Indoor and outdoor atmospheric corrosion of carbon steel and copper in tropical humid climate

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Abstract

This chapter presents the results obtained from indoor exposure for 36 months of carbon steel and electrolytic copper samples in tropical humid marine-urban climate. The indoor condition was used to simulate a rain sheltered cabinet in the climatic conditions of the City of San Francisco de Campeche.
Campeche in the Gulf of Mexico. The corrosion aggressivity of the atmosphere formed inside the box was found to be very high, based on the monitored chlorides and SO$_2$ deposition rates, and the Temperature/Relative Humidity complex.

The concentration of SO$_2$ and chlorides in the atmosphere were measured continuously in both conditions, indoor and outdoor. The Temperature-Relative humidity complex was found to be the main factor that influences in the kinetics of the atmospheric corrosion process, which varies considerably with the time and exposure condition. Indoor atmospheres guaranty high relative humidity during the major part of the year whereas avoid the run-off effect of corrosion products and deposited pollutants on the metallic surfaces due to rainfall.

1. Introduction

Durability and reliability of electric-electronic items depend upon design characteristics and their interaction with the environment during their service lifetime. One of the most important goals of the electric-electronic industry is to know how the way the environment acts during the degradation of metallic micro-components in order to develop technological and low cost solutions to the problem. Due to the increasing requirement for high reliability and performance of electric-electronic products for applications in telecommunications, energy systems, aeronautics, military equipment, car industry, and so on, a lot of effort has been made by manufacturers and research centres in order to get products for applications in tropical-humid climates with a minimum risk of corrosion degradation. Tropical-humid climates represent perhaps the most aggressive condition for electric-electronic products in terms of metal degradation due to indoor and outdoor atmospheric corrosion. This work presents one of the first attempts to methodologically study the factors, variables and mechanisms involved in the indoor atmospheric corrosion damage of metals used for the manufacturing of electric-electronic products. Research work conducted by several authorities around the world about atmospheric corrosion, considered and analysed the effect of the most persistent factors that determine the metals durability: a) chemical composition, b) surface condition, c) characteristics of the environment surrounding the metals [1-4]. Some of these factors are very difficult to control experimentally which finally brings about the need to carry out studies based on statistical treatment of data that allow defining variation ranges of the principal factors mentioned above.

In Mexico there is a huge diversity of climates and micro-climates even in areas not bigger than 100 km$^2$ which makes much more complicated the determination of the atmosphere aggressiveness in terms of metallic corrosion.
In the particular case of Campeche, located in the southeast of Mexico at (19°51’N, 90º32’ W), the city of San Francisco de Campeche has an urban-marine atmosphere. The city is located along the coast in the Gulf of Mexico. Its tropical humid climate exhibits very marked dry and rainy seasons. The effect of distance from the coast line upon the corrosivity of the atmosphere has been determined for the city of San Francisco de Campeche [5-10].

As mentioned by Corvo et al. in chapter 2 of this book, the atmosphere represents the most extended environment to which metallic engineering structures and components are exposed. Degradation of metals for electric-electronic applications due to their interaction with the atmosphere seems to be a negligible problem as in many cases the result of the process is not visually obvious. However, this phenomenon affects many sectors of the economy, mainly telecommunications, which are strongly related to transportation (ships, automobiles, buses, airplanes, trains). Infrastructure in general (bridges, highways, roads, ports) is also affected as well as buildings and tangible cultural heritage. Atmospheric corrosion, due to its electrochemical nature takes place in the presence of thin-film electrolytes, which is enough to produce degradation damage in electronics that in the majority of cases leads to early failures even in indoor atmospheres. Due to this, there is a need to characterize in detail indoor environments and their potential corrosion degradation effects on electronic materials. The corrosivity of indoor environments (atmosphere) can be assessed by exposing coupons of different metals in a specific environment of interest for real applications [11,12].

A very important aspect of atmospheric degradation of metals is the effect of air contaminants such as SO$_2$, NO$_x$ and Cl$^-$ (this one specially at places with tropical-marine climates). The concentration and deposition rate levels of pollutants associated to energy production and car traffic are increasing dramatically in the last 20 years in many developing countries many of which are located in regions with tropical climates, high relative humidity and high annual pluvial precipitation. Is in these regions where metallic degradation due to atmospheric corrosion is expected to be the highest compared even with places with the same average annual temperature under similar emissions of pollutants. As reported by Kucera et al. [4], the most influencing environmental parameter upon atmospheric corrosion rate of the principal engineering alloys, limestone and even for painted steel is the amount of SO$_4^{2-}$. Other parameters with high influence are SO$_2$ for carbon steel, rain pH for zinc and SO$_2$, rain pH and HNO$_3$ for limestone.

The principal aim of this work was to give a base for the methodological study of indoor atmospheric corrosion of carbon steel and copper used for electric-electronic products in tropical-humid climate. This will facilitate the
elaboration of international standards and methodologies as a guide for users to have quality assessment elements for electronic products. For manufacturers, the standards will give them tools to guarantee the proper performance of their products and to attend the market in countries with tropical-humid climates. The present work was conducted parallel to the Iberoamerican project “TROPICORR”, organised by CYTED from 2003 to 2007, although here we present results after three years of exposure.

2. Experimental

Measurement of environmental parameters is normally the faster way to characterise the corrosivity of the atmosphere and will always be required if it is necessary to consider measures for reducing the corrosivity should be carried out. Different combinations of parameters affect the atmospheres. The knowledge about possible sources for environmental effects must be obtained before the decision for the type of measurements needed is taken.

2.1. Sampling site

The exposure site was located 300 m away from the coast line at the Campeche University campus (CICORR), in the city of San Francisco de Campeche, Campeche in the Gulf of Mexico as shown in figure 1. This site has an urban-tropical humid atmosphere and is 6.9 km away from a thermoelectric plant.

![Figure 1](image.png)

**Figure 1.** Location of the exposure site where the cabinet was set up, showing the position of the CICORR and the thermoelectric plant.
plant which is the principal SO₂ emission producer. Its tropical humid climate exhibits very marked dry and rainy seasons. A combination of high temperatures (T) and annual time of wetness (TOW), due to high constant daily and monthly relative humidity (RH), make possible an accelerated electrochemical corrosion process in the presence of hygroscopic surface pollutants, such as chloride present in the coastal region. Veleva L. et al have reported an analysis of the principal characteristics of that climate [9].

2.2. Specimens

Metallic rectangular samples of high purity electrolytic copper (99.99%) of 5x1x0.1 cm and commercial copper (low purity), and low carbon steel samples of 5x1x0.1 cm (of low and high purity) were prepared and exposed inside a cabinet (indoor condition) and outside (outdoor condition).

The specimens were prepared following the procedures of ISO/CD 11844-2 [13] as follows: a hole with diameter 2 mm was drilled at the upper side of the specimens. Cu samples were grinded with silicon carbide paper to 1200 P (600 grit), while steel samples were grinded with paper to 500 P (320 grit). After cleaning with deionised water and degreasing with ethanol in an ultrasonic bath for 5 min, the samples were dried, weighed (on a microbalance with the accuracy of ± 0.1 µg) and stored in plastic bags and placed in a container with minimum humidity.

2.3. Exposure

The metallic samples of pure electrolytic copper and low carbon steel where placed in vertical position inside the cabinet (a rectangular metallic box of 66 x 32 x 71 cm), and in the rack for outdoor exposure. The cabinet was constructed using galvanized sheet, painted with a white corrosion resistive paint with two windows of 22 x 26 cm positioned at the longitudinal ends of the cabinet, at 20 cm from the bottom, in order to leave the wind to flow from side to side. The windows were protected by a steel mesh for free air flow. The box was positioned following the north-west direction, according to the latitude of Campeche City, at the top of a building 10 m high, where the wind passed through freely. Figure 2 shows the cabinet and the exposure rack at the top of the building.

In the outdoor environment samples of both metals were exposed in a metallic rack with ceramic supports to avoid metal-metal contact. The exposure period for outdoor conditions started one year later than indoor. Samples were also placed in vertical position 1.5 m from the floor at the top of the same building in which the cabinet was placed. The samples were exposed in both environments for periods of time of: 1, 3, 6, 12, 24 and 36 months.
During the complete exposure time the relative humidity (RH) and temperature (T) were recorded continuously for both cases, inside the cabinet (indoor condition) and outside (outdoor condition). The rate and direction of the predominant winds, and pluvial precipitation were also recorded. These meteorological parameters were recorded using an automatic record system of the meteorological station installed just few meters away from the site where the cabinet and rack for outdoor exposure were situated.

The set down rate of SO₂ and Chloride ions was measured inside and outside the cabinet following the methodology proposed by the ISO 9225:1992 standard. Sulphate plates were used for determination of atmospheric SO₂ and wet candle for chloride deposit rate.

2.4. Determination of corrosion attack

In the end of each exposure period (1, 3, 6, 12, 24, 36 and 48 months), three identical samples of each metal were removed for analysis. For the evaluation of the corrosion rate the gravimetric method of mass loss measurements was applied. This method has a precision of about ±10 mg/m² with the method described in [13]. The copper and carbon steel specimens were subjected to chemical pickling in specific solutions, to remove the corrosion products from the surface [13]. The immersion time was a function of the severity of the corrosive attack on the surface of the samples and was usually from one to 2 min at room temperature. A reference sample (specimen not exposed) of each metal was subjected to the same pickling treatment. After pickling, the samples were degreased with ethanol in an ultrasonic bath for 5 min, after which they were dried and weighted using a micro-balance with an accuracy of ±1 x 10⁻⁵g. All results present in this study are the average measure from three different samples exposed to the same conditions.
3. Results and discussion
3.1. Mass loss and corrosion rate

Figure 3 presents the mass loss of Cu and low carbon steel samples as a function of exposure time under indoor A) and outdoor B) conditions. At indoor conditions copper presented the highest mass loss after 12 months of exposure. For longer exposure periods, 24 and 36 months, the mass loss copper decreased compared with the obtained after 12 month. Carbon steel samples presented an increasing mass loss during the 36 months of exposure period. For outdoor conditions the mass loss increased continuously during the complete exposure period for both metals. Outdoor environment induced higher mass loss than indoor. In the case of copper the mass loss was 5 times higher than at indoor whereas for carbon steel it was twice. Several factors such as pollutants concentration, time of wetness and temperature ranges are responsible for this result, which will be discussed in detail in the following sections.

On the other hand, the highest corrosion rate of both metals at indoor conditions was reached after six months of exposure as shown in figure 4A. From month six to the end of the test the corrosion rate of both metals decreased as a function of the exposure time at indoor conditions. At outdoor conditions, the maximum corrosion rate was observed after one month of exposure for both, copper and carbon steel. Figure 4B presents the corrosion rate as a function of exposure time for outdoor conditions in which can be seen that after one month the corrosion rate for both metals decreased and after 12 months it was stable at values around 0.28 and 0.35 g m$^{-2}$ day$^{-1}$ for carbon steel and copper respectively. This result indicated that in the tropical-humid climate of Campeche these two metals attain a stable atmospheric corrosion degradation process after one year of exposure.

![Figure 3](image)

Figure 3. Mass loss for Cu and Steel as a function of exposure time at A) indoor and B) outdoor conditions.
Figure 4. Corrosion rate of Cu and Steel as a function of exposure time at A) indoor and B) outdoor conditions.

The indoor conditions generated inside the cabinet induced severe changes in the kinetics of the corrosion degradation of copper and carbon steel. The corrosion rate increased drastically during the first six months reaching the maximum value recorded. From sixth month to the end of the exposure period the corrosion rate decreased. Conversely, outdoor conditions are so aggressive that provoke high corrosion rate of both metals from the first days of exposure, after which both metals presented a corrosion rate 50% lower compared to the obtained at the beginning of the test. The patent difference in pollutants concentration along with differences in relative humidity levels and temperature at indoor and outdoor conditions are the main factors for the different behaviour of the atmospheric corrosion process of these two metals. The characteristics of the corrosion products formed on both metals play an important role in the atmospheric corrosion process. This effect has more influence at indoor conditions where there was not the effect of rain and runoff of corrosion products. It seems that inside the cabinet the environment generated is less aggressive than the one outside (outdoor condition).

3.2. Air pollutants

It has been clearly established that atmospheric corrosion is a process markedly influenced by the relative humidity and temperature of the atmosphere as well as by the concentration and deposition rate of air pollutants [1,2,4,7,13]. These critic variables act interdependently during the atmospheric corrosion process. Polluted atmospheres will always be more corrosive than “clean” atmospheres [14-16]. For the conditions prevailing in the city of San Francisco de Campeche the concentration of the principal air contaminants SO$_2$ and Cl$^-$ inside the cabinet was lower than the measured outside for outdoor conditions as indicated in figure 5. The deposition rate of SO$_2$ and Cl$^-$ was measured continuously and is reported in figure 5 as a function of the exposure time at A) indoor and B) outdoor conditions.
The deposition rate of SO$_2$ at outdoor conditions was 3.3 times higher than at indoor whereas for the case of Cl$^-$ deposition the outdoor/indoor ratio was 2.83. The principal air contaminant that increases the corrosivity of the atmosphere in Campeche is Cl$^-$. It can be proposed that for the specific conditions of the tropical-humid climate of Campeche, outdoor pollutants concentration is 3 times that for indoor conditions (inside the metallic box). Analysis of the information presented in figures 4 and 5 indicates that there is a close relationship between the corrosion rate of copper and carbon steel and the deposition rate of atmospheric pollutants.

### 3.4. Temperature-relative humidity relationship

Figures 6 and 7 present the number of hours at which different temperature (T)-relative humidity (RH) relationships take place during the complete exposure period at indoor and outdoor conditions respectively. The information obtained indicates that the major number of hours corresponds to a short interval of RH and T values. As can be seen in figures 6a) to 6c), at indoor conditions during summer (April-October) the distribution of the complex T-RH was from 22 to 40 °C and from 30 to 100 % RH. In this period the highest temperatures were observed during the three years of test.

The winter period (October-April) was characterised for lower temperatures, which explains the increase in the number of hours for the T-RH complex that ensures condensation of water in the surface of both metals. The information presented in figures 6d to 6f indicates that at indoor conditions the annual climatic parameters practically did not change from 2003 to 2006. However, even in the tropical-humid climate of Campeche, there is a clear difference on the distribution of the number of hours for the T-RH complex for summer and winter periods.
Figure 6a-f. Number of hours for the T-RH complex during the exposure period at indoor conditions.

At outdoor conditions, the temperature and relative humidity range was shorter than for indoor as can be observed in figure 7(a-d). The lowest temperature was the same as for indoor conditions however the maximum temperature was several degrees lower.

As in the indoor condition, the winter period induced more number of hours for the T-RH complex due to lower temperatures as shown in figure 7d.
The RH during summer period was from 34 to 95%, and the annual RH values recorded for 12, 24 and 36 months were 95%. However the minimum RH was 36, 48 and 51 for 12, 24 and 36 months of exposure at outdoor conditions respectively. It was found that indoor condition propitiates higher...
maximum temperatures than at outdoors. In general, indoor conditions presented negligible variation in the proportional distribution on hours for the annual T-RH complex, opposite with the outdoor condition which presented considerable variations. It can be established that annual climatic conditions inside the metallic cabinet (indoor conditions) were very stable during the three years of tests, contrary to the severe changes observed on the climatic conditions at outdoors.

In tables I and II we resume the information of the Temperature (T) and Relative Humidity (RH) as average value of the maximum number of hours, the most frequent and the percentage of hours for 3, 6, 12, 24 and 36 months at indoor and outdoor conditions respectively.

Table I. Temperature and Relative Humidity recorded at different periods at indoor conditions.

<table>
<thead>
<tr>
<th>Exposure time (months)</th>
<th>Maximum quantity of hours</th>
<th>T (°C) most frequent</th>
<th>HR (%) most frequent</th>
<th>T (°C) range</th>
<th>HR (%) range</th>
<th>% of hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>24 - 25</td>
<td>95 - 96</td>
<td>22 - 28</td>
<td>79 - 100</td>
<td>34</td>
</tr>
<tr>
<td>3</td>
<td>27</td>
<td>25 - 26</td>
<td>88 - 89</td>
<td>24 - 27</td>
<td>79 - 95</td>
<td>23</td>
</tr>
<tr>
<td>6</td>
<td>88</td>
<td>24 - 25</td>
<td>95 - 96</td>
<td>24 - 26</td>
<td>91 - 97</td>
<td>14</td>
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<tr>
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<td>104</td>
<td>24 - 25</td>
<td>95 - 96</td>
<td>23 - 26</td>
<td>88 - 97</td>
<td>11</td>
</tr>
<tr>
<td>24</td>
<td>184</td>
<td>24 - 25</td>
<td>93 - 94</td>
<td>23 - 26</td>
<td>85 - 98</td>
<td>18</td>
</tr>
<tr>
<td>36</td>
<td>307</td>
<td>24 - 25</td>
<td>95 - 96</td>
<td>23 - 26</td>
<td>85 - 98</td>
<td>19</td>
</tr>
</tbody>
</table>

Table II. Temperature and Relative Humidity recorded at different periods at outdoor conditions.

<table>
<thead>
<tr>
<th>Exposure time (months)</th>
<th>Maximum quantity of hours</th>
<th>T (°C) most frequent</th>
<th>HR (%) most frequent</th>
<th>T (°C) range</th>
<th>HR (%) range</th>
<th>% of hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>25 - 26</td>
<td>76 - 77</td>
<td>23-27</td>
<td>71-92</td>
<td>34</td>
</tr>
<tr>
<td>3</td>
<td>26</td>
<td>23 - 24</td>
<td>90 - 91</td>
<td>23-28</td>
<td>73-92</td>
<td>40</td>
</tr>
<tr>
<td>6</td>
<td>82</td>
<td>24 - 25</td>
<td>88 - 89</td>
<td>23-26</td>
<td>85-92</td>
<td>19</td>
</tr>
<tr>
<td>12</td>
<td>100</td>
<td>24 - 25</td>
<td>88 - 89</td>
<td>23-27</td>
<td>78-92</td>
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<td>24</td>
<td>195</td>
<td>24 - 25</td>
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<td>295</td>
<td>24 - 25</td>
<td>89 - 90</td>
<td>23-27</td>
<td>79-92</td>
<td>27</td>
</tr>
</tbody>
</table>
For outdoor conditions, the standard ISO 9225:1992 establishes that the time of wetness (TOW) must be determined considering $T \geq 0$ °C and $RH \geq 80\%$. However, for indoor conditions Veleva et al. [11] and Corvo et al. [17-20] have proposed that TOW values should be determined for $T \leq 25$ °C and $RH \geq 70\%$. As can be seen in tables I and II, the maximum number of hours for TOW according to the ISO 9225:1992 are very similar for both, indoor and outdoor conditions as a function of the exposure time in months. The maximum number of hours for the T-RH complex at both conditions occurred at a temperature range from 24 to 25 °C whereas the RH was from 93 to 96% for indoor and from 88 to 90% for outdoor conditions. This result indicates that indoor conditions in tropical-humid climates promote more the condensation of water films on the surface of metals than outdoor conditions.

In general, relative humidity was always higher at indoor (85-98%) than at outdoor (78-92%) conditions. However, the proportion of hours for TOW was bigger for outdoors than indoors. This means that even if indoor conditions facilitate more the presence of water films on the surface of metals than outdoors, the time effective TOW is lower at indoors than at outdoors.

Tables III and IV present the TOW at indoor and outdoor conditions according to the two criteria. At indoor conditions, there is no significant difference of the percentage of annual number of hours between the two criteria ($T \leq 25$ °C, $HR \geq 70\%$) vs ($T > 0$ °C, $HR \geq 80\%$).

Taking into account the criteria proposed by Corvo and Veleva to characterise TOW for indoor conditions, ($T \leq 25$ °C y $HR \geq 70\%$) and the standard ISO 9225:1992 ($T > 0$ °C y $HR \geq 80\%$) for outdoor, the TOW for indoor conditions is higher than for outdoors. The values of TOW, together with the fact that at indoor conditions the runoff effect associated with the rain is not present, which promotes pollutants accumulation, it could be expected higher corrosion rate of carbon steel and copper at indoor than at outdoor conditions.

**Table III.** Indoor TOW and percentage of total number of hours.

<table>
<thead>
<tr>
<th>Exposure time (months)</th>
<th>$T \leq 25$ °C y $HR \geq 70%$</th>
<th>$T &gt; 0$ °C y $HR \geq 80%$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hours</td>
<td>% of hours</td>
</tr>
<tr>
<td>1</td>
<td>265</td>
<td>37</td>
</tr>
<tr>
<td>3</td>
<td>727</td>
<td>33</td>
</tr>
<tr>
<td>6</td>
<td>1576</td>
<td>36</td>
</tr>
<tr>
<td>12</td>
<td>3896</td>
<td>44</td>
</tr>
<tr>
<td>24</td>
<td>7700</td>
<td>44</td>
</tr>
<tr>
<td>36</td>
<td>11505</td>
<td>44</td>
</tr>
</tbody>
</table>
### Table IV. Outdoor TOW and percentage of total number of hours.

<table>
<thead>
<tr>
<th>Exposure time (months)</th>
<th>$T \leq 25^\circ C$ y HR $\geq 70%$</th>
<th>$T &gt; 0^\circ C$ y HR $\geq 80%$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hours</td>
<td>% of hours</td>
</tr>
<tr>
<td>1</td>
<td>232</td>
<td>32</td>
</tr>
<tr>
<td>3</td>
<td>752</td>
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</tr>
<tr>
<td>6</td>
<td>1655</td>
<td>38</td>
</tr>
<tr>
<td>12</td>
<td>3817</td>
<td>44</td>
</tr>
<tr>
<td>24</td>
<td>7740</td>
<td>44</td>
</tr>
<tr>
<td>36</td>
<td>11743</td>
<td>45</td>
</tr>
</tbody>
</table>

**Figure 8.** Corrosion rate of copper and carbon steel at indoor and outdoor conditions.

Results of corrosion rate obtained from short exposure times at the beginning of the test show the effect of the environment aggressiveness on the corrosion degradation of the two exposed metals. As corrosion reaction proceeded the corrosion products formed on carbon steel and copper offered some corrosion protection. Even if they are not proper patinas they had the effect of reduce the corrosion rate and keep it stable from the sixth month of exposure to the end of the test after 36 months. Several studies have shown that depending on atmosphere pollutants concentration, corrosion products provide more or less corrosion protection as the case of copper in rural-urban atmospheres [21]. At outdoor conditions the protection effect of corrosion products was evident from the first month of exposure for both metals whereas at indoor conditions this effect was observed clearly from the sixth month of exposure as can be observed in figure 8.

For longer exposure periods (24 and 36 months), the corrosion rate at indoor conditions is lower than at outdoors even when the corrosion rate was stable and at low for both metals.
For indoor and outdoor conditions in tropical-humid climates like in the city of San Francisco de Campeche in Campeche, Mexico, the corrosion rate for carbon steel and copper are better explained in terms of temperature and relative humidity intervals during the exposure period.

**Conclusions**

The most important parameter for atmospheric indoor and outdoor conditions is the TOW which is considered the time during which corrosion occurs due to the presence of water films on the metals surface. The TOW determined properly must define the probability for atmospheric corrosion to occur. However, corrosion rate will depend mainly in the acceleration caused by contaminants deposition and other factors like maximum temperature at indoor which is higher than outdoors and the level of pollutants concentration in the atmosphere and accumulated on the metallic surfaces.

The principal conclusions from the studies of indoor and outdoor atmospheric corrosion are:

- The corrosion rate of copper and carbon steel exposed to indoor conditions was lower than that obtained at outdoor conditions due to the low level of pollutants concentration and to the high average temperature which made short the periods for corrosion to take place.
- The highest temperatures were recorded inside the cabinet (metallic box), where temperatures as high as 40 °C were measured during the exposure time. This temperature provokes faster water removal from the metallic surfaces even though indoor conditions presented also higher relative humidity (around 95%) than at outdoors.
- High RH at indoor condition stimulate the presence of water films on metallic surfaces, but the high temperature found in that condition makes shorter the effective TOW.
- Based on gravimetric methods for mass gain and loss of the metals exposed, it was found that the metals were exposed to an atmosphere of high corrosivity (category IC5) according to ISO/CD 11844. This condition was originated by mainly by elevated relative humidity present at the interior of the cabinet during the exposure period.

**References**

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