

Power Spectral Density Analysis of the Corrosion Potential Fluctuation of Aluminium in Early Stages of Exposure to Caribbean Sea Water

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Aluminium samples were exposed for six months to Caribbean sea water. The fluctuations of the free corrosion potential values (E_{corr} at o.c.p.), considered as electrochemical noise, were correlated with the aluminium pitting corrosion in sea water, influenced by different crystalline phases formed on the metal surface: $\text{Al}(\text{OH})_3$ as a corrosion product in pits, and likewise crystals of MgCaCO_3 and SiO_2 proceeding from the sea water. At three months the film of bio-fouling had grown on aluminium surface, formed by two diatoms (microalgae). E_{corr} fluctuation analysis was carried out using the power spectral density (PSD) vs frequency. The decrease of the PSD slopes (negative β exponent) indicated a release of spontaneous energy during from the aluminium surface, with the progress of pit formation in sea water. The calculated Hurst exponent values suggested that pits formed randomly on the surface in sea water could be as a consequence of highly persistent processes, dominated by fractional Gaussian noise (fGn) at almost all periods of testing in sea water, with the contribution of fractional Brownian motion (fBm) during some periods of time.

Keywords: Corrosion potential · Electrochemical noise · Power spectral density · Aluminium · Sea water

1. INTRODUCTION

At present, aluminium is one of the structural metals widely used in engineering applications in sea water, having great economic and industrial importance, as part of the structure of ships, submarines, high-voltage transmission cables, equipments and fuel containers. Thermodynamically it is very active and immediately corrodes naturally in the presence of oxygen (high level of free energy and high negative potential value – 1.67 V). According to the electrochemical Pourbaix diagram [1],

aluminium and its alloys could attain the three possible states: passivity, immunity and corrosion (active state). There is a range of pH (from 4 to 9) and electrochemical potentials where the metal acquires passivity, due to the formation of a very thin (transparent), hydrated oxide layer ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and/or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) with low porosity, adhering well to the metal surface. This passive film is the reason for the very good corrosion resistance of aluminium when exposed to environments free of chloride ions. However, in their presence, the passive state of the aluminium could break down and localised corrosion attack occurs, usually in small and specific locations on the metal surface; this phenomenon is known as pitting corrosion (up to 100 μm deep) [2-10].

Sea water is a very aggressive medium for the metals and can cause severe damage to metallic structures in a very short space of time. Usually, this water contains the ions (in decreasing quantities) of Cl^- , Na^+ , SO_4^{2-} , Mg^{2+} , Ca^{2+} , K^+ , HCO_3^- , Br^- , B^{3+} , Sr^{2+} , F^- , and dissolved gases, *viz* O_2 and CO_2 . The percentage average of the most abundant ions in sea water (salinity 35.00%, density 1.023 g cm^{-3} at 25°C) is as follows: 55.3% chloride; 30.8% sodium, 3.7% magnesium, 2.6% sulfates, 1.2% calcium and 1.1% potassium [7, 11]. Oxygen content, salinity, pH, temperature, specific contaminants, biological activity, and flow velocity are the major factors affecting the corrosion behaviour of any metal (and alloys) submerged in sea water, which is a very aggressive environment.

Since aluminium behaviour in sea water is an increasingly frequent topic of study, the generation of new data is of interest to the international civil engineering community. Furthermore, the aluminium surface is subjected to a fixing process of the undesirable growth of harmful deposits of biological origin (bio-fouling), and their identification in the early stages is nowadays an important objective.

A review describing a field of knowledge of the pitting of aluminium has been presented by Szklarska-Smialowska [12] and the critical factors that influence the pitting have been reported by Frankel [13]. The existing hypotheses relating to pitting mechanisms in halogen environments still do not coincide. The pitting mechanism is very complicated, covering: (1) processes occurring in the air-borne oxide amorphous passive film formed on an aluminium surface, at the boundary of this film - solution (electrolyte); (2) processes within the passive film, when no visible microscopic changes occur therein; (3) formation of so-called metastable pits which initiate and grow for a short period of time below the critical pitting potential and then repassivate (intermediate step in pitting); (4) stable pit growth above a certain potential, termed critical pitting potential. A simple passivation and depassivation model for pitting corrosion has been described by Meakin *et al.* [14]. The effect of the metal electronic structure on pitting has been explained by a point defect model, to take account of the kinetics of growth of passive films on metal surfaces exposed to halide aqueous solutions (in particular chloride) [15, 16]. The model leads to a number of important generalisations concerning the kinetics of film growth. On the other hand, the passive film breakdown of metals in aqueous chloride-containing solutions is usually described as following three important processes: adsorption of chloride ions (Cl^-) in the oxide film, chloride ions weakening the oxide bonds, and mechanical film breakdown at various points at the line surface defect sites (vacancies, dislocations, inclusions) [2, 4].

The changes on Al-surface is a relatively slow process that can takes months, i.e. before the pits become visible, since their orifice size may be a matter of micrometres. The small area of pits, compared with that not attacked by corrosion, produces very low mass loss in any steel sample

(structure) and this fact results in a high error in the calculation of the corrosion rate of metals presenting the localised corrosion. The detection of the pits is very difficult in the early stages and studies of the changes occurring in a metal surface, and interest in their characterisation have increased steadily. However, electrochemical techniques allow changes to be detected in the surface of the metal, for example, by monitoring the potential of the metal at open circuit (o.c.p.) over time, often termed as free corrosion potential E_{corr} . This is a direct and non-intrusive method, probably the single most useful measured variable, relatively simple in concept and its values can give an indication of active/passive behaviour of the metal during its exposure to aggressive environments. The fluctuations in E_{corr} are an observable phenomenon, generally of low frequency (<10 Hz) and low amplitude, and they can be classified as electrochemical noise (EN). The EN produced is partly a result of naturally occurring variations in the kinetics of the electrochemical corrosion process [17-19]. For the purpose of EN data acquisition and their analysis, evolution of the corrosion process is usually monitored over time without application of external polarisation (o.c.p.). The first EN measurement for corrosion studies were described by Iverson [20]. As the author claims, the investigations of voltage fluctuations appear to offer much promise for the detection and study of the corrosion process. Thus far, these fluctuations give a qualitative "fingerprint" characterisation of corrosion processes occurring in different metals and alloys. Measurements of self-generated electrochemical potential fluctuations on electrodes undergoing either pitting or crevice corrosion have shown that these forms of localised attack have distinct noise "signatures" and can be detected within second of their initiation [21]. The traditional way to analyse EN has been to transform the frequency domain to obtain power spectral density (PSD) [22]. PSD plots can typically be computed using standard algorithms, for example, the Fast Fourier Transform (FFT) or other algorithms, such as the maximum entropy method (MEM) [23, 24]. The PSD described as signal power is distributed to different frequencies, and by developing other analysis algorithms can be detected deterministic or chaotic features hidden in apparently random data. Thus the spontaneous EN can be a rich source of information concerning the processes simultaneously occurring at a corroding interface [24, 25]. The analysis of EN generated during the corrosion of metallic specimens can be conducted by various techniques to reveal the stochastic and fractal nature of simultaneous phenomena occurring at a corroding interface [26].

1.1. Power spectral density (PSD) analysis

PSD has proved to be very useful to detect reliably long-term dependence (persistence) in data. This method allows to be determined the energy changes in the system. The graphs show the power per unit frequency (V^2/Hz) with respect to the frequency (Hz) on a logarithmic scale [27]. One of the mathematical models for analysing time series data has been proposed by Mandelbrot and van Ness [28]. Mandelbrot and van Ness relation $S(f)$ can be expressed as $1/f^\beta$ in the frequency domain, where f is the frequency and $S(f)$ the corresponding square amplitude; β is estimated by calculating the negative slope ($-\beta$) of the line relating $\log(S(f))$ to $\log(f)$. Obtaining a well-defined linear fit in the $\log - \log$ plot is an important indication of persistence in the original series. According to Eke *et al.* [29], PSD allows a distinction to be made between series with fractional Gaussian noise (fGn) and fractional

Brownian motion (*fBm*), as *fGn* corresponds to β exponents ranging from -1 to +1, and *fBm* to exponents from +1 to +3. The exponent β can be converted into \hat{H} (Hurst coefficient) [30, 31], according to the following equations:

$$\hat{H} = (\beta + 1)/2 \quad \text{for } fGn \quad \text{when } -1 \leq \beta \leq 1 \quad (1)$$

$$\hat{H} = (\beta - 1)/2 \quad \text{for } fBm \quad \text{when } 1 \leq \beta \leq 3 \quad (2)$$

The exponent β is associated with persistent processes (forces) in data series over time [32]. Ordinary Brownian motion corresponds to the special case $\hat{H} = 0.5$ and forms the border between anti-persistent ($\hat{H} < 0.5$) and persistent ($\hat{H} > 0.5$) processes [30, 31]. Although the model of fractional Brownian motion (*fBm*) can help to describe the time series data with complex geometry, analysis can be performed in a very simple way using rescaled range analysis (R/S), originally proposed by Hurst [30]. The fractional Gaussian noise (*fGn*) is considered as a stationary process and the fractional Brownian motion (*fBm*) is non-stationary.

The corrosion behaviour of 6061 Al alloy has been studied in 0.1M NaCl and a borate buffer under potentiostatic condition, using power spectral density to provide a direct method for stressed specimens for the period of minutes after immersion [25]. The physical (EN) and electrochemical (EIS) results gathered during 10 days of exposure of 2519 and 7030 structural aluminium in 3% NaCl indicated that the two materials corrode by very different mechanisms [26]. The authors suggest that some of the key parameters revealed by the analysis of EIS and EN results are directly related to the severity of localised attack of the aluminium materials. Research also reports that a correlation between the EN and corrosion intensity was established on the basis of appropriate treatment of the recorded numerical data and *ex situ* examination of aluminium surface exposed to 4% wt% NaCl, pH 7 [33].

The study of spontaneous potential fluctuations for the characterisation of corrosion processes has received considerable attention in recent years. The aim of this study is to expand the information for aluminium localised corrosion in the early stages of samples exposed to stationary Caribbean sea water during six months. The tendencies of corrosion potential fluctuations (E_{corr} at o.c.p.) were correlated with the surface natural phenomenon occurring on aluminium. The analysis of the data was carried out using the power spectral density (PDS) method. Thus, this procedure enables the slopes of the amplitude spectrum to be determined as well the behaviour of the corrosion mechanism of processes occurring on aluminium surface during exposure in sea water. SEM images of the aluminium surface have supported the discussion of the results obtained. To our knowledge, no other research has been undertaken to date on this aspect. In our previously reported work, corrosion potential fluctuations occurring during the first stages of copper patina formation in sea water were correlated with the multifractal detrended method [34].

2. EXPERIMENTAL

2.1 Aluminium exposure and characterisation

Electrolytic aluminium flat samples (99.99 mass %; with dimensions of 30 x 30 x 1 mm), were previously degreased with ethanol and immersed separately, each in 55 mL of stationary Caribbean sea

water at 21°C in glass containers for 1, 2, 3, 5 days and 1, 3, 6 months. One sample, used as a working electrode, was immersed in sea water, in an electrochemical cell. The changes in the free corrosion potential (E_{corr}) values were measured at o.c.p. during 13,000 s (3.6 h), with a sampling period of 0.05 s (2^{14} data), during the time of exposure of the aluminium in sea water. A potentiostat/galvanostat computerised Series G750 (Gamry Instruments, Inc., software PHE 200), has employed for measurement of E_{corr} . As a reference electrode calomel (SCE $E_{\text{Hg}^{2+}/\text{Hg}/\text{sat.KCl}} = 0.244$ V) was used and, as an auxiliary electrode, platinum wire. The electrochemical E_{corr} potential fluctuations were considered as electrochemical noise (EN) signal amplitudes. When E_{corr} was graphed *vs* time, spectral analysis was performed to obtain the amplitude spectrum by the method of Fast Fourier Transform (FFT) utilised to graph power spectral density (PSD) described above. On conversion to logarithmic scale, the PSD as a function of low frequencies (10^{-2} Hz – 1 Hz) was analysed. These procedures enabled the slopes of the amplitude spectrum to be determined as well the behaviour of the corrosion mechanism of processes occurring on aluminium surface during exposure to sea water.

Samples of aluminium, withdrawn at various periods of exposure in sea water, were dried at room temperature and analysed with different techniques. The crystalline phases formed during the corrosion process were characterised using X-rays diffraction technique (XRD, Siemens D-5000, with grazing beam geometry, 3° angle, 34 kV/25 mA and radiation $\text{Cu}_{\text{K}\alpha}$). The spectra were processed with DIFRACT AT [35] software and the identification of the phases with Powder Diffraction File [36]. Scanning electron microscopes (SEM-EDS, Phillips and XL-30 ESEM JEOL JSM-7600F) were used to provide images of the surface morphology of aluminium samples after their exposure to sea water. After XRD and SEM-EDS analyses, the samples were chemically etched in 50 mL of phosphoric acid (H_3PO_4 , 1.69 g mL^{-1}) and 20 g/L of CrO_3 for 5 -10 min at 80°C, to remove the corrosion products, according to ISO 8407 [37] and reexamined the aluminium surface morphology and corrosion attack with a SEM-EDS microscope.

2.2 Sea water chemistry

The sea water was taken from the Caribbean sea (Telchac port, Yucatan Peninsula, Mexico, 21°7' N, 89°25' W, warm humid tropical climate marine test station of CINVESTAV-Merida), at a depth of 10 m and a distance of 10 km from de coast. At that location stands with aluminium samples were submerged for testing in actual sea environment. The sea water had total salinity of 37.48%, pH=7.69, dissolved oxygen 1.1 ppm and temperature of 21°C at that depth. Specific sea pollutants were ($\mu\text{M/L}$): 1.75 ammonium; 2.61 silicates; 0.28 phosphates; 0.04 nitrites and 1.84 nitrates.

3. RESULTS AND DISCUSSION

3.1. Aluminium free corrosion potential E_{corr}

Table 1 shows E_{corr} (o.c.p) values of an Al electrode sample immersed in Caribbean sea water over 6 months at different periods of time. The initial $E_{\text{corr}} = -0.080$ V (*vs*. SCE) tends towards more

negative values and after 5 days it reached -0.770 V, as a result of the first pitting events (pitting corrosion) due to the chloride ion attack, which break down the naturally air born-formed passive layer of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and/or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Table 1. Free corrosion potential E_{corr} (o.c.p.) values of aluminium during exposure to Caribbean sea water over six months.

Exposure time	Inicial	1 day	2 days	3 days	5 days	1 month	3 months	6 months
E_{corr} (V) vs SCE	-0.080	-0.681	-0.738	-0.734	-0.770	-0.575	-0.745	-0.785

However, at the end of first month E_{corr} (Table 1) reached less negative value (-0.575 V), owing to the formation of a layer on the aluminium surface, composed of several compounds, which works as an Ohmic barrier between the aluminium surface and sea water. XRD analysis revealed the presence of $\text{Al}(\text{OH})_3$ as a corrosion product in pits, and likewise crystals of MgCaCO_3 and SiO_2 proceeding from the sea water (Figure 1).

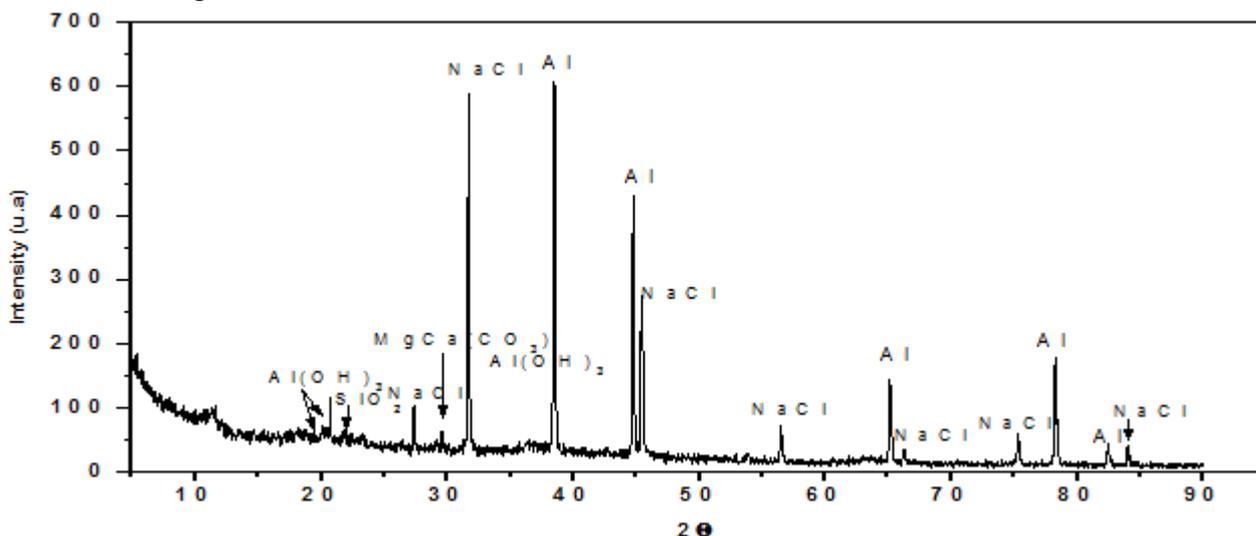


Figure 1. XRD spectra of the crystalline phases formed on the aluminium surface after 1 month of exposure to Caribbean sea water.

However, this layer of different crystalline phases subsequently lost adhesion to the aluminium surface and their precipitation was observed on the bottom of the electrochemical test cell. Because of this fact, the E_{corr} values returned again to a more negative one (-0.785 V, at 6 months). The tendencies of E_{corr} changes (Table 1) during aluminum exposure to Caribbean sea water were correlated with the surface morphology and corrosion attack. Figure 2 presents SEM images of the aluminium surface, which revealed the increasing number of pits of different sizes and area, and at the same time their deepening as corrosion process progressed.

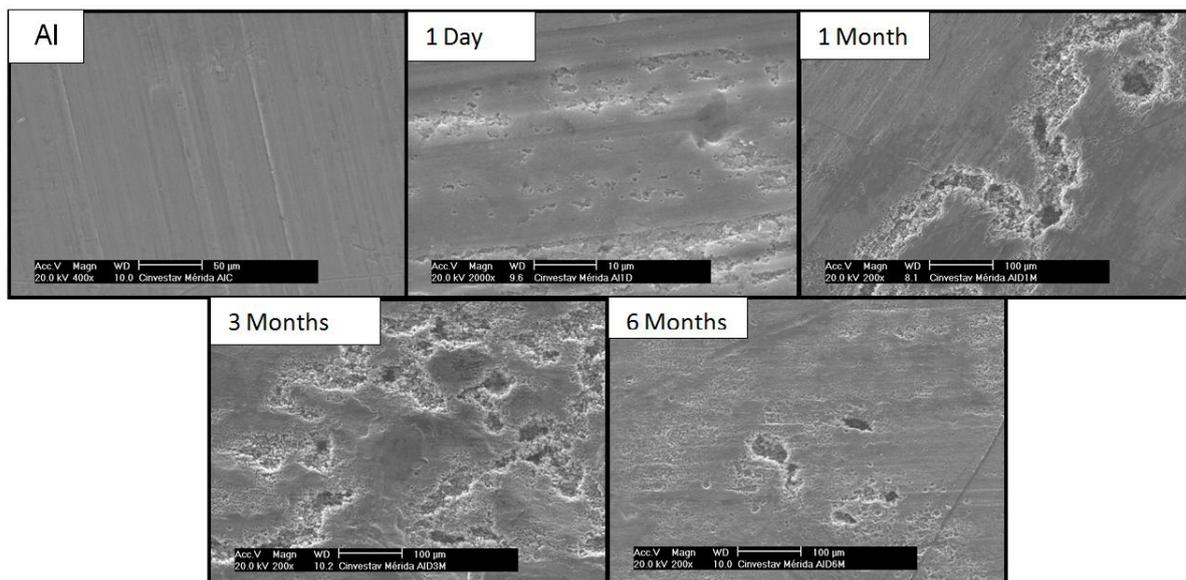


Figure 2. SEM images of aluminium surfaces after removal of corrosion products, at different periods of exposure to Caribbean sea water: Al before exposure (400x); 1 day (2000x); 1, 3 and 6 months (200x).

At a later period of exposure of aluminium to Caribbean sea water, SEM images (Fig. 3) showed, that after 3 months the metal surface began to be partially covered by a well-adhered bio-fouling film, the appearance of which suggests the growth of diatoms [38]. The SEM-EDS analysis confirmed the presence of silica (Fig. 3c), corresponding to the main composition of the diatoms. The diatoms are micro-algae, the wal cell (frustule) of which is composed of silicone dioxide and they are regarded as constituting most microplankton and phytoplankton [39]. The growth of diatoms is influenced by the sea water salinity, oxygen content, nutrients, water temperature and flow velocity. Two types of diatoms were identified and classified as *Amphora sp.* (with apices) and *Cocconeis cf. Placentula* (Ehrenberg) (Fig. 3b). Diatoms normally measure between 20-200 µm. In the present case, at this point in time, the diatoms had a length of the order of 8-12 µm and a width of 5-7 µm.

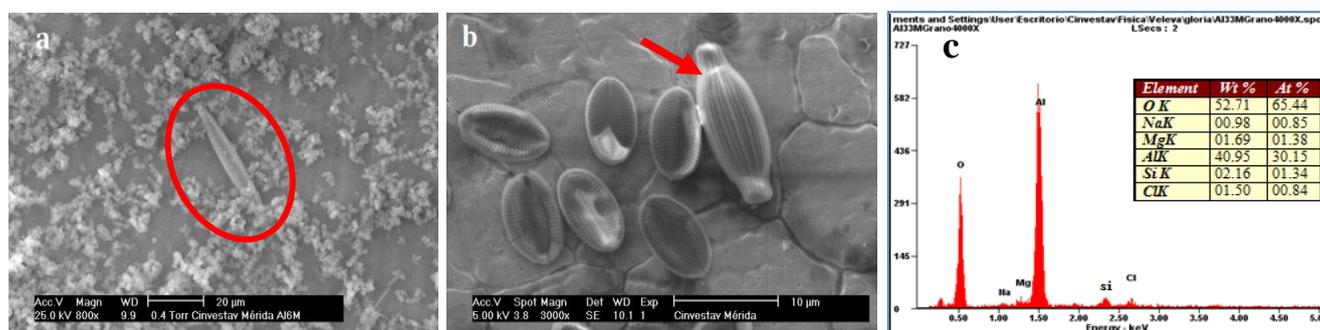
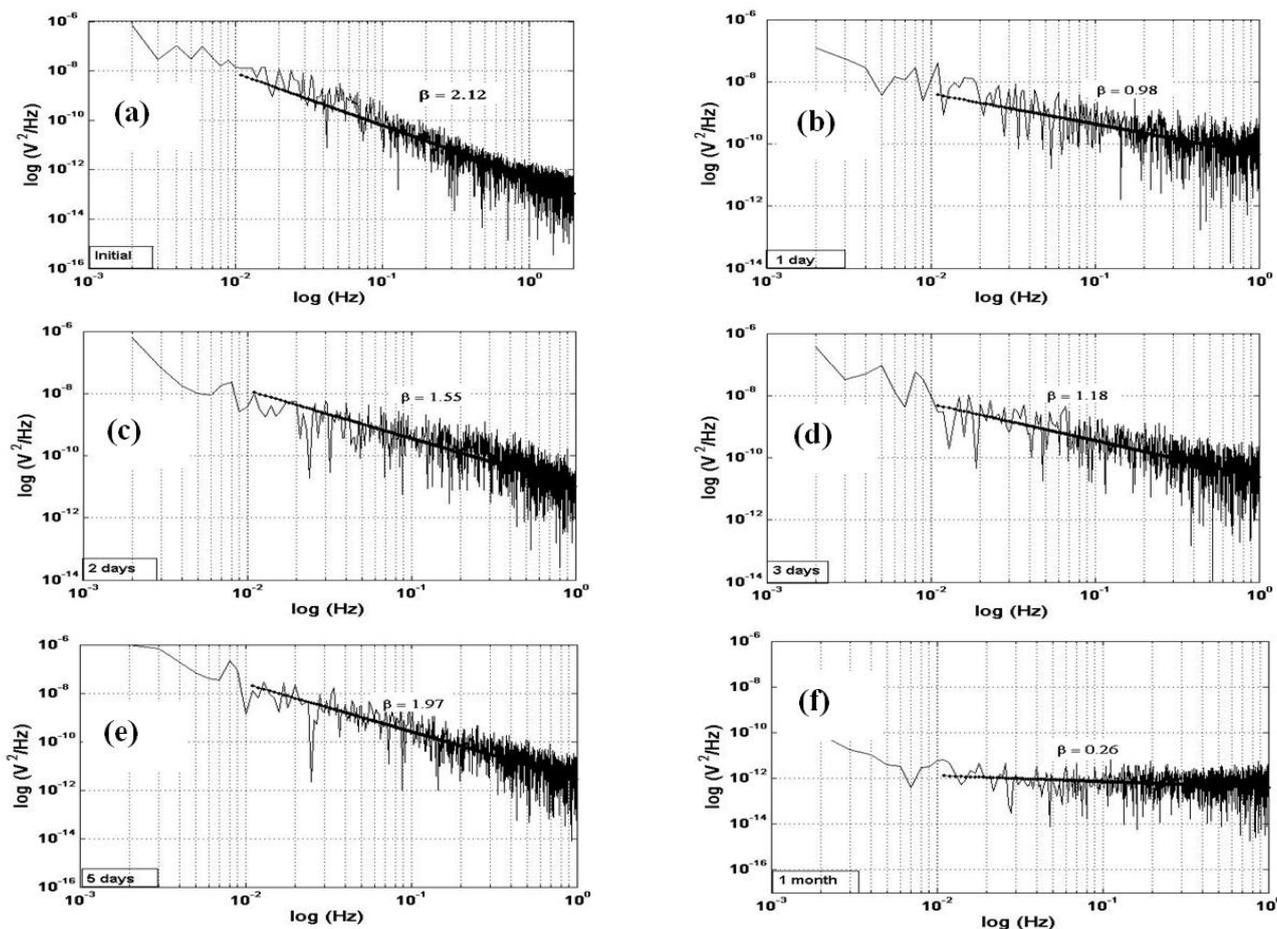


Figure 3. SEM images of bio-fouling of diatoms adhering to the aluminium surfaces after 6 months of exposure to Caribbean sea water: (a) general view of biofilm (800x); (b) Diatoms (3000x): *Amphora sp.* (with apices) and *Cocconeis cf. Placentula* (Ehrenberg);(c) the SEM-EDS analysis of diatom.

The biofilm ensemble is a heterogeneous complex. Within the bio-fouling film, oxygen is involved in the metabolic pathways of many micro-organisms [40]. It acts as a final electron acceptor in the oxidation process of organic molecules, e.g. lipids and sugars, or inorganic species. Due to energetic considerations, the reduction reaction of oxygen leads to the formation of highly reactive free radicals or molecular species. Such intermediate products, commonly called reactive oxygen species (ROS), are involved in bio-corrosion because their reactivity is higher than that of oxygen itself. Oxygen plays a pivotal role in processes associated with bio-corrosion of metals in sea water as it is involved in both abiotic and biotic mechanisms, which influence the electrochemical potential of the metal. One issue of primary importance in bio-corrosion studies still remains poorly understood, *viz.* does ennoblement of the corrosion potential lead to localised corrosion of metals [40]?

3.2. PSD analysis of E_{corr} fluctuations of aluminium exposed to sea water

Localised aluminium corrosion (pit formation) was correlated with the fluctuations of the free corrosion potential (E_{corr} at o.c.p.), recorded at different periods of time. Data series of E_{corr} , considered as EN were previously treated in order to minimise errors, subtracting the average value and removing the linear trend, according to ASTM G 199-09 [41]. As was mentioned in the experimental part, the analysis of E_{corr} fluctuations was carried out with the power spectral density (PSD) vs frequency in logarithmic scale.



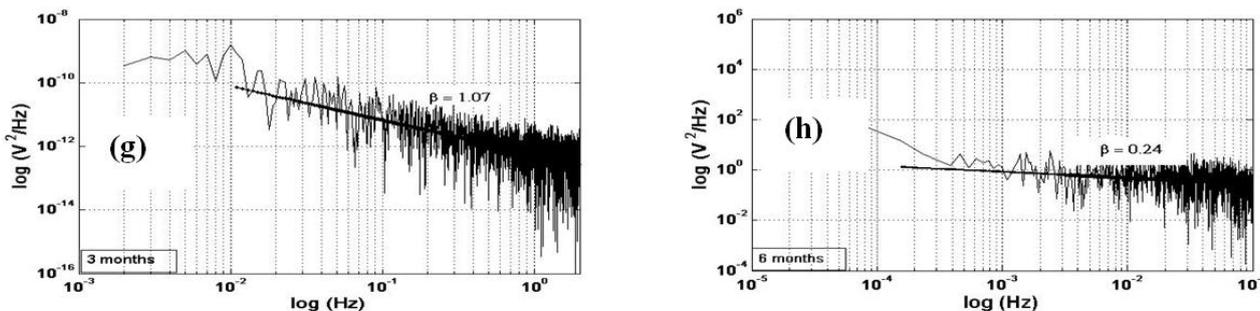


Figure 4. Power spectral density (PSD) plots of aluminium E_{corr} fluctuations vs frequency in logarithmic scale ($\log V^2 \text{ Hz}^{-1}$ vs. $\log \text{ Hz}$): (a) initial time; (b) 1 day; (c) 2 days; (d) 3 days and (e) 5 days; (f) 1 month; (g) 3 months; (h) 6 months of exposure to Caribbean sea water.

Figure 4 presents log-log PSD plots of E_{corr} fluctuations over time as a function of frequency, after different periods of exposure of aluminium to Caribbean sea water. As can be seen, all plots showed a decreasing slope (exponent β) on the bilogarithmic graphs, which could be related to the spontaneous release of energy from the metal surface, with the progress of pit formation (localised corrosion attack) on the aluminium surface in sea water.

Table 2. Experimental values of PSD slopes (exponent β_{exp}) and calculated Hurst (\hat{H}) coefficients (eqs. 1-2), characteristic of the localised surface processes occurring in the aluminium exposed to Caribbean sea water over six months.

Exposure time	β_{exp}	\hat{H}_{exp}	\hat{H}_{fGn}	\hat{H}_{fBm}	\hat{H}_{av}	Type of localised corrosion process
Initial	2.12	1.01	1.56	0.56	1.06	fGn + fBm
1 day	0.98	0.94	0.99	-	-	fGn
2 days	1.55	0.95	1.28	0.28	0.78	fGn + fBm
3 days	1.18	0.97		1.09		fBm
5 days	1.97	0.98	1.49	0.49	0.99	fGn + fBm
1 month	0.26	0.61	0.63	-	-	fGn
3 months	1.07	0.90	1.04	-	-	fGn
6 months	0.24	0.67	0.62	-	-	fGn

The values of the Hurst coefficients (Table 2) allowed us to conclude that the process of localised aluminium corrosion (pit formation), occurring on the surface exposed to Caribbean sea water, is a highly persistent process, which was dominated by fractional Gaussian noise (fGn) at almost all periods of testing, with the contribution of fractional Brownian motion (fBm) during some periods of time. Both, fGn and fBm are representative properties of self-similarity processes.

4. CONCLUSIONS

Flat aluminium flat samples were exposed during 6 months to Carribean sea water. After three months a bio-fouling layer, formed by two diatoms, partially covered the aluminium surface. The tendencies of the free corrosion potential fluctuations (E_{corr} at o.c.p.) were correlated with the aluminium pitting corrosion in sea water, influenced by different crystalline phases formed on the metal surface: $\text{Al}(\text{OH})_3$ as a corrosion product in pits, and likewise the crystals of MgCaCO_3 and SiO_2 proceeding from the sea water. The analysis of E_{corr} fluctuations was carried out with the power spectral density (PSD) vs frequency in logarithmic scale. The decrease of the PSD slopes, exponent β values, indicated a spontaneous release of energy from the aluminium surface, with the progress of pit formation in sea water. The calculated Hurst exponent values suggested that aluminium surface localised corrosion occurring in sea water could be considered as a consequence of highly persistent processes, dominated by fractional Gaussian noise (fGn) at almost all periods of testing, with the contribution of fractional Brownian motion (fBm) during some periods of time.

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