrolytes and also the corrosion rate[38].

Sulfating rate and total chlorides in the atmosphere of Camaçari-Ba

According to Table 4, the sulfur dioxide rate is (38,0 ± 11,3) mg/m^2.day and the chloride rate is (8,0 ± 5,8) mg/m^2.day. The sulfur dioxide rate could be explained by the large number of industries present near the region of data collection. The concentration of chlorides is given by the fact that the sea is at a distance of 20 km in relation to NWS, and chloride is the main contaminant.

Table 4. Average concentration of sulfur dioxide and chloride elements (mg/m^2.dia) collected from September 2008 to January 2010.

Average atmospheric concentration of chlorides (mg/m^2.day)	*Average concentration of atmospheric sulfur dioxide (mg/m^2.day)*
Cl^-	SO_2
8 ± 5,8	38 ± 11,3

Weathering test

The copper and galvanized steel corrosion rates are presented in Tables 5 and 6. According to the tables the corrosion rates average for the copper and galvanized steel samples were (8.0 ± 4.2) mg/m^2.day and (14.0 ± 3.7) mg/m^2.day, respectively. The local environment was classified for both as C2 and C4.

Table 5. Corrosion rates (g/m².year) of copper samples in the city of Camaçari-BA, from September 2008 to January 2010.

COPPER			
	TIME EXPOSURE		CORROSION RATE
INITIAL DATE	FINAL DATE	DAYS OF EXPOSITION	(g/m².year)
29/9/2008	11/12/2008	73	14
29/9/2008	17/3/2009	169	9
29/9/2008	27/5/2009	240	6
29/9/2008	2/8/2009	307	6
29/9/2008	27/1/2010	485	3

Table 6. Corrosion rate (g/m².year) of copper thin plates in the city of Camaçari-BA in the period from September 2008 to January 2010.

GALVANIZED STEEL			
	TIME EXPOSURE		CORROSION RATE
INITIAL DATE	FINAL DATE	DAYS OF EXPOSITION	(g/m².year)
29/9/2008	11/12/2008	73	19
29/9/2008	17/3/2009	169	16
29/9/2008	27/5/2009	240	13
29/9/2008	2/8/2009	307	11
29/9/2008	27/1/2010	485	10

In the Figure 7, is shown the corrosion rate of the copper and the galvanized steel samples. Both of them presented the same mass loss rates, but the galvanized steel plate had higher corrosion degradation. One possible explanation for this fact was the higher concentration of sulfate than chloride in the atmosphere.

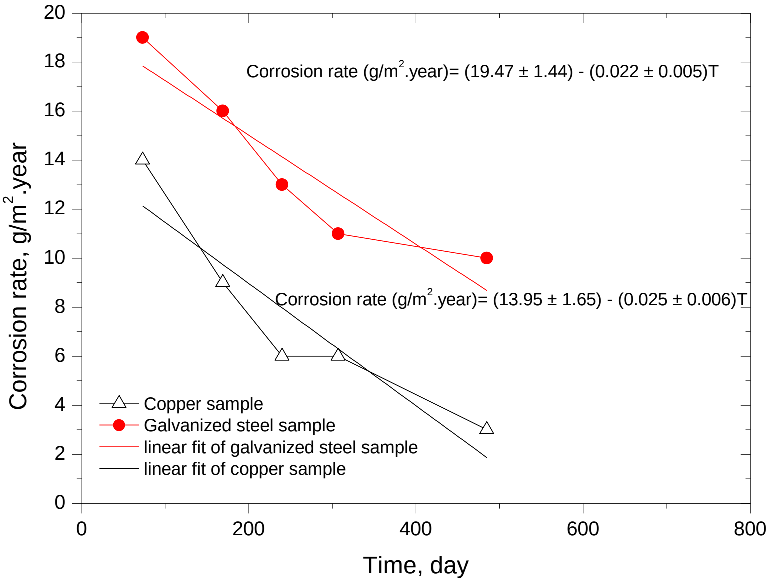


Figure 7. Curves comparing the performance of galvanized steel plates and copper plates in relation to corrosion rate (g/m².year), at the city of Camaçari-BA from September 2008 to January 2010.

In this study the results showed that in Camaçari-BA, the corrosion rate in galvanized steel plates was higher than in copper plates and the average rate of sulfate was so greater than chloride in the period studied.

Conclusion

The research results indicated the region Camaçari-BA could be classified according to the degree of corrosivity as C2 for copper and C4 for galvanized steel samples, i. e., low and high agressivity degree, respectively.

Regarding the corrosion rate in the city of Camaçari-BA, galvanized steel plates had the highest rates than the copper samples.

In that region was recommended to the energy distribution line materials, as electric cables and other main accessories, copper than the galvanized steel metals.

Acknowledgments

The authors would like to thank COELBA, CNPq Process: 303729/2008-2 and LACTEC for their cooperation and providing the infrastructure for accomplishment of this work.

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