Study of X52 steel in seawater with biocides under turbulent flow conditions

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Estudio del acero X52 en agua de mar con biocida bajo condiciones de flujo turbulento

Estudi de l'acer X52 en aigua de mar amb biocida sota condicions de flux turbulent

RESUMEN

El presente trabajo muestra el estudio de la corrosión de un acero de tubería API X52 inmerso en agua de mar sin biocida y con 0,25, 0,5 y 0,75 ppm de biocida, bajo condiciones estáticas y dinámicas (flujo turbulento) a temperatura ambiente y presión atmosférica. El tiempo total de exposición del acero en la solución de evaluación fue de 24 h. Se usó un Electrodo Cilíndrico Rotatorio (ECR) para controlar las condiciones hidrodinámicas. La velocidad de rotación fue de 1000 RPM. Las muestras de acero fueron inmersas en la solución evaluadora y posteriormente se les realizó un estudio electroquímico utilizando las técnicas electroquímicas de resistencia a la polarización lineal (R_p), espectroscopía de impedancia electroquímica (EIE) y curvas de polarización (CP). En el análisis superficial de las muestras de acero se utilizó un microscopio electrónico de barrido.

Los resultados del estudio electroquímico muestran que la velocidad de corrosión es más elevada bajo condiciones de flujo turbulento que a condiciones estáticas, así como también que a medida que la concentración de biocida, en la solución evaluadora, incrementó la velocidad de corrosión disminuyó. Se encontró el tipo de corrosión localizada en las muestras de acero evaluadas.

Palabras claves: Flujo turbulento, EIE, R_p, ECR, Biocida

SUMMARY

This work presents the corrosion study of the API X52 pipeline steel immersed in seawater without biocide and with 0,25, 0,5 and 0,75 ppm of biocide, under static and dynamic (turbulent flow) conditions at room temperature and atmospheric pressure. The total exposure time of the steel sample in test solution was 24h. In order to control the hydrodynamic conditions, a rotating cylinder electrode (RCE) was used. The rotation speed was 1000 RPM. The steel samples were immersed in the test solution, then, an electrochemical corrosion study using linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and polarization curves (PC) was made. In the superficial analysis of the steel samples, a scanning electronic microscopy was used. The results of the electrochemical study shown that the corrosion rate is higher under turbulent flow conditions than static conditions, and as the biocide concentration increased in the test solution, the corrosion rate decreased. A localized corrosion type was found in all the samples tested.

Keyword: turbulent flow, EIS, LPR, RCE, biocide.

RESUM

En el present treball, s'estudia la corrosió d'un acer de canonada API X52 immers en aigua de mar sense biocida i amb 0,25, 0,5 i 0,75 ppm de biocida sota condicions estàtiques i dinàmiques (flux turbulent) a temperatura ambient i a pressió atmosfèrica. El temps total d'exposició de l'acer en la solució d'avaluació ha estat de 24 h. S'empra un Elèctrode Cilíndric Rotatori (ECR) per controlar les condicions hidrodinàmiques. La velocitat de rotació és de 1000 rpm. Les mostres d'acer es submergeixen en la solució avaluadora i posteriorment es realitza un estudi electroquímic emprant les tècniques electroquímiques de resistència a la polarització lineal (R_p), espectroscòpia d'impedància electroquímica (EIE) i corbes de polarització (CP). En l'anàlisi superficial de les mostres d'acer s'utilitza un microscopi electrònic d'escombratge.

Els resultats de l'estudi electroquímic mostren que la velocitat de corrosió es més elevada sota condicions de flux turbulent que en condicions estàtiques, i també que a mesura que la concentració de biocida en la solució avaluadora s'incrementa, la velocitat de la corrosió disminueix. Es troba el tipus de corrosió localitzada en les mostres d'acer avaluades.

Mots clau: Flux turbulent, EIE, R_p, ECR, Biocida

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INTRODUCTION

The negative change of the Gibbs energy indicates that the corrosion process is spontaneous; it is to say, under this condition, the corrosion is a thermodynamically possible process[1]. The steel structures that are exposed to seawater or aqueous solutions generally have many corrosion problems. A great variety of microorganisms live within these waters, and some studies have demonstrated that these microorganisms initiate or accelerate the corrosion[2,3]. Microbiological Induced Corrosion (MIC) accelerates corrosion due to the interaction between the microbial activity and the electrochemical corrosion processes[4]. Sulphate Reducing Bacteria (SRB) is the predominant groups of microorganisms responsible for the MIC[5-9]. One method for corrosion protection is the use of inhibitors[10,11] which have influence over the corrosion process. Inhibitor studies cover a spectrum of activities, ranging from protection mechanisms through the search of new compounds and the appraisal of competitive commercial products to the monitoring of industrial systems in which inhibitors are being used[12]. The inhibitors like biocides can modify the dissolution rate of metals, influencing the kinetics of the electrochemical reactions which constitute the corrosion process.

The action of the corrosion inhibitor is located at the interface metal/electrolyte and is connected with the change of the metal surface properties and the kinetics of the reaction; it can determine the corrosion process[12,13]. On the other hand, it is important to mention the continuing effort to find a corrosion inhibitor that exhibits a greater effect with smaller quantity in the corrosion medium[14].

Turbulent flow is the most common type of flow conditions found in industrial processes. With the increasing necessity to describe the corrosion of metals in turbulent flow conditions some laboratory hydrodynamic systems have been used with different degrees of success[15-17]. Among these hydrodynamic systems, rotating cylinder electrodes (RCEs), pipe segments, concentric pipe segments, submerged impinging jets and close-circuit loops have been used and have been important in the improvement of the understanding of the corrosion process taking place in turbulent flow conditions[17-24]. The use of the rotating cylinder electrode (RCE), as a laboratory hydrodynamic test system, has been gaining popularity in corrosion studies[25,26]. This popularity is due to its characteristics, such as, its operation mainly in turbulent flow conditions, its well-defined hydrodynamics, ease of assembly and disassembly, smaller volume of fluid used, and easier flow and temperature control[27,28].

It has been found that for a RCE enclosed in a concentric cell, the transition between the laminar and turbulent flow occurs at values of Reynolds number of 200 approximately[15,16,28]. The RCE in corrosion laboratory studies is a useful tool for the understanding of mass transfer processes, effects of surface films, inhibition phenomena, etc. [29] taking place in turbulent flow conditions. However, the use of the RCE has been questioned by some researchers[30], due to the differences found between the values of corrosion rates measured on pipe flow electrodes and on the RCE. The reasons for this difference are still not well understood. However, some works have provided ideas on the explanation of this apparent difference[31-33].

EXPERIMENTAL PROCEDURE

Test environment
All test were carried out at room temperature and atmospheric pressure of Veracruz City (1 atm., approximately). Natural seawater without biocide (SW) and seawater with 0.25, 0.5 and 0.75 ppm of biocide were used as corrosive medium. A not-oxidant biocide was used in the present work. The corrosion tests were made under static and dynamic (turbulent flow) conditions. Hydrodynamic conditions were controlled using a Rotating Cylinder Electrode (RCE) system. In dynamic conditions, a rotation speed of 1000 rpm was used.

Materials
An air-tight three-electrode electrochemical glass cell with a three-electrode array was used. Cylindrical working electrodes made of API X52 steel (with similar composition to AISI-SAE 1518) were used in all experiments. The total exposed area of the working electrodes was 5.3 cm^2 for static conditions and 3.4 cm^2 for dynamic conditions. Prior to each experiment the steel working electrodes were polished up to 600 grit SiC paper, cleaned and degreased with acetone. As reference electrode a saturated calomel electrode (SCE) was used. In order to minimize the effect of the solution resistance a Lugging capillary was used. A sintered graphite rod was used as auxiliary electrode.

Electrochemical techniques
All the electrochemical experiments were performed with a potentiostat / galvanostat. These electrochemical measurements were: Corrosion potential (E_{corr}), Linear polarization resistance (LPR), polarization curves (PCs) and electrochemical impedance spectroscopy (EIS).

I   *Corrosion potential against time*.
II   *Potentiodynamic Linear Polarization Resistance*. The potential range used was ± 0.015 V referred to E_{corr} and a sweep rate of 0.001 Vs^{-1}. In all corrosion rate (CR) calculations, a value of 0.026 V for the Stern-Geary constant was considered. LPR measurements were carried out during 24h
III *Polarization curves.* The polarization curves were recorded at a sweep rate of 0.001 Vs^{-1} and the potential range used was ± 0.5 V referred to E_{corr}.
IV   *Electrochemical impedance spectroscopy*. In all EIS tests, the frequency range used was 0.1 Hz to 10 kHz with a 10 mV of amplitude. 10 points per decade of frequency were recorded.

In order to get the morphology of the corrosive process, some exposed steel samples were selected in order to made a superficial analysis using a scanning electron microscope (SEM)

EXPERIMENTAL RESULTS AND DISCUSSION

E_{corr} vs. time.
Figure 1 shows the results obtained in the E_{corr} measures versus time of the X52 steel samples immersed in SW and seawater with 0.25, 0.5 and 0.75 ppm of biocide during 24 h at static and turbulent flow conditions.

The results showed in these figures indicate that the corrosion potential (E_{corr}) values are affected by the turbulent flow conditions, because at turbulent flow conditions, all corrosion potential values are more electropositive than

the E_{corr} values at static conditions. In addition, after 5 hours at static conditions, the E_{corr} trend to stable feature, it has variations from -0.68 to -0.74 V vs. SCE.
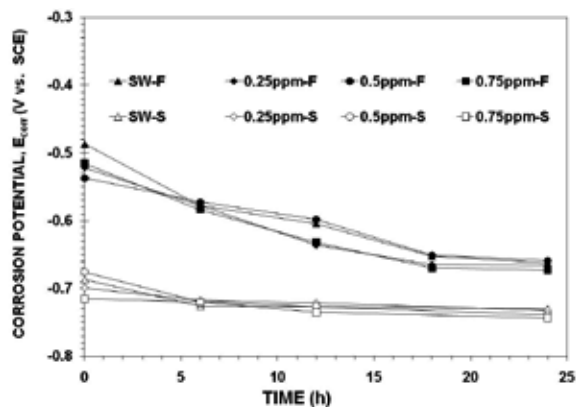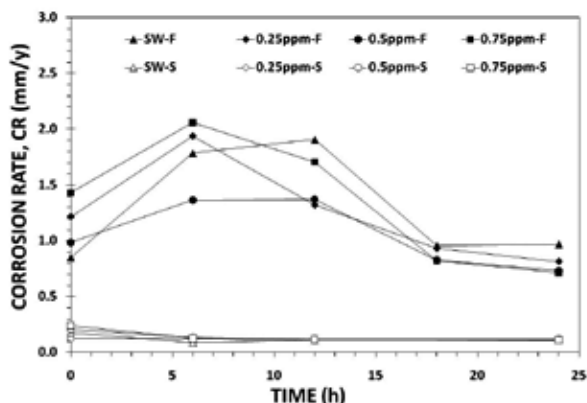

Figure 1 E_{corr} against time. X52 steel sample immersed in natural seawater (SW) and seawater with 0.25, 0.5 and 0.75 ppm of biocide under static (-S) and turbulent flow (-F) conditions during 24 h of the exposure time.

On the other hand, the E_{corr} values at turbulent flow conditions increase as the exposure time also increase. It is important to point out that at the beginning of the tests, at static and turbulent flow conditions, the corrosion potential values are high, but as the exposure time increase, these E_{corr} values decrease and trend to stable feature.

Linear polarization resistance (LPR).
Figure 2 shows the experimental corrosion rate (CR) values against time. This CR was obtained in the LPR tests under static and turbulent flow conditions. The results showed in figure 2 indicate that the CR is affected by the turbulent flow conditions, because all CR values at turbulent flow conditions are higher than the CR values at static conditions.

Figure 2 Corrosion rate (calculated by LPR) against time. X52 steel sample immersed in SW and seawater with 0.25, 0.5 and 0.75 ppm of biocide under static (-S) and turbulent flow (-F) conditions during 24 h of the exposure time.

In curves corresponding to static conditions, is possible to observe that in all concentrations and at the beginning of the test, the CR values are highest, but as the exposure time increased, the CR trend to a stable feature. This behaviour should be attributed to the fact that at the beginning of the test, the surface of the steel sample is active, consequently the CR is high, but as the exposure time increased, the surface of the steel sample was covered by a corrosion products film and consequently the CR decreased until to get a stable feature. On the other hand, in curves corresponding to turbulent flow conditions is possible to see that in all concentrations; the CR values raise and fall as the exposure time increased. This behaviour should be attributed to the mechanical effects of the fluid movement.

The increment of the 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 CR in all concentrations has the same behaviour (raise and fall of the CR), but, after ten hours of exposition approximately, the CR of the steel immersed in seawater without biocide has the highest values, this fact suggest that at dynamic conditions and as the exposure time increase, the not-oxidant biocide has a protector effects on the steel corrosion.

Electrochemical Impedance Spectroscopy (EIS)
Figure 3 and 4 show the experimental results of EIS technique for X52 steel sample immerse in seawater without biocide and seawater with 0.25, 0.5 and 0.75 ppm of biocide, under static and turbulent flow conditions respectively.

Figure 3 shows the Nyquist plots with impedance spectra corresponding to SW (a) and seawater with 0.25 (b), 0.5 (c) and 0.75 (d) ppm of biocide at static conditions. In all these figures are possible to see that the smallest semicircle diameters (charge transfer resistance, R_{ct}) were found at the beginning of the test. This fact should be attributed that, at this exposure time, the steel sample was active because it was polished and cleaned. According to this behaviour is possible to say that the highest CR was found at the beginning of the test. In figure 3(a), the highest R_{ct} was found during the first 6 hours, but after this exposure time, the R_{ct} decreased. On the other hand, in figures 4b to 4d, the R_{ct} increased as the exposure time also increased. In general, it is possible to say that the CR decreased as the exposure time increased; this behaviour is attributed to the fact that after a period of exposure time, the surface of the steel sample was covered by a corrosion products film and consequently the CR decreased.

The EIS spectra in figures 4a to 4d show that the R_{ct} values increased and decreased during all exposure time consequently the CR values also decreased and increased. The increment of the CR values can be attributed to the rupture of the corrosion products film by action of the mechanical effects of the fluid movement. On the other hand, the CR decreased should be attributed to the regeneration of this film. Figure 5 shows the electrical equivalent circuit used in fitting of EIS spectra shown in figure 3 and 4, where: R_s is the solution resistance, R_{film} and C_{film} is the resistance and capacitance respectively, of the film formed on surface of the steel sample and C_{dl} is the double layer capacitance.
Impedance spectra analysis using electrical equivalent circuit. Figure 6 shows the CR (calculated with the R_{ct}) obtained by the impedance spectra fitting with R-C double electrical equivalent circuit (for covered metal) shown in figure 5.
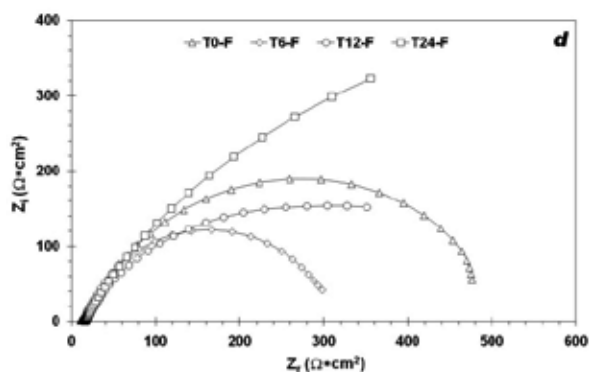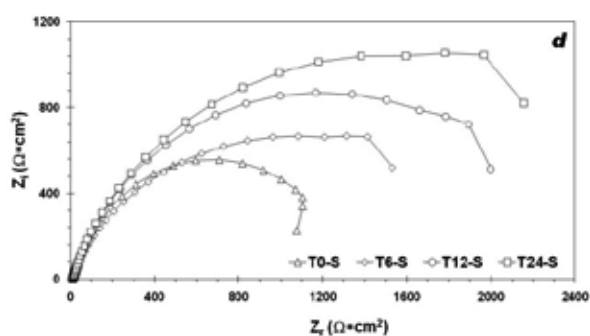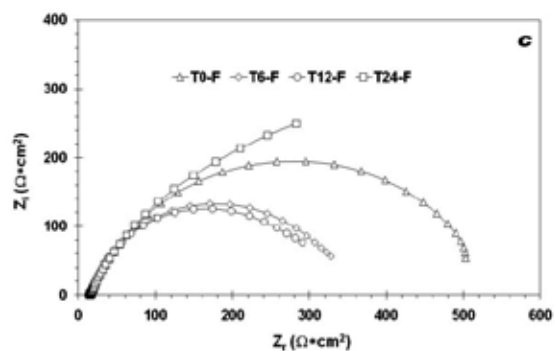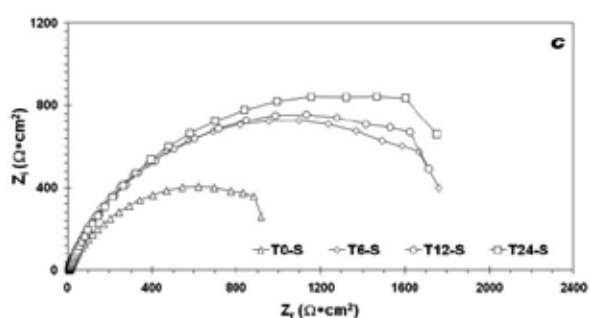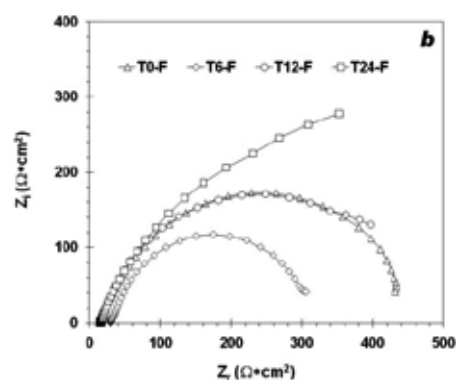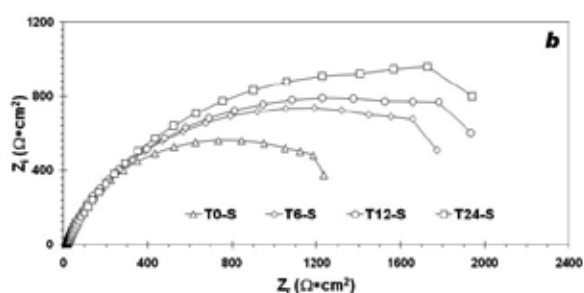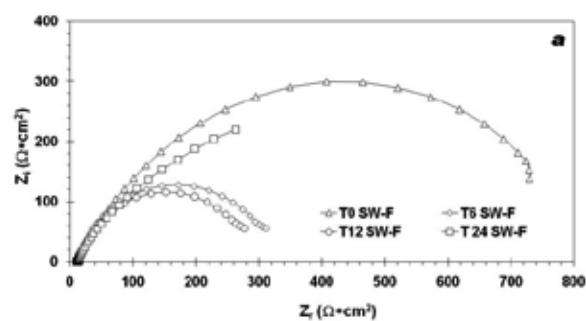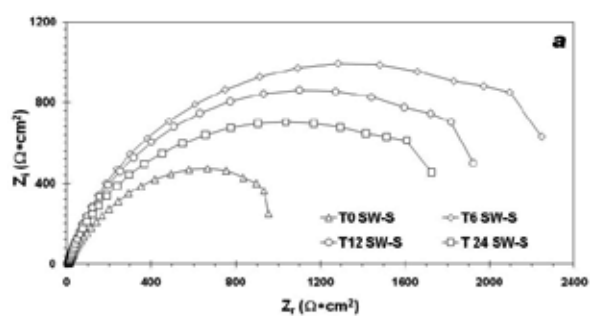
Figure 3 *Measured EIS spectra (Nyquist plot) as a function of time. X52 steel sample immersed in SW (a) and seawater with 0.25 (b), 0.5 (c) and 0.75 ppm (d) of biocide under static conditions during 24 h of the exposure time. Where, 0 (beginning of the test), 6, 12 and 24 corresponds to the hours of the exposure time.*

Figure 4 Measured EIS spectra (Nyquist plot) as a function of time. X52 steel sample immersed in SW (a) and seawater with 0.25 (b), 0.5 (c) and 0.75 ppm (d) of biocide under flow conditions during 24 h of the exposure time. Where, 0 (beginning of the test), 6, 12 and 24 corresponds to the hours of the exposure time
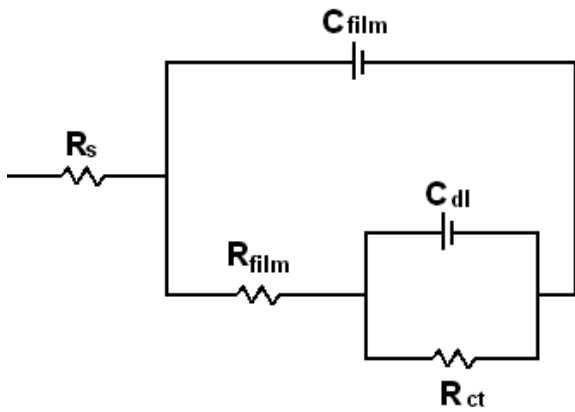
Figure 5 Electrical equivalent circuit used in fitting of EIS spectra shown in figure 3 and 4.

The results showed in figure 6 indicate that the CR is affected by the turbulent flow conditions, as it was mentioned before; it is because all CR values at turbulent flow conditions are higher than the CR values at static conditions. It is important to point out that the behaviour of CR showed in figure 6 is in good agreement with the CR behaviour obtained by LPR (figure 2). In general, at the turbulent flow conditions, the CR in all concentrations has the same behaviour (raise and fall), but, the highest CR values in the majority of the exposure time correspond to SW, this fact suggest that the not-oxidant biocide has a slight protector effects on the steel corrosion.
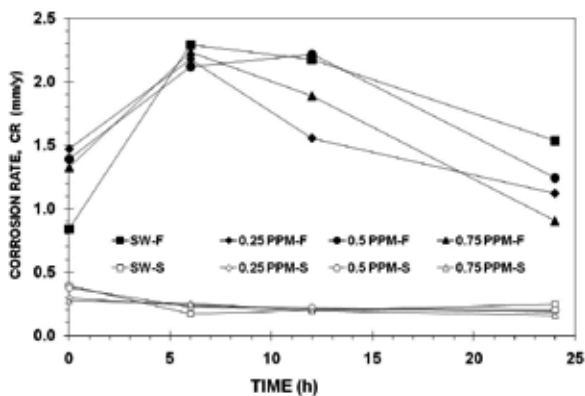
Figure 6 Corrosion rate vs. time obtained by EIS spectra fitting of the figures 3 and 4 by electrical equivalent circuit
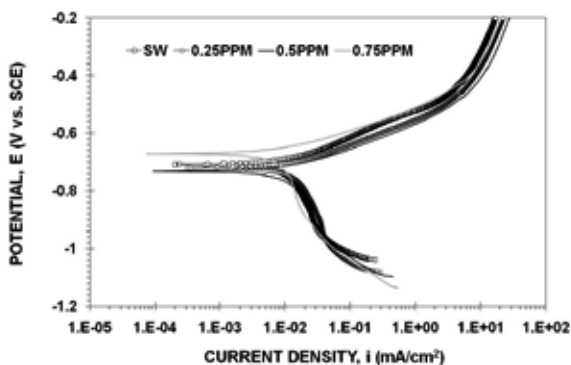
Figure 7 *Polarization curves of X52 steel sample immersed in SW and seawater with 0.25, 0.5 and 0.75 ppm of biocide under static conditions during 24 h of the exposure time.*

Potentiodynamic Polarization curves.

Figure 3 and 4 show the potentiodynamic polarization curves for X52 steel sample immersed in SW and seawater with 0.25, 0.5 and 0.75 ppm of biocide during 24 h at static and turbulent flow conditions.

The anodic branches, in all polarization curves and both conditions (static and turbulent flow) have slopes that should be associated with the charge transfer process. On the other hand, the cathodic branches in all polarization curves and both condition, have slopes that can not be associated with a pure charge transfer resistance process. This fact should be suggesting a contribution of a mass transfer process on the cathodic kinetics mainly at turbulent flow conditions, where the slopes are closer to 90°, it is to say, a limiting current density[34] can be observed.

TABLE 1 *Corrosion parameters obtained from the polarization curves shown in figure 7.*

| Test solution	E_{corr} (mV vs ESC)	i_{corr} (mA cm^{-2})	V_{corr} (mm/year)
SW	-708.0	9.70E-03	0.1125
0.25 ppm	-719.4	1.10E-02	0.1275
0.5 ppm	-731.3	1.40E-02	0.1623
0.75 ppm	-670.4	1.50E-02	0.1739

TABLE 2 Corrosion parameters obtained from the polarization curves shown in figure 8.

Test solution	E_{corr} (mV vs ESC)	i_{corr} (mA cm^{-2})	V_{corr} (mm/year)
SW	-451.6	6.80E-02	0.7884
0.25 ppm	-496.5	9.00E-02	1.0435
0.5 ppm	-479.0	6.20E-02	0.7189
0.75 ppm	-518.0	9.80E-02	1.1363

Table 1 and 2 present the relevant electrochemical parameter calculated from the polarization curves in figure 7 and 8 respectively. The CR values at turbulent flow conditions (table 2) are higher than the CR values at static conditions (table 1). This fact confirms the influence of the turbulent flow on the corrosion process of the steel sample immersed in seawater with different biocide concentration. This behaviour is in good agreement with the behaviours observed in the CR obtained by LPR and EIS techniques.
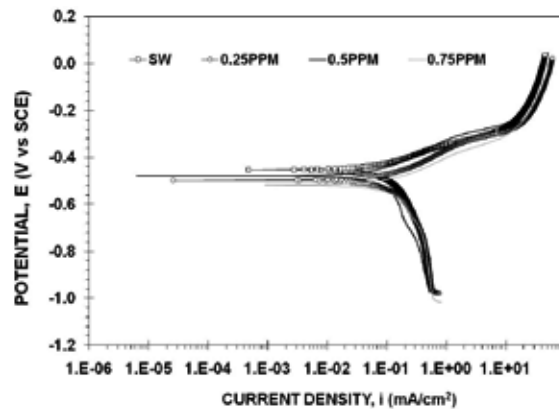
Figure 8 *Polarization curves of X52 steel sample immersed in SW and seawater with 0.25, 0.5 and 0.75 ppm of biocide under turbulent flow conditions during 24 h of the exposure time.*
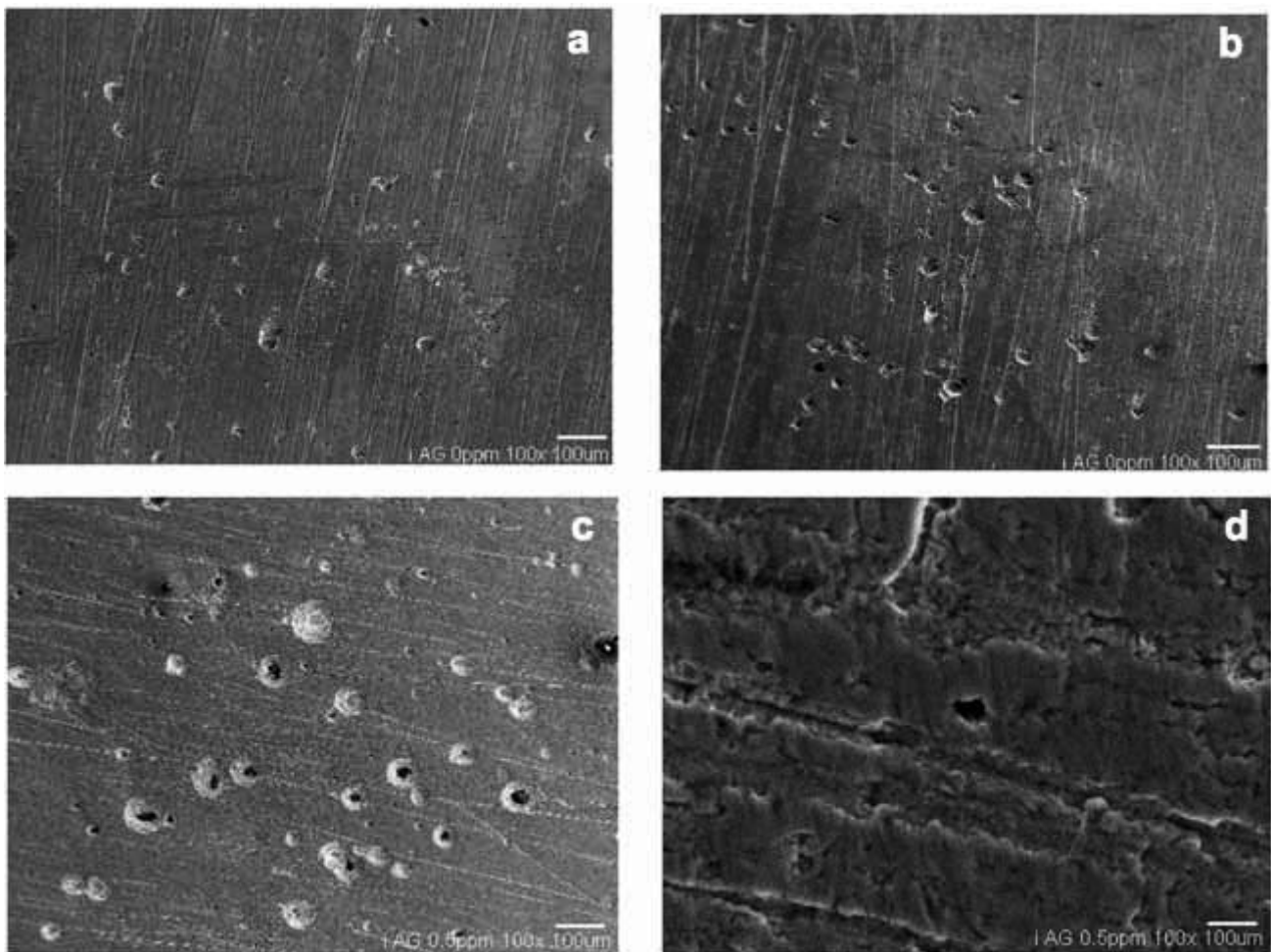
Figure 9 *SEM Micrographs of the morphological attack obtained by the corrosion of the X52 steel immersed in SW (a and b) and seawater with 0.5 ppm of biocide (c and d) at static (a and c) and turbulent flow (b and d) conditions.*

Surface analyses

Figures 9 shows the micrographs obtained by SEM from the selected X52 steel sample exposed to SW (a and b) and seawater with 0.5 ppm (c and d) of biocide at static (a and c) and turbulent flow conditions (b and d). In all microphotographs is possible to see that in both conditions, at static and turbulent flow conditions, a localized corrosion form, specifically, pitting corrosion form was found. It is important to point out that a similar attack was found in the other two test solutions.

CONCLUSIONS

According to electrochemical study of the X52 steel sample exposed to natural seawater and seawater with 0.25, 0.5 and 0.75 ppm of biocide is possible to conclude that the turbulent flow condition can increase the CR of the steel sample immersed in seawater with different biocide concentration. 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. In both conditions and in the cathodic reactions, a contribution of a mass transfer process was found. The results obtained by the LPR, EIS and CPs have good correlation between them. The corrosion form found in the steel sample immersed in seawater and seawater with biocide was localized corrosion.

ACKNOWLEDGMENTS

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