

Evaluation of the Atmospheric Corrosion Indices at Different Sites in Chile Using the (CLIMAT) Wire-on-Bolt Test

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This study classifies the atmosphere of certain sites in Chile in order of corrosivity using the CLIMAT technique (Classification of Industrial and Marine Atmospheres), and compares the results with a more conventional methodology (ISO 9223). The study sites are: Putre, Huasco, Valparaíso, Quintero, Los Andes and Temuco. Aluminum wire was used for the anode, while the cathode was iron in the monitoring of marine environment (Al-Fe), copper for industrial environment (Al-Cu) and polyethylene for general atmospheric corrosion (Al-polyethylene). The Marine Corrosion Index (MCI), the Industrial Corrosion Index (ICI) and the Atmospheric Corrosion Index (ACI) were calculated for each station. The atmospheric corrosion categories are in line with both methodologies and the CLIMAT test can therefore be used to obtain reliable results in a short period of time. The corrosion rate of the aluminum was also measured and the percentage galvanic effect calculated at each station.

Keywords: Atmospheric corrosion, aluminum, weight loss, corrosion index, Climat.

1. INTRODUCTION

Atmospheric corrosion is a complex process and is highly sensitive to the environmental conditions at each particular site [1-4]. Under this perspective, companies from different sectors with metallic infrastructures exposed to different types of atmosphere, such as those in the electricity sector, need to be aware of the impact of atmospheric corrosion in order to be able to select adequate materials, to calculate the useful life of these materials, and to choose the best method for protecting them from a particular atmosphere.

The wire-on-bolt test has established itself as an important tool in the study of atmospheric corrosion. The methodology was used more than 50 years ago in the United States by Bell Telephone

Laboratories to study the galvanic behavior of different bimetal couples exposed to the atmosphere [5]. The company ALCAN Cables used the technique later on to predict the resistance of aluminum to atmospheric attack in a short timeframe (three months), particularly for the case of different metals, mainly iron and copper [6-8]. The test has also been used to measure the resistance of aluminum steel-reinforced cables in coastal zones and as a way to classify the corrosivity of marine and industrial atmospheres for sites with no prior information on atmospheric corrosion or for sites with microclimates [9].

As part of the Ibero-American Atmospheric Corrosion Project (MICAT) [10] and the V Centenary Science and Technology for Development Program (CYTED-D), a series of stations were set up in Mexico to study atmospheric corrosion. One of these stations, located to the southeast of Mexico City, was used to conduct tests to classify the atmosphere around the station using the wire-on-bolt technique and the methodology proposed by the International Standardization Organization [11] to classify atmospheres in accordance with climatological variables and pollutant content, while also classifying the atmospheres on the basis of corrosion rate measured after exposing metal test probes for a period of one year. According to these tests, the station was classified as rural, of low to medium corrosivity, and, in addition, good correlation was found between the two methods [12].

In another study, wire-on-bolt assemblies were exposed to a process of immersion-emersion using the CEBELCOR method with solutions of 10^{-4} M Na_2SO_4 , 10^{-3} M NaCl , a mixture of 10^{-4} M Na_2SO_4 + 10^{-3} M NaCl and distilled water as electrolytes, simulating rainwater from urban, marine, marine-urban and rural atmospheres, respectively. In all media, the Al-Cu system showed the highest corrosion index, and was seen to be the best couple for evaluating atmospheric corrosion. The galvanic effect is the main contribution to total corrosion in this system [13].

Colombian researchers carried out bimonthly classification on atmospheres based on their corrosivity using the CLIMAT test in 21 sampling sites distributed around the country. The classifications were then correlated with the mass loss measured for different materials, and with atmospheric parameters (temperature and relative humidity) and environmental parameters (chloride and sulfate content). They reported that the atmosphere at coastal stations in the period of January-May is more aggressive to the studied materials, which suggested correlation with the higher chloride concentrations found during this period [14-15].

In general, the CLIMAT method can be used to rapidly study environmental corrosivity, but it should be noted that the process considers general corrosion on the exposed surface of the wire, the corrosion in the grooves between the wire and the bolt and the galvanic corrosion between the two metals.

The objective of the present research is to use a simple methodology to classify the atmospheres of different sites within Chile and to compare the results with others obtained by traditional methods as a means of validating the data obtained. It is hoped that this will allow future classification of sites of difficult access where it is not possible to install weather stations and atmospheric pollutant measurement equipment. Six study sites in Chile were used: Putre, Huasco, Valparaíso, Quintero, Los Andes and Temuco. Their geographical characteristics are shown in Table 1.

Table 1. Geographic details of exposure sites.

Site	Latitude (S)	Longitude (W)	Location in Chile	Altitude (m)	Distance to sea (m)
Putre	18°11'47"	69°33'33"	North	3553	84000
Huasco	28°27'55"	71°13'20"	North	21	88
Valparaiso	33°2'39.63"	71°36'45.34"	Center	15	200
Quintero	32°45'10.7"	71°28'58.23"	Center	18	70
Los Andes	32°52'36"	70°35'82"	Center	860	85000
Temuco	38°46'11.4"	72°38'15.69"	South	114	68000

2. MATERIALS AND METHODS

When using the wire-on-bolt technique to evaluate atmospheric corrosion, an anodic material (the wire) is placed in contact with a cathodic material (the bolt). The anodic wire is wrapped around the cathodic bolt and the assembly is exposed to the atmosphere.

In all cases, 1100 aluminum (UNS A91100) was used for the wire anode and the cathode was 1010 steel (UNS G 10100) and CA110 copper (UNS C11000) to monitor the marine environments (Al–Fe) and industrial environments (Al–Cu), respectively. In order to study atmospheric corrosion without considering the galvanic effect, an assembly of the aluminum wire wrapped around a polyethylene bolt was used. At the same time, samples of aluminum wire twisted into spirals were exposed without contact with any other material. Table 2 shows the composition of each material.

Table 2. Chemical composition of materials

Material	Element (%)								
	Al	Si	Fe	Cu	Mn	Zn	C	P	S
Al 1100	99	< 0.50	< 0.50	0.10	< 0.05	< 0.10	---	---	---
Carbon steel 1010	---	---	99	---	0.40	---	0.10	< 0.04	< 0.05
Copper CA110	---	---	---	99.9	---	---	---	---	---

The dimensions and the materials used in the samples are all standardized [16]. The bolts were 10 cm in length with a diameter of 1.27 cm, and with 13 threads per inch. This implies that the wire was in contact with approximately 5.0 cm of the length of the bolt. Each end of the wire was held in place with plastic rings (to avoid unwanted galvanic effects), as shown in Figure 1.



Figure 1. Wire-on-bolt assembly.

The bolts and wires were degreased prior to assembly. The mass of the wires was measured with a precision of 0.1 mg in order to identify the exact mass of the portion wrapped around the bolt [17]. The bolts were placed vertically in plastic supports and stored in hermetically sealed bags to avoid contamination before exposure. At the end of the exposure period, the samples were disassembled, corrosion products were removed from the wires in accordance with conventional methods [18] and the mass loss of the aluminum wire was measured.

The mass loss found on the aluminum wires, expressed as a percentage, after three months of exposure is called the Corrosion Index and is used to classify the different atmospheres in the respective categories, depending on the result obtained for the Atmospheric Corrosion Index (ACI), the Marine Corrosion Index (MCI) and the Industrial Corrosion Index (ICI) [16]. In addition, the values of the mass loss of the wires for the galvanic pairs and the wire wrapped around the polyethylene bolt can be used to calculate the galvanic effect [16].

As the environmental conditions at a particular site can vary by season, the four measurements conducted at each sampling station correspond approximately to the periods of autumn, winter, spring and summer. It is recommendable to carry out the test for each season and thus to be able to observe the differences in the indices as a function of meteorological variables.

Weather stations were also installed at the study sites to obtain monthly data on temperature, relative humidity, amount of rainfall and wind speed and direction. Devices were also installed to take bimonthly measurements of chloride and sulfur dioxide content in the air. The wet candle method was used to measure atmospheric chlorides. This method consists of wrapping a strip of gauze around a glass tube, the ends of the gauze are submerged in a solution of 10% glycerin in distilled water. The chlorides deposited from the air are measured by mercurimetry in the presence of the indicators, diphenylcarbazone and bromophenol blue; the results are expressed in $\text{mg Cl}^- \text{m}^{-2} \text{day}^{-1}$ [19]. For measurements of SO_2 , the lead dioxide candle method was used; SO_2 is deposited on gauze coated with PbO_2 , forming lead sulfate. This compound is solubilized in 5% Na_2CO_3 and the sulfate ion is then measured gravimetrically by precipitation as BaSO_4 ; the result is expressed in $\text{mg SO}_2 \text{m}^{-2} \text{day}^{-1}$ [19].

The morphology of the corrosive attack was observed using a JEOL JSM-5410 scanning electron microscope, coupled to an EDX 9100 energy dispersive spectrometer, and the corrosion products obtained on the aluminum wire were identified using the X'PERT PRO PANalytical diffractometer with CuK α radiation and a pyrolytic graphite monochromator. The equipment power was 40mA and 40kV in grazing beam, using an angle of incidence of 1 degree and a nickel filter.

3. RESULTS AND DISCUSSION

3.1. Characterization of the test atmosphere

Monthly evaluation of the climatic and environmental parameters and the use of ISO 9223 allow classification of the aggression of the atmospheres at the stations [11]. Figure 2 shows the variation in time of wetness (TOW, τ) for each station. This variable is the period of time for which the metal surface is covered by a film of electrolyte (including in an adsorbed form) which significantly stimulates atmospheric corrosion. TOW is calculated by counting the number of hours for which relative humidity (RH) is above a certain threshold, generally above 80%, and the temperature is above 0 °C.

The results obtained for TOW (Figure 2) may be used to separate the stations into three groups: values between 60% and 90%, corresponding to the stations in Quintero, Temuco and Huasco; values around 40%, corresponding to the station in Valparaíso; and around 10% for the stations in Putre and Los Andes. According to these values, which show the length of time the metal or alloy is humid, it may be expected that the more aggressive zones with higher levels of atmospheric corrosion are those in Quintero, Temuco and Huasco.

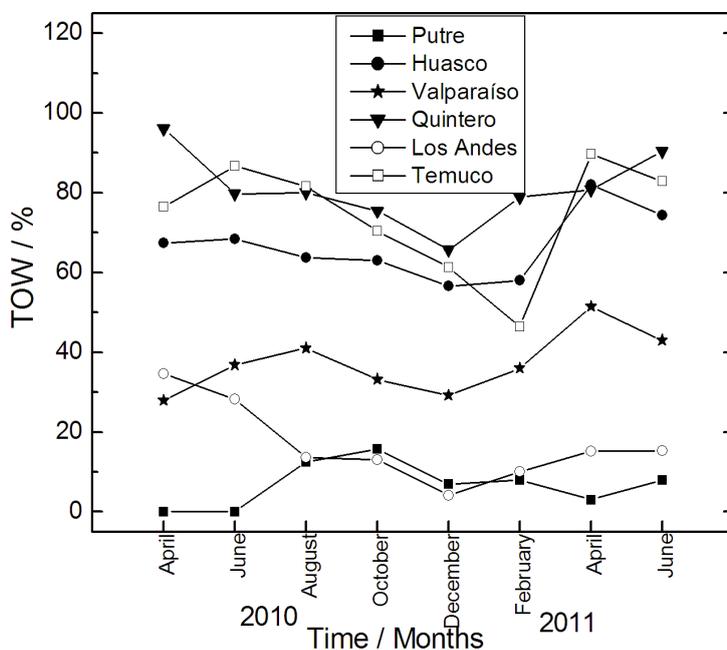


Figure 2. TOW as a function of time, for each study station.

Figure 3 shows the variation in environmental deposits of the pollutants, chloride (salinity, S) and sulfur dioxide (sulfurated compounds, P) during the study period for each site. It can be seen that the highest chloride content levels are found at the Quintero station, which is undoubtedly due to its close proximity to the coastline and to the presence of strong winds in the area which produce a large amount of saline fog that is then deposited on the sample.

The stations in Huasco and Valparaíso show similar behavior as they are both marine stations with similar climatic characteristics. The lowest levels of chloride content are seen in Putre, Los Andes and Temuco, all of which are located far from the coast.

The highest levels of sulfur dioxide pollution are also seen in Quintero due to the presence of mining industry in the area and these values are highest in the periods of spring and summer.

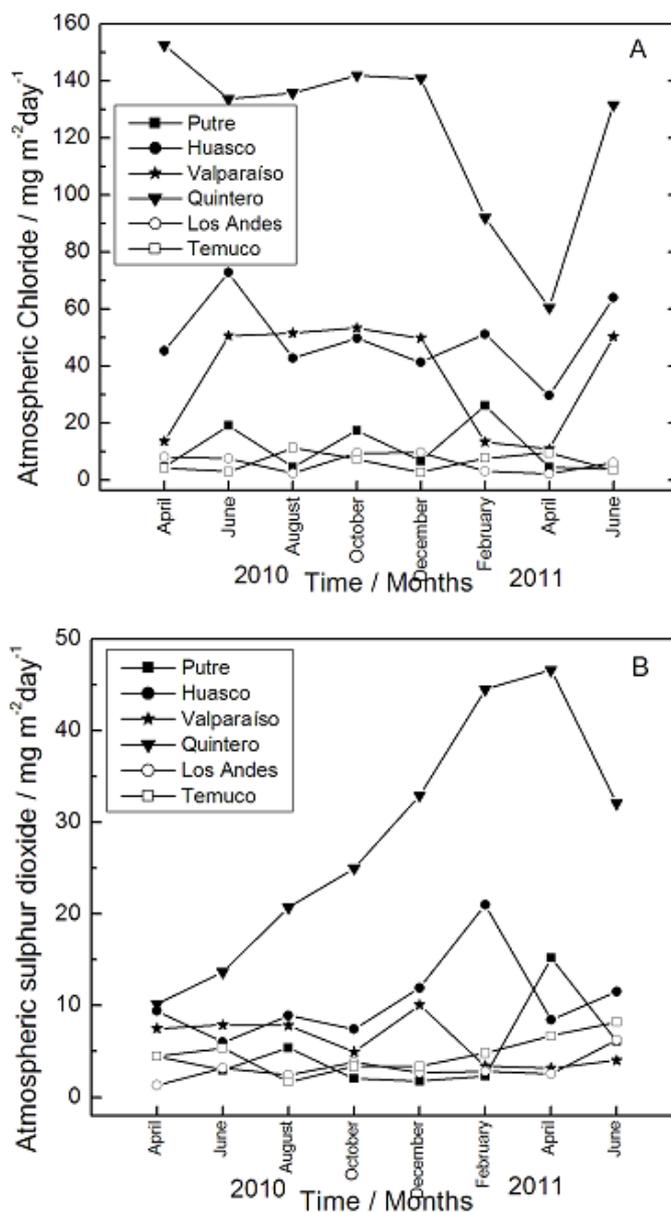


Figure 3. Variation in chloride and sulfur dioxide content as a function of time for each study station.

Figure 4 shows the variation in rainfall during the study period for each site. It can be seen that the Temuco station has the highest level of rainfall during the year, mainly in winter, while the area of Putre presents more rainfall in the summer months.

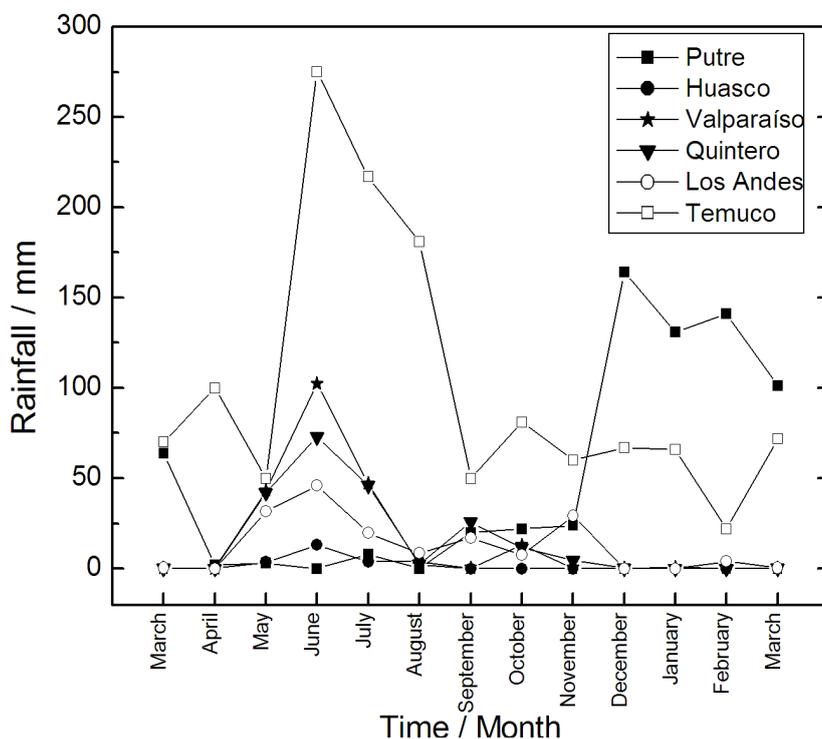


Figure 4. Variation in rainfall as a function of time for each study station.

3.2. Calculation of the atmospheric corrosion index

The results obtained in the four exposure periods from March 2010 to March 2011 are shown in Figures 5 and 6 as the seasons of Autumn, Winter, Spring and Summer. Table 3 shows the classification of atmospheric corrosivity based on the ICI, in comparison with the data obtained using ISO 9223.

In general, for all the study sites the values obtained for the aggressivity indices can be ordered as follows: $ICI > MCI > ACI$. These results were expected given that for ICI the test couple is aluminum/copper, and these two metals present a greater difference in corrosion potential than that of aluminum/steel. Therefore, atmospheric corrosion, galvanic corrosion and corrosion in the grooves between the aluminum wire are evaluated in both cases, while only atmospheric corrosion and the corrosion in the grooves of the wire are evaluated for the aluminum/polyethylene couple.

When comparing the results of the different indices for the same site during the different seasons, certain variations can be seen. These will likely depend on changes in TOW, atmospheric pollutant content, amount of rainfall and wind speed. This variation is more pronounced for MCI and ICI. The aforementioned factors will also influence the composition, adherence and morphology of the corrosion products that are formed, which in turn influences the degree of corrosive attack of the aluminum.

Figure 5 presents the corrosion indices obtained for the three stations located on the coast, Quintero, Huasco and Valparaíso. Quintero is classified as very severe, with corrosion indices considerably higher than the other two stations. This is due to the combined effect of the environmental pollutants, as the samples are exposed at a distance of 70 m from the coastline, with an average chloride content level of $123.6 \text{ mg m}^{-2} \text{ year}^{-1}$ and also to the presence of different industries in the sector (average SO_2 content of $28.0 \text{ mg m}^{-2} \text{ year}^{-1}$). In this area, the differences between the aggressivity indices for the different seasons of the year are minor.

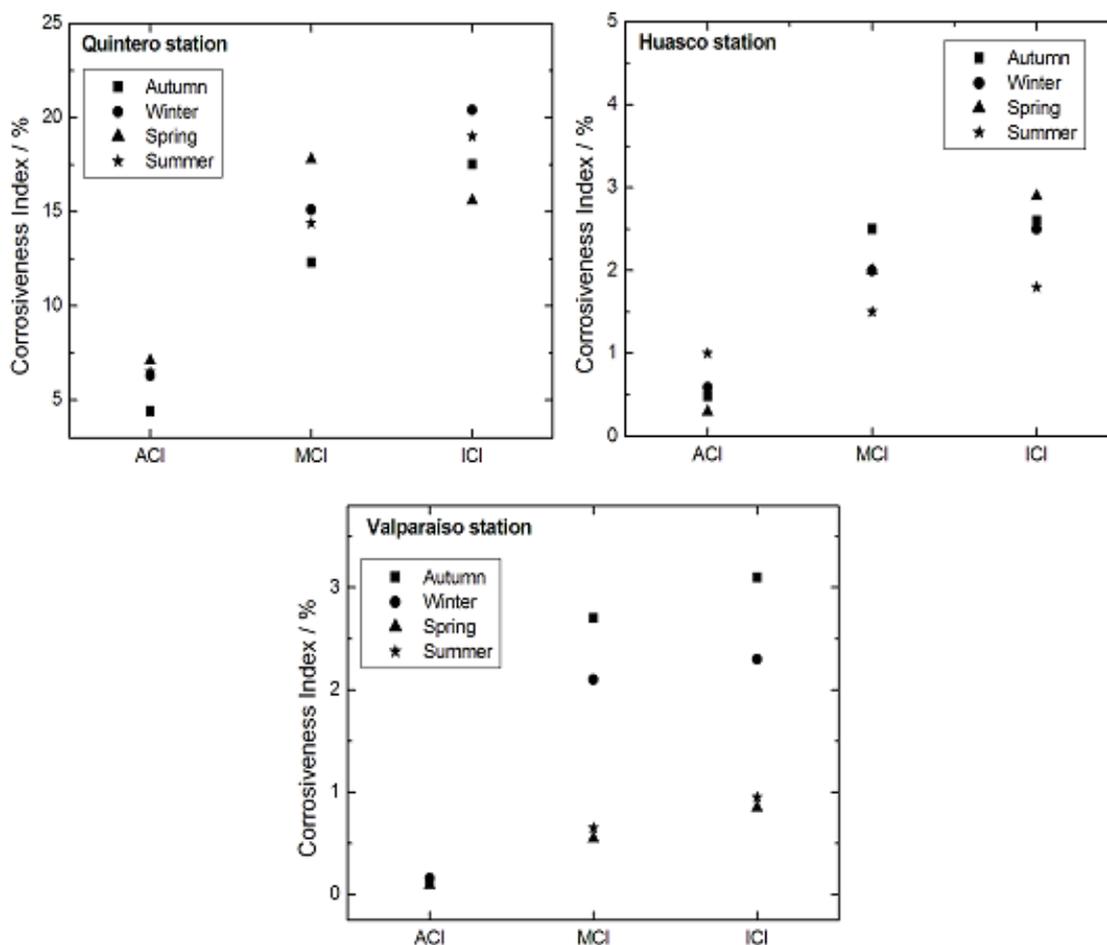


Figure 5. Corrosion indices for the stations at Quintero, Huasco and Valparaíso.

In Huasco, the station located furthest north within the country (average chloride content of $49.6 \text{ mg m}^{-2} \text{ year}^{-1}$), the atmospheric, marine and industrial corrosion indices are around 6 times lower than for the Quintero station, and slightly higher than in Valparaíso. This site is close to a thermoelectric power station, where average atmospheric SO_2 content is $10.6 \text{ mg m}^{-2} \text{ year}^{-1}$ and TOW averages 66.7%. This explains the difference with the Valparaíso station, which is located 200 m from the coast, in an urban area with surrounding buildings that generate a screening effect, giving chloride content of $36.6 \text{ mg m}^{-2} \text{ year}^{-1}$, SO_2 content of $6.1 \text{ mg m}^{-2} \text{ year}^{-1}$ and TOW of 37.3%. The decrease in the corrosion indices for the Valparaíso station in the periods of spring and summer is due to the

increase in temperature, the decrease in relative humidity and also the change in the direction and intensity of the wind, all of which produces a fall in the chloride content of the atmosphere. This fact is what marks the difference between the Huasco station with a moderate/severe atmospheric corrosion classification and Valparaíso, which is classified as moderate. It is important to note that the ACI for aluminum wire that is not tied around a polyethylene bolt exposed in Valparaíso is 0.11 in autumn and 0.15 in winter. These values are slightly lower than when the wire is placed on the polyethylene bolt, and may therefore represent damage suffered due to the process of atmospheric corrosion.

Figures 6 shows the corrosion indices obtained for the stations located in Los Andes, Putre and Temuco. The three corrosion indices for the Los Andes station are very low, and the site is therefore categorized as of negligible corrosivity. This result was predictable as the area is far from the coast, is 860 mamsl, and is characterized by high temperatures in summer and below freezing temperatures in winter, with an average TOW of 14.0%, chloride content of 2.8 mg m⁻² year⁻¹ and SO₂ content of 3.0 mg m⁻² year⁻¹.

The Putre station is located in the extreme north of the country, 3553 mamsl and 8.4 km from the sea. It is a relatively uninhabited area characterized similarly to Los Andes by high temperatures in summer and below freezing temperatures in winter, with a TOW of 7.0%, chloride content of 14.8 mg m⁻² year⁻¹ and SO₂ content of 4.8 mg m⁻² year⁻¹ during the period of this study. The rainfall in Putre is more prevalent in summer, therefore increasing corrosion index values in that period. Given the conditions in the area, the corrosion indices are generally lower than those obtained for Los Andes.

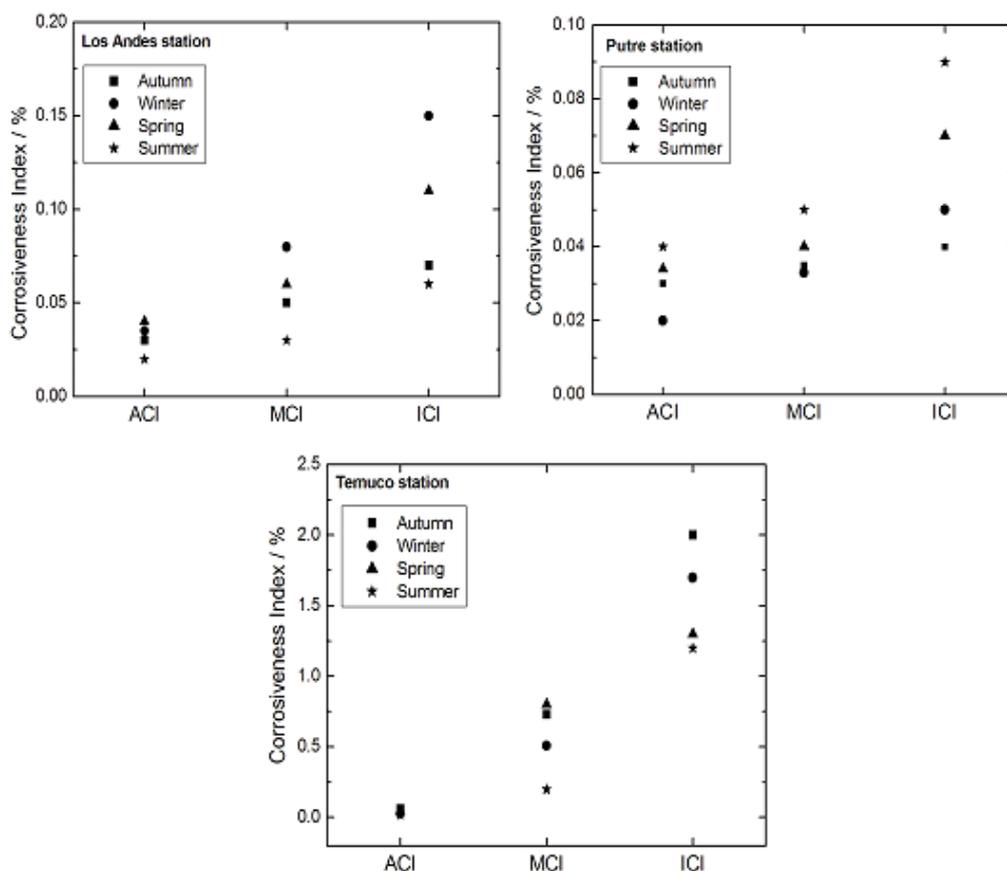


Figure 6. Corrosion indices at the stations in Los Andes, Putre and Temuco.

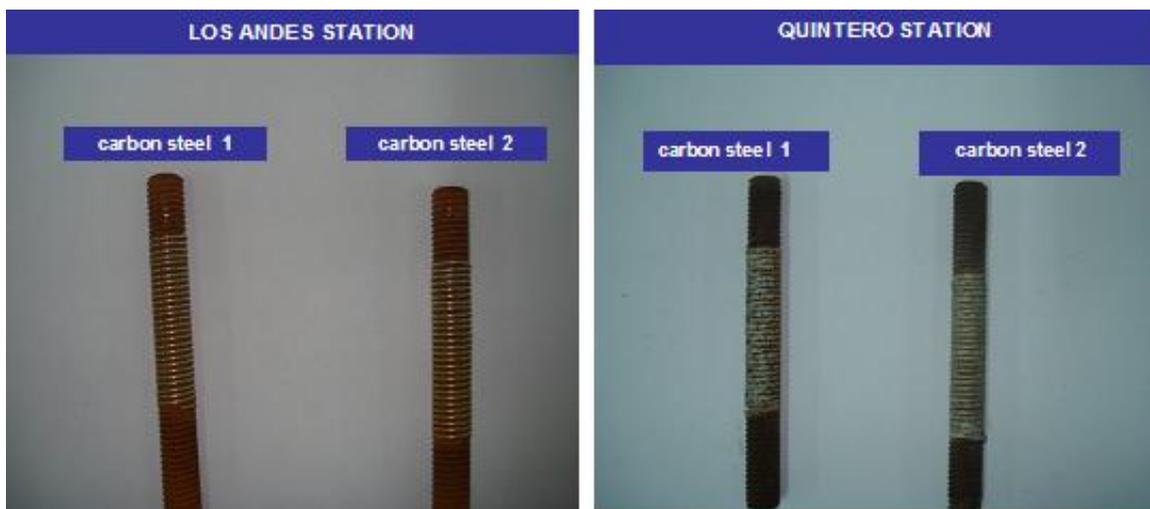


Figure 7. Surface appearance of the aluminum/steel couples exposed at the stations in Los Andes and Quintero, after 3 months of exposure during the period of autumn.

The Temuco station is also at a distance from the sea, but lies in an area of high rainfall, particularly in autumn and winter, with an average TOW of 74.4%. It can be categorized according to the mass loss tests as moderately corrosive. It is important to note that this sampling station is located at the airport, where gases emitted by the airplane engines may contribute to the levels of pollution. Another possible contributing factor is the use, within the city, of heating systems that burn damp firewood. The average atmospheric SO₂ content in the area was measured at 4.8 mg m⁻² year⁻¹ and chloride content at 3.1 mg m⁻² year⁻¹.

Figure 7 shows the surface appearance of the samples exposed for a period of three months at the stations in Quintero (marine/industrial zone) and Los Andes (rural zone), for the period of autumn (the initial stage of the research). The appearance of the aluminum wires is in line with the results obtained for MCI (Al-Fe) at these sites, where the values were calculated at 0.05 for Los Andes and 12.3 for Quintero, showing a higher degree of corrosion for the sample exposed in Quintero.

Table 3 compares the environmental corrosion categories identified for the study sites using the CLIMAT test (specifically the ICI) and the procedure set out in ISO 9223. The results obtained for the different areas within Chile, with their different atmospheric conditions, are similar using both methodologies. This suggests that it is possible to use the CLIMAT test in areas of difficult access, implying lower costs in the implementation of sampling and the subsequent analysis.

Table 3. Classification of atmospheric corrosion at the study sites.

Station	CLIMAT (ICI)	ISO 9223
Putre	Negligible	LowC1 (S ₁ P ₀ τ ₂)
Huasco	Moderate-Severe	HighC4 (S ₁ P ₁ τ ₅)
Valparaíso	Moderate	MediumC3 (S ₁ P ₀ τ ₄)
Quintero	Very Severe	Very highC5 (S ₂ P ₂ τ ₅)
Los Andes	Negligible	LowC2 (S ₀ P ₀ τ ₃)
Temuco	Moderate	MediumC3 (S ₀ P ₀ τ ₅)

The results obtained by other authors, such as Morcillo [10], who generated a map of atmospheric corrosion for the Balearic Islands in Spain, with MCI data after 3 months for Mallorca (2.11), Ibiza (2.53) and Formentera (2.83), are similar to the MCI values for Huasco (2.50) and Valparaíso (2.70). Our results are also comparable to those obtained by Jaén et al. [20] on the Caribbean coast of Panama, at Sherman Open and Sherman Coastal, located 600 m and 50 m from the coast, respectively, with atmospheric classification identified at $S_1P_0 \tau_5$ (C4). This result is particularly similar to that obtained for the Huasco station in the present study.

The Quintero station, which presents the highest value for MCI at 17.8 and an atmospheric classification of ($S_2P_1 \tau_5$), is similar to the behavior of the island of Menorca in Spain, which has a maximum MCI of 11.70, and to the area of Sherman Breakwater, 3 m from the Caribbean coast of Panama, whose atmospheric classification is $S_3P_0 \tau_5$ (>C5).

CLIMAT tests conducted at different stations in Colombia show that the aluminum presents a higher level of deterioration at coastal stations. This is corroborated by the MCI, ICI and ACI indices. These tests also show that aggressivity is increased for costal stations during the third and fourth periods (January to May 2007). This seems to be related to higher levels of chloride concentration seen during these periods. Similar seasonal variation in aggressivity was also seen at the marine stations in Valparaíso and Huasco. Another station located in an industrial area of Cartagena de Indias in Colombia was classified as moderate in terms of ICI. This is similar to the results for the Valparaíso station. Two stations located in the industrial port district of Barranquillas obtained very severe ICI classifications, as did the Quintero station, which can also be described as an industrial port area [14].

3.3. Calculation of aluminum corrosion rate

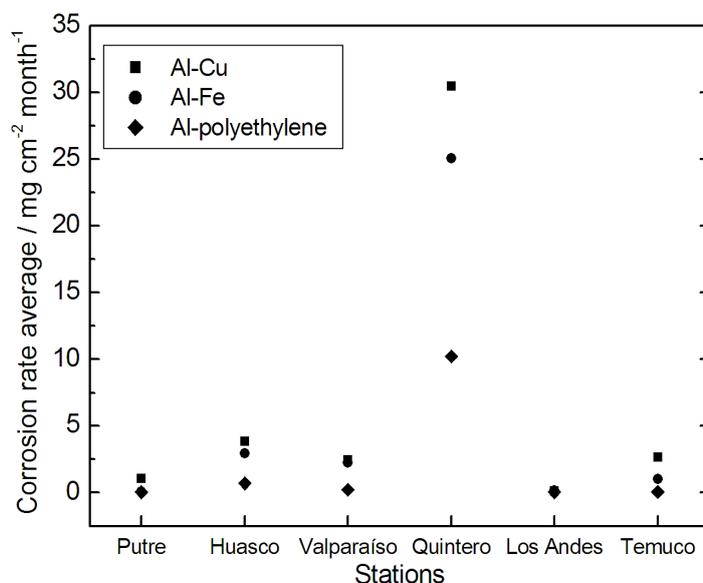


Figure 8. Average corrosion rate of the aluminum in different couples during one year of exposure at different sites.

Figure 8 shows the results obtained for the average corrosion rate of the aluminum in the different seasons and at the different sites. The highest values are seen at the Quintero station for all couples, thus corroborating the atmospheric corrosion index results. In this marine-industrial environment the aluminum shows severe damage, with the presence of cracks, pitting and exfoliation. There is also formation of a large amount of corrosion product, which is mainly composed of aluminum oxide (Al_2O_3), as can be seen in Figure 9. These results are also in line with previous studies by the authors [21]. Unlike the results for Quintero, the corrosion rate of the aluminum at the Los Andes station is considerable low, where the material presents only light superficial damage, as shown in Figure 10.

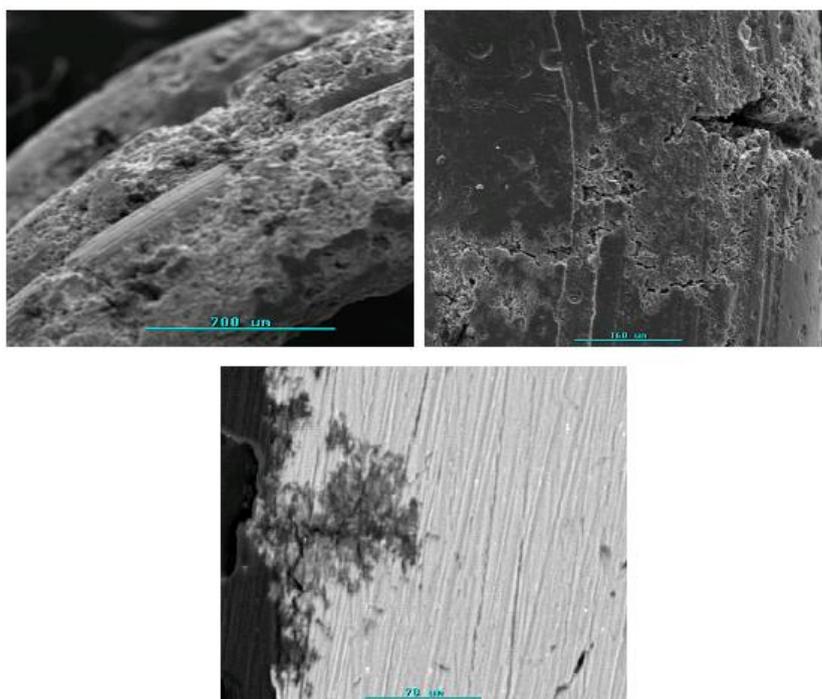


Figure 9. Morphology of the damage suffered by the aluminum wire in the Al/Cu couple at the Quintero station, one year (x50, x200, x500).

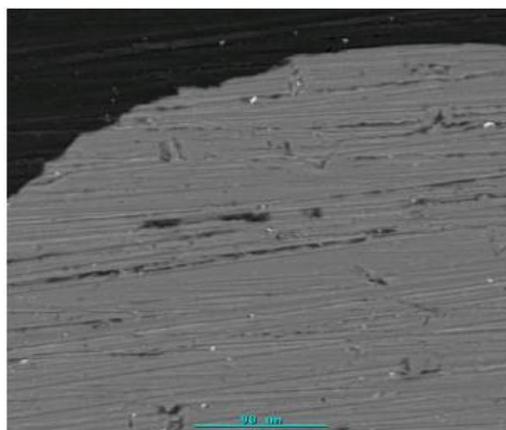


Figure 10. Morphology of the damage suffered by the aluminum wire in the Al/Cu couple at the Los Andes station, one year (x350).

As a compliment to the information above, the average percentage galvanic effect was calculated for the different couples at the study sites; the results are shown in Table 4. The galvanic effect is calculated using the following expression:

$$\text{Percentage Galvanic Effect} = \frac{M_m - M_p}{M_m} \cdot 100$$

where: M_m = mass loss of the aluminum wire coiled on the metal bolt
 M_p = mass loss of the aluminum wire coiled on the polyethylene bolt

Table 4 shows that for all stations the percentage galvanic effect is slightly higher when the aluminum is coupled with copper. This is due to the fact that this pair is not selective, i.e. it is sensitive to both marine and industrial pollution. At the Huasco, Valparaíso and Temuco sites, it can also be seen that the percentage galvanic effect is considerable, reaching between 75 and 97%. This is a result of the low ACI at these stations and is because corrosion increases significantly when the aluminum forms a galvanic pair. For the stations in Los Andes and Quintero, despite having very different corrosivity categories (negligible and very severe, respectively), the percentage galvanic effects are similar. The galvanic effect at the Putre station is low since the corrosion rate of the aluminum in this environment is also minor and the difference between the Al/polyethylene and the other couples is negligible.

Table 4. Percentage galvanic effect (annual average).

Station	Al-Cu (%)	Al-Fe (%)
Putre	33.6	27.4
Huasco	78.8	75.2
Valparaíso	80.4	77.2
Quintero	65.2	56.6
Los Andes	59.6	57.6
Temuco	96.9	91.3

4. CONCLUSIONS

The results obtained in this research suggest that the wire-on-bolt test is an adequate method for classification of atmospheres, given that the results are in line with the classifications obtained by other methodologies that require a greater number of measurements.

This agreement of the classification obtained using a more conventional methodology (ISO 9223) shows that this type of test is a significant tool for classification of areas of difficult access where, for example, it is not possible to install weather stations or units with flat test probes that can be

evaluated after a year of exposure. The use of this technique therefore implies lower costs in the implementation of samples and less time spent on their analysis.

The indices of atmospheric aggressivity differ depending on the season (summer, autumn, winter, spring) of exposure. The variation depends on meteorological variables (T, RH, TOW, amount of rainfall, wind speed and direction) and atmospheric pollutant content (mainly chloride and sulfur dioxide).

The aluminum generally presents low corrosion rates (less than $5 \text{ mg cm}^{-2} \text{ month}^{-1}$) for the stations at Huasco, Valparaíso, Temuco, Los Andes and Putre, unlike the Quintero station, where there is high chloride and sulfur dioxide content, which is clearly reflected in the values obtained for ACI and for the corrosion rate (around $30 \text{ mg cm}^{-2} \text{ month}^{-1}$).

In a mainly marine atmosphere the corrosion of the aluminum wire shows damage in the form of pitting and exfoliation, with the formation of a whitish corrosion product that is mainly composed of aluminum oxide (Al_2O_3) distributed unevenly over the metal surface.

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