Weather Conditions, Corrosivity Indexes and Electrochemical Corrosion of Carbon Steel, Copper and Zinc in the Coastal Atmosphere of Tuxpan, Veracruz, Mexico

E. Gallardo-Castán1, G. Lugo-Islas1*, N. García-Navarro1, J. G. Ibañez Cornejo3, G. Galicia-Aguilar2, J. L. Ramírez-Reyes2

3Universidad Iberoamericana, Campus Santa Fe, Prol. Paseo de la Reforma, Santa Fe, Zedec Sta Fé, Álvaro Obregón, Ciudad de México, CDMX. C. P. 01376.

*Corresponding author: G. Lugo-Islas, email: glugo@uv.mx

Received April 1st, 2023; Accepted July 21st, 2023.

DOI: http://dx.doi.org/10.29356/jmcs.v67i4.2041

Abstract. Tuxpan is a port with economic and industrial important activity subject to atmospheric corrosion of metal structures such as boats, ships, oil platforms, and power stations. The main purpose of this paper is to evaluate the atmospheric corrosion of Tuxpan Veracruz, it was necessary to install an exposition panel with carbon steel specimens, galvanized steel (zinc), and copper to evaluate them in every season by electrochemical methods (electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR) and potentiodynamic polarization curves (CP). In addition, corrosivity indexes of atmospheric are evaluated by CLIMAT and ISO methodology. An exposition panel was installed with specimens of aluminum wire on steel screws, copper screws, and nylon screws to study corrosivity indexes through mass loss in every season of the year and thus classify the different types of atmospheres; marine, industrial, and rural-urban according to the values specified in the standard (ISO 8408, 9223, 9224). The corrosivity indexes are under the standards allowed in the regulations. However, they show the aggressiveness of the marine and industrial atmosphere due to the location and activities of the port in the northern zone. Zinc and carbon steel corrodes due to aggressive agents such as chlorides and sulfur dioxide, forming soluble oxides on the surface of the metallic substrate, while copper forms corrosion products that weakly protect its surface.

Keywords: Corrosion; CLIMAT; corrosivity indexes; electrochemical impedance.

Resumen. Tuxpan es un puerto con importante actividad económica e industrial, ha sido objeto del proceso de corrosión atmosférica en las estructuras metálicas como embarcaciones, botes, plataformas petroleras y Termoeléctricas. El propósito principal de este trabajo es evaluar la corrosión atmosférica de Tuxpan Veracruz, se instaló un panel de exposición con probetas de acero al carbono, acero galvanizado (zinc) y cobre para poder evaluarlas en cada estación del año por métodos electroquímicos (impedancia electroquímica espectroscopía (EIS), resistencia de polarización lineal (Rp) y curvas de polarización potenciódinámicas (CP). Además, se evalúan los índices de corrosividad de la atmósfera mediante la metodología CLIMAT e ISO. Se instaló un panel de exposición con probetas de alambre de aluminio sobre tornillos de acero, tornillos de cobre y tornillos de plástico para estudiar los índices de corrosividad por pérdida de masa en cada estación del año, y así clasificar los
diferentes tipos de atmósferas: marina, industrial y rural-urbana según los valores especificados en la norma (ISO 8408, 9223, 9224). Los índices se encuentran por debajo de los estándares permitidos en la normatividad. Sin embargo, muestran la agresividad del ambiente marino e industrial producto de la ubicación y actividades del puerto en la zona norte. El zinc y el acero al carbono se corroen debido a agentes agresivos como los cloruros y el dióxido de azufre, formando óxidos solubles en la superficie del sustrato metálico, mientras que el cobre forma productos de corrosión que protegen débilmente su superficie.

**Palabras clave:** Corrosión; CLIMAT; índices de corrosividad; impedancia electroquímica.

**Introduction**

Corrosion can be defined as the deterioration of a material produced by a chemical attack on its environment. Since corrosion is a chemical reaction, the rate at which it occurs will depend to some extent on the temperature and concentration of the reagents and products. Most metals are corroded by water and the atmosphere [1]. The most widespread form of corrosion is atmospheric, a general cause of alteration and destruction of most natural or man-made materials. The atmosphere in most of the world is humid, where the main industrial areas of the planet are located. Therefore, it is not strange that this type of corrosion is favored in these areas. Therefore, the study of atmospheric corrosion is important. Civilization has made great advances in materials technologies, but unfortunately, the humidity factor is always present in the atmosphere. Also, atmospheric corrosion is caused by climatic factors and environmental pollution (Cl\textsuperscript{-}, SO\textsubscript{x}, NO\textsubscript{x}, CO\textsubscript{x}, and particles). The climatic parameters have a greater influence on atmospheric corrosion at temperature, relative humidity, rainfall, and wind (direction and speed) [5-6]. Material resistant to the attack of one kind of atmospheric environment is not necessarily resistant in another place with different characteristics. For example, stainless steel and aluminum, which have good corrosion resistance in industrial, urban, and rural atmospheres, are not resistant to corrosion in coastal areas where the marine atmosphere is predominant. The explanation for these conditions is that different climate conditions, such as temperature, relative humidity, rainfall, direction, and wind speed, influence atmospheric corrosion. Besides climate conditions, the severity of corrosion depends on the levels of atmospheric contamination; therefore, it has been classified into indexes of atmospheric corrosivity for marine type, industrial and rural-urban environments [1-4].

In the aqueous phase, the oxidation mechanism \( SO_2 \) according to [1] is the following:

\[
SO_2 + xH_2O \rightarrow SO_2 \cdot xH_2O
\]

\[
SO_2 \cdot xH_2O \rightarrow HSO_3^- + H_3O^+ + (x - 2)H_2O
\]

\[
HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H_3O^+
\]

All metals (aluminum to a lesser extent) can adsorb \( SO_2 \) from the atmosphere. Deposits of \( SO_2 \) on metal surfaces can accelerate corrosion if they give rise to soluble products instead of the sparingly soluble products formed in pure water. The rust layer on the steel adsorbs \( SO_2 \) almost quantitatively, even in the case of dry air at 0º C [41]. Under humid conditions, sulfuric acid is formed:

\[
SO_2 + H_2O + \frac{1}{2}O_2 \rightarrow H_2SO_4
\]

This oxidation of S(IV) to S(VI), which occurs very slowly in the aqueous phase, is catalyzed by metals and metal oxides. Schikorr [41] has proposed that the corrosion of iron proceeds through what he calls the acid regeneration cycle. The sulfuric acid formed by the oxidation of \( SO_2 \), attacks the steel according to the global reaction:
\[ 4H_2SO_4 + 4Fe + 2O_2 \rightarrow 4FeSO_4 + 4H_2O \]

And is regenerated by a hydrolysis process

\[ 4FeSO_4 + O_2 + 4H_2O \rightarrow 4FeOOH + 4H_2SO_4 \]

For some metals, such as copper, the attack by sulfuric acid is probably direct, with the formation of sulfates. Copper sulfates are deliquescent but gradually convert to insoluble basic sulfates. That is, they may be protected or passivated after active corrosion in the presence of sulfuric acid.

NaCl, along with SO_2, is the contaminant that has probably been the subject of the greatest number of studies regarding its effects on corrosion. Like other ions, it increases the electrical conductivity of water, thus facilitating the flow of corrosion currents. It also reduces the effectiveness of natural protective films, which can be permeable to small ions. The effect of chloride on stainless steel is an extreme example, but similar effects have been found on other metals, albeit to a lesser degree. Given the hygroscopic nature of these salts, a lower relative humidity level will be needed for the corrosive process to occur. In this regard, studies such as the one carried out by St. Preston and Sanyal show that under a deposit of NaCl particles on the iron surface, corrosion begins to be noticed when the RH reaches 70 %, accelerating notably at higher relative humidity.

According to the CLIMAT (Classification of the Industrial and Marine Atmosphere) methodology, indexes of atmospheric corrosivity in environments of interest are determined by the direct exposure of metal samples to the environment, evaluating the corrosion rate out of mass loss and the determination of pollutants such as SO_2, deposited chlorides [2,3]. Tuxpan City is located in the northern zone of the state of Veracruz, it extends over an area of 1061.90 km², representing 1.46 % of the state territory being a coastal area and one of the closest seaports to Mexico City. Its climate is warm and humid; during the year, the temperature generally varies from 17 °C to 33 °C. Its humidity indexes range from March to November. Being a coastal area, it has 3 corrosive atmospheres; marine, industrial, and urban-rural. These directly affect metal structures causing pitting and wear of materials by the action of chlorides, sulfates, suspended particles, or polluting gases, including sulfur dioxide, carbon dioxide, and carbon monoxide, the latter from vehicle emissions. In Tuxpan, the environmental conditions of the region favour atmospheric corrosion, being able to implement programs of prevention and protection, industrial and port metals materials, process equipment and facilities, and any equipment being designed according to the prevailing environmental conditions. Therefore, assessing atmospheric corrosivity is relevant to the region because of the economic impact generated in different sectors (industrial, port, naval, and tourism).

Exposure to the atmosphere of aluminum wires (commercial grade) on screws has been widely used to determine the aggressiveness of the environment on the galvanic couple and thus assess the aggressiveness of the different types of atmospheres, according to CLIMAT methodology (Classification of Industrial and Marine Atmospheres) [3-7]. The test "wire on screw" promotes the accumulation of corrosive liquids in the cracks. High surface/ground wire accelerates corrosion, making it an invaluable tool for galvanic corrosion in corrosive atmospheres [6]. Galvanic corrosion experienced by the wire is calculated by the difference between the weight losses of the wires wound on the metal and the nylon screw. The operation of the galvanic couple depends, among other factors, on the atmosphere where it is acting. Earlier studies by Doyle and Godard [4, 8-9] have indicated that the specimen Al-Fe is very sensitive to the marine atmosphere and has little industrial. In contrast, the Al-Cu specimen is sensitive to both types of atmospheres. Thus, the types of atmospheres are usually classified as marine, industrial, and rural-urban. The main purpose of this paper is to evaluate the atmospheric corrosion of Tuxpan View using electrochemical methods to characterize the electrochemical behavior of an electrode-electrolyte interface with the following metallic materials: mild steel with rust remover, zinc, aluminum, and copper. These techniques will be completed with the CLIMAT methodology to determine the corrosion rate by weight loss of the materials listed in the atmosphere.
Experimental

CLIMAT methodology

Around the world, for more than three decades, the CLIMAT test has been used successfully to monitor atmospheric corrosion in different types of atmospheres. This method, originally called "wire on bolt" consists of wrapping aluminum wire in the threads of nylon, steel, and copper bolts with dimensions of 1.27 cm in diameter and 10 cm in length, as shown in Fig. 1. Each bolt acts as a galvanic couple; the Al-nylon combination determines the aggressiveness of the rural-urban atmosphere, the Al-steel marine atmosphere, and Al-Cu for the industrial atmosphere. Exposure of the coupons was performed according to the specifications of ISO 8565 and ASTM G116-93, using a display panel with an inclination angle of 45° to the horizontal and 1m above the floor, directly facing the prevailing winds (usually from the north-east) [5-7].

![Fig. 1. CLIMAT coupons of aluminum wire on nylon, steel, and copper bolts in the atmosphere of Tuxpan.](image)

During a year, at the end of each weather season, coupons were removed from the environment to wash with chemical methods, following the procedures described in ASTM G1 to remove the corrosion products. Subsequently, loss mass was determined by equation (1). Corrosion index (CI) calculation was made using equation (2) and only the aluminum wire values in % [1-6].

\[
\text{Loss mass} = \text{Initial mass} - \text{Final mass}
\]  
\[ (1) \]

\[
CI = \frac{\text{Loss mass}}{\text{Initial mass}} \times 100
\]  
\[ (2) \]

The installation methodology and chemical cleaning of the screws are run under ISO 8408, 9223 and 9224. The symbology standards for the identification of corrosivity indexes were found in the ISO 9223 standard:

<table>
<thead>
<tr>
<th>Atmosphere type</th>
<th>Galvanic Couple</th>
<th>Atmospheric corrosivity index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial</td>
<td>Al-Cu</td>
<td>0.15 – 1.8</td>
</tr>
<tr>
<td>Urban Rural</td>
<td>Al-Nylon</td>
<td>1.0 – 2.0</td>
</tr>
<tr>
<td>Sea</td>
<td>Al-Fe</td>
<td>0.4 – 9.0</td>
</tr>
</tbody>
</table>
Monitoring weather conditions, data recorded by weather station number 766400 located at coordinates (+20°95) latitude, (-97°40) longitude, and (+0028) altitude in the city of Tuxpan were used of Rodriguez Cano, Ver.

**Electrochemical methods**

Electrochemical methods do allow monitoring of atmospheric corrosivity more consistently and continuously. In this study, a biological potentiostat is used. To perform electrochemical measurements, a three-electrode electrochemical cell was used: reference electrode (RE) saturated Ag/AgCl, auxiliary electrode (AE) of graphite, and a working electrode (WE) consisting of a metal sample obtained in each season: with an area of 1 cm$^2$ equivalent exposure (Fig. 2). The experiment used the electrolyte as an ionic conductor, Na$_2$SO$_4$ (sodium sulfate). Potentiostat receives the signal from the electrochemical behavior in the system itself that connects to a personal computer through a software-compatible EC Lab. The electrochemical Impedance Spectroscopy (EIS) technique was applied with an amplitude of ± 10 mV in a frequency range of 0.01-10000Hz, according to the response of each system. The disturbance signal to the technique of linear polarization resistance (LPR) was ± 30 mV, designation: G 59-97, Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements. Finally, as a technique for high-field, the polarization curve was run by applying a signal of ± 500 mV, and a scan rate of 1.67mV / seconds [5-7].

**Fig. 2.** Electrochemical evaluation of the specimens in each season.

**Results and discussion**

**Corrosivity indexes**

The results in Table 2 show atmospheric corrosivity indexes of marine (MA), industrial (IA), and rural-urban (RUA) environments for each season. The highest corrosion indexes correspond to the industrial atmosphere, and the marine and rural-urban atmospheres register less aggressive corrosion indexes within the standard levels. The corrosivity indexes for the industrial atmosphere calculated in the year's three seasons are within the limits established by the regulations (0.15 -1.8). However, they increase from one season to another, having a higher corrosivity index in aluminum in winter, which means that in this season of the year, industrial activity prevails that generates sulfur products such as sulfur dioxide (SO$_2$), a product of the combustion of the processes of plants such as the “Adolfo López Mateos” Thermoelectric Power Plant located near the space where the experimentation system was placed. The corrosivity indexes of the marine atmosphere are within the limits established by the regulations (0.4 -9.0). However, they increase from one season to another, having in winter a higher corrosivity index in aluminum of 1.8546 %, which means that in this season of the year, the action of the winds causes components of the marine atmosphere (Cl$^-$) chlorides are transported in the air and affect metals, in this case causing aluminum corrosion. The urban-rural atmosphere is within the limits.
established by the regulations (1.0 - 2.0). However, in the fall season of the year, the corrosivity index is higher by 1.1668 % compared to the other two seasons of the year, which can be attributed to the increase in vehicle capacity and the burning of wood in the form of firewood derived from domestic activities [1-9].

Table 2. Atmospheric corrosivity indexes in Tuxpan, in 2020. ISO 9223.

<table>
<thead>
<tr>
<th>Galvanic Couple</th>
<th>Atmosphere type</th>
<th>Season</th>
<th>Initial mass, mg</th>
<th>Final mass, mg</th>
<th>Loss mass, mg</th>
<th>Corrosivity indexes, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Cu</td>
<td>IA</td>
<td>Summer</td>
<td>3,501.90</td>
<td>3,485.30</td>
<td>16.6</td>
<td>0.474028385</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fall</td>
<td>3,510.70</td>
<td>3,492.60</td>
<td>18.1</td>
<td>0.515566696</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Winter</td>
<td>3,503.54</td>
<td>3,472.17</td>
<td>31.37</td>
<td>0.895380101</td>
</tr>
<tr>
<td>Al-Fe</td>
<td>MA</td>
<td>Summer</td>
<td>5,112.34</td>
<td>5,098.40</td>
<td>13.94</td>
<td>0.27267357</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fall</td>
<td>5,195.80</td>
<td>5,153.60</td>
<td>42.20</td>
<td>0.812194465</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Winter</td>
<td>5,084.40</td>
<td>4,990.10</td>
<td>94.30</td>
<td>1.854692786</td>
</tr>
<tr>
<td>Al-Nylon</td>
<td>RUA</td>
<td>Summer</td>
<td>5,412.40</td>
<td>5,404.40</td>
<td>8.00</td>
<td>0.147808735</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fall</td>
<td>5,330.50</td>
<td>5,268.30</td>
<td>62.20</td>
<td>1.1668699</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Winter</td>
<td>5,423.40</td>
<td>5,419.59</td>
<td>3.81</td>
<td>0.070251134</td>
</tr>
</tbody>
</table>

The aggressive atmospheric parameters are shown in Table 3. The number of suspended particles and sulfates decreases in the spring and autumn. However, in autumn and winter, the deposition rate of sulfates and particles rises due to the decrease in rainfall and the change in the direction and speed of the prevailing winds. The velocity of chloride deposition increases in spring and summer, when the winds blow from the east (from the sea to the coast), and the temperature and precipitation are significant. When the wind speed is slow, the transport of chlorides is limited, so the concentration decreases in the autumn and winter seasons. 92 rainy days, temperatures higher than 20 °C, and rainfall up to 840.21 mm were recorded. Emphasizing that the more significant the environmental conditions, the electrochemical corrosion of metals acquires greater rate. In the spring season, the direction of the wind has the north and east as dominant components. Similarly, for summer, the eastern component is still present, and the northeast component intensifies; for the autumn season, the direction of the winds is dominated by the western component, and for the winter season, the dominant components are the northwest and the east.

Table 3. Behavior of aggressive parameters and weather conditions (average) in the atmosphere of Tuxpan, Ver. ISO 9223-9225.

<table>
<thead>
<tr>
<th>Aggressive parameters</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
<th>Winter</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂, mg/m²-d</td>
<td>27.5</td>
<td>19.8</td>
<td>7.4</td>
<td>9</td>
</tr>
<tr>
<td>Suspended particles, mg/m²-d</td>
<td>64.3</td>
<td>40.3</td>
<td>18.7</td>
<td>112.8</td>
</tr>
<tr>
<td>Cl⁻, mg/m²-d</td>
<td>228.3</td>
<td>280.9</td>
<td>198.7</td>
<td>193.1</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>28.1</td>
<td>28.5</td>
<td>22.3</td>
<td>20.8</td>
</tr>
<tr>
<td>Relative humidity, %</td>
<td>85.3</td>
<td>88.7</td>
<td>91.6</td>
<td>85.9</td>
</tr>
<tr>
<td>Dew point, °C</td>
<td>25.1</td>
<td>24.2</td>
<td>23.4</td>
<td>17.8</td>
</tr>
<tr>
<td>Precipitation, mm</td>
<td>315</td>
<td>840.8</td>
<td>175.6</td>
<td>56.8</td>
</tr>
<tr>
<td>Wind speed, Km/h</td>
<td>5.8</td>
<td>4.3</td>
<td>3.9</td>
<td>5.2</td>
</tr>
</tbody>
</table>
Electrochemical measurements

Table 4 shows the results of the electrochemical technique Linear Polarization Resistance (LPR) for evaluating corrosion in test tubes or metal plates of iron, copper, and zinc exposed to the atmosphere in the summer, fall, and winter seasons. Iron, zinc, and copper present different corrosion rates in the year's three seasons. What is related to the potential or activity of each material according to its location in the series of standard reduction potentials (−0.44 V for Fe, 0.16 V for copper, and -0.76 V for zinc), where in theory, the smaller the standard potential, the more active the metal is, that is, its possibility of oxidizing is greater. Thus, iron presents corrosion rates in mm/year in the three seasons of the year that are higher than those of copper, which is less active than iron. However, zinc, with a lower potential than iron, has lower corrosion rates, which also has to do with the corrosion products resulting from the corrosion process suffered by the metal. For example, corrosion products such as iron oxides are less protective of iron than zinc oxides, which are protective of zinc [1-4].

Table 4. Results of electrochemical measurements of bare metals exposed in the atmosphere of Tuxpan, Veracruz in 2020.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density, g/cm³</th>
<th>Season</th>
<th>( E_{corr}, \text{mV} )</th>
<th>LPR, ( \Omega \cdot \text{cm}^2 )</th>
<th>( I_{corr} \times 10^6 \text{ A/cm}^2 )</th>
<th>Vcorr, mm/año</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon steel (Fe)</td>
<td>( \rho = 7.874 )</td>
<td>0 exp.</td>
<td>-497.391</td>
<td>257</td>
<td>14.882</td>
<td>0.1744647</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Summer</td>
<td>-360.883</td>
<td>139</td>
<td>27.399</td>
<td>0.3175326</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fall</td>
<td>-326.53</td>
<td>238</td>
<td>19.882</td>
<td>0.2304166</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Winter</td>
<td>-382.658</td>
<td>141</td>
<td>26.232</td>
<td>0.3040080</td>
</tr>
<tr>
<td>Cu</td>
<td>( \rho = 8.96 )</td>
<td>0 exp.</td>
<td>77.430</td>
<td>4749</td>
<td>0.060</td>
<td>0.0006953</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Summer</td>
<td>69.502</td>
<td>38611</td>
<td>0.086</td>
<td>0.0009966</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fall</td>
<td>96.256</td>
<td>12476</td>
<td>0.361</td>
<td>0.0041834</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Winter</td>
<td>110.823</td>
<td>9819</td>
<td>0.427</td>
<td>0.0049483</td>
</tr>
<tr>
<td>Zn</td>
<td>( \rho = 7.13 )</td>
<td>0 exp.</td>
<td>-894.592</td>
<td>6044</td>
<td>0.707</td>
<td>0.0105931</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Summer</td>
<td>-928.098</td>
<td>1501</td>
<td>0.087</td>
<td>0.0013035</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fall</td>
<td>-928.859</td>
<td>17622</td>
<td>0.218</td>
<td>0.0032663</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Winter</td>
<td>-946.29</td>
<td>8872</td>
<td>0.323</td>
<td>0.0048395</td>
</tr>
</tbody>
</table>

Figures 3, 4, and 5 present the results of the electrochemical technique of Electrochemical Impedance Spectroscopy (EIS) carried out on carbon steel, copper, and zinc plates or specimens in the seasons of the year or weather seasons of summer, autumn, and winter. Figure 3 shows the results of the EIS technique for carbon steel. In the three seasons of the year, it is observed that in the carbon steel test tube at zero immersion, the real impedance of 36 ohms/cm² and the imaginary impedance of 22 ohms/cm², having a resistive interface which means that the iron when exposed to the electrolyte It presents degradation by activation or charge transfer, this is the dissolution of solid iron (Fe) to iron ions (Fe²⁺). However, in the summer and winter seasons, the quantities of the imaginary impedance decrease to 17 ohms/cm² because the interface, in comparison with the iron at zero immersion, becomes more resistive, which means that in the months of such stations, iron corrosion products such as porous and soluble oxides and hydroxides were formed on the surface, which do not protect the substrate, causing the metal to continue passing from the solid state to the ionic state, favoring corrosion [8-9].
Fig. 3. EIS in Nyquist for carbon steel exposed in the atmosphere of Tuxpan.

Fig. 4 shows the results of the EIS technique for copper in the year's three seasons. In copper, at zero immersion, the real impedance is 200 ohms/cm² and the imaginary impedance is 100 ohms/cm². The interface is resistive, which means that copper when exposed to the electrolyte, presents degradation by activation or charge transfer. This is the dissolution of solid Copper (Cu) to Copper ions (Cu²⁺). However, in the summer, autumn, and winter seasons, real impedance values of 4756, 5811, and 6841 Ohms/cm², respectively, are observed, with the formation of a 45-degree slope or Warburg-type impedance that implies the diffusion and migration of species. chemicals such as chlorides, sulfates, oxygen, and copper cations to the interface in a differentiated way [8-9].

Fig. 4. EIS in Nyquist for copper exposed in the atmosphere of Tuxpan.

Fig. 5 shows the results of the EIS technique for zinc in the three seasons of the year, observing that in the zinc specimen at zero immersion, the real impedance is 1234 ohms/cm² and the imaginary impedance is 174 ohms/cm², having a resistive interface, means that copper presents corrosion by activation or charge transfer when exposed to the electrolyte. This is the dissolution of solid zinc (Zn) to zinc ions (Zn²⁺) with Warburg-type impedance. However, in the summer, autumn, and winter seasons, real impedance values of 6049, 1142, and 5183 ohms/cm² are observed, respectively. In the summer and winter seasons, the formation
of a 45-degree slope occurs, a Warburg-type impedance that implies the diffusion and migration of chemical species such as chlorides, sulfates, oxygen, and zinc cations to the interface [2-3].

Fig. 5. EIS in Nyquist for zinc exposed in the atmosphere of Tuxpan.

Figures 6, 7, and 8 present the results of the Potentiodynamic Polarization Curves electrochemical technique for carbon steel, copper, and zinc in the year's summer, autumn, and winter seasons. The kinetics of carbon steel's anodic and cathodic reactions (Fig. 6) are mixed at all stations. The corrosion rate is 174.4647 mm/year to 317.5326 mm/year, the highest in autumn, as observed in Table 3 [9-10].

Fig. 6 Potentiodynamic polarization curves for carbon steel in atmospheric exposure of Tuxpan.

Copper (Fig. 7) shows mixed control for both reactions, anodic and cathodic. In winter, copper forms corrosion products that passivate the surface due to a limiting current density in the anodic reaction. However, the dissolution of copper is rapid in the environment, a consequence of the aggressiveness of the marine and industrial atmosphere according to the corrosivity indexes. The corrosion rate is in a range of 0.5963 mm/year to 4.9483 mm/year, being the highest in spring as observed in Table 3.
Fig. 7 Potentiodynamic polarization curves for copper in atmospheric exposure of Tuxpan.

Fig. 8 shows a rapid dissolution of zinc in the cathode zone in the three seasons. The lowest corrosion rate was recorded in the autumn season and with a greater magnitude in the summer season of 10.5931 mm/year.

Conclusions

According to corrosivity indexes, in Tuxpan, the atmosphere is industrial and marine during the winter season, while in autumn, the atmosphere is urban-rural. The corrosivity indexes for the aluminum-copper galvanic pair are within the limits established by the standard. However, according to the series of potentials published in the literature, the corrosivity index for aluminum, as it is an active metallic material, increases from one season to another. This quantity increases, taking winter as the third season, in which the aluminum-copper galvanic pair was exposed. Therefore, industrial activity increases in winter when sulfur, carbon, and nitrogen products are generated, such as sulfur dioxide, obtained in combustion processes, damaging the metallic infrastructure.
In the case of the aluminum-iron galvanic pair used to monitor the behaviour of the marine atmosphere, it was indicated that the corrosivity indexes calculated in the year's summer, autumn, and winter seasons are within what is specified in the regulations (0.4 - 9.0). However, these indexes increase when going from one season to another, having in winter the highest corrosivity index in aluminum of 1.8546 %, which does not exceed what is established in the regulations; this can be attributed to the fact that because it is an investigation where the system For the measurement of experimental data, it was located in a coastal area such as the City of Tuxpan Veracruz, whose proximity to the sea is short, allowing the winds that blow with a certain speed in that season, to contain certain substances from the sea, mainly salts in the form of chlorides (Cl⁻) that are deposited at the interface of the galvanic aluminum-iron pair, causing the oxidation of aluminum until its transformation into a layer of aluminum oxide or alumina, which can be uniformly attacked by other chemical components that conduct to the formation of soluble salts, such as aluminum sulfate Al₂(SO₄)₃ or basic salts that are incorporated into the corrosion product layer.

The corrosivity indexes for the urban-rural atmosphere evaluated with the aluminum-nylon galvanic pair in the year's summer, autumn, and winter seasons are within the established official regulations (1.0 - 2.0). However, the year's autumn season presents a corrosivity index greater than 1.1668 % compared to the other two seasons of the year. This can be attributed to the increase in vehicle capacity that produces concentrations of combustion gases such as monoxide and dioxides of carbon and sulfur, and gases produced by the combustion of wood in the form of firewood to make fires in rural kitchens.

The prevailing atmosphere in the city of Tuxpan is of an industrial type since it is maintained at the permitted levels during the year's four seasons, reaching its highest level recorded in the winter due to the burning of coal and fossil fuels. The main consumer of this type of energy and the main fixed source emitting SO₂ is the Adolfo López Mateos power station, where although the registered wind direction from the northwest-east component drags the particles further south, conditions are propitious for the generation of corrosion thanks to the high relative humidity generated by low temperatures, low dew point, little rainfall, favouring the formation of a film of water on the metal surface, thus favouring electrochemical corrosion.

Carbon steel presents corrosion rates in mm/year in the three seasons (summer, autumn, and winter) higher than copper, which is consistent with the theory since iron is more active than copper. However, the corrosion rates for zinc, which has a potential lower than that of iron, are lower than those of the latter, which indicates that other factors intervene from the potential in the corrosion rate of a metallic material, such as the corrosion products that are deposited in the metal interface, for example in zinc, it is possible the formation of products in the form of zinc oxide that protects it.

Acknowledgements

The participants of the present work are pleased to thank the Faculties of Chemical and Accounting Sciences, both Poza Rica-Tuxpan Region, dependent on the Universidad Veracruzana, for the support granted, in carrying out the different research activities.

References