Application of recurrence plots as a new tool in the analysis of electrochemical oscillations of copper

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Abstract

The main aim of this research is the study of electrochemical oscillations in current by means of recurrence plots at different potentials in which products of corrosion are formed, originating pitting corrosion of copper in different saline solutions containing chlorides and sulphates. The dynamics of the formation of corrosion products was characterized by determining if the passive layer is adequate or not to give origin to the pitting corrosion phenomenon. A key contribution of this work to the study of corrosion is the fact that it was found that pitting corrosion begins at the quasi-periodic oscillation potential and not at the so-called pitting potential, which in this work will be denominated apparent pitting potential. This has been proved by means of SEM micrographs at the quasi-periodic potential and with the aid of electrochemical oscillation measurements and qualitative and quantitative recurrence analysis of electrochemical oscillation time series.

Keywords: Electrochemical oscillations; Pitting corrosion; Recurrence plots

1. Introduction

The corrosion phenomenon as is well-known has an electrochemical nature, which is the reason why one can find out the presence of oscillations in potential and current due to the formation of microcells on a metal surface. Such oscillations contain information of the corrosion process under study, finding an important application in the industry [1] and also as a tool of basic research in electrochemistry [2–4].

As was said above, the oscillating signal is generated by the dynamics which takes place on the metal surface where the double layer is continually modified. Many efforts have been realized in the past to extract information from that signal; which is associated to electrochemical reactions and to the distribution of these reactions taken part on the metal surface, what determines the type of morphology present during the corrosive attack. An example of this can be found in the research done by García-Ochoa and Genescá [5], where it is shown that the fractal dimension of the corroded surface has a direct relationship with the fractal dimension of the electrochemical oscillating signal.

The metal selected by us to study the pitting corrosion phenomenon was copper. This is a metallic material frequently used in pipelines of cooling systems of thermoelectric centrals and petroleum installations employing sea water as refrigerant in which the most abundant anions are chlorides and sulphates. The most important danger suffered by these systems is precisely that of pitting corrosion, phenomenon which is responsible for the production of perforations in pipelines, provoking that recycling water, whose purity is very high,
be polluted with sea water giving origin to very serious problems in all the cooling system.

The pitting corrosion phenomenon is one of fundamental importance to industrial systems as we could appreciate above; and as a matter of necessity, a profound knowledge of the dynamics of the pitting corrosion process to understand this phenomenon should be attained. Some researchers in the past have employed electrochemical oscillating signals to study the dynamics of pitting corrosion [6–8], where it has been found that these electrochemical signals apparently show chaotic behavior [9–13]; opening an enormous panorama of research, in which it was possible to determine some parameters characteristic of the branch of mathematics called nonlinear system dynamic analysis; among the parameters considered in such studies, the correlation dimension and the maximum Lyapunov exponent were calculated. The work done by Corcoran and Sieradzki [14] is remarkable, for they asserted that the electrochemical oscillating signal during the pitting corrosion phenomenon of silver has chaotic behavior. In our work we found that pitting corrosion of copper should be associated to an electrochemical oscillating quasi-periodic signal. As a matter of fact, one can associate pitting corrosion to a lower degree of chaotic behavior; the less the chaos the more the pitting, till the point where the behavior of the dynamical system becomes quasi-periodic, where one has the more developed degree of pitting corrosion. Concerning stochastic behavior, one can now assure that contrary to what had been classically proposed in the early times of the study of pitting corrosion (1933) by Evans et al. [15], one should not associate stochastic behavior of the electrochemical oscillating signal to pitting corrosion, unless some degree of chaotic behavior (measured in terms of the Kolmogorov entropy) be considered as stochastic behavior. Moreover, for practical purposes, in nonlinear physics one does consider highly developed chaotic behavior (one with a high value of the Kolmogorov entropy and a high value of the maximum Lyapunov entropy) as stochastic behavior (even when, strictly speaking, the kind of dynamical behavior detected be of chaotic nature); for in modeling, it would not make sense to solve a huge number of nonlinear coupled differential equations to generate the time series. It is better, in such a case, to associate a probability density to the time series under study as if we were dealing with stochastic behavior. In the theory of random matrices one fits the histogram generated from chaotic dynamical systems by obtaining the probability densities of various types of Hamiltonian random matrices, what includes the so-called Gaussian orthogonal ensemble (GOE) [39]. Usually a low level of chaos is detected measuring a low value of the maximum exponent of Lyapunov or according to Pensi’s theorem; calculating a low value of the Kolmogorov entropy, which is equivalent to the sum of the positive Lyapunov exponents. We will focus this paper in the study of pitting corrosion using the techniques of recurrence analysis. In particular, we will not calculate explicit values of the maximum Lyapunov exponent; we will rather present values of a chaotic descriptor, which is part of the recurrence analysis, known as the maximum line (Max-Line); which can be considered as the inverse of the maximum Lyapunov exponent. Standard nonlinear system dynamic analysis of copper pitting corrosion has been presented elsewhere [16].

1.1. Visual and quantitative recurrence analysis

Traditionally, researchers interested in nonlinear system dynamic analysis deal with phase space reconstruction trajectories. In visual recurrence analysis, which is a different approach to nonlinear dynamical systems one can study recurrent behavior. This procedure has been proposed to differentiate stochastic variability of chaotic variability. Recurrence plots (RPs) are relevant for short and nonstationary data, they are especially useful for the graphical representation of multidimensional dynamical systems by means of two dimensional RPs [17,18]. There are two distinct types of recurrence plots: unthresholded and thresholded recurrence plots, UTRPs and TRPs, respectively. The axes of the recurrence plot are time indices i and j. In TRPs, if points i and j fall within some distance or threshold of each other, then point (i,j) gets a dot. In UTRPs, points (i,j) get a colored dot according to the distance between points i and j. In Fig. 1, as an example, we show the TRP (Fig. 1(a)) and the UTRP (Fig. 1(b)) of a sinusoidal signal. The technique of qualitative recurrence plots was first introduced by Eckman et al. [19]. The quantitative aspect of this theory was first established by Zbilut and Webber [20], who also introduced the very first time the idea of a quantitative metric to characterize and generate RPs. What we know in oscillating signal measurements is a time series of current i(t), obtained under potentiostatic conditions. By monitoring the scalar signal of current, that we shall call \( y_k \equiv (x_1, x_2, \ldots, x_k) \), where k is a discretization of time, one constructs a vector \( y_k \) for \( k = 1, 2, \ldots, M \)

\[
y_k = (x_k, x_{k+1}, x_{k+2}, \ldots, x_{k+M-1})
\]

in the above equation \( d_k \) corresponds to the embedding dimension and \( \tau \) is the time delay.

The embedding dimension \( d_k \) can be estimated through the calculation of the percentage of the global false nearest neighbors [21,22] for the dynamical variable \( y_k \). The estimation of the time lag \( \tau \) corresponds to the first minimum of the average mutual information [21,23,24].

\[
I(\tau) = \sum_{x(k),x(k+\tau)} P(x(k),x(k+\tau)) \log_2 \left( \frac{P(x(k),x(k+\tau))}{P(x(k))P(x(k+\tau))} \right),
\]

(2)
where \( P(x(k), x(k + \tau)) \) is the joint probability for measurements \( x(k) \) and \( x(k + \tau) \) and \( P(x(k)) \) and \( P(x(k + \tau)) \) are the individual probability densities for measurements \( x(k) \) and \( x(k + \tau) \), respectively.

According to Takens and Packard [25,26] from a one-dimensional time series generated by a dynamical system of dimension \( d \), one can generate a multidimensional space denominated embedding space \( E \), with \( d \geq 2d + 1 \). A proper choice of \( d \) and \( \tau \) is critical and must be done wisely in order to reconstruct the phase space attractor and the recurrence plot in an optimal way. The resultant trajectory in \( R^E \) is

\[
\{y_1, y_2, \ldots, y_m\},
\]

where

\[
M = N - (d - 1)\tau.
\]

Let us define the Euclidean \( p \)-norm \( q_p \)

\[
q_p(x, y) = \left(\sum_{k=1}^{n}|y_k - x_k|^p\right)^{1/p}
\]

which in one dimension is equivalent to the maximum norm [27].

A recurrence matrix can be defined by [27]

\[
R(i, j) = q_p(x, y), \quad 1 \leq i, j \leq m
\]

which is used to generate an unthresholded recurrence plot (UTRP) of the oscillating signal time series by plotting the recurrence matrix \( R(i, j) \) as a contour coloured plot.

Due to the fact that the graphical presentation given by recurrence plots might be difficult to be evaluated visually; Zbilut and Webber [20] did propose a set of parameters which are part of the recurrence quantification analysis (RQA). In this investigation, we did consider only the use of the following parameters of RQA: Percent of determinism (%Det) which can be calculated by means of the following formula:

\[
\%\text{Det} = \frac{D\text{Recurrence}}{N\text{Recurrence}},
\]

where \( D\text{Recurrence} \) is the number of points forming part of line segments parallel to the square bisector of the recurrence plot. A line segment is defined as two or more adjacent points. \( N\text{Recurrence} \) is the total number of recurrence points in the superior triangle of the recurrence plot without counting the number of points on the bisector. Maximum Line (MaxLine) is the longest recurrent diagonal line segment found during the computation of %Det. MaxLine is also inversely proportional to the largest positive Lyapunov exponent and is therefore a measurement of the sensitivity to initial conditions of the time series. The great potentiality of recurrence plots have found many applications in multiple branches of scientific research as in chemistry [28], physics [29,30], and physiology [31,32] among others. Computer software used in this work was the Visual Recurrence Analysis package developed by Kononov [21]. A review of existing software packages for the construction of recurrence plots, done by J. Belaire-Franch and D. Contreras, can be found in [38].

2. Experimental procedure

Electrochemical tests were carried out using an electrode holder with a copper sample (99.94% purity) exposing a surface of 1 cm\(^2\) of copper to the selected solution. In Table 1, one shows the set of aggressive anion solutions employed in our research; using for it an analytical reactive (Baker Reagent A.C.S.) and deionized water in their preparation. The metal surface was polished with 1200 sandpaper and degreased with acetone (Baker Reagent A.C.S.). We employed a saturated calomel reference electrode and as a counter electrode a couple of graphite bars. Potential in all cases were measured vs. SCE. This system has a connection isolated for the Electrochemical Interface (Solartron 1287), which
was used to control the potential of the working electrode.

All the system was contained in a five-mounted glass cell of 1000 ml at ambient temperature. The polarization curves (cyclic voltammograms) were carried out to locate the pitting potential zone. Each curve was scanned at 5 mV s\(^{-1}\) from 0.70 to 1.5 V, followed by a reverse scan back to 0.70 V. Current time series were obtained under experimental conditions assuring that stationary state had been reached waiting 20 min before each potentiostatic test. The current data acquisition speed at different potentials was of two data per second (2 Hz). Copper samples for SEM micrographs were prepared using ASTM Norm G1-03 Standard Practice for preparing, cleaning, and evaluating corrosion test.

3. Experimental results

Four polarization curves are shown in Fig. 2, they were obtained with reverse scan polarization at different concentrations of chlorides and sulphates; one can clearly appreciate that there exists a critical potential in which the value of the current does increase after the passivation process. This is due to the generation of some corrosion products on the surface of the working electrode, which are mainly constituted by Cu\(_2\)O, CuCl\(_2\)·3Cu(OH)\(_2\) and CuSO\(_4\)·3Cu(OH)\(_2\)·H\(_2\)O (brochantite) [33]. After doing this, one continued the experiment with a return of potential, where one could clearly appreciate a phenomenon of hysteresis in which the associated current values during reverse scanning voltammetry were remarkably high. This points out to the fact that the metal surface had grown and that this was not due to an increment in the oxidation level of the species formed during the passivation process. This is the reason why, one has classically denominated to this critical potential, the pitting potential (\(E_p\)), for one associates it to the potential in which pitting is apparently generated on the metal surface provoking a sudden increase of the electrode surface due to the formation of the corrosion products above mentioned [34].

The value of the critical potential of pitting (\(E_p\)) which from now on will be called apparent pitting potential is shown in Fig. 3, this potential is related to the chemical composition of the medium. This is the reason why one would expect that the copper electrode would present a corrosive attack by pitting, after reaching this potential in all the concentrations at which the study has been carried out.

The corroded surface of four copper electrodes subject to potentials higher than the corresponding apparent pitting potential (\(E_p\)) is presented in Fig. 4 and is a function of the composition of the medium in which the electrodes were immersed. As is well appreciated there, two electrodes do present pitting corrosion (Figs. 4(a) and (b)), while the two other do not show pitting (Figs. 4(c) and (d)).

In Fig. 5 one presents the time series of four concentrations at the apparent pitting potential (\(E_p\)) and at a potential higher than \(E_p\); there one clearly notes that for the solution at a concentration of 26.5 g/l NaCl and 3.89 g/l Na\(_2\)SO\(_4\) one generates a series of quasi-periodic oscillations at both potentials (Figs. 5(a1) and (a2)); while at 13.25 g/l NaCl and 3.89 g/l Na\(_2\)SO\(_4\) one only observes these quasi-periodic oscillations at potentials higher than the \(E_p\). Let us note that Fig. 5(b1) shows a current time series which begins to exhibit regularity from a value of time equal to 1250 s; however, quasi-periodicity has not been completely developed at this potential (\(E_p = 702\) mV), which is the apparent pitting potential. Actually, at this potential pitting corrosion is

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.62 g/l NaCl</td>
<td>3.89 g/l Na(_2)SO(_4)</td>
</tr>
<tr>
<td>B</td>
<td>8.48 g/l NaCl</td>
<td>3.89 g/l Na(_2)SO(_4)</td>
</tr>
<tr>
<td>C</td>
<td>10.60 g/l NaCl</td>
<td>3.89 g/l Na(_2)SO(_4)</td>
</tr>
<tr>
<td>D</td>
<td>13.25 g/l NaCl</td>
<td>3.89 g/l Na(_2)SO(_4)</td>
</tr>
<tr>
<td>E</td>
<td>19.87 g/l NaCl</td>
<td>3.89 g/l Na(_2)SO(_4)</td>
</tr>
<tr>
<td>F</td>
<td>26.50 g/l NaCl</td>
<td>3.89 g/l Na(_2)SO(_4)</td>
</tr>
<tr>
<td>G</td>
<td>26.50 g/l NaCl</td>
<td>1.75 g/l Na(_2)SO(_4)</td>
</tr>
<tr>
<td>H</td>
<td>26.50 g/l NaCl</td>
<td>1.32 g/l Na(_2)SO(_4)</td>
</tr>
<tr>
<td>I</td>
<td>26.50 g/l NaCl</td>
<td>1.05 g/l Na(_2)SO(_4)</td>
</tr>
<tr>
<td>J</td>
<td>26.50 g/l NaCl</td>
<td>0.85 g/l Na(_2)SO(_4)</td>
</tr>
<tr>
<td>K</td>
<td>26.50 g/l NaCl</td>
<td>0.70 g/l Na(_2)SO(_4)</td>
</tr>
<tr>
<td>L</td>
<td>26.50 g/l NaCl</td>
<td>0.66 g/l Na(_2)SO(_4)</td>
</tr>
<tr>
<td>M</td>
<td>26.50 g/l NaCl</td>
<td>0.64 g/l Na(_2)SO(_4)</td>
</tr>
</tbody>
</table>

Table 1

Solutions containing mixtures of chloride and sulphate anions used during each voltammetry and oscillating current signal generation at different pHs

![Fig. 2. Cyclic voltammograms obtained with reverse scan polarization. At 5 mV s\(^{-1}\): (a) Solution F: 26.50 g/l NaCl and 3.89 g/l Na\(_2\)SO\(_4\); (b) solution D: 13.25 g/l NaCl and 3.89 g/l Na\(_2\)SO\(_4\); (c) solution G: 26.50 g/l NaCl and 1.75 g/l Na\(_2\)SO\(_4\); (d) solution M: 26.50 g/l NaCl and 0.64 g/l Na\(_2\)SO\(_4\).](image-url)
not present. In Fig. 5(b2) we do show a current time series which begins to exhibit quasi-periodic behavior at a time of 1900 s and at a potential which is greater than the apparent pitting potential \( (E_p = 702 \text{ mV}) \). This the potential at which pitting really occurs and shall be denominated quasi-periodic potential or \( E_{qpo} \), and has a value of 1054 mV. For the two remaining concentrations one does not observe these series of quasi-periodic oscillations (Figs. 5(c1), (c2), (d1) and (d2)) and pitting is not present there. It is clear that when quasi-periodic oscillations do appear, the pitting corrosion phenomenon is always present. On the other hand, in the absence of quasi-periodic oscillations we only observed a phenomenon of homogeneous corrosion. The oscillatory potential region (lower and upper potential boundaries) was found departing from the apparent pitting potentials \( (E_{ps}) \) and considering an interval of potential of 800 mV. We analyzed each current time series for values of the potential above and below the apparent pitting potential in steps of 10 mV.

One can see in Fig. 6 the apparent pitting potentials \( (E_p) \) and the potential at which quasi-periodic oscillations \( (E_{qpo}) \) are present in the different saline concentrations considered in Table 1. \( E_{qpo} \) will be denominated quasi-periodic oscillation potential in this work, and is the
potential at which pitting really begins. One clearly note that there is a relationship between the chemical composition of the medium and the potential difference between $E_p$ and $E_{aqpo}$. A very relevant fact occurs when the concentration of Na$_2$SO$_4$ is equal to 3.89 g/l (which corresponds to solutions A to F in Table 1); there the
$E_{\text{qpo}}$ is always present, and we noted, of course, the occurrence of quasi-periodic oscillations and hence the presence of pitting on the surface of the copper electrode. On the other hand, for concentrations of Na$_2$SO$_4$ below 3.89 g/l (which corresponds to solutions G to M in Table 1) one only generates values of the apparent pitting potential which were obtained from the corresponding polarization curves. Actually at this potential, pitting corrosion is never present, with the sole exception of the case corresponding to solution F in Table 1, where $E_p = E_{\text{qpo}} = 622$ mV. Besides, in Fig. 5(a1), which corresponds to the current time series precisely at $E_p = E_{\text{qpo}} = 622$ mV, we note the presence of a quasi-periodic behavior whose dominant frequency is 0.0035 Hz. The value of the quasi-periodic potential $E_{\text{qpo}}$, as have been already mentioned above, was determined from experimental current time series at values of potential below and above the apparent pitting potential $E_p$. Actually, we found out that at potentials below the apparent pitting potential $E_p$, we could not detect quasi-periodic oscillations, and as it was expected, we never saw there pitting corrosion. Quasi-periodic oscillations were present only at potentials equal or higher to $E_p$.

Fig. 7 is the graphical representation of two attractors in phase space at the $E_{\text{qpo}}$. In Fig. 7(a) one observes a series of quasi-periodic trajectories corresponding to current time series in Fig. 5(a1). This is indicative of a phenomenon of self-organization, which demands a highly correlated dynamic behavior. This means that there exists a communication among pits and this is attained by means of waves of concentration and electrical field [35] generated by pitting itself; since there, one has sites where the dissolution of the metallic material (copper) is very intense; while in the surroundings, where the passive layer is present, the dissolution of the material goes to a minimum. This is analogous to what happens on an electrode with a discretized surface, as has been demonstrated by Hudson et al. [36,37]. In the same investigation, Hudson observed chaotic behavior with some degree of periodicity, which was a function of the distribution of the active sites in the particular kind of electrodes used by him and coworkers. On the other hand, Fig. 7(b) shows an attractor with a dense zone (a nucleus) corresponding to the interval in the time series of Fig. 5(b2), which goes approximately from 0 to 1000 s; then one can appreciate in the same attractor of Fig. 7(b) the apparition of a spiral course which finishes forming a quasi-periodic attractor. Note that in Fig. 5(b2) one can see the presence of a beat, which is characteristic of quasi-periodicity starting approximately at a time of 1850 s. Moreover, at the quasi-periodic potential ($E_{\text{qpo}} = 1054$ mV) in which Figs. 5(b2) and 7(b) were generated, we detected pitting corrosion of copper.
Fig. 8. Recurrence plots obtained from current time series at different applied potentials and different mediums. (a1,b1) 200 mV, $dE = 8$, $T = 46$; (a2,b2) 345 mV, $dE = 10$, $T = 45$; (a3,b3) 622 mV, $dE = 9$, $T = 52$; and (a4,b4) 690 mV, $dE = 9$, $T = 52$; in solution F: 26.50 g/l NaCl and 3.89 g/l Na$_2$SO$_4$; (a5,b5) 702 mV, $dE = 9$, $T = 48$; (a6,b6) 895 mV, $dE = 8$, $T = 54$; (a7,b7) 1054 mV, $dE = 9$, $T = 23$; and (a8,b8) 1154 mV, $dE = 10$, $T = 21$; in solution D: 13.25 g/l NaCl and 3.89 g/l Na$_2$SO$_4$; (a9,c9) 183 mV, $dE = 10$, $T = 9$; (a10,b10) 212 mV, $dE = 10$, $T = 7$; (a11,b11) 420 mV, $dE = 10$, $T = 52$; and (a12,b12) 482 mV, $dE = 10$, $T = 29$; in solution G: 26.50 g/l NaCl and 1.75 g/l Na$_2$SO$_4$; (a13,b13) 194 mV, $dE = 10$, $T = 11$; (a14,b14) 328 mV, $dE = 10$, $T = 8$; (a15,b15) 396 mV, $dE = 10$, $T = 12$; (a16,b16) 554 mV, $dE = 10$, $T = 14$; and (a17,b17) 680 mV, $dE = 10$, $T = 88$; in solution M: 26.50 g/l NaCl and 0.64 g/l Na$_2$SO$_4$. 
A collection of electrochemical oscillating signals in different saline media at different potentials and their respective recurrence plots is shown in Fig. 8. Figs. 8(a1) and (a2) do show the current time series with their accompanying recurrence plots (Figs. 8(b1) and (b2)); in which it begins to be manifest that at values below $E_{qpo} = 622 \, \text{mV}$ (200 and 345 mV, respectively); i.e., during the formation of the passive layer, there is an
important degree of correlation in the corresponding electrochemical oscillating signal. So, in recurrence plots of Figs. 8(b1) and (b2) one can notice a fractal recognition pattern whose aspect exhibits self-organization in the form of quasi-parallel structures (not lines). In the set of current time series with their respective recurrence plots at concentrations of 26.5 g/l NaCl, 3.89 g/l Na₂SO₄ and pH 6.5 (solution F); where the $E_p$ and the $E_{qpo}$ do

Fig. 8 (continued)
coincide at a value of 622 mV (Figs. 8(a3) and (b3)), one clearly observes a pattern corresponding to a quasi-periodic process; which consists of a set of diagonal lines parallel to the bisector. Fig. 8(a4) shows a beat, which is typical of quasi-periodic behavior and whose recurrence plot consists also of a set of diagonal parallel lines.
The potential in this case is above $E_{\text{qpo}}$ and is equal to 690 mV. At this potential pitting corrosion is present. At potentials higher than $E_{\text{qpo}}$ persists in a very clear form a type of pattern characteristic of a quasi-periodic signal.

The opposite case to the previous one corresponds to a series of recurrence plots at a concentration of 26.5 g/l NaCl, 0.64 g/l Na$_2$SO$_4$ and pH 6.5 (solution M), where the apparent pitting potential $E_p$ is equal to 554 mV (Figs. 8(a16) and (b16)) and in which $E_{\text{qpo}}$ is not present. This means that there are simply not quasi-periodic oscillations at that potential. It is clearly appreciated that at potentials higher or lower than $E_p$, one never observed a recurrence pattern pertaining to a quasi-periodic signal (Figs. 8(a13), (b13); (a14), (b14) and (a17), (b17)). This means that the dynamics of formation of the passive layer generates an electrochemical oscillating signal which is totally uncorrelated.

The intermediate case corresponds to a concentration of 13.25 g/l NaCl, 3.89 g/l Na$_2$SO$_4$ and pH 6.5 (solution D), where $E_p$ has a value of 702 mV (Figs. 8(a5) and (b5)) and $E_{\text{qpo}}$ is equal to 1054 mV (Figs. 8(a7) and (b7)). Again, it is there appreciated that to lower potentials than $E_{\text{qpo}}$, the formation of a pattern pertaining to a quasi-periodic signal is initiated (Figs. 8(a5), (b5) and (a6), (b6)). This indicates, as was previously said, a signal with some degree of correlation. Let us note again the apparition of quasi-parallel structures. While to the potential $E_{\text{qpo}}$ and upper values (Figs. 8(a7), (b7) and (a8), (b8)) the signal is highly correlated; clearly manifesting, a pattern pertaining to a quasi-periodic signal. This has been already explained for Fig. 8(a7) in relation with its attractor shown in Fig. 7(b). Additionally, the current time series at 1154 mV shows the appearance of beats with different amplitudes (Fig. 8(a8)); which corresponds to time intervals of quasi-periodicity, manifesting important modifications, proper of the dynamics of the process at these conditions. Besides, the corresponding recurrence plot (Fig. 8(b8)) is very sensitive to small changes in the electrochemical oscillating signal.

Another intermediate case does correspond to current time series and recurrence plots at a concentration of 26.5 g/l NaCl, 1.75 g/l Na$_2$SO$_4$ and pH 6.4 (solution G). For potentials lower than the $E_p$ (Figs. 8(a9), (b9) and (a10), (b10)), both, the time series and recurrence plots do not present any kind of structure; what is indicative of stochastic behavior. When $E_p$ is equal to 420 mV (Figs. 8(a11) and (b11)) there is no a value for $E_{\text{qpo}}$, because we neither observed quasi-periodic oscillations nor pitting corrosion (see micrograph of Fig. 4(c)). However, at this condition of concentration, recurrence plot of Fig. 8(b11) shows a set of weakly consolidated quasi-parallel structures (still not parallel lines); which is indicative of some kind of periodicity, but in no case it attains a clear quasi-periodical state in the form of beats (Figs. 8(a11), (b11) and (a12), (b12)).

As we could appreciate above, the characteristic patterns of the saline concentrations in which the phenomenon of pitting corrosion is present, are manifest. The same occurs with the saline media in which the phenomenon of pitting corrosion is not present; what indicates that in this system one can characterize the dynamics by means of the analysis of recurrence plots. Up to this point the evaluation of the system has been merely qualitative. A recurrence quantitative analysis (RQA) can also be done; among the quantities that are usually calculated in a RQA we selected: %Det (which is the percentage of determinism) and the MaxLine; since we could appreciate that these were the most adequate and relevant parameters in the study of copper corrosion.

In Figs. 9 and 10 we have plots of %Det and MaxLine for the four concentrations above mentioned at different potentials. We can observe that for a concentration of 26.5 g/l NaCl, 3.89 g/l Na$_2$SO$_4$ and a pH 6.5 (solution F); which is the medium where the quasi-periodic oscillations in current are manifest; %Det do maintain upper levels at approximately 448 mV above $E_p$ (Fig. 9(a)); and for a value of 52 mV below $E_p = E_{\text{qpo}} = 622$ mV, we can see that %Det falls down to 86.61, attaining a relative minimum at 483 mV;
being \%Det = 60.30. For lower values of potential, i.e., in the range of 178–410 mV, we do observe (in the same figure) that \%Det raises its value to a \%Det of approximately 84% or 90% in the average. Within the range of 178–410 mV, we did not observe beats in the current time series; however, we saw the formation of parallel geometrical structures in the recurrence plots, as can be seen in Figs. 8(b1) and (b2). Fig. 10(a) shows MaxLine vs. potential corresponding to solution F, in which one can easily appreciate that MaxLine maintains, in the average, an almost constant value of approximately 3645; within a range of potential which is 273 mV above the \( E_p = E_{qpo} = 622 \) mV, and 444 mV below \( E_p \). Note that in the range of potentials between 622 and 895 mV we obtained values of \%Det which are approximately of the order of 3645 mV; being remarkable that from a value of 622 mV (which coincides with the apparent pitting potential) we generated part of a beat in the current time series with its corresponding recurrence plot showing the apparition of parallel lines (see Figs. 8(a3) and (b3)). Note that Fig. 8(a4) shows a beat at 690 mV whose corresponding parallel lines are shown in Fig. 8(b4). SEM micrograph corresponding to solution F is presented in Fig. 4(a) and shows pitting corrosion of copper. While in the case where the medium does correspond to 26.5 g/l NaCl, 0.64 g/l \( \mathrm{Na}_2\mathrm{SO}_4 \) and pH 6.5(solution M) which is the opposite case to the above one (solution M), both parameters fall down and take, in general, very low values of \%Det and Maxline, including zero values (Figs. 9(d) and 10(d)). Note that in solution M, \%Det raises its value precisely when \( E_p = 554 \) mV, then attains a relative minimum at value of potential equal to 680 mV, and raises

![Image](https://via.placeholder.com/150)

Fig. 9. Determinism versus applied potential at different media. (a) \% Determinism, measured in solution F: 26.50 g/l NaCl and 3.89 g/l \( \mathrm{Na}_2\mathrm{SO}_4 \); (b) \% determinism, measured in solution D: 13.25 g/l NaCl and 3.89 g/l \( \mathrm{Na}_2\mathrm{SO}_4 \); (c) \% determinism, in solution G: 26.50 g/l NaCl and 1.75 g/l \( \mathrm{Na}_2\mathrm{SO}_4 \); (d) \% determinism, in solution M: 26.50 g/l NaCl and 0.64 g/l \( \mathrm{Na}_2\mathrm{SO}_4 \).
its value again for a potential of 772 mV, falling down at a potential of 840 mV. This can be interpreted considering that between 614 and 772 mV; we were in a region of metastable dynamical determinism. For those points in Fig. 9(d) in which values of %Det = 0, we can assure that we had stochastic behavior, and of course, no pitting corrosion of copper. SEM micrograph corresponding to solution M (Fig. 4(d)) shows a surface which does not present pitting corrosion of copper. In Fig. 10(d), we found two regions in which Maxline was equal to zero, which means stochastic behavior; this coincides with the same regions of Fig. 9(d), in which we do observe %Det = 0. Let us notice the presence of a peak of Maxline = 1747 in Fig. 10(d) at a potential of 328 mV, and a peak in %Det = 10.99 at 257 mV, around which one can associate a region of non-stable dynamical behavior. A comparison of these results with Figs. 8(a13)-(a16) and Figs. 8(b13)-(b16) confirms that in the range of potentials where %Det is equal to zero or has very low values, the dynamical behavior of the system tends to be stochastic, which means that pitting corrosion of copper will not be present.

In the intermediate cases, the tendencies of both media lie between this two extremes. Let us now consider the saline medium at 13.25 g/l NaCl, 3.89 g/l Na₂SO₄ and pH 6.5 (Solution D and Figs. 9(b) and 10(b)), where $E_p = 702$ mV and $E_{qpo} = 1054$ mV. Let us notice that in the vicinity of $E_p$, where %Det = 89.92; for example, at a potential of 652 mV %Det falls down to a value of 61.46 and at a potential of 830 mV %Det has a value of 82.88; so that, in the neighborhood of $E_p$ there is an instability in the kind of dynamical behavior shown by copper in solution D. Actually, for copper in solution D, we observe a fluctuating behavior within the range of values comprising 75–652 mV where we can localize a minimum for %Det. If we consider, in this solution,
the value of $E_{qpo} = 1054$ mV, we note that apparently from this value on %Det begins to show a kind of metastable dynamical behavior which can be associated to the presence of beats. As can be seen in Fig. 8(a8), where we do appreciate a series of beats with different amplitudes and appearing at different periods of time, exhibiting intermittency. Fig. 8(b8) shows the recurrence plot corresponding to the current time series of Fig. 8(a8) at $E_{qpo} = 1154$ mV. Solution D also presents pitting corrosion. Fig. 10(b) shows a similar situation to that of Fig. 9(b), there one can observe a fluctuating interval of MaxLine values from a potential of 75 mV to a potential of 652 mV, reaching a plateau of dynamical instability at $E_p = 702$ mV and then reaching another plateau near the quasi-periodic potential at approximately 1054 mV. Let us note that the in the vicinity of the quasi-periodic pitting potential ($E_{qpo} = 1054$ mV, for solution D), Maxline values reach a constant value of 3911. Finally, the two parameters of the RQA calculated for solution G: 26.5 g/l NaCl, 1.75 g/l Na$_2$SO$_4$ pH 6.4 (see Figs. 9(c) and 10(c)); do indicate that this is a medium in which quasi-periodic oscillations and pitting corrosion of copper were absent. Fig. 9(c) shows a complex dynamical behavior in the range of potentials considered in this work (50–1264 mV), being $E_p = 420$ mV. In the neighborhood of the apparent pitting potential, Fig. 9(c); we found that low levels of the potential lead us to high values of %Det. For example, if the potential is equal to 420 mV, %Det = 65 and when the potential reaches a value of 482 mV, %Det = 20. There is a similar situation in Fig. 10c, in which one can appreciate that around the apparent pitting potential, Maxline is equal to zero; what can be interpreted as associated to stochastic dynamical behavior and also to the non presence of quasi-periodic oscillations and pitting corrosion of copper. On the other hand, Maxline rises to a value of approximately 1500 when the potential is equal to 636 mV. Maxline has a value of approximately 1100, when the potential is equal to 420 mV. Besides, one can observe a region of metastable dynamical behavior for potentials in the range of 309–386 mV. Another region of metastable dynamical behavior can be found in Fig. 10c, for values of potential in the range of 636–913 mV.

Hence, we clearly conclude that the dynamics of formation of the corrosion products do determine how possible is that the pitting corrosion be generated, at least in the case of copper. This opens a very interesting possibility in the study of pitting corrosion from a predictive standpoint for other metals; circumstance which is very
difficult to attain with the classical methods of evaluation of corrosion like, for instance, Fourier Spectra obtained from electrochemical oscillating time series, conventionally used as a tool in the study of pitting corrosion.

4. Conclusions

An important conclusion of this work is that the technique of reverse scanning voltammetry is not sufficient to determine if some metal (copper in this research) exposed to some corrosive medium (composed essentially from chlorides and sulphates) is susceptible to pitting corrosion; which is a form of localized corrosion. It was rather the electrochemical oscillating signal in current, which has shown the presence of pitting on the metallic surface of copper, through the presence of quasi-periodic oscillations in the form of beats, indicating additionally a phenomenon of synchronization among the generated pits. Visual Recurrence Analysis applied to the electrochemical oscillating signal in current was able to characterize the electrochemical dynamics on the metallic surface showing clearly the dynamics of the formation of the passive layer, as well as the presence of pitting corrosion of copper.

From the recurrence quantitative analysis (RQA) shown in Figs. 9(a) and 10(a) one can observe an almost constant value of %Det of approximately 90%; this corresponds physically to pitting corrosion and the behavior of this dynamical system as we pointed out above is quasi-periodic. On the other hand, Figs. 9(d) and 10(d) do correspond to a system where pitting corrosion is absent, there %Det is almost 0 for some ranges of potential; this also corresponds to stochastic behavior, so we can infer from the results discussed above, that a necessary condition for pitting corrosion to appear is quasi-periodic behavior in the form of beats or a low level of chaotic behavior and in consequence a high and almost constant level of %Det. In other words, at lower levels of chaos we do observe a higher intensity of pitting. Additionally, high values of MaxLine presented in Fig. 10(a) do confirm a low level of chaoticity, for MaxLine is the inversely proportional of the maximum Lyapunov exponent. As we have shown, recurrence plots are an excellent tool in

![Fig. 10 (continued)](image-url)
the analysis of electrochemical oscillating signals, opening the possibility of predicting the presence of pitting. Finally, the presence of diagonal parallel lines in the recurrence plot generated from electrochemical oscillating signals in current is directly associated to quasi-periodic behavior and therefore to the diagnosis of pitting corrosion of copper.

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