Atmospheric Corrosion of Steel at Two Sites in Iran: a Comparative Study

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(Received on November 30, 2010; accepted on August 4, 2011)

This paper presents a comparative study on the atmospheric corrosion of steel, at two sites, in Iran. Corrosion rate values, time of wetness and the level of pollutants, namely of SO2 and chlorides, in both atmospheres, 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.

KEY WORDS: atmospheric; corrosion; steel; Iran.

1. Introduction

Atmospheric corrosion is a process of practical importance as it degrades the structures, devices and products exposed to atmosphere. It is mainly depends on exposure time and some climatic factors, like relative humidity, temperature, sulfur content, salinity (chloride) and the presence of some other pollutants.1) Global studies have shown that the overall cost of corrosion, which have been estimated to be in the range of 2–4% GNP and that 20–25% of discussed could be avoided by using appropriate corrosion control technology. Atmospheric corrosion makes the major contribution to this cost.2) 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 phenomena. Atmospheric corrosion processes have been reviewed and analyzed with detail and also several mathematical models have been developed for predicting the corrosion damage of metals in the atmosphere.3) 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 that is considered by the models is much reduced in comparison with the great number of variables that really influence the atmospheric corrosion process.4)

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 SO2), exposure time, time of wetness (defined as the fraction of exposure time during which the relative humidity is equal or higher than 80% and the temperature in higher than 0°C).5) Otherwise the deposits of atmospheric particles (dust and aerosols), the intensity of solar radiation, periods of dryness on metals surface and 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 atmosphere. 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 two sites, in Iran. Corrosion rate values, time of wetness and the level of pollutants, namely of SO2 and chlorides, in both atmospheres, 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 2-exposure stations. Exposure stations were chosen according to the local atmosphere, convenience of installations and facilities for technical assistance. Locations of two exposure stations are shown in Fig. 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 150×100 mm² and thickness of 3 mm and helical samples were constructed using wires, 3 mm in diameter and 1 meter long. Based on Standard ASTM G1-03,7) 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 to 10 seconds) 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 sub layers 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 should be noted 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 supporters were connected to samples table by screws. To prevent galvanic corrosion between samples and aluminum mounts, a set of plastic covers and a plastic label was prepared containing the information for each helical sample. To record the samples secondary weights, a set of codes were employed showing the type of material used and the related sampling number. The flat samples were drilled to install the supports were connected to samples table by screws. Chemical composition of samples is presented in the 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 lost of weight. Weight loss was determined by measuring the difference of 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 gr/lit 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 centigrade degrees. 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 SO2 in the solution. In addition, by considering stukiometry ratio of SO4 to SO2, the SO2 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, 3 samples of the resultant solution were preserved to be used in Mercurimetric Titration Method. 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 milligrams with time (t) can be described by the general empirical equation in the form

\[ C = Kt^n \] .......................... (1)

Townsend and Zoccola\(^9\) in 1982, used linear regression analysis to fit straight line to a log-log plot of corrosion loss (C) vs. time (t) in logarithmic form

\[ \log C = \log K + n \log t \] .................................. (2)

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 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.\(^9\)\(^\text{—}^{11}\)

3. Results and Discussion

3.1. Levels of Pollutants in the Atmosphere

Table 3 gives the average, deposition rates of SO2 and of chloride, at both sites, for the first year of exposure. The deposition rate of SO2 recorded, at site 1 (Abadan), were in general quite low as it would be expected, ranging between 0.44 and 1.53 mg m\(^{-2}\)day\(^{-1}\), while at site 2 (Tehran) values ranging between 2.5 and 5.4 mg m\(^{-2}\)day\(^{-1}\). Considering the data for one year of exposure and accordingly to the ISO 9223 both atmospheres will be classified in the P0 category. The annual average values of Cl\(^-\) were almost identical for
both sites, 25.1 and 24.04 mg m$^{-2}$day$^{-1}$, at Abadan and Tehran, respectively. The variations of Cl$^-$ and SO$_2$ deposition rates could be due to cleansing effect of rain and carrying effect of wind, respectively.$^{4,12}$

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.$^{13}$ 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 is less than site 2, the higher corrosion rates would be expected at Abadan (site 1). Table 4 gives the values and category of time of wetness for both sites.

3.3. Corrosion Rate Values

As defined by ISO 9223$^6$ a way to evaluate the corrosivity categories of atmospheres consists of determination of the corrosion rates for the set of metals after 1-year exposure. This standard classifies the corrosivity category of different environments under class C, where in C$_1$, C$_2$, C$_3$, C$_4$ and C$_5$ correspond to the corrosion rates of very low, low, medium, high and very high, respectively. It can be seen from the Table 5 that the corrosion rates for tested samples, in general, tend to decrease as the exposure time increases and the higher corrosion rates were obtained for site 1 in comparison with site 2.

3.4. Kinetic Studies

When modeling the data relative to the corrosion rate, we have used Eq. (1) for two 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

| Periods of sampling | Site no. | SO$_2$ (mg m$^{-2}$ d$^{-1}$) | Deposition rate category (P) | Cl$^-$ (mg m$^{-2}$ d$^{-1}$) | Deposition rate category (S) |
|---------------------|---------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| 1                   | 1       | 0.44                        | P$_0$                        | 45.4                        | S$_1$                        |
| 2                   | 1       | 1.53                        | P$_0$                        | 35.6                        | S$_1$                        |
| 3                   | 1       | 0.63                        | P$_0$                        | 19.8                        | S$_1$                        |
| 4                   | 1       | 0.68                        | P$_0$                        | 18.32                       | S$_1$                        |
| 5                   | 1       | 0.61                        | P$_0$                        | 18.01                       | S$_1$                        |
| 6                   | 1       | 0.51                        | P$_0$                        | 14                         | S$_1$                        |
| 1                   | 2       | 5.4                         | P$_0$                        | 36.3                        | S$_1$                        |
| 2                   | 2       | 5.08                        | P$_0$                        | 32.94                       | S$_1$                        |
| 3                   | 2       | 3.17                        | P$_0$                        | 22.75                       | S$_1$                        |
| 4                   | 2       | 2.5                         | P$_0$                        | 17                         | S$_1$                        |
| 5                   | 2       | 3.81                        | P$_0$                        | 19.18                       | S$_1$                        |
| 6                   | 2       | 4.71                        | P$_0$                        | 16.07                       | S$_1$                        |

| Site no. | Time of Wetness (hours/year) | Category |
|----------|------------------------------|----------|
| 1        | 590                          | τ$_1$    |
| 2        | 360                          | τ$_1$    |

| No. of periods | Type of samples | Site no. | Corrosion rate$^*$ | Category |
|----------------|-----------------|---------|--------------------|----------|
| 1              | Plate           | 1       | 319.5              | C$_3$    |
| 2              | Plate           | 1       | 218                | C$_3$    |
| 3              | Plate           | 1       | 203.4              | C$_3$    |
| 4              | Plate           | 1       | 155                | C$_2$    |
| 5              | Plate           | 1       | 131                | C$_2$    |
| 6              | Plate           | 1       | 124                | C$_2$    |
| 1              | Helix           | 1       | 52.59              | C$_4$    |
| 2              | Helix           | 1       | 35.45              | C$_3$    |
| 3              | Helix           | 1       | 25.4               | C$_3$    |
| 4              | Helix           | 1       | 23.88              | C$_2$    |
| 5              | Helix           | 1       | 20.23              | C$_2$    |
| 6              | Helix           | 1       | 18.8               | C$_2$    |
| 1              | Plate           | 2       | 27.7               | C$_2$    |
| 2              | Plate           | 2       | 16.68              | C$_2$    |
| 3              | Plate           | 2       | 14.61              | C$_2$    |
| 4              | Plate           | 2       | 11.267             | C$_2$    |
| 5              | Plate           | 2       | 9.98               | C$_1$    |
| 6              | Plate           | 2       | 8.28               | C$_1$    |
| 1              | Helix           | 2       | 23.74              | C$_2$    |
| 2              | Helix           | 2       | 21.06              | C$_2$    |
| 3              | Helix           | 2       | 18.246             | C$_2$    |
| 4              | Helix           | 2       | 13.548             | C$_2$    |
| 5              | Helix           | 2       | 8.808              | C$_1$    |
| 6              | Helix           | 2       | 7.535              | C$_1$    |

*Corrosion rates of flat samples were expressed in the terms of $\frac{\mu \text{m}}{\text{year}}$ and corrosion rates of helical samples were expressed in the terms of $\frac{\mu \text{m}}{\text{year}}$. 

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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 vs. time on log-log coordinates will therefore give points approximately on the straight lines of slope ‘n’.

Figure 2 shows the log-log plots obtained and Table 6 shows the value for ‘n’, ‘K’ and correlation coefficient ‘r²’ for each site. On log-log coordinates, the points lie close to a straight line for two stations. Thus, it is reasonable to accept the verification of power law function to estimate corrosion behavior of steel at these two stations. Reasonable straight lines, analytically described by the equations \( \Delta m = 39.5 \text{ (g m}^{-2} \text{ month}^{-0.39}) t^{0.39} \) and \( \Delta m = 2.06 \text{ (g m}^{-2} \text{ month}^{-0.58}) t^{0.58} \), for the samples exposed at Abadan (site 1) and Tehran (site 2) atmospheres, respectively. The values of the kinetic constants 39.5 (g m\(^{-2}\) month\(^{-0.39}\)) and 2.06 (g m\(^{-2}\) month\(^{-0.58}\)) account for the differences in the kinetics of the corrosion of steel, at both sites. As expected the higher amount of TOW (at site 1) leads to higher initial corrosion rate (K) and protective corrosion products (n<0.5).

Due to less time period of electrochemical corrosion processes, the lower 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 site 1.

### Table 6. Corrosion kinetic parameters K, n, and correlation coefficient r² for steel samples.

| Site no. | ‘n’ value | “K” value          | r²   |
|----------|-----------|--------------------|------|
| 1        | 0.386     | 39.5 (g m\(^{-2}\) month\(^{-0.39}\)) | 0.9381 |
| 2        | 0.5768    | 2.06 (g m\(^{-2}\) month\(^{-0.58}\)) | 0.9817 |

**Fig. 2.** Logarithmic plots of weight losses (g m\(^{-2}\)) of steel samples as a function of time. Exposed at Abadan (a) and Tehran (b).

4. Conclusions

(1) The deposition rate of SO\(_2\), recorded at site 1 (Abadan), were in general quite low as it would be expected, ranging between 0.44 and 1.53 mg m\(^{-2}\)day\(^{-1}\), while at site 2 (Tehran) values ranging between 2.5 and 5.4 mg m\(^{-2}\)day\(^{-1}\).

(2) The annual average values of Cl\(^-\) were almost identical for both sites, 25.1 and 24.04 mg m\(^{-2}\)day\(^{-1}\), at Abadan and Tehran, respectively.

(3) 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 is less than site 2, the higher corrosion rates would be expected at Abadan (site 1).

(4) The corrosion rates for tested samples, in general, tend to decrease as the exposure time increases and the higher corrosion rates were obtained for site 1 in comparison with site 2.

(5) Reasonable straight lines, analytically described by the equations \( \Delta m = 39.5 \text{ (g m}^{-2} \text{ month}^{-0.39}) t^{0.39} \) and \( \Delta m = 2.06 \text{ (g m}^{-2} \text{ month}^{-0.58}) t^{0.58} \), for the samples exposed at Abadan (site 1) and Tehran (site 2) atmospheres, respectively.

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