Atmospheric corrosion in tropical humid climates

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1. Abstract

The tropical climate is characterized by permanently high temperatures and relative humidity with considerable precipitation. A high corrosion rate of metals is usually reported for this climate. Airborne salinity plays an important role in determining corrosion aggressivity in Cuba and in the...
Yucatán Peninsula. The similarities and differences between the Yucatan Peninsula and Cuban atmospheres are reported.

The interaction Chloride Deposition rate-rain regime is important in determining acceleration rate of chloride deposition on metals.

Sulphate is contained in airborne salinity. In tropical coastal atmospheres a significant part of the sulphur compounds determined could be related to the presence of sulphate in sea aerosol. Sulphates have not the same influence on corrosion rate than $SO_2$ so an error is included considering that all sulphur compounds detected have the same influence on corrosion rate.

There is very little information about corrosion behavior indoors. Calculation of TOW-ISO should not be as important as outdoors. Higher TOW-ISO values are reported for indoor conditions where corrosion rate is significantly lower. In coastal regions, corrosion rate diminishes under indoor conditions.

2. Introduction

The atmosphere represents the most extended environment to which structural metals are exposed. Almost all man live and activity is carried out in the atmosphere. Atmospheric corrosion affects many sectors of the economy like infrastructure (bridges, highways, roads), transportation (ships, automobiles, buses, aircraft), communication (electronics and information technology), buildings and cultural heritage. It is also an aspect to consider in risk management.

The presence of a liquid phase, usually a thin aqueous layer formed on the surface of the material is very important for the occurrence of atmospheric corrosion process. This liquid layer is the place were electrochemical reactions occur and also act as a solvent for deposited atmospheric constituents, gaseous as well as particulate.

While $SO_2$ levels in developed countries are decreasing, pollution levels due to energy production and vehicle numbers in many developing countries are rapidly increasing. In addition, many of the developing countries are located in tropical regions with high relative humidity and a high frequency of precipitation. Thus, there is a great risk of extreme corrosion rates in these areas, even higher than in the temperate zone under similar emissions of pollutants, with accompanying high costs due to corrosion damage. Kucera et al [1] made a correlation between corrosion and selected environmental parameters of 12 sites placed in tropical climate of Asia and Africa. The environmental parameter that has the highest correlation with corrosion rate of steel, zinc, copper, limestone and painted steel is the amount of $SO_4^{2-}$.
analyzed from the particulate deposited matter. Other parameters with high correlation are SO$_2$ for carbon steel, rain pH for zinc and SO$_2$, rain pH and HNO$_3$ for limestone. These results have been obtained for an exposure time of one year. The program is still under execution.

The results showed that while the levels of S-pollutants have decreased dramatically in industrial countries, the levels of SO$_2$ are high in several locations in developing countries. Kuala Lumpur has the highest HNO$_3$ values in the network probably due to a combination of the high NO$_2$ emissions, the high temperature, and the humid conditions.

Respecting Iberoamerican Countries, an important collaborative research project was carried out with the participation of 14 countries of this region [2]. The majority of the countries participating in the project are located completely or in part in the tropical region. The results showed a broad range of changes in Time of Wetness, SO$_2$ and Chloride Deposition and consequently, significant changes in atmospheric corrosivity. It is important to remark the high influence of Chloride ions for tropical regions coinciding with high levels of Chloride deposition. The influence of orography is also very important in determining corrosion aggressivity.

The tropical climate is typical of equatorial and tropical regions and is characterized by permanently high temperatures and relative humidity with considerable precipitation, at least during part of the year. A high corrosion rate of metals is usually reported for this climate.

The humid tropical climate of Cuba and the Yucatán Peninsula (México) is characterized by an average air temperature always higher than 15 °C, frequently high relative humidity, a summer or wet season (may to october) with frequent and heavy precipitations and a winter of dry season (november to april) with lower precipitations.

In the case of these two regions there is a natural source of airborne salinity: the waters of the Atlantic Ocean, the Gulf of Mexico and the Caribbean Sea. Airborne salinity plays an important role in determining corrosion aggressivity in Cuba [3-6] and in the Yucatán Peninsula [4, 7-8]. Other anthropogenic contaminants can be present also in this region, particularly sulfur compounds coming from the oil production and manufacture industries and transportation. Nitrogen oxides can also be present. Depending on the contaminants sources existing in different regions, the kind of contaminants may change, but in general, the main types of contaminants are Chlorides and Sulfur compounds, particularly outdoors, although in developed countries, where the levels of sulphur dioxide, nitrogen oxides and other pollutants have significantly diminishes, a new multipollutant approach is been tested.
The relatively high temperatures of tropical climate could increase the presence in the atmosphere of contaminants produced by decomposition of organic matter such as \( \text{H}_2\text{S} \) [9] and dry deposition of \( \text{NH}_3 \) and ammonium compounds[10].

Air temperature in the Yucatán Peninsula reaches higher values than in Cuba, the top average air temperature in Cuba is 26 °C in the eastern shoreline [11]. In the Yucatán Peninsula part of the territory can be classified as Tropical very warm with an average temperature over 26 °C [12]. Absolute maximum temperature in Cuba is of 38.6 °C, meanwhile a temperature over 40 °C is frequently reported in sites of the Yucatán Peninsula, particularly in Campeche.

About ¼ of the Cuban territory is composed by mountains and the rest is mainly terrain flatness. The Yucatán Peninsula has no mountains. The lower temperatures and higher precipitations rates in Cuba are localized in the mountain regions. Orography is a transformation factor of local wind regime.

Average relative humidity in the west side of Cuba is frequently higher than in Campeche, the average is about 80% for Cuba and about 76% for Campeche. Daily maximum relative humidity values are over 90% for the west part of Cuba and over 88% for Campeche. In spite of this, the classification of TOW according to ISO-9223[13] is the same for the two territories: \( \tau_4 \), corresponding to “Outdoor atmospheres at all climates, excepting dry and cold climates”.

The influence of air temperature may change depending on the conditions. The effect of increasing temperature appears to be an increase in corrosion rate under conditions of permanent surface wetting, such as those obtained during precipitation. Under conditions of varying surface wetting, however, the corrosion rate increases with temperature up to a certain maximum value, and thereafter decreases [14]. ISO 9223 standard established that for purposes of corrosivity determinations the use of temperature-humidity complex data is the recommended methodology, because corrosion rate depends on this complex and not only on temperature or humidity independently. Taking into account this report, a decrease in corrosion rate should be expected in tropical climate for an increase in average air temperature.

2.1. Time of wetness (TOW) and ISO 9223 definition

Taking into account the electrochemical nature of the atmospheric corrosion process it is absolutely necessary to use the concept of Time of Wetness (TOW). It is a concept commonly used in atmospheric corrosion of metallic materials and refers to the time when the metal is sufficiently wet for
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corrosion reaction to occur, that is, when an electrolyte is present on the metallic surface. Under the particular characteristics of atmospheric corrosion there are time periods where corrosion could not occur due to the absence of an electrolyte in the metallic surface. The lowest outdoor TOW values are observed in the desert regions, as also in the Antarctic and Arctic regions. Atmospheric corrosion rates of metals at these climatic conditions are also very low and in the case of cold regions, the increase of temperature leads to the increase of TOW and corrosion rate [15]. In principle, TOW is a parameter that depends upon both the climatic conditions and in the characteristics of the metallic surface.

The definition of TOW presented on ISO standard 9223 is the following: “The period during which a metallic surface is covered by adsorptive and/or liquid films of electrolyte that are capable of causing atmospheric corrosion”. In addition, the new document ISO WD/9223 [15] defines: The wetting of surfaces is caused by many factors, for example, dew, rainfall, melting snow and a high humidity level. The length of time when the relative humidity is greater than 80% at a temperature greater than 0 °C is used to estimate the calculated time of wetness (τ) of corroding surfaces. Information on calculated time of wetness is helpful for informative atmosphere corrosivity estimation. In this standard, TOW is “estimated” based on the characteristics of the temperature humidity complex, independently of the pollutant level and the nature of the metal or alloy. It is not the actual time of wetness, but it is an estimation based only on climatic factors (temperature and relative humidity) and independent of the nature and characteristics of the metallic surface. For tropical climate the estimation is reduced to “the length of time when the relative humidity is greater than 80%”, because temperature is always over 0°C. Some results obtained in the tropical regions of the Gulf of Mexico suggest that an upper limit in temperature for the definition of TOW could be established [5-6, 16-18]. TOW as defined in ISO 9223 does not cover all the aspects of climate. According to the ISO definition, in the case of tropical climate where air temperature never reaches 0°C, TOW is estimated as the time when relative humidity is over 80%. The diminution of the electrolyte layer at relative humidity over 80% when temperature is over 25 °C has been reported for Santiago de las Vegas rural station in Cuba [16] using TOW sensors based in a circuit print covered with a gold layer. By other way, metal temperature and TOW were registered in a rural station at 30 km of the seashore located in Merida, Yucatan Peninsula, using copper/gold sensors [18] according to ASTM Practice G84-89 (1999). It was reported the influence of the nature of the metal and their corrosion products, the orientation of the sample (skyward or groundward), the direction of the winds and rain precipitation on the measured TOW values. None of this
factor is taken into consideration by ISO 9223. A quite different temperature was determined for the metal surface respecting air temperature. It is perhaps an explanation to the very possible increase in evaporation of the surface electrolyte when air temperature is over 25 °C.

Water adsorption on silver surfaces exposed into a ventilated shed in an urban-rural site of Cuba was studied [17] using quartz resonators covered with a silver layer. It was determined that in these indoor conditions water adsorption significantly diminishes when air temperature increases over 25 °C at relative humidity ranges of 80-90% and 90-100%. All these results confirm the idea that an upper limit of temperature should be established for the estimation of time of wetness.

The presence of water does not only create conditions for the existence of an electrolyte, but it acts as a solvent for the dissolution of contaminants [14]. Oxygen plays an important role as oxidant element in the atmospheric corrosion process. The thickness of the water layer determines the oxygen diffusion toward the metallic surface and also the diffusion of the reaction products to the outside interface limited by the atmosphere. Another aspect of ISO definition is that “a metallic surface is covered by adsorptive and/or liquid films of electrolyte”. According to new results, the presence of adsorptive or liquid films of electrolyte perhaps could be not in the entire metallic surface, but in places where there is formed a central anodic drop due to the existence of hygroscopic particles or substances surrounded by microdrops where the cathodic process takes place. This phenomenon is particularly possible in indoor conditions [19-22].

Using ISOCORRAG, MICAT and Russian data, Tidblad et al [23] showed that the inclusion of temperature among the environmental parameters improves considerably the usefulness of the dose-response functions and should be adapted in the revision of ISO 9223 standard. It is reported an increase in corrosion rate with average air temperature in the range of -15 to 30 °C.

In the eighties of the last century the adsorption of water layers on surfaces was studied [24]. It was demonstrated that the change in thickness of these layers depends on the physico-chemical properties of water in these thin water layers. It is reported that on iron surfaces, the number of adsorbed water layers is about 15 at RH 55% and 90 at 100%. Similar values are obtained for Copper and Zinc; however significant differences are reported for Platinum, gold, aluminum and silver. These monolayers have been calculated, in general, only in presence of water (without oxygen) where the corrosion process is very slow and, consequently, in conditions far from the reality.
Almost all tests carried out to study the starting process of atmospheric corrosion have been performed in a surface without corrosion products; however, in real conditions, the metal is covered with corrosion products after a given time and these products begin to play its role as retardants of the corrosion process in almost all cases. Corrosion products act as a barrier for oxygen and contaminants diffusion, the free area for the occurrence of the corrosion is lower; however, the formation of the surface electrolyte is enhanced. Only in highly polluted areas the corrosion products accelerate the corrosion process. Water adsorption isotherms were determined to corrosion products formed in Cuban natural atmospheres [25]. Sorption properties of corrosion products (taking into account their salt content-usually hygroscopic) determine the possibilities of surface adsorption and the possibility of development of corrosion process.

For a single type of climate it could be more practical and easy to use time instead of TOW, because it is expected the same category of TOW according to ISO 9223. In other words, it makes no sense to work using TOW-ISO in tropical climate, because in general it is in the same category at all places, so its influence is the same. Using data for different climates or wide regions a significant change in TOW-ISO could take place, including changes in wet/dry cycles. In these conditions it should be recommendable to use TOW according to ISO definition.

2.2. Time and TOW-ISO

Outdoor TOW-ISO

Corrosion rate is a function of time of wetness, considered as the time during which corrosion occurs, but in general it should not be a linear function because corrosion rate changes with time. There are different factors influencing, for example, the protective properties of the corrosion products, the increase or decrease of the acceleration caused by contaminants, increase or decrease of the thickness and conductivity of the electrolyte layer, i.e.

If the definition of TOW established by ISO is used (TOW-ISO), a linear relationship between time and TOW is obtained, in spite of the different possible changes in corrosion rate caused by changes in the nature of TOW. It has to be remarked that it is not the same effect on corrosion rate caused by a heavy rain than dew, fog or water adsorption, so for the same interval of relative humidity (80-100%), notable changes in nature of TOW-ISO and consequently in corrosion rate could take place.

If a linear regression is fitted between time (sum of time in months) and TOW-ISO (sum of TOW corresponding to every month up to one year), a perfect linear relationship is obtained [26] (see tables 1, 2, 3, 4 and 5). The results show that a perfect linear relation exists between time and TOW-ISO.
Table 1. Simple regression of TOW-ISO data and time for Campeche PCGM coastal test station in a period of 2 years. Equation \( t = a + b \) TOW-ISO, \( r \) = correlation coefficient, \( r^2 \) = percentage of variation explained by the independent variable, \( P \) = Statistical Probability.

<table>
<thead>
<tr>
<th>Year</th>
<th>a</th>
<th>b</th>
<th>r</th>
<th>( r^2 )</th>
<th>( P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2004</td>
<td>-230.42</td>
<td>234.39</td>
<td>0.979</td>
<td>95.90</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>2005</td>
<td>-300.15</td>
<td>258.77</td>
<td>0.974</td>
<td>94.88</td>
<td>&lt;0.0000</td>
</tr>
</tbody>
</table>

Table 2. Simple regression of TOW-ISO data and time for Viriato coastal test station in a period of 10 years. Equation \( t = a + b \) TOW-ISO., \( r \) = correlation coefficient, \( r^2 \) = percentage of variation explained by the independent variable, \( P \) = Statistical Probability.

<table>
<thead>
<tr>
<th>Year</th>
<th>a</th>
<th>b</th>
<th>r</th>
<th>( r^2 )</th>
<th>( P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1987</td>
<td>-487.20</td>
<td>406.48</td>
<td>0.987</td>
<td>97.49</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1988</td>
<td>-14.83</td>
<td>423.15</td>
<td>0.997</td>
<td>99.38</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1989</td>
<td>-160.20</td>
<td>365.59</td>
<td>0.998</td>
<td>99.58</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1990</td>
<td>89.30</td>
<td>299.48</td>
<td>0.996</td>
<td>99.11</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1991</td>
<td>-167.38</td>
<td>395.20</td>
<td>0.998</td>
<td>99.52</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1992</td>
<td>-237.26</td>
<td>375.55</td>
<td>0.996</td>
<td>99.16</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1993</td>
<td>-91.18</td>
<td>348.37</td>
<td>0.996</td>
<td>99.29</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1994</td>
<td>-70.60</td>
<td>380.73</td>
<td>0.999</td>
<td>99.71</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1995</td>
<td>-428.05</td>
<td>413.16</td>
<td>0.994</td>
<td>98.73</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1996</td>
<td>83.97</td>
<td>252.75</td>
<td>0.997</td>
<td>99.489</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1997</td>
<td>-101.30</td>
<td>390.60</td>
<td>0.999</td>
<td>99.73</td>
<td>&lt;0.0000</td>
</tr>
</tbody>
</table>

Table 3. Simple regression of TOW-ISO data and time for Holguin coastal station (located in the eastern side of Cuba) in a period of 3 years. Equation \( t = a + b \) TOW-ISO., \( r \) = correlation coefficient, \( r^2 \) = percentage of variation explained by the independent variable, \( P \) = Statistical Probability.

<table>
<thead>
<tr>
<th>Year</th>
<th>a</th>
<th>b</th>
<th>r</th>
<th>( r^2 )</th>
<th>( P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1987</td>
<td>126.42</td>
<td>469.84</td>
<td>0.999</td>
<td>99.79</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1988</td>
<td>27.13</td>
<td>435.98</td>
<td>0.999</td>
<td>99.88</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1989</td>
<td>54.44</td>
<td>403.36</td>
<td>0.999</td>
<td>99.96</td>
<td>&lt;0.0000</td>
</tr>
</tbody>
</table>

It means that both variables are equivalent, so for purposes of long term prognosis, work carried out time give the same result than using TOW-ISO. It does not mean that the actual time of wetness should be the same as estimated according to ISO, because as it has been pointed out above, the ISO
Table 4. Simple regression of TOW-ISO data and time for Cojimar coastal station in a period of 10 years. Equation $t = a + b \text{TOW-ISO}$, $r$ = correlation coefficient, $r^2$ = percentage of variation explained by the independent variable, $P$ = Statistical Probability.

<table>
<thead>
<tr>
<th>Year</th>
<th>a</th>
<th>b</th>
<th>r</th>
<th>$r^2$</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>1991</td>
<td>-127.68</td>
<td>389.13</td>
<td>0.998</td>
<td>99.52</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1992</td>
<td>-172.08</td>
<td>367.73</td>
<td>0.996</td>
<td>99.14</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1993</td>
<td>-54.0</td>
<td>342.23</td>
<td>0.998</td>
<td>99.53</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1994</td>
<td>-51.32</td>
<td>381.34</td>
<td>0.999</td>
<td>99.78</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1995</td>
<td>-289.58</td>
<td>389.58</td>
<td>0.993</td>
<td>98.60</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1996</td>
<td>-164.67</td>
<td>376.75</td>
<td>0.997</td>
<td>99.41</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1997</td>
<td>-51.44</td>
<td>369.95</td>
<td>0.999</td>
<td>99.83</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1998</td>
<td>-75.36</td>
<td>344.79</td>
<td>0.997</td>
<td>99.40</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1999</td>
<td>-286.80</td>
<td>352.04</td>
<td>0.989</td>
<td>97.89</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>2000</td>
<td>-159.21</td>
<td>371.14</td>
<td>0.995</td>
<td>99.02</td>
<td>&lt;0.0000</td>
</tr>
</tbody>
</table>

Table 5. Simple regression of TOW-ISO data and time for Quivican rural station in a period of 8 years. Equation $t = a + b \text{TOW-ISO}$, $r$ = correlation coefficient, $r^2$ = percentage of variation explained by the independent variable, $P$ = Statistical Probability.

<table>
<thead>
<tr>
<th>Year</th>
<th>a</th>
<th>b</th>
<th>r</th>
<th>$r^2$</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>1990</td>
<td>-89.37</td>
<td>405.78</td>
<td>0.997</td>
<td>99.34</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1991</td>
<td>-121.50</td>
<td>421.15</td>
<td>0.997</td>
<td>99.34</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1992</td>
<td>-66.07</td>
<td>440.34</td>
<td>0.998</td>
<td>99.59</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1993</td>
<td>-33.53</td>
<td>443.97</td>
<td>0.999</td>
<td>99.85</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1994</td>
<td>-75.86</td>
<td>448.22</td>
<td>0.999</td>
<td>99.73</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1995</td>
<td>-105.04</td>
<td>458.38</td>
<td>0.999</td>
<td>99.72</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1996</td>
<td>-62.50</td>
<td>444.04</td>
<td>0.999</td>
<td>99.53</td>
<td>&lt;0.0000</td>
</tr>
<tr>
<td>1997</td>
<td>-71.86</td>
<td>457.37</td>
<td>0.999</td>
<td>99.78</td>
<td>&lt;0.0000</td>
</tr>
</tbody>
</table>

definition does not take into account the nature of the different components of TOW regarding climate (rain, dew, fog, water adsorption) and the nature of the metal and the corrosion products.

**TOW-ISO under heat trap conditions**

A simple regression was made between time and TOW-ISO for the different test stations under heat trap conditions for a two year exposure time. The results were the following: Heat trap conditions [26-27] refer to the exposure of samples inside metallic boxes. In those conditions of partially closed metallic boxes, sun irradiation causes a significant increase in temperature and the maximum values of air temperature are obtained under
these conditions. Some electro-electronic items are used under these conditions.

The results of the regression are the following:

Quivican rural test station, Cuba:
\[ t = -0.005 + 0.0026 \text{ TOW-ISO} \]
\[ r = 0.999 \quad r^2 = 99.94 \quad P < 0.0000 \]

Campeche PCGM coastal test station, Mexico:
\[ t = 0.177 + 0.0032 \text{ TOW-ISO} \]
\[ r = 0.999 \quad r^2 = 99.79 \quad P < 0.0000 \]

CNIC urban rural test station, Cuba:
\[ t = 0.0011 + 0.003 \text{ TOW-ISO} \]
\[ r = 0.999 \quad r^2 = 99.84 \quad P < 0.0000 \]

Cojimar coastal test station, Cuba:
\[ t = 0.097 + 0.0035 \text{ TOW-ISO} \]
\[ r = 0.999 \quad r^2 = 99.9383 \quad P = 0.0000 \]

The results show that a perfect relation exists between time and TOW-ISO, so both variables are equivalent and can be used for purposes of long term prognosis.

There are some small differences between the metallic boxes used in Cuba and Campeche. On figures 1 and 2 it can be observed that Cuban metallic boxes are relatively more closed than the one used at Campeche PCGM corrosion station.

**Figure 1.** Metallic box exposed at Cojimar coastal station in the north shore of the City of Havana. Similar metallic boxes are exposed at CNIC and Quivican Cuban stations. Samples and contaminant detector are placed inside the metallic boxes.
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Figure 2. Metallic boxes exposed at Campeche PCGM coastal station at 300 m of the shoreline in the City of Campeche (front view). Samples and contaminant detectors are placed inside the metallic boxes. As it can be observed, this metallic box has a wider window than those used in Cuban stations.

TOW-ISO under heat trap conditions at long term exposure

It is very well known the equation:

\[ K = a \tau^b \]

Where:

- \( a \) = constant
- \( b \) = coefficient that indicates the protective properties of the corrosion products layer
- \( \tau \) = Actual time of wetness (effective time during which corrosion process occurs)

It is very wide used in studying the atmospheric corrosion process and its development with time. As smaller will be coefficient \( b \), it is supposed that the protective properties of the corrosion products layer are higher.

On Table 6 it is shown a comparison between data fitness using TOW calculated according to ISO 9223 and time. It can be observed that there are not significant differences in using TOW or time because \( r^2 \) is almost the same in both cases. It could be explained supposing a direct relationship between time and TOW, that is, TOW increases with time. If, in general, there should be differences in TOW for the different climatic seasons, these are not significant for the total time.
Table 6. Statistical fitness of data of corrosion of Copper, Steel, Nickel and Tin inside a metallic box (heat trap conditions) respecting time and TOW according to ISO definition.

<table>
<thead>
<tr>
<th>Station</th>
<th>Metal</th>
<th>$K = a \tau^b$</th>
<th>$K = a \tau^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$a$  $b$  $r^2$</td>
<td>$a$  $b$  $r^2$</td>
</tr>
<tr>
<td>Cojimar</td>
<td>Copper</td>
<td>0.0009 0.847 0.138</td>
<td>0.805 49.76</td>
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<td>Steel</td>
<td>0.0038 1.185 4.284</td>
<td>1.455 97.11</td>
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<tr>
<td></td>
<td>Tin</td>
<td>0.0014 0.817 0.177</td>
<td>0.795 98.41</td>
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<td></td>
<td>Nickel</td>
<td>n.w.l. n.w.l. n.w.l.</td>
<td>n.w.l. n.w.l.</td>
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<tr>
<td>CNIC</td>
<td>Copper</td>
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<tr>
<td>(urban)</td>
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<td>0.716 82.98</td>
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<tr>
<td></td>
<td>Tin</td>
<td>0.0044 0.766 0.949</td>
<td>0.545 97.81</td>
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<tr>
<td></td>
<td>Nickel</td>
<td>9.7180 1.216 0.015</td>
<td>1.163 95.98</td>
</tr>
<tr>
<td>Quivicán</td>
<td>Copper</td>
<td>0.0017 0.986 9.412</td>
<td>1.083 98.68</td>
</tr>
<tr>
<td>(rural)</td>
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<td>0.0206 1.087 9.412</td>
<td>1.083 98.68</td>
</tr>
<tr>
<td></td>
<td>Tin</td>
<td>0.0135 0.705 9.412</td>
<td>1.083 98.68</td>
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<td>Nickel</td>
<td>7.2561 0.953 9.412</td>
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<tr>
<td>Campeche</td>
<td>Copper</td>
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<tr>
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<td>1.083 98.68</td>
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<tr>
<td></td>
<td>Nickel</td>
<td>0.0000002 1.851 9.412</td>
<td>1.083 98.68</td>
</tr>
</tbody>
</table>

n.w.l.= No weight loss detected.

2.3. Indoor humidity

Under indoor conditions, in the same way than outdoors, it is necessary the presence of surface humidity for corrosion to occur due to the electrochemical nature of the atmospheric corrosion process; however, in indoor conditions there are no precipitations and the presence of surface water depends mainly on water content in the air and changes in temperature on the surface, as well as the presence of hygroscopic substances on the metallic surface.

Indoor temperature and relative humidity appreciably depends on the ventilation level, on the use or not of air conditioner or heating systems and of the thermal isolation. Leygraf reports [28] that indoor relative humidity ranges from 15 to 85% with an average value of 50%. In Cuba [29] average values significantly different to 50% have been found, because inside a closed storehouse (no windows) during one year an average value of 89,5% is reported. In a storehouse having windows the average value is of 79,5%. In a storehouse having a dehumidifier system the annual average relative humidity diminishes to 74,5%, still significantly high respecting Leygraf report. In two storehouses without climatic control it is reached a 100% of relative humidity, while in the storehouse submitted to dehumidification the relative humidity reaches 85%. Changes in indoor relative humidity are lower
than those occurring outdoors, without the strong change caused by the difference between night and day. In this way, the most probable way the metallic surface can be humid is through water adsorption, although it can be observed that a significant relative humidity is reported indoors respecting Europe, so a higher corrosion should be determined. The higher temperature of the Cuban climate causes also the existence of higher water content and increases the possibilities of water condensation.

Under indoor conditions, wind rate is lower than outdoors [30]. In this way, outdoor conditions promotes a fast surface drying due to the influence of air and sun radiation, and also a more frequent surface wetness, thicker water layers due to rainfall, factors almost nonexistent in indoor conditions. Another factor nonexistent in indoor conditions is the washing effect on the metallic surface by precipitations.

It is important to remark that indoors, TOW-ISO is higher in storehouses without ventilation than outdoors in tropical humid climates. ISO 9223 classifies TOW for no ventilated storehouses as $\tau_5$ (more than 5500 h/y), whereas for outdoor conditions it is $\tau_4$ (2500-5500 h/y). Taking into account that indoors corrosion rate is significantly lower respecting outdoors, it can be perfectly understood that the development of corrosion under adsorbed water is very low respecting outdoors. In these conditions, the magnitude of corrosion will be determined by the possibilities of acceleration that could cause contaminants, being the presence of water on the surface a requirement for the occurrence of corrosion, but not for determining the rate of the corrosion reaction.

When the wind velocity is lower, drying process could be larger and could be a significant part of the dry/wet cycle. It also depends on the temperature existing on the metallic surface. On ISO-9223 there are not considered changes in the dry/wet cycles.

The deposition of contaminants in the surface usually causes an acceleration of the corrosion process; however, there should not be excluded the possibility that a given contaminant could diminish corrosion rate, as it could be the case of ammonia and its influence on steel (due to its alkaline properties, it could induce the passivation of steel).

An important difference between outdoor and indoor conditions is that in the last one there is no washing of contaminants by precipitations. Contaminants deposition is lower, but it increases with time. In these conditions, the presence of adsorbed water is necessary for corrosion to occur, but the rate of the process depends on the acceleration cause by contaminants. The calculation of TOW-ISO should not be as important as outdoors, because adsorbed water could be present all time. It has been reported a significant decrease in adsorbed water as temperature increases in Cuban climate [17].
In indoor conditions, the role of airborne salinity significantly diminishes, because the deposition rate is significantly lower than outdoors [29].

Stratmann reports [31-32] polarization curves on metallic surfaces covered by electrolyte layers as thin as 2 micrometers without using Luggin capillary, but using a Kelvin probe as reference (it is not necessary a contact to the surface). In this way there is avoided the effect in the polarization curve caused by the presence of a capillary having aqueous solution inside. It was possible to study the drying process, observing that at the beginning oxygen reduction increases due to a fast transport of this element through the thin electrolyte layer. Corrosion rate was determined by the oxygen consumption in a closed volume. It was shown that corrosion rate of pure steel could be divided into three parts: the increase in the oxygen diffusion current at the beginning, passivity of the surface in a second period and the diminishing in the oxygen reduction at the end of the drying process.

Recent reports about the microdroplets formation in the starting periods of atmospheric corrosion [19-22] show that the idea of a thin uniform water layers is not completely in accordance with the reality. It has been observed that when a water drop is on the metallic surface, formed in the place where a salt deposit existed before, microdroplets are formed around this central drop. The cathodic process takes place in these surrounding microdroplets, meanwhile the anodic process takes place in the central drop. This idea is not consistent with the proposal of a uniform water layer on the surface and it is very probable that this situation could be obtained under indoor conditions. It has been determined that microdrops (about 1 micrometer diameter) clusters are formed around a central drop. An important influence of air relative humidity is reported on microdrops formation. There is a critical value of relative humidity for the formation of microdrops. Under this value no microdroplets are formed. This value could be considered as the critical relative humidity. This situation is very similar to the process of indoor atmospheric corrosion: presence of humid air, deposition of hygroscopic contaminants in the surface, formation of microdrops. Water is necessary for corrosion reaction to occur, but the reaction rate depends on the deposition rate and nature of contaminants.

ISO 11844-3[33] establishes that the combination of different parameters is what determines the corrosivity of the atmosphere. Under indoor conditions, corrosion process depends on a more complex number of parameters than outdoors; however in the same way than outdoors two types of parameters are considered:

- Air temperature and humidity
- Air contaminants (gas and particulates)
The effect of these two groups of parameters is linked, because contaminants need a given level of humidity to act on the corrosion process. A combination of contaminants could have different effects than the sum of the individual effects. In ISO 11844-1 [34] it is explained that the impact of temperature and relative humidity cannot be expressed according to ISO-9223. It could be explained taking into account that the nature of TOW is very different to outdoors conditions.

Recent reports [35-36] on the use of atmospheric corrosion sensors based on changes in electrical resistance showed that when there were no contaminants, in tests of 100-110 h., corrosion rate was zero or insignificant. These sensors can determine changes in metal thickness lower than one nanometer. However, in the presence of 0.08 ppm of SO$_2$ or 200 mg/m$^2$ of NaCl in the system, changes in thickness where always detected over 75% of relative humidity. Corrosion rate was determined at temperatures of 20, 30 and 40 °C and the Arrhenius equation was used to calculate the activation energy of the reactions. This method is very similar to the natural conditions.

2.4. TOW at different exposure conditions

TOW depends mainly on the meteorological parameters, the nature of the metal, the properties of the metallic surface and of the corrosion products layer formed. The most important climatic factors on the corrosion process are relative humidity, sunshine hours, temperature of the air and the metal surface, wind velocity and duration and frequency of the rain, dew and fog.

Dew or condensation of humidity is considered an important cause of the corrosion of metals. Its formation depends on the relative humidity and on the changes of temperature. Dew does not wash the metallic surface so the concentration of pollutants is relatively high and could be more aggressive than rain. Rain gives rise to the formation of a thick layer of water and also adds corrosive agents such as H$^+$ and SO$_4^{2-}$; however it can wash away the contaminants as well. It will depend on the intensity and duration of the rainfall.

The results of a wide evaluation carried out on different exposure conditions in Cuba have already been published [5-6]. The following Cuban corrosion test stations and conditions were considered:

- Coastal test station under outdoor, sheltered and ventilated shed conditions
- Urban-industrial test station under outdoor and sheltered conditions
- Rural test station under outdoor, sheltered, ventilated shed and closed space conditions

As was expected, the higher corrosivity corresponds to the coastal station. It was also noted that the higher the corrosivity of the atmosphere, the higher the difference between the outdoor corrosion rate and the indoor corrosion rate.
The atmospheric corrosion rate of metals depends mainly on TOW and pollutants; however, if the differences in the corrosion process between outdoor and indoor conditions are taken into account, the influence of direct precipitation such as rain is very important for outdoor and negligible for indoor conditions. The acceleration effect of pollutants could change depending on wetness conditions of the surface, so the influence of the rain time and quantity should be very important in determining changes in corrosion rate.

A model was proposed which considers the influence of the relationship between rain quantity/time and the interaction between pollutants at different TOW. TOW-ISO was divided into two parts, when air temperature was lower than 25 °C and when air temperature was higher than 25 °C (up to 35 °C). In this way three different times of wetness are considered: time due to rain (included independently of TOW-ISO), time including rain, dew and fog (TOW-ISO at air temperature <25 °C), and time when evaporation of the electrolyte layer prevails (air temperature >25 °C)-in some cases this last variable should also include rarely time of rain. This model was developed based on previous results indicating that when air temperature is over 25 °C a significant diminution of the surface water layer takes place, possible due to a significant increase in evaporation of this water layer.

The suggestion of dividing the time of wetness into three different contribution parts was made in order to get a more quantitative approach step to study the atmospheric corrosion process. The influence of time and quantity of rain is very important for characterizing differences between indoor and outdoor corrosion. It was observed that in all cases the variable TOW 25-35 is affected by a negative sign, indicating a diminishing of corrosion rate when this variables increases, what is according to the fact that when temperature is over 25 °C the electrolyte layer significantly diminishes instead of existing a high relative humidity.

The cleaning effect of rain is important in the corrosion process. In many cases this variable is significant, as well as the inclusion of time of rain as an independent variable in explaining the influence of different parameters in atmospheric corrosion rate of basic metals.

2.5. Air temperature, relative humidity, TOW-ISO, corrosion of steel and deposition of contaminants at different exposure conditions

A comparison of the behavior of air temperature for different exposure conditions in Cuba and Campeche using data corresponding to one year is presented on figure 3. It is only an approximated behavior because there was not used the same year for all exposure conditions. Average air temperature is around 25 °C for all conditions, slightly higher in the storehouses in urban
Atmospheric corrosion in tropical humid climates and rural sites, as also at Campeche outdoor coastal station. No data of average minimum and maximum temperatures were available for storehouses. It can be observed that higher temperatures are reported for conditions of heat trap and lowers for storehouses. The wider interval of temperature is also obtained at heat-trap conditions, probably due to the emission of heat of the painted galvanized steel used in the construction of the metallic boxes. The lower interval between maximum and minimum temperature is obtained in the case of storehouse. It is due to the fact that these are wide and close spaces with concrete walls where air temperature changes are relatively low. The lower temperature interval is reported for the storehouse with air conditioner.

In outdoor, sheltered conditions and ventilated sheds there is reported a second wide interval of temperature. The lower and higher temperature is reported for the outdoor rural station, because it is relatively far from the seashore and its influence is lower.

The behavior of relative humidity is shown of figure 4. It is interesting to note that maximum relative humidity is obtained in almost all exposure conditions, excepting the storehouse having air conditioner, rural ventilated

![Outdoor and indoor air temperature](image)

**Figure 3.** Changes in average, average maximum and minimum, maximum and minimum air temperature depending on exposure condition and type of atmosphere for test stations located in the western side of the Cuban Isle and Campeche PCGM coastal station.
shed and Campeche heat-trap conditions, the last two with a very small difference. It means that regarding relative humidity the possibilities of condensation of moisture are significantly higher if the required conditions are available. Average relative humidity is around 80%, higher in the storehouse having no windows and lower in the ventilated shed located in the coastal site. It is very well known that in a closed place relative humidity increases. No data of average maximum and minimum relative humidity for storehouses were available. The lower average in relative humidity between storehouses is reported for the storehouse having air conditioner as it should be expected. The lower average RH is reported for Campeche PCGM (outdoor and indoor) coastal station. This station is located on a roof, where humidity should be lower regarding a soil covered by grass as Cuban stations. By other way, in general, relative humidity at Campeche is lower than in Cuba (and temperature higher). Both territories are classified as humid tropical (τ₄), but Campeche presents lower values of relative humidity regarding Cuba.

These two figures refer to the temperature-relative humidity complex, but there is an important difference in the environment between outdoor, sheltered, ventilated shed and indoor corrosion. Precipitation is only possible in outdoor conditions, although condensation of moisture is possible in sheltered conditions and less probable in ventilated storehouses and

![Outdoor and indoor relative humidity](image)

**Figure 4.** Changes in average, average maximum and minimum, maximum and minimum air relative humidity depending on exposure condition and type of atmosphere for test stations located in the western side of the Cuban Isle and Campeche PCGM coastal station.
heat trap conditions there are no possibilities of precipitation and condensation of moisture is more difficult.

A calculation of time of wetness according to ISO 9223, considered as the time when relative humidity is over 80% and air temperature over 0 °C is presented on figure 5.

It can be noted that the lower TOW is obtained for the storehouse having air conditioner and the higher for the storehouse located in the coastal site and the metallic box located in the rural site. According to these results, the higher possibilities of corrosion should be in these last conditions if we only consider the definition of TOW and the values obtained. However, it is very well known that the higher corrosion rate is usually obtained in outdoor or sheltered conditions. This figure shows that the concept of TOW established on ISO 9223 could not be used simply and many considerations have to be made. It should be limited to outdoor conditions and some considerations have to be made respecting the nature and characteristics of different meteorological parameters such as rain, dew, fog, i.e.

In other words, the concept of time of wetness (established in ISO 9223) shows limitations, because the nature and the changes occurred in the electrolyte formed on the metallic surface have clear differences between exposure conditions. There is a significant difference between outdoor time of wetness and sheltered or indoor TOW.
Figure 6. Average corrosion rate (g/m²) depending on exposure condition and type of atmosphere for test stations located in the western part of the Cuban Isle and Campeche PCGM coastal station.

Actually, the general concept of TOW (time during which corrosion reaction occurs) is, undoubtedly, correct and generally applicable, taking into account the electrochemical nature of the atmospheric corrosion process, but the estimation made by ISO 9223 has to be limited to specific conditions, mainly outdoors and taking into consideration the differences in the corrosion reaction as a function of the way the water is present on the surface, because, for example, rain forms an electrolyte in the metallic surface different to dew, and the formation of the electrolyte during rain also causes a diminishing rate of deposition of contaminants in the surface depending on the extent of rain. How can this complicated process be represented? Obviously, not by the simple concept established by ISO 9223. It should be also considered the nature of the metal and the corrosion products. Under outdoor conditions, the lower TOW-ISO value reported corresponds to Campeche coastal station. Average annual corrosion rate of steel reported for test stations depending on exposure conditions and type of exposure (see figure 6) is significantly different to the behavior of time of wetness for the same conditions. It is perfectly explained based on the influence of contaminants. Chloride deposition rate causes a significant acceleration of corrosion rate, which is the reason why the maximum annual corrosion lost is reported for outdoor conditions in the coastal zone, following sheltered and ventilated shed in the same coastal zone. Urban industrial atmospheres (outdoor, sheltered and ventilated shed) are the second one in weight lost and rural stations the less aggressive atmosphere. Regarding indoor corrosion, the lower weight lost is determined in the storehouses and heat trap conditions increase respecting the last one.
A significant difference in steel corrosion exists between Campeche and Cuban coastal stations. It is mainly caused by a significant difference in chloride deposition.

As it can be observed, in the storehouse where there is determined the maximum time of wetness, it is reported the lower corrosion rate. It is explained based in the fact that in this case TOW consists mainly in air humidity without the contribution of any precipitation or condensation (no rain, no dew, no significant condensation). It is a demonstration that the estimation of time of wetness according to ISO 9223 presents limitations.

Changes in steel corrosion rate for different exposure conditions and types of atmosphere are better explained based on average deposition rate of Chlorides, as can be observed on figure 5. It can be note that chloride deposition is higher in Cuban coastal stations, as it should be expected, and it is in agreement with a higher weight lost for these stations. In the case of Campeche chloride deposition is lower as also corrosion of steel.

The lower values of chloride deposition are reported for the storehouses, where coincidently, there are reported the lower weight losses. Under heat trap conditions there is a given increase in Chloride deposition, that is why corrosion rate of steel is higher than in storehouses.

On figure 7 there is represented average chloride deposition rate determined in Cuba and Campeche coastal station for different types of atmosphere and exposure conditions. The results are very similar to those

**Figure 7.** Annual average Chloride deposition rate for test station located at the western side of the Cuban Isle and Campeche PCGM coastal station depending on exposure conditions and type of atmosphere. Wet Candle method was used for determination of chloride deposition at Campeche and Dry deposition methods for Cuba. A correct comparison can not be made under these conditions.
presented on figure 6, particularly respecting outdoor and ventilated shed conditions. Chloride deposition is determined under shelter, that is why it is assumed the same value for outdoor and sheltered conditions; however, it is very well known, the significant influence of precipitations upon outdoor corrosion and its negligible effect under sheltered conditions. In storehouses and heat trap conditions the influence of Chloride deposition significantly diminishes; however, under heat trap conditions the higher corrosion of steel is reported for the Cuban coastal test station. Corrosion at Campeche coastal station is lower. Respecting chloride deposition, the determination at Campeche coastal station was carried out by the Wet Candle Method and at Cuba by a dry procedure reported in [37]. Taking into account that a different method for determination of chloride deposition was used a correct comparison can not be made.

The average deposition of sulfur compounds found at the Cuban western side test station and Campeche PCGM coastal station is presented on figure 8. As can be expected, the higher sulfur compound deposition rate corresponded to the urban industrial station in outdoor conditions. There is no report for ventilated shed. Part of the sulfur compound deposition for coastal stations should not be attributed to gaseous SO$_2$ or SO$_3$, because it is well known that airborne salinity contains sulphate ions and the procedure used for determining sulfur compounds deposition is sensible to sulphate ions(see ISO 9225 [38]). A direct relationship between average corrosion rate and sulfur compound deposition is not observed as in the case of chloride deposition. It confirms the importance of Chloride deposition in determining corrosion aggressivity in Cuba.

![Sulphur compounds deposition rate at different exposure conditions](image)

**Figure 8.** Annual average sulfur compound deposition rate for test stations located in the western side of the Isle of Cuba and Campeche PCGM coastal station depending on exposure conditions and type of atmosphere.
2.6. TOW-ISO and rain

Chloride ion is one of the most important natural pollutants influencing corrosion; particularly in the tropical humid conditions of Cuba and Campeche in Mexico; however, its role may change depending on climate. A very humid climate can cause a fast leaching of the chloride ions and decreases its effect on the acceleration of corrosion rate. A different acceleration rate has been reported for chloride ions between Eastern and Western Caribbean [4]. In a given climate the influence of rain could change the acceleration caused by chloride ion on metal corrosion. Differences between rainy and dry periods could be important in determining such acceleration. The electrochemical mechanism of corrosion by chloride ions does not change, but the time during which chloride ions acts on the metallic surface and their concentration may appreciable change, depending on factors such as climatic conditions and nature of corrosion products.

A research about the role of the rainfall characteristics on the acceleration rate caused by chloride ions between two stations having noticeable differences in rain regime was already published [39]. The influence of chloride ions at Medellin and Havana corrosion stations was studied by submitting samples of steel and copper to salt spray during exposure to the open atmosphere. Up to 12 months of exposure, the acceleration on the deterioration caused by chloride ions was notably up to 12 months of exposure, being higher at Havana station for steel and copper.

The corrosivity category for steel and copper (C3) in natural conditions in Havana increases to C5 for copper and over C5 for steel when salt spray is applied; however at Medellin, copper corrosion increases to C4 for copper and C5 for steel under the application of salt spray.

The acceleration rate caused by the addition of a salt spray under natural conditions causes a higher acceleration of corrosion rate at Havana. For copper, the difference does not appreciably change with time; but it does for steel. A more aggressive action of chloride ions is observed in the case of steel.

The remarkable difference in the acceleration caused by chloride deposition rate in Havana and Medellin could be due to the considerable difference in the rain regime between both sites. Other characteristic of the environment could also have influence, but rain should play an important role.

Samples were submitted to the same artificial chloride deposition rate at Havana and Medellin stations (supposing that differences concerning natural values of chloride deposition rate are not very significant). Samples were prepared from the same origin material, so the differences on the corrosion behavior can be associated only to climatic characteristics. In the case of Medellin the washing effect of rain should be higher than in Havana because
the rain amount is more than four times than the reported for Havana during the exposure period. It explains why a lower acceleration rate of chloride ions is obtained at the former station. Based on this fact, a model for studying the influence of the washing or cleaning effect of rain in the determination of the acceleration rate of chloride ions is proposed.

The bi-logarithm equation for atmospheric corrosion establishes that:

\[ K = a t^b \]

where \( K \) = mass loss; \( a \) and \( b \) = constants; \( t \) = time of exposure.

In the presence of a given value of chloride deposition rate, an acceleration of corrosion takes place; this acceleration means that corrosion increases with time. At the same time, the acceleration of corrosion caused by chlorides depends on the washing or cleaning effect of rain. Under this condition the following model is proposed:

\[ K = a t^b [\text{Cl}]^c (W/D)^d \]

where \( K \) = mass loss; \( a, b, c \) and \( d \) = constants; \([\text{Cl}]\) = chloride deposition rate; \( W \) = rainfall (mm); \( D \) = rainy days; \( t \) = time of exposure.

It has been considered that the washing or cleaning effect of rain could be represented by the ratio \( W/D \) (amount of rain/frequency of rain). This washing effect could affect the influence of chloride deposition rate on corrosion.

A regression analysis including steel mass loss data for Havana and Medellin showed the following results:

\[ K = 18.8516 t^{1.0947} [\text{Cl}]^{0.4313} (W/D)^{-0.2447} \]
\[ r^2 = 98.11 \]

where \( K \) = mass loss (g/m\(^2\)); \( t \) = time of exposure (months); \([\text{Cl}]\) = chloride deposition rate (mg/m\(^2\) d); \( W \) = rainfall amount (mm); \( D \) = number of rainy days.

A regression analysis including copper mass loss data for Havana and Medellin showed the following results:

\[ K = 1.2466 t^{0.7858} [\text{Cl}]^{0.2616} (W/D)^{-0.2379} \]
\[ r^2 = 98.08 \]

A good data fit is also obtained for copper. It confirms that the complex chloride deposition rate–rain regime is important for determining mass loss of copper and steel. In this model TOW-ISO has not been used and a good fitness has been obtained.

It confirms that the acceleration rate caused by chloride ions on atmospheric corrosion of steel and copper depends on the characteristics of
Atmospheric corrosion in tropical humid climates

rain regime. For a place having high amount and time of rain, a lower acceleration on corrosion rate should be expected for a given chloride deposition rate.

Data of outdoor exposure of carbon steel and copper during two years using samples sizing (1 x 5 cm) were processed together with data for the same exposure periods of TOW-ISO at temperature 25 °C or below, TOW-ISO at temperature higher than 25 °C, time of rain and amount of rain. The regression equation obtained was the following:

\[ K_{\text{steel}} = 59.93 + 0.021 \text{ TOW-ISO } T \leq 25 + 0.218 \text{ TOW-ISO } T > 25 - 2.05 t_{\text{rain}} - 1.28 \text{ mm } / t_{\text{rain}}. \]

As it can be observed, the washing and cleaning effect of rain causes that time of rain and the ratio amount/time of rain show a negative sign, indicating a diminution of corrosion when time and ratio amount/time of rain increases, confirming the importance of washing and cleaning effect at Campeche tropical climate.

The washing and cleaning effect of rain is not included and is far from the concept of TOW established on ISO 9223 standard.

2.7. Corrosion in tropical coastal atmospheres. Role of TOW-ISO

Airborne salinity can be determined using different methods. In corrosion research the standard method (Wet Candle method) is established in ISO-9225: 1992 [38]; however, it is not the only method traditionally used. In the case of Cuba it has been widely used the method named as dry plate method, consisting in the employment of a dry cotton fabric of known area exposed under a shed. The amount of chloride deposition on the gauze is determined analytically at the end of the exposure period (two months) and the deposition rate is calculated.

A report [40] about the simultaneous comparison between values obtained using Wet Candle and Dry plate methods at different corrosion stations in Cuba showed that there is not a good correlation for the rural station having lower values of salinity; however, a good correlation was obtained for stations having higher values of salinity. The following regression equation was obtained:

\[ [\text{Cl}^-]_{\text{W.C.}} = -54.5 + 1.6 [\text{Cl}^-]_{\text{D.P.}} \]

\[ r = 0.98 \quad n=14 \quad P<0.005 \]

where:

\( [\text{Cl}^-]_{\text{W.C.}} = \) Chloride deposition rate determined using Wet Candle method

\( [\text{Cl}^-]_{\text{D.P.}} = \) Chloride deposition rate determined using Dry Plate method
Chloride deposition rate was determined using Wet Candle and Dry Plate methods in the corrosion stations Santiago de las Vegas (rural-urban), Casa Blanca (industrial-marine-urban), Via Blanca (industrial-urban-marine) and Cojimar (marine).

On figure 9 it can be noted a significant difference between Steel corrosion rate and Chloride deposition between the north and the south shores. It is caused because, in general, trade winds in the north shore come from the Ocean and in the south shore from the earth. In addition, cold fronts always come from the north. The territory is flat, presenting only small hills, so Chloride deposition reaches almost all the territory. It can be seen that even in places located at 15-30 km from the north seashore a significant Chloride deposition rate is determined (3.4-8.5 mg/m²d-classified as S₁ according to ISO-9223). Sulfur compounds deposition has also some relation with Chloride deposition. The higher values correspond to coastal and industrial stations. It means that, taking into account that the determination using alkaline surfaces is sensible to different sulphur compounds, it includes, in addition to sulphur oxides, sulphates coming in airborne salinity. Another possible sulphur compound determined could be H₂S. Changes in TOW-ISO are negligible between all the test stations of the Cuban western side. All values are classified as τ₄ according to ISO 9223. In these conditions main changes depend on contaminants deposition.

Figure 9. Changes in annual Corrosion rate of mild steel flat samples, annual average Chloride deposition rate determined by the dry plate method and annual average Sulfur compounds deposition rate determined by alkaline surfaces method in the west side of the Cuban Isle.
Due to the hygroscopic properties of the salts deposited in the surface there is no doubt that corrosion should occur at a relative humidity lower than 80%, so in this case the use of TOW-ISO has no sense.

On figure 10 the annual average Chloride deposition rate determined at three zones of the Yucatán Peninsula is presented: Puerto Progreso and Puerto Morelos in the mouth of the Gulf of Mexico and Campeche and Veracruz inside this Gulf as function of the distance to the shoreline. As can be seen, Chloride deposition is very similar at Puerto Progreso, Puerto Morelos and Veracruz; however, the values of Chloride deposition are significantly lower for Campeche. It could be explained based on the fact that predominant winds in Campeche most of the year are from earth to the Gulf of Mexico. Another factor is that sea Campeche usually has no wave movement. It is a similar situation to the south shore of the Cuban Isle where a lower Chloride deposition is determined.

Changes of corrosion rate of steel as function of distance to the shoreline are lower respecting Veracruz. It is in perfect agreement with the influence of Chloride deposition. In the case of Puerto Morelos and Puerto Progreso it is also reported a significantly higher corrosion rate respecting Campeche.

Changes in corrosion rate depending on the climatic season in coastal atmospheres

Chloride ion is one of the most important natural pollutants influencing corrosion; however, its role may change depending on climate. A very humid climate can cause a fast leaching of the chloride ions and diminish their effect on the acceleration of corrosion rate. A different acceleration rate has been reported for chloride ions between Eastern and Western Caribbean [4].

It has been reported that the acceleration rate caused by chloride ions on atmospheric corrosion of steel and copper depends on the characteristics of rain regime. For a place having high amount and time of rain, a lower acceleration on corrosion rate should be expected for a given chloride deposition rate [39].

It is very well known that in tropical climate there are two main seasons, rainy season and dry season. Under this conditions, the acceleration caused by chlorides should be higher in the dry season (winter period) and lower in the rainy season. As an example, on Table 7 presents statistical parameters calculated for corrosion rate of steel at Viriato coastal stations for periods of six months corresponding to the wet season (may to october) and dry season (november to april). All steel samples were exposed for a six months period corresponding, starting on may or on november. Data correspond to the period may/1987 to November/1991.
Figure 10. Annual average of deposition rate of Chlorides for different sites of the Yucatán Peninsula: Puerto Progreso and Puerto Morelos (Yucatán and Quintana Roo States), Campeche and Veracruz States.

Figure 11. Annual average corrosion rate of carbon steel at Campeche, Veracruz and Puerto Morelos as function of distance to the shoreline.

As can be seen, a remarkable difference is determined for samples exposed in winter and in summer six months period at Viriato coastal station. It shows that a marked difference in aggressivity exists between climatic seasons in tropical climate. It is confirmed by the ratio Summer/Winter.
Table 7. Average corrosion rate of steel, standard deviation, average Chloride deposition rate, standard deviation and average TOW-ISO (h) for six months exposure periods at Viriato coastal station, Cuba.

<table>
<thead>
<tr>
<th>Climatic season</th>
<th>Average Corrosion rate of steel (g/m²)</th>
<th>Standard deviation</th>
<th>Average Chloride deposition rate (mg/m²d)</th>
<th>Standard deviation</th>
<th>TOW-ISO (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer (May/oOct)</td>
<td>569.4</td>
<td>167.6</td>
<td>225.0</td>
<td>107.7</td>
<td>2112</td>
</tr>
<tr>
<td>Winter (Nov/Apr)</td>
<td>2111.5</td>
<td>892.8</td>
<td>486.3</td>
<td>174.2</td>
<td>2000</td>
</tr>
<tr>
<td>Summer/Winter</td>
<td>2.53</td>
<td>--</td>
<td>4.34</td>
<td>--</td>
<td>1.06</td>
</tr>
</tbody>
</table>

Table 8. Average Chloride deposition rate for different test stations of Campeche.

<table>
<thead>
<tr>
<th>Test station</th>
<th>Average Chloride deposition rate (mg/m²d)</th>
<th>Summer/04</th>
<th>Summer/05</th>
<th>Winter/03-04</th>
<th>Winter/04-05</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMN</td>
<td></td>
<td>16,16</td>
<td>26,31</td>
<td>18,82</td>
<td>26,05</td>
</tr>
<tr>
<td>PCGM</td>
<td></td>
<td>26,40</td>
<td>18,02</td>
<td>27,42</td>
<td>25,24</td>
</tr>
<tr>
<td>CRIP</td>
<td></td>
<td>47,97</td>
<td>74,95</td>
<td>157,24</td>
<td>114,99</td>
</tr>
<tr>
<td>TEC</td>
<td></td>
<td>45,77</td>
<td>42,86</td>
<td>77,47</td>
<td>67,11</td>
</tr>
</tbody>
</table>

It means that a higher acceleration caused by Chloride ions take place in the season having lower amount of rain. Changes in TOW-ISO are not remarkable. A slightly higher TOW-ISO is reported for summer period, the time when corrosion rate is lower. It seems that it has no sense to use TOW-ISO in studying atmospheric corrosion in tropical coastal atmospheres, because due to the hygroscopic nature of coastal salts, corrosion rate could take place very often at RH lower than 80%.

On Table 8 presents data for four test sites in Campeche (having lower deposition rates than in Havana). Chloride deposition is higher in winter periods for Campeche CRIP and Campeche TEC, the two sites nearer to the shoreline and with S1 ISO classification. In the case of Campeche SMN and Campeche PCGM (classification So according to ISO) the tendency is to a higher Chloride deposition in winter, but there are values of average deposition higher during the summer period.
Dependence between Chloride and sulphur compounds deposition rate in coastal zones

Airborne salinity contains not only sodium Chloride, but also other anions like carbonate, sulphate, nitrate and so on. Near the shoreline it is possible that the main source of sulphur compounds should be airborne salinity and under these conditions the main type of sulphur compound presented should be sulphate instead of sulphur dioxide. To confirm this supposal, Chloride and Sulphur compounds deposition rate determined at Viriato coastal station during 3 years (1986-1989) were processed.

The relationship obtained between Chloride and Sulphur compounds deposition rate for Viriato coastal station is shown on figure 12. A significant correlation coefficient of 0.68 is obtained. It means that at this coastal station, the main source of sulphur compounds is sulphate coming from airborne salinity and not SO₂ coming from human activity.

When the type of sulphur compounds changes, the values of deposition rate obtained are representative of more than one sulphur compound (this method have been developed for SO₂ deposition). The influence on corrosion rate of SO₂ is normally different to sulphate. It means that a different acceleration rate on corrosion should be determined depending on the main source of sulphur compounds, because the methods established on ISO 9225 are sensible to all sulphur compounds and sometimes the type of compound changes. Under these conditions, methods for determining the different sulphur compounds should be used or, in a more simple way, the results of the determination should be used taking into account the main source of sulphur compound, for example, sulphate in coastal sites, H₂S near oil wells, SO₂ in industrial sites and so on.

![Figure 12. Dependence between Sulphur compounds deposition rate and Chloride deposition rate determined at Viriato coastal station during 3 years.](image-url)
Conclusions

TOW considered as the time during which corrosion occurs is an important parameter in atmospheric corrosion of metals. It defines the possibility for atmospheric corrosion to occur based on its electrochemical nature, but corrosion rate will depend mainly in the acceleration caused by contaminants deposition and other factors.

TOW according to ISO definition shows several limitations in tropical climate:

- It is a variable perfectly linked to time. It is not necessary to calculate TOW-ISO when the development of corrosion rate on time is studied because a linear relationship exists between time and TOW-ISO.
- Its nature changes from outdoor to indoor conditions. Higher TOW-ISO values are reported for indoor conditions where corrosion rate is significantly lower. It is mainly due to the absence of precipitations.
- It has no sense to calculate TOW-ISO for coastal tropical atmospheres, because in those conditions corrosion process occurs at relative humidity lower than 80%. It has been determined that water adsorption by corrosion products is polymolecular in these conditions. As analogy, in highly polluted atmospheres, corrosion process should proceed at RH lower than 80%, so it has no sense to use TOW-ISO.
- TOW-ISO does not take into account the washing and cleaning effect of rain, a very important aspect in atmospheric corrosion outdoors.
- An upper limit for air temperature has not been included in TOW-ISO definition. Several results show that a significant change in TOW-ISO takes place at air temperature higher than 25°C and RH >80%.

In order to improve the estimation of TOW-ISO it is proposed:

- To establish an upper limit of temperature for TOW-ISO calculation, dividing TOW-ISO in two categories: Air temperature 0>25< and air temperature >25.
- To include time and amount of rain as an additional variable, taking into account the washing and cleaning effect of rain.
- To limit the use of TOW-ISO to outdoor and not highly contaminated environments.
- Always take into account the influence of contaminant deposition and its interaction with TOW.
- The concept of an adsorptive or liquid film of electrolyte on the metallic surface should include the possibility of the existence of localized presence of adsorptive or liquid films on the metallic surface, particularly in indoor conditions.
Respecting tropical coastal atmospheres:

- Corrosivity in tropical coastal atmospheres ranges between C3 and >C5 levels of ISO 9223. Depending mainly on wind patterns, in some coastal places of the Yucatan Peninsula and Cuba a lower corrosivity is determined. In the Yucatan Peninsula and Cuba, most of the values of corrosion rate over the maximum established by ISO standard are reported for sites at less than 150 m of the shoreline.

- The influence of chloride ions on outdoor corrosion changes depending on the climatic season. A higher corrosion rate is determined for winter or dry season respecting wet or summer season. It could be explained mainly based in the washing effect of rain (taking into account the increase in airborne salinity of winter season).

- Corrosion rate significantly decrease in tropical coastal atmospheres when metals are exposed in relatively closed environments.

- The determination of sulphur compounds according to ISO 9225 does not allow to distinguish between the different types of sulphur compounds presented in the atmosphere. In the case of coastal regions, the presence of sulphate as main type of sulphur compounds is very possible. Under these conditions, a different behaviour should be obtained in comparison with regions where main sulphur compound is SO₂.

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