

Atmospheric Corrosion of Galvanised Steel in Different Environments in Chile and Mexico

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The behaviour of the atmospheric corrosion of galvanised steel is evaluated in three cities in Chile and Mexico. Meteorological variables were measured (T, RH, rainfall, wind speed) along with the principal air pollutants (SO₂ and Cl⁻ ions). Comparing the data from the Chilean and Mexican weather stations, there is a clear trend of decreased corrosion with the increase in mean temperature, and statistically significant influence from air pollutants was not seen under the conditions in question. The corrosion process does not develop uniformly, with the formation of voluminous corrosion products distributed heterogeneously over the galvanised surface. The main corrosion products in both environments, identified by XRD analysis, are: Zincite (ZnO), Zinc Hydroxide Sulphate Hydrate (Zn(OH)₂)₃(ZnSO₄)(H₂O)₅, Zinc Oxide Sulphate Hydrate (Zn₄O₃(SO₄).7H₂O), Zinc Sulphate Hydroxide Hydrate (Zn₄SO₄(OH)₆.4H₂O) and Simonkolleite (Zn₅(OH)₈Cl₂.H₂O). The presence of sulphate in the corrosion products shows that sulphur dioxide pollution plays an importance role in galvanised-steel corrosion, though no statistical evidence was found.

Keywords: Metal coatings, galvanised, atmospheric corrosion, SEM, XRD.

1. INTRODUCTION

Atmospheric corrosion is fundamentally due to the variety of types of atmospheres and their corrosive pollutants as part of the environment surrounding the metal or alloy in question. This type of corrosion occurs on the metal/environment interface and involves an aqueous phase. The film of electrolyte formed on the metal is one of the necessary conditions for initiating corrosion. Different gases in the environment are dissolved into the aqueous phase; these include O₂, CO₂, SO₂, etc. [1-4].

The variety of applications of galvanised steel in industry is mainly due to its good corrosion resistance in atmospheric conditions. The property imbued by the zinc due to the formation of a protective coating during its oxidation, consisting of zinc oxide and hydroxide or several basal salts depending on the nature of the environment to which it is exposed. This layer, though not very adhesive, acts as a physical barrier between the metal and the environment surrounding it, thus significantly decreasing the zinc corrosion rate [4-6].

The zinc also gives galvanic protection to the steel, playing the role of anode in the zinc-iron (steel) pair, as its electrochemical potential is more negative (-0.76V vs. SHE) than the potential of iron (-0.44V vs. SHE). The protective power of zinc against steel corrosion depends on numerous factors: porosity and thickness of the zinc coating, its adhesion to the steel, the nature of the oxide layer formed on the zinc surface, etc. [7].

The factors that determine the corrosion rate of galvanised steel exposed to an atmosphere are: humidity and temperature of the air, periods of rainfall, atmospheric acidity, salinity (chloride content) of the air and contamination with SO₂, etc. Temperature accelerates electrochemical reactions, but at the same time it accelerates evaporation of the humidity deposited on the metal, decreasing the time of wetness for the metal surface [5].

Zinc corrosion has historically been studied as part of research into galvanised steel, a material used extensively in industry [8-14]. However, there are also studies focused on the pure metal form [15-27]. The corrosion rate of zinc is generally higher than that of copper and lower than steel (iron). The project "Ibero-American Map of Atmospheric Corrosiveness" (MICAT) conducted in Mexico [24] reports different annual corrosion rates for zinc depending on the corrosiveness of the atmosphere: 0.82 $\mu\text{m year}^{-1}$ (Mexico City), 1.37 $\mu\text{m year}^{-1}$ (Cuernavaca), 1.77 $\mu\text{m year}^{-1}$ (San Luis Potosí – high SO₂ concentration) and 1.46 $\mu\text{m year}^{-1}$ (Acapulco – high chloride concentration). In south-eastern Mexico (Yucatan), in a wet tropical climate [25], the results reveal zinc corrosion rates ranging from 0.82 $\mu\text{m year}^{-1}$ (rural/urban atmosphere of Merida) to 16.40 $\mu\text{m year}^{-1}$ (marine atmosphere of Progreso). In Europe, annual zinc corrosion rates have been reported between 0.6 and 4.5 $\mu\text{m year}^{-1}$ [21-27].

Studies carried out in the city of Valparaiso in Chile after 15 months of exposure report that the corrosion potential of galvanised steel increases over time, thus corroborating the formation of a protective film of zinc corrosion products, which were identified as zincite (ZnO) and simonkolleite (Zn₅(OH)₈Cl₂·H₂O). In this research the Zn mass loss for the total exposure time was calculated at 8.5 $\mu\text{m year}^{-1}$ [28-29].

The station located in Mexico is the south-east of the state of Tabasco. Its low elevation above sea level promotes the development of a warm humid climate influenced by the Gulf of Mexico and the Atlantic Ocean. The mean annual temperature is 27°C, average annual relative humidity is estimated at 82%, annual precipitation varies depending on the influence of cold fronts, recording mean annual values of 2008 mm [30]. The wet tropical climate leads to a high value for annual time of wetness (TOW) for the metal samples exposed to the elements [31], and similarly it has a corrosiveness category of t₅, the highest level according to ISO 9223:92 [32]. Combined with this, and in the presence of pollutants generated by industrial activity, the deterioration of metal materials occurs more rapidly.

Chile is renowned for its diversity of climates, including coastal areas (chloride pollution from marine spray) and industrial areas polluted with sulphur dioxide (SO₂) which combined with humidity leads to acid rain. Northern Chile generally has low precipitation and a foggy coastal desert climate with abundant morning fog, a phenomenon called “camanchaca” that is caused by the cold Humboldt Current. This is the case in the cities of Antofagasta and Huasco. The weather station located on Easter Island is exposed to a climate that varies between temperate with sufficient humidity and a tropical climate. Its thermal patterns are fully influenced by the ocean and anticyclones. Its precipitation must therefore be convective in origin, particularly in summer, while in winter the arrival of some frontal systems produces frontal precipitation [33-34].

Given the diversity in meteorological and environmental conditions between Mexico and Chile, this study presents a comparative analysis of the influence of meteorological variables and main air pollutants (SO₂ and NaCl) on the corrosion rate of galvanised steel test probes exposed for a period of 2 years in three environment types in Chile (Antofagasta, Huasco, Easter Island) and in the Mexican state of Tabasco (Cunduacán, Villahermosa, Paraíso)

2. MATERIALS AND METHODS

2.1. Testing Stations

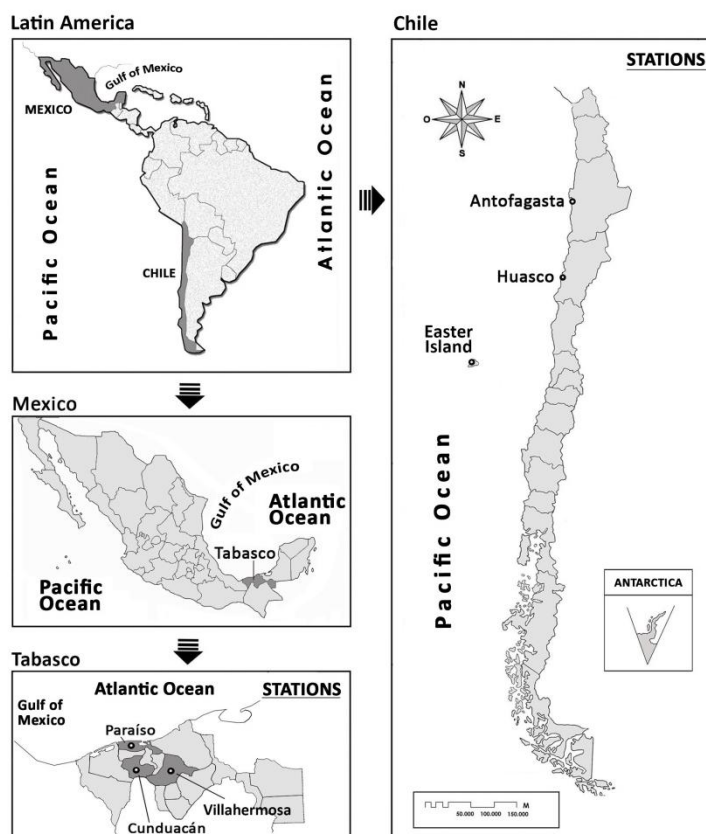


Figure 1. Locations of the testing stations.

The testing stations in Chile are located on the Pacific Ocean coastline in Antofagasta (23°65' south, 70°40' east, 0.32 km from the sea and 0.01 km above sea level), Huasco (28°46' south, 71°22' east, 0.09 km from the sea and 0.02 km above sea level) and Easter Island (27°15' south, 109°43' east, 0.5 km from the sea and 0.02 km above sea level). The testing sites in Mexico are located in three areas in the state of Tabasco: Cunduacán (18°03' north, 93° 10' east), 50 km from the Gulf of Mexico, on the Atlantic Ocean and 10 km from Samaria-Iride (PEMEX); Villahermosa (18°20' north, 93°15' east), 68 km from the Gulf of Mexico and 18 km from oil company facilities; and Paraíso, 1500 m from the shore and 1000 m from the South-East Marine Region of the District of Dos Bocas (Fig. 1).

The samples were installed exposed to the elements on aluminium panels for a period of two years, in accordance with the procedures set out in ISO 8565 and ASTM G 50-76 [35-36].

2.2. Pollutant deposit rates and climate parameters

During the testing period, environmental deposit rates of chlorides and sulphur dioxide were analysed every 2 months, in line with the method of ISO 9225:92 [37]. At the same time data was obtained from the weather stations on temperature, relative humidity, amount of rainfall and wind speed. The data on temperature and relative humidity were used to determine time of wetness (TOW) in accordance with ISO 9223:92 [32].

2.3. Calculation of corrosion rate

Before exposure, the galvanised steel samples (100x150x0.95 mm in Mexico and 100x100x4 mm in Chile) were degreased with acetone and alcohol and then weighed on an analytical balance (± 0.0001 g). The corrosion rate of the galvanised steel samples was evaluated using the gravimetric technique, eliminating corrosion products with an ammonium hydroxide solution at a temperature of 25°C, in accordance with ISO 8407 [38]. The calculations were carried out on 3 repetitions and the respective control for each evaluation period.

2.4. Characterisation of the Corrosion Products

The corrosion products were studied by X-ray diffraction (XRD) in a SIEMENS D-5000 diffractometer using Cu-K α radiation. The morphology of the metal attack was evaluated using scanning electron microscopy (SEM) with a Carl Zeiss Evo MA 10 microscope coupled to an EDS Oxford x-act analyser for element characterisation.

3. RESULTS AND DISCUSSION

3.1. Characterisation of the material

The galvanised steel plates used at the stations in Chile were prepared by hot dipping A-36 carbon steel in a galvanising bath with a composition of 0.005 % Al, 0.35 % Sn, 0.30 % Pb, 0.5 % Ni

and the remainder Zn. Fig. 2a shows the surface appearance of the galvanized steel, with the Zn coating displaying a certain degree of porosity. Fig. 2b shows the respective cross-section. The EDS results obtained show a composition of 95.8% Zn, 0.65% Fe, 2.91% Pb and 1.47% Al, as the main elements. Prior results obtained by the authors on a cross-section of a pure Zn layer (η) gave an approximate thickness of 30 μm and an approximate total thickness of 114 μm [28-29]. For the galvanized steel samples used in Mexico, the SEM-EDS analysis showed four areas with different zinc content (86.01%-98.23%) at different depths of coating and a total thickness of 9.9 μm , and aluminium in the alloys at a level of 1.12% (Fig. 2c).

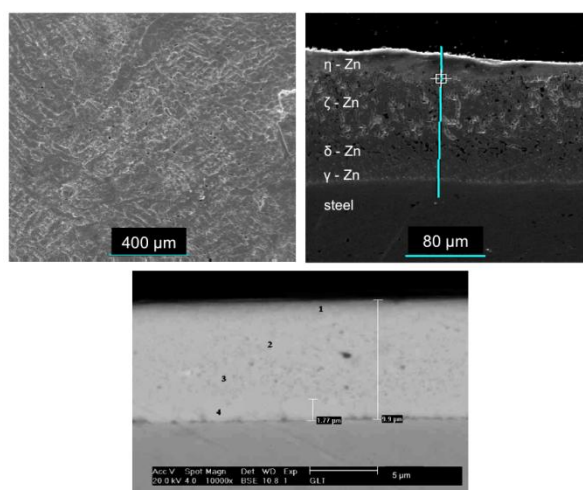


Figure 2. Metallographs of the hot-dip galvanized SAE steel (a) Surface appearance and (b) Cross section, exposed in Chile (c) SEM-EDS of the galvanized steel coating exposed in Mexico.

3.2. Climate parameters at testing sites

Records were taken of the climate parameters at local weather stations in each country (Mexico and Chile) throughout the two-year period. Table 1 shows the average data for the two years for Temperature (T), Relative Humidity (RH), wind speed (m/s), amount of rainfall (mm) and time of wetness (TOW). Time of wetness was calculated in accordance with ISO 9223:92.

In Table 1, it can be seen that the testing stations in Mexico have higher values for some climate parameters compared to the testing stations in Chile. These parameters are T, RH, TOW and amount of rainfall. Higher values were recorded in Chile for wind speed. Fig. 3 shows the behaviour of Temperature over the two years of testing. It can be seen that T is higher in Mexico than in Chile. Temperature change directly or indirectly affects the corrosion process. Increased temperature increases the velocity of electrochemical reactions, though at the same time it accelerates evaporation of the humidity deposited on the metal surface, thus decreasing the concentration of oxygen and other dissolved gases. Changes may also occur in the protective property of corrosion product layers.

Table 1. Climate parameters at testing stations in Chile and Mexico (averages for the two-year testing period).

Climate parameter	Antofagasta	Huasco	Isla de Pascua	Cunduacán	Villahermosa	Paraíso
Climate classification	Desert	Desert	Tropical rainy	Tropical humid	Tropical humid	Tropical humid
Characteristics	Coastal, 0.320 Km to the shoreline	Coastal, 0.90 Km to the shoreline	Isle, 0.500 Km to the shoreline	Flat territory, 50 km the shoreline and 10 km to oil production plant	Flat territory, 68 km to the shoreline and 18 km to oil production plant	Coastal, 1.5 Km to the shoreline
T °C	16	15	21	29	29	27
RH (%)	73	83	77	80	82	83
TOW (h)	185	507	338	569	582	598
Rain (mm)	0.17	19	121	137	142	145
Wind (m/s)	4.50	3.95	4.95	1.70	1.92	4.01

Below a level of 0°C, when the electrolyte film does not form, corrosion practically stops, but it should be taken into account that in heavily polluted atmospheres, corrosion may still occur even at -5°C due to the increased saline concentration in the electrolyte layer on the metal, thus delaying freezing. As a result of the research of Feliu and Morcillo, it is known that corrosion rate remains practically constant between 5 and 15°C, when humidity and pollution on the metal surface are detectable. However, it is important to know the temperature range in which the metal surface remains wet, as this will determine the rate of the process of atmospheric corrosion. A change of 10°C in temperature can accelerate the corrosion process by up to 100 times [4,39].

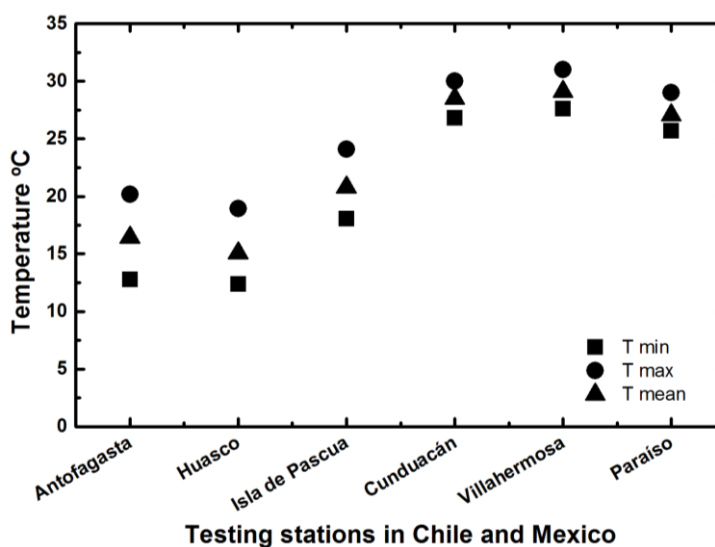


Figure 3. Behaviour of Temperature during atmospheric corrosion testing in Chile and Mexico.

In general, the effect of temperature is considerably lower than that of environmental pollution and time of wetness [40-41]. The present study does not comply with this notion, showing a significant influence from temperature due to the differences in geographical latitude and therefore in temperature between Chile and Mexico.

The humidity in the environment is a measure of the amount of water vapour in the air and relative humidity is the proportion of absolute humidity and saturation humidity, expressed as a percentage. This percentage is an inverse function of temperature, i.e. relative humidity increases with a decrease in temperature and vice versa. In the present research, the average RH values are from 1 to 10% higher in Mexico than in Chile. The order of the stations from highest to lowest RH values is as follows for the two countries: Paraíso>Easter Island>Villahermosa>Huasco>Cunducacán>Antofagasta. Fig. 4 shows the behaviour of the minimum and maximum RH values over the two-year period.

The variation in RH for the different stations is as follows: Easter Island 68 - 89 %, Paraíso 80 - 89%, Villahermosa 76 - 86%, Huasco 80 - 85%, Cunducacán 78 - 83%, Antofagasta 71-76%.

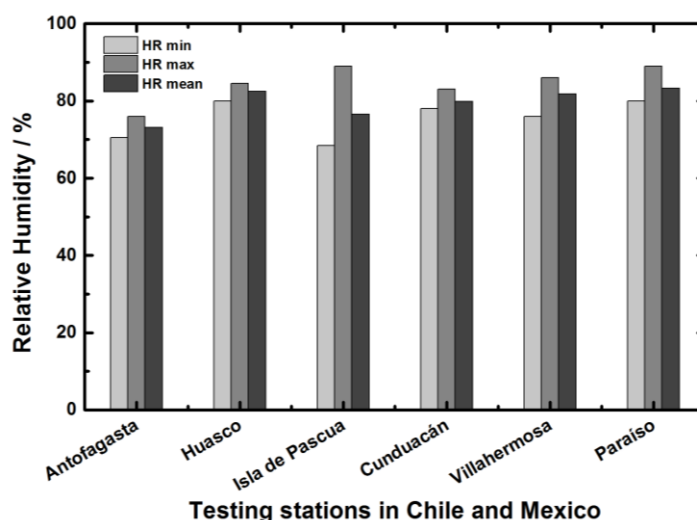


Figure 4. Minimum and maximum RH values for each testing station in Chile and Mexico.

Rainfall is of vital importance to atmospheric corrosion, especially the frequency with which it occurs and the subsequent dry periods in between. Due to the washing away of pollutants accumulated on the metal surface, rainfall can slow the corrosion process. Similarly, some corrosion products that are soluble in water can be removed, thus accelerating the corrosion.

During the period of exposure of the galvanised steel the rainfall events differed in duration and amounts. At the cities in Chile, fewer rainfall events occurred than in Mexico; in Antofagasta only two periods of rainfall were recorded of 1.02 mm for the second and fourth months of the year. For the testing stations located in Mexico, rainfall was 80% higher than in Chile. From highest to lowest, considering maximum rainfall values (mm), the order was as follows: Cunducacán (472 mm) > Paraíso (420 mm) > Villahermosa (302.5 mm) > Easter Island (279.14 mm) > Huasco (73.89 mm) > Antofagasta (1.02 mm). Fig. 5 shows that during the second year of testing, a higher amount of rainfall was recorded.

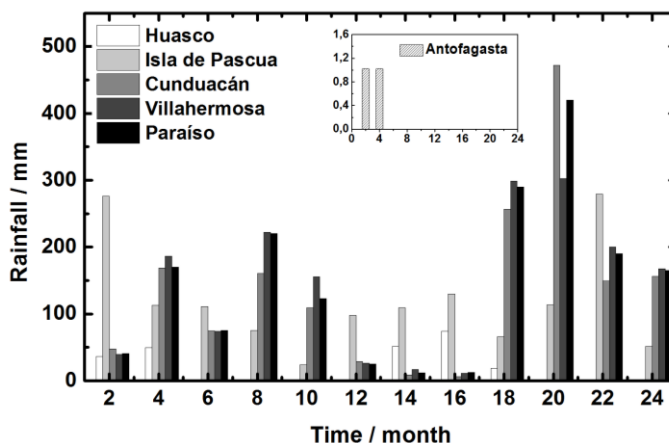


Figure 5. Behaviour of rainfall at the study sites in Chile and Mexico.

Wind speed and direction are also important factors in atmospheric corrosion, as they favour the transport and dispersion of air pollutants, while wind speed also influences time of wetness, since higher wind speed on the metal surface will dry it faster. The wind generally favours the distribution of pollutants as it displaces air masses as a function of pressure and temperature. The effect caused by the wind depends fundamentally on accidents on site or even the configuration of buildings in local urbanised zones (atmospheric pollution).

Fig. 6 shows the behaviour of the wind as average values over the two years, with minimums and maximums for the testing sites in Chile and Mexico. The order by maximum recorded wind speed is as follows: Easter Island (10.54 m/s) > Antofagasta (5.26 m/s) > Huasco (5.19 m/s) > Paraíso (5 m/s) > Cunducán (4.05 m/s) > Villahermosa (2.5 m/s).

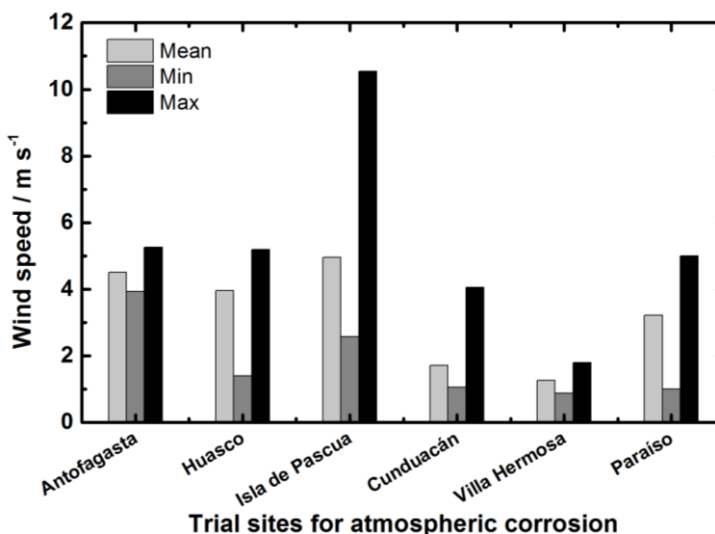


Figure 6. Wind speed at testing sites in Chile and Mexico.

Time of wetness was calculated using the relation between T and RH, in accordance with ISO 9223:92 [32]. TOW is the time during which the metal surface remains wet and the process of corrosion can occur. The corrosion process advances significantly during periods of visible wetness (presence of dew) on the metal surface [3,37].

In the two countries in question, the highest values of TOW were recorded at the sites in Mexico. Ordering the maximum TOW values from highest to lowest gives the following (Table 2): Paraíso (741 h) > Villahermosa (738 h) > Cunduacán (730 h) > Huasco (568 h) > Easter Island (324 h) > Antofagasta (225 h). Table 2 shows that TOW is higher for the wet tropical climate in the Mexican cities which have high corrosiveness categories (t_4). The cities in Chile are assigned categories of t_3 and t_4 , in accordance with ISO 9223, i.e. low and high environmental corrosiveness.

Table 2. Behaviour of annual TOW (h) at testing sites in Chile and Mexico.

		Chile						México					
		Antofagasta		Huasco		Isla de Pascua		Cunduacán		Villahermosa		Paraíso	
Year	TOW(h)	TOW(h)	TOW(h)	TOW(h)	TOW(h)	TOW(h)	TOW(h)	TOW(h)	TOW(h)	TOW(h)	TOW(h)	TOW(h)	TOW(h)
1	656	t_3	2984	t_4	1488	t_3	3214	t_4	3151	t_4	3323	t_4	
2	1160	t_3	3099	t_4	2160	t_3	3772	t_4	3834	t_4	3859	t_4	

Generally, wind speed influences TOW values, especially in the dry/wet cycles experienced by the materials, which can occur periodically with different frequencies depending on air flow around the exposed surface. The nature of the corrosion products formed also influences the dynamics of the dry/wet cycle, as their morphology and structure (porosity and roughness) differs for different metals. Another factor that influences TOW is the concentration and nature of dissolved salts in the layer of wetness on the surface. It is well known that a saline solution evaporates slower than pure water and that the water pressure balance is lower in the presence of saline solutions compared to pure water. The evaporation rate (or drying rate) also depends on the area of the wet surface region and the molar concentration of the saline solution. With the evaporation of the water the concentration of the solution increase and the drying rate and the size of the wet surface area both decrease [31].

3.3 Deposit rate of sulphur dioxide (SO_2) at the testing stations

During the study period, the sulphur dioxide deposit rate was recorded every two months, as it is one of the main corrosive agents, following the method described in ISO 9225:92 [37]. SO_2 is one of the most important agents in zinc corrosion as it determines the changes in pH of the wet coating formed on the metal's surface and can thus accelerate the atmospheric corrosion. Fig. 7 shows the variation in SO_2 deposit rates for the testing stations in Chile and Mexico.

In general, higher SO₂ deposit rates were recorded at the stations in Chile. However, the corrosiveness of the three environments in Chile was categorised as very low (P_0) to low (P_1). The classification of the stations in accordance with the minimum and maximum ranges and the standard deviation of the data over the two years is as follows: Huasco recorded the highest SO₂ deposit rates of $6.82-16.82 \pm 3.46 \text{ mg m}^{-2} \text{ day}^{-1}$, giving a category of low corrosiveness (P_1). In Antofagasta, the SO₂ deposit rate was $3.05-9.44 \pm 2.0 \text{ mg m}^{-2} \text{ day}^{-1}$, giving a category of low corrosiveness (P_0). Easter Island recorded values of SO₂ deposit rates in the range of $0.51-5.47 \pm 1.39 \text{ mg m}^{-2} \text{ day}^{-1}$, giving a category of low corrosiveness (P_0).

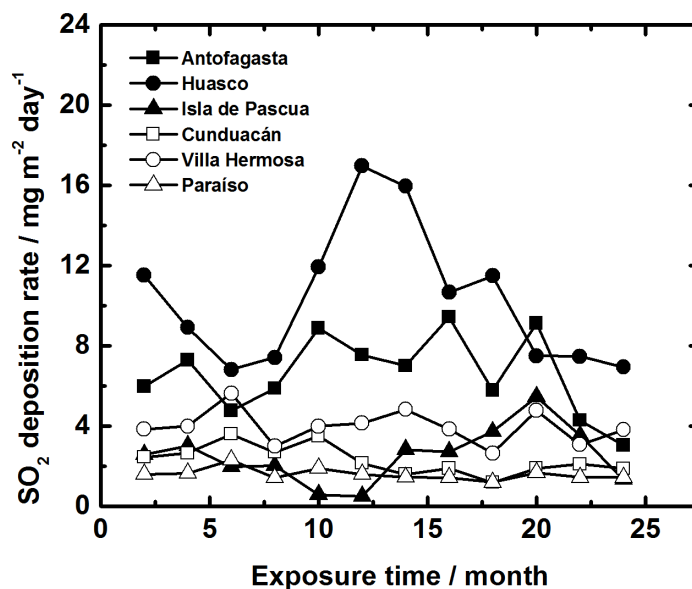


Figure 7. SO₂ deposit rates at testing stations in Mexico and Chile.

In the case of Mexico, the city of Villahermosa recorded the highest SO₂ deposit rates of the three sites. The classification of the stations according to the minimum and maximum ranges and the standard deviations for the data over two years is as follows: Villahermosa saw SO₂ deposit rates of $2.65-5.62 \pm 0.84 \text{ mg m}^{-2} \text{ day}^{-1}$, giving a category of low corrosiveness (P_0). Cunduacán recorded SO₂ deposit rates of $1.19-3.60 \pm 0.72 \text{ mg m}^{-2} \text{ day}^{-1}$, giving a category of low corrosiveness (P_0). Paraíso saw SO₂ deposit rates in the range of $1.20-2.31 \pm 0.28 \text{ mg m}^{-2} \text{ day}^{-1}$, also giving a category of low corrosiveness (P_0). In general, the corrosiveness of the environments studied in Mexico is very low (P_0) according to ISO 9223:92 [32].

3.4 Deposit rate of chlorides at the testing stations

During the two-year study period, chloride deposit rates were recorded every two months, as this is one of the main agents of atmospheric corrosion (Fig. 8), following the method described in ISO 9225:92 [37]. It should be noted that the stations in Chile are close to the Pacific Ocean, where salinity

in the north is 35 g L^{-1} , decreasing to 34.3 g L^{-1} when moving southward. In Mexico, on the Atlantic Ocean, the salinity was recorded at approximately 36 g L^{-1} .

The classification of the stations according to the minimum and maximum ranges and the standard deviations of the data for the two-year period is as follows: Easter Island recorded the highest Cl^- deposit rates of $21\text{-}78 \pm 20 \text{ mg m}^{-2} \text{ day}^{-1}$, giving a category of low corrosiveness (S_1 , S_2). In Huasco Cl^- deposit rates were $26.3\text{-}72.8 \pm 13 \text{ mg m}^{-2} \text{ day}^{-1}$, giving a category of low corrosiveness (S_1 , S_2). Antofagasta recorded Cl^- deposit rates of $11.21\text{-}38.35 \pm 7 \text{ mg m}^{-2} \text{ day}^{-1}$, giving a category of low corrosiveness (S_1). In general, according to the ISO 9223:92, the corrosiveness of the three environments in Chile based on chloride deposit rates was categorised as low (S_1) to medium (S_2). Though Antofagasta is 0.32 km from the coast, it has low values because the corrosion testing station is not at sea level, but is located on the terrace of a 4-storey building, and therefore wind speed and direction is important in allowing saline to reach the exposed samples. In addition, the proximity of other buildings partially blocks saline fogs from reaching the testing station.

The station in Huasco is located 0.09 km from the shoreline and is fully exposed to the elements. Its values fluctuate between the categories of S_1 and S_2 , and depend solely on the environment, with lower temperatures that do not favour seawater evaporation, and on the arrival of saline fog. For Easter Island, the higher temperatures lead to more evaporation, though the chloride values are not very high because the station is located far from the coast (0.5 km) and on a hill that is inaccessible to saline fog.

The amount of chlorides deposited at the three testing sites in Mexico indicates that the behaviour of this pollutant is directly related to the distance from the coast. Its presence depends on periods with cold fronts from the north passing across the Gulf of Mexico before entering the state of Tabasco. The classification of the stations in Mexico according to the minimum and maximum ranges and the standard deviation of the data for the two years of study are as follows: Paraíso recorded the highest Cl^- deposit rates of $72.1\text{-}117.8 \pm 14.6 \text{ mg m}^{-2} \text{ day}^{-1}$, giving a category of slightly high corrosiveness (S_2). In Cunduacán the Cl^- deposit rates were $11.0\text{-}28.1 \pm 6.19 \text{ mg m}^{-2} \text{ day}^{-1}$, giving a category of low corrosiveness (S_0). Villahermosa recorded Cl^- deposit rates of $3.82\text{-}13.50 \pm 2.94 \text{ mg m}^{-2} \text{ day}^{-1}$, giving a category of low corrosiveness (S_0).

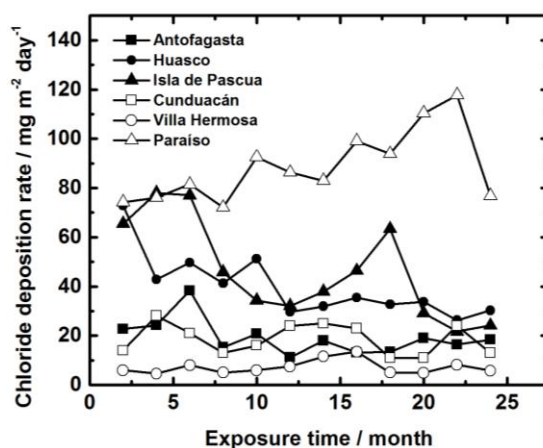


Figure 8. Cl^- deposit rates at testing stations in Chile and Mexico.

3.5. Mass loss of the galvanised steel

Fig. 9 shows a comparison of the mass loss for the galvanised steel samples exposed at the testing sites in Chile and Mexico, as a function of exposure time for the two years of testing.

At the testing sites in Chile (Fig. 9) it can be seen that Huasco has the highest mass loss values of $0.321\text{--}3.1 \pm 0.99 \text{ mg cm}^{-2}$. The high level of mass loss is associated with its proximity (0.09 km) to the coastline, and the higher content of the pollutant SO_2 . Since the chloride category is S_1 to S_2 , the degradation of Zn depends solely on the medium. Easter Island recorded mass loss values of $0.53\text{--}2.7 \pm 0.66 \text{ mg cm}^{-2}$, which is also associated with the presence of chlorides (S_1 , S_2). It should also be considered that the higher wind speed erodes the samples. Antofagasta recorded mass loss values of $0.43\text{--}2.35 \pm 0.63 \text{ mg cm}^{-2}$. The chlorides at this site gave a low corrosiveness category (S_1) and the SO_2 deposit rates were also a low corrosiveness category (P_0).

In Mexico, the highest mass loss due to corrosion was seen in Paraíso with values of $0.77\text{--}1.61 \pm 0.25 \text{ mg cm}^{-2}$, which is attributed to the presence of chlorides (S_1). In Villahermosa the mass loss figures were $0.167\text{--}1.413 \pm 0.413 \text{ mg cm}^{-2}$. At this site the corrosion is associated with the SO_2 deposit rate (P_0). Cunduacán recorded mass loss values of $0.127\text{--}1.3 \pm 0.38 \text{ mg cm}^{-2}$. At this site both the content of Cl and SO_2 exert influence on the corrosion, since the area is located 50 km from the coast and close to oil company facilities. Thus, the wet tropical climate of the state of Tabasco is assigned a corrosiveness category of C_3 in accordance with ISO 9223:92 [32].

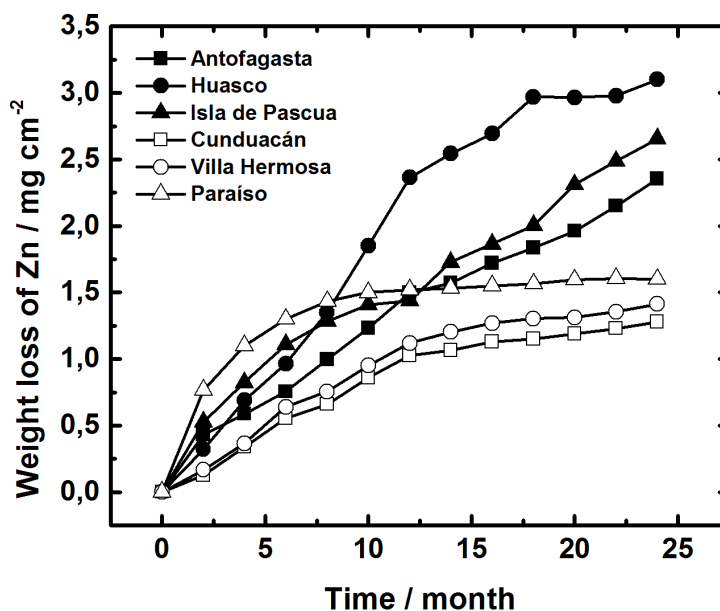


Figure 9. Mass loss at the testing sites in Chile and Mexico.

It is important to note that the stations in Mexico reach a stable level of mass loss after 10 months, though this does not occur in Chile, this behaviour is attributed mainly to the higher temperature, which accelerates the corrosion over a short time, leading to the formation of corrosion

products distributed more homogeneously and acting as a barrier, i.e. the corrosion products formed in Mexico have better protective properties than those forming in Chile.

3.6 Corrosion rate of the galvanised steel in Chile and Mexico

Fig. 10 shows the corrosion rate over the two years of study at the testing sites in Chile and in Mexico. It can be seen that the corrosion rate was higher in the first year for both countries, as is expected. The order from highest to lowest for corrosion rate of the galvanised steel was as follows: Huasco > Paraíso > Antofagasta > Easter Island > Villahermosa > Cunduacán.

Since Chile is a coastal country, the stations close to the sea show increased environmental chloride content, thus favouring the corrosion process. Under these conditions, the free chloride retained on the corroded metal will depend, among other things, on the composition and properties of the corrosion products formed on the metal, such as hygroscopicity, morphology and porosity, as well as on the amount of rainfall during the period of exposure [42]. The corrosion rate in the first and second year of exposure was higher for the stations in Huasco (C₄). Easter Island and Antofagasta were given a medium category (C₃) according to ISO 9223:92. Huasco and Antofagasta have low rainfall, meaning that the pollutants are not washed away, thus significantly influencing corrosion.

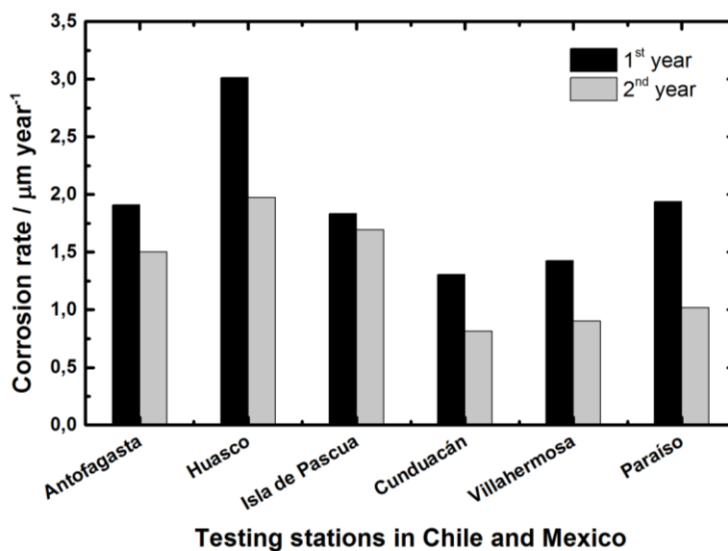


Figure 10. Corrosion rates at testing sites in Chile and Mexico in the first and second years of testing.

In the case of Mexico, given that Paraíso is very close to the coast of the Gulf of Mexico, this area saw higher chloride deposit rates and therefore higher corrosion rates, with a medium to high category (C₃-C₄) according to ISO 9223:92. Therefore, in Cunduacán and Villahermosa the corrosion rate falls due to the lower presence of chlorides in these environments, while SO₂ is more significant in affecting corrosion here, leading to a medium category (C₃) according to ISO 9223:92. It is important to note that the differences between the data obtained for corrosion rates between the first and second

years for the stations in Mexico show that the corrosion products formed at these sites are more protective.

3.7. Statistical processing of the data on corrosion, atmospheric pollutants, temperature and relative humidity

It is known that atmospheric corrosion occurs in the presence of an electrolyte layer and can be accelerated by deposits of pollutants such as chlorides and sulphur compounds.

Currently, the power function (eq.1) is widely used to describe the corrosion effects obtained in tests for various periods of time in various regions of the world $K = At^n$ or in logarithmic coordinates [42]:

$$\log K = \log A + n \log t \quad (\text{eq. 1})$$

where K represents the corrosion losses after time t, A is a constant coefficient of corrosion losses over the first year and n is a constant coefficient that characterises the protective properties of the corrosion products. A multi-linear equation between mass loss and different parameters considered of importance in corrosion processes can also be used. These parameters may include pollutants, time of wetness, humidity, temperature, etc.

The data on the corrosion of galvanised steel for the stations in Chile and Mexico was processed using multi-linear or linear correlations, maintaining the corrosion always as the dependent variable. The results of the statistically significant equations are shown below:

Chile (data from all testing stations)

$$K (\text{mg/cm}^2) = 0.1948 + 0.11 t (\text{months}) \quad (\text{eq. 2})$$

$$r = 0.944 \quad r^2 = 89.16 \quad P = 0.0000$$

The variables corresponding to pollutants, temperature and relative humidity were not found to be significant. This shows that all Chilean stations maintain similar behaviour over time and that the statistical influence of pollutants, temperature and humidity was not significant. It is possible that pollutants, temperature and relative humidity are within a range of variation that does not affect the behaviour of the corrosion during the testing period.

The corrosion and time data were also fit to an exponential function of time and the result obtained is shown in eq. 3. The fit is slightly better than the linear equation and it also confirms the homogeneity in the behaviour of the atmospheric corrosion of the galvanised steel at the Chilean stations.

$$K (\text{mg/cm}^2) = 0.18 t^{0.76} \quad (\text{eq. 3})$$

$$r = 0.96 \quad r^2 = 92.77 \quad P = 0.0000$$

Mexico

The data from all Mexican stations was processed jointly as with the data from the Chilean stations. As in Chile, the pollutants were not found to be statistically significant in the behaviour of the corrosion. The mathematical expression obtained is shown in eq. 4.

$$K (\text{mg/cm}^2) = 0.0067 + 0.068 t (\text{months}) - 0.13 \text{Temp } (^\circ\text{C}) + 0.048 \text{RH } (\%) \quad (\text{eq. 4})$$

$$r^2 = 91.23 \quad P = 0.0000$$

In this case, the variables of temperature and relative humidity were statistically significant. The results show that when mean temperature increases there is a decrease in the corrosion process, and that the same occurs with a decrease in relative humidity. It is known that when pollution and other meteorological variables do not change significantly, there is a decrease in atmospheric corrosion with an increase in temperature.

Chile and Mexico

When jointly processing the data from all stations in Chile and Mexico, the results shown in eq. 5 are obtained:

$$K \text{ (mg/cm}^2\text{)} = -0.015 + 0.08 t \text{ (months)} - 0.06 \text{ Temp (}^\circ\text{C)} + 0.02 \text{ RH (\%)} \quad \text{(eq. 5)}$$

$$r^2 = 86.85 \quad P = 0.0000$$

It can be noted that the merger of all the data from all stations shows a statistical trend in which the mass loss of Zn increases along with time, as should always be expected. However, it can also be seen that an increase in mean temperature causes decreased corrosion, thus leading to higher corrosion levels at the stations in Chile. The increased relative humidity is also a factor of this higher level of corrosion.

3.7. Characterisation of the corrosion products

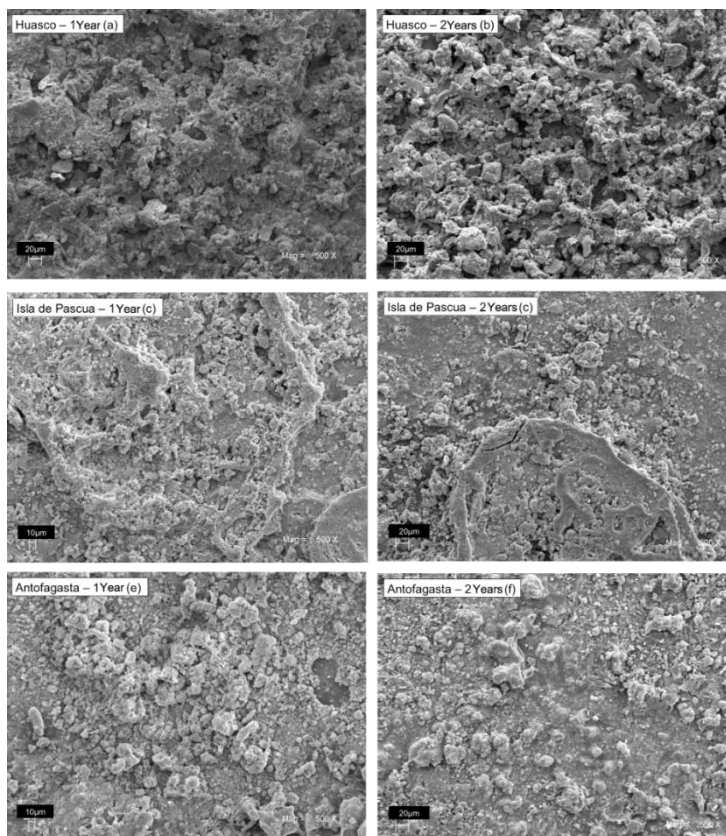


Figure 11. SEM Micrographs of the galvanised steel exposed in Chile during the first and second years of testing, respectively: Huasco (a, b), Easter Island (c, d), Antofagasta (e, f).

Fig. 11 (a, b, c, d, e, f) presents the microstructure of the galvanised steel for the first and second years of exposure, respectively, in the Chilean environments (Huasco, Easter Island, Antofagasta). The morphology of the corrosion products shows widespread deposits of granules formed due to the relative humidity in the air and its interaction with oxygen in the air and the presence of pollutants in the atmosphere (Cl^- and SO_2). Huasco shows the highest amount of corrosion products, thus corroborating its higher corrosion rate value. Easter Island shows corrosion products with a flat morphology due to the presence of stronger winds.

For the case of Mexico, the SEM micrographs show that part of the corrosion products on the galvanised steel from the three environments were affected by the influence of rainfall during the two years of exposure (Fig. 5), showing deeper attacks in the metal by the second year, as seen in Figures 12 (b) (d) and (f). According to the results in the literature [12], during rainfall events some soluble zinc salts (corrosion products), such as basal zinc sulphate, a corrosion product of low adherence, can be removed from the metal surface by dissolution. The galvanised steel surface is very sensitive to environmental conditions, and it was affected by the frequency of rainfall/dry cycles recorded at the testing sites and by the influence of high figures for time of wetness (Tables 1 and 2) and the higher proportion of pollutants present in the atmosphere, i.e. SO_2 in Villahermosa (Fig. 8) and chlorides in Paraíso and Cunduacán (Fig. 9).

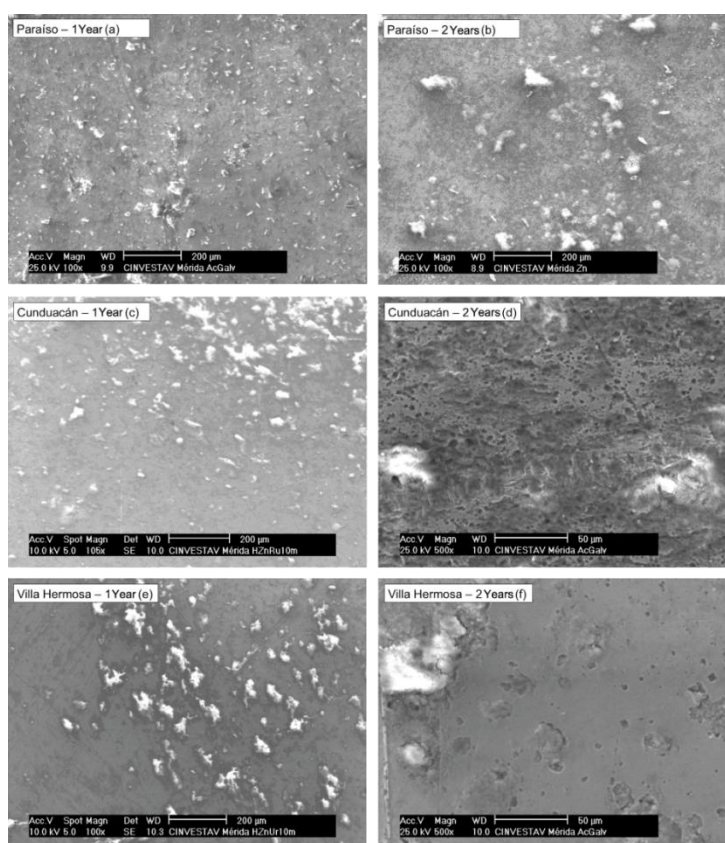


Figure 12. SEM Micrographs of galvanized steel samples exposed in Mexico during the first and second years, respectively: Paraíso (a, b), Cunduacán (c, d) Villahermosa (e, f).

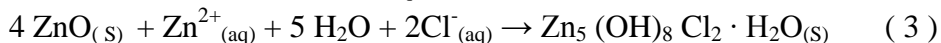
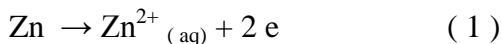
The time for which the metal is exposed to the atmosphere is a parameter that can be used to study the evolution of crystalline phases and their morphological changes. In Figs. 11 and 12 for Chile and Mexico, it can be seen that at the different analysis times, the surface characteristics of the zinc did evolve from a lesser to a greater degree of oxidation. Different types of agglomerations of circular white granules were formed on the zinc microstructure in a non-localised manner. With the increased exposure time (2 years), there is increased grouping of the agglomerations of white granules and greater heterogeneity on the galvanised steel surface. For the case of Chile, in the second year the white granules grew to twice the size, particularly at the station in Huasco, and were distributed across the entire surface of the material.

Table 3 shows the X-ray results for the corrosion products formed on the Zn surface during the two years of exposure at the stations in Chile and Mexico. The major phase of the corrosion products is marked with the symbol (Δ) and the minor phase with (x).

Table 3. Corrosion products on the galvanised steel at the testing sites in Chile and Mexico.

Station	1 st year	2 nd year
Huasco	Zn (x) Carbon (x) ZnO (x) Zinc hydroxycarbonate (Δ) Zn hydroxy-sulphate chlorohydrate (Δ) Simonkolleite (Δ)	Hydrozincite (Δ) Zinc hydroxychloride (x) Zn hydroxy-sulphate chlorohydrate (x) Zn oxide sulphate (Δ) Simonkolleite (Δ)
Isla de Pascua	Simonkolleite (Δ) Hydrozincite (Δ) Zn hydroxide sulphate hydrate (x) Sulphur (x)	ZnO (x) Hydrozincite (x) Simonkolleite (Δ) Zn Hydroxycarbonate hydrate (Δ)
Antofagasta	Zn (x) ZnO, zincite (x) Hydrozincite (x) S (x) Zn hydroxide sulphate hydrate (Δ) Zn hydroxy-sulphate chlorohydrate (Δ) Simonkolleite (Δ)	Zn hydroxide sulphate hydrate (x) Zn hydroxy-sulphate chlorohydrate (Δ) S (x) ZnO, zincite Hydrozincite (x) Simonkolleite (Δ)
Paraíso	Zn hydroxide sulphate hydrate (Δ) Zinc Hydroxide (x) Zinc and sodium chlorohydroxysulphate (x) Simonkolleite (Δ)	Simonkolleite(Δ) Zinc and sodium chlorohydroxysulphate (Δ)
Cunduacán	Zinc and sodium chlorohydroxysulphate (Δ) Zinc trihydroxysulphate hydrate (Δ) Simonkolleite (Δ) Zinc Hydrogen Sulfate (x)	Zinc hydroxysulphate tetra-hydrate (Δ) Zinc tetrasulphate acid (Δ) Simonkolleite (Δ)
Villahermosa	Zinc trihydroxysulphate hydrate (Δ) Zinc tetrasulphate acid (Δ) Simonkolleite (Δ) Zinc Hydrogen Sulfate (x)	Zinc trihydroxysulphate hepta-hydrate (Δ) Zinc hexahydroxysulphate tetra-hydrate (Δ) Simonkolleite (Δ)

In both countries Simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$) was shown as the major phase in the first and second year of exposure; its formation is presented in reactions 1-3. This phase is considered soluble in weak acid solutions (rainfall pH between 5 and 6) [43] and can be isolated from the (generally acidic) aqueous surface layer. Furthermore, since it forms rapidly it is a meta-stable phase, and therefore it gradually transforms into Zn hydroxysulphate, which has a low degree of solubility.



Another major phase of which the corrosion products are composed in both countries is zinc sodium chlorohydroxysulphate, $\text{Zn}_4\text{Na}(\text{OH})_6(\text{SO}_4)\text{Cl}(\text{H}_2\text{O})_6$, which has been reported by other researchers [44,45,46] for marine environments. It is estimated that this corrosion product comes from initial crystalline phases in which zinc hydroxycarbonate is formed, which immediately transforms into zinc hydroxychloride (intermediary phase) and sodium and zinc chlorohydroxysulphates as the final phase, which in turn have high solubility.

4. CONCLUSIONS

The station in Huasco is classified as highly corrosive (C_4), while Paraíso ($\text{C}_3\text{-C}_4$) and the stations in Antofagasta, Easter Island, Cunducacán and Villahermosa (C_3) are categorised as being of medium corrosiveness.

The main phase in the corrosion products formed on the galvanised steel surface is simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$), irrespective of the environmental conditions at the different testing stations.

The behaviour of the galvanised steel at the Chilean stations with regard to atmospheric corrosion is quite similar and the variations in corrosion rate mainly occur as a function of exposure time. On the other hand, at the Mexican stations the variables of temperature and relative humidity were also found to be statistically significant.

The results obtained indicate a clear trend of decreased corrosion on the galvanised steel with the increase in mean temperature, irrespective of the level of pollution present at all testing stations. This trend suggests that the corrosion of galvanised steel should decrease with the increased effects of climate change, which will bring higher mean temperatures.

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References

1. L. Rozenfeld, Atmospheric Corrosion of Metals, B.H. Tytel (Ed.), National Association of Corrosion Engineers (NACE), Houston, TX, 1973.
2. V. Kucera, E. Mattsson, Atmospheric Corrosion, W.H. Ailor (Ed.), Stockholm, Sweden, 1982.

3. L.L. Shreir, R.A. Jarman, G.T. Burstein, (Eds.), Corrosion, Vol.1-2, Metal /Environment reactions, 3ra ed., Butterworth-Heinemann, Oxford, U.K., 1994.
4. L. Veleva, R. Kane, Atmospheric Corrosion (Chapter 2.2), en Vol.13A – Corrosion: Fundamentals, Testing and Protection, S. D. Cramer y B. S. Covinio (Eds.), ASM International, OH, 2003, pp.196-209.
5. I. Odnevall, C. Leygraf, Environmental effects of metals induced by atmospheric corrosion, “Outdoor Atmospheric Corrosion”, ASTM STP 1421, H. E. Townsend Ed., ASTM, West Conshohocken. PA, 2002, pp. 185-199.
6. F. Zhu, D. Person, D. Thierry, C. Taxen, *Corrosion*, 56 (2000)1256.
7. R. A. Legault, V.P. Pearson, Atmospheric Factors Affecting the Corrosion of Engineering Metals, ASTM STP 646, Ed. American Society for Testing and Materials, Philadelphia 1978, 83.
8. Fred H. Haynie, The Degradation of metals in the Atmosphere, ASTM STP 965, Ed. American Society for Testing and Materials, Philadelphia, 1998, 282.
9. Fred H. Haynie, John W. Spence, Fred W. Lipfert, S. D. Cramer, L.G. Mc Donald, Corrosion Testing and Evaluation: Silver Anniversary Volume, ASTM STP 1000, Ed. American Society for Testing and Materials, Philadelphia, 1990, 225.
10. J. W. Spence, E. O. Edney, F. H. Haynie, Corrosion Testing and Evaluation: Silver Anniversary Volume, ASTM STP 1000, Ed. American Society for Testing and Materials, Philadelphia, 1990, 191.
11. J.W. Spence, F. H. Haynie, F.W. Liepfert, S.D. Cramer, Atmospheric Corrosion Model for Galvanized Steel Structures, *Corrosion*, 48 (1992)1009.
12. F. Zhu, D. Persson, D. Thierry, *Corrosion* 57 (2001) 582.
13. A. P. Yadav, A. Nishikata, T. Tsuru, *Corros. Sci.*, 46 (2004) 361.
14. D.A. Worsley, H.N. McMurray, J.H. Sullivan, I.P. Williams, *Corrosion*, 60 (2004) 437.
15. L. Odnevall, C. Leygraf, *Corros. Sci.*, 34 (1993)1213.
16. L. Odnevall, C. Leygraf, *Corros. Sci.*, 36 (1994)1077.
17. P. Quintana, L. Veleva, W. Cahuich, R. Pomes, J.L. Peña, *Appl. Surf. Sci.*, 99 (1996) 325.
18. D. De la Fuente, J. G. Castaño, M. Morcillo, *Corros. Sci.*, 49 (2007)1420.
19. X.G. Zhang, *Corrosion*, 55 (1999) 787.
20. T. Ohtsuka, M. Matsuda, *Corrosion*, 59 (2003) 407.
21. S. Oesch, M. Faller, *Corros. Sci.*, 39 (1997) 1505.
22. J. E. Svensson, L.G. Johansson, *Corros. Sci.*, 34 (1993) 721.
23. F. Zhu, D. Pearson, D. Thierry, C. Taxen, *Corrosion*, 56 (2000) 1256.
24. Corrosividad Atmosférica (MICAT-MÉXICO), Compiladores L. Mariaca, J. Genesca, J. Uruchurtu, L. Hernández, Primera Edición, México, D.F., 1999.
25. L. Maldonado, L. Veleva, Corrosión atmosférica en el norte de la península de Yucatán y el Caribe Mexicano, MICAT-México 1999; 165.
26. C. Leygraf, T. Graedel, Atmospheric Corrosion, Ed. Wiley and Sons, Inc. 2000; 341.
27. I. Odnevall, M. Westdahl, *Corros. Sci.*, 34 (1993) 1231.
28. Rosa Vera, Fabian Guerrero, Diana Delgado, Raquel Araya, *J. Braz. Chem. Soc.*, 24 (2013) 449.
29. Rosa Vera, Fabian Guerrero, Diana Delgado, Raquel Araya, *Revista de la Construcción*, 8 (2009) 8.
30. Instituto Nacional de Información Estadística y Geográfica, 2004 (INEGI).
31. E. Del Angel-Meraz, L. Veleva, M. Acosta-Alejandro, *Revista Universidad y Ciencia*, 25 (2009) 111.
32. ISO 9223, Corrosion of Metals and Alloy. Corrosivity of Atmospheres. Classification, International Organization for Standardization, Geneva, Switzerland, 1992.
33. R. Vera, M. Puentes R. Araya, P. Rojas, A. M. Carvajal, *Revista de la Construcción*, 12 (2012) 61.
34. Diana Delgado, Rosa Vera, *Int. J. Electrochem. Sci.*, 8 (2013) 7687.

35. ISO 8565, "Corrosion of Metals and Alloys- Atmospheric Corrosion Testing-General Requirements for Field Tests", International Organization for Standardization, Geneva, Switzerland, 1992.
36. ASTM G50-76 (2003), "Standard Practice for Conducting Atmospheric Corrosion Test on Metals", ASTM International, 2003.
37. ISO 9225, Corrosion of Metals and Alloys, Corrosivity of Atmospheres. Measurement of pollution, International Organization for Standardization, Geneva, Switzerland, 1992.
38. ISO 8407, "Corrosion of Metals and Alloys, Removal of corrosion products from corrosion test specimens", International Organization for Standardization, Geneva, Switzerland, 1991.
39. J.M. Costa, A.Vilarrasa, *British Corrosion Journal*, 28 (1993) 117.
40. S. Feliu, M. Morcillo, S. Jr. Feliu, *Corros. Sci.*, 34 (1993) 403.
41. J. M. Costa, M. Morcillo, S. Feliu, Effect of Environmental Parameters on Atmospheric Corrosion of Metals. In *Encyclopedia of Environmental Control Technology*, vol. 2, ed. P.N. Cheremisinoff (Houston, TX: Gulf Publishing Company, 1989), p 197.
42. Yu.M. Panchenko, A.I. Marshakov, T.N. Igonin, V.V. Kovtanyuk, L.A. Nikolaeva, *Corros. Sci.* 88 (2014) 306.
43. G.A. El Mahdy, *Corrosion* 59 (2003) 505.
44. P. Quintana, L. Veleza, L. Baños, JCPDS- Internacional Centre for Diffraction Data 1997; 10.

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