

# Atmospheric corrosion in the Canary Islands

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## ABSTRACT

Corrosion is a process that occurs naturally and irreversibly. It is defined as the deterioration of a material (usually a metal) due to its interaction with the surrounding environment. Economic losses related to corrosive processes account for about 5% of the Gross National Product (GNP) of Western countries, China and India. Only in the United States, the costs related to metal corrosion are estimated at app. \$1,000 annual *per capita*, and responsible for a substantial portion of this cost is atmospheric corrosion. Within the various types of corrosive processes, atmospheric corrosion attracts great interest since it affects the entirety of metal materials exposed to air, including urban and industrial infrastructures. It is a widely studied process, and there are national and international standardized norms for its characterization classifying the aggressiveness of a given environment for a specific metal type (usually those most widely used by the industry). However, major discrepancies between the results of direct exposure and those obtained from the application of standardized norms and predictive models occur for fragmented geographical areas, as in the case of archipelagos. In the Canary Islands, due to their characteristic orography and the regime of winds that affects the archipelago, a multitude of microclimates is generated in a very small geographical area. This variability of atmospheric environments in different islands means, even for the same metal, that the extent of the atmospheric attack may vary substantially between two locations separated only a few miles away. This fact imposes the need for the development of specific prediction models to characterize the corrosion rate for different metals. Investigations carried out in the Canary Islands allowed the characterization of the atmospheric corrosion for metals of wide industrial use (namely mild steel, galvanized steel, zinc, copper, and aluminium), and to obtain maps of atmospheric corrosivity for all the islands. Specific mathematical models have been developed for the prediction of the corrosion rates for these metals exposed on the various islands that make up the archipelago.

**Keywords:** Atmospheric corrosion; Corrosion category; Canary Islands; Weight loss; Metals; Predictive models.

## 1.- INTRODUCTION

Corrosion is both the cause and the effect of the chemical interaction of a material with the surrounding environment. In the case of metals, this process of deterioration is called metallic corrosion.

The corrosion of metallic materials is a major financial and ecological plague since repairs due to corrosion account for about 5% of the Gross National Product (GNP) in Western Countries, China, and India [1]. The consequences are a loss of resources, energy, and the release of toxic substances to the environment due to the oxidation reactions. The most

important type of corrosion process is of electrochemical nature. In this process, anodic and cathodic reactions are involved. In order to prevent a corrosion process, one or both redox reactions must be hindered.

Metallic corrosion is a natural process that is thermodynamically favored. As any physicochemical process, the corrosion rate depends on the metal and the environmental variables. When a metal, alloy or metal coating is exposed to the action of the atmosphere, the occurring spontaneous process is called *atmospheric corrosion*. Its rate, as in any other corrosion process, depends on a large number of variables such as the nature of the metal, environmental factors (rain, fog, dew, relative humidity, wind, temperature...), and the amounts of contaminants (SO<sub>2</sub>, NO<sub>x</sub>, chloride, etc.).

Atmospheric corrosion is the most important cause of deterioration of metals given the enormous number of structures and metal parts of all kinds (e.g., bridges, electrical transmission towers, roofs, gates,...) that operate exposed to the atmosphere. Thus, the availability of atmospheric corrosivity maps facilitate the task of selecting the right material for a particular application in a given location based on the local atmospheric aggressivity.

Numerous studies on atmospheric corrosion have been performed and published [2,3], including the development of international standard norms aimed at normalizing this type of studies. One of the limitations presented by these works is that they refer to continental areas with minor geographical and seasonal climatic variabilities. By contrast, the analysis of the atmospheric corrosivity in an archipelagic region like the Canary Islands presents many complexities. We have observed important limitations in the existing international standard norms [4] and a great variability of results compared to those found in continental areas.

## 2.- ATMOSPHERIC CORROSION

Atmospheric corrosion can be defined as the corrosion of materials exposed to the air and its pollutants rather than immersed in a liquid phase. Due to the electrochemical nature of atmospheric corrosion, the metal must be in contact with an electrolyte that can range from an extremely thin film of moisture to an aqueous layer, when the metal appears noticeably wet. Indeed, at room temperature and in a fully dry atmosphere, metallic corrosion progresses at an infinitesimal rate and, for practical purposes, it can be ignored.

The intensity of the atmospheric corrosion process is determined mainly by the relative humidity of the air (RH), the number of days that aqueous precipitation occurs (namely, rain, snow, fog...) and their duration, the contaminants present in the air like gases, vapors, acids and marine aerosols, the presence of solid particles in the air, and the ambient temperature.

RH plays a decisive role in the atmospheric corrosion process. Below a certain amount of relative humidity (i.e., critical relative humidity), where there is no appreciable film of electrolyte on the metal, the corrosion rate is negligible. Different authors have attempted to establish a threshold of relative humidity above which the corrosive reactions take place, but this has become a very complicated process since such a threshold may be influenced by many different variables. Thus, the presence of contaminants or corrosion products may considerably decrease the necessary RH for the corrosive process to occur. For instance, the presence of SO<sub>2</sub> in the air effectively reduces the RH level required for the corrosive process to be initiated for a specific metal.

Another variable used in atmospheric corrosion that is related to RH is known as the time of wetness (TOW). The general process of atmospheric corrosion is the sum of (individual) partial processes that occur whenever a layer of electrolyte is formed on the metal surface for a certain duration. Metal corrosion is possible during these partial processes. It has been found that there is a good correlation between the TOW and the time in which the RH exceeds a certain level of humidity, generally greater than 80%. This feature has led to defining the TOW as the number of hours per year (h/year) during which the RH is higher than 80% and the temperature > 0°C [5].

Another important factor within a particular temperature-humidity condition is the pollution caused by sulfur dioxide or the airborne salinity level. Accordingly, the ISO 9223:1992(E) norm [5] exclusively considered pollution by SO<sub>2</sub> and chlorides when establishing the corrosivity category. Atmospheric corrosion depends on the type of atmosphere in which the metal or metal structure is exposed. Traditionally, atmosphere types have been classified into rural, urban, industrial and marine, depending solely on the SO<sub>2</sub> content according to the ISO 9223 norm [5,6].

In relation to its effect on corrosion, NaCl is another pollutant that has been the subject of a great number of studies. NaCl is incorporated into the atmosphere from the sea. Its effects are very important for areas close to the seashore, where marine aerosol is continuously produced, and thus large amounts of salt may be transported by the air. This aerosol can be carried by winds allowing chlorides to be present at considerable distances from the coast.

Other contaminants may be present in the atmosphere, such as nitrogen compounds in the form of NO<sub>x</sub>, nitric acid (HNO<sub>3</sub>), industrial dust, chlorine (Cl<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S), though they usually have a negligible impact on atmospheric corrosion, and should be taken into account solely for very specific atmospheres. However, the presence of

suspended dust particles can have a significant effect on the corrosion rate of objects exposed to the atmosphere in some regions. According to the chemical and physical properties of the particles present, they can exert a variety of effects as a result of metal surface blasting, leading to acceleration in the corrosive processes, and a reduction in the threshold RH level due to these particles hygroscopic nature.

Although there are multiple factors that can influence atmospheric corrosion, the simultaneous concurrence of several of them frequently causes synergistic phenomena. Thus, the coincidence of SO<sub>2</sub> and Cl<sup>-</sup> makes the resulting effect greater than the sum of them separately.

### 3.- CORROSION MAPPING

Atmospheric corrosion maps are a very useful tool to have available to make a correct selection of the metals, alloys or metal coatings to be used in a given area, as well as to adequately select the protection systems to be employed. The methodology for the elaboration of atmospheric corrosion maps has been established in a series of ISO standards norms. Namely, the methodology for the measurement of the relevant environmental parameters is set by the ISO 9225 [7], the determination of corrosion rates in standard specimens by the ISO 9226 [8], the selection of optimized corrosion protection systems in atmospheric environments by the ISO 11303 [9] and, finally, the classification of the atmospheric corrosion into different categories by the ISO 9223 [5,6]. The ISO 9223 standard has been revised recently, incorporating major changes with respect to the previous version. The most important modification is the addition of a new corrosion category, CX, corresponding to extreme corrosive environments, as shown in Table 1. These categories have been established based on the monitoring of corrosion rates for standard specimens (namely carbon steel, zinc, copper, and aluminium) by weight loss measurements. Table 2 establishes the relation between the corrosion rate and the corrosion category for different metals.

The need for this new corrosion category CX was initially justified in a previous publication of our research group [4], and it was confirmed by other similar studies [3]. Although the second version of the ISO 9223 norm considers a wider range of situations, the possibility of classifying the corrosion of atmospheres according to environmental parameters is not possible anymore, which was possible in its earlier version. However, it does allow a classification of atmospheres according to environmental parameters such as the time of wetness, SO<sub>2</sub> and chlorides contents, without establishing a direct correlation between this classification and the corrosion categories described above.

The main discrepancy between the two versions of ISO 9223 lies in the assignment of atmospheric corrosion categories according to environmental parameters and using weight loss measurements. The first classification required prior alphanumeric classification of the environment levels of SO<sub>2</sub>, chloride and TOW. A code *S* was then assigned for chloride levels ranging from *S*<sub>0</sub> (lowest) to *S*<sub>3</sub> (highest), a code *P* for the SO<sub>2</sub> contents from *P*<sub>0</sub> (lowest) to *P*<sub>3</sub> (highest), and a code *τ* for the TOW from *τ*<sub>1</sub> (lowest) to *τ*<sub>5</sub> (highest) (see Table 3). From this classification, the first version of the ISO 9223:1992(E) standard allowed the assignment of corrosion categories between values C1 to C5. In many cases, the assignment of a corrosion category was not conclusive, since the standard, itself, allowed the coexistence of two levels of corrosion for the same situation.

The comparison of the results obtained using this method with corrosion categories derived from weight loss measurements evidenced discrepancies for the data recorded in the Canary Islands [4], likewise those described by D. C. Cook *et al.* [10] during the development of a corrosion map of the Gulf of Mexico. A relevant conclusion from that study, further confirmed in a similar work [3], was that reliable corrosion categories are only those obtained from weight loss of specimens exposed to the atmosphere. Accordingly, in the second edition of the standard ISO 9223:2012(E), although referring to the same classification of environments, according to the concentration of chlorides, SO<sub>2</sub> and TOW, it was only possible to derive a corrosion category from weight loss data.

Apart from this discrepancy, another disadvantage consists of the limited number of corrosion categories available for tropical and subtropical environments. This is relevant since it has been observed that the corrosion rate increases significantly with atmospheric chloride content for carbon steel, zinc, and copper [11]: a fact that has been confirmed for subtropical environments such as those present in the Canary Islands [4].

## 4.- ATMOSPHERIC CORROSION IN THE CANARY ISLANDS

### 4.1.- Canary Islands Weather traits

The Canary Islands (27° 37' to 29° 27' N; 13° 20' to 18° 20' W) are positioned off the hyper-arid coast of Northwest Africa (see Figure 1). It is the most extensive and populated archipelago in the region of Macaronesia, with a census of 2,108,121 inhabitants in the year 2017, and with a forecasted population growth of 13% by 2018 and 15% by 2019 [12].

The archipelago is formed by seven large islands, organized administratively into two provinces, namely Las Palmas (Gran Canaria, Lanzarote and Fuerteventura islands) and Santa Cruz de Tenerife (Tenerife, La Palma, La Gomera and El Hierro islands). Table 4 shows the characteristics of each island.

The seasonal climate of the Canary Islands is determined by the local atmospheric conditions and by geographical factors such as the location of the islands in the Atlantic Ocean, the orography of the different islands, and their proximity to Africa.

The atmospheric dynamics of subtropical latitudes, and the combined effects of abrupt orography, proximity to a continent, and bathed by a cold ocean current, confer very specific climatic characteristics on the Canary Islands. Among them, the regime of Trade Winds (Azores High Winds) is the most determinant one. Azores High Winds are moisture-laden marine winds blowing from the NE, which already possess a very marked seasonal variation. Thus, over the summer months, they blow 90 to 95% of days, while in winter their frequency drops to app. 50% of days. The prevalence of these winds provides a stable weather, with very cloudy skies with stratocumulus clouds in the midlands and the northern coasts, and clear skies on the leeward side of the islands.

On the islands with the greatest relief, and related to this wind regime, there is another fundamental feature: the stratification of the troposphere in two layers. One is moist and fresh at low heights, whereas the other is dry and warm, thus producing a thermal inversion situation at around 1,500 m of altitude. Visual observation of these clouds from a higher point produces the impression of being like a sea. Occurrences of such a “sea of clouds” means that, contrary to usual, the RH in coastal areas is lower than in midland areas. At these locations, so-called *horizontal rain* results from the condensation of the clouds. On the other hand, on the islands of lesser relief (i.e., Lanzarote and Fuerteventura) this process does not occur at all.

The climates of the islands vary greatly. The eastern islands (namely, Lanzarote and Fuerteventura) exhibit a desert-like climate, with an orography presenting low mountains that cannot retain the humidity of the Azores High Winds. On the other side, Gran Canaria, Tenerife, La Palma, La Gomera and Hierro Islands present a Mediterranean-type climate [13]. On these islands, the mountains act as a topographical barrier to the low-altitude and moist Trade Winds, creating a toposequence of contrasting climatic conditions. These climatic variations originate different microclimates on each island. For this reason, the Canary Islands are popularly known as “*miniaturized continents*”. In addition, a third major climatic sector can be distinguished in Tenerife and Gran Canaria Islands, and to a smaller extent even on the smallest island (El Hierro). These different climatic sectors were ascertained in a recent study developed by the University of La Laguna, the University of Las Palmas de Gran Canaria and the Regional Government of the Canary Islands that was named CLIMCAN-010 [14]. The main objective of the project was to achieve the complete climate characterization of the Canary Islands in the Technical Building Code (CTE) of Spain [15]. The information about the climatic conditions of the Canary Islands was insufficient at that time, and it did not account for the major weather variations arising from geographical conditions of the fragmented territory and the altitude and orientation of the relief on each of the islands. That work attempted to improve, expand and eventually correct the information describing the climate of the Canary Islands. As a result, the climatic characteristics were classified into “*climatic sectors*” for each island. The various climatic sectors and the orography of the islands are graphically shown in Figure 2.

The delimitation of the climatic sectors was performed considering:

- the variation and the vertical gradients of temperature and precipitation with altitude;
- the orientation against the air flows; and
- the quantification of thermometric (<14°C, from 14° to 16°C, from 16° to 18°C and > 18°C), pluviometric (<300 mm/year, between 300 and 500, between 500 to 1,000 and > 1,000 mm/year) and radiation (<4.2, from 4.2 to 4.6, from 4.6 to 5.0 and > 5.0 kWh/m<sup>2</sup>) thresholds for the different altitudes.

Tenerife presents the greatest microclimatic variation with six climatic sectors. Even the smallest island (El Hierro), which has an area of only 268.7 km<sup>2</sup>, exhibits three climatic sectors.

Given that atmospheric corrosion is a process strongly influenced by the climatic characteristics of the region, large variations in the behavior of the different metals can be expected depending on the climate sector they are exposed to.

#### **4.2.- The development of atmospheric corrosivity maps for the Canary Islands project**

The “Development of atmospheric corrosivity maps for the Canary Islands” research project was conducted to characterize the aggressiveness of the different atmospheres occurring on the seven Canary Islands [16]. The availability of these maps should greatly assist the correct selection of materials, protection or maintenance policy of metallic structures exposed to weather conditions.

Project implementation was a complex process due to the wide variety of parameters involved, which were determined from direct measurement of the atmospheric corrosivities experienced by various bare metals exposed to air. A total of 74 test sites were installed across the seven major islands comprising the Canary Archipelago. Figure 3 shows the distribution of the 74 test sites, whereas Tables 4 and 5 give the main characteristics corresponding to each one. It was considered that this distribution of test sites should suffice to cover climatic areas observed on the islands.

Corrosion test stations consisted of a metal frame at which standard bare metal coupons of dimension 10 cm x 4 cm x 2 mm were stacked according to ISO 9223. In order to achieve maximum insolation, the plates were oriented towards the south with an inclination of 45°. The exposed metals were carbon steel, zinc and copper of nominal compositions given in Table 7.

The components employed to measure the amount of pollutants (i.e., SO<sub>2</sub> and chlorides), according to the standard ISO 9225, as well as a thermal hygrometer to monitor the relative humidity, were placed at the back of the frame holding the metal coupons. Figure 4 shows photographs taken at two representative corrosion test sites.

The amounts of pollutants were analyzed monthly, while RH monitoring was accomplished using a continuous procedure. Two methods were employed to determine SO<sub>2</sub> contamination, namely the Husy method in the Santa Cruz province, and the lead dioxide candle according to ASTM D 2010-85 [19] in Las Palmas province. The concentration of chloride was monitored by the wet candle method, according to ISO 9225. Weight loss of the metal coupons was measured during the first year of exposure. The retrieved samples were first cleaned following the ASTM G1-90 standard [20].

#### **4.3.- SO<sub>2</sub>, chlorides and TOW data in the Canary Islands.**

Figures 5-10 show SO<sub>2</sub>, chlorides and TOW data determined at the corrosion sites over a sampling period of 3 years. These data evidenced that the concentration of chlorides, carried by the Trade Winds, are very high in the atmospheres of the Canary Islands. In the province of Santa Cruz de Tenerife, from 35 studied atmospheres, only 5 correspond to rural atmospheres (those in which the concentration of NaCl is less than 15 mg/(m<sup>2</sup>·day), and in all cases the chloride concentration is higher than 6 mg/(m<sup>2</sup>·day). A similar situation occurs in the province of Las Palmas, where, with the exception of sites 20LP, 26LP, 27LP, 34LP and 35LP, high chloride concentrations are found highlighting the stations located on the islands of Lanzarote and Fuerteventura and the corrosion stations located on the east side of Gran Canaria Islands. Remarkably high salinity values were found at the sites 22LP, presenting a maximum of 1152 mg/(m<sup>2</sup>·day), 29TF, with a chloride concentration reaching the value of 237.617 mg/(m<sup>2</sup>·day), and 20TF, whose chloride concentration was 119.545 mg/(m<sup>2</sup>·day).

Sulphur dioxide data are quite low in all locations. With regard to the province of Santa Cruz de Tenerife, even for stations installed in urban areas close to a petroleum refinery (namely sites 1TF and 2TF), the concentration of sulphur dioxide is much lower than those observed in other similar locations in continental geography. This feature can be justified considering the wind regime affecting Santa Cruz de Tenerife. In addition to these two stations, only stations 16TF, 20TF and 29TF, exceeded 4 mg/(m<sup>2</sup>·day). In the rest of the stations of the province of Santa Cruz de Tenerife, SO<sub>2</sub> concentration was minimal. In the province of Las Palmas, the highest values were registered in proximity to thermal power stations (i.e., 13LP, 15LP and 36LP test sites), as well as in harbour locations (22LP and 38LP stations). In the latter locations, these high values may not have arisen exclusively from atmospheric SO<sub>2</sub>, and instead may have been sulfate carried there with the marine aerosol.

In summary, from the standpoint of pollutants, the atmospheres of both provinces are characterized by high values of salinity, and mostly very low levels of SO<sub>2</sub> pollution. TOW levels determined across the islands are at the same order of magnitude as those obtained elsewhere in Spain, except in the case of station 28TF (El Hierro Island), whose relative humidity surpassed even the wettest locations of continental Spain. By contrast, station 15TF exhibited the lowest TOW. Sulphur dioxide, chloride and TOW data were employed to assign corrosivity categories to each individual site according to ISO 9223, and they are listed in Table 8. For the sake of comparison, corrosivity categories were also established from weight loss measurements according to the first version of the ISO 9223:1992(E) norm as reported in the next section.

#### 4.4.- Atmospheric corrosivity maps of the Canary Islands

Table 9 gives the corrosivity categories assigned to each test station for carbon steel, zinc and copper.

##### 4.4.1. Atmospheric corrosion map for carbon steel

Figure 11 shows the atmospheric corrosivity map for carbon steel derived using experimental data from all 74 test sites. Diverse corrosivity categories are distributed across the archipelago, with approximately 58% of the sites exhibiting category C2, 30% with C3, 5% with C4, and 7% with C5. None of the stations corresponded to the corrosivity category C1. In general, the corrosivity levels observed for carbon steel are low and medium levels (more than 83% of the cases) in both provinces.

The initial stages of the atmospheric corrosion process on carbon steel involves the intake of oxygen and water to produce rust layers containing a rich variety of iron oxides and hydroxides. The corrosion rate of iron depends on various environmental parameters. In the Canary Islands, the most important of these are relative humidity, chloride level and solid particle deposition on the metal surface, the latter being more influential on the easternmost islands (i.e., Lanzarote and Fuerteventura).

Near the sea, the corrosiveness of carbon steel is extremely high (high salinity) as can be seen on the east coast of Gran Canaria. By contrast, close to the shore at locations in less exposed areas, salinity levels are lower, and the corrosion process is moderate. For values of salinity up to about 15 mg/(m<sup>2</sup>·day) (i.e., rural atmospheres), the corrosion rates for carbon steel were very low. For salinity values ranging between 15 and 30 mg/(m<sup>2</sup>·day) (not very aggressive marine atmospheres), but with significant levels of TOW, corrosion rates increased dramatically.

Indeed, a major factor for carbon steel corrosion is the TOW. Stations located in areas where the relative humidity was high and, therefore, the metal surface remained coated by moisture for rather long periods (for example, at sites 4TF, 5TF, 6TF, 7TF, and 8TF), even if salinity was not very high, the observed corrosion rate was high. A very significant example is provided by station 28TF located at El Hierro Island, where over a period of three years the TOW has been 2.25 years (75% of the total), and the measured corrosion rate was the highest for all the archipelago. Yet salinity data were relatively low at this site (namely, 18.5 mg/(m<sup>2</sup>·day)). By contrast, at stations 1TF, 2TF and 21TF, although they were placed in marine atmospheres, low corrosion rates were found due to the low TOW values occurring in them.

In the province of Las Palmas, TOW data were generally lower than in Santa Cruz de Tenerife province, making it difficult to ascertain unambiguously the influence of this variable by itself on the corrosion of carbon steel. A special mention should be made of the behavior observed at inland locations in Lanzarote and Fuerteventura Islands; the corrosion rates of carbon steel measured there were higher than the rates observed at stations located close to the shore (i.e., marine environment). This is because the corrosive process is also favored by the presence of atmospheric particles, which have different roles in atmospheric corrosion. Firstly, they retain moisture for longer periods; therefore, effective TOW is higher than the values recorded by the thermohygrometers. As result, metallic surfaces become moistened even during apparent dry periods, and the corrosive process can take place. In addition, they also erode the metal surface as they are thrown by the wind against the surface (that is, erosion corrosion).

X-ray diffraction (XRD) studies showed that the corrosion products for carbon steel probes were akagaenite ( $\beta$ -FeOOH), lepidocrocite ( $\gamma$ -FeOOH), goethite ( $\alpha$ -FeOOH), magnetite (Fe<sub>3</sub>O<sub>4</sub>), and hematite (Fe<sub>2</sub>O<sub>3</sub>), in good agreement with observations from other studies [17,18,21].

Among them, akagaenite is the predominant component. XRD data also evidenced the formation of green rust 2 (GR2(SO<sub>4</sub><sup>2-</sup>)) in the corrosion products formed on a carbon steel rod exposed to atmospheric corrosion. The occurrence of green rust 2 as atmospheric corrosion product of carbon steel exposed in industrial-marine stations has been related to the presence of sulfate reducing bacteria (SRB) in the marine aerosol [22].

In the case of test sites located in low pollutant atmospheres (namely, 20LP, 21LP, 26LP, 27LP, 7TF, 10TF, 15TF, and 27TF), the oxide film was found to consist of a very thin inner Fe<sub>3</sub>O<sub>4</sub> and an external of Fe<sub>2</sub>O<sub>3</sub> polycrystalline layers. This species may become  $\gamma$ -FeOOH, oxi-ferric hydroxide (lepidocrocite) under the action of the water vapour present in the atmosphere. Furthermore, in weakly acidic solutions, this species is transformed into  $\alpha$ -FeOOH (goethite) which is the most stable (and so much more protective) oxy-ferric hydroxide. The transformation process of lepidocrocite into goethite depends on the concentration of sulfate and the temperature. Therefore, the observation of goethite in addition to lepidocrocite could be expected for those stations installed at urban and industrial locations, as well as those in close proximity to highways and airports, due to the high SO<sub>2</sub> levels present in those environments.

On the other hand, at locations near the seashore, where the electrolyte film formed on the metal surface contains concentrations of chloride,  $\beta$ -FeOOH (akaganeite) is formed. This compound contains chloride ion contents above 5 wt.%, and can be described as  $\beta$ -FeO(OH,Cl). Indeed, akaganeite has been detected at stations exhibiting the highest chloride contents. Thus, akaganeite was present in 18 out of 35 stations in the province of Santa Cruz de Tenerife, while it was present in almost all the stations placed in the Las Palmas province with the only exception of locations in the interior of Gran Canaria Island.

#### 4.4.2.- Atmospheric corrosion map for zinc

Figure 12 shows the corresponding atmospheric corrosivity map for zinc. In general, the level of atmospheric corrosivity of this metal is higher when chlorides are present in the air, reaching the C5 category or even higher at 59% of the sites. As for the two provinces, the prevailing atmosphere in Las Palmas was more aggressive than that in the province of Santa Cruz de Tenerife.

Zinc has a high natural corrosion tendency. As result, zinc surface exposed to the atmosphere is covered instantly by a film of zinc oxide (zincite) ZnO, which evolves with the humidity of the environment to hydroxide of zinc, Zn(OH)<sub>2</sub> and, subsequently, a protective layer of basic zinc carbonate, ZnOH(CO<sub>3</sub>)<sub>0.5</sub>. The initial stability of these corrosion products, resulting from the dissolution of Zn<sup>2+</sup>, is controlled by the pH of the aqueous layer developed on the surface of the metal.

Prolonged exposure of zinc to different atmospheres will result in the formation of different corrosion products. The formation rate of these corrosion products will depend on the rate of deposit of the pollutants presents in the atmosphere (i.e., Cl<sup>-</sup> and SO<sub>2</sub>). The main corrosion products observed in our study were hydrozincite (Zn<sub>4</sub>CO<sub>3</sub>(OH)<sub>6</sub>·H<sub>2</sub>O) and simonkolleite (Zn<sub>5</sub>(OH)<sub>8</sub>Cl<sub>2</sub>), revealing that chloride and carbon dioxide are the most aggressive pollutants present in the atmosphere [23-25]. Sulfate-containing species, namely zinc oxysulfate (Zn<sub>3</sub>O(SO<sub>4</sub>)<sub>2</sub>), zinc diamminehydroxynitrate (Zn<sub>5</sub>(OH)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>·2NH<sub>3</sub>), and zinc chlorohydroxysulfate (NaZn<sub>4</sub>Cl(OH)<sub>6</sub>SO<sub>4</sub>·6H<sub>2</sub>O), were also found though in smaller amounts.

This last product shows the synergistic action of Cl<sup>-</sup> and SO<sub>2</sub>. A wide variety of corrosion products is formed in the Canary Islands, typical of these types of atmospheres, a feature not observed in other climatic regions [11].

In the case of rural atmospheres, it was observed that the corrosion rate of zinc, expressed as penetration rate ( $\mu\text{m}/\text{year}$ ) decreased linearly with the exposure time. This fact evidences the protective nature of the ZnOH(CO<sub>3</sub>)<sub>0.5</sub> formed on the surface of the zinc, because the initially-formed layer of zinc carbonate has continued to grow, although at a slow pace. Contrary to description in the literature [26,27], the formation of a basic protective layer of zinc hydroxosulfate (Zn<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub>·H<sub>2</sub>O) has not been observed.

In marine atmospheres, as result of the deposition of chloride on the surface, a basic chloride Zn<sub>5</sub>Cl<sub>2</sub>(OH)<sub>8</sub>·H<sub>2</sub>O grew covering the entire surface. The presence of this basic zinc chloride, which is less protective than the basic zinc carbonate, prevents a decrease in the zinc corrosion penetration with the exposure time in marine environments, contrary to what happened in the stations placed in rural areas. A special mention is deserved for stations 20TF and 30TF in the province of Santa Cruz de Tenerife, and stations 15LP and 22LP. They were located in very windy areas with high salinity values.

The corrosion rates exceed by far those determined in the remaining stations, due to the effects of erosion that breaks the passive layer of corrosion products.

As an exception, a mention should be made of 29TF station. The exceptionally high salinity conditions occurring at this location accounted for the complete degradation of the zinc coupons after three years of exposure.

#### 4.4.3.- Atmospheric corrosion map for copper

Figure 13 shows the corresponding atmospheric corrosivity map for copper. The aggressivity of the atmospheres to copper is high, reaching up to ISO 9223 category C5 in 75% of the cases.

Copper is a metal with little tendency to rust. When a copper coupon is exposed to the atmosphere, a protective patina is formed on it. This patina is made up of either a single  $\text{Cu}_2\text{O}$  film or a  $\text{Cu}_2\text{O}/\text{CuO}$ ,  $\text{Cu}(\text{OH})_2$  bilayer. This patina will react with the species contained in the atmosphere such as the  $\text{SO}_x$ ,  $\text{Cl}^-$ ,  $\text{CO}_2$  y  $\text{NO}_x$ , giving rise to the formation of basic salts.

The corrosion rate increases with the chloride content in the atmosphere. There seems to be a critical salinity level around  $20 \text{ mg}/(\text{m}^2 \cdot \text{day})$  after which the action of the chloride ion is clearly noticed [11], with the formation of atacamite ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ) among the corrosion products.

The corrosion rates observed in urban areas varied between 1 and  $2 \mu\text{m}/\text{year}$ , decreasing with increased time of exposure mainly as a result of the formation of a protective copper patina of cuprite ( $\text{Cu}_2\text{O}$ ), hydroxy chloride dimorphs, atacamite and paratacamite ( $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ), hydroxy sulfates brochantite ( $\text{Cu}_4(\text{OH})_6\text{SO}_4$ ) and antlerite ( $\text{Cu}_3(\text{OH})_4\text{SO}_4$ ).

The corrosion products were cuprite ( $\text{Cu}_2\text{O}$ ), malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ), atacamite and paratacamite ( $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ) all being typical of marine environments. None of the stations presented corrosion products containing sulfates in their composition. In the studies carried out in urban areas in continental regions, brochantite ( $\text{Cu}_4(\text{OH})_6\text{SO}_4$ ) was found to be the main component of the patina, something which did not occur in our case.

In addition, the layer of corrosion products has a complex composition, which varies from one place to another. The main components were copper (I) oxide and one or more basic salts of copper. In both provinces, the main corrosion product detected has been atacamite, which can be explained by taking into account the chloride levels in the stations under study, much higher than the of  $\text{SO}_2$  levels.

The corrosion rates of copper in the Canary Islands were much greater than the rates reported in the literature. This fact can be justified by the combined effect of the salinity of the atmospheres (salinity values exceeding  $10 \text{ mg}/(\text{m}^2 \cdot \text{day})$ , observed in all cases, even at station 27LP located in the center of Gran Canaria Island), and the high average temperatures (temperatures were never lower than  $10^\circ\text{C}$ , except at station 15TF situated at 2367 m altitude). As a result, in accordance with ISO 9223 norm, the corrosivity categories of copper for the atmospheres of the Canary Islands should be either the most aggressive category or even beyond those described by the standard.

In the rural atmospheres of the province of Santa Cruz de Tenerife (i.e., for  $\text{Cl}^-$  and  $\text{SO}_2$  concentrations below  $15 \text{ mg}/(\text{m}^2 \cdot \text{day})$ ), the formation of the patina film may require some time and, as a consequence, the corrosion rate would increase until reaching an approximately constant value, corresponding to the formation of the passivating film.

In the case of the surfaces of the copper coupons exposed to marine environments, due to the arrival of chlorides carried by the wind, and whenever the humidity is sufficiently high, a patina of basic copper salts is soon deposited. In the case of copper coupons exposed in atmospheres where the values of salinity exceeded  $15 \text{ mg}/(\text{m}^2 \cdot \text{day})$  without reaching  $30 \text{ mg}/(\text{m}^2 \cdot \text{day})$ , and where the humidity was high, the initial corrosion rate was high and decreased with time to attain an approximately constant value. In stations where salinity exceeded  $30 \text{ mg}/(\text{m}^2 \cdot \text{day})$ , (e.g., stations 26TF, 20TF, 29TF, 30TF and 32TF in the province of Santa Cruz de Tenerife, and stations 3LP, 4LP, 5LP, 8LP, 13LP, 15LP and 22LP in the province of Las Palmas), the aggressiveness of the environment hindered the formation of the passive film even after three years of exposure.

When the air was very dry, as is the case in the capital of Tenerife, at some locations in the south of Tenerife, Lanzarote, Fuerteventura and the south of Gran Canaria, the patina formation was slow. However, despite the very aggressive exposure conditions, the corrosion rate increased until the protective layer was formed.



## 5.- MATHEMATICAL MODELLING

Once the corrosivity maps were obtained, the next effort focused on the prediction of the durability of a specific material exposed to the atmosphere. The ability to predict the durability of a given material is very useful for the design of new structures, as well as to predict eventual failures in materials already exposed.

The actual ISO 9224 and ISO 9223 standards specify mathematical models as a starting point for the estimation of corrosion rates with time. These models, while responding to a base derived from many years of observation and experimentation, did not fit well with the data obtained in the atmospheres of the Canary Islands [28].

A rather wide variety of models has been proposed in the literature for the prediction of corrosion rates. Among them, the models obtained in the ISO CORRAG project [29,30], and the models obtained by The International Cooperative Program on Effects and The Iberoamerican Atmospheric Corrosion Map Project MICAT (Mapa Iberoamericano de Corrosión Atmosférica) [31] are of special interest. In the specific case of the Canary Islands, we have tested the models obtained in the MICAT project without good results [28].

In general, the mathematical model traditionally used in atmospheric corrosion fits the bilogarithmic law [17] and is shown in Equations (1) and (2)

$$C = k \cdot t^n \quad (1)$$

$$\log C = \log k + n \cdot \log t \quad (2)$$

where  $C$  is the depth of the corrosion expressed in  $\mu\text{m}$  after  $t$  years of atmospheric exposure,  $k$  is the corrosion rate in  $\mu\text{m}$  for the first year of exposure, and  $n$  is an exponent that depends on the type of metal, the type of atmosphere and the conditions of exposure [16]. A modification of this model includes a term related to the concentration of pollutants and the TOW, as shown in Equation (3),

$$C = k \cdot t^n \cdot 10^{\left[ a \cdot (SO_2) + b \cdot (Cl^-) + c \cdot TOW \right]} \quad (3)$$

where,  $a$ ,  $b$ , and  $c$  are constants,  $(SO_2)$  is the concentration of sulfur dioxide in  $\text{mg}/(\text{m}^2 \cdot \text{day})$ ,  $(Cl^-)$  is the concentration of chlorides in  $\text{mg}/(\text{m}^2 \cdot \text{day})$  and TOW is the time of wetness (h/year).

This change in the bilogarithmic law provided higher quality fits when individual stations were modeled, or within stations grouped by corrosivity category [16], but they did not provide a satisfactory general model.

A variation to the tested models consisted of the establishment of a new kind of variable, namely qualitative variables related to a variable inherent to the corrosion stations (i.e., corrosivity category for the station, amount of a given pollutant, etc.). For the development of these new models, the corrosion rates and pollutant values recorded over a three-year period were employed.

### 5.1.- Mathematical modelling of the atmospheric corrosion of carbon steel

In order to obtain a general model for the set of stations distributed across the Canary Islands, the following models were tested:

$$\ln(C) = k_0 + k_1 \cdot t \quad (4)$$

$$\ln(C) = k_0 + k_1 \cdot t + \delta_2 \cdot D2 + \delta_3 \cdot D3 + \delta_4 \cdot D4 \quad (5)$$

$$\ln(C) = k_0 + k_1 \cdot \ln(t) \quad (6)$$

$$\ln(C) = k_0 + k_1 \cdot \ln(t) + \delta_2 \cdot D2 + \delta_3 \cdot D3 + \delta_4 \cdot D4 \quad (7)$$

$$\begin{aligned} \ln(C) = & k_0 + k_1 \cdot (SO_2) + k_2 \cdot (Cl^-) + k_3 \cdot \ln(TOW) + k_4 \cdot (SO_2) \cdot (Cl^-) + k_5 \cdot \ln(t) \\ & + k_6 \cdot (SO_2) \cdot \ln(t) + k_7 \cdot (Cl^-) \cdot \ln(t) + k_8 \cdot (SO_2) \cdot (Cl^-) \cdot \ln(t) + k_9 \cdot (TOW) \cdot \ln(t) \end{aligned} \quad (8)$$

$$\begin{aligned} \ln(C) = & k_0 + k_1 \cdot (SO_2) + k_2 \cdot (Cl^-) + k_3 \cdot \ln(TOW) + k_4 \cdot (SO_2) \cdot (Cl^-) + k_5 \cdot \ln(t) \\ & + k_6 \cdot (SO_2) \cdot \ln(t) + k_7 \cdot (Cl^-) \cdot \ln(t) + k_8 \cdot (SO_2) \cdot (Cl^-) \cdot \ln(t) + k_9 \cdot (TOW) \cdot \ln(t) \\ & + \delta_2 \cdot D2 + \delta_3 \cdot D3 + \delta_4 \cdot D4 \end{aligned} \quad (9)$$

$$\begin{aligned} \ln(C) = & k_0 + k_1 \cdot \ln(SO_2) + k_2 \cdot \ln(Cl^-) + k_3 \cdot (Cl^-) + k_4 \cdot \ln(TOW) + k_5 \cdot (SO_2) \cdot \ln(t) \\ & + k_6 \cdot (TOW) \cdot \ln(t) \end{aligned} \quad (10)$$

$$\begin{aligned} \ln(C) = & k_0 + k_1 \cdot \ln(SO_2) + k_2 \cdot \ln(Cl^-) + k_3 \cdot (Cl^-) + k_4 \cdot \ln(TOW) + k_5 \cdot (SO_2) \cdot \ln(t) \\ & + k_6 \cdot (TOW) \cdot \ln(t) + \delta_2 D2 + \delta_3 D3 + \delta_4 D4 \end{aligned} \quad (11)$$

Unlike the previous models, these new equations include some qualitative variables ( $D2$ ,  $D3$  and  $D4$ ) in Equations (5), (7), (9) and (11) in order to allow changes in the independent term ( $k_0$ ) to be achieved on basis of the different initial characteristics of a given station expressed by its corrosivity category.

Therefore, in a first stage, corrosion stations were grouped in different corrosivity categories for carbon steel (cf. Table 9):

- G1 group: stations with corrosivity category C2,
- G2 group: stations with corrosivity category C3,
- G3 Group: stations with corrosivity category C4 in the province of Las Palmas and categories C4 and C5 in the province of Santa Cruz de Tenerife,
- G4 group: stations with corrosivity category C5 in the province of Las Palmas.

The following qualitative variables were defined to represent the four groups of stations:

- $D1 = 1$ , if the observation belonged to the first group (G1),
- $D1 = 0$  for the remaining cases;
- $D2 = 1$  if the observation belonged to the second group (G2),
- $D2 = 0$  for the remaining cases;
- $D3 = 1$  if the observation belonged to the third group (G3),
- $D3 = 0$  for the remaining cases;
- $D4 = 1$  if the observation belonged to the fourth group (G4),
- $D4 = 0$  for the remaining cases.

The introduction of qualitative variables greatly improved the fit of the mathematical models because the distortion caused by the different initial corrosion rates could be effectively eliminated. However, the effects that different environmental parameters produced on the corrosion rate were not taken in account yet.

The mathematical model for the carbon steel for the Canary archipelago is the following:

$$\begin{aligned} \ln(C) = & 2.9378 + 0.0738 \cdot (SO_2) + 0.0097 \cdot (Cl^-) + 0.1987 \cdot \ln(TOW) - 0.0018 \cdot (SO_2) \cdot (Cl^-) \\ & - 0.5985 \cdot \ln(t) + 0.0067 \cdot (SO_2) \cdot \ln(t) - 0.0014 \cdot (SO_2) \cdot (Cl^-) \cdot \ln(t) + 0.554 \cdot D2 + 1.1423 \cdot D3 \\ & + 1.4916 \cdot D4 \end{aligned} \quad (12)$$

The errors in predicted rates produced using this model were evaluated using the data recorded during the first two years of exposure. The magnitude of the errors observed for each station was expressed as percentage intervals in Table 10. Only two stations (that is, 2.74% of the total) produced 100% error

## 5.2.- Mathematical modelling of the atmospheric corrosion of zinc

These models were also applied to the corrosion rate data obtained for zinc from the stations located in the province of Santa Cruz de Tenerife. In this case, the corrosion stations were distributed into different groups according to their corrosion rates [32], and not according to their corrosivity categories. Thus,

- G1: Between 0 and 22 g/(m<sup>2</sup>·year) (Stations 1TF, 2TF, 5TF, 6TF, 7TF, 10TF, 14TF, 15TF, 19TF, 24TF, 27TF, 28TF, 25TF, 35TF);
- G2: Between 22 and 40 g/(m<sup>2</sup>·year) (Stations 4TF, 8TF, 9TF, 12TF, 17TF, 21TF, 23TF, 33TF);
- G3: Between 40 and 70 g/(m<sup>2</sup>·year) (Stations 3TF, 16TF, 18TF, 26TF, 31TF, 32TF, 34TF);
- G4: Between 70 and 140 g/(m<sup>2</sup>·year) (Station 30TF);
- G5: Between 300 and 400 g/(m<sup>2</sup>·year) (Station 20TF);
- G6: Between 1500 and 1600 g/(m<sup>2</sup>·year) (Station 29TF).

The following qualitative variables were introduced:

- $D1 = 1$ , if the observation belonged to group (G1),
- $D1 = 0$  for the remaining cases;
- $D2 = 1$ , if the observation belonged to group (G2),
- $D2 = 0$  for the remaining cases;
- $D3 = 1$ , if the observation belonged to group (G3),
- $D3 = 0$  for the remaining cases;
- $D4 = 1$ , if the observation belonged to group (G4),
- $D4 = 0$  for the remaining cases;
- $D5 = 1$ , if the observation belonged to group (G5),
- $D5 = 0$  for the remaining cases;
- $D6 = 1$ , if the observation belonged to group (G6),
- $D6 = 0$  for the remaining cases.

The mathematical model obtained for zinc for the assembly of four islands in the province of Santa Cruz de Tenerife was:

$$\begin{aligned} \ln(C) = & 2.2635 + 0.0723 \cdot (Cl^-) + 0.188 \cdot \ln(TOW) - 0.0076 \cdot (SO_2) \cdot (Cl^-) \\ & - 0.7943 \cdot \ln(t) + 0.0386 \cdot (Cl^-) \cdot \ln(t) - 0.0155 \cdot (SO_2) \cdot (Cl^-) \cdot \ln(t) + 0.5794 \cdot D2 \\ & + 1.0107 \cdot D3 + 1.4649 \cdot D4 + 1.4704 \cdot D5 \end{aligned} \quad (13)$$

In 25 cases, the error was less than 50%, and in 14 of them was even below 5%. Only in 5 cases, the error ranged between 50 and 80%.

In conclusion, the predicted corrosion rates obtained after incorporating qualitative variables into the mathematical models led to improved results compared to the original models. Although the errors obtained in a few cases are high, it should be noted that the whole fitting process operated exclusively using three variables when attempting to characterize a process involving many other variables, some of them hardly quantifiable at this stage.

## 6.- CONCLUSIONS

Atmospheric corrosion occurs in a rather complex system consisting of a metal, corrosion product layers, an electrolyte and the atmosphere. It is an electrochemical process in which an electrolyte is a thin layer of moisture on the surface. Electrolyte composition mainly depends on the deposition rate of air pollutants and fluctuates with humidity conditions.

Atmospheric corrosion depends, apart from on the type of metal, on the relative humidity (expressed as TOW) and the presence of certain compounds in the atmosphere such as chlorides, CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>x</sub>, among others. The climatic conditions observed in a given region usually show little variability for large tracts of land in continental locations. However, the special topography of the Canary Islands in combination with the operating wind regime mainly characterized by high humidity, produce a wide climate variability throughout the archipelago within a small geographical area. Several microclimate sectors can clearly be differentiated throughout the Islands.

This microclimate variability in a small geographical area greatly influences the corrosivity of its atmospheres. The study and development of Atmospheric Corrosivity Maps for the Canary Islands involved the assignment of corrosivity categories to the 74 test stations installed on the seven major islands that make up the archipelago. Although numerous studies have been performed by the scientific community in order to characterize the corrosive processes taking place both in inland areas well as in tropical and sub-tropical zones, their proposals do not satisfactorily describe the corrosion behaviors observed in the Canary Islands.

The results described in this work confirm the uniqueness of the Canarian climate. In many cases, the corrosivity categories would exceed those given by the ISO 9223 standard in its various editions. For the sake of comparative purposes, corrosivity categories were determined based on both environmental parameters according to ISO 9223:1992, and weight loss measurements. The observed discrepancies confirm the limitation of this standard norm and the unique atmospheres of the Canary Islands.

Atmospheric corrosivity of the Canary Islands varies greatly in the case of carbon steel (from C2 to C5). The highest corrosion rates were obtained in coastal areas and the hinterland of the most arid islands, and corrosion rates were almost negligible at high altitudes (stations with low TOW values). A great variety of corrosion products were formed on the surface of carbon steel coupons, corresponding to both urban and marine atmospheres. The occurrence of corrosion products with anaerobic microbial origin such as green rust 2 were also described.

As result of the local salinity and humidity characteristics of the atmospheres in the Canary Islands, the corrosiveness for copper and zinc were generally very high. In the case of zinc, above 82% of the stations were assigned corrosivity category C5 or higher in the province of Las Palmas and 32% of those located in the province of Santa Cruz de Tenerife. Among them, the highest corrosion rates were exhibited by stations 15LP, 22LP, 20TF, 13LP and 30TF, which were located in very windy areas with high salinity. In addition, the high corrosivity produced on carbon steel exposed on arid islands such as Lanzarote and Fuerteventura was attributed to the combined impact of suspended particles against the surface of the metal.

In the case of copper, more than 69% of the stations of the province of Las Palmas were assigned the C5 corrosivity category or even above it, while this condition was exhibited by 80% of the stations in the province of Santa Cruz de Tenerife.

The introduction of qualitative variables for mathematical modeling produced a major improvement in corrosion rate predictions for both carbon steel as well as for zinc, although only TOW, SO<sub>2</sub> and chloride levels were taken into account at this stage.

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**Table 1.-** Corrosivity categories of atmospheres according to ISO 9223:1992(E) [5] and ISO9223:2012 [6].

Corrosivity	Category	
	ISO 9223:1992(E)	ISO 9223:2012
Very low	C1	C1
Low	C2	C2
Medium	C3	C3
High	C4	C4
Very high	C5	C5
Extreme	-	CX

**Table 2.-** Corrosion rates,  $r_{\text{corr}}$ , for the first year of exposure, and corrosivity category assignment according to ISO 9223 [5,6].

Corrosivity category	Corrosion rates ( $r_{\text{corr}}$ ) in $\mu\text{m}/\text{year}$		
	Carbon steel	Zinc	Copper
C1	$r_{\text{corr}} \leq 1.3$	$r_{\text{corr}} \leq 0.1$	$r_{\text{corr}} \leq 0.1$
C2	$1.3 < r_{\text{corr}} \leq 25$	$0.1 < r_{\text{corr}} \leq 0.7$	$0.1 < r_{\text{corr}} \leq 0.6$
C3	$25 < r_{\text{corr}} \leq 50$	$0.7 < r_{\text{corr}} \leq 2.1$	$0.6 < r_{\text{corr}} \leq 1.3$
C4	$50 < r_{\text{corr}} \leq 80$	$2.1 < r_{\text{corr}} \leq 4.2$	$1.3 < r_{\text{corr}} \leq 2.8$
C5	$80 < r_{\text{corr}} \leq 200$	$4.2 < r_{\text{corr}} \leq 8.4$	$2.8 < r_{\text{corr}} \leq 5.6$
CX	$200 < r_{\text{corr}} \leq 700$	$8.4 < r_{\text{corr}} \leq 25$	$5.6 < r_{\text{corr}} \leq 10$

**Table 3.-** Classes for SO<sub>2</sub>, chloride and TOW according to ISO 9223:1992(E) [5].

Deposition rate of SO <sub>2</sub> in mg/(m <sup>2</sup> ·day)	Class	Deposition rate of chloride in mg/(m <sup>2</sup> ·day)	Class	Time of wetness in h/year	Class
$P_d \leq 10$ $P_d \leq 4^*$	$P_0$ - Rural atmosphere	$S_d \leq 3$	$S_0$	$\tau \leq 10$	$\tau_1$
$10 < P_d \leq 35$ $4 < P_d \leq 24^*$	$P_1$ - Urban atmosphere	$3 < S_d \leq 60$	$S_1$	$10 < \tau \leq 250$	$\tau_2$
$35 < P_d \leq 80$ $24 < P_d \leq 80^*$	$P_2$ - Industrial atmosphere	$60 < S_d \leq 300$	$S_2$	$250 < \tau \leq 2500$	$\tau_3$
$80 < P_d \leq 200$	$P_3$ - Highly polluted industrial atmosphere	$300 < S_d \leq 1500$	$S_3$	$2500 < \tau \leq 5500$	$\tau_4$
*Change introduced in the second version of the ISO 9223 norm				$5500 > \tau$	$\tau_5$

**Table 4.-** The Canarian Archipelago.

	Geographic coordinate		Elevation (m)	Area (km <sup>2</sup> )	Population (2017)
	North latitude	West longitude			
Islas Canarias	28° 28' 00" N	16° 15' 00" W	3718	7446.9	2,108,121
Las Palmas Province					
Gran Canaria	28° 07' 30" N	15° 25' 42" W	1949	1560.1	843,158
Fuerteventura	28° 19' 60" N	14° 01' 12" W	807	1659.7	110,299
Lanzarote	29° 00' 36" N	13° 38' 27" W	671	845.9	147,023
Santa Cruz de Tenerife Province					
Tenerife	28° 17' 23" N	16° 37' 20" W	3718	2034.4	894,636
La Palma	28° 40' 00" N	17° 52' 00" W	2423	708.3	81,350
La Gomera	28° 06' 00" N	17° 08' 00" W	1487	369.8	20,976
El Hierro	27° 45' 00" N	18° 00' 00" W	1501	268.7	10,679

**Table 5.-** Location of the corrosion stations and their characteristic environment type for Las Palmas province [17].

Test Site	Elevation (m)	Geographic coordinate		Atmosphere
		North latitude	West longitude	
<i>Fuerteventura</i>				
1LP Puerto del Rosario	23	28° 30' 00" N	13° 51' 06" W	Marine
2LP Corralejo	50	28° 42' 13" N	13° 54' 02" W	Marine
3LP Power Station	38	28° 32' 01" N	13° 50' 22" W	Industrial
4LP El Cotillo	35	28° 40' 54" N	14° 00' 45" W	Marine
5LP Gran Tarajal	10	28° 12' 49" N	14° 01' 13" W	Marine
6LP Costa Calma	100	28° 09' 42" N	14° 13' 55" W	Marine
<i>Lanzarote</i>				
7LP Arrecife	25	28° 57' 29" N	13° 33' 47" W	Marine
8LP P.S. Punta Grande	25	28° 58' 47" N	13° 31' 93" W	Marine
9LP Aeropuerto	15	28° 56' 51" N	13° 35' 58" W	Marine
10LP Haría	278	29° 08' 51" N	13° 30' 02" W	Marine
11LP Tegüise	280	29° 03' 40" N	13° 33' 21" W	Humid industrial
12LP Yaiza	180	28° 57' 08" N	13° 45' 55" W	Marine
<i>Gran Canaria</i>				
13LP P. S. Jinámar	30	28° 02' 30" N	15° 24' 39" W	Industrial marine
14LP Arucas	250	28° 07' 14" N	15° 30' 36" W	Rural
15LP P. S. Juan Grande	30	27° 48' 93" N	15° 26' 63" W	Industrial marine
16LP Santa Brígida	520	28° 02' 02" N	15° 29' 13" W	Marine
17LP Las Palmas de G.C.	40	28° 06' 27" N	15° 25' 04" W	Marine
18LP Sardina del Norte	50	28° 09' 10" N	15° 41' 10" W	Marine
19LP San Nicolás	70	27° 59' 10" N	15° 46' 40" W	Marine
20LP Moya	485	28° 06' 40" N	15° 34' 17" W	Marine
21LP Guía	185	28° 08' 27" N	15° 37' 12" W	Marine
22LP Taliarte	20	27° 59' 28" N	15° 22' 66" W	Industrial marine
23LP Telde	200	28° 00' 00" N	15° 24' 20" W	Marine
24LP San Agustín	40	27° 46' 17" N	15° 33' 12" W	Marine
25LP Aeropuerto	50	27° 56' 20" N	15° 23' 20" W	Humid industrial
26LP San Mateo	850	28° 00' 48" N	15° 31' 00" W	Rural
27LP Tejeda	1060	28° 00' 00" N	15° 36' 25" W	Rural
28LP Arguineguín	30	27° 45' 16" N	15° 40' 15" W	Marine
29LP Santa Lucía	100	27° 51' 00" N	15° 27' 32" W	Marine
30LP Mogán	280	27° 53' 10" N	15° 43' 09" W	Marine
31LP Agaete	50	28° 06' 24" N	15° 42' 05" W	Marine
32LP Valle de Agaete	255	28° 05' 19" N	15° 39' 38" W	Marine
33LP Agüimes	290	27° 54' 24" N	15° 26' 01" W	Marine
34LP Valleseco	150	28° 07' 30" N	15° 26' 47" W	Rural
35LP Teror	600	28° 03' 40" N	15° 32' 08" W	Rural
36LP Jinámar	100	28° 01' 48" N	15° 24' 46" W	Industrial marine
37LP Tafira	350	28° 04' 29" N	15° 26' 28" W	Marine
38LP Muelle de la Luz	15	28° 08' 50" N	15° 25' 10" W	Industrial marine
39LP Las Torres	980	28° 01' 59" N	15° 34' 44" W	Marine



**Table 6.-** Location of the corrosion stations and their characteristic environment type for Santa Cruz de Tenerife province [4].

Test site	Elevation (m)	Geographic coordinate		Atmosphere
		North latitude	West longitude	
<i>Tenerife</i>				
1TF Meteorológico	36	28° 27' 18" N	16° 14' 56" W	Rural
2TF Policía Local	30	28° 27' 32" N	16° 15' 29" W	Rural
3TF Oceanográfico	2	28° 30' 03" N	16° 11' 49" W	Marine
4TF Montaña Ofra	300	28° 27' 10" N	16° 18' 13" W	Marine
5TF Química	600	28° 28' 10" N	16° 19' 04" W	Marine
6TF Pajalillos	110	28° 32' 04" N	16° 21' 33" W	Marine
7TF El Boquerón	400	28° 31' 06" N	16° 23' 42" W	Marine
8TF Garimba	500	28° 29' 52" N	16° 23' 05" W	Marine
9TF Puerto Cruz	7	28° 25' 04" N	16° 32' 54" W	Marine
10TF Botánico	120	28° 24' 06" N	16° 32' 30" W	Marine
11TF Montañeta	650	28° 20' 21" N	16° 45' 25" W	Rural
12TF Buenavista	125	28° 22' 20" N	16° 51' 04" W	Marine
13TF El Palmar	525	28° 20' 44" N	16° 50' 51" W	Marine
14TF Las Raíces	965	28° 25' 54" N	16° 21' 58" W	Rural
15TF Izaña	2367	28° 17' 55" N	16° 29' 25" W	Rural
16TF Unelco Caletillas	220	28° 22' 54" N	16° 21' 29" W	Industrial marine
17TF La Planta	120	28° 18' 43" N	16° 22' 24" W	Marine
18TF La Oficina	100	28° 17' 55" N	16° 29' 25" W	Marine
19TF El Bueno	830	28° 12' 16" N	16° 28' 34" W	Marine
20TF P. S. Granadilla	12	28° 02' 34" N	16° 34' 14" W	Industrial marine
21TF Los Cristianos	150	28° 03' 79" N	16° 42' 54" W	Marine
22TF Vilaflor	1414	28° 09' 23" N	16° 38' 68" W	Rural
23TF Cueva del Polvo	80	28° 13' 36" N	16° 49' 57" W	Marine
24TF Guía de Isora	715	28° 14' 10" N	16° 47' 23" W	Marine
<i>La Gomera</i>				
25TF San Sebastián	15	28° 05' 18" N	17° 07' 03" W	Marine
26TF Valle Gran Rey	10	28° 05' 47" N	17° 20' 42" W	Marine
27TF El Cedro	960	28° 07' 50" N	17° 13' 05" W	Rural
<i>El Hierro</i>				
28TF Valverde	600	27° 48' 38" N	17° 54' 53" W	Marine
29TF Aeropuerto	10	27° 48' 50" N	17° 53' 10" W	Industrial marine
<i>La Palma</i>				
30TF Aeropuerto	30	28° 37' 14" N	17° 45' 12" W	Industrial marine
31TF El Paso	847	28° 39' 10" N	17° 51' 05" W	Marine
32TF Puerto Naos	30	28° 34' 57" N	17° 54' 32" W	Marine
33TF Los Llanos	350	28° 39' 37" N	17° 54' 58" W	Marine
34TF Fuencaliente	570	28° 29' 58" N	17° 49' 30" W	Marine
35TF San Andrés y Sauces	280	28° 47' 59" N	17° 46' 19" W	Marine

**Table 7.-** Composition of carbon steel, zinc and copper test probes [4,18].

<b>Metal</b>	<b>Composition (wt. %)</b>									
	<b>Si</b>	<b>Fe</b>	<b>C</b>	<b>Mn</b>	<b>Zn</b>	<b>Ti</b>	<b>Cu</b>	<b>Mg</b>	<b>Al</b>	<b>Others</b>
Carbon steel	0.08	99.47	0.06	0.37	-	-	-	-	-	0.023
Copper	0.28	0.9	-	0.05	0.09	0.05	98.5	0.05	-	0.09
Zinc	-	-	-	-	99.77	0.02	0.2	-	0.006	-

**Table 8.-** Chloride and sulphur dioxide deposition rates, time of wetness values (TOW), and atmosphere classification according to airborne salinity (*S*), sulphur-containing substances (*P*), and time of wetness ( $\tau$ ) for the corrosion stations according to ISO 9223 norm [4,16].

Test site	Cl <sup>-</sup> d.r.	<i>S</i>	SO <sub>2</sub> d.r.	<i>P</i>	TOW	$\tau$	Test site	Cl <sup>-</sup> d.r.	<i>S</i>	SO <sub>2</sub> d.r.	<i>P</i>	TOW	$\tau$
1LP	29.61	1	0.34	0	5713	5	1TF	13.37	1	7.25	0	1976	3
2LP	39.06	1	0.26	0	2901	4	2TF	13.97	1	7.92	0	1976	3
3LP	138.13	2	3.50	0	5543	5	3TF	30.94	1	6.36	0	2260	3
4LP	158.69	2	0.38	0	1245	3	4TF	16.10	1	5.95	0	2680	4
5LP	59.50	2	0.37	0	2315	3	5TF	18.65	1	6.42	0	5680	5
6LP	56.36	2	0.18	0	2628	4	6TF	18.79	1	3.84	0	5142	4
7LP	33.14	1	0.65	0	3926	4	7TF	15.36	1	4.43	0	5856	5
8LP	42.35	1	2.81	0	3714	4	8TF	22.50	1	4.67	0	6516	5
9LP	61.87	2	0.31	0	2265	3	9TF	34.79	1	3.82	0	4520	4
10LP	32.45	1	0.21	0	3109	4	10TF	15.60	1	2.41	0	5160	4
11LP	38.83	1	0.23	0	3816	4	11TF	12.98	1	1.03	0	5500	5
12LP	32.99	1	0.20	0	3614	4	12TF	18.42	1	2.47	0	3682	4
13LP	168.94	2	12.30	1	3824	4	13TF	17.46	1	2.025	0	6700	5
14LP	14.05	1	0.49	0	1425	3	14TF	13.91	1	2.46	0	6044	5
15LP	133.04	2	18.47	1	1021	4	15TF	13.55	1	1.04	0	552	3
16LP	19.42	1	0.33	0	3604	3	16TF	38.39	1	4.66	0	3160	4
17LP	18.90	1	0.70	0	1257	3	17TF	24.29	1	2.54	0	3160	4
18LP	51.64	1	0.11	0	2213	3	18TF	30.32	1	4.26	0	3160	4
19LP	23.88	1	0.15	0	1324	3	19TF	17.28	1	2.66	0	5290	4
20LP	16.93	1	0.09	0	2900	4	20TF	163.10	1	5.41	0	2158	3
21LP	28.58	1	0.27	0	1936	3	21TF	21.10	1	3.13	0	2158	3
22LP	933.75	3	12.90	1	7215	5	22TF	12.34	1	1.73	0	3650	4
23LP	30.53	1	8.01	0	1515	3	23TF	25.02	1	2.44	0	6922	5
24LP	22.15	1	3.27	0	2675	4	24TF	18.90	1	4.79	0	4192	4
25LP	53.16	1	6.40	0	3651	4	25TF	20.92	1	3.30	0	3086	4
26LP	14.42	1	0.13	0	2510	4	26TF	31.65	1	3.84	0	3086	4
27LP	12.90	1	0.20	0	2441	3	27TF	14.67	1	1.28	0	5542	5
28LP	30.91	1	0.14	0	2315	3	28TF	21.16	1	2.70	0	7458	5
29LP	28.82	1	2.12	0	2132	3	29TF	334.69	3	8.74	0	4626	4
30LP	38.65	1	0.21	0	1391	3	30TF	41.26	1	3.45	0	2236	3
31LP	21.56	1	0.35	0	274	3	31TF	17.55	1	1.14	0	2964	4
32LP	20.27	1	0.08	0	1574	3	32TF	34.16	1	3.28	0	2900	4
33LP	26.24	1	1.05	0	2031	3	33TF	15.71	1	1.31	0	4816	4
34LP	14.47	1	0.95	0	1107	3	34TF	22.22	1	2.01	0	5240	4
35LP	13.25	1	0.22	0	2403	3	35TF	16.83	1	1.30	0	3212	4
36LP	39.32	1	14.40	1	3537	4	d.r. = deposition rate (mg/(m <sup>2</sup> ·day))						
37LP	24.30	1	1.65	0	2481	3	TOW (h/year)						
38LP	34.44	1	9.72	0	3723	4	<i>P</i> , <i>S</i> = pollution classes						
39LP	19.19	1	0.20	0	2490	3	$\tau$ = time of wetness classes						

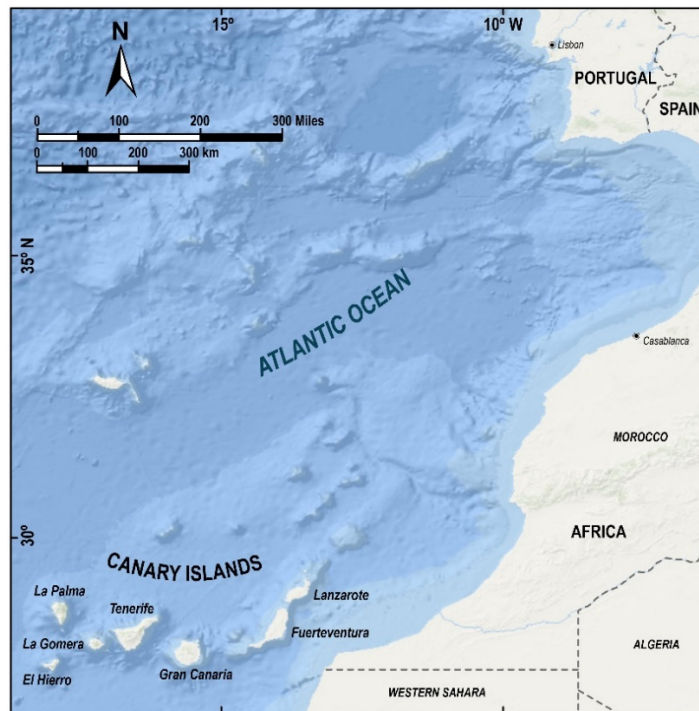
**Table 9.-** Corrosivity categories of the 74 corrosion stations across the Canary Islands, according to ISO 9223:1992(E) norm [4].

Test site	Corrosivity category (w.l./env.)*			Test site	Corrosivity category (w.l./env.)*		
	Carbon steel	Zinc	Copper		Carbon steel	Zinc	Copper
1LP	2/3 or 4	>5/3 or 4	>5	1TF	2/2 or 3	3/2	5/2
2LP	3/3	>5/3	>5/3	2TF	2/2 or 3	3/2	5/2
3LP	5/5	>5/5	>5/5	3TF	2/2 or 3	5/2	5/2
4LP	4/3 or 4	>5/3	5/3	4TF	3/3	4/3	5/3
5LP	2/2 or 3	>5/3	>5/3	5TF	3/3	3/3	5/3
6LP	2/3	>5/4	5/4	6TF	2/3	3/3	5/3
7LP	3/3	>5/3	5/3	7TF	2/3	4/3	5/3
8LP	3/3	>5/3	>5/3	8TF	3/3	4/3	5/3
9LP	2/3 or 4	>5/3	>5/3	9TF	2/2 or 3	5/2	>5/2
10LP	3/3	>5/3	5/3	10TF	2/3	3/3	4/3
11LP	5/3	>5/3	>5/3	11TF	2/3	3/3	4/3
12LP	2/3	>5/3	5/3	12TF	2/3	4/3	5/3
13LP	4/4	>5/4	>5/4	13TF	2/3	3/3	5/3
14LP	2/2 or 3	>5/3	4/3	14TF	2/3	3/3	4/3
15LP	4/3 or 4	>5/3	>5/3	15TF	2/2 or 3	3/2	4/2
16LP	2/3	5/3	2/3	16TF	3/2 or 3	5/2	>5/2
17LP	2/2 or 3	>5/3	5/3	17TF	2/2 or 3	4/2	>5/2
18LP	3/2 or 3	>5/3	>5/3	18TF	3/2 or 3	5/2	>5/2
19LP	2/2 or 3	>5/3	5/3	19TF	3/2 or 3	3/2	5/2
20LP	3/3	>5/3	4/3	20TF	5/4	>5	>5
21LP	2/2 or 3	>5/3	>5/3	21TF	2/3	4/3	>5/3
22LP	>5/5	>5/5	>5/5	22TF	-/2 or 3	2/2	-/2
23LP	3/2 or 3	>5/3	5/3	23TF	2/3	4/3	>5/3
24LP	3/3	>5/3	5/3	24TF	2/3	3/3	5/3
25LP	3/3	>5/3	>5/3	25TF	3/3	4/3	5/3
26LP	2/3	>5/3	2/3	26TF	3/2 or 3	5/2	>5/2
27LP	2/2 or 3	4/3	3/3	27TF	2/3	2/3	4/3
28LP	3/2 or 3	>5/3	5/3	28TF	>5/3 or 4	5/3 or 4	>5/3 or 4
29LP	3/2 or 3	>5/3	5/3	29TF	>5/5	>5/5	>5/5
30LP	2/2 or 3	4/3	5/3	30TF	3/3	>5/3	>5/3
31LP	2/2 or 3	5/3	5/3	31TF	2/3	5/3	4/3
32LP	2/2 or 3	4/3	4/3	32TF	2/3	5/3	>5/3
33LP	2/2 or 3	4/3	4/3	33TF	2/3 or 4	4/3 or 4	5/3 or 4
34LP	3/2 or 3	>5/3	5/3	34TF	2/3 or 4	5/3 or 4	>5/3 or 4
35LP	2/2 or 3	5/3	2/3	35TF	2/2 or 3	3/2	5/2
36LP	3/3	5/3	5/3				
37LP	3/2 or 3	>5/3	5/3				
38LP	4/3	>5/3	>5/3				
39LP	3/2 or 3	>5/3	3/3				

\*Corrosivity category from weight loss (w.l.) and from environmental data (env.) according to ISO 9223:1992(E)

**Table 10.-** Error ranges observed for the prediction of early carbon steel corrosion rates within the test sites.

<b>Error range</b>	<b>Percentage of stations</b>
Error < 10%	30.14
10% ≤ Error < 20%	26.03
20% ≤ Error < 30%	17.81
30% ≤ Error < 40%	12.32
40% ≤ Error < 50%	4.11
50% ≤ Error < 100%	6.85

**Figure 1.-** Geographical locations of the Canary Islands.

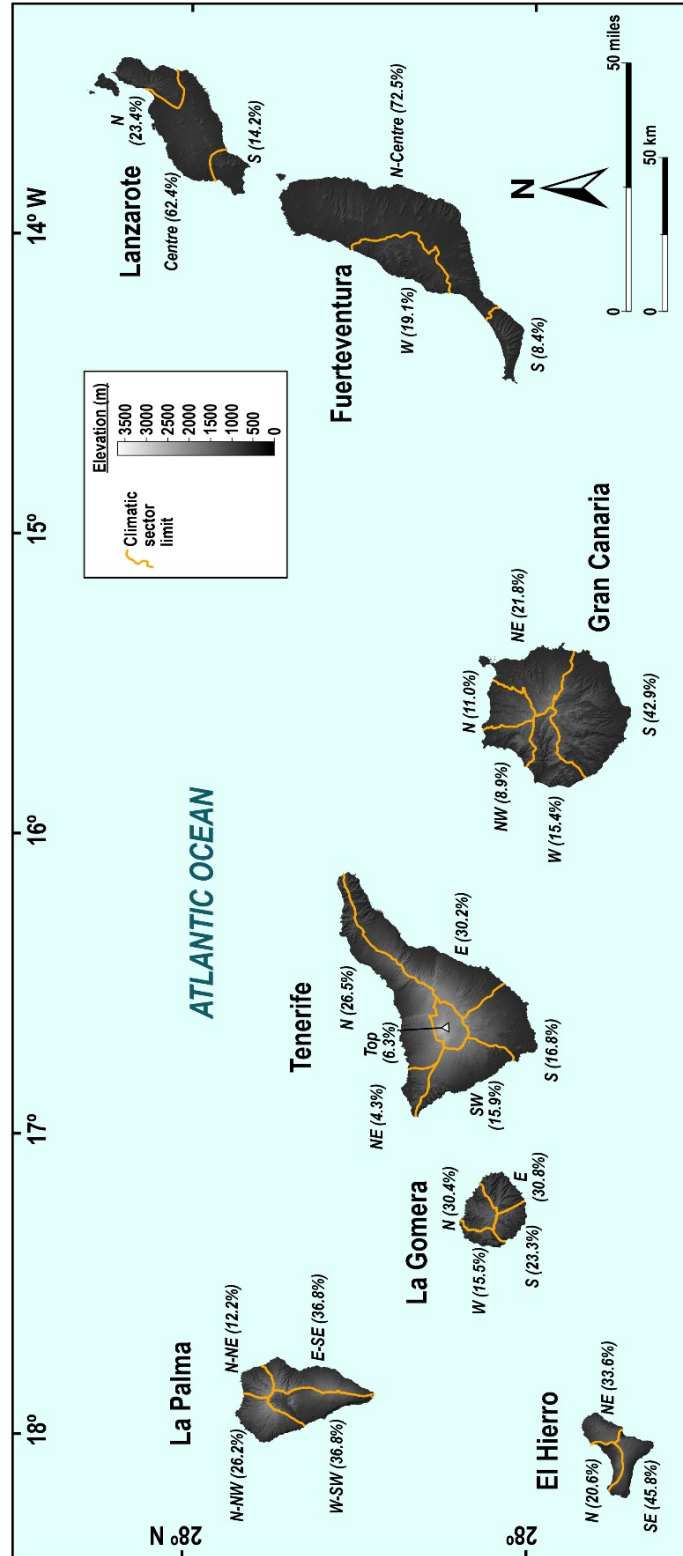


Figure 2.- Climatic sectors and orography of the Canary Islands (adapted from [14]).

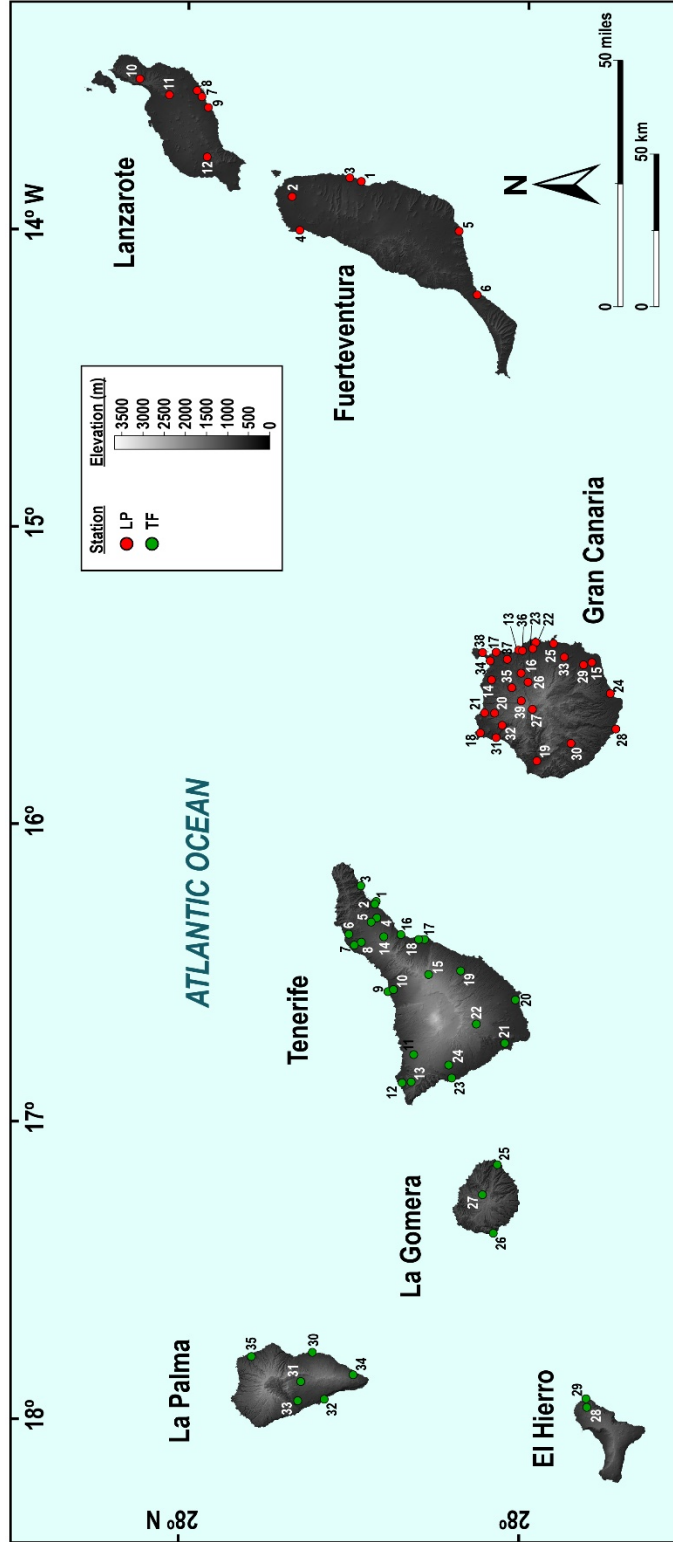
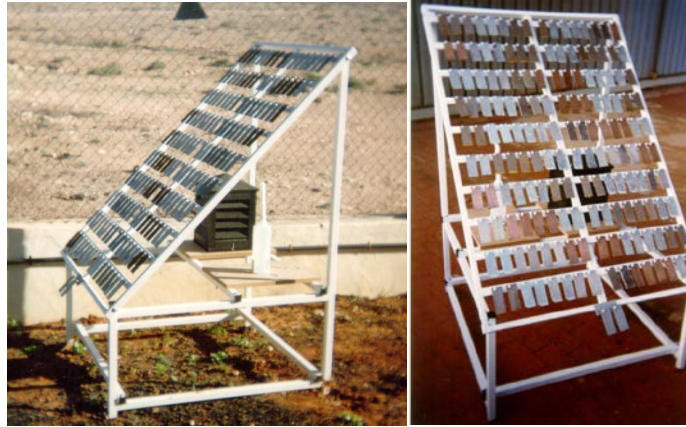
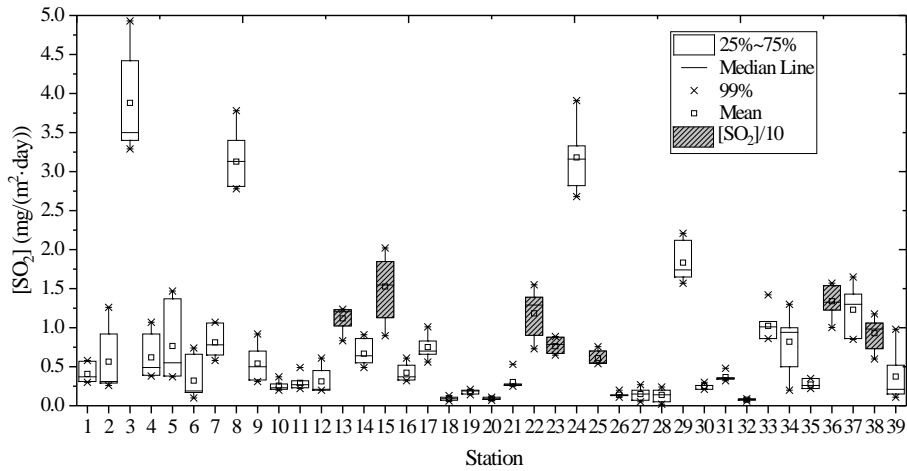


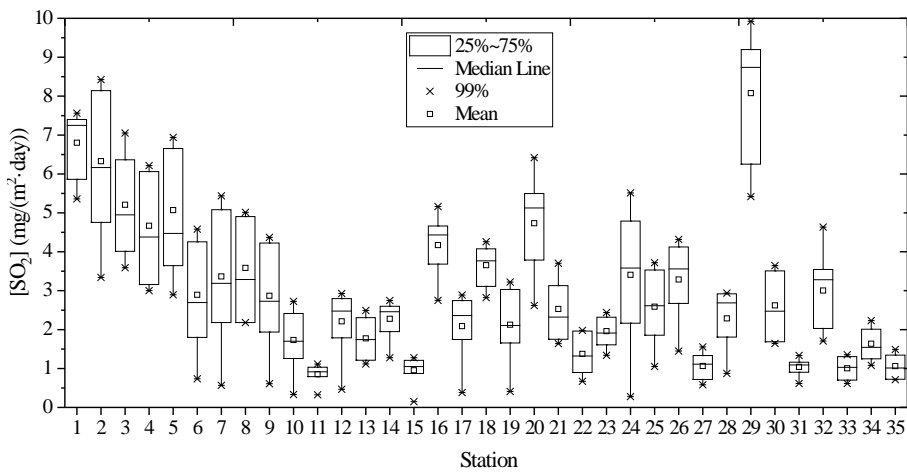
Figure 3.- Location of the corrosion test sites in the Canary Islands.



**Figure 4.-** Photographs taken at selected corrosion test sites.



**Figure 5.-** Sulphur dioxide amounts monitored over three years at the corrosion stations located in Las Palmas province.



**Figure 6.-** Sulphur dioxide amounts monitored over three years at the corrosion stations located in Santa Cruz de Tenerife province.



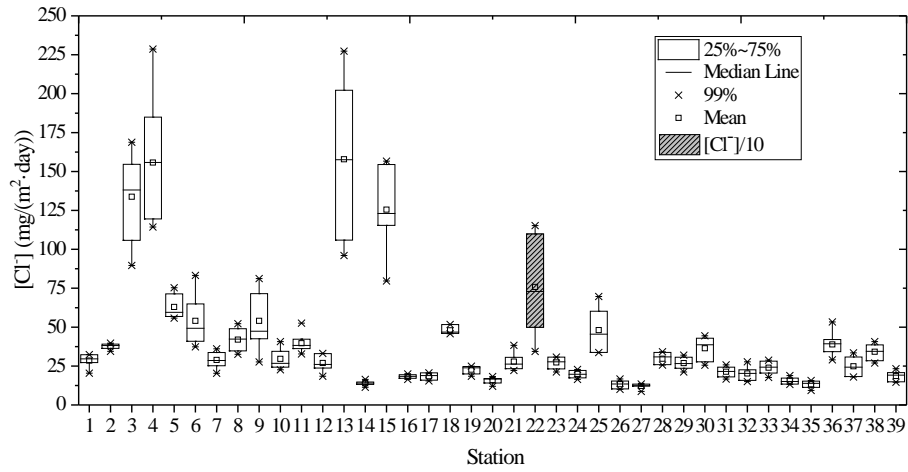


Figure 7.- Chloride amounts monitored over three years at the corrosion stations located in Las Palmas province.

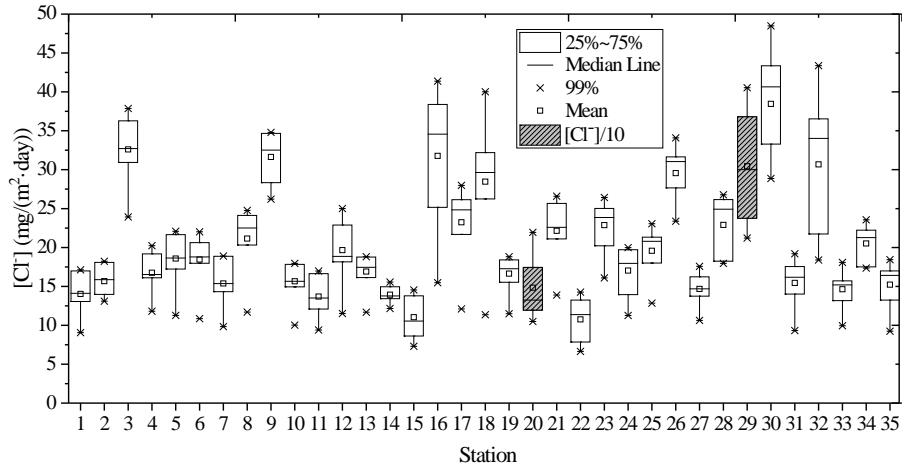


Figure 8.- Chloride amounts monitored over three years at the corrosion stations located in Santa Cruz de Tenerife province.

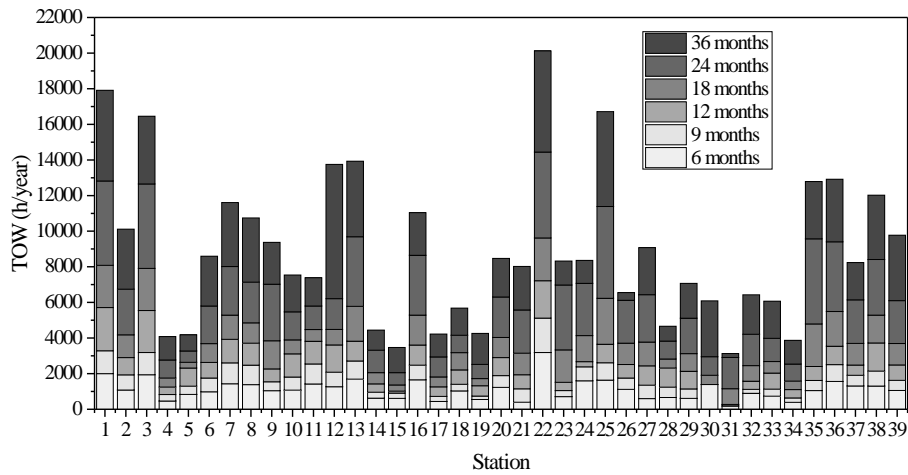
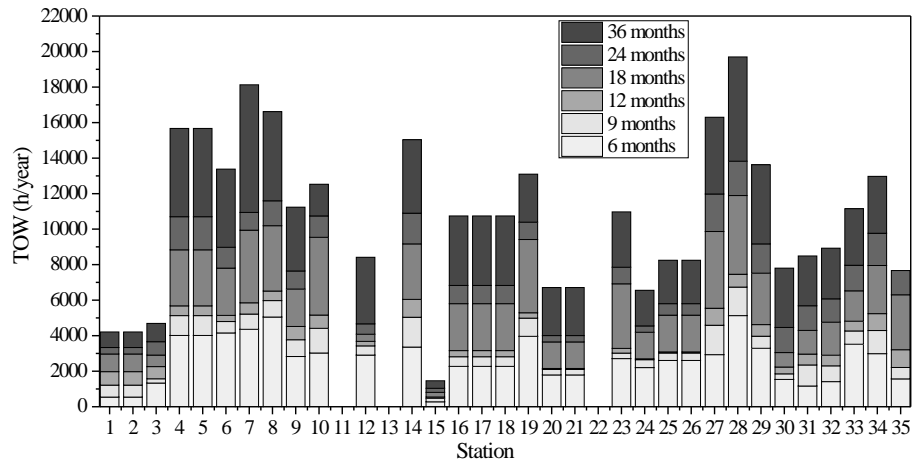


Figure 9.- TOW data monitored over three years at the corrosion stations located in Las Palmas province.



**Figure 10.-** TOW data monitored over three years at the corrosion stations located in Santa Cruz de Tenerife province.

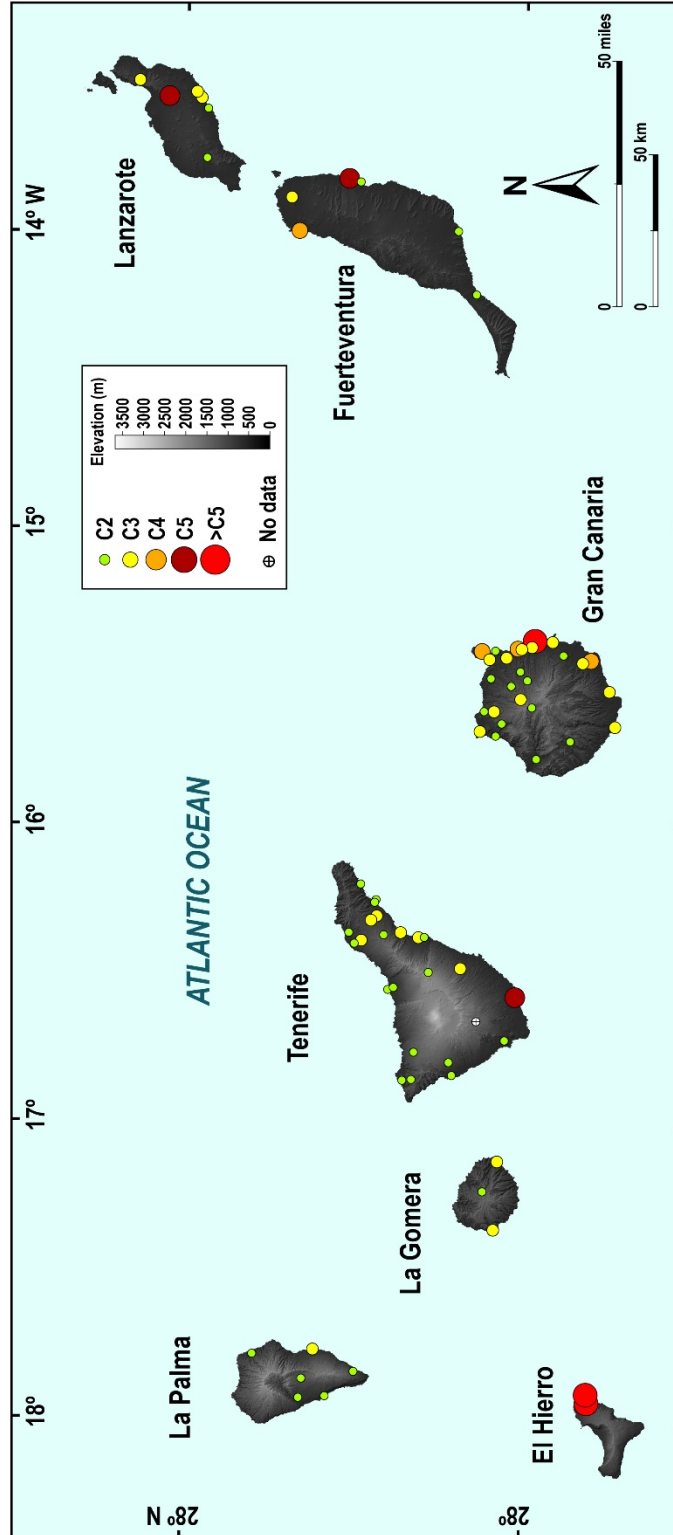


Figure 11.- Corrosivity map for carbon steel.

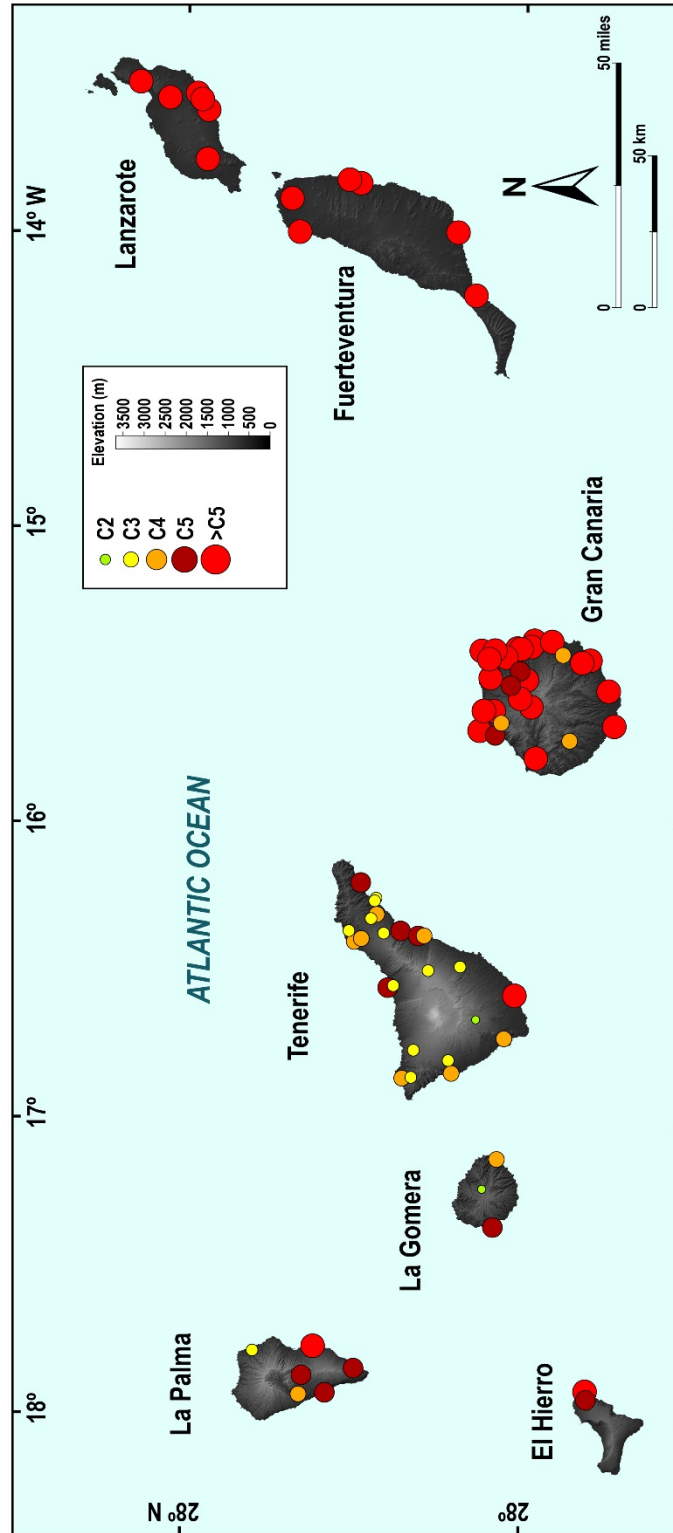


Figure 12.- Corrosivity map for zinc.

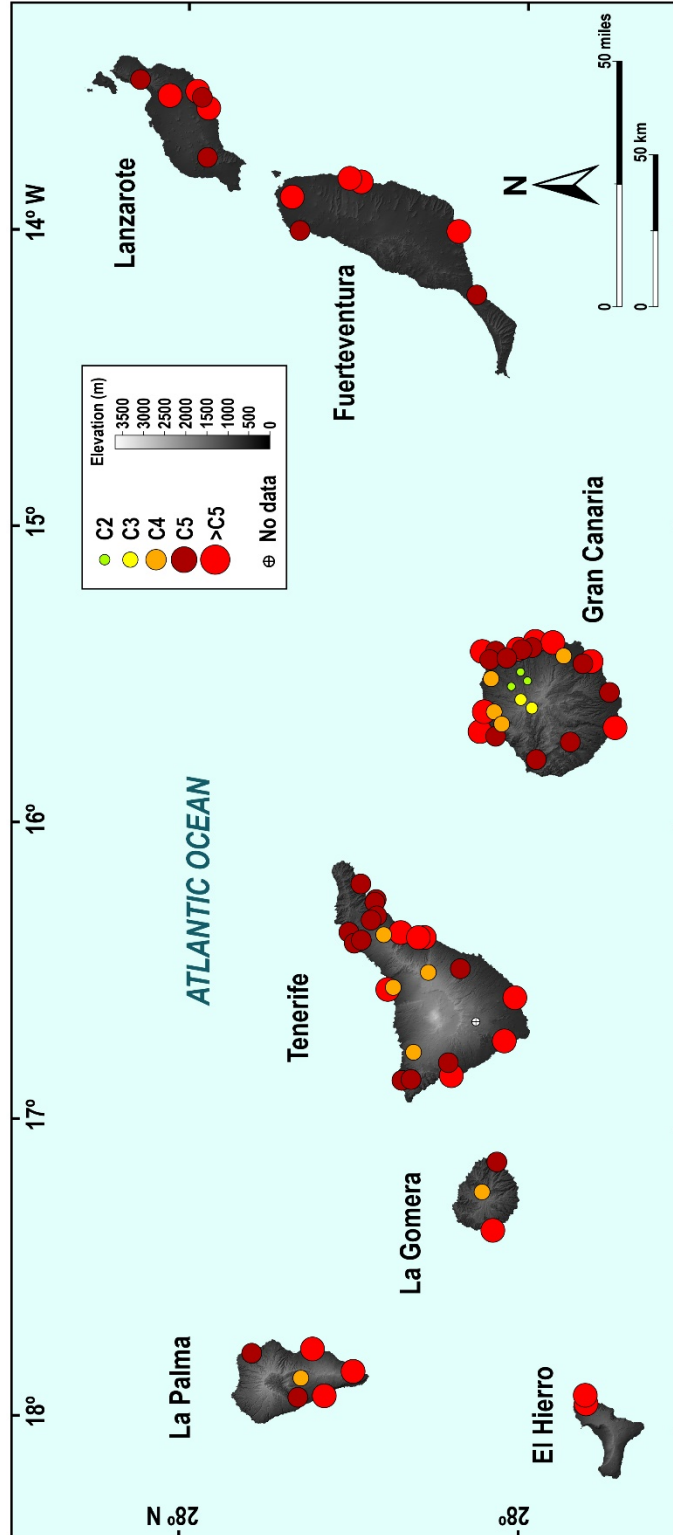


Figure 13.- Corrosivity map for copper.