

Effect of Hypochlorite Ions on Corrosion of Cu-Ni Alloys Immersed in Seawater at Turbulent Flow Conditions

R. Galvan-Martinez^{1,*}, M.A. Baltazar², E. Mejia³, M. Salaza⁴, A. Contreras⁵, R. Orozco-Cruz¹

¹ Unidad Anticorrosión-Instituto de Ingeniería, Universidad Veracruzana, Av. S. S. Juan Pablo II, Zona Universitaria, Veracruz, 94294, México.

² Facultad de Ingeniería Civil, Universidad Veracruzana, Xalapa, Veracruz, CP 91000, México.

³ Facultad de Ingeniería, Universidad Veracruzana, Campus Cordoba-Orizaba, Veracruz México.

⁴ Clúster Politécnico Veracruz, Av. IPN s/n, C.P. 93400, Papantla, Veracruz, México.

⁵ Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152 C.P. 07730, CD MX, México.

*E-mail: rigalvan@uv.mx

Received: 24 February 2018 / Accepted: 5 July 2018 / Published: 1 September 2018

A corrosion study of Cu-Ni (90-10) alloy was carried out in natural seawater adding several concentrations of an oxidant biocide (hypochlorite-based biocide). The corrosion tests were made at atmospheric pressure, static and turbulent flow conditions (1000 rpm) and room temperature during 24 hours. A rotating cylinder electrode (RCE) was used in order to get the hydrodynamic conditions. The electrochemical techniques used in the corrosion studies were lineal polarization resistance (R_p), electrochemical impedance spectroscopy (EIS) and polarization curves (PC). A scanning electron microscope (SEM) to carry out the superficial analysis and characterize the corrosion type was used. At turbulent flow condition, the corrosion rate (CR) of the Cu-Ni sample decreased as the concentration of hypochlorite ions increase, while at static condition the CR increased as the hypochlorite ions also increase. A mix corrosion process was observed. Pitting and crevice corrosion was detected, and the mechanism was a differential aeration cell.

Keywords: Turbulent flow, Cu-Ni Alloy, Hypochlorite Ions, Impedance, polarization curves.

1. INTRODUCTION

The corrosion of the steel structures submerged in seawater can occurred by differential aeration cells where the macro and microorganisms can participate [1-2]. This situation can get great importance when some alloys, such as stainless steel or Cu-Ni alloys are used in heat exchangers of cooling systems and these systems using seawater as refrigeration fluid provoking with this fact that the alloys will be damaged [3, 4].

The marine biofouling is an organism's community that they are in constant growth on metallic surface immersed in the sea permanently or temporarily. The growing of these microorganisms can interfere with the efficient use of some metallic surfaces. Some examples of these troubles are the velocity reduction of a ship, the reduction of the internal diameter of the pipeline that transport the refrigerant fluid and the incrustation of the macro and microorganisms in the surface of the metallic structures that supporting the oil platforms [2, 5].

The most common biocide for chemical anti-biofouling treatments used in the industrial waters seawater used in the cooling tower, is chlorination. The term "chlorination" is often used inappropriately by the plants operators in referring to the dosage/production of other oxidant species than chlorine (or hypochlorite), as the alternative product chlorine dioxide. However, an excessive chlorination may cause the formation of harmful disinfection products that they can react to form aggressive species to environment [6-8].

Additionally to the problems caused by the macro/microorganisms, there is an effect produced by the relative movement between the metal and the corrosive environment, where this movement can increase the velocity of the suspended solid producing an increase of the corrosion rate (CR) by the shear stress. Galvan [9] studied the corrosion of X52 pipeline steel immersed in seawater with a no oxidant biocide under turbulent flow conditions using a rotating cylinder electrode (RCE). They found that at static condition, the influence of the biocide concentration on the corrosion steel sample is low, whereas at turbulent flow conditions, the not-oxidant biocide has a slight protector effect on the steel corrosion.

The influence of the turbulent flow conditions on the corrosion process of the metallic structures is really complex and it has been analyzed in the oil industry [10-13], where the effects of the flow in synergy with dissolved gases (mainly CO₂ and H₂S) in aqueous media is really important. The most common flow regimen in the industrials processes is the turbulent flow and according to this fact, many researchers have tried to analyze and describe the corrosion process under this type of flow by using different hydrodynamic systems and obtaining different degree of acceptance and successful [14].

Some hydrodynamic systems used in the corrosion studies are RCE, loops, concentric pipeline and jet impingement. All of these systems have been important in the study, improvement and understanding of the metallic corrosion that it develop under turbulent flow conditions [14-20]. In order to reduce the growth and prevent the settlement of the microorganism, many methods have been developed. Some of these methods are physical removal (mechanic or with heat application), superficial treatment and chemical treatment of the water. In case of the chemical treatment, it is important to point out that biocides are toxic substances to macro/microorganisms [3, 21, 22]. The biocide more used in the cooling systems that using seawater as cooling fluid is the chlorine and its aqueous solutions. The chlorine has some disadvantages but one of the most important is that it can corrode all metals or alloys used in the industrial process.

This paper is focused in the results of Cu-Ni (90-10) alloy corrosion immersed in natural seawater at 1000 rpm (turbulent flow conditions) using the electrochemical techniques linear polarization resistance, potentiodynamic polarization curves and electrochemical impedance

spectroscopy. In order to control the hydrodynamic conditions of the corrosion process, a RCE was used [9, 23-25].

2. EXPERIMENTAL

2.1. Materials

Cylindrical working electrodes made of a Cu-Ni (90-10) alloy were used in all experiments. Exposure area in all the working electrodes was 3.4 cm^2 . Prior to each experiment the Cu-Ni working electrodes were polished up to 600 grit SiC paper, cleaned with distilled water and degreased with acetone.

In order to identify the corrosion morphology, some corroded Cu-Ni samples were analyzed by scanning electron microscope (SEM).

2.2. Test solution

The solution used in all electrochemical tests was natural seawater without biocide (0 ppm) and with biocide at three different concentrations, 0.25, 0.5 and 0.7 ppm. The exposure time in all corrosion tests was 24 h at room temperature and atmospheric pressure (Veracruz Port, Mexico). The biocide used was sodium hypochlorite (called in this paper as "biocide"). In order to control the hydrodynamic conditions, a RCE at 1000 rpm was used. It is important to point out that the electrochemical measurements were also carried out at static conditions.

2.3. Experimental set-up

A three-electrode electrochemical cell was used (working, reference and auxiliary electrode). Cu-Ni alloy as working electrode, a saturated calomel electrode (SCE) as reference electrode and a sintered graphite rod as auxiliary electrode was used. In order to minimize the effect of the solution resistance a Lugging capillary employed.

2.4. Electrochemical techniques

All the electrochemical experiments were performed with a Potentiostat / Galvanostat. These electrochemical measurements were:

- I. Corrosion potential (E_{corr}) against time.
- II. Linear polarization resistance (LPR). A potentiodynamic method was used, with a potential range of $\pm 0.015 \text{ V}$ referred to E_{corr} and a sweep rate of 0.001 Vs^{-1} . In all corrosion rate (CR) calculations, an experimental value for the Stern-Geary constant (B) was considered; this constant was obtained from the anodic and cathodic Tafel slopes of the polarization curves (*ba* and *bc* respectively).
- III. Potentiodynamic polarization curves (PC). The polarization curves were re- corded at a sweep rate of 0.001 Vs^{-1} and the potential range used was $\pm 0.3 \text{ V}$ referred to E_{corr} .

IV. Electrochemical impedance spectroscopy (EIS). In all EIS tests, the frequency range used was 0.01 Hz to 10 kHz with an amplitude of 10 mV referred to E_{corr} . Ten points per decade of frequency were recorded.

The corrosion current density (i_{corr}) was obtained using LPR and the Stern and Geary equation [26]:

$$i_{corr} = \frac{B}{R} \tag{1}$$

Where B is a Stern and Geary constant and R is the LPR value. The constant of Stern and Geary and the corresponding corrosion rate was calculated according to [27]:

$$B = \frac{ba * bc}{2.303 (ba + bc)} \tag{2}$$

3. RESULTS

3.1. Potential corrosion vs. time.

Figure 1 shows the results of corrosion potential (E_{corr}) measurements for Cu-Ni sample immersed in natural seawater without biocide (0ppm) and 0.25 ppm of biocide (Figure 1a) and with 0.5 and 0.7 ppm of biocide (Figure 1b) at static (S) and turbulent flow (F) conditions.

The behavior of the potential in figure 1a shown that the turbulent flow has a great influence over the corrosion potential, in both concentrations (0 and 0.25 ppm of biocide) the values of E_{corr} under turbulent flow conditions changed to more electronegative values. E_{corr} at these two concentrations had a stable behavior after 7 h of exposure time. In addition, this E_{corr} was not affected with the increment of the biocide concentration.

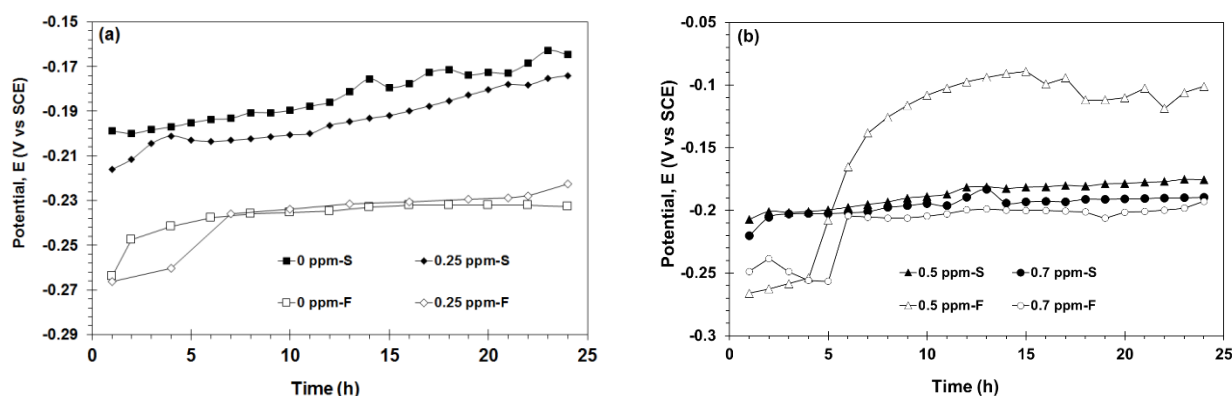


Figure 1. E_{corr} vs time for Cu-Ni sample immersed in natural seawater, a) without biocide and 0.25 ppm, b) 0.5 and 0.7 ppm, at static (S) and turbulent flow (F) conditions.

On the other hand, at 0.5 and 0.7 ppm of biocide, the E_{corr} was affected by the biocide concentration because as the biocide concentration increased, the E_{corr} goes to more electronegative values.

3.2. Linear polarization resistance (LPR).

Figure 2 shows the comparison of the corrosion rate (CR) obtained by LPR of Cu-Ni alloy immersed in natural seawater with different concentrations of biocide (0, 0.25, 0.5 and 0.7 ppm) at static and turbulent flow conditions.

Figure 2a shows the corrosion rate values of the Cu-Ni alloy with 0 and 0.25 ppm at static and turbulent flow conditions. These CR values show a similar behavior because the corrosion rate of the metallic sample was not affected by the increment of the biocide concentration during all exposure time. In addition, for the static conditions and at the beginning of the test, the values of CR were high, but as the exposure time increases the CR decreased to 0.03 mm/year approximately and get a stable value. This behaviour is attributed to the fact that at the beginning of the test, the surface of the Cu-Ni sample was active consequently the CR is high, but as the exposure time increases, a corrosion products film covered the surface of the Cu-Ni sample and consequently the CR decreased until to get a stable value. According to Bautista [28], the corrosion products formed is mainly copper dioxide.

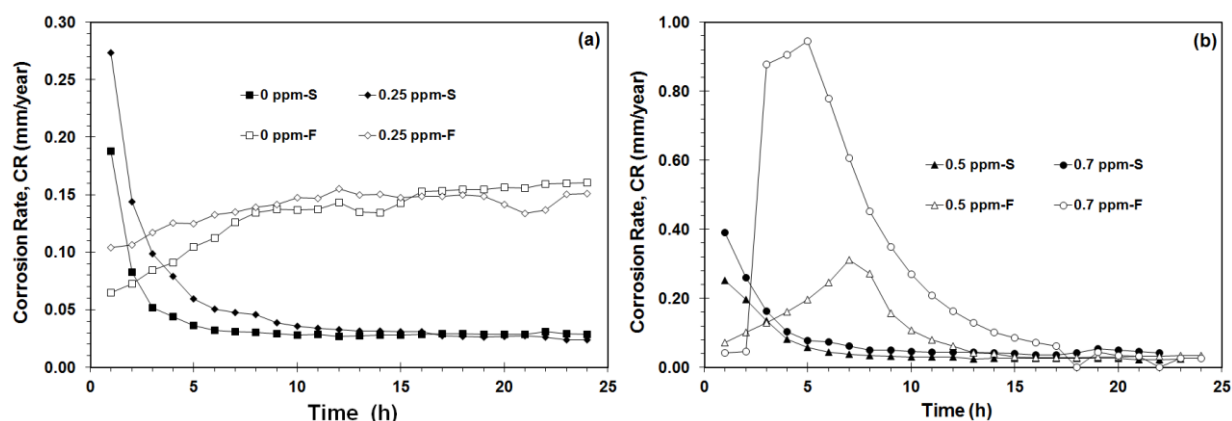


Figure 2. CR (obtained by LPR) as a function of time. Cu-Ni sample immersed in seawater with biocide, a) without biocide and 0.25 ppm, (b) 0.5 and 0.7 ppm, at static (S) and turbulent flow (F) conditions.

On the other hand, in values corresponding to turbulent flow conditions is possible to observe that the CR values raise and fall as the exposure time increases. The increment in CR values should be attributed to the rupture of the corrosion products film formed on surface of the steel sample and the regeneration of this film reduce the CR. It is important to point out that the rupture of the film is attributed to the mechanical effects of the fluid movement (shear stress) and to the rupture provoked by the hypochlorite ions. It is important to mention that at the end of the test, the CR had a stable value of 0.14 mm/year approximately. The stable behavior observed in the corrosion rate at static and turbulent flow conditions can be attributed to the corrosion products film, mainly chloride copper and copper

oxide [29-31] formed on surface of the alloy which acts an interface between natural seawater and Cu-Ni alloy. It is important to point out that the turbulent flow conditions have influence on CR of the Cu-Ni sample because after 4 hours of the exposure time, the CR values of Cu-Ni sample at turbulent flow conditions were higher than CR values at static conditions.

In figure 2b is possible to observe that both curves (at 0.5 and 0.7 ppm) at static conditions show a similar behavior to observed in the CR of the Cu-Ni immersed in seawater with 0 and 0.25 ppm of biocide where the increment of biocide concentration did not affected the corrosion rate of the metallic sample during all exposure time. In addition, it is important to point out that CR also has a similar behaviour with respect to time to observe at 0 and 0.25 ppm of biocide. At the beginning of the test, the values of CR were high but as the exposure time increased, the CR decreased until get a stable value of 0.04 mm/year approximately.

In case of the CR curve corresponding to 0.5 ppm of biocide at turbulent flow condition, the CR increased from 0.07 to 0.30 mm/year in the first 7 hours, later it decreased to 0.04 mm/year approximately. On the other hand, the CR at 0.7 ppm and at this condition, at the beginning of the test the CR value was 0.04 mm/year, then it increased to 0.96 mm/year to finally get a stable value after 18 hours of exposure time (0.04 mm/year approximately).

The CR behavior presented by the Cu-Ni sample immersed in seawater with 0.5 and 0.7 ppm of biocide can be attributed to the protective effect of the corrosion products film formed on surface of the metallic sample consequently the CR decreased. The increment of the CR is attributed to rupture of this corrosion products film. At static and turbulent flow conditions, All CR at 0.5 and 0.7 ppm of biocide and after 17 hours of the exposure time have similar values indicating that the turbulent flow condition has not influenced on the CR at the end of the test. This fact is attributed to the stability of the corrosion products film that it can isolate to the surface of the metallic sample from the corrosive medium [32].

3.3. Electrochemical impedance spectroscopy (EIS).

Figure 3 and 4 shows the experimental results obtained by EIS technique for Cu-Ni alloy sample immersed in natural seawater with 0, 0.25, 0.5, and 0.7 ppm of biocide under static and turbulent flow conditions during an exposure time of 24 h.

Figure 3a shows the Nyquist plot with the impedance spectra of the Cu-Ni alloy immersed in seawater without biocide (0 ppm) and figure 3b with 0.25 ppm of biocide where T0 and T24 correspond to 0 (beginning of the test) and 24 hours of exposure time.

EIS spectra at static conditions and 0 ppm of biocide (figure 3a) show that the charge transfer resistance (R_{ct}) increased as the exposure time also increased, while the EIS spectra at turbulent flow have a contrary behavior because the R_{ct} decreased as the exposure time increased. This fact indicate that at static conditions, the CR decreased with time, but in case of turbulent flow, the CR increased as the exposure time also increased.

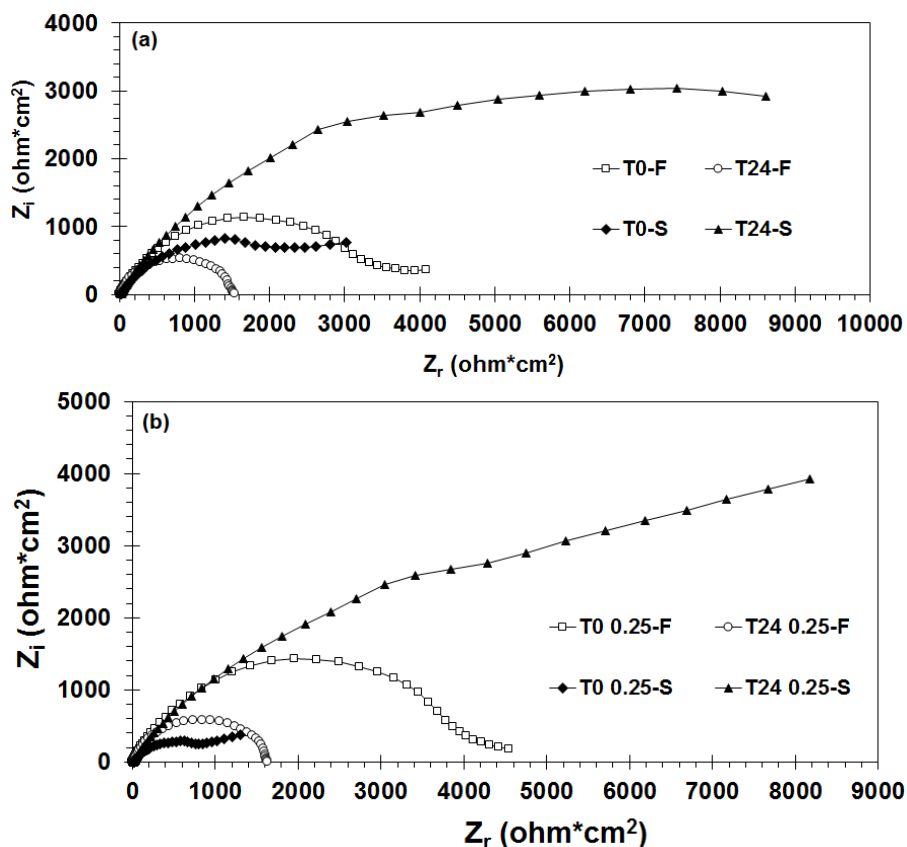


Figure 3. Impedance spectra obtained for Cu-Ni alloy immersed in natural seawater a) without biocide, b) with 0.25 ppm of biocide at static (S) and turbulent flow (F) conditions during 24 h.

On the other hand, the CR at 0.25 ppm has a similar behavior that the CR at 0 ppm. The behavior of CR at static conditions is attributed to the fact that a corrosion products film was formed on metallic surface and protected partially; while at turbulent flow condition the film was broken by action of hypochlorite ions and the shear stress. It is important to point out that at in both conditions (0 and 0.25 ppm) and at the end of the exposure time (24 h) the highest CR was obtained at turbulent flow condition.

Figure 4 shows the Nyquist plot with the impedance spectra for Cu-Ni alloy immersed in natural seawater with 0.5 ppm (4a) and 0.7 ppm (4b) of biocide. All impedance spectra in figure 4a show two time constant; the first time constant at high frequencies is attributed to the corrosion products film, while the second time constant at low frequencies, is attributed to the charge transfer resistance of the corrosion process [33, 34].

In figure 4b the EIS spectra at static conditions (0.7 ppm) also shows two time constant but at turbulent flow conditions, just one time constant is observed. According the EIS spectra, the lowest values of CR was obtained at 0.7 ppm and at turbulent flow conditions. At this highest concentration of the hypochlorite ions, the effect of turbulent flow condition does not have influence in the CR. This fact can be attributed to the chaotic system in this flow regime and the corrosion products film adsorbed on surface of the metallic sample [35].

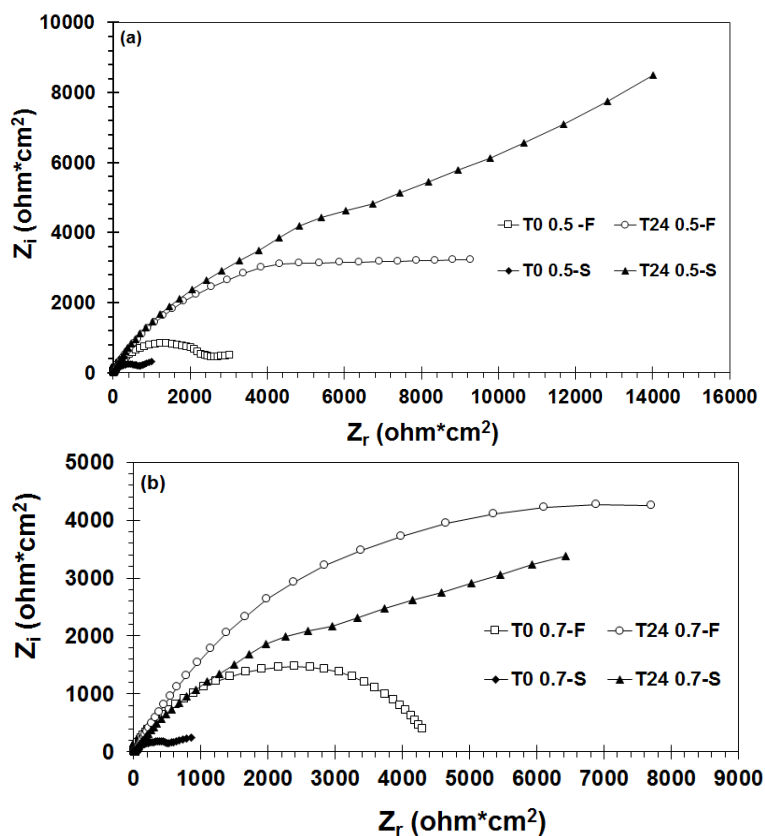


Figure 4. Impedance spectra obtained for Cu-Ni alloy immersed in natural seawater, a) with 0.5 ppm, b) with 0.7 ppm of biocide at static (S) and turbulent flow (F) conditions during 24 h.

Figure 4 shows that the R_{ct} has a similar behavior in 0.5 and 0.7 ppm of biocide where the R_{ct} increases as the exposure time also increases. According to this fact is possible to say that CR decreased with time.

3.4. Potentiodynamic polarization curves (PC).

Figure 5 shows the PC obtained for the Cu-Ni alloy immersed in seawater with 0, 0.25, 0.5, and 0.7 ppm of biocide at static and turbulent flow conditions. In PC at static condition (figure 5a) and at the beginning of the all anodic branches, a process associated with a charge transfer is observed but after a polarization of 0.12 V approximately, a mass transfer process influenced the anodic reaction. On the other hand, at turbulent flow condition (figure 5b) a similar behavior is observed, but in this case the mass transfer process had influence close to the end of the anodic polarization.

Table 1 shows the electrochemical parameters of the polarization curves obtained at static and turbulent flow conditions, where E_{corr} is the corrosion potential, B is the Stern and Geary constant and i_{corr} is the corrosion current density.

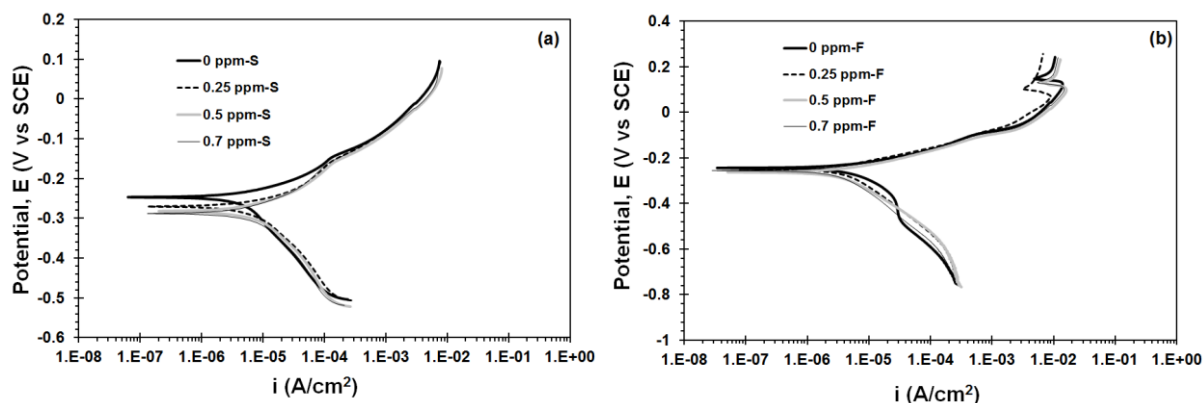


Figure 5. Potentiodynamic polarization curves of Cu-Ni alloy immersed in seawater with 0, 0.25, 0.5 and 0.7 ppm of biocide, a) at static and b) turbulent flow conditions.

The cathodic branches in the PC at static condition have slopes that can be associated to charge transfer process but in case of the cathodic branches and at turbulent flow condition, these have slopes that can be associated to mass transfer process in the cathodic kinetics [36]. In general, the total corrosion of the Cu-Ni is associated to a mix process, where at static condition the corrosion reactions are dominated by a charge transfer process, but at turbulent flow condition, the main process is the mass transfer. It is important to point out that the charge transfer process is related to the corrosion of the Cu-Ni samples while the mass transfer is associated at two diffusion process. The diffusion of the oxygen from the bulk to the metallic surface and the diffusion of the oxygen through the corrosion products film adsorbed on surface of the metallic sample [32, 37].

Table 1. Electrochemical parameter obtained from the PC shown in figure 5

| Concentration Biocide in Seawater | Static Condition | | | Turbulent Flow Condition | | |
|---|-------------------|-----------------|------------------------|--------------------------|-----------------|------------------------|
| | E_{corr} (V) | B (V/decade) | i_{corr} (A/year) | E_{corr} (V) | B (V/decade) | i_{corr} (A/year) |
| 0.00 ppm | -0.247 | 0.014 | 2.8E-6 | -0.250 | 0.024 | 8.2E-6 |
| 0.25 ppm | -0.271 | 0.018 | 4.1E-6 | -0.251 | 0.023 | 7.5E-6 |
| 0.50 ppm | -0.281 | 0.022 | 7.3E-6 | -0.264 | 0.021 | 6.6E-6 |
| 0.70 ppm | -0.288 | 0.030 | 1.5E-5 | -0.253 | 0.022 | 6.5E-6 |

Figure 6 shows the corrosion rate obtained from PC of Cu-Ni sample at static and turbulent flow conditions with different biocide concentrations.

In figure 6 is possible to observe that turbulent flow has influence just in the first two biocide concentrations (0 and 0.25 ppm), but when the concentration increased to 0.5 and 0.7 ppm the CR values obtained at static condition was lower than the values of CR obtained at turbulent flow condition. The fact observed at 0.5 and 0.7 ppm of biocide should be attributed to the chaotic behaviour in the turbulent flow regimen and to the passive film formed on metallic surface that it can protect the metallic sample. This passive behavior is possible to observe in the PC shown in figure 5b.

It is important to point out that at static condition the values of CR have a clear tendency to increase as the biocide concentration also increase. This behavior it should be attributed to the effects of the hypochlorite ions on the corrosion products film adsorbed in metallic surface without fluid movement.

On the other hand, at turbulent flow condition, the values of CR have tendency to decrease when the hypochlorite ions concentration increase, this behaviour is attributed to the distribution of these ions in the chaotic system by turbulent flow regime and to the passive film formed on metallic surface.

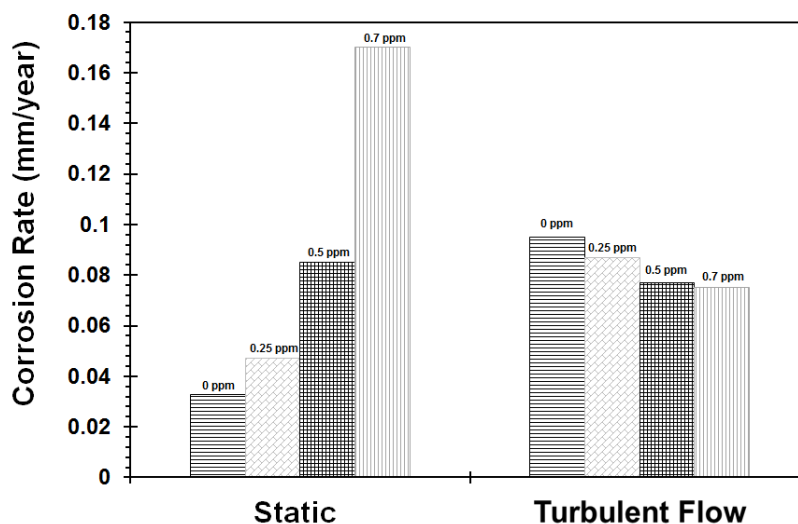


Figure 6. CR obtained from PC as a function of biocide concentration.

The results of the polarization curves have good agreement with the behaviour of the results obtained by LPR and EIS.

3.5. Superficial analysis by SEM.

Figure 7 shows the micrographs obtained by SEM from the Cu-Ni samples exposed to seawater with 0 ppm (Figure 7a-b), and 0.7 ppm (Figure 7c-d) of biocide. The Figures 7a and 7c show the micrographs obtained at static condition while figure 7b and 7d were obtained at turbulent flow condition. In order to get a better analysis, this paper only presents the conditions where the highest and lower of CR values were obtained.

SEM observations of surface of Cu-Ni alloys samples showed localized corrosion, specifically, pitting and crevice corrosion. These two-corrosion forms indicate that the mechanism of the corrosion process is a differential aeration cell [26]

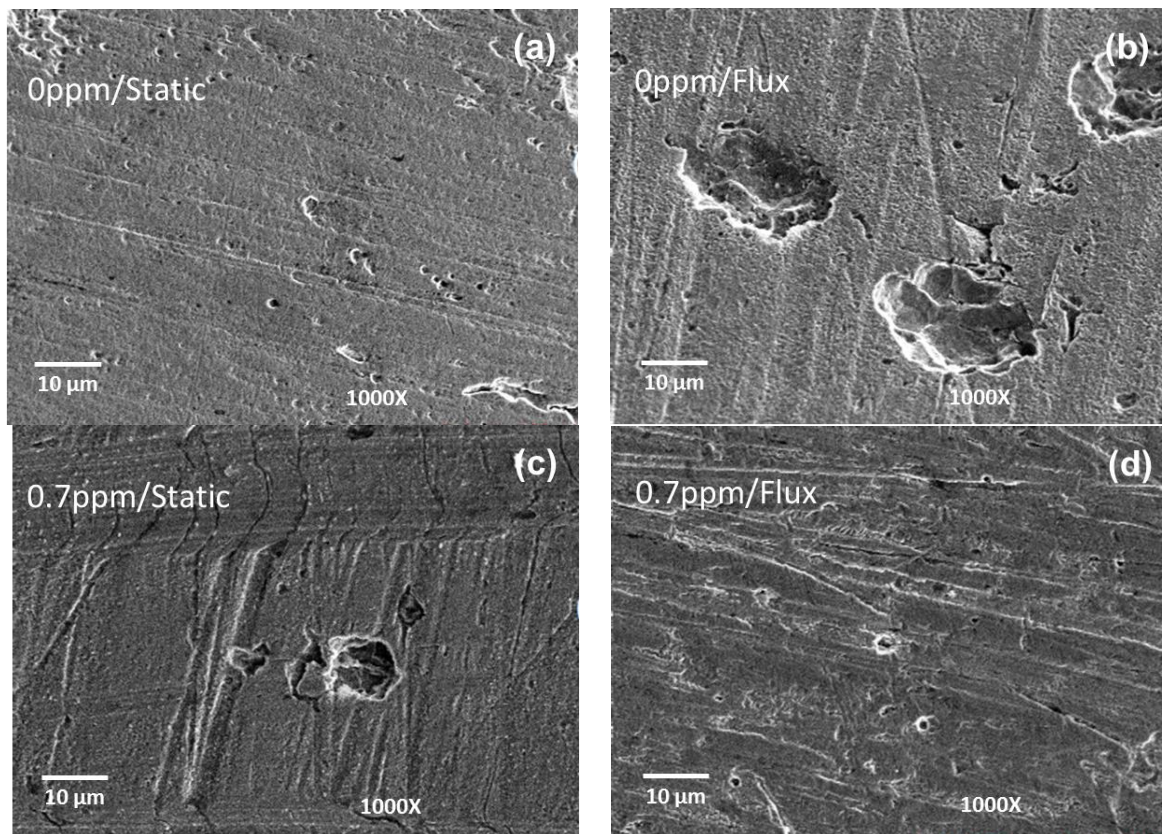


Figure 7. SEM micrographs of the morphological damage by corrosion of Cu-Ni samples immersed in seawater under static and turbulent flow.

4. CONCLUSIONS

According to electrochemical study of the Cu-Ni alloy exposed to natural seawater without biocide 0 ppm and with 0.25, 0.5 and 0.7 ppm of biocide under static and turbulent flow conditions, it is possible to conclude that at turbulent flow condition, the corrosion rate of the Cu-Ni alloy decreases as the concentration of hypochlorite ions increases. This behaviour could be attributed to the chaotic system and the passive film formed on metallic surface constituted mainly by copper chloride and copper dioxide. On the other hand, at static condition, the CR increases as the hypochlorite ions concentration also increases, in this case the behaviour is attributed to the action (without any disturbance) of the hypochlorite ions against to the corrosion products film. The corrosion of the Cu-Ni was associated to a mix process, where at static conditions the corrosion reactions was dominated by a charge transfer process, but at turbulent flow conditions the main process is the mass transfer. In addition, the results obtained by LPR, EIS and PC have good correlation between them. The corrosion form observed on the Cu-Ni samples was pitting and crevice corrosion and the mechanism was a differential aeration cell.

References

1. D. J. Blackwood, C. S. Lim, S. L. M. Teo, H. Xiaoping, P. Jianjun, *Corros. Sci.* 129 (2017) 152.
2. A. H. Videla, C. R. Salvarezza, *Introducción a la Corrosión Microbiológica*, 1a ed., Editorial Agropecuaria (1984) Buenos Aires Argentina.
3. A. D. Mercer, *Corrosion in Seawater Systems (Ellis Horwood Series in Corrosion and its Prevention)*, Ed. ELLIS HORWOOD, (1990) Great Britain, United Kingdom.
4. A. Colombo, L. Oldani, S. P. Trasatti, *Eng. Fail. Anal.*, 84 (2018) 46.
5. Kh. Rahmani, R. Jadidian, S. Haghtalab, *Desalination* 393 (2016) 174.
6. P. Cristiani, G. Perboni, *Bioelectrochemistry*, 97 (2014) 120.
7. D. K. Gray, I. C. Duggan, H. J. MacIsaac, *Mar. Pollut. Bull.*, 52 (2006) 689.
8. M. Al-Bloushi, J. Saththasivam, S. Al-Sayeghc, S. Jeong, K. Choon Ng, G. L. Amy, T. Leiknes, *J. Ind. Eng. Chem.*, 59 (2018) 127.
9. R. Galvan-Martinez, R. Orozco-Cruz, R. Torres-Sánchez, *Afinidad*, 550 (2010) 442.
10. E. Huttunen-Saarivirta, P. Rajala, M. Marja-aho, J. Maukonen, E. Sohlberg, L. Carpen, *Bioelectrochemistry*, 120 (2018) 27.
11. M. E. Olvera-Martínez, J. Mendoza-Flores, J. Genesca, *J. Loss Prevent. Proc.*, 35 (2015) 19.
12. W. Li, B. F. M. Pots, X. Zhong, S. Nestic, *Corros. Sci.* 126 (2017) 208.
13. L. Garverick, *Corrosion in the Petrochemical Industry - Essential Research*, ASM International, (2011) United States of America.
14. M. N. Zafar, R. Rihan, L. Al-Hadhrami, *Corros. Sci.* 94 (2015) 275.
15. F. C. Walsh, G. Kear, A. H. Nah, J. A. Wharton, L.F. Arenas, *Corros. Sci.*, 123 (2017) 1.
16. B. Poulson, *J. Appl. Electrochem.* 24 (1994) 1.
17. C. Sedano-de-la Rosa, M. Vite-Torres, G. Godínez-Salcedo, E. A. Gallardo-Hernández, R. Cuamatzi-Melendez, L. I. Farfán-Cabrera, *Wear*, 376-377 (2017) 549.
18. H. Huang, J. Tian, G. Zhang, Z. Pan, *Mater. Chem. Phys.* 181 (2016) 312.
19. D. C. Silverman, *Corrosion*, 40 (1984) 220.
20. D. C. Silverman, *Rotating Cylinder Electrode - An Approach for Predicting Velocity Sensitive Corrosion*, CORROSION/90, NACE International, Houston, U.S. A. 1990, 1.
21. Md. A. Islam, Z. Farhat, *Wear* 376-377 (2017) 533.
22. A. Rochdi, R. Tourir, M. El Bakri, M. E. Touhami, S. Bakkali, B. Mernari, *J. Environm. Chem. Eng.*, 3 (2015) 233.
23. W. Su, Y. Tian, S. Peng, *Appl. Surf. Sci.*, 315 (2014) 95.
24. F. Mansfeld, *Mater. Corros.*, 54 (2003) 489.
25. R. Galván-Martínez, J. Mendoza-Flores, R. Duran-Romero, J. Genesca-Llongueras, *Mater. Corros.* 55 (2004) 586.
26. P. R. Roberge, *Handbook of Corrosion Engineering*, Second edition, Ed. McGraw Hill Professional (2012) New York, U.S.A.
27. ASTM G59-97. "Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements", ASTM International (2014).
28. B. E. Torres-Bautista, M. L. Carvalho, A. Seyeux, S. Zanna, P. Cristiani, B. Tribollet, P. Marcus, I. Frateur, *Bioelectrochemistry*, 97 (2014) 34.
29. K. M. Ismail, A. M. Fathi, W. A. Badawy, *Corros. Sci.* 48 (2006) 1912.
30. P. Druska, H. H. Strehblow, S. Golledge, *Corros. Sci.* 38 (1996) 835.
31. A. M. Fenelon, C. B. Breslin, *Corros. Sci.* 45 (2003) 2837.
32. B. Yin, Y. Yin, Y. Lei, L. Dong, Y. Zhang, *Chem. Phys. Lett.*, 509 (2011) 192.
33. H. Castañeda, X.D. Benetton, *Corros. Sci.*, 50 (2008) 1169.
34. R. Galvan-Martinez, R. Orozco-Cruz, R. Torres-Sanchez, E. A. Martinez, *Mater. Corros.*, 61 (2010) 872.
35. W. Su, Y. Tian, S. Peng, *Appl. Surf. Sci.*, 315 (2014) 95.

36. R. Galvan-Martinez, J. Mendoza-Flores, R. Duran-Romero, J. Genesca, *Mater. Corros.* 58 (2007) 514.
37. E. K. Mioč, Z. H. Gretić, H. O. Čurković, *Corros. Sci.*, 134 (2018) 189.

© 2018 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).