

Full Length Research Paper

Electrochemical behaviour of some copper alloys in sodium chloride solutions containing different inorganic additives

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The corrosion behavior of Cu-Fe and Cu-Fe-Al was studied in NaCl solutions without and with different concentrations of some inorganic additives, Na_2MoO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, and KIO_3 . The measuring techniques used were, open-circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The potentiodynamic polarization measurements indicated that the corrosion current, I_{corr} , of Cu-Fe is less than that of Cu-Fe-Al. The investigated additives in 3.5% NaCl shift corrosion potential E_{corr} to more positive values (except in $\text{K}_2\text{Cr}_2\text{O}_7$ reverses the action for Cu-Fe alloy) and increase I_{corr} . Impedance measurements indicated that Nyquist plots for Cu-Fe and Cu-Fe-Al may be regarded as part of semicircle (arc), the values of R_p for Cu-Fe are higher than those for Cu-Fe-Al except in $\text{K}_2\text{Cr}_2\text{O}_7$. On the other hand, the values of C_{dl} for Cu-Fe are lower than those obtained for Cu-Fe-Al. The presence of these additives in NaCl solutions increases the values of polarization resistance (R_p) and decreases the values of (C_{dl}).

Key words: Copper alloys, corrosion, passivators, NaCl.

INTRODUCTION

Copper is one of the oldest metals known to man, so the corrosion of this material has been studied for many years (Bengough et al., 1920; Bonfiglio et al., 1973; Faita et al., 1975; Ohsawa et al., 1979; Lee et al., 1985; Barcia et al., 1993). Cu-Fe alloys are materials that are more and more extensively applied in industry, they are utilized as master alloys to produce new copper alloys for very special purposes. They are used as materials for electrical device components, for example, semiconductor lead frames, electrical connectors and electrical fuses. Also, copper and its alloys are widely used as preferred materials for the transport of water in domestic and industrial water utilities, in plumbing within buildings and heat exchangers. They are also used in the petrochemical, marine, food, paper, and textile industries. This is related to their corrosion resistance, mechanical workability, excellent electrical and thermal conductivity and resistance to macrofouling (Nomoto et al., 1999). It has been reported that iron-alloying addition to copper alloys

may be used to improve their corrosion resistance (Cairs et al., 1990). The corrosion resistance of copper alloys has been attributed to the formation of a protective film of cuprous oxide (Cu_2O) and to the doping of Cu_2O layer with ions such as iron (Blundy et al., 1972; North et al., 1970). This doping reduces the ionic or electronic conductivity of the film, improving the corrosion resistance. In practice, alloying additions of Al, Zn, Sn, Fe and Ni are used to dope the corrosion product films. The films retard both the anodic dissolution of the alloy and the rate of O_2 reduction (De Sanchez et al., 1982). Therefore, it is not surprising that failure is always associated with the deterioration of the protective film (Gudas et al., 1979; El-Feky et al., 2009), the corrosion behavior of Cu-Fe and Cu-Fe-Al was studied. Sury (1970) showed that the thickness of the corrosion layers of Cu-Al alloys decreases with increasing Al-content of the corrosion layer. The protection nature of these films was ascribed to the formation of a Cu_2O layer which was detected on binary Cu-Al alloys in NaCl solution by X-ray technique. The asymptotic drop of the corrosion rate during the layer formation process was explained with the simultaneous decrease of the anodic reaction inside growing Cu_2O

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layer, and the cathodic reaction on its surface. The role of Al in passivation was assumed to be due to its incorporation in the Cu_2O lattice, reducing the rate of O_2 reduction on the Cu_2O surface. The protection of metals against corrosion in neutral electrolytes can be achieved either with inhibitors or with passivators (Rozenfeld, 1981). Ateya et al. (1994) studied the corrosion behaviour of α -Al bronze (Cu-7% Al) in 3.4% NaCl solution for extended periods and stated that corrosive attack occurred very early leading to general corrosion and pit nucleation, coalescence, growth and eventual merging of neighboring pits together to give multiple tough-like cavities. In the present work, the kinetic studies on the stability of the passive layer formed on copper-iron and copper-aluminium-iron alloys in different media are aimed. These are performed by studying the effect of some inorganic additives (passivators) on the corrosion and passivation behaviours on the investigated alloys in neutral media. The inorganic additives, used in the present work are: sodium molybdate, potassium iodate and potassium dichromate.

MATERIALS AND METHODS

Materials

Two types of the copper alloys are used in this study having the chemical composition (%wt): Alloy (I) Cu-4.47%Fe and Alloy (II) Cu-10.67%Al-5%Fe. The electrodes were jammed in a small copper mould with about 30 cm wire tail which was fixed in a glass tube with Araldite (Ciba- production, Switzerland) epoxy adhesive resin. The apparent cross sectional area of all electrodes were 0.2826 cm^2 .

Test medium

The test solution of 3.5% NaCl used in this work was prepared from Analar grade reagents. The inorganic additives were: potassium iodate, potassium dichromate, and sodium molybdate. These additives are chemically pure grades and obtained from Aldrich

Chemical Co Ltd. All measurements were carried out at temperature of 20 °C. The measurements were carried out in an EA876G- 20 Jacket Cell Bottom. The thermostat used is Compact Thermostat Model PC-Italy. The reference electrode (RE) was Ag/AgCl/ Cl- electrode and the counter electrode was Pt electrode. The electrodes were mechanically polished with successive grades of 600, 800, 1000 and 1200 emery papers till the surface appears as a bright mirror. The electrodes were then rinsed several times with deionized water and degreased with acetone.

Electrochemical tests

The potential of the working electrode under open circuit conditions was measured against Ag/AgCl/Cl- (3M KCl) reference electrode ($E_0 = -197$ mV vs NHE) and Pt- electrode as a counter electrode. The potential were recorded by means of multimeter (Keithley, Model 130 A, USA). Electrochemical impedance spectroscopy (EIS) measurements were carried out using impedance measurements system (IM6 Zahner electric, Meßtechnik, Germany). Impedance measurements were conducted, with excitation amplitude of 10 mV peak to peak, and the frequency domain from 0.1 Hz to 100 kHz.

Potentiodynamic polarization technique experiments were performed after obtaining a more or less steady state at 35 min open circuit potential using the same instrument and software with a scan rate 10 mV /sec.

RESULTS

Open-circuit conditions

In these series of experiments, the potential of Cu-Fe and Cu-Fe-Al was recorded as a function of time in 3.5% NaCl solution in absence and in presence of different concentrations of the inorganic additives: Na_2MoO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ and KIO_3 under open-circuit conditions. Figures 1a, b, and c shows open circuit potential (OCP) for Cu-Fe in 3.5% NaCl solutions without and with different concentrations of Na_2MoO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ and KIO_3 . The potential of the electrode was measured up to 45 min or more exposure time. The values of the electrode potential are listed in Table 1 for the different concentrations of the inorganic additives. Figures 2a, b, and c represent the potential-time plots under open-circuit conditions for the Cu-Fe-Al in 3.5% NaCl solutions without and with different concentrations of Na_2MoO_4 . Similar plots are obtained in presence of different concentrations of $\text{K}_2\text{Cr}_2\text{O}_7$ and KIO_3 . The values of the electrode potential are listed in Table 2 for the different concentrations of the inorganic additives. Generally, the potential of Cu-Fe is shifted to more positive values with time except in case of presence of $\text{K}_2\text{Cr}_2\text{O}_7$, it shifts the potential to more negative direction. The potential of Cu-Fe-Al is shifted to more negative values with time in all solutions except in presence of KIO_3 , the potential is shifted to positive direction. The addition of inorganic compounds shifts the steady state potential to positive and negative direction. The ranging in potential with time is due to heterogeneity of layer formed.

Potentiodynamic polarization

Figures 3a, b and c shows cathodic and anodic polarization curves recorded for Cu-Fe in 3.5% NaCl solutions without and with different concentrations of Na_2MoO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ and KIO_3 respectively. The values of different electrochemical parameters for corrosion (corrosion potential E_{corr} , corrosion current density i_{corr} , and anodic and cathodic Tafel slopes β_a , β_c) are listed in Table 3 for Cu-Fe in 3.5% NaCl solutions without and with the inorganic additives. The similar curves are showed for Cu-Fe-Al in Figures 4a, b and c in 3.5% NaCl containing different concentrations of $\text{K}_2\text{Cr}_2\text{O}_7$, Na_2MoO_4 and KIO_3 . The corrosion parameters for the alloy in different media are listed in Table 4. Generally, the addition of inorganic compound shifts the E_{corr} to more positive values except in $\text{K}_2\text{Cr}_2\text{O}_7$, where it shifts E_{corr} to more negative direction for Cu-Fe alloy. The presence of inorganic additives causes shifting of E_{corr} to more positive value

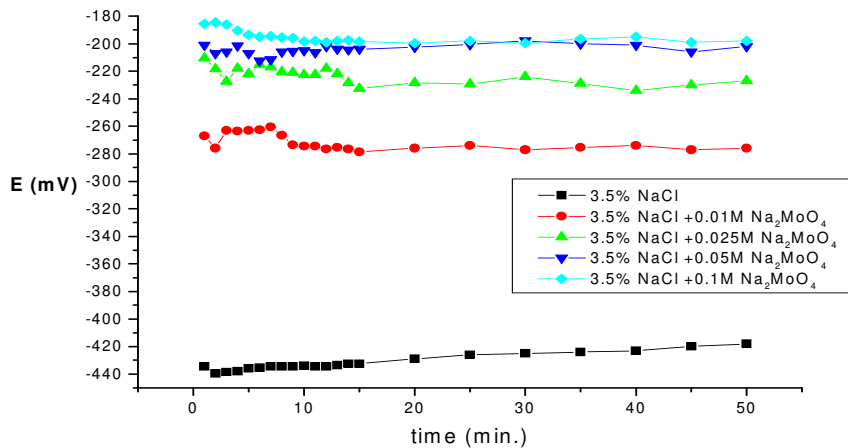


Figure 1a. Variation of the open-circuit potential of Cu-Fe with time in 3.5% NaCl solution in the presence of different concentration of Na_2MoO_4 at 20°C .

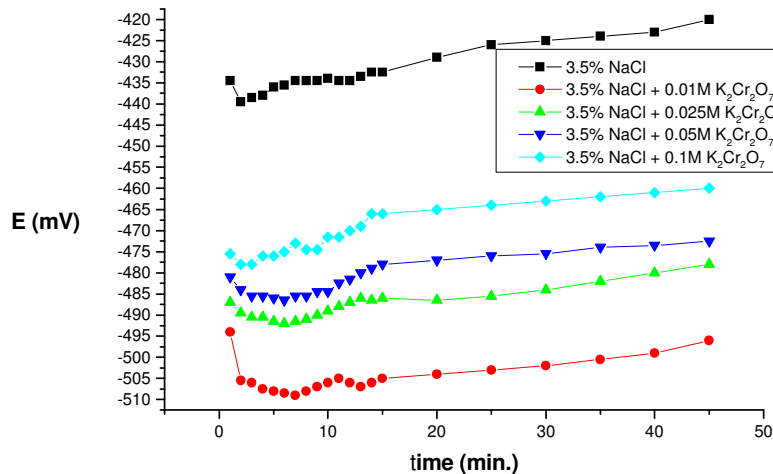


Figure 1b. Variation of the open-circuit potential of Cu-Fe with time in 3.5% NaCl solution in the presence of different concentration of $\text{K}_2\text{Cr}_2\text{O}_7$ at 20°C .

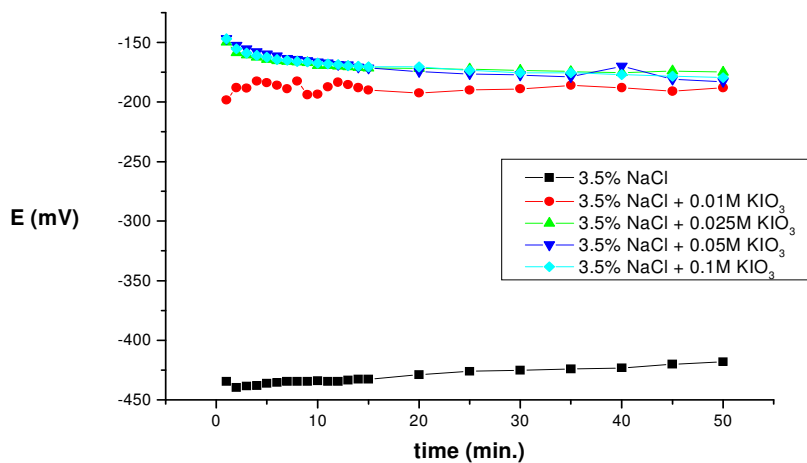


Figure 1c. Variation of the open-circuit potential of Cu-Fe with time in 3.5% NaCl solution in the presence of different concentration of KIO_3 at 20°C .

Table 1. Data of open circuit potential measurements for Cu-Fe immersed in 3.5% NaCl solutions without and with different concentrations of inorganic additives at 20°C.

Additive conc. (M)	Na ₂ MoO ₄	K ₂ Cr ₂ O ₇ Potential E (mV)	KIO ₃
0.00	-430	-430	-430
0.01	-370	-510	-180
0.025	-310	-485	-170
0.05	-290	-480	-170
0.1	-270	-460	-170

Electrochemical impedance spectroscopy

The impedance measurements is used to study the corrosion behavior of Cu-Fe and Cu-Fe-Al alloys in 3.5% NaCl solutions with presence of different concentrations of the above mentioned inorganic additives. In principle, the method involves direct measurements of impedance of the electrochemical system in the frequency domain from 0.1 to 105 Hz. The electrode impedance, Z and the phase shift (φ) are presented in Bode and Nyquist plots. These experiments are carried out at steady state under open circuit conditions. Figure 5a - c, 6a - c and 7a - c show the Bode, Nyquist and phase plots for Cu-Fe alloy in presence of different inorganic additive (0.01 M KIO₃, 0.01 M K₂Cr₂O₇ and 0.01 M Na₂MoO₄, respectively) at different immersion time. In the presence of 0.01 M K₂Cr₂O₇, the resistance of passive films that formed on the alloy surface increases with time and displays one phase maxima. This means that one electrode processes occur on the alloy surface. But with 0.01 M Na₂MoO₄ and 0.01M KIO₃, the film resistance decreases with increasing of immersion time, in addition to the electrode display one phase maxima. The values of polarization resistance R_p and capacitance of double layer Cdl for the electrode are listed in Table 5. Figures 8a - c, 9a - c and 10a - c shows the Bode, Nyquist and phase plots for Cu-Fe-Al alloy, in presence of different inorganic additive (0.01 M Na₂MoO₄, 0.01 M K₂Cr₂O₇ and 0.01 M KIO₃, respectively). The film resistance and reciprocal of charge transfer increases with elapsing of time in presence of inorganic additives. The addition of different concentrations of dichromate, malybdate and iodate, lead to increasing of the film resistance than that was recorded with 3.5% NaCl inorganic compound-free.

The values of polarization resistance R_p and capacitance of double layer Cdl are listed in Table 6.

DISCUSSION

The potential of Cu-Fe is shifted to more positive values with time, while in the presence of K₂Cr₂O₇, the potential is shifted to negative direction. The potential of Cu-Fe-Al shifted to more negative values with time, while the

presence of KIO₃ shifts the potential to positive direction. The addition of inorganic compounds shifts the steady state potential to positive and negative direction. Also, there are ranging in potential with time in most cases due to heterogeneity of layer formed (Rezenfeld et al., 1961). In pure chloride solution, the electrode is in active-passive state and the observed oscillations of the potential, which is associated with the fact that two concurrent processes are taking place at the electrode: activation and passivation. If passivating ions are added to the electrolyte, the electrode potential becomes stable and oscillations cease. Such an electrode can be polarized without activation up to the positive potentials. A concurrent adsorption of the passive state of the metal depends on the ratio between the numbers of activating and passivating ions, the charge, the potential of the electrode and the composition of the alloy. The role of anions as accelerators or inhibitors is directly related to their polarizability, is a measure of their deformability (Piontelli et al., 1951). Polarization determines the ability of the ion to inter the double layer and influence the electrode reaction. Mayre (1960) found that the attack on the protective film on the metal is sufficiently low in the presence of ions having polarizability equal to or lower than OH⁻. In the presence of ions of larger polarizability than OH⁻, film formation does not take place. The mechanism of action of inhibitors of the non-oxidizing type can be assumed to be as follows: after retarding the anodic reaction of ionization of the metal by forming sparingly soluble compounds or by direct electrochemical oxidation of the metal, these inhibitors shift the potential of the metal to values at which oxidation of the metal by oxygen of water becomes possible. Covering a considerable part of the electrode with sparingly soluble compound reduces the passivation current. Thus the current densities which are produced by the ordinary reaction of oxygen reduction are sufficient to keep the potential at the level necessary for passivation. Here a unique internal synergistic effect is involved, whereby the inhibitor facilitates passivation of the metal by oxygen of water, without participating in the cathodic reaction.

The inhibitors with strong properties act primarily as stimulators of the cathodic process and indirectly retarding the anodic reaction. Based on the effect of anions of the type M on iron, Cartledge (1955) and Lee (1955) advanced their electrostatic polarization hypothesis. The M anions do not exhibit certain behaviour. Thus, Mn reacts readily with iron to give non-protective film, S does not inhibit, P is only effective in the presence of oxygen and Cr causes passivity even in absence of oxygen. According to this hypothesis, an inhibitor should have suitable geometry for adsorption, a high for central charge, a high degree of internal polarity and low enough redox potential to prevent its reduction. The action of KIO₃ may be attributed to its oxidizing properties even in neutral solutions according to the following half reaction: This oxidizing property primarily stimulates the cathodic

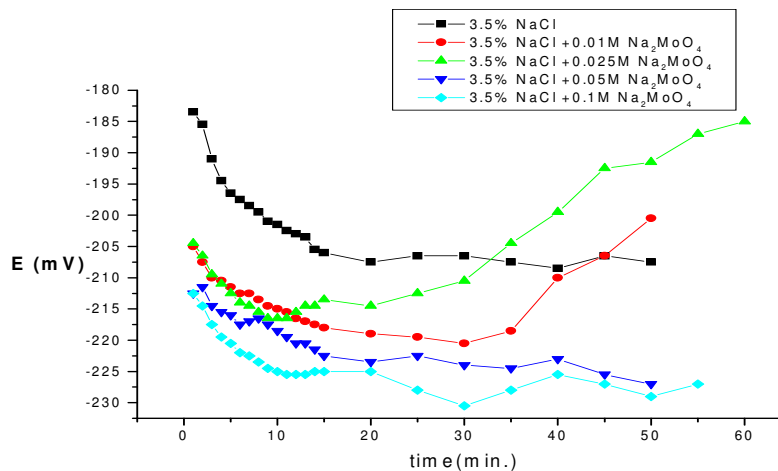


Figure 2a. Variation of the open-circuit potential of Cu-Fe-Al with time in 3.5% NaCl solution in the presence of different concentration of Na_2MoO_4 at 20°C .

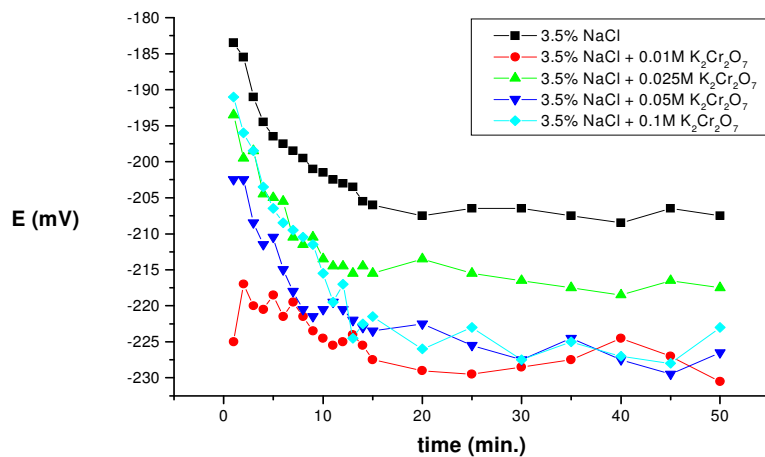


Figure 2b. Variation of the open-circuit potential of Cu-Fe-Al with time in 3.5% NaCl solution in the presence of different concentration of $\text{K}_2\text{Cr}_2\text{O}_7$ at 20°C .

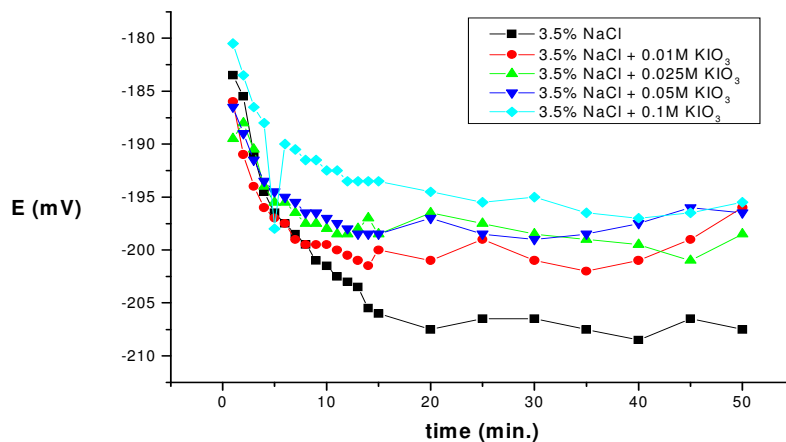


Figure 2c. Variation of the open-circuit potential of Cu-Fe-Al with time in 3.5% NaCl solution in the presence of different concentration of KIO_3 at 20°C .

Table 2. Data of open circuit potential measurements for Cu–Fe–Al immersed in 3.5% NaCl solutions without and with different concentrations of inorganic additives at 20°C.

Additive conc. M	Na ₂ MoO ₄	K ₂ Cr ₂ O ₇	Potential E (mV)	KIO ₃
0.00	-206		-206	-206
0.01	-216		-227	-202
0.025	-212		-216	-199
0.05	-221		-226	-199
0.1	-225		-225	-195

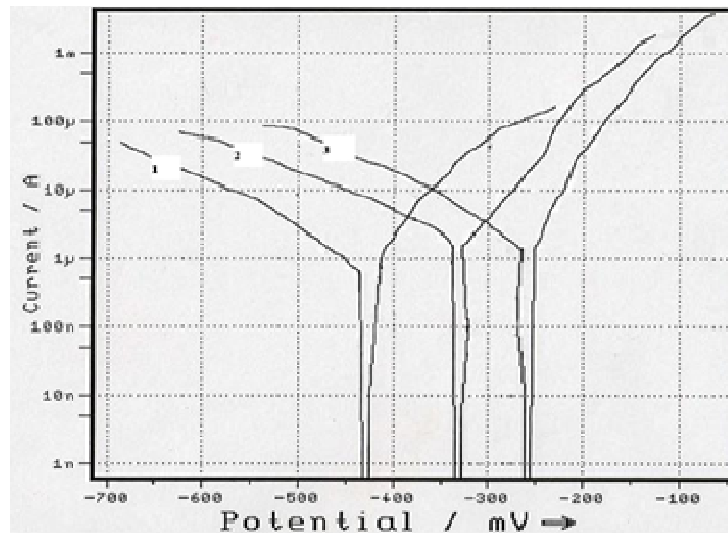


Figure 3a. Potentiodynamic polarization plots for Cu-Fe alloy 3.5 %NaCl at 35 min of immersion time at 20°C. 1=3.5% NaCl, 2= 3.5% NaCl+ 0.01M Na₂MoO₄, 3= 3.5% NaCl +0.1M Na₂MoO₄.

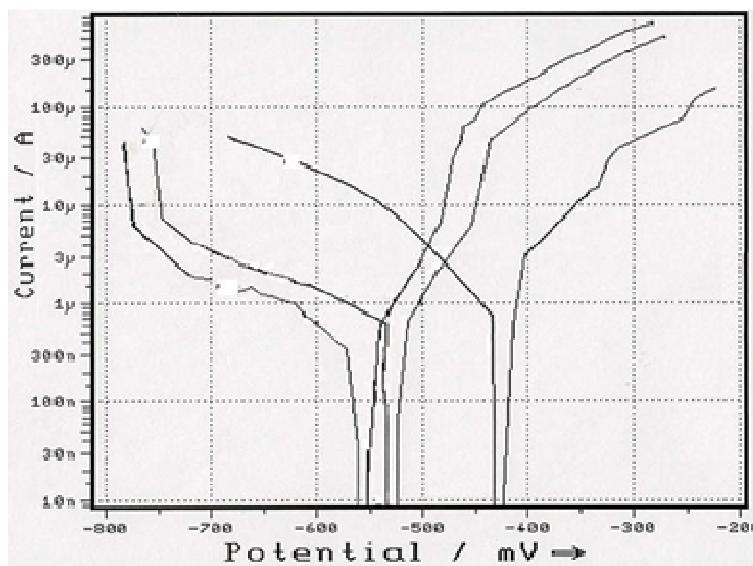


Figure 3b. Potentiodynamic polarization plots for Cu-Fe alloy 3.5 %NaCl at 35 min of immersion time at 20°C. 1=3.5% NaCl, 2= 3.5% NaCl+ 0.01M K₂Cr₂O₇, 3=3.5% NaCl + 0.1 M K₂Cr₂O₇.

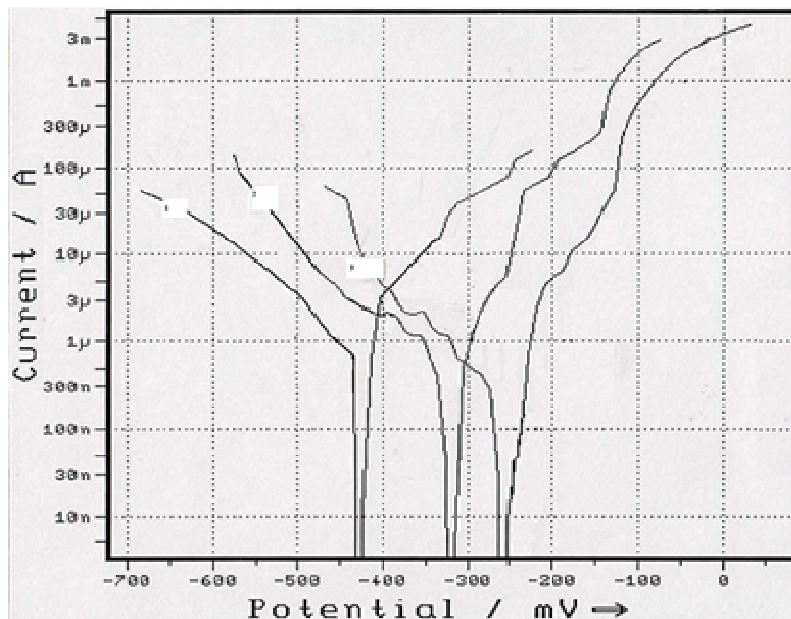


Figure 3c. Potentiodynamic polarization plots for Cu-Fe alloy 3.5 %NaCl at 35 min of immersion time at 20°C. 1 = 3.5% NaCl, 2 = 3.5% NaCl + 0.01 M KIO₃, 3= 3.5% NaCl +0.05 M KIO₃.

Table 3. Corrosion parameters for Cu-Fe in 3.5% NaCl Solutions without and with different concentrations of inorganic additives at 20°C.

Additive	Conc. mol/dm ³	-β _c (mV/d)	β _a (mV/d)	i _{corr.} (μA/cm ²)	E _{corr.} (mV)
NaCl	3.5%	118	66.3	0.241	-453.4
	0.01	75.5	38.7	0.488	-323.4
Na ₂ MoO ₄	0.025	108	62.9	0.968	-317.2
	0.05	83.3	45.3	0.509	-263
	0.1	615	184	1.31	-274.1
K ₂ Cr ₂ O ₇	0.01	217	50.4	0.497	-515.3
	0.025	133	65.8	0.453	-536.7
	0.05	159	52.8	0.428	-546
	0.1	102	49.8	0.238	-558.9
KIO ₃	0.01	136	51.1	0.539	-313.9
	0.025	105	81.7	1.91	-237.7
	0.05	104	55.3	0.126	-226.6
	0.1	72.3	47.4	0.242	-228.3

process and indirectly retarding the anodic reaction. In addition, the above half-reaction shows that the hydroxyl ions are produced. For a sufficiently high concentration of hydroxyl ions in the electrolyte, it becomes possible for a passivating oxide to form at the expense of hydroxyl oxygen according to the reaction: without the anodic

polarization (Rozenfeld, 1981). Also Cu₂O and Cu₂(OH)₃Cl, may be formed by the following reactions: Also such a behaviour of the electrode is undoubtedly associated with concurrent adsorption of chloride ions, and the produced iodide ions, and the hydroxyl ions. The amount of adsorbed chloride ions decreases when is introduced into

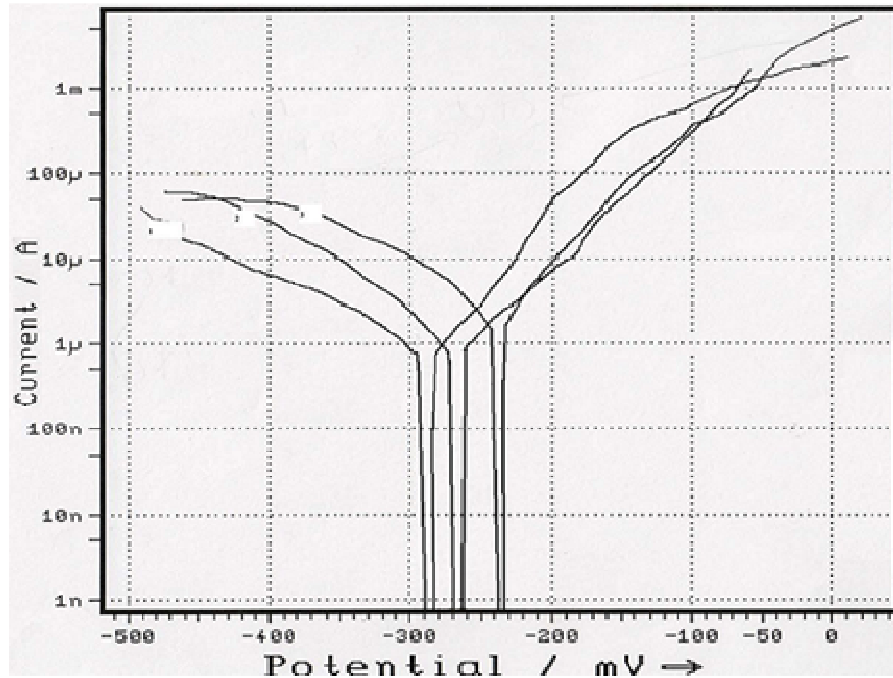


Figure 4a. Potentiodynamic polarization plots for Cu-Fe-Al alloy 3.5 %NaCl at 35 min of immersion time at 20°C. 1 = 3.5% NaCl, 2 = 3.5% NaCl+ 0.01 M Na_2MoO_4 , 3 = 3.5% NaCl +0.1 M Na_2MoO_4 .

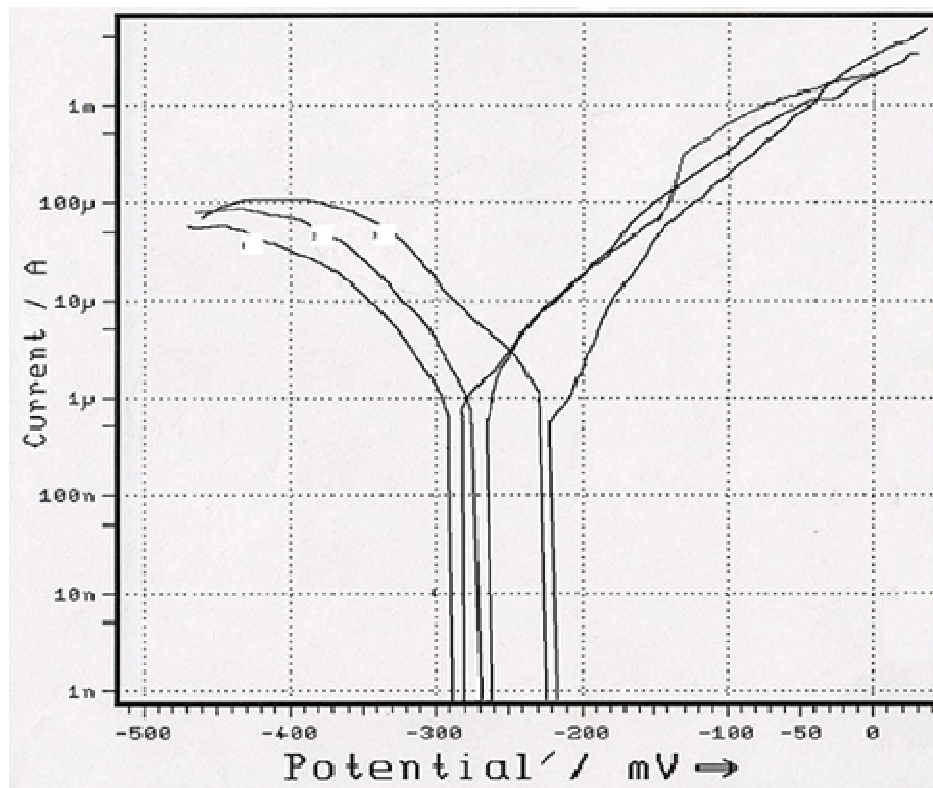


Figure 4b. Potentiodynamic polarization plots for Cu-Fe-Al alloy 3.5 %NaCl at 35 min of immersion time at 20°C. 1 = 3.5% NaCl, 2 = 3.5% NaCl + 0.01 M $\text{K}_2\text{Cr}_2\text{O}_4$, 3 = 3.5% NaCl + 0.1 M $\text{K}_2\text{Cr}_2\text{O}_4$.

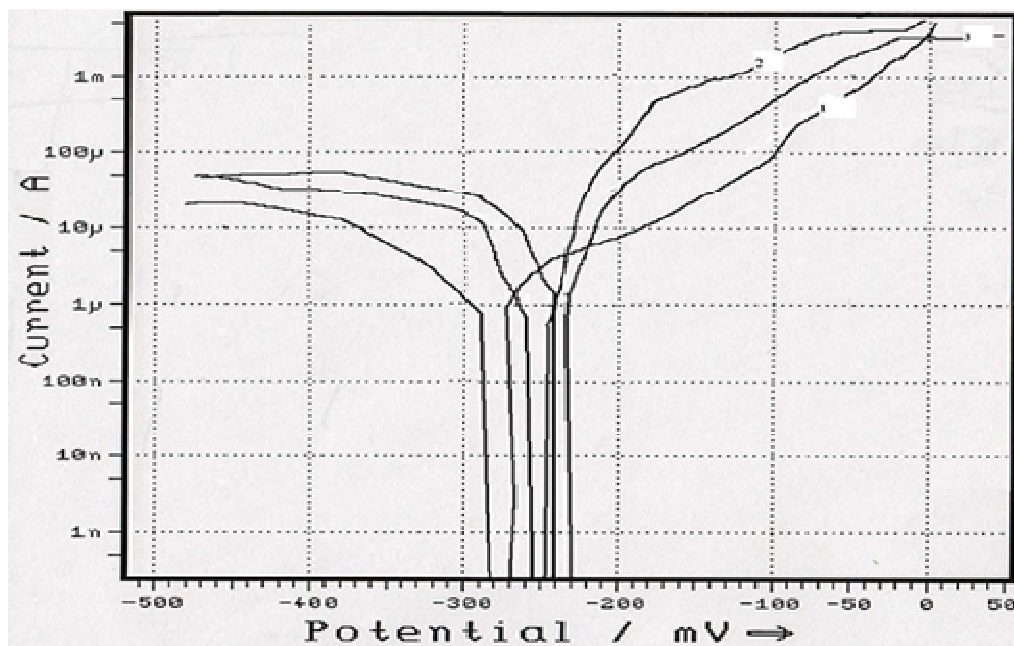


Figure 4c. Potentiodynamic polarization plots for Cu-Fe alloy 3.5 %NaCl at 35 min of immersion time at 20°C. 1 = 3.5% NaCl, 2 = 3.5% NaCl + 0.01 M KIO₃, 3 = 3.5% NaCl + 0.1 M KIO₃.

Table 4. Corrosion parameters for Cu-Fe-Al in 3.5% NaCl solutions without and with different concentrations of inorganic additives at 20°C.

Additive	Conc. mol/dm ³	-βc (mV/d)	βa (mV/d)	i _{corr} (μA/cm ²)	E _{corr} (mV)
NaCl	3.5%	1350	149	0.993	-286.1
	0.01	116	10.7	0.771	-263.5
Na ₂ MoO ₄	0.025	142	69.1	0.795	-241.5
	0.05	166	71	0.889	-256
	0.1	136	43.6	1.152	-231.5
K ₂ Cr ₂ O ₇	0.01	35.2	79.8	0.98	-266.6
	0.025	32.9	14.5	0.574	-260
	0.05	112	36.9	0.955	-217.7
	0.1	53.8	170	0.986	-217.8
KIO ₃	0.01	31	40	0.439	-262.1
	0.025	105	90.9	0.747	-286
	0.05	63.5	161	1.19	-294.9
	0.1	106	110	2.12	-254.8

the electrolyte. For higher concentrations of passivating ions, the adsorption of activating ions can be excluded completely.

Compounds such as Na₂MoO₄ can protect the alloy against corrosion. Upon hydrolysis of these compounds,

which are salts of weak acid and strong base, hydroxyl ions appear which are capable of forming a passivating oxide. Salts of a weak acid and strong base take preference over ordinary alkali, since the hydroxyl ions used in the formation of the passivating oxide are automatically

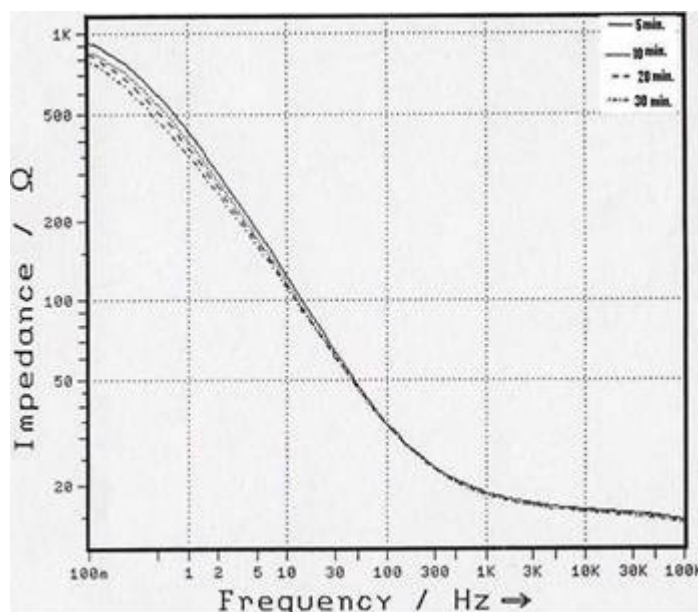


Figure 5a. Bode plot for Cu-Fe alloy in 3.5 NaCl +0.01 M KIO_3 solution as a function of immersion time at 20°C.

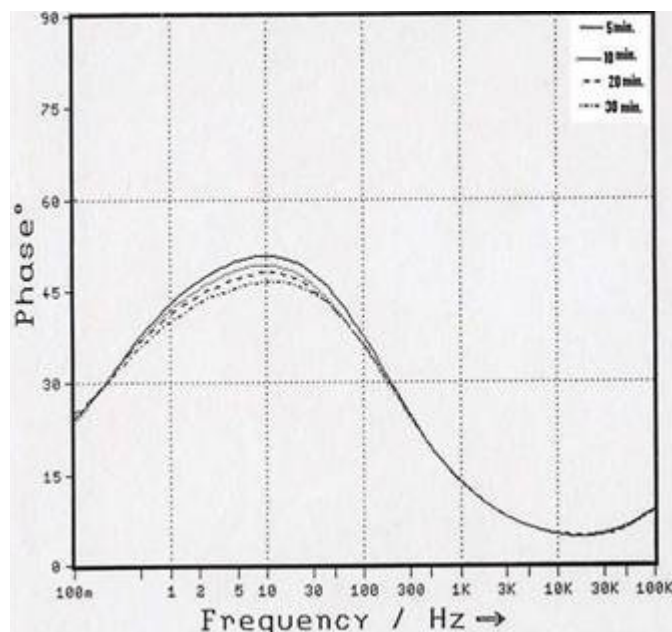


Figure 5c. Phase plot for Cu-Fe alloy in 3.5 NaCl +0.01 M KIO_3 solution as a function of immersion time at 20°C.

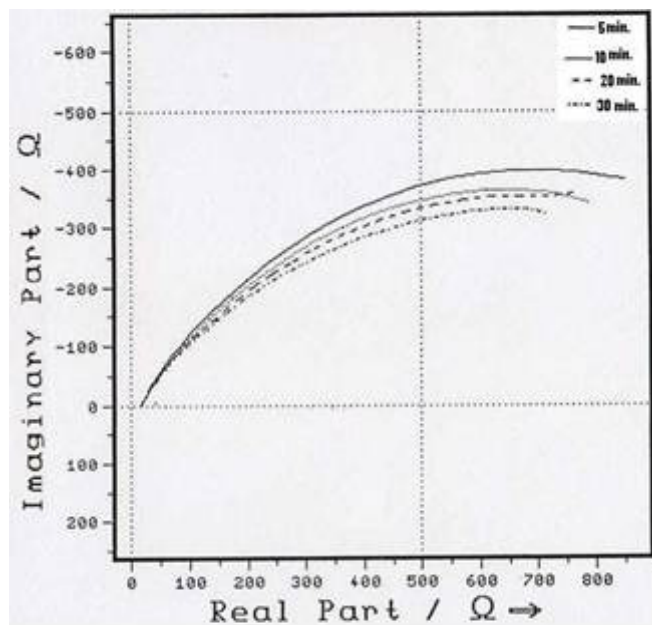


Figure 5b. Nyquist plot for Cu-Fe alloy in 3.5 NaCl + 0.01 M KIO_3 solution as a function of immersion time at 20°C.

replenished by hydrolysis. For a sufficiently high concentration of hydroxyl ions in the electrolyte, it becomes possible for a passivating oxide to form at the expense of the hydroxyl oxygen according to the above mentioned reactions. Also, the formed hydroxyl ions may compete the activating chloride ions, for the adsorption on the electrode surface. Compound such as $K_2Cr_2O_7$, the dichromate ions, can exist only in the acidic media

Table 5. Impedance parameters for Cu-Fe in 3.5% NaCl solutions without and with different concentrations of inorganic additives at 20°C.

Additive	Conc. (mol / dm ³)	C _{dl} (μF. cm ⁻²)	R _p (Ω-cm)
NaCl	3.5%	383.6	1343.29
	0.01	802.5	1684.73
	0.025	283.6	1733.7
	0.05	322.8	2094.4
$K_2Cr_2O_7$	0.1	246	2443.63
	0.01	227	2269.25
	0.025	240.6	2644.45
	0.05	141	2740.92
KIO_3	0.1	63.4	2091.4
	0.01	471.6	917.56
	0.025	259.5	2874.7
	0.05	321.6	3433.08
	0.1	433.6	3199.08

and in neutral media these ions transform to chromate ions according to the equilibrium: and the dichromate ions can not behave as an oxidizing agent in this neutral medium. For this reason the presence of in low concentrations in NaCl solution is accompanied by shifting of the

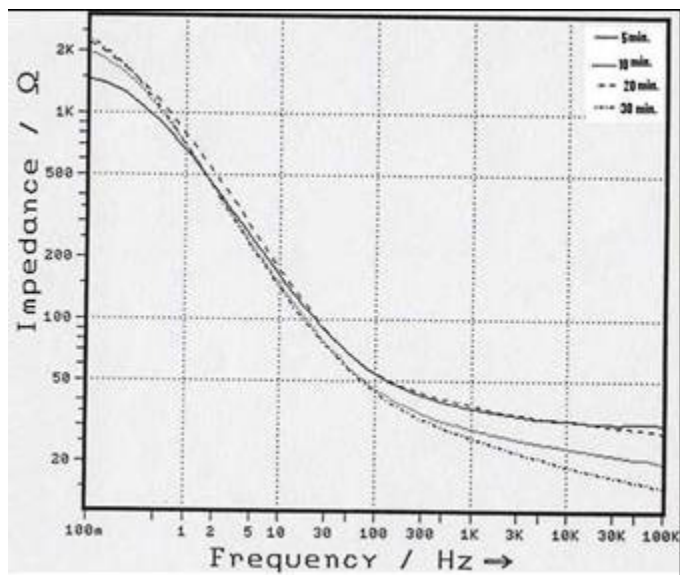


Figure 6a. Bode plot for Cu-Fe alloy in 3.5 NaCl + 0.01 M $K_2Cr_2O_7$ solution as a function of immersion time at 20°C.

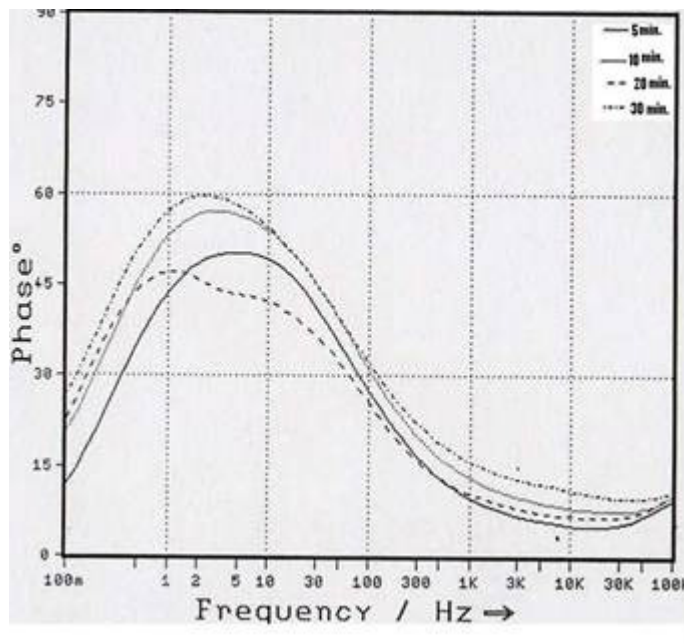


Figure 6c. Phase plots for Cu-Fe alloy in 3.5 NaCl + 0.01 M $K_2Cr_2O_7$ solution as a function of immersion time at 20°C.

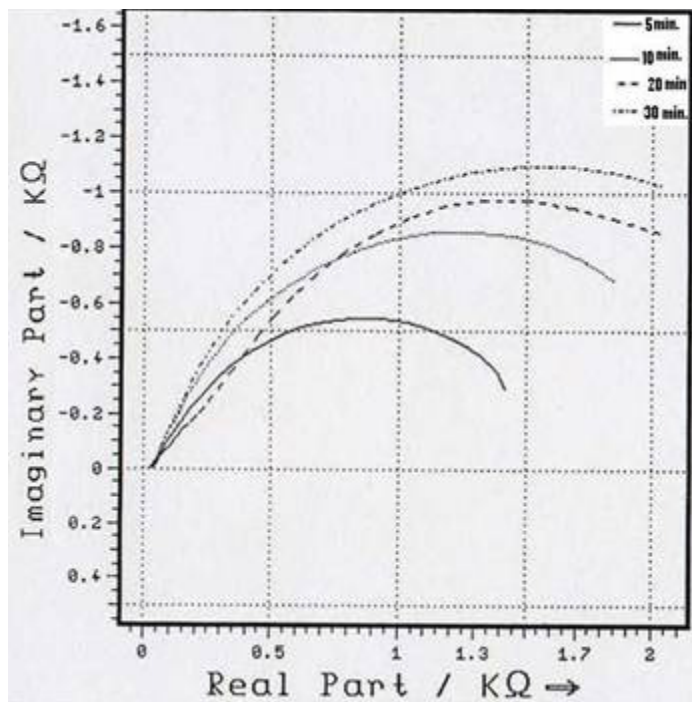


Figure 6b. Nyquist plots for Cu-Fe alloy in 3.5 NaCl + 0.01 M $K_2Cr_2O_7$ solution as a function of immersion time at 20°C.

electrode potential to the more negative value than that obtained in sodium chloride solution. This means that the low concentration of these additives may accelerate the corrosion of the alloy in sodium chloride solution. The negative shift of electrode potential decreases with the increase of the additive concentration and may become

Table 6. Impedance parameters for Cu-Fe-Al in 3.5% NaCl solutions without and with different concentrations of inorganic additives at 20°C.

Additive	Conc. (mol /dm ³)	C _{dl} (μF. cm ⁻²)	R _p (Ω-cm ²)
NaCl	3.5%	978.3	789.87
	0.01	901.9	749.73
Na ₂ MoO ₄	0.025	489.2	1300.87
	0.05	313	1727.98
	0.1	549.3	1641.21
K ₂ Cr ₂ O ₇	0.01	63.5	10019.33
	0.025	105.1	4554.92
	0.05	92.9	4410.38
	0.1	304.9	3225.95
KIO ₃	0.01	157.2	2294.36
	0.025	184.97	2340.61
	0.05	153.1	2208.58
	0.1	184.5	2021.89

positive at higher concentrations. This behaviour occurs at a certain concentration, depending on the type of additive. The ennoblement of the electrode potential in the presence of higher concentration of $K_2Cr_2O_7$ means that it can behave as an inhibitor and can retard the corrosion effect of sodium chloride. The retarding effect of $K_2Cr_2O_7$ can be explained by adsorption of the ions of inhibitor which reduce the free energy of the system and

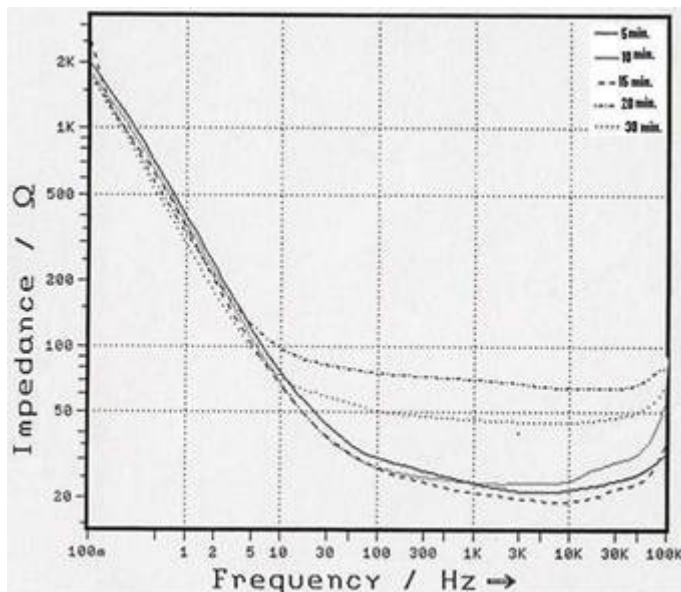


Figure 7a. Bode plot for Cu-Fe alloy in 3.5 NaCl + 0.01 M Na_2MoO_4 solution as a function of immersion time at 20°C.

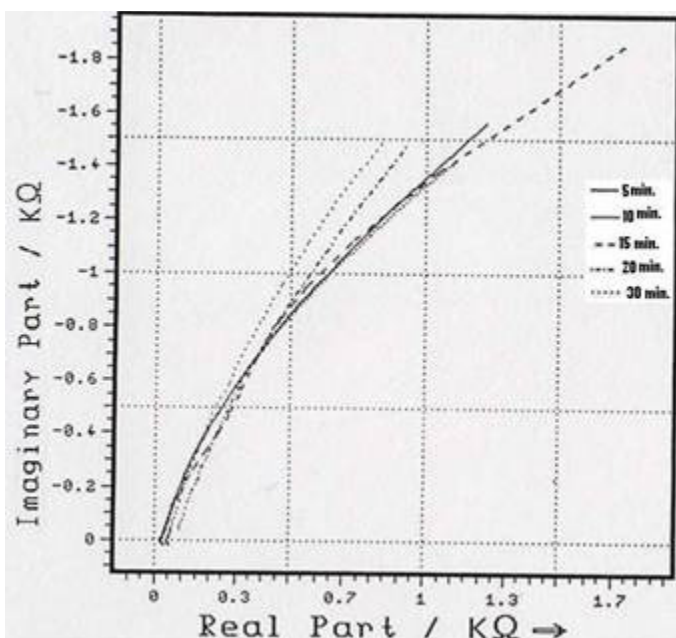


Figure 7b. Nyquist plot for Cu-Fe alloy in 3.5 NaCl + 0.01 M Na_2MoO_4 solution as a function of immersion time at 20°C.

impedes the passage of ion-atoms of metal from the lattice into the solution. It must, however, be kept in mind that the passivating properties of these additives depend greatly on the presence of activating ions (e.g. Cl^-) in solution and the ratio between them. Also, such behaviour of the electrode is undoubtedly associated with concurrent adsorption. In NaCl solutions and under the

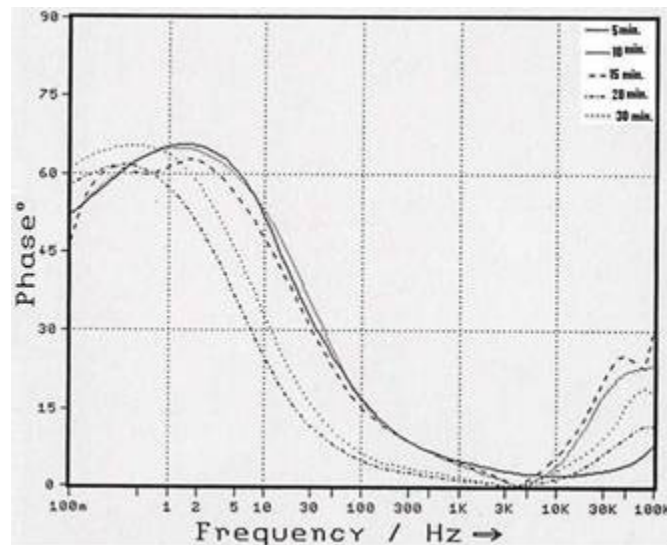


Figure 7c. Phase plot for Cu-Fe alloy in 3.5 NaCl + 0.01 M Na_2MoO_4 solution as a function of immersion time at 20°C.

anodic polarization Cu_2O , CuCl and CuO can form respectively (De chialov et al., 1985; Brossard, 1983) in the potential region from 0.2 to + 0.1 V (SCE).

For copper alloys in the potential range between -0.2 and 0.0 V (SCE), the corrosion reactions should yield Cu_2O , CuCl , Cu(I) , and Cu(II) such as Cu(OH)_2 and were found in solution depending on the chloride concentration (Lee et al., 1984). Paratacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$) is stable at 0.12 V (SCE) and $\text{pH} = 7.5$ (Bianchi et al., 1978).

In the case of alloy (II) the presence of aluminum in the alloy leads to the formation of heterogeneous phases which have a potential difference. The phases of CuAl_2 and FeAl_3 may precipitate at the grain boundaries, where these phases are cathodic to the matrix. The passivation of this alloy occurs on the account of the formation of iron oxides, copper oxides and copper oxchlorides or also aluminum oxides.

The results of Sury (1970) showed that the thickness of the corrosion layers of Cu-Al alloys decreases with increasing Al-content of the corrosion layer. The protection nature of these films was ascribed to the formation of Cu_2O layer which was detected on binary Cu-Al alloys in NaCl solution by X-ray technique. The asymptotic drop of corrosion rate during the layer formation process was explained with the simultaneous decrease both of the anodic reaction inside growing Cu_2O layer and the cathodic reaction on its surface. The role of Al in passivation was assumed to be due to its incorporation in the Cu_2O lattice, reducing the rate of O_2 reduction on the Cu_2O surface.

Ateya et al., 1994 on studying the corrosion behaviour of α -Al bronze (Cu-7% Al) in NaCl solution stated that corrosive attack occurred very early leading to general corrosion and pit nucleation. The corrosion products formed under free corrosion conditions appeared as a

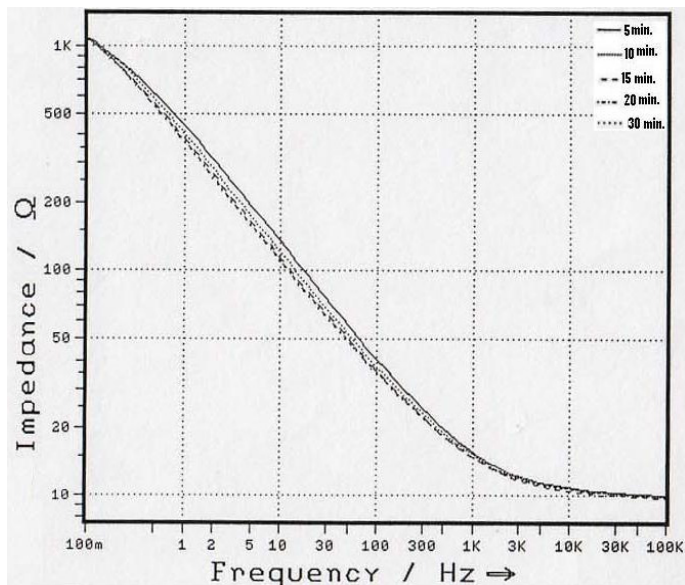


Figure 8a. Bode plot for Cu-Al-Fe alloy in 3.5 NaCl + 0.01 M Na_2MoO_4 solution as a function of immersion time at 20°C.

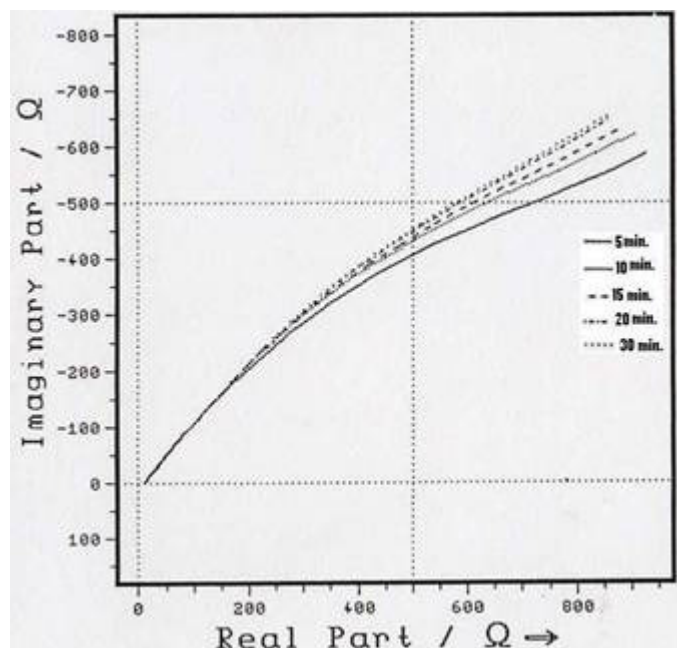


Figure 8b. Nyquist plot for Cu-Al-Fe alloy in 3.5 NaCl + 0.01 M Na_2MoO_4 solution as a function of immersion time at 20°C.

duplex film with an inner-adherent layer of Al_2O_3 and an outer layer of Cu_2O , $\text{Cu}_2(\text{OH})_3\text{Cl}$ and $\text{Cu}(\text{OH})\text{Cl}$. The polarization measurements carried out for Cu-Fe and Cu-Fe-Al alloys in NaCl solution indicated that the corrosion current of Cu-Fe is less than that of Cu-Fe-Al. Addition of Na_2MoO_4 and KIO_3 in NaCl solution for Cu-Fe causes shifts of the corrosion potential (E_{corr}) to more

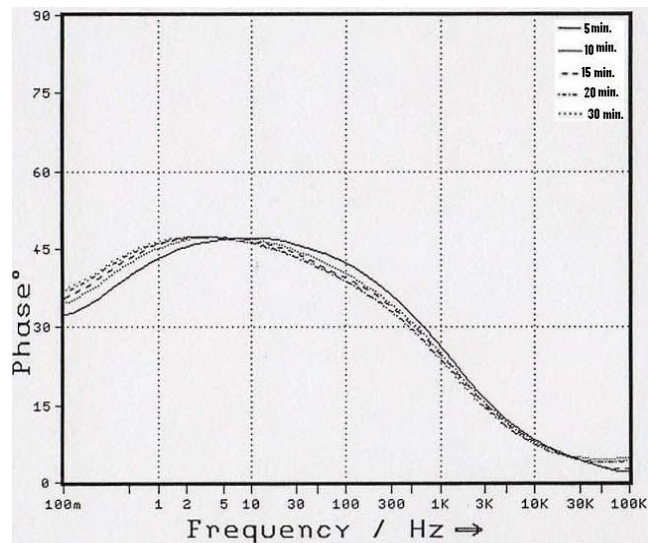


Figure 8c. Phase plot for Cu-Al-Fe alloy in 3.5 NaCl + 0.01 M Na_2MoO_4 solution as a function of immersion time at 20°C.

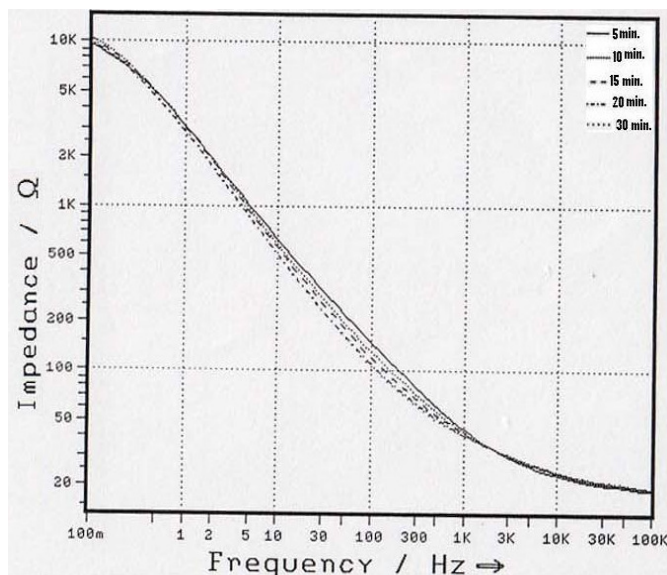


Figure 9a. Bode plot for Cu-Fe-Al alloy in 3.5 NaCl + 0.01 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution as a function of immersion time at 20°C.

positive values and increases the values of corrosion current density (I_{corr}), while the presence of high $\text{K}_2\text{Cr}_2\text{O}_7$ shifts the corrosion potential of the working electrodes to more negative values. Immersion of Cu-Fe-Al in the test solution shifts the corrosion potential, E_{corr} , to more positive values and increases the values of I_{corr} .

From impedance measurements, Nyquist curves may be regarded as semi-circle and arc (semi-circle) with elapse of time. Increase or decrease of the diameter of the semi-circle with time that proportionally direct with passive film resistance was recorded, indicating an increase or

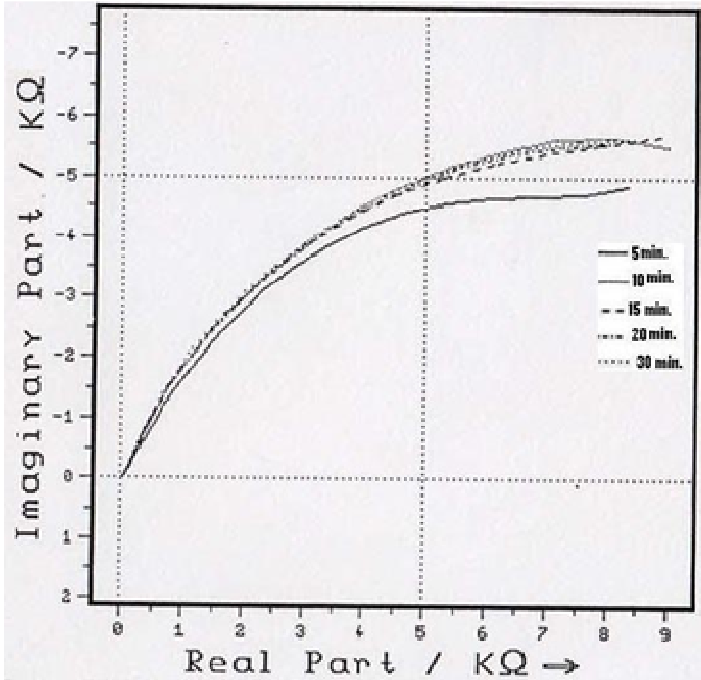


Figure 9b. Nyquist plot for Cu-Fe-Al alloy in 3.5 NaCl + 0.01 M $K_2Cr_2O_7$ solution as a function of immersion time at 20°C.

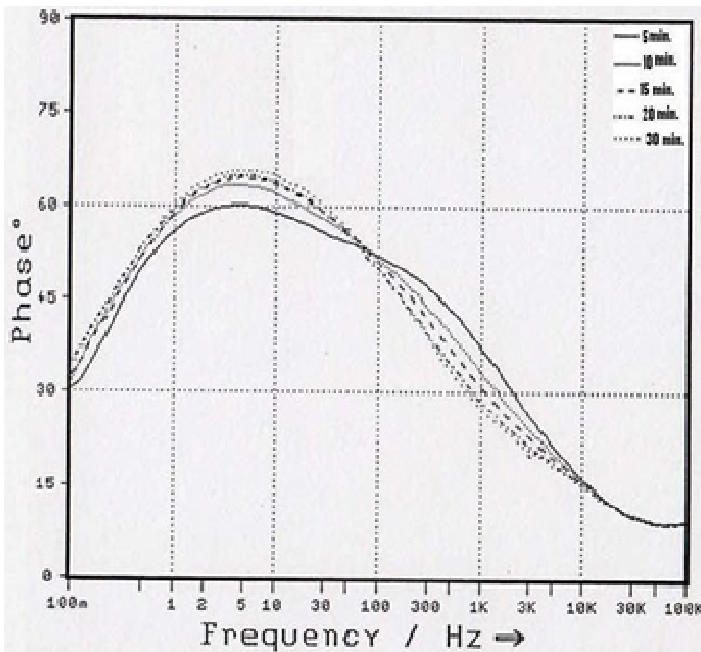


Figure 9c. Phase plot for Cu-Fe-Al alloy in 3.5 NaCl + 0.01 M $K_2Cr_2O_7$ solution as a function of immersion time at 20°C.

decrease of the protective properties of the surface layer. Bode plots indicated that at both high and low frequency limit the phase angle (θ°) assumes a value of about 0° , corresponding to the resistive behavior of solution resis-

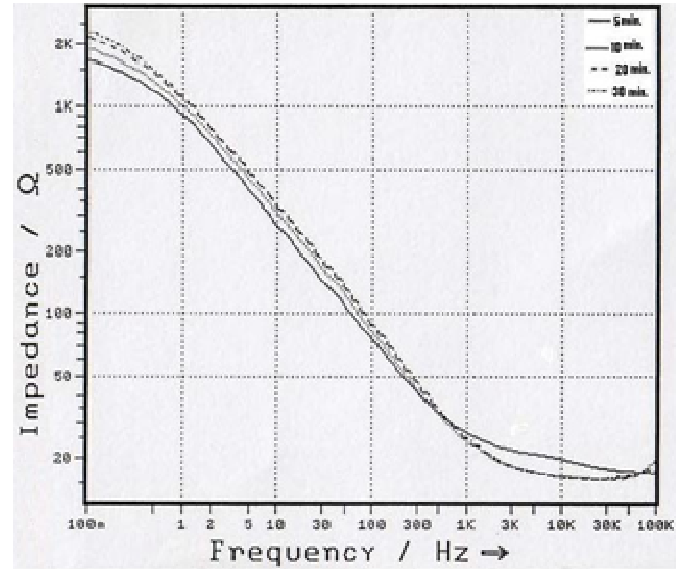


Figure 10a. Bode plot for Cu-Fe-Al alloy in 3.5 NaCl + 0.01 M KIO_3 solution as a function of immersion time at 20°C.

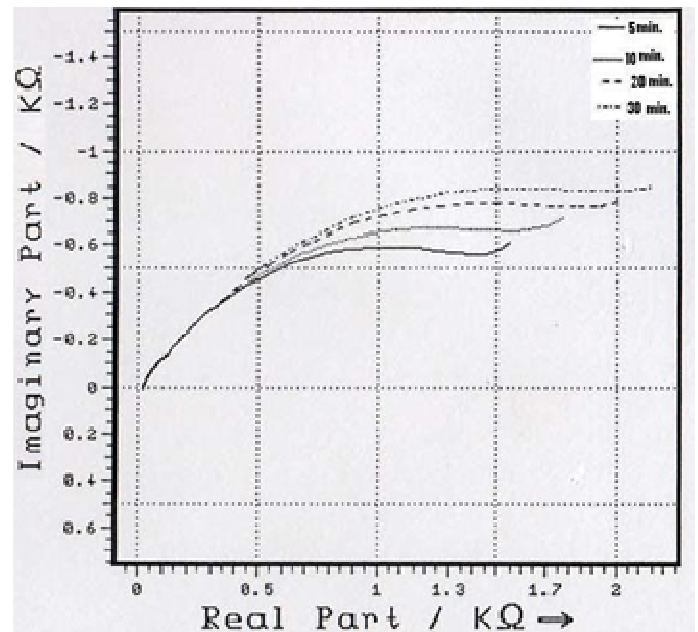


Figure 10b. Nyquist plot for Cu-Fe-Al alloy in 3.5 NaCl + 0.01 M KIO_3 solution as a function of immersion time at 20°C.

tance, R_p and (R_s+R_p) , respectively. The dielectric constant of the oxide film is a proof for the capacitive behavior of the system at intermediate frequency. The value tend to be more than 65° , the capacitive time constant is attributed to the formation of the oxide layer or the oxide layer itself, that is, the oxide film can be considered to be a parallel circuit of a resistor (due to the

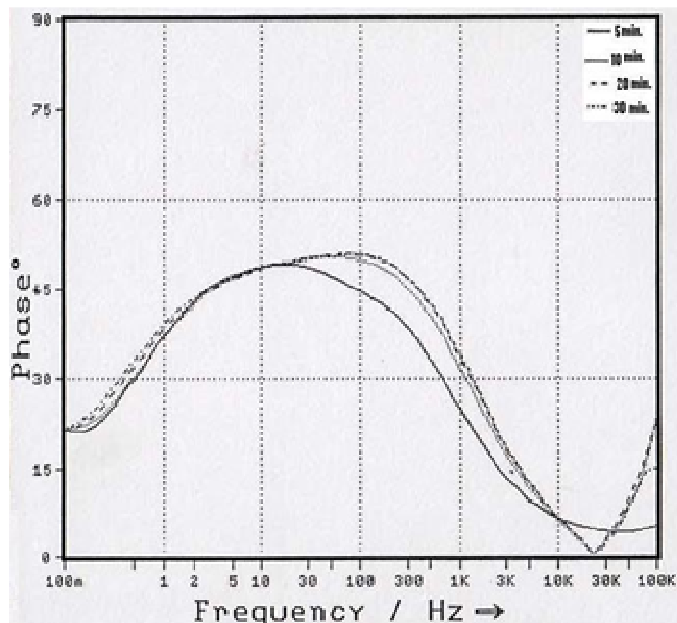


Figure 10c. Phase plots for Cu–Fe–Al alloy in 3.5 NaCl + 0.01 M KIO_3 solution as a function of immersion time at 20°C.

ionic conduction in the oxide) and a capacitance (due to the dielectric properties of this oxide). The impedance diagrams obtained were found to best fit for the simple Randle circuit: where R_p is the polarization resistance and C_{dl} is the capacitance of double layer. Nyquist plots tend to be semi-circle. The depression angles of these circles are correlated to the microscopic roughness of the metal/solution interface and with modification in the morphology of the electrode surface (Levie, 1965). Depressed capacitive semi-circles are often referred to as surface inhomogeneity (Metikos et al., 1994). The main parameters that can be deduced from the analysis of the Nyquist diagram are the charge transfer of the corrosion reaction, R_{ct} and the capacity of the double layer, C_{dl} . R_p values are calculated from the difference in impedance at lower and higher frequencies (Mansfeld et al., 1981; Tsuru et al., 1978). The double-layer capacitance, C_{dl} , can be calculated from the following relationship (Bentiss et al., 2000):

$$C_{dl} = \pi R_p f(z_{im,max})$$

Where $f(z_{im,max})$ is the frequency at which the imaginary part of the impedance is maximum. The calculated values of R_p and C_{dl} are listed in Tables 3a and b, for the alloys (I, II), respectively, in NaCl solutions containing different concentrations of the investigated additives.

Conclusion

The investigated inhibitors behave as anodic ones, where they increase the anode polarization and hence move the corrosion potential, E_{corr} , in the positive direction, some of these inhibitors and under definite conditions behave as cathodic inhibitors, where in the corresponding manner displaces the corrosion potential, E_{corr} , in the negative direction. Also, these inhibitors greatly retard the localized attack on the electrodes surface.

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