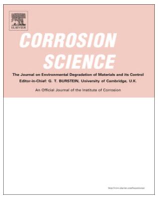
Corrosion Science xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci



Airborne chloride deposit and its effect on marine atmospheric corrosion of mild steel

J. Alcántara, B. Chico, I. Díaz, D. de la Fuente, M. Morcillo *

National Centre for Metallurgical Research (CENIM-CSIC), Avda. Gregorio del Amo, 8, 28040 Madrid, Spain

ARTICLE INFO

Article history:
Received 8 October 2014
Accepted 18 April 2015
Available online xxxx

Keywords:
A. Mild steel
B. SEM
B. XRD
C. Atmospheric corrosion
C. Rust

ABSTRACT

Research has been carried out for one year in six pure marine atmospheres with annual average chloride deposition rates of 70–1906 mg Cl^-/m^2 day. A study of some environmental parameters and their influence in the airborne chloride deposit on the site has been accomplished. The paper also considers mild steel corrosion rate and the resulting corrosion products and layers, and its dependence of atmospheric salinity of the site. In addition to lepidocrocite and goethite, high akaganeite and magnetite contents were found in the corrosion products. Additional magnetite formation is possible due to the transformation of lepidocrocite.

1. Introduction

The atmospheric corrosion of metals is an electrochemical process which is the sum of the individual processes that take place when an electrolyte layer forms on the metal. This electrolyte can be either an extremely thin moisture film (just a few monolayers) or an aqueous film of hundreds of microns in thickness (when the metal is perceptibly wet). Aqueous precipitation (rain, fog, etc.) and humidity condensation due to temperature changes (dew) are the main promoters of metallic corrosion in the atmosphere.

Atmospheric salinity in coastal regions generates a notable increase in the atmospheric corrosion rate compared to a clean atmosphere, as marine chlorides dissolved in the moisture layer considerably raise the conductivity of the electrolyte film on the metal and tend to destroy any passivating films. The corrosion rate is a function of the Cl^- ion activity.

In 1973 Barton noted that the mechanism governing the effects of Cl^- ions in atmospheric corrosion had not been fully explained, and that the higher corrosion rate of steel in marine atmospheres could also be due to other causes [1]: (a) being hygroscopic, chloride species (NaCl, $CaCl_2$ or $MgCl_2$) promote the electrochemical corrosion process, favouring the formation of electrolytes at relatively low relative humidity (RH) values; and (b) the solubility of the corrosion products formed also plays an important role. Thus, in the case of iron, which does not form stable basic chlorides, the action of chlorides is more pronounced than with other metals (Zn, Cu, etc.) whose basic salts are only slightly soluble. Since then, there has been great progress in scientific knowledge of atmospheric corrosion in marine environments. A brief review of state of the art on the matter is subsequently presented.

In addition to the corrosion products commonly found in the atmospheric exposure of steel, namely lepidocrocite (γ-FeOOH) and goethite (α-FeOOH), in marine atmospheres the formation of akaganeite (β-FeOOH) and magnetite (Fe_3O_4) is particularly important. The formation mechanisms and the identification of these phases in corrosion layers have been and continue to be the cause of considerable controversy.

The research presented in this paper has a double aim. On the one side a study of some environmental parameters and their influence in the airborne chloride deposit on the site has been accomplished: spectral wave height in the nearby sea, the wind speed and the marine wind run. It is of interest to carry out studies in relation with this matter. A greater knowledge of this effect would enable us, for example, to make a rough estimate atmospheric salinities simply by analysing information about wave high in the nearby and wind characteristics already existing in the environmental databases of any country. The inclusion of salinity values in the numerous published damage functions between corrosion and environmental factors [2–4] would also make it possible to estimate atmospheric corrosion simply from environmental databases without having to carry out natural corrosion tests in a specific site, which involve long waiting times and considerable expenses. On the other hand the paper assesses the mild steel corrosion rate and analyses the resulting corrosion products and layers, and its dependence of atmospheric salinity of the site of exposure.

---

* Corresponding author. Tel.: +34 91 553 8900; fax: +34 91 534 7425.
E-mail address: morcillo@cenim.csic.es (M. Morcillo).

http://dx.doi.org/10.1016/j.corsci.2015.04.015

Please cite this article in press as: J. Alcántara et al., Airborne chloride deposit and its effect on marine atmospheric corrosion of mild steel, Corros. Sci. (2015), http://dx.doi.org/10.1016/j.corsci.2015.04.015

The exceptional weather conditions experienced at the test site over the year in which the study was carried out (April 2013–March 2014) led to very high Cl^- ion deposition rates of up to 1906 mg Cl^-/m^2 day, not normally found in the scientific literature on marine atmospheric corrosion, which have given rise to high levels of akaganeite and magnetite/maghemite in the corrosion layers formed in the different testing stations.

1.1. Atmospheric corrosion of mild steel in marine atmospheres. A brief state of the art

Atmospheric salinity in coastal regions promotes a notable increase in the atmospheric corrosion rate of steel compared to a clean atmosphere. The corrosion rate is a function of Cl^- ion activity in the moisture film, under which the steel corrodes according to the anodic reaction:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (1)$$

where the cathodic process consists of the reduction of oxygen dissolved in the moisture film:

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \qquad (2)$$

The OH^- ions formed migrate towards the anodic zones forming $Fe(OH)_2$ as the initial rust product:

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

There is currently consensus that in pure atmospheres (free of pollutants) or atmospheres with low Cl^- deposition the main corrosion products formed on steel are lepidocrocite, goethite and magnetite. The oxidation by oxygen from the air of Fe^{2+} ions produced as a consequence of the dissolution of Fe in the thin aqueous films formed in periods of wetting of the metallic surface, lead to the precipitation and crystallisation of lepidocrocite in the drying stage via the prior formation of $Fe(OH)_2$; the atmospheric corrosion process starts with the formation of lepidocrocite [5].

Evans [6] was the first researcher to electrochemically postulate that the oxidation of iron was balanced by the reduction of rust in periods of high water content within the porous structure of the rust. Subsequently, Strattmann et al. [7], in an electrochemical study of phase transitions in already formed rust layers, proposed a three-stage rust formation mechanism (wetting, wet surface, and drying), demonstrating that the anodic reaction of iron dissolution in the first stage was not balanced by the cathodic reaction of reduction of the oxygen present in the moisture layer, but by the reduction of the pre-existing oxide, giving rise to a "reduced lepidocrocite" transition phase.

$$\gamma\text{-FeOOH (lepidocrocite)} + H^+ + e^- \rightarrow \gamma\text{-Fe} \cdot OH \cdot OH \text{ (reduced lepidocrocite)} \qquad (4)$$

Once the reducible lepidocrocite is exhausted, importance is acquired by the cathodic reaction of reduction of the oxygen dissolved in the rust layer (2), whose slow diffusion in the electrolyte-filled pores in the rust layer means that the metallic dissolution rate is highly limited. During drying, oxygen diffusion is extremely high due to the thinning of the electrolyte film, giving rise to high corrosion rates, where (2) is the cathodic reaction, accompanied by the reoxidation of the previously formed reduced lepidocrocite to lepidocrocite.

$$2\gamma\text{-Fe} \cdot OH \cdot OH + 1/2O_2 \rightarrow 2\gamma\text{-FeOOH} + H_2O \qquad (5)$$

In Cl^--rich atmospheres, Nishimura et al. note that more than the role played by lepidocrocite in the corrosion process of steel in chloride-free atmospheres, the formation of akaganeite is the cause that extremely accelerates the atmospheric corrosion process [8]. In a laboratory study these researchers saw that at low Cl^- concentrations the oxyhydroxide that formed was lepidocrocite, while high Cl^- concentrations led to the formation of akaganeite via the formation of green rust, $Fe(OH, Cl)_{2.55}$ (GR1), a process that required a certain time for the complete disappearance of GR1. They show that akaganeite can also be reduced electrochemically in the corrosion process, being consumed in the wetting period of the metallic surface. Subsequently, Antony et al. [9] and Lair et al. [10] also experimentally saw that lepidocrocite was not the only species of the different phases comprising the rust that was electrochemically reducible by Fe (galvanic couple), and that the order of reducing capacity was as follows:

$$\text{ferrihydrite, GR} > \text{akaganeite and feroxyhyte} > \text{lepidocrocite}$$

The reduction of goethite by iron was not favoured, and if it occurred it would only be at an extremely low reaction rate.

Nomura et al. [11], in a laboratory study in which Fe is made to react with a 3% NaCl solution, note that lepidocrocite forms on the rust surface that is easily accessible to oxygen dissolved in the aqueous layer, whereas the formation of akaganeite and magnetite takes place in the interior of the rust layer, specifically at the steel/rust interface, where the access of oxygen from the air is more limited. The formation of these phases takes place by the transformation, after a certain time, of basic iron complexes containing Cl^- and the slow oxidation of Fe, respectively. Thus the oxygen deficit and the presence of a high Cl^- content are fundamental factors for akaganeite formation.

Nowadays it is fully accepted that the iron oxychloride β-$Fe_2(OH)_3Cl$ is involved in the formation of akaganeite and that this requires a certain time to develop from the metastable precursors $[Fe(OH)_2]$. In research carried out by Remazeilles and Refait [12] it was seen that for low $R = [Cl^-]/[OH^-]$ ratios ($R < 1.16$) the formation of $Fe(OH)_2$ takes place, while for $R > 2.25$ only β-$Fe_2(OH)_3Cl$ forms and for intermediate R values ($1.40 < R < 2.25$) both form. These same researchers have also carried out very important laboratory studies that have enormously clarified the akaganeite formation mechanism, controlling the reaction of $FeCl_2{\cdot}4H_2O$ with NaOH by varying the $R = [Cl^-]/[OH^-]$ ratio [13]. For $R \geqslant 8$, i.e. in conditions of great excess of ferrous chloride, akaganeite formation only takes place via the formation of intermediate GR1 components, whereas at small excesses of $FeCl_2$ only lepidocrocite forms. When $R \leqslant 6$ the formation of goethite takes place, and when $6.5 \leqslant R \leqslant 8$ both goethite and akaganeite form. The akaganeite formation mechanism implies the presence of high Cl^- concentrations (at least 2–3 mol L^{-1}) and acid conditions (pH 4–6), by the hydrolysis of ferrous chloride ($FeCl_2$), conditions that occur in confined spaces where Cl^- ions accumulate: metal/corrosion products interface, crevice zones, etc.

With regard to the formation of magnetite, attention is drawn to the work of Ishikawa et al. [14]. These researchers saw that in oxygen-free aqueous solutions the reaction of the oxyhydroxides (goethite, akaganeite and lepidocrocite) with Fe^{2+} ions led to the formation of magnetite across a broad range of temperatures (25–100 °C) and pH (3–13), with a notable reduction in the oxyhydroxide content. The magnetite concentration depended on the $R = [Cl^-]/[OH^-]$ molar ratio of the suspension, showing a maximum for $R = 2$, and Fe_3O_4 is produced by the reaction of dissolved species of FeOOH with those $Fe(OH)_2$. The maximum Fe_3O_4 content was in the order:

$$\text{akaganeite} > \text{lepidocrocite} \gg \text{goethite}$$

In a recent study of Tanaka et al. [15], in which the oxyhydroxides were made to react with iron powder, the amount of magnetite formed was greater with akaganeite than with lepidocrocite, not taking into account when the oxyhydroxide was goethite.

The high steel corrosion rates promoted by the presence of akaganeite give rise to an expansion of the rust volume which leads to

Please cite this article in press as: J. Alcántara et al., Airborne chloride deposit and its effect on marine atmospheric corrosion of mild steel, Corros. Sci. (2015), http://dx.doi.org/10.1016/j.corsci.2015.04.015