

Study of the Corrosion Products Formed on Low-Carbon Steel Exposed to Different Environments in Egypt

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Abstract

The corrosion performance of carbon steel X52 was studied after exposure up to 12 months in three atmospheric environments in Egypt. The results are in agreement with kinetic equations of the form $P=At^B$, where P is the corrosion penetration, t is time, and A , and B are constants. The corrosion resistance of carbon steel, especially in industrial and urban sites are better than in coastal site. The corrosion products were characterized by XRD and SEM.

Keywords

Carbon steel; Industrial; Urban; Coastal; Atmospheric corrosion.

Introduction

Steel is used for making a wide range of equipment and metallic structures due to its low cost and high mechanical strength. Manufactured steel is usually exposed to outdoor conditions; often in highly polluted atmospheres where corrosion is considerably more severe than in clean rural environments. Carbon steel is an alloy of wide applications along the human civilization. The atmospheric corrosion of carbon steel has always been of prime interest for electrochemists and corrosion engineers because as it is the most widely spread corrosion process found in nature. Leading to the destruction of the materials, shaping the industrial age and is therefore responsible for immense financial loss. The corrosion products which form on carbon steel are influenced by the environmental condition, such as temperature, relative humidity, and the presence of atmospheric constituents such as SO_2 and chlorides [1-4]. Many researchers have studied the corrosion products formed on carbon steels exposed to various atmospheres [5-8]. The main corrosion products on the surface of steel reported are mainly γ - $FeOOH$ (lepidocrocite), α - $FeOOH$ (goethite), Fe_3O_4 (magnetite), and γ - Fe_2O_3 [9-10]. These products can coexist partly as crystalline and partly as amorphous structures, the relative amounts of which will vary depending on the environmental conditions. The rust layer formed on carbon steel is generally porous, with poor adherence, and cracked in its outer part. This structure gives a poor protection to steel against atmospheric corrosion, because it is not a barrier to the passage of electrolyte and corrosive species towards the metallic substrate [1, 11-12]. In the present work, SEM/EDX and XRD were used to characterize the corrosion products formed on carbon steel when exposed to various environments in Egypt.

Experimental work

Exposure tests

The material examined was used for the field test carbon steel plates with the dimensions 100mm*150mm*3mm. Table 1 gives the analysis of this steel obtained from the Egyptian Iron and Steel Company (EISCO). Surface preparation of steel plates consisted of mechanical grinding with 800 grade silicon carbide paper, cleaning and then dried. Immediately before testing, they were weighed on analytical balance of 0.01g sensitivity. According to ASTM G 50-76 [13], specification the test panels were exposed at 30° to the horizontal, with skyward surface facing south, at three test sites: Cairo university (urban site), Tabbin institute (industrial site) and Alexandria (coastal site). The study was carried out over 12 month's period between May 2009 and May 2010. After exposure, corrosion products on the specimen surfaces were removed by dipping in Clarke's solution (1 L HCl +20 g Sb_2O_3 +50 g $SnCl_2$ obtained from El Nasr Pharmaceutical Chemicals.co) at room temperature up to 25 minutes. After corrosion products removing, the specimens were rinsed with distilled water, dried with ablower, and then weighed to determine their weight loss. The weight loss in each test is the average obtained by using two samples. The climatic parameters influencing atmospheric corrosion were measured by Egyptian Environmental Affairs Agency and Tabbin Institute for metallurgical Studies (EEAA and TIMS), parameters measured during the exposure period. They are listed in Table 2.

Table 1 Chemical analysis of carbon steel.

Element	Fe	C	Si	Mn	P	S
Composition (wt. %)	99.43	0.06	0.07	0.4	0.028	0.011

Table 2 Environmental conditions of exposure sites.

Test site	Environment	Average temp °C	Average rain fall mm/year	Average RH, %	Average wind speed m/s	Cl ⁻ mg/m ³	SO ₂ mg/m ³
Alex	Coastal	21.417	190	69.250	4	2.265	5
El-tabbin	Industrial	22.083	26	35.167	3	0.240	38.923
Cairo uni	Urban	22.083	26	35.167	3	0.255	24.438

Rust analysis

X-ray Diffraction (XRD)

The test specimens, approximately 10x10x3mm were subjected to atmospheric corrosion for 12 months at each site. One sample was taken from each site after 12 months exposure to investigate the rust analysis by XRD (conducted using a computer controlled D8ADVANCE X-R diffractometer-Germany, employing CuK- α radiation).

SEM/EDS

Other coupons were used for SEM/EDS, after 12 months exposure. The corrosion products were characterized using scanning electron microscope (SEM)-type Inspect S50.

Results and Discussion

Atmospheric corrosion rates as a function of time

Atmospheric corrosion penetration usually is not linear with time. The buildup of corrosion products often tends to reduce the corrosion rate. Pourbaix [14] utilized the so called linear the bilogarithmic law for atmospheric corrosion, to describe atmospheric corrosion damage as a function of time on a mathematical basis. According to the linear bilogarithmic law expressed by Eq. (1)

$$P = At^B \text{ or } \log P = A + B \log t \quad (1)$$

Where p is the corrosion penetration and t is the exposure time. The corrosion penetration of carbon steel can be calculated from the weight loss measurements using equation (2).

$$P = W/ad \quad (2)$$

Where W is the weight loss, in g, a , is the surface area of the specimens, in cm² and d is the density of carbon steel (7.86g/cm³). According to the linear bilogarithmic law, the atmospheric behavior of a specific material at a given location can be defined by the two parameters A and B . The initial corrosion rate, observed during the first year of exposure, is described by A , while B is a measure of the long term decrease in corrosion rate. When B equals 0.5, corrosion penetration increase is parabolic, with diffusion through the corrosion product layers as the rate controlling step. At B values appreciably smaller than 0.5 the corrosion products show protective, passivating characteristics. Higher B values, greater than 0.5, are indicative of no protective corrosion

products. An important aspect of the linear bilogarithmic law is that it facilitates the prediction of long term corrosion damage from short exposure tests. According to Pourbaix, this extrapolation is valid for up to 20 to 30 years. Table 3 shows the estimated values for A , B and the correlation coefficient of the fitted curves shown in Fig. 1 for low carbon steel exposed at three sites. It is noted that in case of low carbon steel in urban and industrial stations (Cairo University and El-Tabbin sites), the values of B (0.52640 and 0.51228 respectively) correspond to a non-protective layer of rust, but it is close to the threshold that determines the protective behavior. In case of low carbon steel in the Alexandria station (coastal site) the value of B (0.89830) is close to 1, indicating that the rust layer had a linear growth and therefore the corrosion products were not sufficiently protective.

Table 3 Values of initial corrosion rate observed during the first year of exposure "A", long term decrease in corrosion rate "B" and correlation coefficient of the fitted curves "R²".

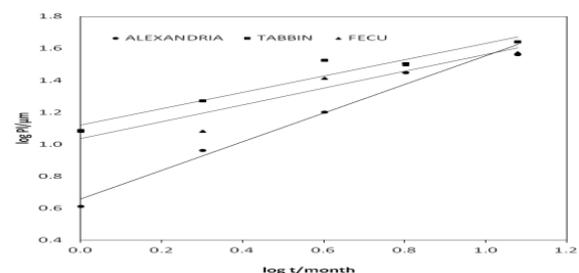
Test site	A	B	R ²
Alexandria	0.65612	0.89830	0.97910
El-tabbin	1.11990	0.51228	0.93644
Cairo University	1.03572	0.52640	0.90341

As can be observed from Figure 1 the corrosion penetration increased in the first 4 months in the order of El - Tabbin (1.52652) > Cairo University (1.4118) > Alexandria (1.20143). This behavior seems to be related to the content of SO₂ at the industrial station.

Rust Analysis

XRD

Figure 2 shows XRD spectra of corrosion products of carbon steel obtained after an exposure time 12-months. In case of Cairo University station (urban site) and El-Tabbin station (industrial site), the phases detected were mainly γ -FeOOH, α -FeOOH and Fe₃O₄. In case of samples taken from Alexandria station (coastal site), only β -FeOOH and Fe₃O₄ phases, were detected.

**Figure 1** Corrosion penetration of carbon steel in different environments as a function of time.

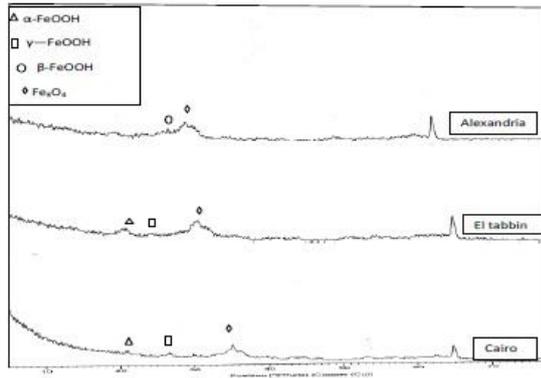


Figure 2 XRD obtained after 12-month (El-Tabbin) Industrial area, (Cairo University).

In the specimen exposed at El-Tabbin station (industrial site), (flowery structure) typical of lepidocrocite and globular (cotton balls) typical of goethite were found as shown in (Fig.4-a). (Fig. 4-b) depicts a cross – section of carbon steel specimen exposed at El-Tabbin, it shows an irregular layer of corrosion products which exhibits horizontal and longitudinal cracking. In the specimen exposed at El-Tabbin station (industrial site), (flowery structure) typical of lepidocrocite and globular (cotton balls) typical of goethite were found as shown in (Fig.4-a).

(Fig. 4-b) depicts a cross – section of carbon steel specimen exposed at El-Tabbin, it shows an irregular layer of corrosion products which exhibits horizontal and longitudinal cracking. According to Table 2, air analysis of the industrial (El- Tabbin site) as well as urban (Cairo site) was characterized by high SO_2 content (38.923 and 24.438 mg/m³, respectively). In atmospheres polluted by SO_2 , however, the surface of electrolyte is usually mildly acidic and $\text{Fe}(\text{OH})_2$ does not precipitate[15].

Hiller [16] considers $\gamma\text{-FeOOH}$ as the primary crystalline corrosion product. In mildly acidic solutions $\gamma\text{-FeOOH}$ is transformed into $\alpha\text{-FeOOH}$ in a process that is dependent on the sulphate concentration and temperature. $\alpha\text{-FeOOH}$ seems to be the most stable modification of ferric oxide hydroxides. The solubility of $\alpha\text{-FeOOH}$ is approximately 105 times lower than that of $\gamma\text{-FeOOH}$ [17].

According to the kinetic study in industrial and urban atmospheres, the rust layer formed on carbon steel correspond to a non-protective layer of rust, but it is close to the threshold that determines the protective behavior. The XRD and SEM analyses confirm the relatively protective character of this rust layer in an atmosphere which is relatively dry and slightly rich in SO_2 . However, when the climate is usually humid or rainy, this effect is reduced.

Figure (5-a) shows cigar-shaped crystals of akaganite found in the specimen exposed at Alexandria station (coastal site). (Fig.5-b) shows the cross section area in the specimen exposed at Alexandria station (coastal site); a thin layer of

irregular shape which exhibits horizontal and longitudinal cracking.

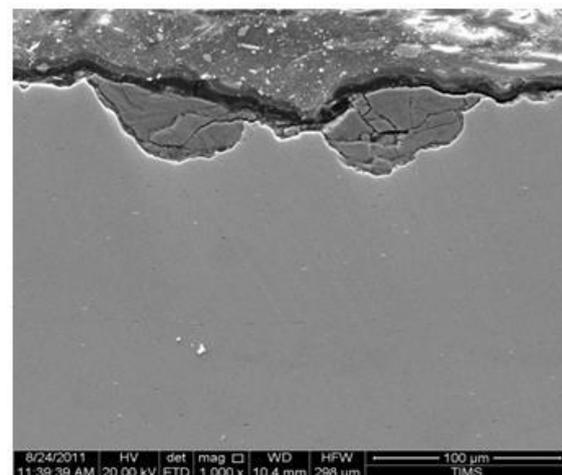
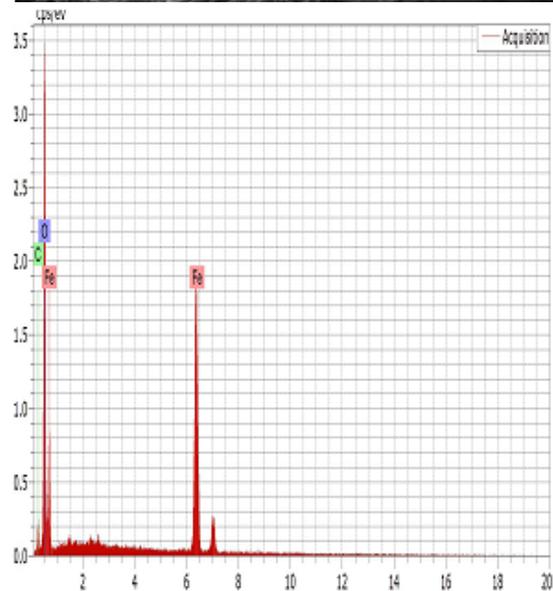
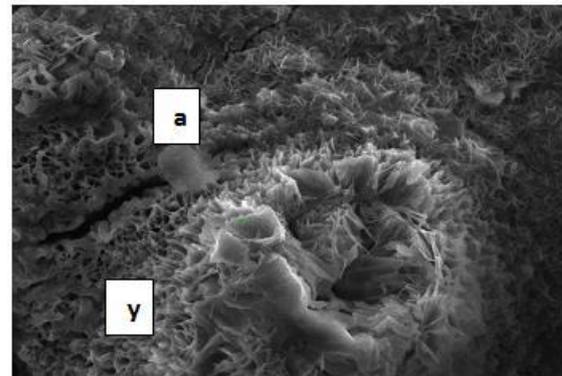
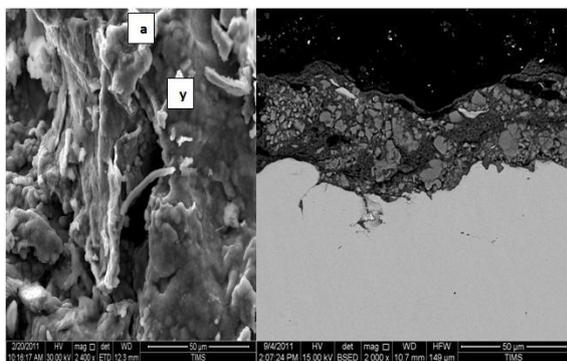


Figure 3 Morphology of corrosion products in case of urban area (Cairo University).

(Figure 5-c) shows mapping of chlorine through the cross section area in the specimen exposed at Alexandria station (coastal site); uniform distribution of chlorine ions. In Alexandria (marine atmosphere), the surface of electrolyte contains chlorides, $\beta\text{-}$



FeOOH is found which is in accordance with the findings of Keller [18].

Figure 4 Morphology of corrosion products in case of industrial area (El-Tabbin).

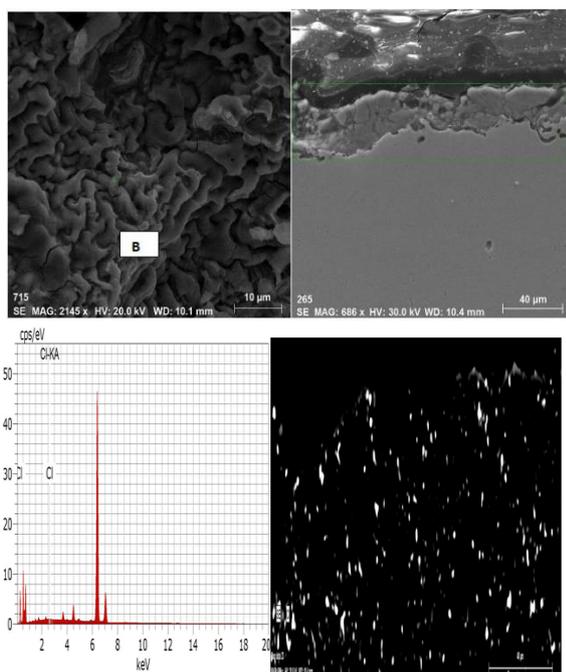


Figure 5 Morphology of corrosion products in case of coastal area (Alexandria).

The formation of detectable amounts of β FeOOH on freely exposed steel surfaces seems to require high yearly average chloride deposition rates. However on rain protected steel surfaces, β -FeOOH was found to be abundant in rust also when the chloride deposition rates were as low as 40 mg/m²/day [19]. Magnetite is also formed as one of the main constituents. Magnetite may form by oxidation of Fe(OH)₂ or intermediate ferrous–ferric species such as green rust [20]. It may also be formed by reduction of FeOOH in the presence of limited oxygen supply [21] according to;



Magnetite is usually detected in the inner part of rust adhering to the steel surface of specimens that have been subjected to prolonged exposure, where oxygen depletion may occur [22-23]. From the kinetic results the rust layer had a linear growth and therefore the corrosion products were not sufficiently protective. This is confirmed by the SEM analysis which shows the non-protective character of this rust layer in an atmosphere slightly rich in chlorine. In all cases, a good correlation was found between the

protective characteristics of rust calculated from mass loss data and observations made by SEM and XRD.

Conclusions

- The carbon steel showed good atmospheric corrosion resistance especially at industrial and urban sites.
- The corrosion behavior of the carbon steel tested in three different environments is kinetically well represented by linear the bilogarithmic law for atmospheric corrosion.
- Rust layer on carbon steel formed in case of industrial as well as urban areas was composed of mono layer. The main phases detected were γ -FeOOH, α -FeOOH and Fe₃O₄.
- In case of coastal area, samples were covered by a discontinuous corrosion product layer of low compactness. This layer was mainly composed of β -FeOOH and Fe₃O₄ phases.

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