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In situ Corrosion Study of Copper and Copper-Alloys Exposed to Natural Seawater of the Veracruz Port (Gulf of Mexico)

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In this study, the effect of seasonal variability on the marine environment in the corrosion of Cu and Cu-Alloys was analyzed in situ with respect to exposure time. The possible changes in the mechanism of degradation, considering the physicochemical parameters of seawater were studied. An electrochemical study was carried out with three metallic materials industrially used (copper, bronze and brass) for 10 months of continuous exposure in seawater surrounding the San Juan de Ulua Fortress in Veracruz port, Mexico. Electrochemical impedance spectroscopy (EIS) was the electrochemical technique used. Additionally, a characterization of the metal surface with scanning electron microscopy (SEM) and X-ray diffraction (XRD) was carried out. All materials showed good corrosion resistances; however, copper showed higher resistance which took their best values in the last months of exposure presenting a layer of products of Cu_2O. Additionally, some silicates and sulfates were detected. Pitting and localized corrosion type was observed.

Keywords: Seasonal variability, copper, copper alloys, corrosion, EIS, seawater.

1. INTRODUCTION

Corrosion of metallic materials exposed to seawater is of great interest in the scientific community because of the amount of metallic structures that are submerged in this water body. The naval and petrochemical industry are affected by sea water corrosion in their structures used, such as platforms, ships, storage tanks, pipelines, water injection systems, distribution systems and chemical processes in general. The sea water can be affected by the climatic change through the alteration of some aspects such as: changes in precipitation patterns, corrosivity of coastal regions, and increased stresses on marine systems, that can alter the corrosive behaviour of the environment and increase the risk of corrosion failures. [1]

The main chemical components of seawater around the world are consistent. However, sea water is still a complex chemical system affected by several factors. Besides this, it should be noted that sea water has undergone changes in its characteristics, for example sea level and temperature increase and changes in physicochemical parameters (pH, salinity, dissolved oxygen, conductivity, etc.) due to the weather changes [2]. The sea water due to its content of chlorides and various salts, corrode the majority of metals, and this is reflected in the damage to the structures before mentioned. Another problem in this phenomenon called biofouling, which are microorganisms that are able to adhere to the metal surface, causing problems in the cathodic protection systems and variations in the electrochemical behavior [2,3].

Researches about marine corrosion [4] suggest to find different materials for this environment and reduce direct and indirect costs caused mainly by corrosion. Some of the materials used in the submerged marine environment due to their resistance to corrosion, good resistance to biofouling as well as other characteristics is copper and its alloys. The corrosion resistance of these metallic materials has been attributed to the formation of a protective corrosion products film of cuprous oxide (Cu_2O) on surface of the metal [5]. Various studies have been conducted in seawater substitutes and salt solutions at 3.5%, but a few in situ analyses.

Localized corrosion is an important corrosion attacks that Cu and its alloys can suffer in different environments, especially in those containing chloride ions [6]. Some corrosion products films (mainly passivated films) are susceptible to the localized breaking causing the increment of the metal corrosion rate [7,8]. It is important to point out that the marine environment besides that, it has high chloride concentration, it has phytoplankton and zooplankton where, they can sediment on metals surface forming a not uniform film (biofilm) and causing differential aeration cells that it induces to the localized corrosion form.

The study of metallic corrosion “in situ” (field measurements) is very important [4], but it presents a big and complex problem because at “in situ” studies include many parameters that in the laboratory is difficult (sometimes impossible) to simulate and control, such as the exact oxygen and salts concentrations, temperature and pH variations. Although, with some limitations in the corrosion studies, the electrochemical techniques provide the necessary parameters to predict the useful life of the metals and alloys immersed in a corrosive medium like natural seawater with tests of short time [9]. Some of these electrochemical techniques are linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS). Therefore, it is very important to generate research on corrosion behavior of metallic materials commonly used in metal structures of our country, monitoring the variation of the physicochemical parameters, and trying to find a correlation between these variables as investigations carried out by Jeffrey and Melchers [10], Palraj et al. [11] and Joseph et al. [12], at “in situ” conditions.

In this work, seasonal variability and its direct effect on the marine environment as corrosive environment on copper, bronze and brass for 10 months of continuous exposure in seawater was carried out. Degradation of metallic materials “in situ” with respect to exposure time also was analyzed. Electrochemical impedance spectroscopy (EIS) was the electrochemical technique used in the corrosion study.

2. EXPERIMENTAL

2.1 Electrodes

Three working electrodes were machined from commercial copper, brass and bronze. These were embedded in resin to isolate environment and leaving free one metal face for the exposure. Prior to exposure electrodes in seawater, each working electrode was polished up to 600 grit SiC paper, cleaned and degreased with acetone. The electrodes were immersed for 10 months in natural seawater of San Juan de Ulua Fortress in Veracruz port, Mexico. The total exposure area was 2.8 cm^2.

2.2. Physicochemical parameters of seawater

During the 10 months of metallic samples exposure, selected physicochemical parameters were measured. These parameters are pH, temperature, salinity, conductivity, solids and dissolved oxygen. A Multiparameter Hach HQ40d was used.

2.3. Electrochemical techniques

The evaluation was performed with electrochemical impedance spectroscopy (EIS) technique, with frequency since 10000 to 0.1 Hz and an amplitude of 10 mV with 10 points per decade. A typical three-electrode arrangement was used, where samples of Cu, brass and bronze were used as working electrodes (WE), electrode of Ag/seawater as reference electrode (RE) and a sintered graphite bar as auxiliary electrode (AE). A field potentiostat (ACM Field Machine) was used to get the electrochemical parameters.

2.4. Surface analysis

Specimens were prepared for analysis of each studied metal (copper, brass and bronze) after have been immersed for 10 months in seawater. Samples at different time of exposure were selected: 1, 12, 28 and 44 weeks. After these times, the samples were removed from the seawater and immediately the metallic surface was analyzed using a stereoscopic microscope and following the ASTM G1 standard [13]. Additionally, the surface of each metallic specimen after 10 months exposure was analyzed with SEM and XRD.

3. RESULTS AND DISCUSSION

3.1. Electrodes.

Figure 1 shows an image of the three working electrodes (copper, bronze, brass) before exposure to seawater. These electrodes were embedded into resin to isolate environment and leaving only free one metal face for the exposure. Prior to exposure electrodes in seawater, each working electrode was polished up to 600 grit SiC paper.

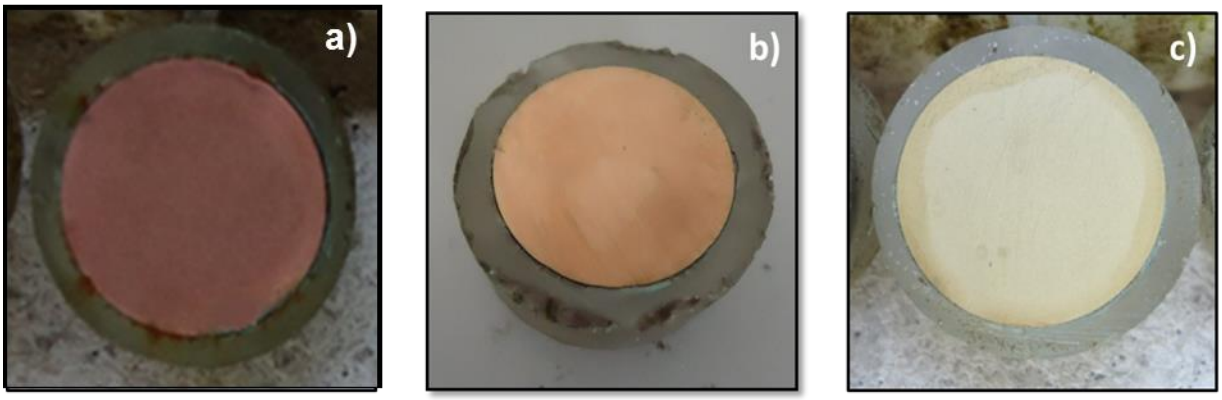

Figure 1. Images of the three electrodes before to be exposed into the seawater, a) copper, b) bronze, c) brass.

3.2. Monitoring of the physicochemical parameters of seawater

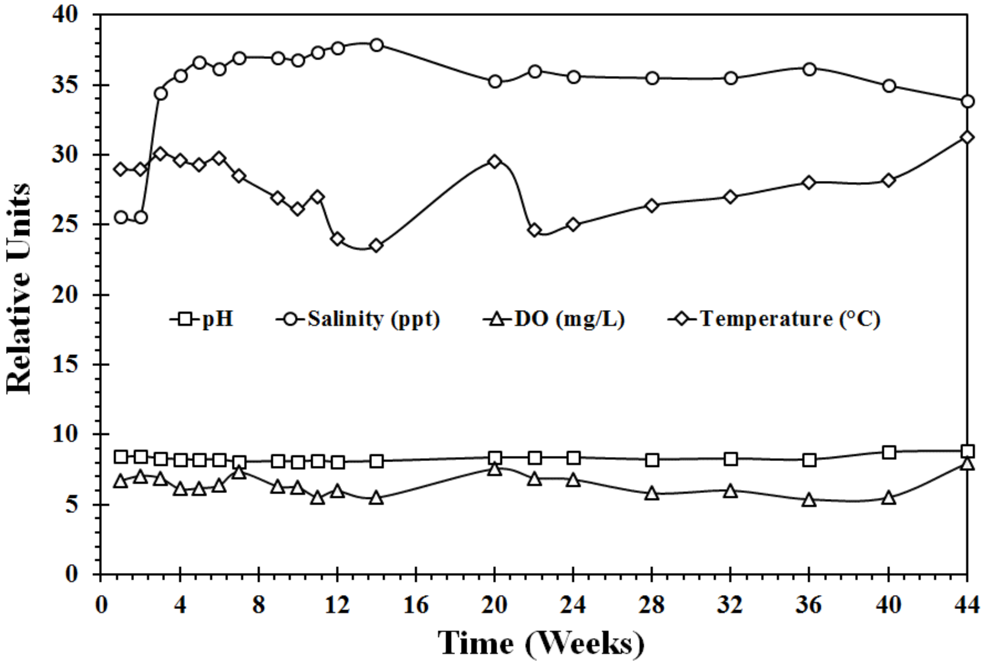

Figure 2. Variation of physicochemical parameters in 10 months of immersion.

Figure 2 shows the physicochemical parameters measured in seawater during exposure time (10 months). The parameters shown in figure 1 are within range reported in the literature [14,15], there was no unusual values that may modify the analysis of the seawater chemical composition, and the action of this electrolyte on the metallic corrosion. pH values between 7.8 and 8.3 were obtained. According to this pH is possible to point out that the pH trend to be an alkaline solution. This behavior is agreed with the reported literature for tropical waters [16]. This is mainly due to the presence of Na^+, K^+, Ca^{2+}, Mg^{2+}, the reactions resulting from the exchange of carbon dioxide present in the air and dissolved in the seawater, and the process of photosynthesis by marine plants. The carbonates and boric acid act as a buffer.

Parameters as salinity, conductivity and total dissolved solids (TDS) have variations. The salinity values are in a range between 34.43 and 37.87 parts per thousand (ppt). Furthermore, the conductivity showed a minimum and maximum at 52.20 and 56.87 mS/cm, respectively, and finally, total dissolved solids have variations from 33 to 36.23 g/L.

Another really important factor is the concentration of dissolved oxygen (DO), which has a huge influence on the corrosivity, this factor is influenced by the temperature and salinity gradient. These values may increase substantially, by factors as the photosynthesis of marine plants and the action of sea waves in splash area and, produced by decomposition of organic matter [16]. The values shown in this study indicate that the oxygen content is very intermittent, tides and surface currents promote mixing of ocean waters, which has effects on the oxygen concentration in the seawater and it generates continuous oxygen gradients, which it is reflected in the ranging values from 5.53 to 7.32 mg/L.

Finally, the temperature is the parameter that it has the most significant changes from 23.5º to 30ºC, as expected since the changes in the seasons of fall to winter or from winter to summer are quite marked. Figure 1 shows how the temperature plays an important role in other parameters, for example, as temperature increases the salinity also increases. On the other hand, increase in temperature produces an increase in the dissolved oxygen. The pH did not show significant variations with the time and temperature; and it did not generate any correlation with the other seawater physicochemical parameters in this study.

The most important changes in the physicochemical parameters are influenced by the temperature; and temperature changes are abrupt with the seasons of the year (for example in summer temperatures are between 28-30°C and temperature in winter is around 24-26°C).

3.3. Copper

3.3.1. Electrochemical analysis

Figure 3 shows the “in situ” measurements of the electrochemical impedance spectroscopy (EIS) for copper sample immersed in natural seawater during 44 weeks. It can be observed that in the first week a charge transfer process (R_{ct}) has the control of the corrosion phenomenon, this due to the continuous movement of seawater in the ocean, where this movement did not allow the stabilization of the corrosion product film on metallic surface, leaving some active areas for interaction with the environment, for that reason the R_{ct} obtained was the lowest (437.9 $\Omega.cm^2$). Figure 3a and 3b permit to corroborate this fact. The increment of R_{ct} indicates that as the exposure time increased, a corrosion product films mixed with organic material (phytoplankton and zooplankton) covered the surface of the Cu sample. It is important to point out that a single time constant was observed in the Bode plot (phase angle vs frequency; see Figure 3c). As the exposure time increased from 5 to 44 weeks, a second time constant is observed at high frequency which it is attributed to a complex layer, that is a mixture of the phytoplankton, zooplankton (biofilms) and corrosion products, adsorbed on surface of the Cu sample. It is important to point out that the R_{ct} increased from 4821 to 106580 $\Omega.cm^2$ indicating with this behavior that the metallic degradation trend to decrease with time.

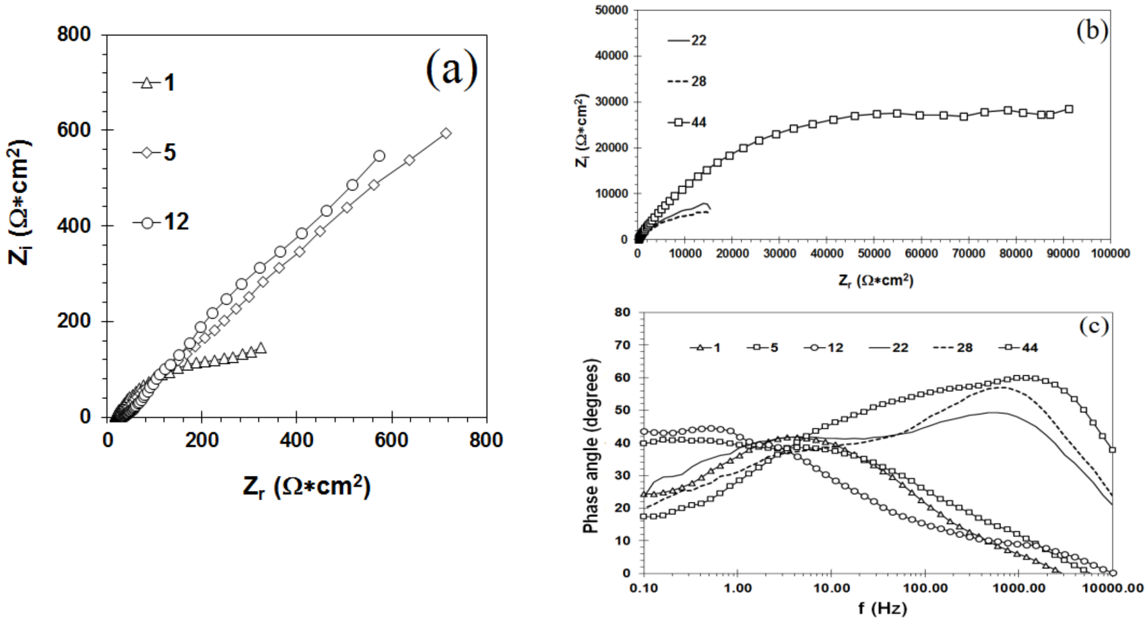

Figure 3. EIS spectra measured as a function of time for copper exposed to natural seawater during 44 weeks.

In the last time period, the majority of the superficial exposed area was covered by biofilms as can be observed in the images showed in figure 4. For that reason, the oxygen reduction was limited causing a diffusion process of the oxygen throughout the complex layer. This fact had influence in the total corrosion process causing the reduction of the CR.

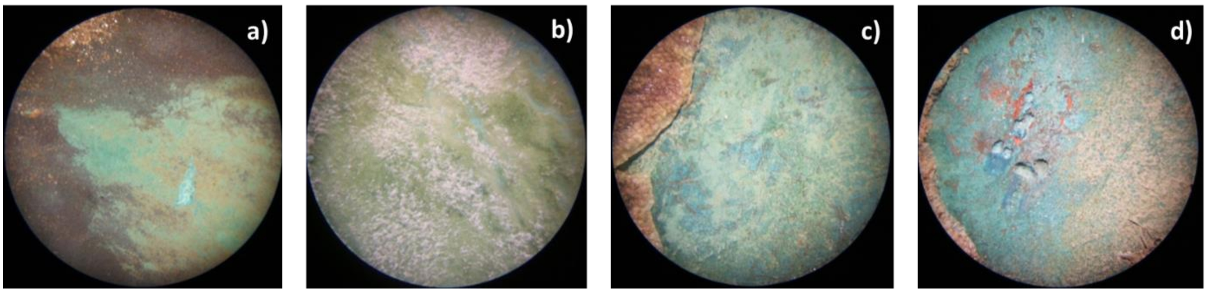

Figure 4. Optical micrographs showing the evolution of superficial topography of copper samples immersed in natural seawater during: a) 1, b) 12, c) 28 and d) 44 weeks.

3.3.2. Equivalent electric circuit (EEC) for EIS spectra of copper

Figure 5 shows the equivalent electric circuit used for the data analysis of the measured Cu impedance spectra obtained "in situ" conditions showed in figure 3. In this figure R_s is the solution resistance, R_{film} is the resistance of the complex layer of the corrosion products film formed on the surface of the metallic sample, R_{ct} is charge transfer resistance and CPE is the constant phase element.

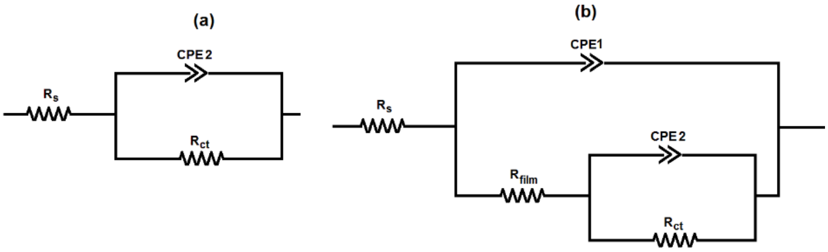

Figure 5. Equivalent electric circuit used for EIS data analysis of copper.

Table 1 shows the results obtained in the numerical simulation of the process, using the equivalent circuit shown in figure 5.

The current density (I_{corr}) was calculated applying the Stern-Geary relationship, where the values of R_p ($R_{ct,}$ in EIS results) were taken from the difference between the high frequency and low frequency intercepts with the real axis in EIS results. (Stern and Geary,

$$i_{corr} = \frac{\beta}{Rp}$$

The corrosion current in A/m2 can be used to determine the amount of corroded material as a result of the corrosion process. Current can be directly converted into mass using Faraday´s law. [26]

Table 1. Electric parameters obtained from EIS spectra for copper using the EEC.

Time (week)	**R_s ($\Omega.cm^2$)**	**R_{ct} ($\Omega.cm^2$)**	**R_{film} ($\Omega.cm^2$)**	**I_{corr} (A/cm^2)**	**CR (mm/year)**
1	12.92	437.9	---	5.94E-05	0.6926
5	24.54	4821	914.09	5.39E-06	0.0629
12	39.57	5118	723.06	5.08E-06	0.0593
22	41.1	34194	3696	7.60E-07	0.0089
28	58.96	30661	2908	8.50E-07	0.0099
44	77.51	106580	24940	2.40E-07	0.0028

In this table is possible to see that as the time increased, the corrosion rate (CR) decreased. This behavior is attributed mainly to the complex layer (biofilm plus corrosion products) adsorbed on surface of the copper sample exposed to seawater. In addition, R_{film} has a trend to increase as the exposure time also increase, this fact is attributed to the thickness complex layer that increased with time. The presence of copper oxide into the complex layer can provoke a diffusion process, but in this work, the investigation was performed with the minimum frequency of 0.1 Hz, and for that reason it is possible that this process did not appear in the EIS spectra.

Figure 6 shows the capacitance of the corrosion products (C_{film}) and the CR as a function of the time. Both C_{film} and CR were obtained by the corrosion process of the Cu immersed in natural seawater at “in situ” conditions. According to previous studies and Scully results [17,18], is possible to point out that as the capacitance of complex layer decreases, the thickness of the complex layer increases (biofilm plus corrosion products), provoking that the R_{film} increased and consequently the CR decreased.

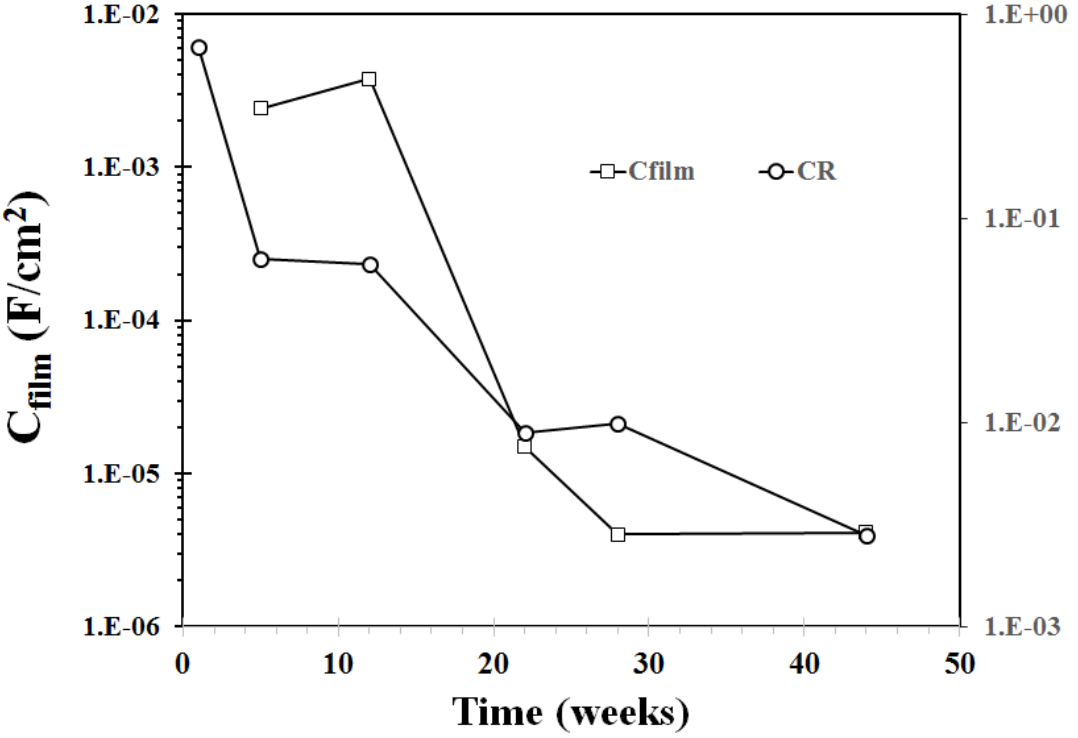

Figure 6. Capacitance of the complex layer and CR as a function of the time for copper.

Palraj et al., [11] worked with Cu samples immersed in natural seawater during one year. In this study, he applied the electrochemical impedance technique and the impedance spectra measured has the same behavior as the present work. That is to say, the CR decreases with the time; at the beginning of the test the CR value was 0.15 mm/year, and as the immersing time passed the resistance of the film increased and consequently the corrosion rate decreased to 0.04 mm/year. The increment of resistance of the film is attributed to the synthesis of the Cu_2O films. Nagiub [3] carried out some experiments where he showed that the movement can influence in the stability time of the corrosion products film on surface of the metallic samples.

3.3.3. X-ray diffraction analysis

After 44 weeks of the immersion in seawater, a topography analysis of the copper surface was carried out. Additionally, the different phases formed on the corrosion product film were analyzed. Figure 7 show the X-Ray diffraction spectrum of the corrosion products film formed on copper sample. The X-Ray spectra show that the corrosion product with major concentration is the copper oxide (Cu_2O), but another corrosion products were found, such as copper (Cu) and copper-sodium silicate [$Cu_3Na_2(Si_4O_{12})$].

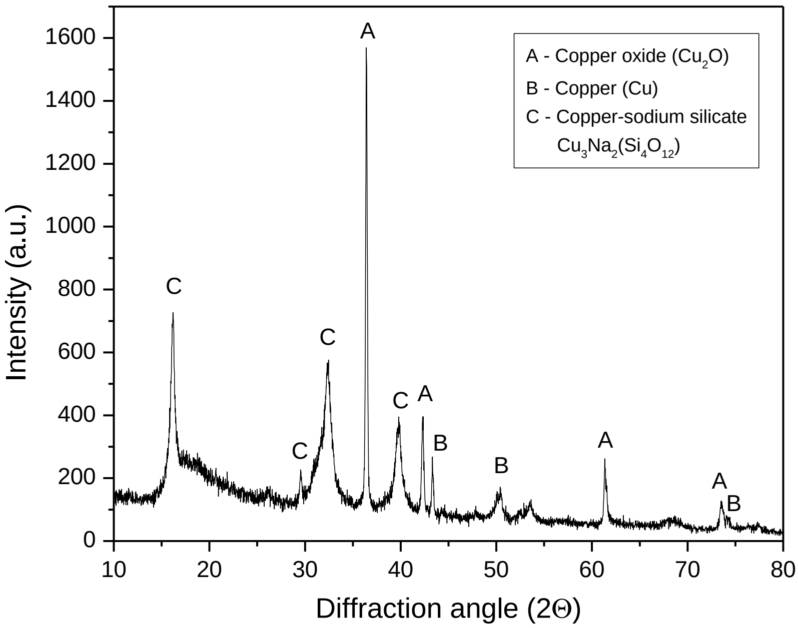

Figure 7. X-Ray diffraction spectrum of the corrosion products film formed on surface of the Cu sample after 44 weeks of exposure.

3.3.4. SEM analysis

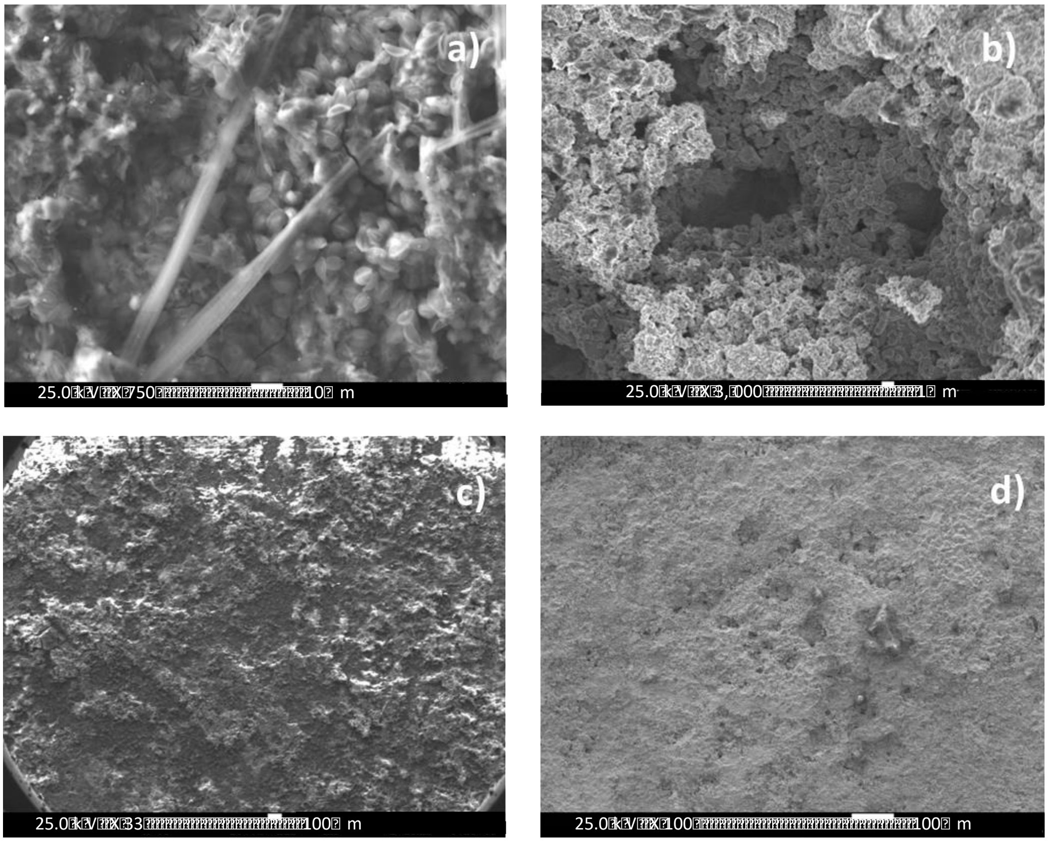

Figure 8. SEM image for copper sample after 44 weeks of exposure in natural seawater showing pitting and localized corrosion type.

Figure 8a-b shows SEM micrographs of the complex layer formed on surface of the Cu sample after 44 weeks of exposure in natural seawater. Figure 8a shows that on surface of the complex layer, only phyto and zooplankton were observed, mainly shell and some aquatic plants. At higher magnification some type of seaweed was observed, such as diatoms (figure 8b).

Figure 8c-d shows SEM micrographs of the coper surface without complex layer after 44 weeks of exposure in natural seawater. Figure 8c shows a localized corrosion which could be attributed to crevice and pitting corrosion mainly as is shown in figure 8d.

3.4. Bronze

3.4.1. Electrochemical analysis

Figure 9 shows the "in situ" measurements of the electrochemical impedance spectroscopy (EIS) technique for bronze sample immersed in natural seawater during 44 weeks. In the firsts weeks (from 1 to 5), a charge transfer process (R_{ct}) has the control of the corrosion phenomenon, this behavior, in same way that copper, is attributed to the continuous movement of seawater in the ocean, where this movement did not allow the stabilization of the corrosion product film on metallic surface.

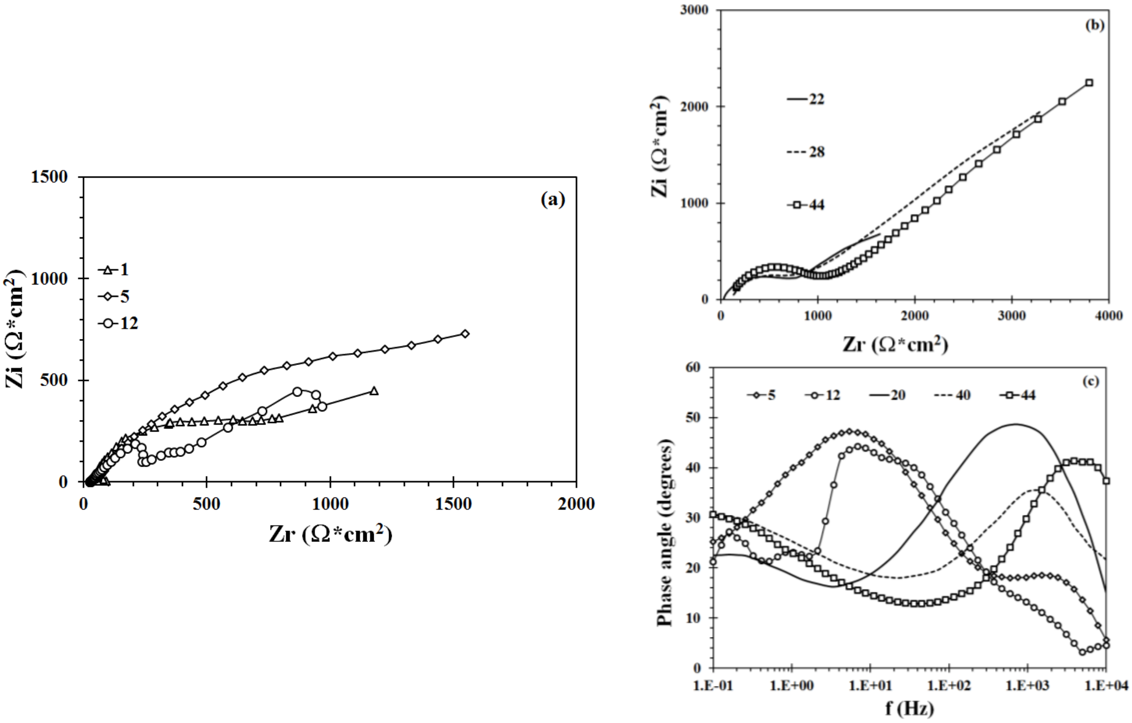

Figure 9. EIS spectra measured as a function of time for bronze exposed to natural seawater during 44 weeks.

It is important to point out that the time constant obtained at high frequencies is attributed to the complex layer and the time constant obtained at low frequencies is attributed to the corrosion process. In this period of time, the R_{film} increased from 605.9 to 1187 $\Omega.cm^2$; this behavior indicates that the complex layer could have covered the total surface of the bronze sample, as is shown in figure 10.

Table 2. Electric parameters obtained from EIS spectra for bronze using the EEC.

Time (week)	R_s ($\Omega.cm^2$)	R_{ct} ($\Omega.cm^2$)	R_{film} ($\Omega.cm^2$)	I_{corr} (A/cm^2)	CR (mm/year)
1	48.53	798.4	---	3.26E-05	0.3799
5	44.46	2383	---	1.09E-05	0.1273
12	28.47	1325	605.9	1.96E-05	0.2289
22	22.00	2830	886.4	9.19E-06	0.1072
28	25.08	6236	457.7	4.17E-06	0.0486
44	130.72	9360	1187	3.80E-07	0.0045

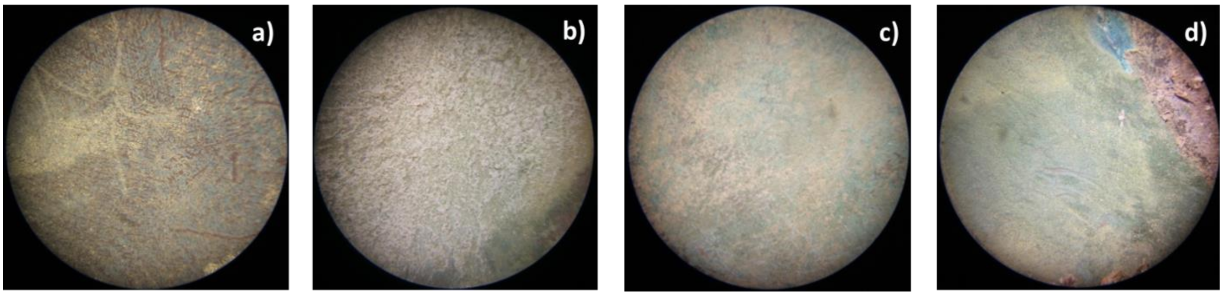

Figure 10. Optical micrographs showing the evolution of superficial topography of bronze samples immersed in natural seawater during: a) 1, b) 12, c) 28 and d) 44 weeks.

3.4.2. Equivalent electric circuit (EEC) for EIS spectra of bronze

The equivalent electrical circuit proposed for this system is the same that was proposed for the system copper-seawater. Table 2 shows the results obtained in the numerical simulation of the process, using the equivalent circuit shown in figure 5a for EIS analysis from 1 to 5 weeks; and using the circuit showed in figure 5b for 12 to 44 weeks.

The behavior of CR values of bronze is similar to behavior of CR values of the copper. That is to say, the CR decreases as the immersion time increases. The R_{film} has a trend to increase as the exposure time also increase; this fact is attributed to the thickness complex layer that increase as the time evolved. In addition, the low frequency was not enough to observe the diffusion process.

Similar studies by Xiao-Ning [19] shown results about the corrosion of bronze samples immersed in 3.5 % NaCl. This researcher concluded that in the first 36 hours, a charge transfer process limited the corrosion, but after this time, a corrosion products film had influence in the process, provoking that the CR decreases.

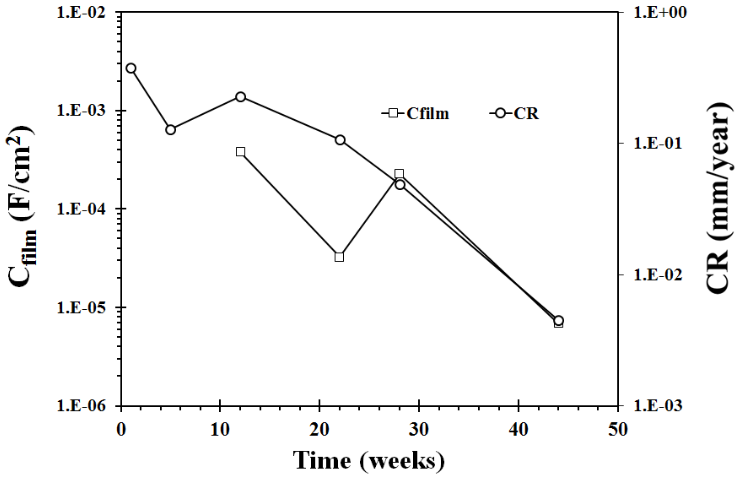

Figure 11. Capacitance of the complex layer and CR as a function of the time for bronze.

Figure 11 shows the capacitance of the corrosion products (C_{film}) and CR as a function of the time. Both C_{film} and CR, were obtained by the corrosion process of the bronze immersed in natural seawater at “in situ” conditions. In this figure is possible to observe that in general, as the capacitance decreases, the thickness of the complex layer increases (biofilm plus corrosion products film), indicating that the R_{film} increased and consequently the CR decreased [17,18].

3.4.3. X-ray diffraction analysis

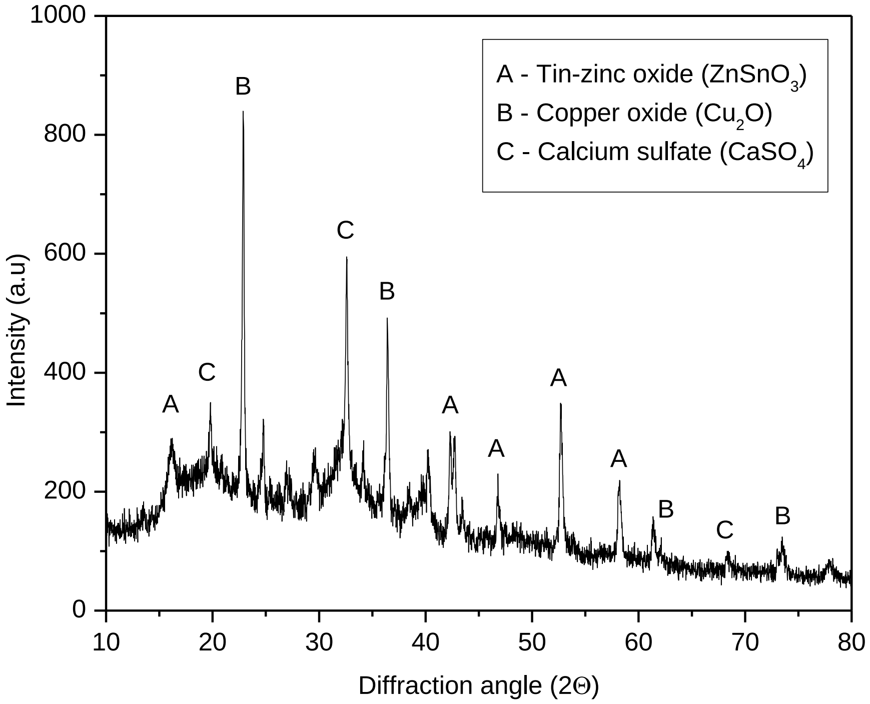

Figure 12. X-Ray diffraction spectrum of the corrosion products film formed on surface of the bronze sample after 44 weeks of exposure.

Figure 12 shows the X-Ray diffraction spectrum of the corrosion products film formed on bronze sample after 44 weeks of the immersion in seawater. Copper oxide (Cu_2O) is the main phase detected; but other corrosion products were found, such as copper-tin oxide ($ZnSnO_3$) and calcium sulfate ($CaSO_4$). It is important to point out that the bronze is a copper alloy, for that reason the tin and copper were found in the corrosion products.

3.4.4. SEM analysis

Figure 13a shows SEM micrographs of the complex layer formed on surface of the bronze sample after 44 weeks of exposure in natural seawater. This figure shows that on surface of the complex layer, only phyto and zooplankton were observed.

Figure 13b shows SEM micrographs of the bronze surface after removing the complex layer. This figure shows that a localized corrosion type was found in the bronze sample. They can be to crevice and pitting corrosion mainly.

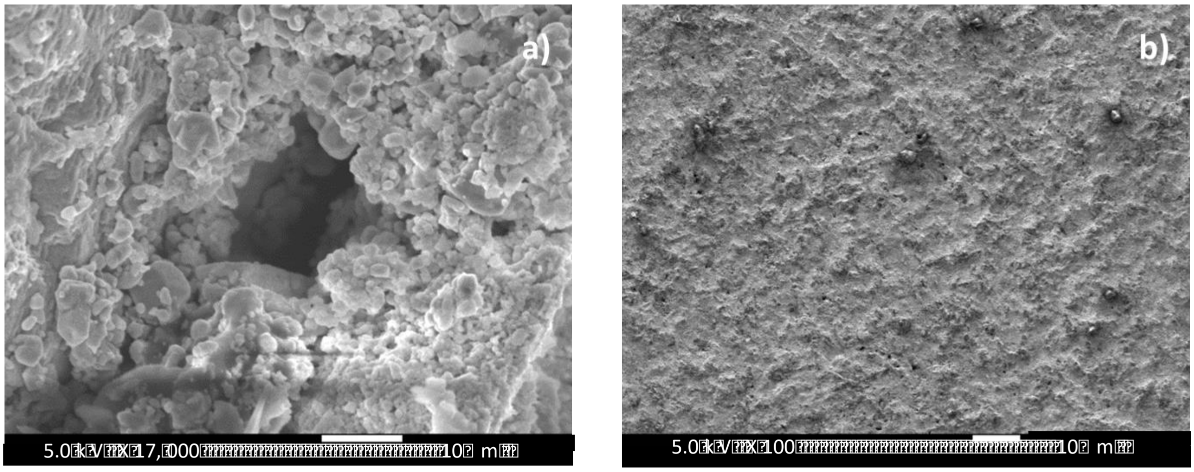

Figure 13. SEM images for bronze sample after 44 weeks of exposure in natural seawater showing pitting and localized corrosion type, a) before and b) after remove the film.

3.5. Brass

3.5.1. Electrochemical analysis

Figure 14 shows the "in situ" measurements of the electrochemical impedance spectroscopy (EIS) technique for brass sample immersed in natural seawater during 44 weeks. In the first week, a charge transfer process (R_{ct}) has the control of the corrosion phenomenon, this behavior in the same way as copper and bronze, is attributed to the continuous movement of seawater in the ocean, where this movement did not allow the stabilization of the corrosion product film on metallic surface.

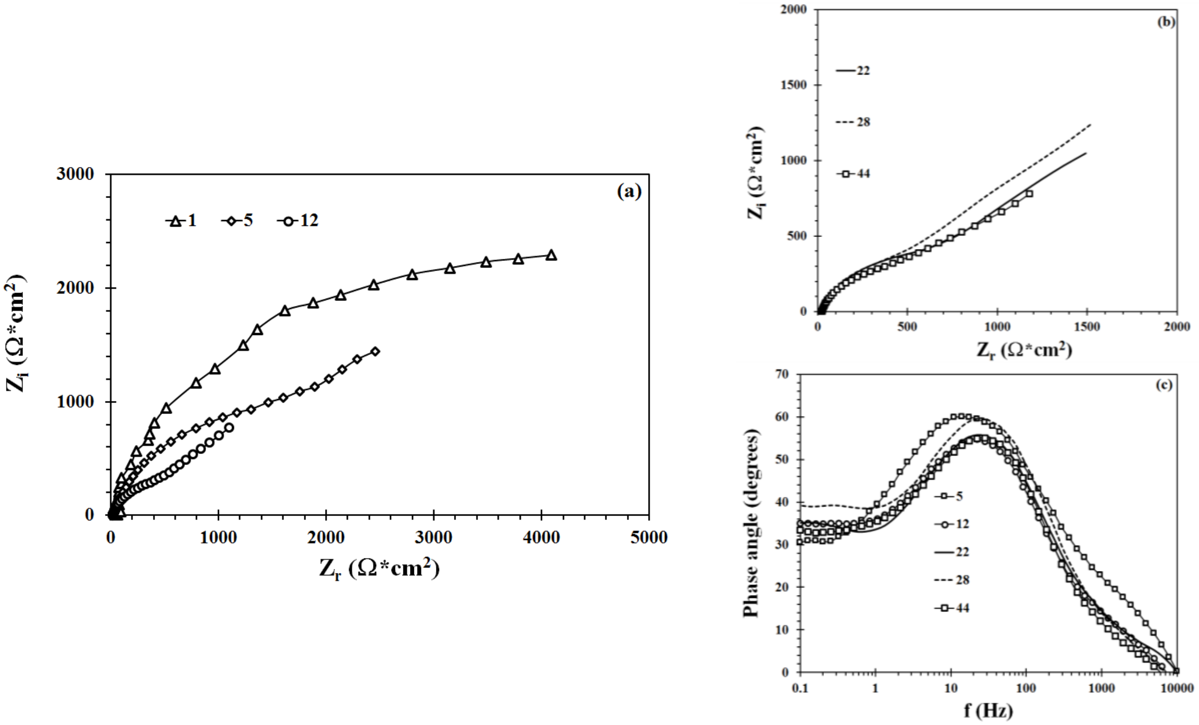

Figure 14. EIS spectra measured as a function of time for brass exposed to natural seawater during 44 weeks.

Since 5 to 44 weeks, a second time constant is observed in the Nyquist and Bode plots (phase angle vs frequency). This behavior indicates that a complex layer (phytoplankton plus zooplankton and corrosion products film) was adsorbed on surface of the brass. According to Table 3, the R_{film} decreases as the immersion time increases, this behavior is attributed to the rupture of the complex layer, which it is provoked by the splash and the continuous movement of seawater in the ocean. It is important to point out that in addition to the complex layer resistance, a diffusion process could have influenced in the corrosion process. In figure 15 is possible to observe that on surface of the brass sample, in same way that Cu and bronze, from the weeks 28 to 44, a typical green color of the patina is observed (formed by copper oxide mainly).

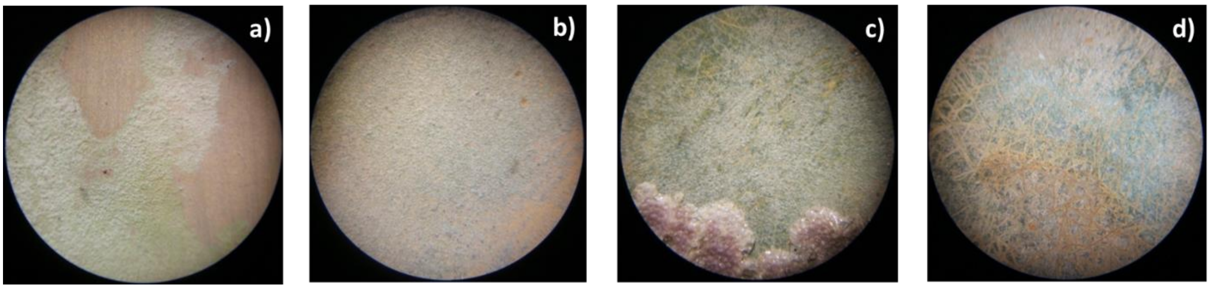

Figure 15. Optical micrographs showing the evolution of superficial topography of brass samples immersed in natural seawater during: a) 1, b) 12, c) 28 and d) 44 weeks.

Studies carried out by Sherif [20] about brass samples immersed in 3.5% NaCl solution show that in the first hour of the immersing time, the corrosion process was dominated by charge transfer.

Meanwhile Mansfeld [21] shows that the corrosion of the brass in synthetic saline solution is dominated by a charge transfer process, only in the first day. The results obtained in this investigation showed that the activation process remains up to the first week. The difference between research from Mansfeld-Sherif and this work is attributed mainly to the movement of the seawater and the complex layer (biofilms plus corrosion products film), that they can be obtained only under "in situ" conditions.

3.5.2. Equivalent electric circuit (EEC) for EIS spectra of brass

The equivalent electrical circuit proposed for this system is the same that was proposed for the system copper-seawater. Table 3 shows the results obtained in the numerical simulation of the process, using the equivalent circuit shown in figure 5a for EIS analysis from 1week; and using the circuit showed in figure 5b for 5 to 44 weeks.

Table 3. Electric parameters obtained from EIS spectra for brass using the EEC.

Time (week)	R_s (Ω.cm^2)	R_{ct} (Ω.cm^2)	R_{film} (Ω.cm^2)	I_{corr} (A/cm^2)	CR (mm/year)
1	27.13	5595	---	4.64E-06	0.0555
5	25.04	4046	2627	6.40E-06	0.0767
12	20.34	1488	744.6	1.75E-05	0.2085
22	26.06	2167	1171	1.20E-05	0.1432
28	19.21	2115	1002	1.23E-05	0.1467
44	23.03	1223	726.1	2.12E-05	0.2537

In general, the R_{film} has a trend to decrease as the immersion time increases indicating that the thickness of the corrosion products film decreased. This fact is attributed to the shear stress provoked by the splash and continuous movements of the seawater against surface of the brass sample [22,25]. On the other hand, the CR values of the brass has an opposite behavior to the CR values of copper and bronze; the corrosion rate increased as the immersion time also increased. The CR behavior is attributed to the high porosity of the corrosion products film (zinc oxide) localized into the complex layer, and mainly to the dezincification process that the brass suffers in seawater [23,25].

Figure 16 shows the capacitance of corrosion products (C_{film}) and CR as a function of the time. In this figure is possible to observe that the capacitance increased in the first 12 weeks, but after 13 weeks, the C_{film} decreased until it had an almost stable value. According to this behavior, is possible to point out that the thickness of the corrosion products film decreases up to a stable value [17,18]. The thinning and dezincification process provoke higher values of corrosion rate as the time evolved.

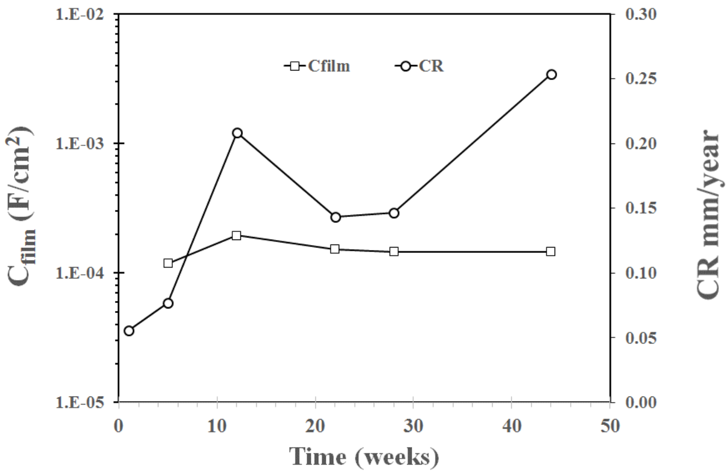

Figure 16. Capacitance of the complex layer and CR as a function of the time for brass.

3.5.3. X-ray diffraction analysis

Figure 17 shows the X-Ray diffraction spectrum of the corrosion products film formed on brass sample after 44 weeks of the immersion in seawater. Zinc oxide (ZnO) and copper oxide (Cu_2O) are the main phase detected; but other corrosion products were found, such as copper-tin oxide ($ZnSnO_3$). It is important to point out that the brass is a Cu-Zn alloy, for that reason the zinc was found in the corrosion products.

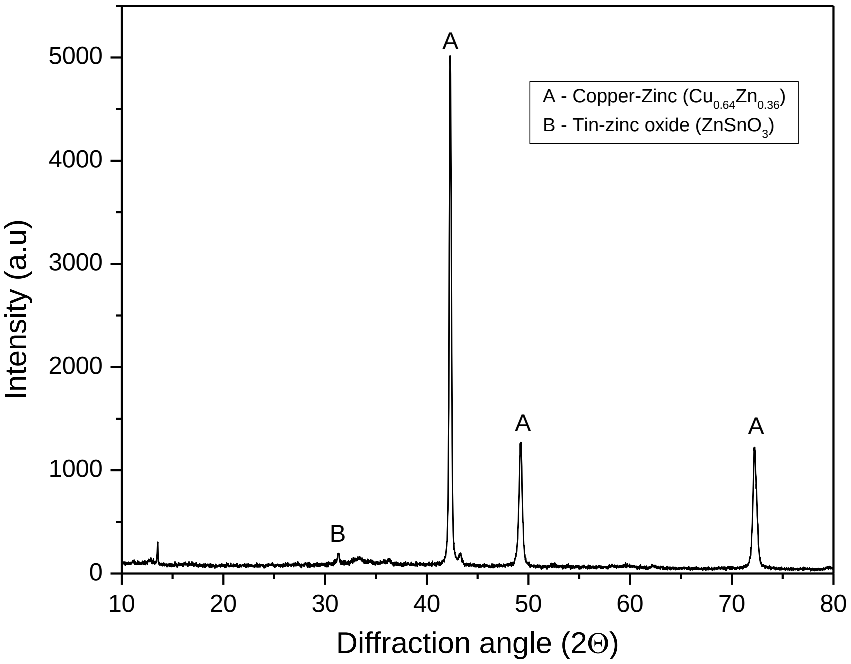

Figure 17. X-Ray diffraction spectrum of the corrosion products film formed on surface of the brass sample after 44 weeks of exposure.

Research performed by Saricimen [24] about the brass exposed to seawater has shown that corrosion products were found as oxides and chlorides of Cu and Zn, according to this fact and to the composition of the brass, the results shown in this work agree with Saricimen results.

3.5.4. SEM analysis

Figure 18a shows SEM micrographs of the complex layer formed on surface of the brass sample after 44 weeks of exposure in natural seawater. This figure shows biofilms (phyto and zooplankton) formed on surface of the complex layer.

Figure 18b shows SEM micrographs of the bronze surface after removing the complex layer. This figure shows that a localized corrosion type was found in the brass sample. They can be to crevice and pitting corrosion due to dezincification mainly.

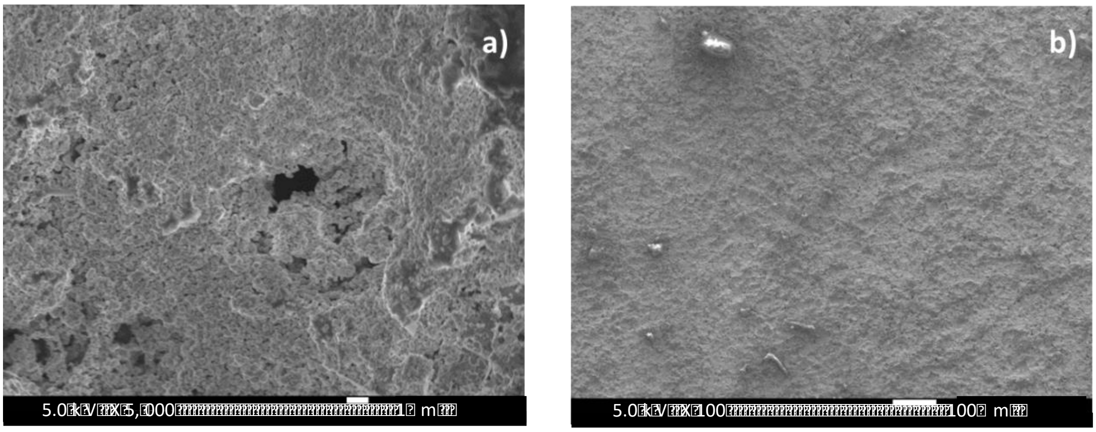

Figure 18. SEM images for bronze sample after 44 weeks of exposure in natural seawater showing pitting and localized corrosion type, a) before and b) after remove the film.

3.6. Influence of the pH, dissolved oxygen and temperature in the CR

Figure 19 shows the behavior of CR for the three alloys in function of the time, and its relationship with the physicochemical parameter measured in seawater. Figure 19a shows the behavior of CR for the three alloys in function of the time. In this figure is possible to observe that Cu and bronze at the beginning have the highest values, but as the immersion time pass, the CR trend to decrease. This behavior is attributed to the complex layer (biofilm plus phyto and zooplankton) that it was adsorbed on surface of the metallic sample and protect it, this fact is possible because the complex layer can partially isolate the metallic surface from the seawater. On the other hand, CR values for brass tend to increase, as the exposure time passes, this behavior could be attributed to the dezincification process that this copper alloy suffers.

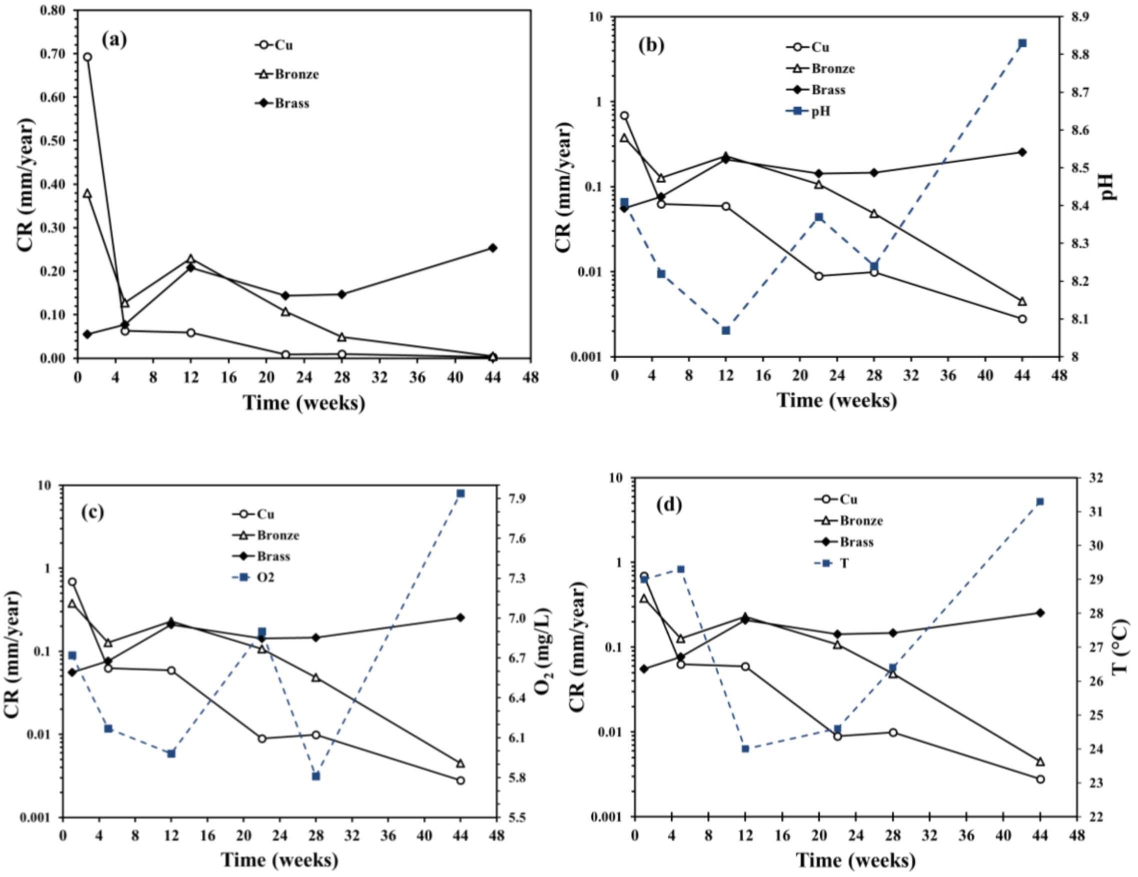

Figure 19. a) Comparative behavior of corrosion rates for the three materials studied, b) Relationship between CR with pH, c) with oxygen concentration and d) with temperature.

Figure 19b-d shows the effects of the physicochemical parameters on the CR for copper and its alloys. These figures show that pH, dissolved oxygen, (O_2) and temperature (T) in general have the same behavior along the 44 weeks. The effect of pH, O_2 and T throughout 44 weeks had a lot of influence in the CR. In the firsts 12 weeks, the values of these parameters tend to decrease, from week 12 to 44 the values of these three parameter increase. In general, if the pH decreases the CR increases. At the beginning of the immersion, the CR of the Cu and its alloys was high, since 1 to 5 weeks the CR decreases fast; this fact is attributed to the high temperature, which was measured in summer season, where the temperature arise 31°C. Additionally, in the first weeks there is a biofilm formation in the surface of metals. In the winter season, the temperature in the seawater is slightly low (from 12 to 22 weeks) and the corrosion rate tend to decrease with time. Cu and bronze present a similar behavior during 44 weeks exposure. However, the brass exhibits a different behavior; the CR during the 44 weeks increases continuously.

4. CONCLUSIONS

The effect of seasonal variability on the marine environment in the corrosion of Cu and Cu-Alloys was analyzed in situ with respect to exposure time. Physicochemical parameters of seawater were related to corrosion behavior. The corrosion process was monitored through EIS during 10 months. Nyquist diagrams show in the three materials the presence of charge transfer processes for the first weeks and diffusion limited processes after film appeared.

In situ studies corroborated that there is significant influence on the corrosion process due to water dynamics, stability of the layers adhered to metal surface, the amount of living organisms, degree of adhesion to the surface and changes in the physicochemical parameters intermittent seawater during each season. All these parameters differently impact on the electrochemical behavior of each material. These results are the beginning of a series of studies to relate the effect of climate change, through the seasonal variability, in the marine environment and the possible repercussions in the corrosion processes of submerged metals in this environment.

After electrochemical analysis and SEM observations, it can be concluded that the material that presented the best results was copper, despite maintaining lower resistance at the beginning. Copper improved its performance once the film was stabilized; this material exhibit faster presence of a homogeneous and stable corrosion product film of Cu_2O.

XRD revealed the formation of some Cu, Sn and Zn oxides mainly. Additionally, some silicates and sulfates were detected. Pitting and localized corrosion type was observed.

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