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MATERIALS ENGINEERING | REVIEW ARTICLE

A brief review on the atmospheric corrosion of mild steel in Iran

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Abstract: This paper presents a review on the atmospheric corrosion of steel, at three sites, in Iran. Corrosion rate values, time of wetness, and the level of pollutants, namely of SO₂ and chlorides were determined for the first year of exposure in order to establish the aggressiveness of the atmospheres. The results obeyed well with the empirical kinetics equation of the form $C = Kt^n$.

Subjects: Corrosion-Materials Science; Metals & Alloys; Surface Engineering-Materials Science

Keywords: metals; alloys; corrosion; deposition; atmospheric pollutant

1. Introduction

Atmospheric corrosion is a process of practical importance as it degrades the structures, devices, and products exposed to atmosphere. It mainly depends on exposure time and some climatic factors, like relative humidity, temperature, sulfur content, salinity (chloride), and the presence of some other pollutants (Natesan, Venkatachari, & Palaniswamy, 2006). Global studies have shown that the overall cost of corrosion, which has been estimated to be in the range of 2–4% GNP and that 20–25% of discussed, could be avoided using appropriate corrosion control technology. Atmospheric corrosion makes the major contribution to this cost (Bhaskaran, Palaniswamy, Rengaswamy, & Jayachandran, 2005; Shafiei, Zeinali, & Nasresfahani, 2011). The aggressiveness of the atmospheric constituents can be assessed by measuring climatic and pollution factors or by determining the corrosion rate of exposed metals. As a result, there are numerous theoretical and experimental studies about atmospheric corrosion which resemble the increasing interest in these types of

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PUBLIC INTEREST STATEMENT

Atmospheric corrosion is the deterioration and destruction of a material and its vital properties due to electrochemical as well as the other reactions of its surface with the constituents of the atmosphere surrounding the material. This paper presents a review study on the effect of atmospheric pollutants on corrosion of steel at three sites in Iran.



phenomena. Atmospheric corrosion processes have been reviewed and analyzed in detail and also several mathematical models have been developed for predicting the corrosion damage of metals in the atmosphere (Mendoza & Corvo, 2000). In an approximate manner, these equations (that related corrosion rate values to environmental data) are useful for answering questions regarding the durability of metallic structures and determining the economic costs associated with the metallic corrosion. However, these mathematical models developed to explain atmospheric corrosion at a particular region cannot be extrapolated to other places, mainly because the number of variables considered by the models is much reduced in comparison to the great number of variables that really influence the atmospheric corrosion process (Morales, Díaz, Hernández-Borges, González, & Cano, 2007).

Although corrosion rate depends on a numerous amount of factors, only a few of them can be generalized with time as, for instance, deposition rate of pollutant (chloride and SO_2), exposure time and time of wetness (defined as the fraction of exposure time during which the relative humidity is equal or higher than 80% and the temperature higher than 0°C) (ISO/WD 9223, 1992). Otherwise, the deposits of atmospheric particles (dust and aerosols), the intensity of solar radiation, periods of dryness on metals surface, evaporation of electrolyte layer, etc. cannot be generalized and, therefore, mathematical models, most frequently used for corrosion prediction, are very simple because they only consider generalized variables.

In countries like Iran, due to wide-spread use of steel, it was considered desirable to study the corrosion behavior of this material in a wide variety of atmospheres. Because of excellent mechanical properties and relatively low prices, carbon steels are now chosen for the structures for petroleum, marine, and agricultural industries.

This paper presents a comparative study on the atmospheric corrosion of steel, at three sites, in Iran. Corrosion rate values, time of wetness, and the level of pollutants, namely of SO_2 and chlorides, were determined for the first year of exposure in order to establish the aggressiveness of the atmospheres. The results obeyed well with the empirical kinetics equation of the form $C = Kt^n$.

2. Experimental procedure

Scope and methodology of conducting the atmospheric corrosion studies were similar for the three exposure stations. Exposure stations were chosen according to the local atmosphere, convenience of installations, and facilities for technical assistance. Locations of three exposure stations are shown in Figure 1. The exposure stations are numbered and the corresponding numbers are used in subsequent citations.

First, 15 flat samples (PLATE) and 15 helical samples of steel were prepared for each site. Flat samples had a metallic surface of $150 \times 100 \text{ mm}^2$ and thickness of 3 mm, and helical samples were constructed using wires, 3 mm in diameter and 1 m long. Based on Standard ASTM G1-03 (2003), the samples were rinsed by acid prior to sampling in order to remove surface dirt and corrosion products. To do so, the samples were soaked in acid, as mentioned in Table 1, for a short time interval (5–10 s), and then they were washed in water; besides, in some cases, sticky surface layers were removed using a soft brush.

The amount of weight loss for samples was being fixed (steady) at each stage, indicating that all the surface layers have been removed and if the washing operation continued, the sublayers would be corroded. Finally, the overall washing time was calculated by multiplying the number of cycles by the time needed in each cycle. Of course, it is noteworthy to mention that the time is calculated correctly if other factors such as temperature and chemical composition of the solution are kept fixed. In order to select the samples easily to be washed by acid and to record the samples secondary weights, a set of codes were used showing the type of material used and the related sampling number. The flat samples were drilled to install the codes and a plastic label was prepared containing

Figure 1. Location of corrosion test sites in Iran.

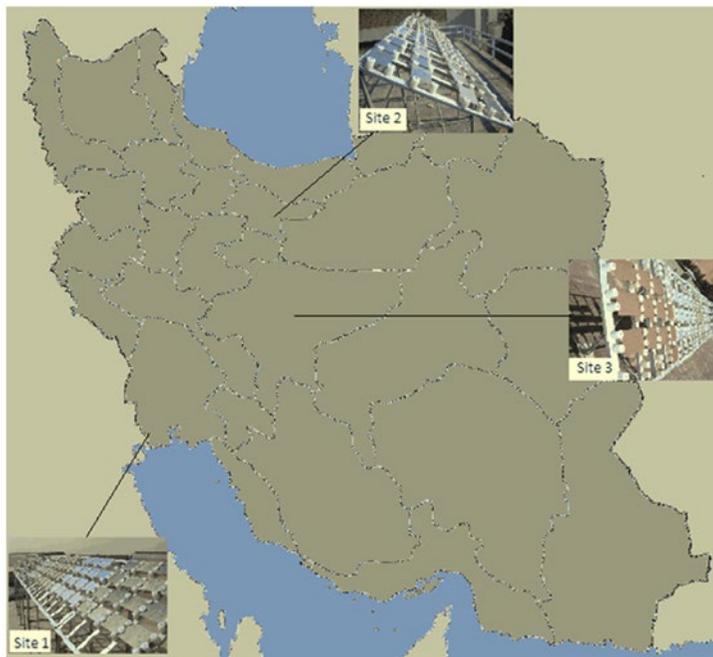


Table 1. Chemical cleaning solutions for removal of corrosion products

| Metal | Solution | Temperature |
|-------|--|-------------|
| Steel | 1 l HCl + 20 g Sb ₂ O ₃ + 50 g SnCl ₂ | 25°C |

Table 2. Chemical composition of steel samples (% wt.)

| Metal | Si | Cd | Mg | Pb | Sn | Zn | Al | Cu | Mn | S | P | Fe | C |
|-------|-------|----|----|----|----|----|-------|-------|------|------|------|-------|------|
| Steel | 0.008 | - | - | - | - | - | 0.065 | 0.048 | 0.17 | 0.01 | 0.01 | 99.54 | 0.27 |

the information for each helical sample. To prevent galvanic corrosion between samples and aluminum mounts, a set of plastic supporters were connected to sample table by screws. Chemical composition of samples is presented in Table 2.

After initial washing, the samples were sealed and stored in plastic containers to be transported to the sampling site. As it went on, sampling was done in definite time intervals. After the first period one sample, for the second period two samples, and for the following periods three samples of each material and type were collected. Then all the samples were washed by the same acids and weighed with a higher precision than before. All the plates which were collected in each period were used to measure the corrosion rate by loss of weight. Weight loss was determined by measuring the difference in weight before and after the exposure time.

In order to determine the deposition rate of sulfur dioxide, the alkaline surface method was used. Sulfation plates were prepared by the following method; paper filter plates of 150 mm × 100 mm × 3 mm were immersed in a 70 g/l sodium carbonate solution. When the plates were completely saturated, they were taken out of the solution and were relatively dried for an hour by an oven at 105 ± 2 °C. At the next stage, one of three plates was selected as blank and kept in laboratory and the rest were packed in nylon and were transferred to the sampling site to be installed on the stated equipment. Since the titration method and Thorin indicator were not very accurate, in order to calculate the mass of deposited SO₂, Palmtest 7100 machine was used by employing photometry method. It must

be noted that this method shows the amount of SO_4 in the solution. In addition, by considering the stoichiometric ratio of $\text{SO}_4\text{-SO}_2$, the SO_2 deposited mass can be calculated. Wet candle method was also employed to measure the deposition rate of chloride. Besides, in order to maintain the recurrence of the experiment, three samples of the resultant solution were preserved to be used in Mercurimetric Titration Method. According to wet candle method described in ISO 9225 (2007), if the Mercurimetric titration method is used, the deposition rate of chloride (Cl^-), expressed in $\text{mg m}^2 \text{ day}^{-1}$, $R_{(\text{Cl}^-)}$, is given by Equation 1:

$$R_{(\text{Cl}^-)} = \frac{2(V_3 - V_4)C_2 \times 35.5V_T}{V_A \cdot A \cdot T} \quad (1)$$

where V_3 is the volume, in ml, of mercury (II) nitrate standard volumetric solution used for titration of the aliquot of sample solution; V_4 is the volume, in ml, of mercury (II) nitrate standard volumetric solution used for nitration of the blank; V_A is the volume, in ml, of the aliquot of the sample solution; V_T is the total volume, in ml, of the sample solution; C_2 is the exact concentration, in moles of Hg (No_3)₂ per liter, of mercury (II) nitrate standard volumetric solution used; A is the area, in m^2 , of the exposed gauze surface; and t is the exposure time.

The measurement of relative humidity during the sampling made it possible to determine the Time of Wetness category.

To predict the mathematical model, the data for one year of exposure were used. The variation of weight loss (C) due to corrosion expressed as mg with time (t) can be described by the general empirical equation in the form

$$C = Kt^n \quad (2)$$

Townsend and Zoccola (ASTM G101-01, 1997) in 1982, used linear regression analysis to fit a straight line to a log-log plot of corrosion loss (C) vs. time (t) in logarithmic form

$$\log C = \log K + n \log t \quad (3)$$

where K is the intercept (equal to the corrosion loss in first year) and “ n ” is the slope of the log-log plot. The first-year corrosion rate is an important parameter not only for the determination of corrosivity of the atmosphere but also for long-term corrosion forecasting. Both “ K ” and “ n ” are dependent on the type of metal and climatic parameters. The validity of the equation and its reliability to predict long-term corrosion has been demonstrated by many authors (ASTM G101-01, 1997; Feliu, Morcillo, & Feliu, 1993; Rodríguez, Javier Hernandez, & Gonzalez, 2003).

3. Results and discussion

3.1. Levels of pollutants in the atmosphere

Figure 2 gives the average, deposition rates of SO_2 and of chloride, at three sites, for the first year of exposure. Because of the lower amount of population and industrial zones, the deposition rate of SO_2 recorded, at sites 1 and 3, were, in general, quite low as it would be expected, ranging between 0.44 and 1.53 $\text{mg m}^{-2} \text{ day}^{-1}$ and 0.38–0.94, respectively, while at site 2, values were ranging between 2.5 and 5.4 $\text{mg m}^{-2} \text{ day}^{-1}$. Considering the data for one year of exposure and accordingly to the ISO 9223, all atmospheres will be classified in the P_0 category. The annual average values of Cl^- were almost identical for sites 1 and 2, 25.1 and 24.04 $\text{mg m}^{-2} \text{ day}^{-1}$, at Abadan and Tehran, respectively, while the annual average value of Cl^- at site 3 (Isfahan) was obtained lower than the aforementioned values. Also, the variations of Cl^- and SO_2 deposition rates could be due to the cleansing effect of rain and carrying effect of wind, respectively (Fonseca, Picciochi, Mendonca, & Ramos, 2004; Mendoza & Corvo, 2000).

Figure 2. Deposition rate of atmospheric pollutants: (a) SO₂ and (b) chloride.

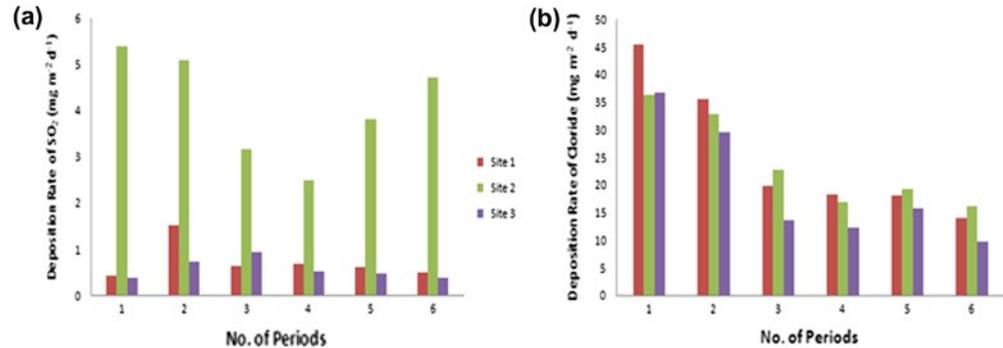


Table 3. Data of time of wetness

| Site No. | Time of wetness (hours/year) | Category |
|----------|------------------------------|----------------|
| 1 | 590 | τ ₃ |
| 2 | 360 | τ ₃ |
| 3 | 470 | τ ₃ |

3.2. Time of wetness

TOW, as defined in ISO 9223, does not cover all the aspects of climate. According to the ISO definition, TOW is “estimated” based on the characteristics of the atmosphere–humidity complex, independently of the pollutant level and the nature of the metallic material (Corvo et al., 2008). It should be apparent that the time of wetness of the corroding surface is a key parameter, directly determining the duration of the electrochemical corrosion processes and because of this, although, the average values of SO₂ deposition rate at site 1, approximately equals to that of site 3, are less than site 2, the higher corrosion rates would be expected at site 1. Table 3 gives the values and category of time of wetness for all sites.

3.3. Corrosion rate values

As defined by ISO 9223 (ISO/WD 9223, 1992), a way to evaluate the corrosivity categories of atmospheres consists of determination of the corrosion rates for the set of metals after one-year exposure. This standard classifies the corrosivity category of different environments under class C, where in C₁, C₂, C₃, C₄, and C₅ correspond to the corrosion rates of very low, low, medium, high, and very high, respectively. It can be seen from Figure 3 that the corrosion rates for tested samples, in general, tend to decrease as the exposure time increases and the average corrosion rate at site 2 is the lowest and the least attacked by general corrosion, followed by sites 3 and 1, respectively. Also, Table 4 shows the corrosivity class of the three atmospheres.

Figure 3. Corrosion rate values: (a) flat samples and (b) helical samples.

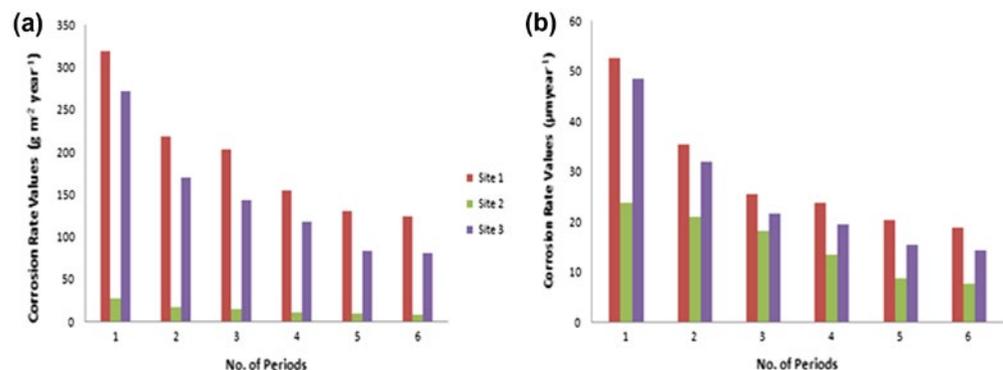


Table 4. Corrosivity class at all sampling stations

| Site No. | Corrosivity class |
|----------|--------------------------------|
| 1 | C ₂ -C ₃ |
| 2 | C ₁ -C ₂ |
| 3 | C ₂ |

3.4. Kinetic studies

When modeling the data relative to the corrosion rate, we have used Equation 2 for all stations. According to this equation, the atmospheric behavior of a certain material at a certain location can be defined by the two parameters “n” and “K,” which are supposed to depend on environmental measurable factors. The initial corrosion rate (say, during the first year of exposure) is described by “K,” while “n” is a measure of the long-term decrease in corrosion rate. When n = 0.5, the law of corrosion penetration increase is parabolic, with diffusion through the corrosion product layers as the rate-controlling step. At “n” values appreciably <0.5, the corrosion products show protective, passivating characteristics. Higher “n” values, >0.5, are indicative of non-protective corrosion products. Loosely adherent, flaky rust layers are an example of this case. Very high correlation coefficient “r²” was found in all the cases. The representation of the corrosion data versus time on log-log coordinates will therefore give points approximately on the straight lines of slope “n.” Figure 4 shows the log-log plots obtained and Table 5 shows the values for “n,” “K,” and correlation coefficient “r²” for each site.

On log-log coordinates, the points lie close to a straight line for all stations. Thus, it is reasonable to accept the verification of power law function to estimate corrosion behavior of steel at these stations. Reasonable straight lines, analytically described by the equations $\Delta m = 39.5 \text{ (g m}^{-2} \text{ month}^{-0.39}) t^{0.39}$, $\Delta m = 2.06 \text{ (g m}^{-2} \text{ month}^{-0.58}) t^{0.58}$, and $\Delta m = 34.3 \text{ (g m}^{-2} \text{ month}^{-0.22}) t^{0.22}$ for the samples exposed at site 1, site 2, and site 3 atmospheres, respectively. The values of the kinetic constants 39.5

Figure 4. Logarithmic plots of weight losses (g m⁻²) of steel samples as a function of time. Exposed at site 1 (a), site 2 (b), and site 3 (c).

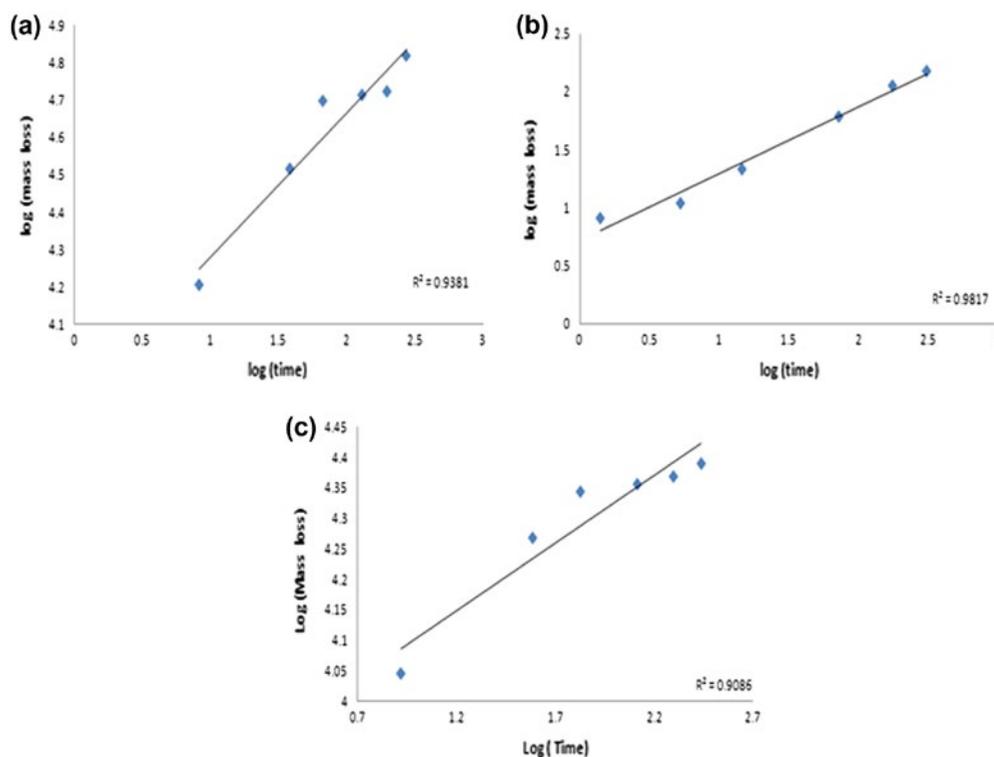


Table 5. Corrosion kinetic parameters K , n , and correlation coefficient r^2 for steel samples

| Site No. | " n " value | " K " value | r^2 |
|----------|---------------|--|--------|
| 1 | 0.386 | 39.5 ($\text{g m}^{-2} \text{ month}^{-0.39}$) | 0.9381 |
| 2 | 0.5768 | 2.06 ($\text{g m}^{-2} \text{ month}^{-0.58}$) | 0.9817 |
| 3 | 0.22 | 34.3 ($\text{g m}^{-2} \text{ month}^{-0.22}$) | 0.9086 |

($\text{g m}^{-2} \text{ month}^{-0.39}$), 2.06 ($\text{g m}^{-2} \text{ month}^{-0.58}$), and 34.3 ($\text{g m}^{-2} \text{ month}^{-0.22}$) account for the differences in the kinetics of the corrosion of steel at the three sites. As expected, the highest amount of TOW (at site 1) leads to highest initial corrosion rate (K) and protective corrosion products ($n < 0.5$) and due to less time period of electrochemical corrosion processes, the lowest amount of TOW at site 2 leads to lower initial corrosion rate (K) and formation of non-protective corrosion products ($n > 0.5$); however, the deposition rate of SO_2 at site 2 is higher than others.

4. Conclusions

- Because of the lower amount of population and industrial zones and consequently SO_2 emission sources, the deposition rate of SO_2 recorded, at sites 1 and 3, were, in general, quite low as it would be expected, ranging between 0.44 and 1.53 $\text{mg m}^{-2} \text{ day}^{-1}$ and 0.38–0.94, respectively, while at site 2, values were ranging between 2.5 and 5.4 $\text{mg m}^{-2} \text{ day}^{-1}$.
- The annual average values of Cl^- were almost identical for sites 1 and 2, 25.1 and 24.04 $\text{mg m}^{-2} \text{ day}^{-1}$, at Abadan and Tehran, respectively, while the annual average value of Cl^- at site 3 was obtained lower than the aforementioned values due to long distance from the sea and other Cl^- sources.
- It should be apparent that the time of wetness of the corroding surface is a key parameter, directly determining the duration of the electrochemical corrosion processes and because of this, although, the average values of SO_2 deposition rate at site 1, approximately equals to that of site 3, is less than site 2, the higher corrosion rates would be expected at site 1.
- The corrosion rates for tested samples, in general, tend to decrease as the exposure time increases and the average corrosion rate at site 2 is the lowest and the least attacked by general corrosion, followed by sites 3 and 1, respectively.
- Reasonable straight lines, analytically described by the equations $\Delta m = 39.5 (\text{g m}^{-2} \text{ month}^{-0.39}) t^{0.39}$, $\Delta m = 2.06 (\text{g m}^{-2} \text{ month}^{-0.58}) t^{0.58}$, and $\Delta m = 34.3 (\text{g m}^{-2} \text{ month}^{-0.22}) t^{0.22}$ for the samples exposed at site 1, site 2, and site 3 atmospheres, respectively.
- As expected, the highest amount of TOW (at site 1) leads to highest initial corrosion rate (K) and protective corrosion products ($n < 0.5$) and due to less time period of electrochemical corrosion processes, the lowest amount of TOW at site 2 leads to lower initial corrosion rate (K) and formation of non-protective corrosion products ($n > 0.5$); however, the deposition rate of SO_2 at site 2 is higher than others.

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References

- ASTM G1-03. (2003). *Standard practice for preparing, cleaning, and evaluating corrosion test specimens*.
 ASTM G101-01. (1997). *Standard guide for estimating the atmospheric corrosion resistance of low alloy steels*.

- Bhaskaran, R., Palaniswamy, N., Rengaswamy, N. S., & Jayachandran, M. (2005). *ASM hand book* (Vol. 13, p. 619). Materials Park, OH: ASM International.
- Corvo, C., Perez, T., Martin, Y., Reyes, J., Dzib, L. R., Gonzalez, J., & Castaneda, A. (2008). Time of wetness in tropical climate: Considerations on the estimation of TOW according to ISO 9223 standard. *Corrosion Science*, 50, 206–219. <http://dx.doi.org/10.1016/j.corsci.2007.06.012>
- Feliu, S., Morcillo, M., & Feliu, Jr., S. (1993, March). The prediction of atmospheric corrosion from meteorological and pollution parameters—II. *Corrosion Science*, 34, 415–422. [http://dx.doi.org/10.1016/0010-938X\(93\)90113-U](http://dx.doi.org/10.1016/0010-938X(93)90113-U)
- Fonseca, I. T. E., Picciochi, R., Mendonca, M. H., & Ramos, A. C. (2004). The atmospheric corrosion of copper at two sites in Portugal: A comparative study. *Corrosion Science*, 46, 547–561.
- ISO/WD 9223. (1992). *Corrosion of metals and alloys, corrosivity of atmospheres, classification*.
- ISO/WD 9225. (2007). *Corrosion of metals and alloys, measurement of pollution*.
- Mendoza, A. R., & Corvo, F. (2000). Outdoor and indoor atmospheric corrosion of non-ferrous metals. *Corrosion Science*, 42, 1123–1147. [http://dx.doi.org/10.1016/S0010-938X\(99\)00135-3](http://dx.doi.org/10.1016/S0010-938X(99)00135-3)
- Morales, J., Díaz, F., Hernández-Borges, J., González, S., & Cano, V. (2007). Atmospheric corrosion in subtropical areas: Statistic study of the corrosion of zinc plates exposed to several atmospheres in the province of Santa Cruz de Tenerife (Canary Islands, Spain). *Corrosion Science*, 49, 526–541. <http://dx.doi.org/10.1016/j.corsci.2006.04.023>
- Natesan, M., Venkatachari, G., & Palaniswamy, N. (2006). Kinetics of atmospheric corrosion of mild steel, zinc, galvanized iron and aluminium at 10 exposure stations in India. *Corrosion Science*, 48, 3584–3608. <http://dx.doi.org/10.1016/j.corsci.2006.02.006>
- Rodríguez, J. J. S., Javier Hernandez, F., & Gonzalez, J. E. G. (2003). The effect of environmental and meteorological variables on atmospheric corrosion of carbon steel, copper, zinc and aluminium in a limited geographic zone with different types of environment. *Corrosion Science*, 45, 799–815. [http://dx.doi.org/10.1016/S0010-938X\(02\)00081-1](http://dx.doi.org/10.1016/S0010-938X(02)00081-1)
- Shafiei, E., Zeinali, M., & Nasresfahani, A. R. (2011). Atmospheric corrosion of steel at two sites in Iran: A comparative study. *ISIJ International*, 51, 1878–1881.



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