

Atmospheric corrosion of mild steel in chloride-rich environments. Questions to be answered

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

This paper describes the peculiarities of carbon steel corrosion in very severe marine atmospheres and points out a number of uncertainties that still need to be explained, such as the following: (a) Data on the evolution of carbon steel corrosion (C) with exposure time (t) obeys the power function $C = At^n$. The variables upon which n depends are not fully known, though the salinity of the atmosphere undoubtedly plays a prominent role. (b) In marine atmospheres, the presence of akaganeite and magnetite phases among the corrosion products is especially significant. In relation with these corrosion products, a number of important questions remain unanswered: What conditions are necessary for their formation? Where are they preferentially located? Is there a critical atmospheric salinity concentration below they are unlikely to form? It is also of great interest to know the typical surface microscopic morphologies resulting from the presence of akaganeite, where the confusion among researchers is well known. (c) In very severe marine atmospheres, the morphology of the corrosion layers formed on steel can be highly unusual, such as sheet-type or mound rust. There is a lack of basic knowledge on the formation mechanisms and internal microstructure of these rust types.

1 Introduction

The atmospheric corrosion of metals is an electrochemical process, which is the sum of 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 chloride ion activity.

The rate of the corrosion reaction increases with the concentration of ionising substances (e.g., chlorides) in the moisture film. Under this film the metal corrodes in a cathodic process of reduction of oxygen from the air. The hydroxide ions

that are formed migrate to anodic areas, forming ferrous hydroxide as the initial corrosion product.

In 1973 *Barton* noted that the mechanism governing the effects of chloride ions in atmospheric corrosion had not been completely 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 (sodium chloride, calcium chloride, or magnesium chloride) 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 (zinc, copper, etc.) whose basic salts are only slightly soluble.

Since then, there has been great progress in scientific knowledge of atmospheric corrosion [2]. *Nishimura et al.* [3] noted in the year 2000 that with the exception of a few studies, research on the fundamental mechanisms of rust formation in chloride-rich marine atmospheres had been rather scarce. In a laboratory study, *Nishimura et al.* observed that in this type of atmosphere, akaganeite formation was the cause that enormously accelerated the atmospheric corrosion process, being electrochemically reduced and consumed during the wetting of the metallic surface, instead of the important role played by lepidocrocite in

M. Morcillo, B. Chico, J. Alcántara, I. Díaz, J. Simancas, D. de la Fuente
National Centre for Metallurgical Research (CENIM-CSIC), Avda.
Gregorio del Amo, 8 28040, Madrid, (Spain)
E-mail: morcillo@cenim.csic.es

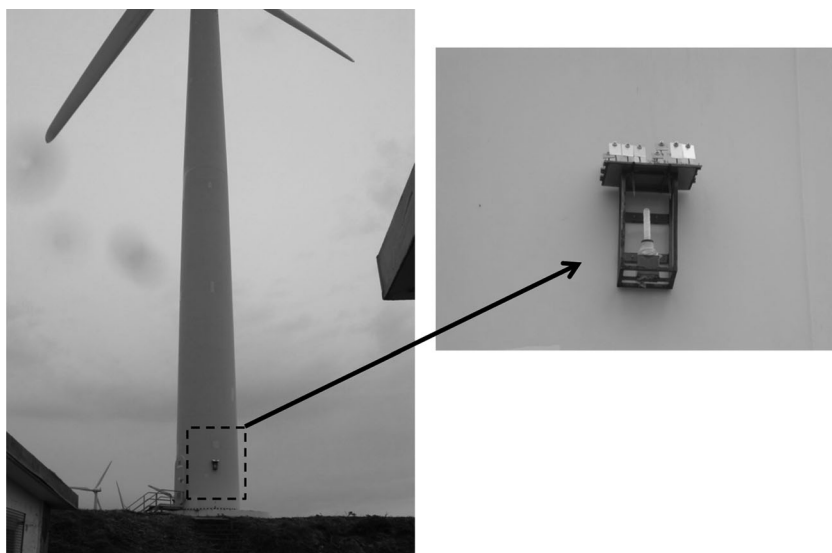


Figure 1. Atmospheric corrosion testing station

steel corrosion in chloride-free atmospheres. High chloride concentrations led to the formation of akaganeite.

This work sets out the peculiarities and uncertainties related with carbon steel corrosion in very severe marine atmospheres, and ends by highlighting some of the questions that still remain unanswered.

2 Experimental

Research was carried out at two atmospheric testing stations located at Cabo Vilano wind farm (Camariñas, Spain) at different distances from the shoreline: 270 m (Station 1) and 332 m (Station 2), respectively. Each station (Fig. 1) was fixed by magnets to the leg of a wind turbine, facing north, which according to historic records is a dominant wind direction at the exposure site.

The station consisted of a rack holding the atmospheric salinity-measuring device (wet candle [4]) at the bottom and the mild steel specimens, whose composition is shown in Table 1, at the top. The specimens measured $5 \times 10 \text{ cm}^2$ and had a thickness of 1 mm. Specimens were withdrawn after 3, 6, 9, and 12 months of exposure.

Steel corrosion due to exposure to the atmosphere has been determined (in triplicate) by the mass loss technique [5]. The corrosion products formed have been characterised by XRD using a BRUKER AXS X-ray diffractometer, model D8 Advance, equipped with a cobalt X-ray tube and a diffracted beam monochromator. The applied voltage was 40 kV and the filament current was 30 mA. Angular scanning was carried out from 10° to 80° , with a step width of 0.03° and a step acquisition time of 3 s.

Table 1. Chemical composition (wt%) of the mild steel used

C	Si	Mn	P	S	Cr	Ni	Cu
0.13	0.09	0.55	<0.02	0.018	0.02	0.02	0.02

Prior to XRD analysis, the rust was screened in order to obtain a particle size of $125 \mu\text{m}$. Semi-quantitative analysis of the rust phases was performed by using the relationship I/I_c (also known as the relative intensity ratio (RIR) method) from the powder diffraction files (PDF) card and MATCH 2 software.

Microscopic observation of the rust layers formed has been carried out using a Nikon model Epiphot 300 polarised light optical microscope equipped with an Infinity 2 camera, and a Hitachi S4800 high resolution scanning electron microscope (SEM) (3 nm in high vacuum mode) equipped with secondary electron and backscattered electron detectors and an Oxford Inca energy dispersive microanalysis system (EDS). Microscopic analysis was carried out on cross sections, observing the structure of the rust layer, pit formation and chlorine distribution in the rust, and on the metal surface, observing the morphology of the different corrosion products comprising the rust.

3 Results and discussion

3.1 Meteorological characteristics of Cabo Vilano wind farm test site

Table 2 shows climate parameters characterising the environment in the study period of April 2013–March 2014, taken from the Spanish Meteorological Agency (AEMET) database for Cabo Vilano weather station located just a few metres away from Station 2.

Table 2 also shows the significant spectral wave heights in the study period supplied by Villano-Sisargas buoy, of the State Port Authority buoy network, close to Cabo Vilano.

The area is seen to present a high relative humidity (RH_{avg} 83.5%), mild temperature (T_{avg} 13°C), and high precipitation ($9908 \text{ L/m}^2/\text{year}$ and >150 days of precipitation/year). These values indicate high times of wetness of the metallic surface, which favour atmospheric corrosion processes. It is also seen that the test site is subjected to strong winds, mainly north-easterly, and the average wind speed is high (21–36 km/h), as is the

Table 2. Meteorological characteristics of the test site at Cabo Vilano wind farm

	<i>T</i> (°C)	HR (%)	Total precipitation (L/m ²)	Days of precipitation	Average wind speed (km/h)	Significant spectral wave height (m)	Number of days with maximum gusts ≥ 70 km/h	Wind direction with frequencies ≥ 20%
April'13	11.7	78.0	874	15	35	3.38	10 ^{a)}	NE, NNE
May'13	12.4	78.8	917	14	30	2.46	2 ^{a)}	NE
June'13	14.3	85.8	464	13	29	2.28	9 ^{a)}	NE
July'13	16.8	86.8	138 ^{a)}	>6	^{b)}	1.61	2 ^{a)}	^{b)}
August'13	17.6	85.0	202	9	29	1.52	9 ^{a)}	NE
Sept.'13	^{b)}	^{b)}	74 ^{a)}	>7	21	1.84	2 ^{a)}	NE, NNE
Oct.'13	14.9	85.8	634 ^{a)}	>4	29	2.42	18 ^{a)}	SSW, S
Nov.'13	12.2	77.8	9814	17	32	3.24	13 ^{a)}	NE
Dec.'13	^{b)}	^{b)}	1140 ^{a)}	>9	^{b)}	4.14	7 ^{a)}	^{b)}
Jan.'14	9.7	88.0	1636 ^{a)}	>22	26	5.08 ^{a)}	8 ^{a)}	WSW
Feb.'14	9.5	84.5	2242 ^{a)}	>20	36	4.97 ^{a)}	14 ^{a)}	WSW, SSW
March'14	10.9	84.0	606 ^{a)}	>14	25	3.22	8 ^{a)}	WSW _(15–20) , N _(15–20)
Annual average	13.0 ^{a)}	83.5 ^{a)}	9908 ^{a)}	>150	29.2 ^{a)}	3.01 ^{a)}	97 ^{a)}	

^{a)}Value obtained with available data.

^{b)}Data not available.

number of days per year with gusts of more than 70 km/h (97 days). The preferential wind direction and the proximity of the stations to the shoreline indicate that the test stations have been subjected to strong marine winds with considerable entrainment of marine aerosol (atmospheric salinity), which has greatly boosted the metallic corrosion process.

The wind, which stirs up and entrains seawater, is the force responsible for the salinity present in marine atmospheres. The waves, whose breaking leads to the formation of marine aerosol, originate in the so-called 'generating zones', which are generally associated with the strong winds or storms. Wave height depends not only on the wind speed, but also on the size of the generating zone across which the wind blows (fetch) and the number of hours the wind has been blowing (wind persistence). When waves propagate outside the generating zone, through an area of calm, a sea swell is originated. Finally, when the swell reaches the coast, the waves become unstable and break [6].

On the high seas, the breaking of waves depends on the speed of the wind blowing over them. In the coastal surf zone, waves can break without the need for simultaneous wind action, and the amount of aerosol generated is largely dependent on the type of sea floor (uniformity, slope, etc.) and the width of the surf zone [7,8].

Aerosol particles can be entrained inland by marine winds, settling after a certain time and after covering a certain distance. The wind regime directly influences aerosol production and transportation, and is significantly affected by geostrophic winds, large-scale atmospheric stability, and the difference between diurnally-averaged land and sea temperatures, which varies according to the season of the year. It is also dependent on the latitude, ruggedness of the coastline, and undulation of the land surface [7,8].

It is therefore of interest to carry out studies in relation with these matters [9,10]. Greater knowledge of these effects would enable us, for instance, to estimate the atmospheric salinity simply by analysing information on sea swell and winds in

meteorological and sea-state databases. The inclusion of salinity values in the numerous published damage functions between annual corrosion and environmental factors (for instance, [11]) would also allow the estimation of atmospheric corrosion simply from those data, without having to carry out natural corrosion tests in a specific site, which involve long waiting times and considerable expense.

3.2 Corrosion losses

3.2.1 Short-term tests

From the graphs of variation in salinity and corrosion at the two stations during the first 6 months of exposure (Fig. 2), attention is drawn to a number of relevant facts that need to be clarified:

- The atmospheric salinity values are extremely high, which is uncommon in marine atmospheric corrosion studies carried out in different parts of the world [12].

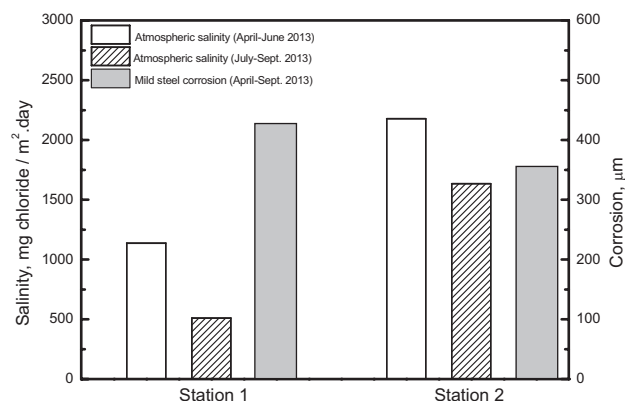


Figure 2. Atmospheric salinity values found in stations 1 and 2 in the first two 3-month exposure periods and mild steel corrosion after 6 months of exposure

- (b) Station 1 is slightly closer to the shoreline than station 2, yet its salinity is lower.
- (c) Steel corrosion is slightly lower at station 2, which receives much more salinity.

With regard to the first matter, it should be pointed out that the study year has been atypical in comparison with previous years in the same test site [13], as a high number of storms and very strong marine winds have given rise to exceptionally high entrainment of marine aerosol.

With regard to (b), there is a cliff between station 1 and the shoreline in a northerly direction, which partly blocks the transportation of marine aerosol inland, and the testing station is partly shielded from the marine winds that blow from this quarter. In contrast, there is no barrier between station 2 and the shoreline to interrupt the transportation of marine aerosol inland.

Finally, with regard to the lower corrosion found in station 2, where enormously high salinity values have been measured, the explanation lies in the less oxygen solubility in the aqueous layer of precipitated water on the metallic surface, with a very high chloride concentration. Oxygen is a fundamental element for the cathodic process of metallic corrosion. This finding is not an isolated occurrence. *Pascual Marqui* [14] explains this effect in terms of competitive adsorption: for high chloride concentrations, the absorbed oxygen concentration on the metal surface is lower, in contrast to the adsorption of chloride ions. *Espada et al.* [15] also observed this effect with salt fogs at high sodium chloride concentrations. In another ancient study by *Hache* [16], it was experimentally seen in immersion tests that both steel corrosion and dissolved oxygen decreased when the saline solution concentration exceeded a threshold of 10 g sodium chloride/L.

For salinities above 600 mg chloride/m² day there is not much steel corrosion data in the literature [12]. It would be important to have more information from very severe marine atmospheres in order to rigorously confirm this fact.

3.2.2 Long-term tests

For long-term atmospheric corrosion, most of the experimental data have been found to adhere to the following kinetic relationship:

$$C = At^n \quad (1)$$

where C is the corrosion after time t , and A and n are constants.

Thus, corrosion penetration data are usually fitted to a power model involving logarithmic transformation of the exposure time and corrosion penetration.

$$\log C = \log A + n \log t \quad (2)$$

This power function (also called the bilogarithmic law) is widely used to predict the atmospheric corrosion behaviour of metallic materials even after long exposure times, and its accuracy and reliability have been demonstrated by a great number of authors: *Bohnenkamp et al.* [17], *Legault and Preban* [18],

Pourbaix [19], *Feliu and Morcillo* [20], and *Benarie and Lipfert* [21], among others.

If the parabolic law is fulfilled, corrosion behaviour will clearly be characterised by only two parameters: corrosion A after the first year of exposure and the time exponent n . When A and n are known for a given steel and exposure site, the predictions may be extended to any length of time. *Pourbaix* [19] also stated that the bilogarithmic law is valid for different types of atmospheres and for a number of materials and is helpful in extrapolating corrosion results up to 20–30 years from 4-year test results.

According to *Benarie and Lipfert* [21], Equation (1) is a mass-balance equation showing that the diffusion process is rate-determining, and this rate depends on the diffusive properties of the layer separating the reactants. The exponential law, Equation (1), with n close to 0.5, can result from an ideal diffusion-controlled mechanism when all the corrosion products remain on the metal surface. This situation seems to occur in slightly polluted inland atmospheres. On the other hand, n values of more than 0.5 arise due to acceleration of the diffusion process (e.g., as a result of rust detachment by erosion, dissolution, flaking, cracking, etc.). This situation is typical of marine atmospheres, even those with low chloride contents. Conversely, n values of less than 0.5 result from a decrease in the diffusion coefficient with time through recrystallisation, agglomeration, compaction, etc. of the rust layer. Therefore, the exponent n value can be used as an indicator of the physico-chemical behaviour of the corrosion product layer and thus of its interaction with the atmospheric environment. The value of n will depend on the local atmosphere, exposure conditions, nature of wetting/drying cycles, etc. However, there is unfortunately a shortage of data in the literature on steel atmospheric corrosion for long exposure times in varied marine atmosphere exposure conditions, and only by the analysis of such data would it be possible to establish what mathematical relationships would be most consistent to define the kinetics of the atmospheric corrosion process and be able to predict the long-term behaviour of steel in marine atmospheres.

According to *Benarie and Lipfert* [21], as a rule $n < 1$ and there is no physical sense for $n > 1$, as $n = 1$ is the limit for unimpeded diffusion (high permeable corrosion products or no layer at all). Thus, values of $n > 1$ have been dismissed in many atmospheric corrosion studies as being due to outliers in mass loss determinations.

However, the corrosion mechanism that acts on steel exposed to very severe marine atmospheres can differ notably from that based on the existence of a consolidated layer of corrosion products through which diffusion processes involving aggressive species from the environment take place. In very severe marine atmospheres, rust layers present heavy cracking and tend to exfoliate and become partly or completely detached from the base steel, which in turn presents heavy pitting with very deep pits. The high chloride concentration in the aqueous layer deposited on the metal and the high moisture retention in very deteriorated areas of the rust give rise to the formation of ferrous chloride, which hydrolyses the water:



notably raising the acidity of the electrolyte. In this situation the cathodic reaction



becomes important accelerating the corrosion process; the anolyte on the steel surface and in the pits that have formed becomes saturated (or close to saturation) with the highly acidic ferrous chloride solution.

Both the metallic cations and the hydrogen ions require neutralisation, which occurs by the entry of chloride ions, but this leads to an increase in the chloride concentration which intensifies the metal dissolution, giving rise in turn to the entry of more chloride which further intensifies the corrosion process. This attack mechanism is fed by the corrosion products themselves (feedback mechanism), and it is sometimes referred to as 'autocatalytic' [22].

For this reason, in highly severe marine atmospheres, Equation (1) – based on diffusion mechanisms – cannot sometimes be applicable. When applied, it is very common to find exponent n values of close to 1 due to the existence of highly permeable (and barely protective) corrosion layers or the absence of corrosion layers because of their detachment by delamination (exfoliation), or even values of $n > 1$ due to acceleration of the corrosive attack as a result of the aforementioned mechanisms [22], in contrast to the diffusion mechanism upon which Equation (1) is based. Figure 3 shows the evolution of steel corrosion with exposure time in marine atmospheres with high deposited chloride ion contents. The acceleration of the attack as exposure time advances is evident [23,24].

In an attempt to relate the exponent n value with atmospheric salinity at the exposure site in marine atmospheres, the scheme in Fig. 4 has been prepared using data supplied by the MICAT network [24] for marine atmospheres with low sulphur dioxide levels (<35 mg sulphur dioxide/m² day) (Table 3). It is seen how the exponent n value increases with the marine atmosphere salinity. It would be important to have a greater volume of

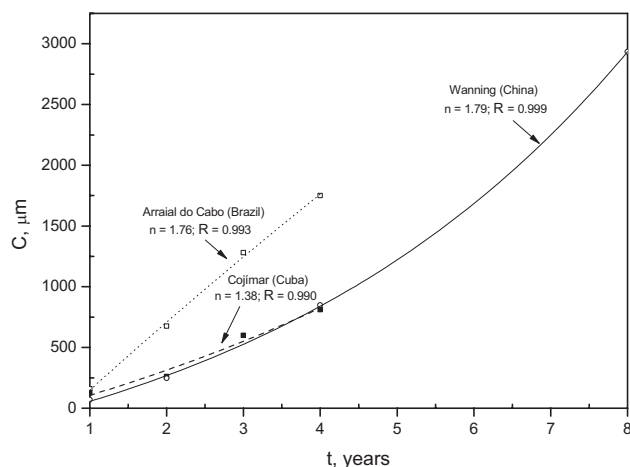


Figure 3. Evolution of mild steel corrosion with exposure time in severe marine atmospheres: Wanning, China [23], Arraial do Cabo, Brazil [24], and Cojimar, Cuba [24]. Values of exponent n and correlation coefficient (R) have been obtained from log C –log t plots for each site

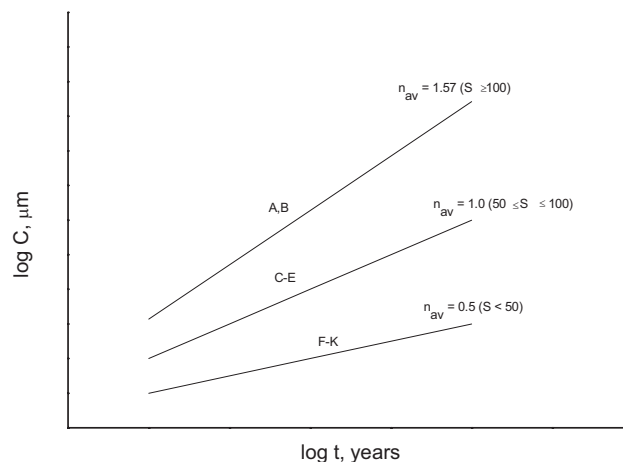


Figure 4. Variation (scheme) in log–log coordinates of mild steel corrosion with exposure time in stations of the MICAT network [24]. It is possible to see the influence of atmospheric salinity (S , mg chloride/m² day) with the average value of the exponent n in Equation (1) (see Table 3)

information in order to perfect Fig. 4, which has been drawn up with just a small amount of data (Table 3).

3.3 Nature of the corrosion products

The rust layer composition depends on the characteristics of the surface electrolyte layer that forms during exposure of the steel to the atmosphere and which originates the atmospheric corrosion process, and therefore varies according to the type of atmosphere [25]. Lepidocrocite and goethite are the major products most commonly found. Magnetite is also an important though minor rust constituent. Its differentiation from maghemite is extremely difficult; both show X-ray diffractograms practically identical. It is usually detected in the inner part of the rust, close to the base steel, where the oxygen concentration is lower.

In the present study, large magnetite formations have been found on the underlying steel that had lost the previously formed rust layer due to exfoliation. Figure 5 shows the typical (doughnut-like) morphology of this compound [26].

In marine atmospheres, where the surface electrolyte contains chlorides, akaganeite may also form. In many marine atmospheric corrosion studies it has not been possible to detect the presence of akaganeite among the corrosion products by XRD, even in atmospheres with not negligible chloride concentrations. Its presence must depend not only on the chloride concentration in the atmosphere (perhaps there is a critical threshold for its formation) but also on other factors such as the steel type, exposure time, moisture retention time of the corrosion product layers, regime of chloride entry in the rust layer during atmospheric exposure, etc. In this respect, it would be important to carry out field studies in order to clarify the conditions that lead to the formation of akaganeite and its concentration in rust as exposure time increases. *Rémazeilles* and *Refait* [27,28] have published important papers in relation with this issue.

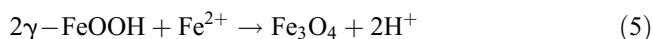
Table 3. Values of exponent n in Equation (1) and correlation coefficients (R) obtained in atmospheric corrosion stations of different salinities in the MICAT network [24]. Exposure time: 4 years

Code	Test site (Country)	Annual average salinity in the exposure period (mg chloride/m ² d)	Value of exponent n in Equation (1)	Correlation coefficient (R)
A	Arrail do Cabo (Brazil)	208.6	1.76	0.993
B	Cojimar (Cuba)	100.0	1.38	0.990
			Av: 1.57	
C	Tablazo (Venezuela)	63.3	0.64	0.992
D	Isla Naval (Colombia)	57.2	1.39	0.977
E	Camet (Argentina)	52.7	0.98	0.988
			Av: 1.00	
F	Salinas (Ecuador)	47.3	0.63	0.988
G	P.Fijo (Venezuela)	33.9	0.49	0.978
H	Coro (Venezuela)	29.7	0.45	0.998
I	Acapulco (México)	23.8	0.38	0.948
J	Barcelona (Venezuela)	21.8	0.73	0.997
K	CIQ (Cuba)	10.9	0.52	0.999
			Av: 0.53	

In the severe marine atmospheres of our study, high akaganeite contents have been found in the rust even after 1 year of exposure, and the magnetite content has also been higher than that found in atmospheres of lower salinity. Contrarily, the lepidocrocite content was notably lower (Fig. 6).

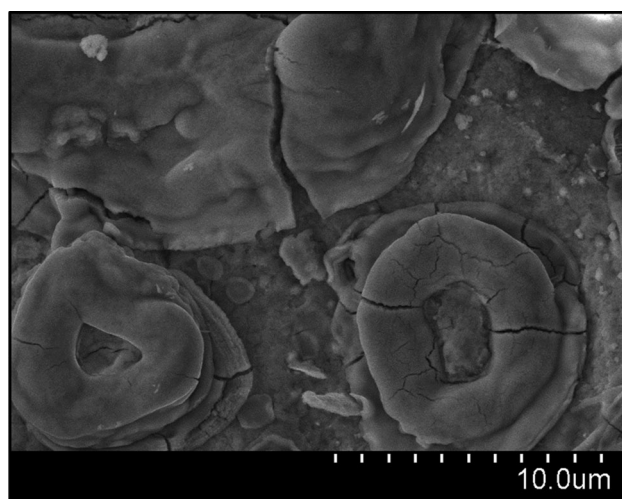
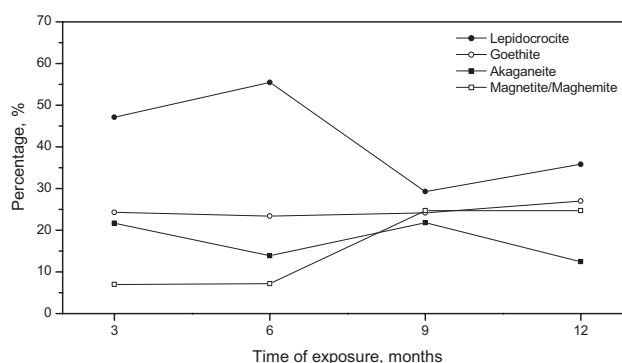
For exposure times of more than 6 months there is seen to be an increase in the magnetite/maghemite content and at the same time a considerable decrease in the lepidocrocite content. Therefore the mechanism formulated by *Ishikawa* et al. [29,30], and also suggested by *Asami* and *Kikuchi* [31], according to which magnetite could form at the expense of akaganeite, i.e., when the magnetite content increases, the akaganeite content decreases, is not confirmed in our case. In contrast, the results obtained confirm the mechanism proposed by *Tamaura* et al. [32],

according to which lepidocrocite is transformed into magnetite in the absence of oxygen, following the reaction:



Therefore it would be important to carry out research in order to clarify this point.

The morphologies of the different rust phases can be highly varied, depending on numerous factors such as the synthesis method used in the laboratory, formation conditions in the atmosphere, etc. In the literature there is a lack of rigorous studies on the morphologies of the different rust phases found on the surface of carbon steels as a consequence of their exposure in different types of atmospheres. Mention may be made of the work of *Raman* et al. [26,33–37], who used SEM to identify the rust phases formed on weathering steels on bridges in Louisiana, United States, in comparison with rusts synthesised in the

**Figure 5.** 'Doughnut-like' magnetite formation on underlying steel that has lost the previously formed rust layer due to exfoliation**Figure 6.** Evolution with exposure time of lepidocrocite, goethite, akaganeite, and magnetite/maghemite percentages in rust formed on mild steel in station 2. XRD analysis was done with the rust remaining on the sample after removing the exfoliation layers

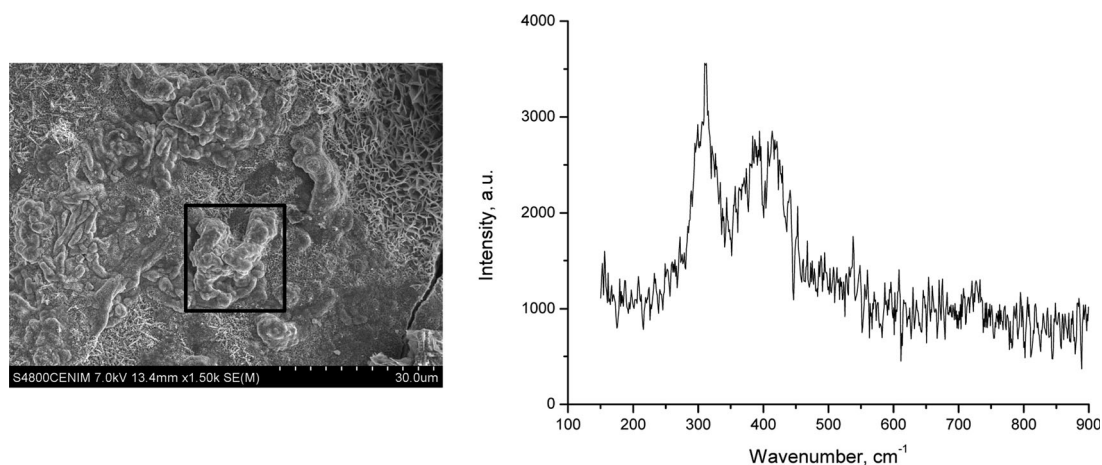


Figure 7. SEM observation of an akaganeite aggregate (left) and the corresponding characteristic Micro-Raman spectrum of this compound (right)

laboratory identified by infrared spectroscopy. Many other researchers have published papers assigning morphologies to the different phases, often making shows of their interpretation without a rigorous analytical check.

In the aforementioned studies, *Raman* et al. [26,33–37] do not unequivocally identify the possible morphologies resulting from akaganeite on the surface of the rust layers. In the present study it has been possible, albeit with great difficulty, to assign by SEM/Micro-Raman a morphology of this compound on one of the rusts formed (Fig. 7). Thus it would be important to carry out further studies on this issue using suitable characterisation techniques to identify the different corrosion products in the rust.

3.4 Structure and morphology of the rust layers

The rust layers formed on steel in rural, urban, industrial, and moderate marine atmospheres are well constituted and present a dual structure when observed in cross-section by optical microscopy with polarised light (Fig. 8). Two strata are observed

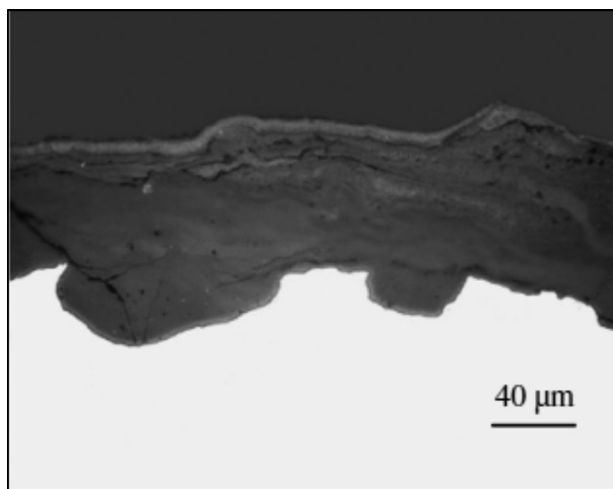


Figure 8. Observation by optical microscopy with polarised light of a cross section of a rust layer formed over 12 months in a marine atmosphere of moderate salinity [13]

in the rust layer: an outer rust layer, which is anisotropic (active under polarised light) and orangey in colour, and an inner rust layer, which is isotropic (non-active under polarised light), and not coloured (greyish in colour) [13]. Figure 8 shows a cross section of a rust layer formed on mild steel after 12 months of exposure in a marine atmosphere of moderate salinity (75 mg chloride/m² day) [13].

In the very severe marine atmospheres in our study the rust layers that are formed present heavy cracking (Fig. 9 top) or are detached (exfoliation), leaving the base steel partly uncovered (Fig. 9 bottom), and subject to severe pitting. The interior of the pits contain a high percentage of chlorine.

From visual observation of the rusts formed in the atmosphere it is possible to identify different types of morphology: powdery rust particles, grains, flakes and sheets or laminations that peel off easily [38]. In severe marine atmospheres, in conditions with a high chloride content and long moisture retention times (edges of plates, boxed locations, etc.), it is common to see the formation of coarse flakes and layered sheets [38–41]. After long exposure times it is sometimes also possible to see the formation of rust mounds [38], which we have only found in the severe marine atmosphere of Cabo Negro (Asturias, Spain), with an average annual salinity of 150 mg chloride/m² day [20].

Figure 10 presents these two singular types of rust formations. The formation of sheet-type rust has been reported in the literature [38–41]. Reference to the formation of rust mounds has only been found in the paper of *Raman* [38].

3.4.1 Sheet-type rust

Also known as heavy rust layer, laminated layer, multilayered sheet, stratified rust, rust laminations, exfoliated rust, etc. *Raman* reported that rust layers were usually comprised of multiple layers adhered to each other, although at times they could peel unevenly. The layering could be the result of a seasonal effect, whereby the existence of a totally dry stage of the rust layer leads to the subsequent formation of a completely new layer. During the drying stage, phase transformations take place in the rust and the stresses generated in the interlayers give rise to a loss of adhesion (decohesion), which promotes delamination [38].

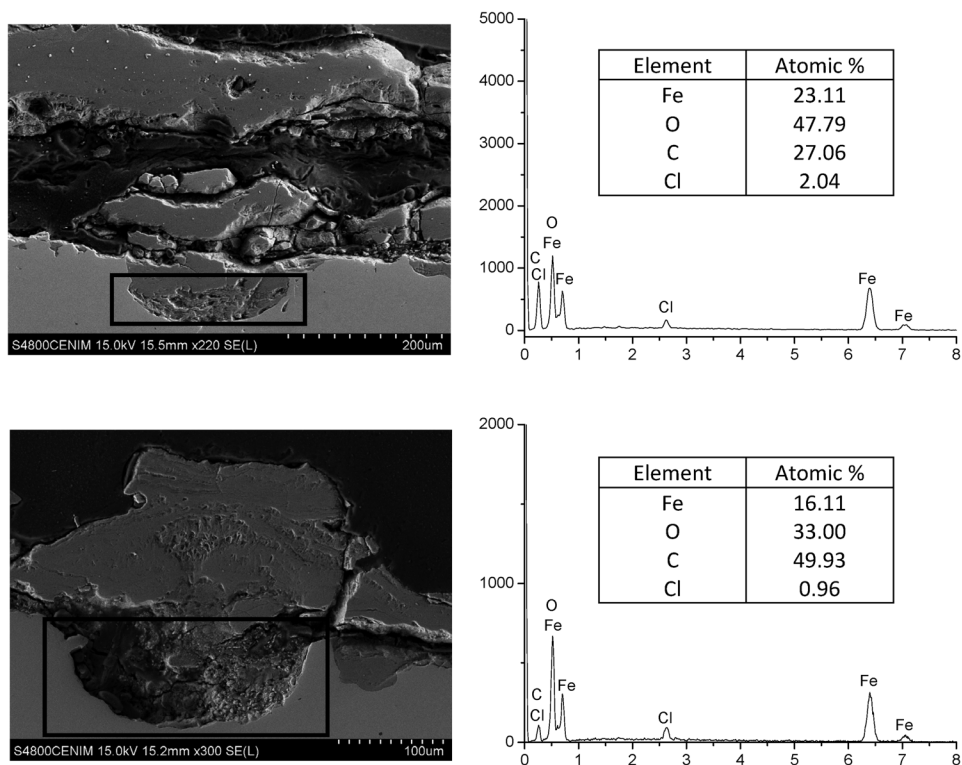


Figure 9. SEM/EDS observation of a rust layer formed over 3 months in a severe marine atmosphere with a very high chloride content (1906 mg chloride/m² day): groundward specimen side (up) and skyward specimen side (down)

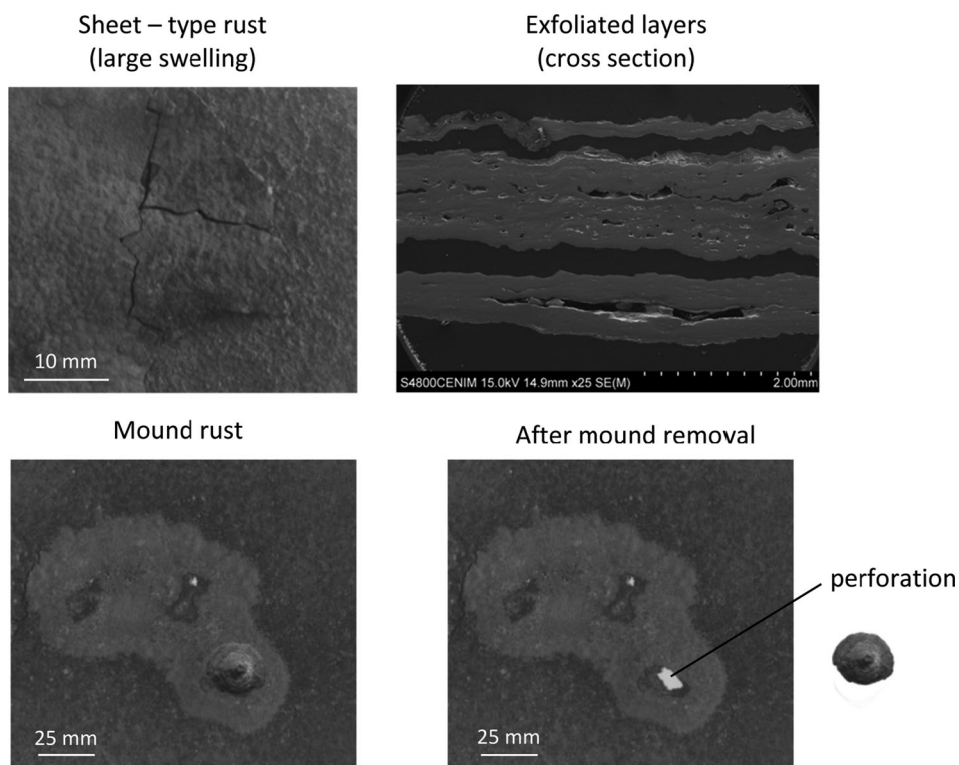


Figure 10. Unusual rust morphologies formed in marine atmospheres with high chloride contents and long moisture retention times: sheet-type (up) and rust mound (down)

Raman et al. also reported the presence of interlayer cavities and cracks in the laminations [34,38]. Using IRS they found the presence of magnetite on the face of the layers closest to the underlying steel, in dense, compact and adherent formations visualised by SEM. On the outer surface (air side) they found maghemite formations, but they did not detect the formation of akaganeite. In contrast, Cook et al. [41], using XRD and Mössbauer spectroscopy, reported high akaganeite and low lepidocrocite contents in the exfoliated layers.

Using conventional XRD and synchrotron XRD, Hara et al. [39,40] found high magnetite and goethite contents, 40% and 38%, respectively, in heavy rust layers with large swellings and laminated layers, along with considerable akaganeite contents (16%) and a very low lepidocrocite content. These researchers noted the presence of large interlayer gaps between the outer and inner layers, as well as many linearly arrayed voids (LAV) and cracks. The mass ratio of magnetite in the local parts, i.e., outer layer, interlayer, and inner layer position, was not higher in general, but the mass ratio of akaganeite was higher. They proposed a multilayer model structure for these heavy rust layers which are made of a spinel poor, rich, and poor unit cell structure (SPRaP-cell) compartmentalised by LAV.

In the exfoliated rust layers produced on the steel exposed in our very severe marine atmospheres we found magnetite enrichment and low lepidocrocite contents in the inner layer closest to the base steel (Table 4), confirming the results obtained by other researchers [39,40]. Both faces present similar percentages of akaganeite and goethite. In Fig. 11, corresponding to one of the laminas comprising the exfoliated rust layer, it is possible to observe its internal structure, which contains interlayers and LAVs as also observed by Hara et al. [39,40].

3.4.2 Mound-type rust

Figure 10 shows this conically-shaped unusual type of rust morphology in which the formation of stratified rust layers is visible to the naked eye. These rust mounds are separated from the steel substrate without much difficulty, and below them the formation of broad perforating pits can be seen.

Raman [38] suggests that the formation must be initiated by the existence of isolated rust nuclei on the steel surface which can retain moisture for long time periods and can act in a similar way to the classic Evans salt solution droplet model [22], leading to the formation of a pit due to a differential aeration cell mechanism. The surface of the steel below the rust nucleus will act anodically, while the edges of the nucleus will act cathodically due to the greater oxygen supply to this region. In a similar way to the mechanism proposed in Section 3.2.2 to explain the formation of

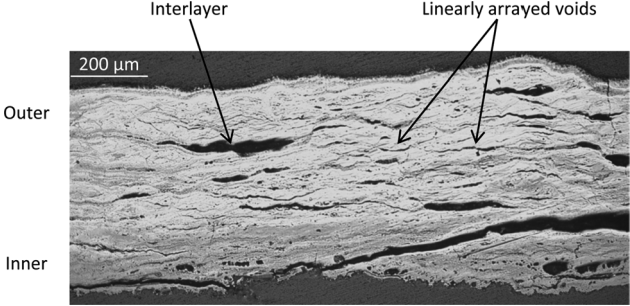


Figure 11. Internal structure of one of the laminas comprising the exfoliated rust layer formed on steel exposed for 1 year in the severe marine atmosphere of Cabo Vilano (Station 2). The existence of interlayers and multiple linearly arrayed voids can be seen

rust layer exfoliations in severe marine atmospheres, along with broad and deep pits in the underlying steel, in the case of these rust mounds there must also be high Cl[−] concentrations in the central regions below the mound, and the long moisture retention times will greatly intensify the attack in these areas, giving rise to the formation of pits.

The existence of complete drying stages will give rise to the formation of a new stratum in the mound, similar to the formation of a new lamina in the sheet-type rust as noted under the preceding heading. The pits in this case grow deep and spread laterally because of the well-known power of alkalis (which diffuse to the peripheral cathodic sites) to creep over dry metal [42]. The formation of rust in these acidic areas inside the mound, where there is a shortage of oxygen, will give rise to the formation of magnetite.

The morphology that we have observed in the mounds formed in the severe marine atmosphere of Cabo Negro (Fig. 10) is identical to the scheme of the stratified rust mound reported by Raman in his paper [38]. Using a binocular magnifier it was possible to see the existence of alternate strata of orangey and blackish colours (Fig. 12 (left)). XRD identified the presence of akaganeite in the former and a high magnetite content in the latter (Table 4). Optical microscopy of a central area of the mound revealed the presence of interlayers and LAVs (Fig. 12 (right)) with a very similar structure to that presented by the exfoliated laminas in the sheet-type rust (Fig. 11), suggesting that both types of rust forms could obey the same formation mechanism.

In the literature there is a lack of studies on the formation mechanisms of these unusual rust types and their internal structure, which will need to be clarified in future research.

Table 4. Semiquantitative XRD analysis of the corrosion products found in sheet and mound-type rust layers formed at Cabo Vilano station 1 and Cabo Negro, respectively (both being severe marine atmospheres)

Rust type	Layer	Lepidocrocite (wt%)	Goethite (wt%)	Akaganeite (wt%)	Magnetite/maghemite (wt%)
Sheet-type rust	Outer	51.6	18.8	18.6	11.0
	Inner	18.9	10.3	18.4	52.4
Mound rust	Black layer	7.8	30.9	Negligible	61.3
	Interlayer (orange)	24.2	44.9	5.4	25.5

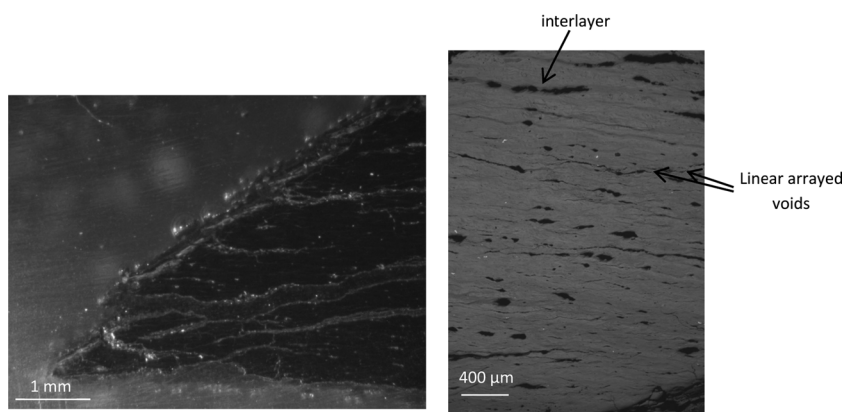


Figure 12. Microscopic observations of a cross section of the rust mound. Observation by binocular magnifier in an area of the mound close to its edge (left) and observation by optical microscopy of a central area of the mound (right)

4 Questions pending

Throughout this work we have drawn attention to a number of points in relation with which additional research would be desirable in order to improve our understanding, namely:

1. Estimation of the atmospheric salinity of a marine atmospheric site from information on sea swell and marine winds already existing in meteorological and sea-state databases.
2. Performance of rigorous long-term corrosion (C) studies (≥ 10 years) in marine atmospheres of various salinities (S) in order to know the influence of this variable on the value of exponent n in the power function $C = At^n$. In particular, it would be desirable to have more information on corrosion and salinity in very severe marine atmospheres ($S > 1000 \text{ mg Cl}^-/\text{m}^2 \text{ day}$) where existing information is very scarce.
3. To understand in depth the formation of akaganeite as an atmospheric corrosion product in field tests: formation conditions, dependence on salinity, location in the rust layer, morphology, evolution with exposure time, etc.
4. To understand in depth the formation of magnetite and to clarify the precursor species. In particular it would be useful to clarify whether its formation takes place from lepidocrocite or akaganeite, a matter, which is the cause of some discrepancy in the scientific literature.
5. Understanding of the formation mechanisms of singular rust types (sheet and mound-type rusts), which occur in severe marine atmospheres and of their internal microstructure.

Acknowledgements: We would like to thank ENEL and Gas Natural for the facilities provided at Cabo Vilano wind farm for the setting up of corrosion stations and data collection. We would also like to thank the LASPEA laboratory at the University of the Basque Country for the performance of SEM/Micro-Raman measurements.

5 References

- [1] K. Barton, *Protection Against Atmospheric Corrosion*, John Wiley and Sons, New York 1973.
- [2] M. Morcillo, I. Díaz, B. Chico, H. Cano, D. de la Fuente, *Corros. Sci.* **2014**, 83, 6.
- [3] T. Nishimura, H. Katayama, K. Noda, T. Kodama, *Corrosion* **2000**, 56, 935.
- [4] ISO9225: Corrosion of Metals and Alloys. Corrosivity of Atmospheres. Measurement of Environmental Parameters Affecting Corrosivity of Atmospheres, International Standards Organization, Geneva 2012.
- [5] ISO 9226: Corrosion of Metals and Alloys. Corrosivity of Atmospheres. Determination of Corrosion Rate of Standard Specimens for the Evaluation of Corrosivity, International Standards Organization, Geneva 2012.
- [6] S. Neshyba, *Oceanography*, Wiley, New York 1987.
- [7] D. C. Blanchard, A. H. Woodcock, *Ann. NY Acad. Sci.* **1980**, 338, 330.
- [8] J. W. Fitzgerald, *Atmos. Environ.* **1991**, 25A, 533.
- [9] S. Feliu, M. Morcillo, B. Chico, *Br. Corros. J.* **2001**, 36, 157.
- [10] S. Feliu, M. Morcillo, B. Chico, *Corrosion* **1999**, 55, 883.
- [11] S. Feliu, M. Morcillo, S. Feliu, Jr, *Corros. Sci.* **1993**, 34, 403.
- [12] M. Morcillo, B. Chico, E. Otero, L. Mariaca, *Mater. Perform.* **1999**, 38, 72.
- [13] I. Díaz, H. Cano, D. de la Fuente, B. Chico, J. M. Vega, M. Morcillo, *Corros. Sci.* **2013**, 76, 348.
- [14] R. D. Pascual Marqui, *Rev. Iberoam. Corros. Prot.* **1980**, XI, 37.
- [15] L. Espada, A. M. González, A. Sánchez, P. Merino, *Rev. Iberoam. Corros. Prot.* **1988**, XIX, 227.
- [16] A. Hache, *Rev. Metall.* **1956**, 76, 53.
- [17] K. Bohnenkamp, G. Burgmann, W. Schwenk, *Stahl. Eisen.* **1973**, 93, 1054.
- [18] R. A. Legault, A. G. Preban, *Corrosion* **1975**, 31, 117.
- [19] M. Pourbaix, in: W. H. Ailor, (Ed.), *Atmospheric Corrosion*, The Electro Chemical Society, John Wiley and Sons, New York 1982, pp. 107–121.
- [20] S. Feliu, M. Morcillo, in: W. H. (Ed.), *Atmospheric Corrosion*, John Wiley and Sons, New York 1982, pp. 913–922.
- [21] Benarie, M. Ailor, F. L. Lipfert, *Atmos. Environ.* **1986**, 20, 1947.
- [22] L. L. Shreir, R. A. Javman, G. T. Burstein, in: *Corrosion*, Butterworth-Heinemann, Oxford 1993, p. 1.146.
- [23] W. Hou, C. Liang, *Corrosion* **1999**, 55, 65.

- [24] M. Morcillo, E. Almeida, B. Rosales, J. Uruchurtu, M. Marrocos, *Corrosion y Protección de Metales en las Atmósferas de Iberoamérica. Parte I—Mapas de Iberoamérica de Corrosividad Atmosférica*, CYTED, Madrid 1998.
- [25] M. Morcillo, D. De la Fuente, I. Díaz, H. Cano, *Rev. Metal. (Madrid, Spain)* **2011**, 47, 426.
- [26] A. Raman, S. Nasrazadani, L. Sharma, *Metallography* **1989**, 22, 79.
- [27] C. Rémazeilles, P. Refait, *Corros. Sci.* **2007**, 49, 844.
- [28] C. Rémazeilles, P. Refait, *Corros. Sci.* **2008**, 50, 856.
- [29] T. Ishikawa, Y. Kondo, A. Yasukawa, K. Kandori, *Corros. Sci.* **1998**, 40, 1239.
- [30] H. Tanaka, R. Mishima, N. Hatanaka, T. Ishikawa, T. Nakayama, *Corros. Sci.* **2014**, 78, 384.
- [31] K. Asami, M. Kikuchi, *Corros. Sci.* **2003**, 45, 2671.
- [32] Y. Tamaura, K. Ito, T. Katsura, *J. Chem. Soc. Dalton Trans.* **1983**, 189.
- [33] A. Raman, A. Razvan, B. Kuban, K. A. Clement, W. E. Graves, *Corrosion* **1986**, 42, 447.
- [34] A. Razvan, A. Raman, *Pract. Metallogr.* **1986**, 23, 223.
- [35] A. Raman, S. Nasrazadani, L. Sharma, A. Razvan, *Pract. Metallogr.* **1987**, 24, 535.
- [36] A. Raman, S. Nasrazadani, L. Sharma, A. Razvan, *Pract. Metallogr.* **1987**, 24, 577.
- [37] A. Raman, B. Kuban, *Corrosion* **1988**, 44, 483.
- [38] A. Raman, in: *Degradation of Metals in the Atmosphere*, ASTM STP 965, ASTM, Philadelphia **1988**, pp. 16–29.
- [39] S. Hara, M. Yamashita, T. Kamimura, M. Sato, *J. Jpn. Inst. Met.* **2007**, 71, 346.
- [40] S. Hara, *Corros. Eng. Jpn.* **2008**, 57, 70.
- [41] D. C. Cook, *Corros. Sci.* **2005**, 47, 2550.
- [42] U. R. Evans, *Metallic Corrosion, Passivity and Protection*, E. Arnold & Co., London **1946**.

(Received: July 25, 2014)

W7940

(Accepted: August 20, 2014)