

Corrosion Inhibition of 316L Stainless Steel in LiBr+Etileneglycol+H₂O By Using Inorganic Inhibitors

E. Sarmiento, J. G. González-Rodríguez, A.M. Ramirez-Arteaga, J. Uruchurtu

Universidad Autonoma del Estado de Morelos-CIICAp; Av. Universidad 1001, Col. Chamilpa, 62209-Cuernavaca, Mor., Mexico

*E-mail: ggonzalez@uaem.mx

Received: 9 August 2013 / Accepted: 25 September 2013 / Published: 20 October 2013

A study of the corrosion inhibition of 316L type stainless steel in LiBr (614 g/l) + ethylene-glycol +H₂O by using inorganic inhibitors has been carried out by using potentiodynamic polarization curves, free corrosion measurements and linear polarization resistance measurements. Inhibitors include LiNO₃, Li₂MoO₄ and Li₂CrO₄ at concentrations of 5, 20 and 50 ppm and at 25, 50 and 80⁰C. Polarization curves showed that the addition of 5 ppm of either inhibitor did not affect the corrosion behavior of 316L SS. However, with the addition of higher inhibitor concentrations, both the corrosion and passivation current density values increased, reaching the highest values with the addition of 20 ppm, but the passive region was widened and the pitting potential value was increased. At 25 and 50⁰C the passive behavior of the steel was kept but it did not exist at 80⁰C. For long time testing, linear polarization resistance measurements showed that the corrosion rate was not increased with the addition of either 5 or 20 ppm but it decreased with the addition of 50 ppm of inhibitor. The corrosion resistance decreased with increasing the temperature but the inhibitor efficiency increased. **Nitrates** had a slightly better performance than nitrates and molybdates.

Keywords: Lithium bromide, ethylene glycol, corrosion inhibitors.

1. INTRODUCTION

Lithium bromide (LiBr) has been widely used in absorption refrigeration systems due to its favorable thermophysical properties. Pumps and pipes are required for circulating LiBr solution during the operation of these systems [1]. Although LiBr possesses favorable thermophysical properties it can cause serious corrosion problems in the metallic components in refrigeration systems and heat exchangers in absorption plants [2-21]. Some other disadvantages of the LiBr/water mixtures are: a) low working pressure, b) high corrosion rates at high temperatures, and c) tendency to crystallize at

high LiBr concentrations. An alternative way to reduce some of these disadvantages of the water/LiBr mixture is to add ethylene glycol to the system [22] because some thermo physical properties of the LiBr/water mixture, such as thermal conductivity, viscosity, maximum concentration etc.. are improved [23]. However, there are not data available concerning the corrosion problems that can be found in this system.

Stainless steels are widely used in absorption systems components such as condensers, evaporators and absorbers [2,4,9] due to their high corrosion resistance. Among the different stainless steels, austenitic ones and specially AISI 316L SS is often used for its high corrosion resistance. However, due to the high temperature, LiBr concentration, etc... stainless steels can suffer from severe corrosion problems [2,4,9-11]. For this reason, the expected high corrosion effects of the LiBr aqueous solutions guide us to use corrosion inhibitors added to these environments. However, there exist very few inhibitors which satisfy at the same time both technological and ecological requirements [3]. In practice, inhibitors are used for corrosion control in closed systems and as an alternative of efficiency-cost for materials use. The affectivity of some corrosion inhibitors depends upon the type of material, its properties and the corrosive environment. Chromate (CrO_4^{2-}) is a very effective passivating inhibitor at relatively high levels. It is very effective for ferrous alloys in the presence of halide ions. It can passivate metals by forming mono-atomic or polyatomic oxide film on the electrode surface. Thus, chromates are very good inhibitors to prevent pitting corrosion for stainless steels. Nitrates (NO_3^{2-}) and molybdates (MoO_4^{2-}) are inorganic, passivating inhibitors which have been used satisfactorily in many corrosive environments. For instance, molybdates have been used to prevent mild steel [24] and cold rolling steel [25] corrosion in simulated cooling water, in the zinc corrosion inhibition in acidic solutions [26], used to seal phosphate coatings on hot-dip galvanized steel [27] or on the bacterial corrosion of iron [28]. On the other hand, nitrates have been used on the corrosion inhibition of galvanized steel and aluminum [29] and zinc [30] in NaCl solutions, and on the pit initiation of pure aluminum in HCl solutions [31]. Previously [16], the authors reported the use of chromates, nitrates and molybdates in the corrosion inhibition of 1018 carbon steel in LiBr+ethylene-glycol +H₂O solution and found that both, the corrosion rate and the passive current density decreased with these inhibitors, and, in general terms, inhibitors efficiency increased with inhibitor concentration. Thus, the goal of this work is to evaluate the corrosion rate of 316L type stainless steel (316L SS) in the LiBr+ethylene glycol + water, as new absorber fluid, and evaluate the use of inorganic inhibitors such as CrO_4^{2-} , NO_3^{2-} , MoO_4^{2-} as alternative candidates for organic compounds, less toxic, cheaper, etc...

2. EXPERIMENTAL PROCEDURE

Material tested was commercial 316L type stainless steel, 316L SS, encapsulated in a commercial polymeric resin. Cylindrical probes with 5.9 mm in diameter and an exposed area of 0.2728 cm² to the solution were used. All of them were abraded with papers 600 SiC emery paper, and finally rinsed with distilled water and ethanol (C₂H₅OH). Solution used was a LiBr+ethyleneglycol+H₂O mixture at room temperature, in a concentration of 614 and 217 g/l for LiBr

and ethylene glycol respectively, with additions of 5, 20 and 50 ppm of either LiNO_3 (Lithium Nitrate), Li_2MoO_4 (Lithium Molybdate) and Li_2CrO_4 (Lithium Chromate) as corrosion inhibitors. Polarization curves were obtained by polarizing the specimens from -600 to 600 mV respect to the free corrosion potential value, E_{corr} , at a scanning rate of 60 mV/min. Corrosion current density values, i_{corr} , were calculated by using Tafel extrapolation method. A saturated silver/silver chloride (Ag/AgCl) electrode was used as reference electrode whereas a platinum wire was the auxiliary electrode. Free corrosion potential values as a function of time were taken 3 times a day during 170 hours. The polarization resistance (R_p) was evaluated by running linear polarization resistance (LPR) curves, which were obtained by polarizing the electrode from -10 to +10 mV_{SCE} respect to the free corrosion potential, E_{corr} , at a scan rate of 1 mV/s. All tests were performed at room temperature (25 °C). Some tests were performed at 50 and 80 °C to evaluate the effect of temperature by using a hot plate.

3. RESULTS AND DISCUSSION

The effect of the addition of LiNO_3 in the variation of the E_{corr} value for 316L SS in the LiBr+ethylene-glycol +H₂O solution during 170 hours is shown in Fig.1.

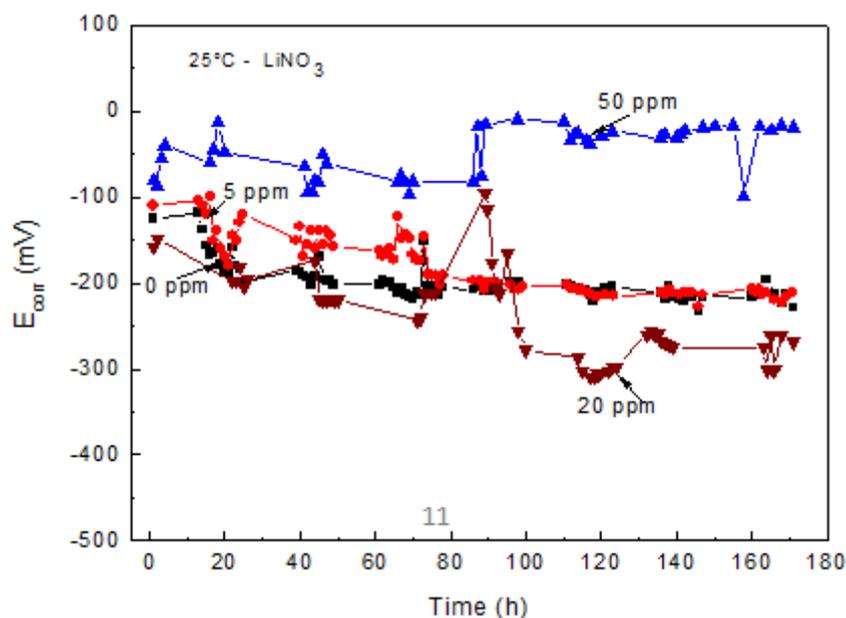


Figure 1. Effect of LiNO_3 concentration in the change of E_{corr} with time for 316L SS in LiBr+ethylene-glycol +H₂O at 25°C.

Generally speaking, the most active potential values, around -300 mV, were obtained with the addition of 20 ppm, whereas the noblest values, around 0 mV, were obtained by adding 50 ppm. The addition of 5 ppm of LiNO_3 had only a marginal effect on the E_{corr} value as compared to the uninhibited solution. In all cases except when 50 ppm of LiNO_3 were added, the E_{corr} value shifted towards more active values as time elapsed, indicating that the steel surface is becoming more active.

The E_{corr} value remained more or less constant with the addition of 50 ppm of LiNO_3 , indicating a very stable film formed by corrosion products and inhibitor. Nitrate is normally an anodic type of inhibitor. If nitrate concentration is low, all anodic sites will not be passivated, and the cathodic sites will remain unchanged. As a consequence, the nitrate activity on the remaining anodic sites will be severe, leading to pitting. However, the inhibiting effect of nitrate decreases gradually (and not sharply) below the critical concentration due to its second inhibiting function as a cathodic polarizer [35]. This is the reason why for low nitrate concentrations, the E_{corr} value shifts towards more active values, while at the highest concentration, i.e. 50 ppm, the E_{corr} value remains more or less constant, indicating the presence of a more protective film on the steel surface.

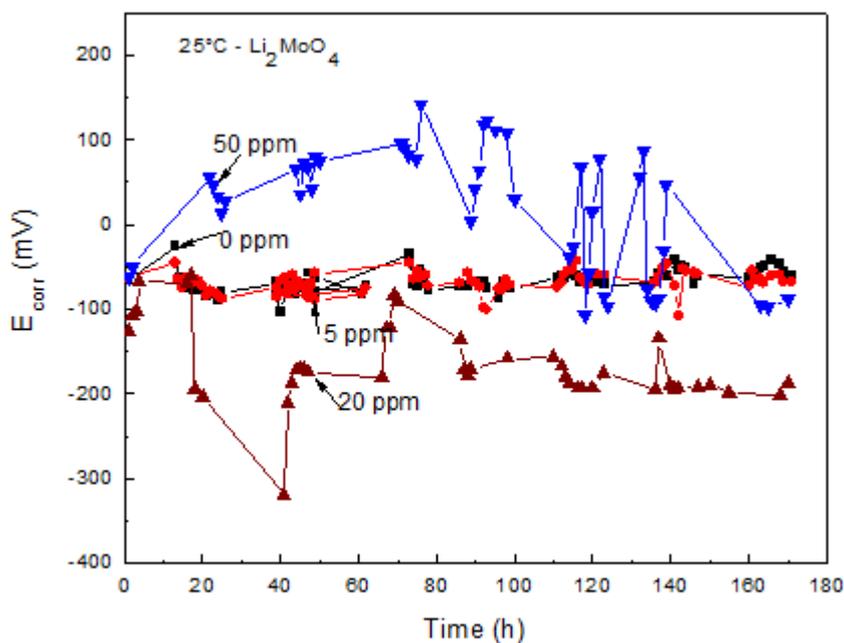


Figure 2. Effect of Li_2MoO_4 concentration in the change of E_{corr} with time for 316L SS in $\text{LiBr} + \text{ethylene-glycol} + \text{H}_2\text{O}$ at 25°C .

When Li_2MoO_4 was added, Fig. 2, the E_{corr} values for the uninhibited solution and that with the addition of 5 ppm of inhibitor were virtually the same and remained more or less constant throughout the test. The most active E_{corr} values, nearly -200 mV, were obtained when 20 ppm of Li_2MoO_4 were added whereas the noblest values, approximately 100 mV, were obtained with 50 ppm. It has been observed that the diminution of the active dissolution of the metal when molybdenum is added to the alloy, such as the amount content in 316L type stainless steel is attributed to the formation of a sub-film on the molybdenum enriched surface [30]. Although the observation of the Mo concentration on the electrode surface has not been done it has been considered that Mo could not enrich this surface in bromide solutions. Thus, it is very likely that in the case of 316L type stainless steel, MoO_2 is incorporated into the $\text{Cr(III)-oxide/hydroxide}$ and $\text{Fe(II)/(III)-oxide/hydroxide}$ layer.

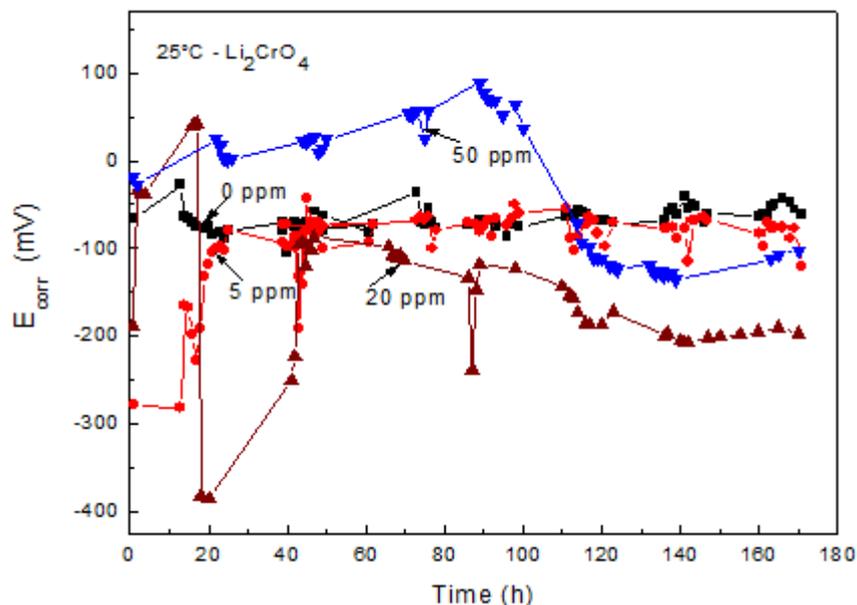


Figure 3. Effect of Li_2CrO_4 concentration in the change of E_{corr} with time for 316L SS in LiBr+ ethylene-glycol + H_2O at 25°C .

A similar situation was obtained when Li_2CrO_4 was used, Fig. 3: the most active E_{corr} value, close to -200 mV, was obtained with the addition of 20 ppm of inhibitor, whereas the noblest value, close to 100 mV, was reached when 50 ppm of Li_2CrO_4 were added. Igual-Muñoz et al. ¹⁵ found that the E_{corr} value shifted towards nobler values, as compared with the uninhibited solution, when low Li_2CrO_4 concentrations were used, i.e. 0.016M , but when the inhibitor concentration increased up to 0.032M , the E_{corr} value shifted towards more active values. Chromate is normally an anodic type of inhibitor. If chromate concentration is low, all anodic sites will not be passivated, and the cathodic sites will remain unchanged. As a consequence, the chromate activity on the remaining anodic sites will be severe, leading to pitting. However, the inhibiting effect of chromate decreases gradually (and not sharply) below the critical concentration due to its second inhibiting function as a cathodic polarizer [35]. This is the reason why for low chromate concentrations, the E_{corr} value shifts towards more active values, while at the highest concentration, i.e. 50 ppm, the E_{corr} value remains more or less constant, indicating the presence of a more protective film on the steel surface. Thus, it has been shown that the noblest E_{corr} value is obtained with the addition of either inhibitor, whereas the most active value is obtained when 20 ppm of inhibitor are added. Isaacs et al. [36] proved that Cr(VI) is only weakly adsorbed on to passive films and does not withstand simple washing of the surface except after exposure to concentrated solutions and only when the growth rate of the oxide has dropped. This means that under these conditions the Cr(VI) is probably incorporated into the oxide formed of an inner Cr(III)-oxide layer and a very thin outer layer of Fe(II)/(III)-oxide ³²⁻³⁴ and when the LiBr solution does not contain chromate the only way to incorporate Cr(VI) to the surface is from the alloy,

The effect of LiNO_3 addition in the polarization curves for 316L steel in the LiBr+ ethylene-glycol + H_2O solution is shown in Fig. 4. It can be seen that in the uninhibited solution, steel shows an active-passive behavior, with an E_{corr} value around -210 mV and an i_{corr} value close to 10^{-7} A/cm². The

passive region was very stable and started at a passivation potential value, E_{pas} , around -170 mV and a pitting potential, E_{pit} , close to 10 mV. The passive current density value was the same as the i_{corr} value, i.e. $10^{-7} A/cm^2$. It has been shown that passive films formed in stainless steels consists mainly of a mixture of iron and chromium oxides, with hydroxide and H_2O -containing compounds concentrated in the outermost region of the film and chromium oxide enrichment in the inner region (metal/film interface) [32-34]. Thus the passive film formed on the stainless steel surface consists of an inner Cr(III)-oxide/hydroxide layer and a very thin outer layer of Fe(II)/(III)-oxide hydroxide.

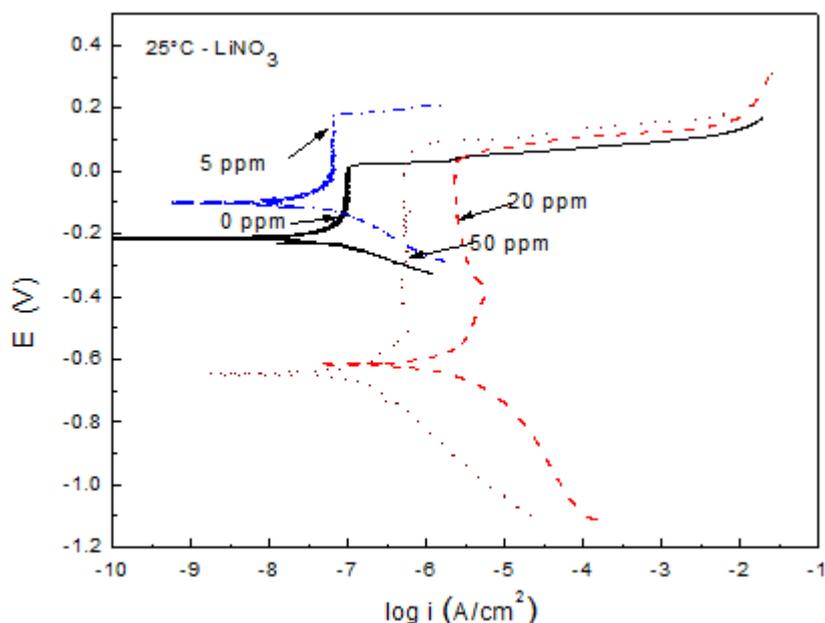


Figure 4. Effect of $LiNO_3$ concentration in the polarization curves for 316L SS in LiBr+ ethylene-glycol + H_2O at $25^{\circ}C$.

With the addition of 5 ppm of $LiNO_3$ all these parameters are improved, including a decrease in the i_{pas} and an increase in the E_{pit} values. However, with the addition of either 20 or 50 ppm of $LiNO_3$, the passive current density value increased and the pitting potential value decreased, obtaining the worst values when 20 ppm of inhibitor are added. However, the passive region becomes wider than that found for the uninhibited solution or with the addition of 5 ppm, since it was around 160-180 mV wide in the latter, compared with 500 mV wide when 50 ppm of inhibitor was added.

When Li_2MoO_4 is used, Fig. 5, the polarization curves for the uninhibited solution and that obtained with the addition of 5 ppm of inhibitor were virtually the same, however, the i_{corr} and i_{pas} values increased with the addition of either 20 or 50 ppm, reaching their highest values with 20 ppm, but the E_{pit} value increased slightly. Once again, similar to that found with $LiNO_3$, the passive region was very stable and much wider with the addition of either 20 or 50 ppm, nearly 700 mV wide for the latter, wider than that obtained for the uninhibited solution or with the addition of 5 ppm of Li_2MoO_4 . Liang et al. [37] evaluated the inhibition performance of Li_2MoO_4 for carbon steel in 55% LiBr

solution by means of chemical immersion, electrochemical measurements, and physical detection technologies.

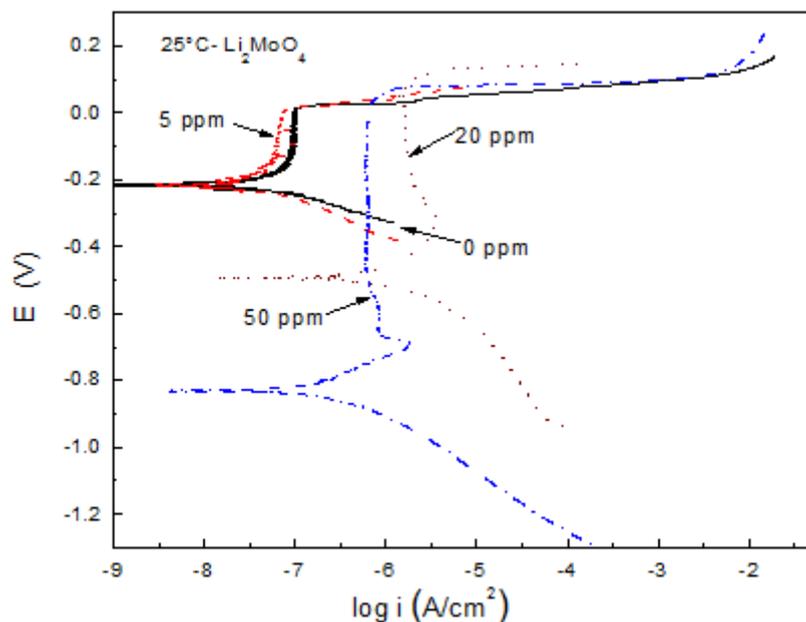


Figure 5. Effect of Li_2MoO_4 concentration in the polarization curves for 316L SS in LiBr+ ethylene-glycol + H_2O at 25°C .

Results indicated that Li_2MoO_4 showed excellent inhibition performance of carbon steel in 55 % LiBr solution, especially at high temperature. With increasing the temperature of solution from 160 to 240°C , the corrosion rates of carbon steel increased from 17.67 pm/a to 33.07 pm/a. Li_2MoO_4 might improved the anodic polarization performance of carbon steel and widen the passive potential region of carbon steel in 55% LiBr solution. Passive film was composed mainly of Fe_3O_4 and MoO_2 . Tanno et al. [38] found similar results when evaluating the corrosion inhibition of carbon steel by MoO_4^{2-} in LiBr solutions at 120 and 160°C and found that passive films were always composed of magnetite with incorporation of inhibitor.

Finally, when 5 ppm of Li_2CrO_4 is added, Fig. 6, the polarization curve was virtually the same to that exhibited in the uninhibited solution, with an active-passive behavior and a very stable passive film which has been reported to be formed on the stainless steel surface consists of an inner Cr(III)-oxide/hydroxide layer and a very thin outer layer of Fe(II)/(III)-oxide/hydroxide and some Cr(VI) from inhibitor is only weakly adsorbed on to passive films.³⁶ However, when 20 or 50 ppm of Li_2CrO_4 were added, the passive film is not as stable as that shown in the previous cases, since this time it was not so clear where the passive region started, and therefore an E_{pas} was not so evident, and the i_{pas} values were very close to each other in both cases.

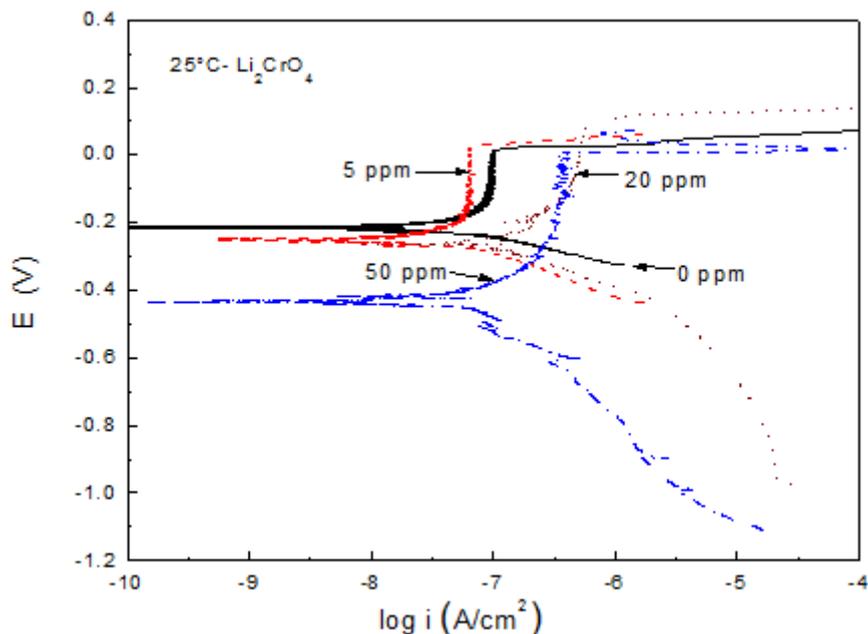


Figure 6. Effect of Li_2CrO_4 concentration in the polarization curves for 316L SS in LiBr+ ethylene glycol + H_2O at 25°C .

The anodic current density value in the passive region exhibited some transients, indicating that the passive film formed with the addition of either 20 or 50 ppm of Li_2CrO_4 was not very stable, and the pitting potential values were very close to those found in the uninhibited solution. Thus, the worst passive film seems to be found with the addition of Li_2CrO_4 , whereas in the case of LiNO_3 or Li_2MoO_4 , the highest passive current density values were found with the addition of 20 ppm of inhibitor, the widest passive zone is found with 50 ppm, and the addition of 5 ppm of inhibitor practically did not have any effect in the polarization curve. Igual-Muñoz et al. [15] evaluated the electrochemical behavior of duplex stainless steel (DSS) in LiBr media was investigated by anodic cyclic polarization curves and AC impedance measurements. The effects of bromide concentration and the presence of chromate in the solutions on the corrosion behavior of AISI 2205 were studied. Cyclic polarization curve analyses showed that there was different pitting susceptibility of passive films depending on the LiBr concentration. Pitting potential decreases with LiBr concentration. Chromate presence displaced pitting potentials towards more positive values at low LiBr concentrations but it did not have any effect when LiBr concentration increased.

In order to evaluate the effect of the temperature, since most of refrigeration systems and heat exchangers in absorption plants operate at temperatures higher than 25°C , some tests were performed at 50 and 80°C but only during 24 hours due to evaporation and crystallization problems, and the results of the effect of temperature in the polarization curves for uninhibited solution and the one with the addition of 5 ppm of Li_2CrO_4 are shown in Fig. 7.

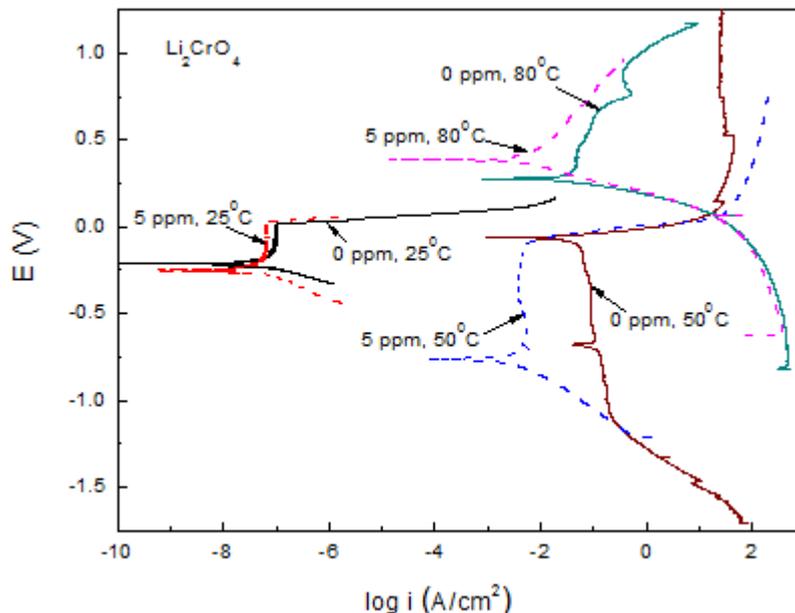


Figure 7. Effect of temperature in the polarization curves for 316L SS in LiBr+ ethylene-glycol +H₂O at 25⁰C+ Li₂CrO₄.

This figure shows that the steel shows a passive region at the three temperatures with or without the addition of inhibitor, although the passive current density at 80⁰C is not as stable as it is at 25 or 50⁰C, indicating that the passive film at this temperature is not as stable as at low temperatures.

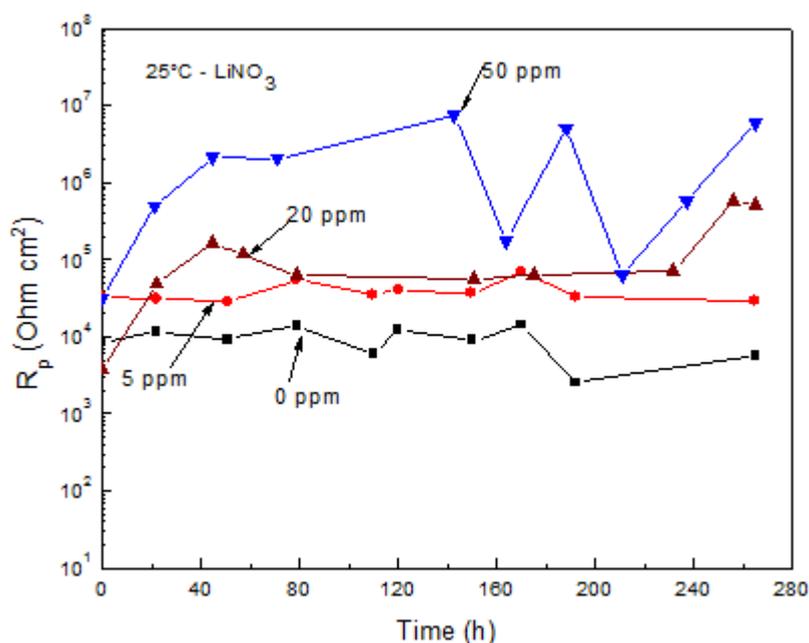


Figure 8. Effect of LiNO₃ concentration in the change of R_p with time for 316L SS in LiBr+ ethylene-glycol +H₂O at 25⁰C.

The passivation range widened when the temperature increased from 25 to 50°C. At the same inhibitor concentration, both the i_{corr} and i_{pas} values increased with the temperature, however this effect was much more pronounced when the temperature increased from 25 to 50°C than when the temperature increased from 50 to 80°C. It can also be seen that, at a given temperature, both the i_{corr} and i_{pas} values decreased with the addition of the inhibitor, indicating that the beneficial effect of the inhibitor is kept at least up to 80°C. Igual-Muñoz et al. [21] evaluated the corrosion resistance of different austenitic stainless steels in chromate-containing LiBr solutions at 25, 50, 75 and 85°C, and found that the E_{corr} value shifted towards nobler values with increasing the temperature, and the i_{corr} value increased with the temperature. They also found that there was passivation at temperatures lower than 50°C and the passivation range narrowed with increasing the temperature.

The change in the R_p value with time at different $LiNO_3$ concentrations is given in Fig. 8, where it can be seen that the R_p value increased with the inhibitor concentration; the lowest value, and thus the highest corrosion rate, was for the uninhibited solution, with a value around 10,000 ohm cm², whereas the highest value, more than two orders of magnitude, was obtained with the addition of 50 ppm of $LiNO_3$. With a few exceptions, the R_p values in all cases were very stable as time elapsed, indicating a very stable protective film. The R_p values obtained by adding either 5 or 20 ppm were very similar with each other, slightly higher than those values obtained for the uninhibited solution, but lower than those obtained with 50 ppm. Inhibition efficiencies [IE(%)] can be determined according to the following equation:

$$E(\%) = \frac{R_{p,i} - R_{p,b}}{R_{p,i}} \times 100 \tag{1}$$

where $R_{p,b}$ is the linear polarization resistance without inhibitor and $R_{p,i}$ is the linear polarization resistance with inhibitor.

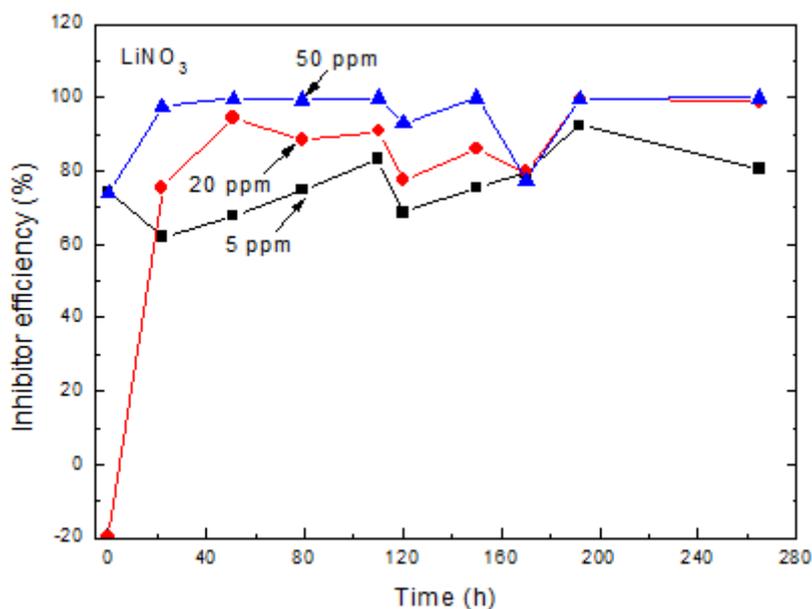


Figure 9. Effect of $LiNO_3$ concentration in the inhibitor efficiency for 316L SS in LiBr+ ethylene-glycol +H₂O at 25°C.

Results for LiNO_3 are shown in Fig. 9. This figure shows that the inhibitor efficiency increased with the concentration, and the lowest efficiency was obtained with the addition of 5 ppm of LiNO_3 , with an average value of 70%, although towards the last days values as high as 80-90% were reached. The highest inhibitor efficiency was obtained by adding 50 ppm of LiNO_3 , with values higher than 90% throughout the test. At the beginning of the test, the inhibitor efficiency values for 20 and 50 ppm of inhibitor were similar or lower than obtained with 5 ppm, as evidenced by polarization curve in Fig. 4, which may be due to the fact that, at the beginning of the experiment the protective film formed at high inhibitor concentrations is not very stable, but it becomes more stable as time elapsed.

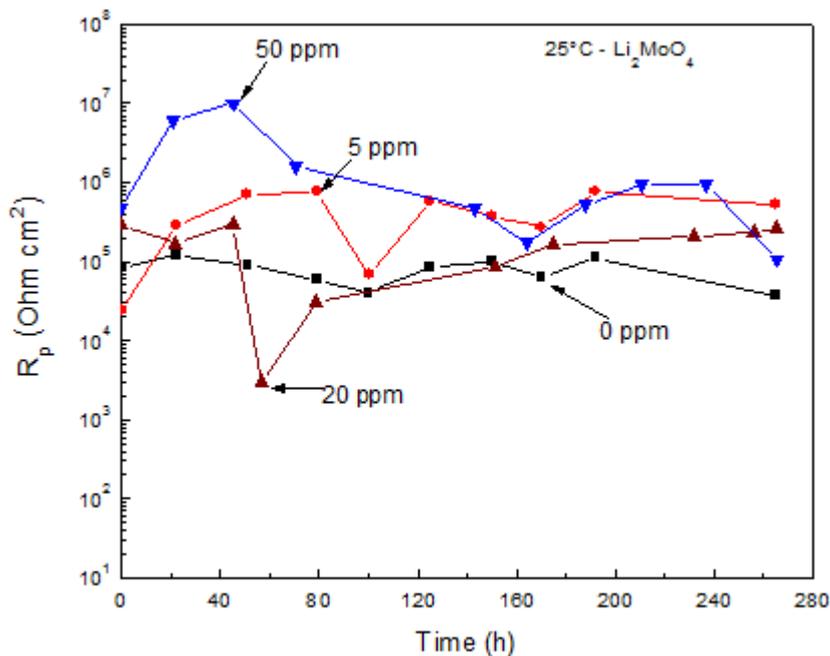


Figure 10. Effect of Li_2MoO_4 concentration in the change of R_p with time for 316L SS in LiBr+ethylene-glycol + H_2O at 25°C .

When Li_2MoO_4 is added to the system, Fig. 10, the lowest R_p values, and thus the highest corrosion rates, were obtained for the uninhibited solution and with the addition of 20 ppm of inhibitor, whereas the lowest corrosion rates were found with the addition of 50 ppm. This is confirmed with Fig. 11, where the lowest inhibitor efficiency values were obtained when 20 ppm of inhibitor are added, obtaining even negative efficiency values, which means that in these cases, the corrosion rate increases with the addition of the inhibitor. On the other hand, the highest inhibitor efficiency values were obtained with the addition of 50 ppm of Li_2MoO_4 , very similar to those found with 50 ppm of LiNO_3 , with a slight trend to decrease towards the end of the test.

Molybdenum is an essential element for the improvement of pitting corrosion resistance, since it acts synergistically with chromium and nitrogen [26]. The enhanced passivation behavior in the presence of Mo was reported to be caused by adsorption of molybdates or formation of Mo-rich precipitates, which decreased the rate of anodic metal dissolution.

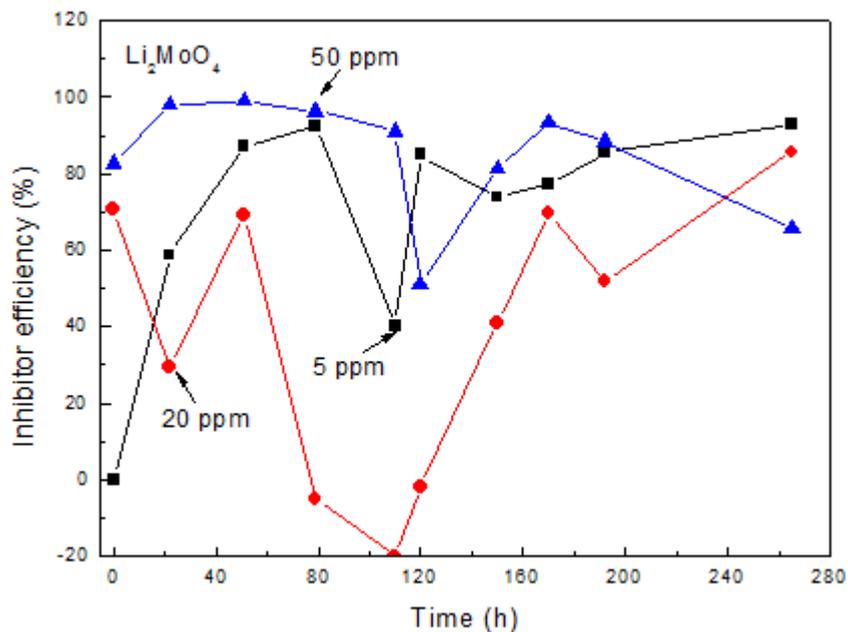


Figure 11. Effect of Li_2MoO_4 concentration in the inhibitor efficiency for 316L SS in LiBr+ ethylene-glycol + H_2O at 25°C .

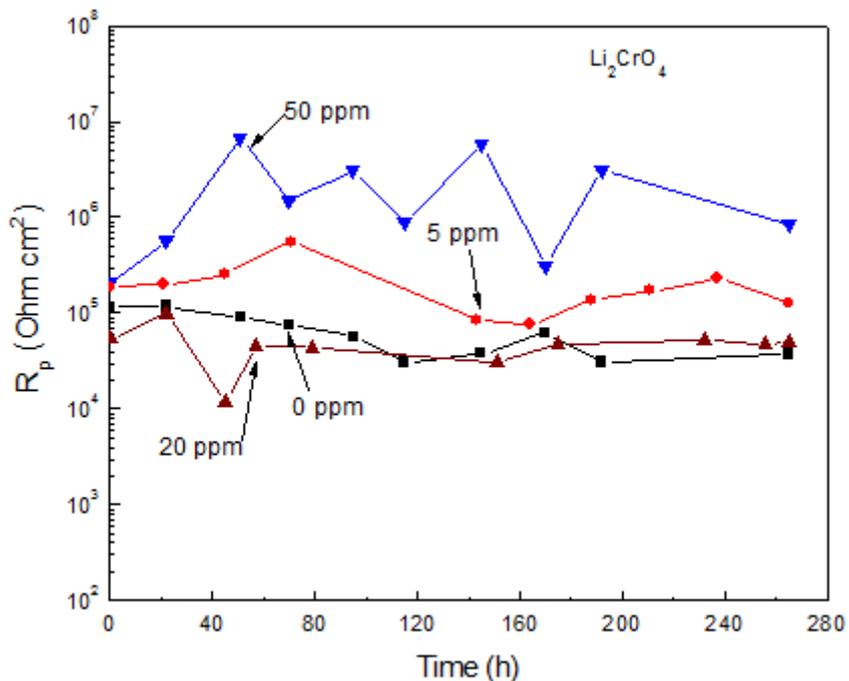


Figure 12. Effect of Li_2CrO_4 concentration in the change of R_p with time for 316L SS in LiBr+ ethylene-glycol + H_2O at 25°C .

Finally, with the addition of Li_2CrO_4 , Fig. 12, the highest corrosion rates were obtained in the uninhibited solution and by adding 20 ppm of inhibitor, whereas the lowest corrosion rates were

obtained with the addition of 50 ppm. This behavior was very similar to the effect found with Li_2MoO_4 , Fig. 10. It is well known that although Cr_2O_3 can passivate by forming insoluble films, it may also promote corrosion by activating the cathodic reaction [30]. It is generally accepted that Cr_2O_3 based products form barrier layers and they are responsible for the superior corrosion resistance of stainless steels [30].

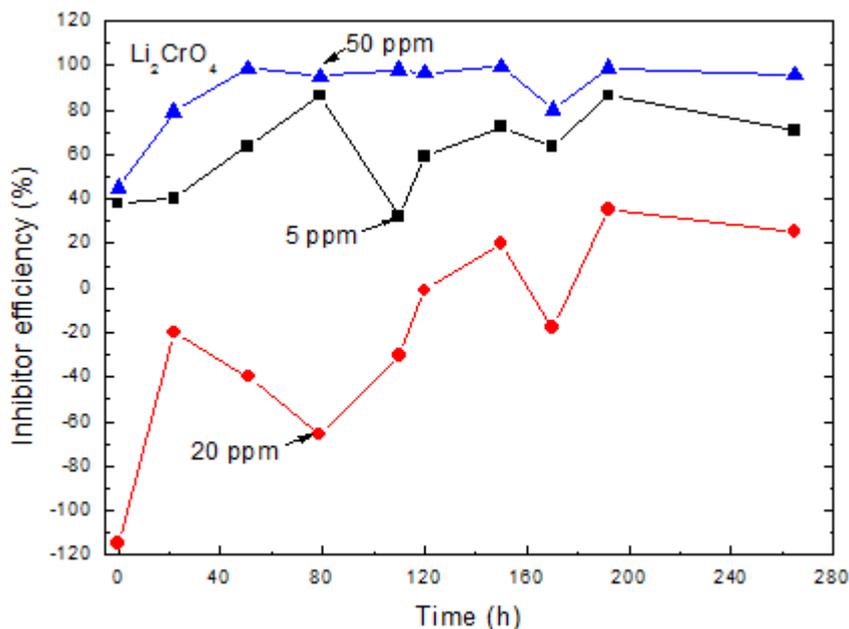


Figure 13. Effect of Li_2CrO_4 concentration in the inhibitor efficiency for 316L SS in $\text{LiBr} + \text{ethylene-glycol} + \text{H}_2\text{O}$ at 25°C .

Table 1. Summary of the effect of the inhibitor concentration and temperature in the inhibitor efficiency value (%).

Inhibitor concentration (ppm)	LiNO_3	Li_2MoO_4	Li_2CrO_4
5	79	65	64
20	91	42	1
50	97	91	97

The lowest inhibitor efficiency values were obtained by adding 20 ppm of inhibitor, Fig. 13, and, as expected, the highest efficiency was obtained with 50 ppm. Inhibitor efficiency values obtained with 50 ppm of Li_2CrO_4 was very similar to those found with either LiNO_3 or Li_2MoO_4 , higher than 90%, but this time this efficiency value was kept during the whole test, indicating that the film formed inhibitor by chromates is very stable with time. These results can be summarized in table 1, which shows that for LiNO_3 the inhibitor efficiency increased with its concentration, however, for both Li_2MoO_4 and $\text{Li}_2\text{Cr}_2\text{O}_4$ a decrease can be seen at 20 ppm but at 50 ppm the inhibitor efficiency

increases. From this table it is also evident that at 5 and 20 ppm, the lowest inhibitor efficiency value was obtained with $\text{Li}_2\text{Cr}_2\text{O}_4$ with the best performance obtained with the addition of LiNO_3 . Igual-Muñoz et al. [15] found similar results but by using electrochemical impedance spectroscopy (EIS) measurements when using 3M LiBr solution, since when 0.016M $\text{Li}_2\text{Cr}_2\text{O}_4$ was added, the film and charge transfer resistance values were decreased as compared to those values found for uninhibited solution, increasing, thus the corrosion rate, but these parameter values increased with a further increase in the $\text{Li}_2\text{Cr}_2\text{O}_4$ concentration, decreasing the corrosion rate [15]. Chromate is an anodic, passivating inhibitor, which if applied in low concentrations, the passive film might not be complete and all anodic sites will not be passivated, and the cathodic sites will remain unchanged. As a consequence, the chromate activity on the remaining anodic sites will be severe, leading to pitting. Once a critical concentration is reached, the passive film covers most of the surface leaving very few anodic sites uncovered and the corrosion rate decreases. In uninhibited solutions, passive films on 316L type stainless steel is composed mainly of iron and chromium oxides, but when they are in presence of anodic type of inhibitors such as nitrate, molybdate or chromates, these ions are incorporated into the passive film to improve it. At the beginning of the test, passive film is not as protective as when these ions are being incorporated into it, and as time elapses, the protectiveness of the passive film improves and the corrosion rate decreases if there is enough inhibitor. If there is not enough inhibitor, the protectiveness of the passive film will last a short time as indicated in Figs. 8-13.

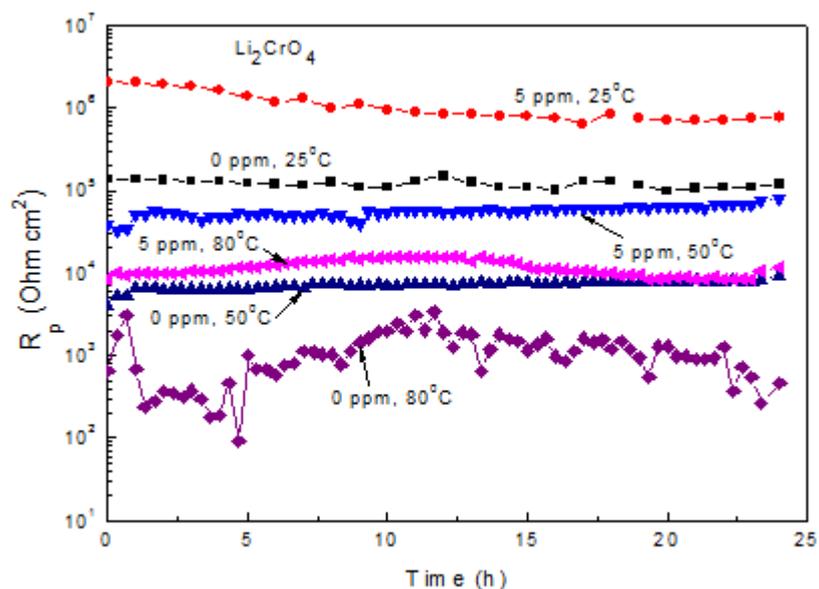


Figure 14. Effect of temperature in the R_p value for 316L SS in LiBr+ ethylene-glycol + H_2O + Li_2CrO_4 at 25°C.

Since the efficiency values obtained with 5 ppm of Li_2CrO_4 was very similar to those obtained with 50 ppm, some tests at higher temperatures, i.e. 50 and 80°C were performed, and the results are shown in Figs. 14-15 during 24 hours only. Fig. 14 shows that at the same temperature, the R_p value for uninhibited solution was always lower when the inhibitor was added, and that the R_p value decreases with the temperature, indicating an increase in the corrosion rate. When the temperature

increases from 25 to 50°C, Fig. 15, the inhibitor efficiency either decreases or remains constant, but when it increases up to 80°C, the inhibitor efficiency increases, but the corrosion rates remain high.

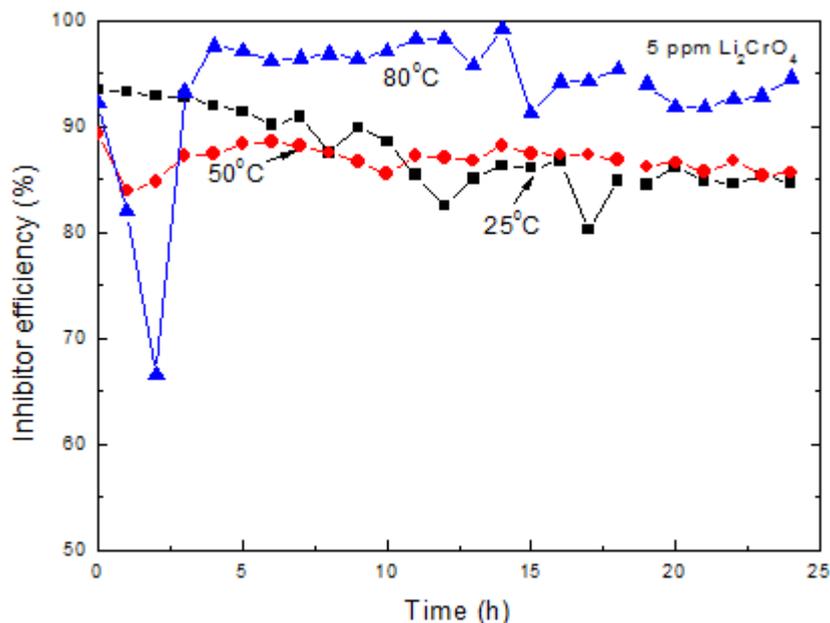


Figure 15. Effect of temperature in the inhibitor efficiency for 316L SS in LiBr+ ethylene-glycol +H₂O+ Li₂CrO₄.

The results reveal that the properties of the passive film can be degraded as temperature increases. Temperature favors the activity of aggressive anions. Moreover, temperature decreases the protective properties of the film. Researchers propose two reasons for this behavior [40]: (a) the porosity of the passive film increases with temperature, (b) the passive film undergoes an intrinsic modification of its chemical composition and/or physical structure. The passive film degradation is observed in the pitting potential drop, the passivation current density increment and its absence as the solution temperature increases. The resistance to generalized and localized corrosion decreases as temperature increases for 316L type stainless steel. This influence of the temperature on the corrosion behavior of 316L type stainless steel seems similar to that reported by other authors for halide pitting in stainless steels [39,40].

4. CONCLUSIONS

A study of the effect of nitrates, molybdates and chromates on the corrosion behavior of 316L type stainless steel at 5, 20 and 50 ppm and 25, 50 and 80 °C in LiBr+ ethylene-glycol +H₂O has been carried out. It was found that at short times, i.e. in the polarization curves, the addition of 5 ppm of either inhibitor did not affect the corrosion behavior of 316L SS. However, with the addition of higher inhibitor concentrations, both the i_{corr} and i_{pas} values increased, reaching the highest values with the

addition of 20 ppm, but the passive region was widened and the E_{pit} value was increased. At 50 °C the passive behavior of the steel was kept but it did not exist at 80 °C. For long time testing, linear polarization resistance measurements showed that the corrosion rate increased with the addition of 20 ppm but it decreased with 50 ppm of inhibitor. The corrosion resistance decreased with increasing the temperature but the inhibitor efficiency increased. Nitrates had a slightly better performance than nitrates and molybdates.

References

1. S.K. Verma, M.S. Mekhjian, G.R. Sandor, N. Nakad, "Corrosion inhibitor in lithium bromide absorption fluid for advanced and current absorption cycle machines", ASHRAE Trans. 105 (1999), p. 813.
2. R. Sánchez-Tovar, M.T. Montañés, J. García-Antón, *Corros. Sci.* 73 (2013) 365.
3. Chunhuan Luo, Qingquan Su, *Corros. Sci.* 74, (2013) 290
4. M.T. Montañés, R. Sánchez-Tovar, J. García-Antón, V. Pérez-Herranz, *Int. J. Electrochem. Sci.*, 5 (2010)1934.
5. D. Itzhak, O. Elias , Y. Greenberg, *Corrosion* 52 (1996) 72.
6. R. Leiva-García, M.J. Muñoz-Portero, J. García-Antón, *Corros. Sci.* 52 (2010) 950.
7. E. Martínez Meza, J. Uruchurtu Chavarín and J. Genescá Llongeras, *Corrosion* 65 (2009) 461.
8. E.A. Abd El Meguid, N.K. Awad, *Corros. Sci.* 51 (2009) 1134.
9. V. Guiñón-Pina; A. Igual-Muñoz; J. García-Antón, *Int. J. Electrochem. Sci.* 6 (2011) 6123.
10. A. Igual Muñoz, J. García Antón, J. L. Guiñón and V. Pérez Herranz, *Corrosion* 60 (2004) 982.
11. R. Sánchez-Tovar, M.T. Montañés, J. García-Antón, *Corros. Sci.* 60 (2012) 118.
12. Masayuki Itagaki, Yoichi Hirata, Kunihiro Watanabe, *Corros. Sci.* 45, (2003) 1023.
13. E. Sarmiento, J. Uruchurtu, J.G. González-Rodríguez, C. Menchaca, O. Sarmiento , *Corrosion* 67 (2011) 105004-1.
14. R. Leiva-García, M.J. Muñoz-Portero, J. García-Antón, R. Sánchez-Tovar, *Int. J. Electrochem. Sci.* 7 (2012) 1332.
15. A. Igual Muñoz, J. García Antón, J.L. Guiñón, V. Pérez Herranz, *Corros. Sci.* 49 (2007) 3200.
16. E. Samiento-Bustos, J.G. González Rodríguez, J. Uruchurtu, G. Dominguez-Patiñoa, V.M. Salinas-Bravo, *Corros. Sci.* 50, (2008) 2296.
17. A. Igual Muñoz, J. García Antón, J.L. Guiñón, V. Pérez Herranz, *Corros. Sci.* 48 (2006) 4127.
18. Xianqi Hu, Chenghao Liang, *Mat. Chem. Phys* 110 (2008) 285.
19. D.M. García-García, E. Blasco-Tamarit, J. García-Antón, *Int. J. Electrochem. Sci.* 6 (2011) 1237.
20. D. Itzhak and O. Elias, *Corrosion* 50 (1994) 131.
21. A. Igual Muñoz, J. García Antón, S. López Nuévalos, J.L. Guiñón, V. Pérez Herranz, *Corros. Sci.* 46 (2004) 2955.
22. W. Rivera, R.J. Romero, M.J. Cardoso, J. Aguillón, R. Best, *Int. Journal Energy Research* 26 (2002) 747.
23. R.J. Romero, P.M.A. Basurto, H.A.H Jiménez, M.J.J. Sánchez, *Solar Energy* 80 (2006) 177.
24. Guannian Mu, Xianghong Li, Qing Qu, Jun Zhou, *Corros. Sci.* 48 (2006) 445.
25. Dihua Wang, Xiao Tang, Yinyan Qiu, Fuxing Gan, George Zhweng Chen, *Corros. Sci.* 47 (2005) 2157.
26. Bi-Lang Lin, Jin-Tang Lu, Gang Kong, *Corros. Sci.* 50 (4) (2008) 962.
27. Y.C. Chen, C.M. Lee, S.K. Yen, S.D. Chyou, *Corros. Sci.* 49 (2007) 3917.
28. A.M. Cabral, W. Trabelsi, R. Sierra, M.F. Montemenor, M.L. Zheludkevich, M.G.S. Ferreira, *Corros. Sci.* 48 (2006) 3740.
29. Kunitsugu Aramaki, *Corros. Sci.* 43 (2001) 2201.

30. Kyung-Hwan Na, Su-II Pyun, *Corros. Sci.* 48 (2007) 2663
31. Heming Wang, Robert Akid, *Corros. Sci.* 50 (2008) 1142
32. J.L. Polo, E. Cano, J.M. Bastidas, *J. Electroanal. Chem.* 537 (2002) 183.
33. A. Galal, N.F. Atta, M.H.S. Al-Hassan, *Mat. Chem. Phys.* 89 (2005) 38.
34. C.M. Abreu, M.J. Cristo´bal, X.R. Nóvoa, G. Pena, M.C. Pérez, *Electrochim. Acta* 49 (2004) 3049.
35. A. Bahadur, *Canadian Metallurgical Quarterly* 37 (1998) 459.
36. H.S. Isaacs, S. Virtanen, M.P. Ryan, P. Schmuki, L.J. Oblonsky, *Electrochim. Acta* 47 (2002) 3127.
37. C. Liang, X. Hu, *J. Iron. Steel Res. Int.*, 15 (2008) 49.
38. K. Tanno, M. Itoh, H. Sekiya, H. Yashiro, N. Kumagai, *Corros. Sci.* 34 (1993) 1453.
39. A. Pardo, E. Otero, M.C. Merino, M.D. Lopez, M.V. Utrilla, F. Moreno, *Corrosion* 56 (2000) 411.
40. L.F. Garfias-Mesias, J.M. Sykes, *Corros. Sci.* 41 (1999) 959.