Multifractal Detrended Analysis of the Corrosion Potential Fluctuations During Copper Patina formation on Its First Stages in Sea Water

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The analysis of multifractal time series (MFDFA) has been carried out for copper patina corrosion potential E_{corr} fluctuations in the period of 10 days, when flat samples were immersed in Caribbean sea water. The results showed that there are ranges of s-sizes for potential signals and q-order fluctuations, where $F_q(s)$ exhibits a power law behavior. The Hurst exponent $h(q)$ values, the nonlinear multifractal spectrum $\tau(q)$ and the shape of the singularity spectrum $f(\alpha)$ confirmed that E_{corr} series of copper exposed in sea water are compatible with a multifractal behavior. The tendencies of E_{corr} change were correlated with the copper ions release (runoff) during dissolution of corrosion products in sea water and with the significant transformation in the copper patina (Cu_2O) composition as time of corrosion process advanced.

1. INTRODUCTION

Copper is one of the structural metals widely used in engineering applications in sea water. However, in the presence of chloride ions, the copper and its alloys corrode forming thin layers of corrosion products, known as patina [1−3]. They are generally brown-greenish or green-bluish in color and protect the copper against faster subsequent deterioration. In the marine corrosion the sea water is the main corrosive agent, since it is a natural complex electrolyte of a great number of dissolved ionic salts, besides the additional presence of other suspended or dissolved substances, as dissolved gases, alive organic matter or in decomposition [4−9]. Usually, the sea water contains the ions (in a falling order for their quantities) of Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+, HCO^-_3, Br^-, B^{3+}, Sr^{2+}, F^-, and dissolved

gases as O_2 and CO_2. The percentage average of the most abundant ions in sea water (salinity 3.5%, density 1,023 g/cm^3 at 25°C) is the following: 55.3% chloride; 30.8% sodium, 3.7% magnesium, 2.6% sulfates, 1.2% calcium and 1.1% potassium [8]. Sea water is a very aggressive medium for the metals and it can cause severe corrosion damages to the metallic structures in very short lapses of time and the formed corrosion products could contaminate the surrounding environment (seawater, alive matter, etc.). The factors that determine the type of corrosion attack on metal and its rate are usually classified as chemical, physical and biological activity.

The copper corrosion in sea water has been relatively less studied than its atmospheric corrosion. Sea water environment includes several zones (splash/spray; tidal (high and low); sub-merged/full immersion (shallow water and deep ocean); and mud zone) to which a metal structure can be exposed and those zones will determine the degree of corrosion and specific corrosive attack. In a previous study we observed that the highest annual copper patina formation rate (0.071 mm/year) occurred within the half-point line of tidal-water boundary, while the lowest rate (0.016 mm/year) was in the atmospheric zone [10]. The splash (0.025 mm/year) and full immersion (0.032 mm/year) zones were less aggressive environments for copper. X-ray diffraction analysis indicated that cuprite (copper oxide) and atacamite (copper chloride compound) were the phases which contributed most to patina formation [3]. Their relative XRD spectra intensities were very similar for patina formed in the tidal sea zone, but atacamite became the sole majority phase in the full immersion zone. As patina formation advanced, the cuprite phase decreased and two copper sulfate minority phases appeared: posnjakite and chalcanthite ($CuSO_4$). Additional factor, such as bio-fouling pollutants adhered in copper patina, changed consequently its structure (porous or compact).

The potential of a corroding metal, often termed as E_{corr} is probably the single most useful measured variable and monitored during metals exposed in field situations. The measurement of E_{corr} is a relatively simple concept and its values can give an indication of active/passive behavior of the metal during its corrosion process. When viewed in the context of Pourbaix diagrams, the corrosion potential can additionally give fundamental information of the thermodynamic corrosion risk [11]. Corrosion potential measurement at open circuit (o.c.p.) is a direct and non-intrusive method and E_{corr} fluctuations could be classified as Electrochemical Noise (EN) [12, 13]. Fluctuations of potential or current of a corroding metallic specimen are a well-known and easily observable phenomenon and the interest of EN analysis as a corrosion tool has increased steadily. The study of corrosion potential fluctuations has been applied, for example, to monitor the onset of events, characterizing localized corrosion such as pitting or stress corrosion cracking (SCC), ex-foliation, erosion-corrosion in either laboratory or diverse and complex industrial environments. No other technique, electrochemical or otherwise is even remotely as sensitive as EN to system changes and upsets. During localized corrosion EN is believed to be generated by a combination of stochastic processes, such as passivation breakdown and repassivation events, and deterministic processes, which can be caused by film formation or pit propagation processes.

The most traditional way to analyze electrochemical noise data has been to transform time records in the frequency domain, in order to obtain power spectra. Spectral or power density plots would thus be computed using fast Fourier transforms (FFT) or other algorithms, such as the maximum entropy method (MEM) [14]. Another very useful mathematical model has been proposed

to specifically reveal the fractal characteristics of signals. The electrochemical noise is considered to be non-stationary process and referred to as random fluctuations of the potential (or current) observed in corrosion process and can be regarded as a result of random nature of the corrosion reactions [15, 16]. EN analysis is a direct technique, which has been provided useful for studying corrosion process [17, 18], and can be analyzed in the time domain and described by the Hurst exponent [19].

The microscopic interactions among of many individual components is the root of non-stationary and non-linear features of corrosion process and the microscopic interactions may refer to low-frequency (large time scale) and/or high-frequency (small time scale) information contents. The presence of various mechanisms with broad range of time scales is likely to complicate the analysis. On noise signals such characteristics arise in novel techniques to study non-linear and non-stationary signals. One method which has proved to be quite useful to detect reliably long–range correlations in data with trends is the *detrended fluctuation analysis* (DFA) introduced by Peng et al. [20]. Later, this method was generalized to the analysis of multifractal time series (MFDFA) by Kantelhardt et al. [21]. MFDFA has showed to work very well for short time series with some 2^{10} or more [22] and their multiresolution properties permit also natural measurement of self-similar properties of signal, which are inherent in fractal *1/f* signals. There are many processes in the nature and society, which exhibit a fractal or multifractal behavior. Some authors have reported on the fractal nature of corrosion processes and corresponding electrochemical noise signals [23].

The aim of this research was to enlarge the information for copper corrosion potential behavior at open circuit during copper patina formation, after 10-days long-test of exposure of flat samples in Caribbean sea water, through the mono-multifractal dynamics changes with time and to correlate the tendency of E_{corr} changes with the surface phenomenon that occur on copper. To our knowledge, no other research has been done to date on this aspect.

1.1. Multifractal detrended fluctuation analysis

The multifractal DFA (MFDFA) procedure introduced in [21] consists of five steps. Suppose that *x(i)* is a time series of finite length *N* and that this series has a compact support; i.e., that only a negligible fraction of the elements *x(i)* is zero.

   a)   Compute the profile *Y(j)*, where *j = 1, ….N*:

$$Y(j) = \sum_{i=0}^{j} [x(i) - < x >] \tag{1}$$

   b)   Divide the new series $Y(j)$ in N_s non-overlapping contiguous segments of time scales of size s starting from the beginning of the series and then repeat starting from the end to obtain $2N_s$ segments.

   c)   Calculate, for all segments ϑ and all sizes s, the local polynomial trend of order m, y_ϑ^m, via a least-square fit and compute the variance:

$$F^2(\vartheta, s) = \frac{1}{s}\sum_{i=0}^{j}\{Y[(\vartheta - 1)s + i] - y_\vartheta^m(i)\}^2 \qquad (2)$$

Linear, quadratic, cubic or higher order polynomials can be used in the fitting procedure.

d)   Average overall segment of a given size s to obtain the q-order fluctuations:

$$F_q(s) = \left\{\frac{1}{2N_s}\sum_{\vartheta=1}^{2N_s}[F^2(\vartheta, s)]^{\frac{q}{2}}\right\}^{\frac{1}{q}} \qquad (3)$$

or for $q = 0$

$$F_0(s) = exp\left\{\frac{1}{4N_s}\sum_{\vartheta=1}^{2N_s} \ln[F^2(\vartheta, s)]\right\} \qquad (4)$$

e) For signals with fractal properties there is a range of sizes, $s_{min} < s < s_{max}$, at given order q for which:

$$F_q(s) \sim s^{h(q)} \qquad (5)$$

The $h(q)$ are called *generalized Hurst exponents* and are the output of the MFDFA algorithm.

Generally we are interested in how the generalized q dependent fluctuation functions $F_q(s)$ depend on the timescale s for different values of q. Hence, we must repeat steps b-d (Eq. 2, 3 and 4) for several time scales s. In general, the exponent $h(q)$ may depend on q and it is related to the multifractal scaling exponents $\tau(q)$ through the following relations:

$$\tau(q) = qh(q) - 1 \qquad (6)$$

For a monofractal signal $\tau(q)$ corresponds to a straight line and for a multifractal signal $\tau(q)$ is nonlinear function.

The singularity spectrum $f(\alpha)$ is related to $h(q)$, where α is called the *Hölder exponent*, through the following relations:

$$\alpha = h(q) + qh'(q) \qquad (7)$$

and

$$f(\alpha) = q[\alpha - h(q)] + 1 \qquad (8)$$

where $h'(q)$ denotes the derivative of h with respect to q.

2. EXPERIMENTAL SETUP

2.1. Exposure of copper samples and their characterization

During 6 months test 10 flat samples of electrolytic copper (99.99 mass %; 20x20x1mm), were immersed separately each one in 50 ml of Caribbean sea water (at 21°C), after degreasing with methanol. One of the samples was used as electrode and the corrosion potential (E_{corr}) changes were monitored the first 10 days by means of a computerized potentiostat/galvanostat Series G 750 Gamry Instruments Inc. and the software PHE 200. After that period of time (10 days) particles of copper patina (corrosion products having a poor adhesion) started to detach from the surface and as a consequence E_{corr} potential was monitored during the first 10 days, corresponding to the first stages of patina formation. The calomel reference electrode (E $_{Hg/Hg2Cl2}$ = 0.244 V) and Pt wire counter electrode were used. The E_{corr} values were registered at open circuit (o.c.p., without external polarization) in an electrochemical cell, during 13,000 seconds (3.6 h) at a sample period of 0.05 s, after different periods of exposure of the copper samples in sea water: 0, 1, 2, 3 and 10 days. The electrochemical E_{corr} potential fluctuations, considered as electrochemical noise, were analyzed with MFDFA method described above.

At those monitored periods of time copper samples were removed and their surface were analyzed with different techniques. To identify the presence of several crystalline phases in the patina, X-ray diffraction (XRD) analysis was done, using Siemens D 5000 diffractometer with grazing geometry (3° angle, 43 kV and current of 30 mA). The resulting spectra were processed by DIFRACT AT software [24] and phase identification was done with the Powder Diffraction File [25]. The surface change of the copper patina morphology was followed with SEM-EDAX "Phillips"microscope.
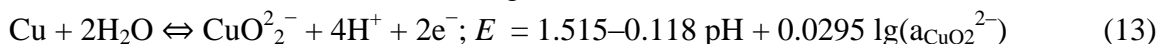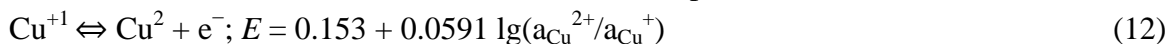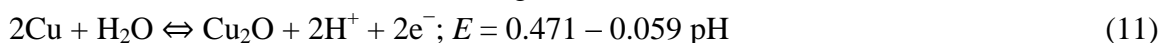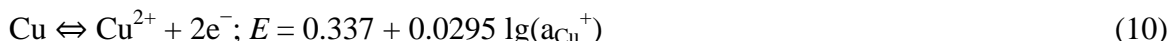
2.2. Sea water chemistry

Caribbean sea water was taken at 10 km from the coastal beach of Telchac marine station of CINVESTAV-Mérida (Yucatán state of Mexico; 21°7' north latitude and 89°25' western longitude) and at 10 m depth, where stands with copper samples were submerged for testing in real sea environment. The sea water had total salinity of 3.75%, pH = 7.69, dissolved oxygen 1.1 ppm and temperature of 21°C (at that depth). Specific sea pollutants were (μM L^{-1}): 1.75 ammonium; 2.61 silicates; 0.28 phosphates; 0.04 nitrites and 1.84 nitrates. Copper ions release (*runoff*), as a part of dissolved corrosion products formed on the samples, was monitored with HANNA 83-200 Multiparameter Ion Photometer for Laboratory. Hach procedures use primarily the bicinchoninic acid, reducing Cu^{2+} to Cu^+ ions and producing purple-colored complex.

3. RESULTS AND DISCUSSION

Copper corrodes in water as copper precipitated compounds or soluble copper salts. According to the data reported in the literature [1–3], in the system Cu-H$_2$O several anodic reactions occur having

different equilibrium potentials:

$$Cu \Leftrightarrow Cu^+ + e^-; E = 0.520 + 0.059 \lg(a_{Cu}^+) \tag{9}$$
$$Cu \Leftrightarrow Cu^{2+} + 2e^-; E = 0.337 + 0.0295 \lg(a_{Cu}^+) \tag{10}$$
$$2Cu + H_2O \Leftrightarrow Cu_2O + 2H^+ + 2e^-; E = 0.471 - 0.059 \text{ pH} \tag{11}$$
$$Cu^{+1} \Leftrightarrow Cu^2 + e^-; E = 0.153 + 0.0591 \lg(a_{Cu}^{2+}/a_{Cu}^+) \tag{12}$$
$$Cu + 2H_2O \Leftrightarrow CuO_2^{2-} + 4H^+ + 2e^-; E = 1.515 - 0.118 \text{ pH} + 0.0295 \lg(a_{CuO2}^{2-}) \tag{13}$$

Those anodic reactions of copper corrosion are developed with a very low overvoltage and in chloride solutions (sea water) they occurs under conditions very close to equilibrium potential, controlled by the diffusion of the formed species. Regarding the cathodic corrosion reactions, the only possible one from the thermodynamic point of view is the reduction of the atmospheric oxygen on the copper surface, although with a high overvoltage. Both Cu(I) and Cu(II) ions concentration increases in the presence of the sea water anions, because of the formation of soluble complexes and this fact could give rise to a change of the equilibrium potential. Cuprous copper ions form complexes only with the chloride ions. Chemical model for freely corroding copper in sea water has been proposed [26] and a more detailed picture of the variety of chemical reactions involved with the corrosion of copper in sea water can be obtained from the electrode potential–pH diagrams [27].

Table 1 shows the large variation with time in the release (*runoff*) rates of total copper ions: 2.83×10^{-5} g m^{-2} at the first 24 hours and up to 6.25×10^{-3} g m^{-2} after 10 days of immersion in sea water, as a result of copper dissolution of corrosion products. The *runoff* rates were measured during 6 months and the copper release reached a value of 1.22 g m^{-2}, three orders higher than that obtained after 10 days of copper exposure in seawater. As was mentioned above (experimental setup), at 10 days copper patina was partially detached, losing its adhesion and this fact contributed to open a fresh copper surface for acceleration of the copper corrosion and release (dissolution) of copper patina.

Table 1. Rates of total copper ions release (*runoff*) with time of exposure of copper flat samples in Caribbean sea water

Time of Cu exposure in sea water	Copper ions release (g m^{-2})
1 day	2.83×10^{-5}
2 day	6.66×10^{-5}
4 day	2.11×10^{-4}
6 day	3.05×10^{-4}
10 days	6.25×10^{-3}
1 months	6.02×10^{-2}
3 months	7.20×10^{-1}
6 months	1.22

It is probable that part of the copper ions release is also as a result of complexation towards organic matter in the sea water. The *runoff* process is completely different from the metal corrosion

(oxidation) process, which is mainly of electrochemical nature, while the *runoff* is of chemical nature and occurs at the interface between the corrosion products and the aggressive environment. The toxicology of copper to marine organisms has been a subject of reviews and it is considered to be the most toxic metal [28, 29]. Probably due to this fact we did not found marine microorganisms on the copper samples in exposure during the 10 days test. The cupric ion (Cu(II)) is recognized as the most lethal form and it is known to overload enzyme systems and to interfere with the basic molecular structure of the organism.

One–year field exposure of fresh copper sheet has been performed in a marine environment and the authors report annual *runoff* rates of total copper of 1.5 g m^{-2} year^{-1} [30], which is close to *runoff* rate of 1.22 g m^{-2} (Table 1) obtained after twice lower period of time (6 months) for copper exposed in sea water. This fact confirms the high aggressivity of the seawater, since it is a natural complex electrolyte of a great number of dissolved ionic salts, specific pollutants, besides the additional presence of other suspended or dissolved substances, as dissolved gases, alive organic matter or in decomposition.

The gradual degradation (corrosion) of the initial patina (Cu$_2$O, cuprite) in sea water and the release of copper ions (Table 1) were followed by a chemical transformation of the copper patina layer. The XRD-spectra analysis indicated that as the time advanced, (Fig. 1, 11 months) the *paratacamite* (copper chloride compound, Cu$_2$(OH)$_3$Cl) increased its relative intensity,while that of cuprite decreased. As a minority phase appeared *nantokite* (CuCl, another copper chloride). Crystals of *halite* (NaCl) were detected by SEM-EDX in the porous copper patina, as a part of the sea water, and magnesian calcite (Ca,Mg)CO$_3$ crystals precipitated on the copper surface at 30 days of exposure (Fig. 2 d).
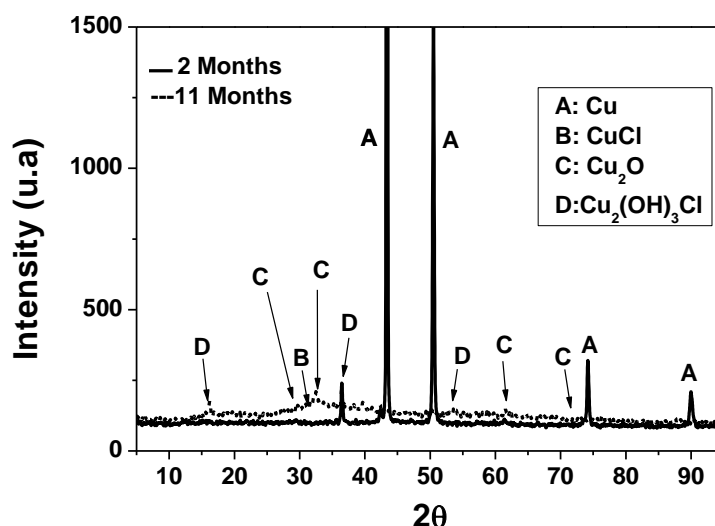

Figure 1. Crystalline phases (XRD) of copper corrosion products formed in artificial sea water after 2 and 11 months of exposure.

The corrosion process was not uniform and SEM images revealed that localized pits were formed (Fig. 2 a-c) in the porous of cuprite (Cu$_2$O, the unique initial copper phase). At the end of 30

days (Fig.2 d) the surface was almost covered by precipitated crystals of magnesian calcite (carbonate) and that fact should create an additional resistance element in the electrical circuit when copper corrosion potential was measured. Later, days after, the magnesian calcite crystals were detached step by step from the patina surface and their protective barrier on the copper patina surface against the corrosion process diminished.
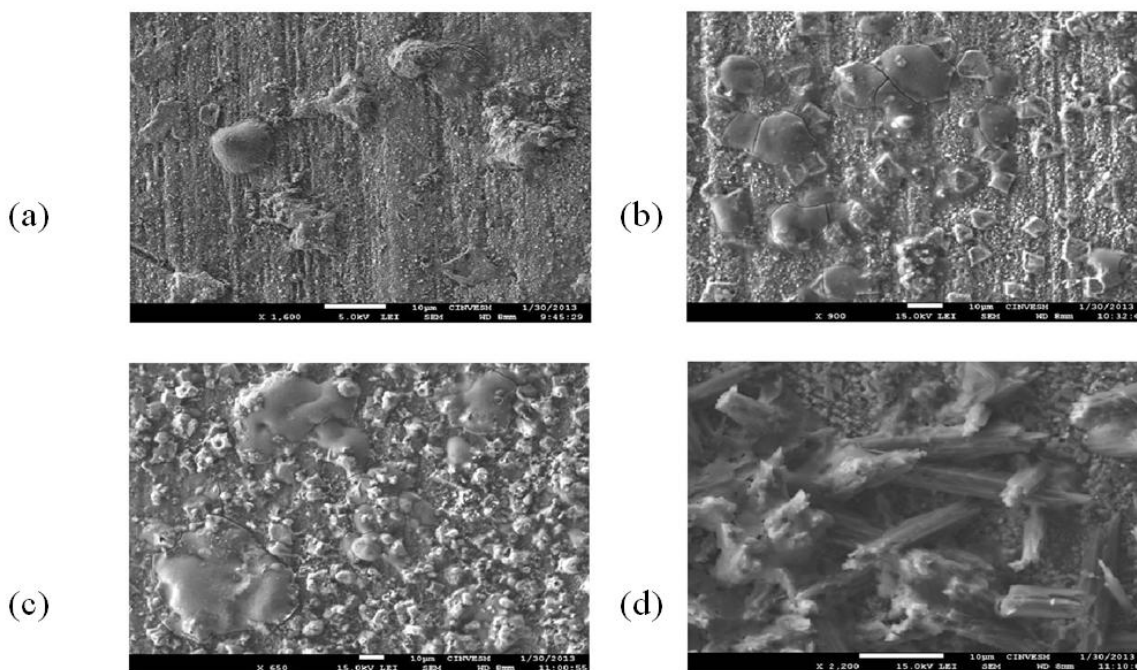

Figure 2.. Morphology (SEM) of the copper surface after exposure in sea water: (a) 2 days; (b) 3 days; (c) 10 days and (d) 30 days.

The electrochemical corrosion potential (o.c.p.) fluctuations of Cu electrode immersed in sea water during 10 days were recorded periodically after different period of times: 0, 1 (24 h), 2, 3 and 10 days. Figure 3 shows examples of those records. On each series of records we selected a stable potential region of 2^{16} continuous data entries and they were analyzed with MFDFA.

Time records of the open circuit potential revealed that after 10 days of exposure in sea water (Fig.2), E_{corr} shifted up with 74 mV to more positive value than the initial one (-0.254 V), reaching a potential of -0.180 V, even the release of copper ions was detected (Table 1).

The MFDFA analysis has been carried in the potential time series E_{corr} (Fig.3). In all exposure periods of copper in sea water, the signals were detrended with a polynomial of order two in the third step of the MFDFA method, described in Section 1.1c. The key assumption of the MFDFA procedure is that $F_q(s) \sim s^{h(q)}$ (Eq.5) for some range in s, so the generalized Hurst exponent $h(q)$ can be extracted in that s range by a fit to a line in a *log-log* scale.
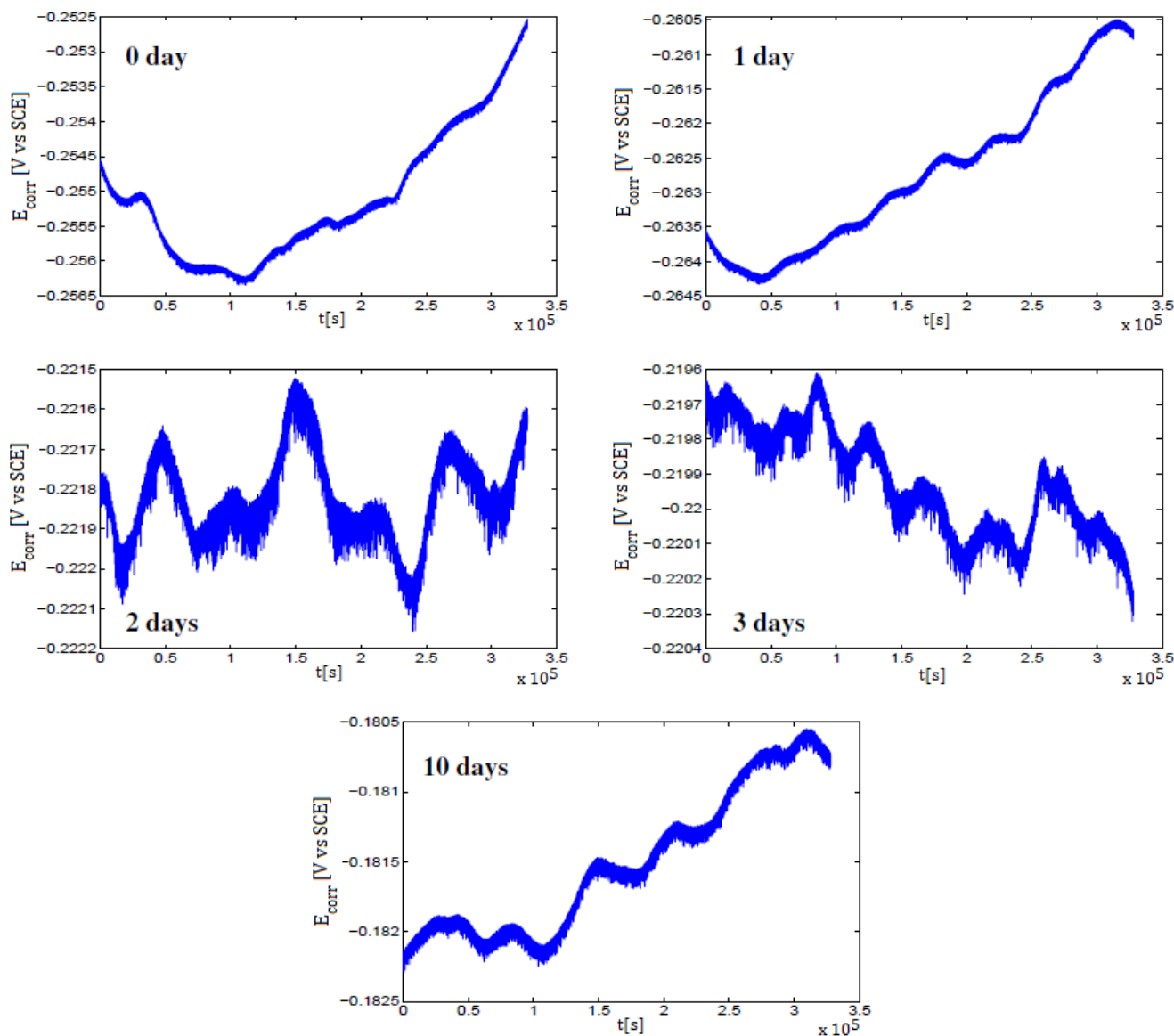
Figure 3. Time records of E_{corr} potential fluctuation of copper electrode during the first 0, 1, 2, 3 and 10 days of exposure in sea water.

The fit of the extracted values of the generalized Hurst exponent was done by a linear least square from $s_{min} = 70$ to $s_{max} = 1000$ time scales s, for q-order values, within −5 and 5 with 0.5 increments in all copper exposure time series. The behavior of q-order fluctuations ($F_q(s)$) for two stages of exposure time are depicted in Figure 4.

The both panels in Figure 4 show $F_q(s)$ for three representative values of q. There is an important observation to be made from this figure: there is a range of box sizes s where $F_q(s)$ exhibits a power law behavior. It is important to remember that the fifth point of the MFDFA algorithm requires the range of sizes where the power law behavior is valid, in order to extract from this range the generalized Hurst exponent $h(q)$ [22].
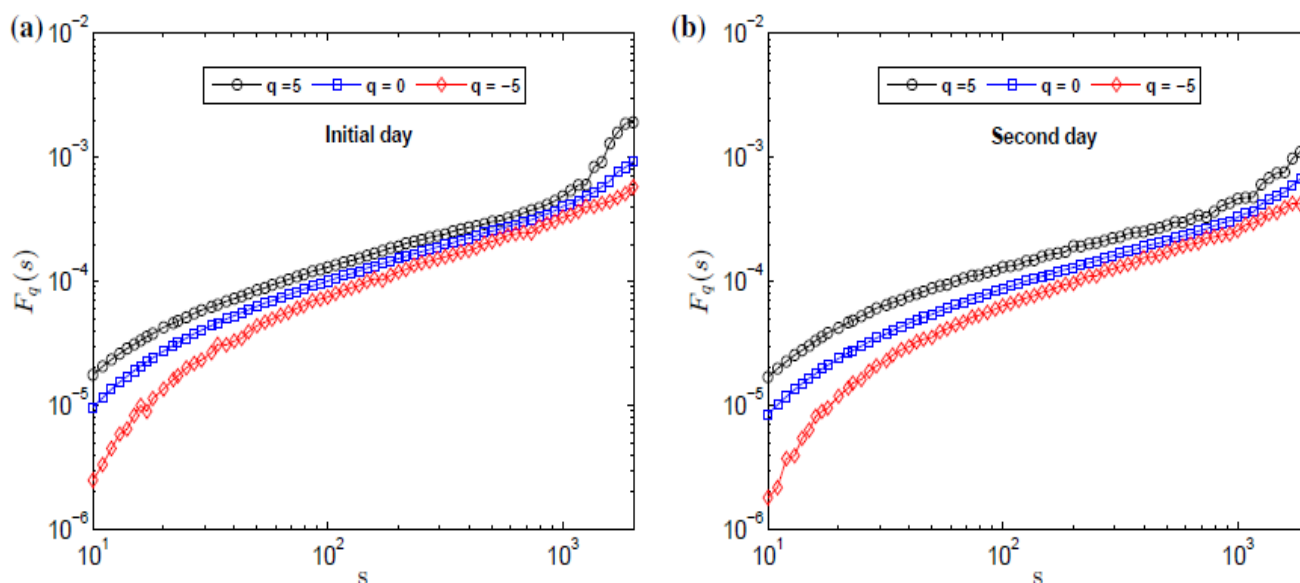
Figure 4. Representative fluctuations of q–order as a function of the scale size s of Cu electrode exposed at sea water: test initiation (a) and second day (b).

The results of the MFDFA are presented in Figure 5. The Figure 5a shows that $h(q)$ decreases with q. There is an important observation to be made: the Hurst exponents $h(q)$, corresponding to the different exposure time of copper in sea water had values $0.53 < h < 0.63$. Those results indicate that the E_{corr} fluctuations exhibit a persistent dynamics: $h < 1/2$ corresponds to anti- persistent behavior; $h = 1/2$ can indicate a completely uncorrelated behavior and $h > 1/2$ corresponds to persistent behavior. This kind of behavior was similar to that observed in [22], for the case of monofractal signals with Hurst exponent $h = 0.5$. From the analysis of monofractal signals with $h = 0.5$, the authors concluded that series of lengths as 2^{16} could be analyzed with a precision less than 3% at values of $|q| < 5$ [22]. The precision of MFDFA applied to the time series of copper exposed in sea water is shown on Table 2.

Table 2. Values of the variation Δ_q for *h(q)* with respect to *h(q=0)* in each period shown in Figure 5.

$$\Delta h_q = |\, h(q=0) - h(q)\,|\,/\,h(q)$$

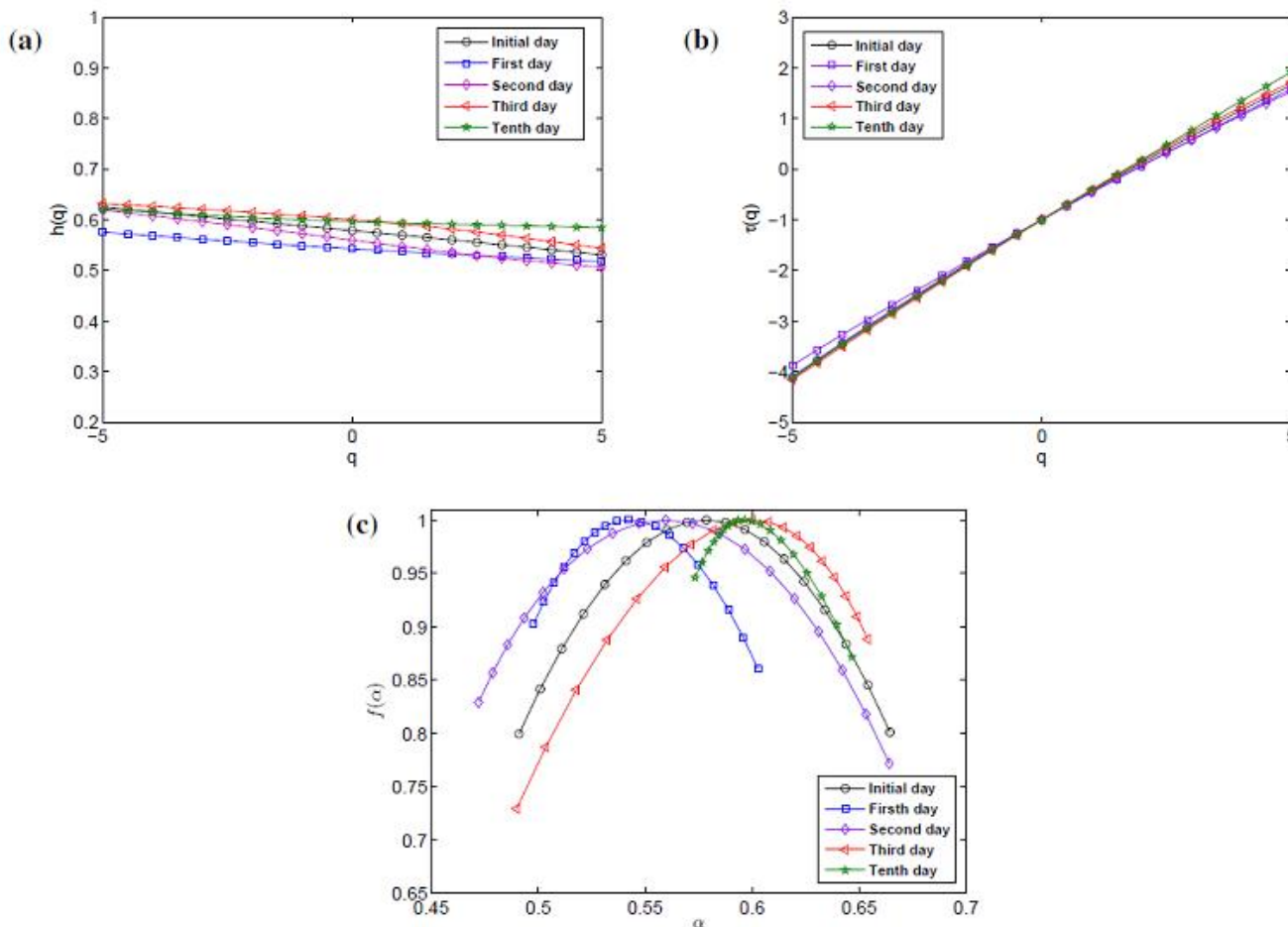| Period	$\Delta h_{q= -5}$	$\Delta h_{q= -2}$	$\Delta h_{q= 2}$	$\Delta h_{q= 5}$
0 day	0.08	0.03	0.03	0.08
1 days	0.06	0.02	0.02	0.05
2 days	0.11	0.04	0.04	0.10
3 days	0.05	0.02	0.03	0.09
10 days	0.04	0.01	0.01	0.02

Figure 5. (a) Behavior of generalized Hurst exponent as a function of the q-order (Eq.5) of E_{corr} potential of copper during its exposure in sea water for different periods of time; (b) multifractal scaling exponent $\tau(q)$ (Eq.6); (c) singularity spectrum $f(\alpha)$ (Eq.8).

The results (Table 2, Fig.5) suggest that the periods 0, 1, 2 and 3 days present a behavior consistent with a *multifractal* signal. However the fifth period of 10 days is consistent with a *monofractal* behavior with long-range correlation and a Hurst exponent around 0.6. The multifractal scaling exponent $\tau(q)$ and the singularity spectrum $f(\alpha)$ for all exposure times of copper in sea water are depicted in Figure 4b and Figure 4c, respectively. Our results showed that the copper corrosion process has non-zero values of $f(\alpha)$ for a broad range of Hölder exponents α (Fig.5c). The Hurst exponents $h(q)$, the nonlinear function of the multifractal spectrum $\tau(q)$, the shape of the singularity spectrum $f(\alpha)$ and the variation Δ_q for $h(q)$ confirmed that E_{corr} series of copper are compatible with a multifractal behavior. However, from the MFDFA procedure applied to the E_{corr} fluctuations, it is difficult to decide if the monofractal behavior of fifth period of 10 days is due the uncertainties expected. This fact could be atributed to the partial detachment of copper patina particles and also to the start of precipitated micro-crystals of magnesian calcite (carbonate) on the copper patina surface, which created an additional resistance element in the electrical circuit when copper corrosion potential was measured.

4. CONCLUSIONS

Six months laboratory exposure of copper samples in Caribbean sea water has been performed with the goal to analyze the corrosion potential (E_{corr}) fluctuations at open circuit, and to correlate the results with corresponding changes in patina formation and barrier properties. The E_{corr} measurement was possible during the yearly stages (up to 10 days) of copper patina formation, as a result of corrosion particles detachment and initiation of precipitated magnesian calcite (carbonate) crystals on the patina surface. One method which has proved to be quite useful to detect reliably long-range correlations in data with trends is the detrended fluctuation analysis (DFA), which later has been generalized to the analysis of multifractal time series (MFDFA). The following main conclusions have been drawn:

- The generalized Hurst exponents $h(q)$ as output of the MFDFA algorithm, have been extracted of some range of sizes (*s*) for E_{corr} potential signals, by a linear least-squares in a log-log scale. The results showed that there is a range of *s* and *q*-order fluctuation range ($-5 \leq q \leq 5$) where $F_q(s)$ exhibits a power law behavior.

- The corrosion process of copper in sea water has ranges of Hurst exponents $0.53 < h < 0.63$, and these results suggest that the corrosion potential oscillations exhibit a persistent behavior.

- The copper corrosion process has non-zero values of the singularity spectrum $f(\alpha)$ for a broad range of Hölder exponents.

- The Hurst exponents $h(q)$, the nonlinear function of the multifractal spectrum $\tau(q)$, the shape of the singularity spectrum $f(\alpha)$ and the variation Δ_q for $h(q)$ confirmed that E_{corr} series of copper exposed in sea water to 0, 1, 2 and 3 days are compatible with a multifractal behavior.

- The mono- or multifractal behavior of fifth period of 10 days is difficult to decide, due the uncertainties expected from the application of MFDFA to the E_{corr} fluctuations. This fact was attributed to detachment of corrosion products and initiation of precipitated crystals of magnesian calcite (carbonate) on the copper patina surface, which created an additional resistance element in the electrical circuit when copper corrosion potential was measured.

- The tendencies of changes in corrosion potential values (E_{corr}, o.c.p.) were correlated with the copper ions release (runoff) in the sea water. During the test period, copper patina (Cu_2O) changed its composition as time of corrosion process advanced.

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