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STUDIES OF CARBON STEEL CORROSION IN ATMOSPHERIC CONDITIONS

■ **ABSTRACT:**
One of the most frequently corrosion type is the atmospheric corrosion. Carbon steel behavior at atmospheric corrosion is presented on base of the literature data study. This has been reported to account for more failures in terms of cost and tonnage than any other type. About 80% from all degradations produced by corrosion in the metallic constructions are due to the atmospheric corrosion. The atmospheric conditions for corrosion are very complex and the corrosion rates vary in function of geographic zone, of season and daily time. The complexity of the atmosphere, as corrosion environment, results from atmosphere composition and from presence of some factors as pollutants, temperature, humidity, wind speed and direction, etc. These variables make meaningful results from laboratory experiments very difficult to obtain. The object of this work is to outline the principles that govern atmospheric corrosion of the carbon steel – the construction material with the largest application – how is influenced his corrosion rate by the atmospheric variables and that are the corresponding corrosion products.

■ **KEYWORDS:**
carbon steel, atmospheric corrosion

INTRODUCTION

One of the most frequently corrosion type is the atmospheric corrosion. This has been reported to account for more failures in terms of cost and tonnage than any other type. About 80% from all degradations produced by corrosion in the metallic constructions are due to the atmospheric corrosion. The atmospheric conditions for corrosion are very complex and the corrosion rates vary in function of geographic zone, of season and daily time. The complexity of the atmosphere, as corrosion environment, results from atmosphere composition and from presence of some factors as pollutants, temperature, humidity, wind speed and direction, etc. [1]. These variables make meaningful results from laboratory experiments very difficult to obtain.

The atmospheric corrosion is conveniently classified in three [2, 3] types: (1) dry oxidation, (2) damp corrosion and (3) wet corrosion. Dry oxidation takes place in the atmosphere with all metals that have a negative free energy of oxide formation. For metals forming non-porous oxides, the films rapidly reach a limiting thickness since ion diffusion through the oxide lattice is extremely slow at ambient temperatures, and at the limiting thickness, the oxide films on metals are invisible. For certain metals and alloys, these films confer remarkable protection on the substrate, e.g. stainless steel, titanium and chromium. The damp and wet atmospheric corrosion are characterized by the presence of a thin, invisible film of electrolyte solution on the metal surface (damp type) or by visible deposits of dew, rain, sea-spray etc. (wet type). In these categories may be placed the rusting of iron and steel, 'white rusting' of zinc (wet type) and the formation of patina on copper and its alloys (both types).

The corrosion products may be soluble or insoluble. Usually, those insoluble reduce the corrosion rate by isolating the substrate from the corrosive environment. Less commonly, they may stimulate corrosion by offering little physical protection while retaining moisture in contact with the metal surface for long periods. The soluble products may increase corrosion rates.

The severity of atmospheric corrosion depends on the environment type [4, 5]: rural, urban, industrial, marine and combined.

The rural atmosphere generally the least corrosive and normally does not contains chemical pollutants. The principal corrosive agents are moisture, oxygen and carbon dioxide.

The urban atmosphere is similar to the rural type in that there is little industrial activity. Additional contaminants are of the SO_x and NO_x variety, from motor vehicle and domestic fuel emissions.

The industrial atmospheres are associated with heavy industrial processing facilities and can contain sulphur dioxide, chlorides, phosphates and nitrate.

The marine atmospheres are usually highly corrosive, due to the presence of chlorides, and corrosivity tends to be significantly dependent on wind direction, wind speed and distance from the coast.

The object of this work is to outline the principles that govern atmospheric corrosion of the carbon steel - the construction material with the largest application - how is influenced his corrosion rate by the atmospheric variables and that are the corresponding corrosion products.

## CORROSION PRINCIPLES OF CARBON STEEL IN ATMOSPHERE

A fundamental requirement for electrochemical corrosion process is the presence of an electrolyte. This film 'invisible' electrolyte tends to form on metallic surfaces under atmospheric exposure conditions after certain critical humidity level is reached. The critical humidity level is not constant and depends on the corroding material, the tendency of corrosion products and surface deposits to adsorb moisture, and the presence of atmospheric pollutants. For iron, the relative critical humidity is 60% in atmosphere free of sulphur dioxide.

In absence of the pollutants, in an atmosphere with relative humidity of least 70%, the carbon steel corrodes with formatting in time of $Fe(OH)_2$, after the electrochemical mechanism [6], conform to the reactions:

Anodic reaction:
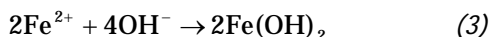
$$2Fe \rightarrow 2Fe^{2+} + 4e \qquad (1)$$

Cathodic reaction:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \qquad (2)$$
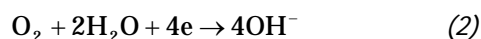
The products of these reactions combine forming ferrous hydroxide - a compound insoluble at neutral pH - that deposits on the metal surface:

$$2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2 \qquad (3)$$

In presence of the oxygen, the ferrous hydroxide oxidizes and forms the rust.

If oxygen from the atmosphere diffuses through the electrolyte film to the metal surface, a diffusion-limiting current density should apply. It has been shown that a diffusion transport mechanism for oxygen is applicable only to an electrolyte-layer of approximately of 30 μm and under strictly isothermal conditions [3]. The predicted theoretical limiting current density of oxygen reduction in an electrolyte-layer of 30 μm significantly exceeds the practical observations on atmospheric corrosion rates. Therefore, the overall rates of the atmospheric corrosion are likely to be controlled not by the cathodic oxygen reduction process, but rather by the anodic reaction(s).

In the presence of gaseous air pollutants, other reduction reactions, involving ozone, sulphur dioxide and nitrogen species have to be considered [7]. It be noted that corrosive contaminant concentrations can reach relatively high values in the thin electrolyte films, especially under conditions of alternate wetting and drying.

THE ROLE OF THE IMPORTANT VARIABLES IN ATMOSPHERIC CORROSION OF CRBON STEEL

Humidity. From the above theory, it should be apparent that presence of electrolyte on the corroding surface (time of wetness) is a key parameter, directly determining the duration of the electrochemical corrosion process. This variable is a complex one, since all the means of formation and evaporation of an electrolyte solution on a metal surface must be considered.

The time of wetness is strongly dependent on the critical relative humidity. The relative humidity of the air varies in large limits, in function of geographic zone, of season and daily time.

Apart from the primary humidity, associated with clean surfaces, secondary and tertiary critical humidity levels may be created by hygroscopic corrosion products and capillary condensation of moisture in corrosion products, respectively. A capillary condensation mechanism may also account for electrolyte formation in microscopic surface cracks and the metal surface-dust particle interface. Other sources of surface electrolyte include chemical condensation (by chloride, sulphates and carbonates), adsorbed molecular water layers, and direct moisture precipitation (ocean spray, dew, rain).

Temperature. The effect of temperature on the atmospheric corrosion rates is quite complex. An increase in temperature will tend to stimulate corrosive attack by increasing the rate of electrochemical reactions and diffusion processes. For a constant humidity level, the increase in temperature would lead to a higher corrosion rate. However, raising the temperature will, generally, lead to a decrease in relative humidity and more rapid evaporation of the surface electrolyte. When the time of wetness is reduced in this manner, the overall corrosion rate tends to diminish.

For closed air spaces, it has been pointed out that the increase in relative humidity associated with a drop in temperature has an overriding effect on corrosion rate [8]. This implies that simple air conditioning that decreases the temperature without additional dehumidification will accelerate atmospheric corrosion damage. An important factor in corrosion favoring is the continue oscillations of temperature.
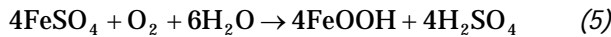
For atmospheric corrosion of metals, the extreme temperatures do not an important role.

Atmospheric contaminants. The electrolyte film that forms on metallic surface contains various compounds resulted from the atmospheric pollutants. Karlson et al [9] observed a severe corrosion of steel if in atmosphere there is sulphur dioxide (SO_2) or alkaline chlorides (in principal NaCl).

Sulphur dioxide. SO_2, a product of combustion of fossil fuels containing sulphur, play an important role in atmospheric corrosion in urban and industrial atmospheres. For all metals, SO_2 appears to be selectively adsorbed from the atmosphere, less so for aluminum than for other metals, and for rusty steel it is almost quantitatively adsorbed even from dry air at
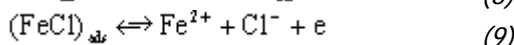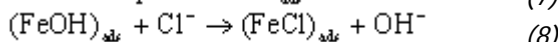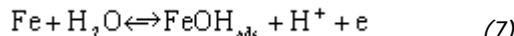
0^oC [2]. *Under humid conditions sulphuric acid is formed, the oxidation of SO_2 to SO_3 being catalysed by metals and by metallic oxides.*

For non-ferrous metals, SO_2 is consumed in the corrosion reaction whereas in the rusting of iron and steel it is considered [2] that ferrous sulphate is hydrolysed to form oxides and thus the sulphuric acid is regenerated. Sulphur dioxide thus acts as catalyst such that one SO_4^{2-} ion can catalyse the dissolution of more 100 atoms of iron [2]. The reactions can be summarized as follows:

$$\mathrm{Fe + SO_2 + O_2 \rightarrow FeSO_4} \qquad (4)$$

$$\mathrm{4FeSO_4 + O_2 + 6H_2O \rightarrow 4FeOOH + 4H_2SO_4} \qquad (5)$$

$$\mathrm{4H_2SO_4 + 4Fe + 2O_2 \rightarrow 4FeSO_4 + 4H_2O, \, at \, seq.} \qquad (6)$$

The high solubility of SO_2 (of 1300 times more soluble than O_2 in water) [2] would make it a more effective cathodic reactant than dissolved oxygen even though its concentration in the atmosphere is comparatively small.

Chlorides. The corrosion rates of the carbon steel increase in marine atmosphere due to its salinity [3]. Apart from enhanced surface electrolyte formation by hygroscopic salts such as NaCl and $MgCl_2$, direct participation of chloride ions in the electrochemical corrosion reactions is also likely. In case of the ferrous metals, chloride anions are known to compete with hydroxyl ions, to combine with ferrous cations produced in the anodic reaction. In the case of hydroxyl ions, stable passivating species tend to be produced. In contrast, iron chloride complexes are soluble, resulting in further stimulation of corrosive attack, according to reactions [10]:

$$\mathrm{Fe + H_2O \Leftrightarrow FeOH_{ads} + H^+ + e} \qquad (7)$$

$$\mathrm{(FeOH)_{ads} + Cl^- \rightarrow (FeCl)_{ads} + OH^-} \qquad (8)$$

$$\mathrm{(FeCl)_{ads} \Leftrightarrow Fe^{2+} + Cl^- + e} \qquad (9)$$

Other atmospheric contaminants, related to industrial emissions in specific microclimates are: hydrogen sulphide, hydrogen chloride, and chlorine that can intensify atmospheric corrosion damage. Hydrogen sulphide is known to be extremely corrosive producing Hydrogen Embrittlement Corrosion of alloys [11]. The corrosive effects of gaseous chlorine and hydrogen chloride in presence of moisture tend to be stronger than those of chloride salts anions because of the acidic character of the former species.

The deposition of solid matter from atmosphere can have a significant effect on atmospheric corrosion rates, particularly in the initial stages. Such deposits can stimulate the atmospheric attack by three mechanisms:

(1) reduction in the critical humidity levels by hygroscopic action;

(2) the provision of anions, stimulating metal dissolution, and

(3) microgalvanic effects by deposits more noble than the corroding metal (carbonaceous deposits deserve special mention in this context) and by different aeration, so it shows in Fig. 1.
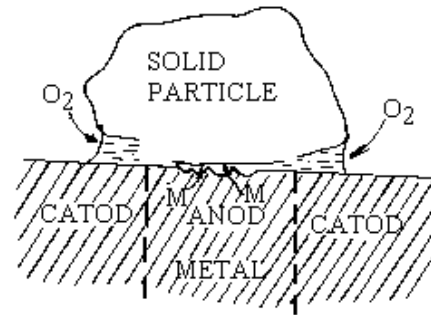

Figure 1 - Corrosion in centre of a surface covered by a solid particle

THE CORROSION PRODUCTS FORMATTED ON CARBON STEEL IN ATMOSPHERIC CORROSION

In presence of oxygen the ferrous hydroxide (reaction 3) oxidizes forming the rust. The iron corrosion products, the rust, have complex composition.

Hiller [12] given a scheme (figure 2) that shows the principal crystalline components of the rust and possible way of their formatting.
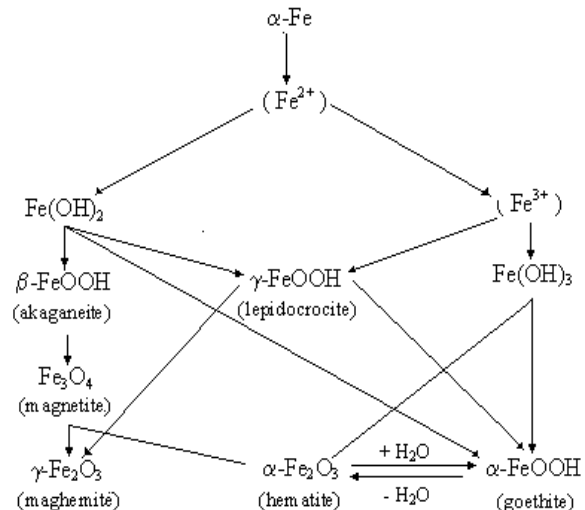

Figure 2 - Hiller scheme for the iron rust compounds [12]

In the first phase of the steel rusting forms $Fe(OH)_2$, which it oxidizes suddenly forming lepidocrocite (γ-FeOOH), a crystalline phase with rhombic structure. In function of water presence or absence, this isomerises in goethite (α-FeOOH), with rhombic structure also. If the corrosion rate is low, a part of lepidocrocite it transforms in maghemite (γ-Fe_2O_3), having a cubic structure.

Akaganeite(β-FeOOH), with tetragonal structure, it forms in the environments with high chlorides content. After Keller [13] akaganeite is the most unstable oxihydrate formed at corrosion steel. In humidity conditions this it transforms in magnetite (Fe_3O_4), having cubic structure. After Hiller [12] magnetite it forms only in direct contact with metal surface and in presence of a high humidity. This compound does not appear in the incipient phases of rusting; it is a product that forms in time from akaganeite, conform to the reaction:

$$\mathrm{2FeOOH + Fe(OH)_2 \rightarrow Fe_3O_4 + 3/2H_2} \qquad (10)$$
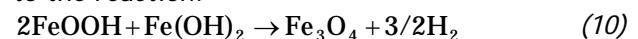
Another oxihydroxide of iron, crystallite (δ-FeOOH), having a hexagonal structure, it forms especially in the

27

atmosphere with low humidity [14]. This can find and in the amorphous state- feroxite.

After K.A. van Oecteron [15] the most important compounds of the rust are oxihydroxides of iron and magnetite.

In presence of the pollutants and in the incipient stages of the carbon steel corrosion, sometimes, forms on metal surface the, so called 'green rust' [16-20].

Green rust is a mixture of hydroxide-salts of Fe(II, III) with formulae:

$$\left[Fe^{II}_{(1-x)}Fe^{III}_{x}(OH)_2\right]^{x+} \cdot \left[\frac{x}{n}A^{n-} \cdot \frac{m}{n}H_2O\right]^{x-} \qquad (11)$$
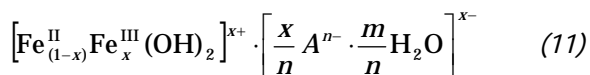
This has a structure in which the iron hydroxide layers with positive charge alternate with negative charged anion layers and with water molecules, leading to a hexagonal symmetry. The green rust is classified [21] in two types:

❖ green rust I, in which A^{n-} are anions with planar structure, as Cl^-;
❖ green rust II, in which A^{n-} are anions with three-dimensional structure, as, sulphate, carbonate, etc.

The change in corrosion rate with time varies markedly for different metals due to the differing degrees of protection conferred by the corrosion products. The behavior of steel is conditioned by the alloying elements present for any given environment. Thus the decrease in corrosion rate with time for carbon steel is very much slower than for low-alloy steel. This can attributed to the much more compact nature of the rust formed on the latter type.

CONCLUSION

The atmospheric corrosion, the most frequently corrosion type of the carbon steel takes place in presence of the humidity surface layer after the electrochemical corrosion mechanism. The principal parameters that determine the corrosion rate are: humidity temperature and presence of pollutants as sulphur dioxide and chloride ions. The carbon steel corrosion products - the rust - have a complex composition, being formatted of various iron oxides and oxihydroxides types.

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