Int. J. Electrochem. Sci., 1(**2006**)258-267

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Behavior of Cr-Mo Steel Alloy in High Temperature Aqueous Sodium Chloride Solution

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Received: 16 July 2006 / *Accepted:* 26 July 2006 / *Published:* 1 September 2006

The electrochemical behavior of a low alloy steel (Fe-2.25 Cr-1Mo) was investigated in 1 m NaCl over a range of temperatures (75-250^{0}C) with various levels of contaminations with $CuCl_2$. The change in free corrosion potential with time and the anodic and cathodic potentiodynamic polarization were measured. Cyclic potentiodynamic polarization was also measured on a previously corroded electrodes for different times (7 and 72 hrs) either in the same or in a fresh electrolyte. The results revealed that the corrosion potential is shifted, at all temperatures, towards more noble values to an extent which increases with the concentration of $CuCl_2$. The cathodic current density also increases as the concentration of $CuCl_2$ increases. $CuCl_2$ acts as cathodic depolarizer. It undergoes electrodeposition leading to the formation of Cu metal onto the corrosion product, which becomes less adherent and less protective. Most of this Cu metal falls off the alloy surface along with the spalled corrosion product. The shift in the corrosion potential towards more noble values with the increase in the precorrosion time, in absence of Cu^{2+} ions, indicates that the corrosion product which forms protect the surface against further attack. In the presence of Cu^{2+} ions, the passivation occurred after the effect of copper is diminished.

Keywords: high temperature, high pressure, electrochemistry, aqueous saline, corrosion

1. INTRODUCTION

Considerable interest has arisen in recent years on the properties of high temperature aqueous solutions [1-7]. These were used in many industrial fields such as steam generators in electric power stations [2, 3, 8], boiling water reactors (BWR) or pressurized water reactors (PWR) [4,9], desalination plants [2, 10], high temperature aqueous fuel cells [7, 11] and hydrothermal treatment of organic waste [6]. In these environments, the bad maintenance and feed water chemistry are the main causes of the failure, leading to corrosion [1-3]. Contaminations, which may arise from corrosion of other parts e.g. condensers [12], are concentrated with an order of 3-6 to form highly corrosive solutions [13].

In aqueous solutions, Iron corrodes leading to the reduction of water and evolution of hydrogen according to the overall reaction:

$$3\,Fe + 4\,H_2O \rightleftharpoons Fe_3O_4 + 4\,H_2 \tag{1}$$

However, it has been proposed that, in deaerated waters, the reaction proceeds in stages [14]

$$3\,Fe + 6\,H_2O \rightleftharpoons 3Fe(OH)_2 + 3\,H_2 \tag{2}$$

$$3\,Fe(OH)_2 \rightleftharpoons Fe_3O_4 + H_2O + H_2 \tag{3}$$

in the absence of oxygen, the cathodic reaction is the reduction of water [15] according to:

$$H_2O + e^- \rightleftharpoons OH^- + 1/2\,H_2 \tag{4}$$

The magnetite which forms due to reaction (1) protects the corroding surface.

Our previous work [16] on the corrosion of a low alloy steel in high temperature aqueous sodium chloride revealed a change in corrosion mechanism after a transition time, the magnitude of which decreases as the temperature increases. At and beyond this transition time, an adherent layer of the corrosion product was shown to protect the substrate alloy by acting as a diffusion barrier. The behavior of the alloy before the onset of this diffusion control was found to be compatible with the nucleation and subsequent lateral growth of islands of the corrosion product onto the alloy surface. The coalescence of these islands into a continuous layer, leads to protection of the substrate against corrosion. When $CuCl_2$ is added, the inclusion of Cu metal within the corrosion product layer was found to render it more brittle and less adherent to the corroding surface and hence less protective. Pitting corrosion with a lace like morphology was also observed. The extent of pitting increases with the temperature and $CuCl_2$ concentration. The lace like morphology of these pits was previously reported [17] at ambient temperature.

The purpose of this work is to explain the nature of partial reactions and the rate determining step(s). The free corrosion potential and the polarization behavior of a low alloy steel (Fe-2.25 Cr-1 Mo) in NaCl was investigated. The effects of temperature, the addition of various concentrations of $CuCl_2$ and the precorrosion on the electrode processes were also tested.

2. EXPERIMENTAL PART

2.1 Materials

The Cr-Mo steel alloy was supplied by the Electricity Authority of Egypt, with the following composition: Cr, 2.3; Mo, 1.0; Mn, 0.46; Si, 0.2; C, 0.13; P, 0.015; S, 0.007; Fe balance, wt%. The alloy was used in the form of sheets of 2 x 2 x 0.2 cm. They were annealed at 900^0C in argon atmosphere for 1 hr and furnace cooled.

2.2. Methods

An autoclave was fabricated from 316 type stainless steel. It consisted of two parts (Fig. 1), as discussed in detail elsewhere [18]. A (Teflon) PTFE cell was machined to fit tightly into the autoclave, to accommodate the electrolyte. The cell was preheated for about 5 hrs to obtain thermal stabilities [19, 20]. The electrodes were insulated in such a way that the resistance was a bout 10^{10} ohm. The autoclave was placed in a furnace, connected with the temperature regulator to the heating source.

The test solutions were 1 molal (m) NaCl (sol. I), 0.999 m NaCl + 5 x 10^{-4} m $CuCl_2$ (sol. II) and 0.9 m NaCl + 5 x 10^{-2} m $CuCl_2$ (sol. III). These were prepared from analytical grade reagent and doubly distilled water. The tests were performed in deaerated electrolytes at 75, 125, 175 and 250^0C. Deaeration was achieved by boiling the electrolyte under reflux for 15 min. This technique is reported to reduce the level of oxygen down to the ppm level [10].

The working electrode consisted of a rectangular sheet spot welded to a Pt wire and was insulated with PTFE in such a way as to expose an area of 1 cm^2 at its end. Prior to each experiment the surface was prepared by polishing with silicon carbide abrasive grits down to 1200 mesh, ultrasonically cleaned in ethyl alcohol, rinsed with distilled water and dried in air. A Pt rod of 0.3 cm diameter and about 15 cm length was used as a counter electrode. It was passed through the autoclave head through a Teflon sheath that is tighten to the autoclave head. The reference electrode was Ag/AgCl which has been frequently used at high temperature [19, 21]. Its equilibrium potential is known at high temperatures [22] .

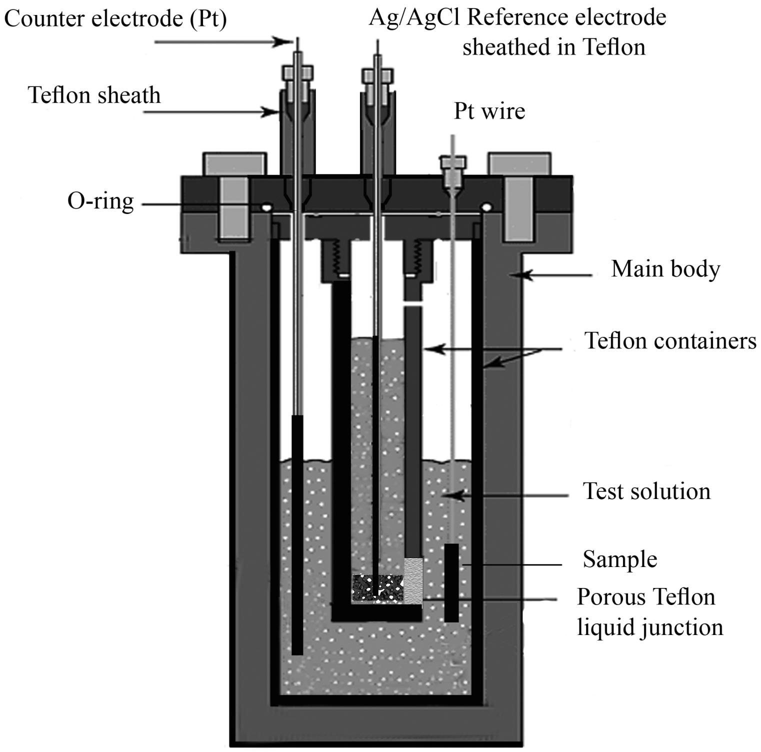

Figure 1. Schematic illustration of the autoclave used for the measurements.

Potentiodynamic polarization curves were obtained using EG & G Potentiostat/Galvanostat Model 273 A at a scan rate of 1.6 mV s^{-1}. Measurements on the precorroded specimens (after 7 and 72 hrs) were made using a fresh and the same corroding solution in which the alloy was corroded e.g. solutions I and III at 175^0C.

3. RESULTS AND DISCUSSION

3.1 Potential-Time Curves

Figure 2 illustrates the time variation of the free corrosion potential, E_{corr} , of the alloy at different temperatures in electrolytes I, II and III. It is seen that E_{corr} shifts toward the noble direction as the concentration of $CuCl_2$ increases. This is in agreement with the results of Lin et al [23]. The increase in temperature, above 75^0C, shifts the values of E_{corr} in electrolytes I and II closer to each other than they are at 75^0C. In electrolyte III, increasing the temperature shifts the free corrosion potential to more noble values. A comparison of these values of free corrosion potential with the equilibrium potentials of the hydrogen evolution (H_2O/H_2) and copper reduction (Cu/Cu^{++}) reactions is necessary in order to identify the cathodic half reactions. Table 1 lists the values of the equilibrium potential of both systems at various temperatures in electrolytes I, II and III. Note that these values of E_{corr} are considerably negative (cathodic) with respect to the reversible equilibrium potentials of the Cu/Cu^{++} or the H_2O/H^+ electrode systems [24]. The approximate values for Cu/Cu^{++} system in electrolytes II and III are calculated at various temperatures using Nernst equation, i.e.

$$Cu^{2+} + 2e^- \rightleftharpoons Cu \tag{5}$$

$$E = E^0_{Cu/CuCl_2} + \frac{2.303RT}{2F}\log\left[Cu^{2+}\right] \tag{6}$$

The values of E^o were obtained after Latimer [25], the activity of the Cu^{2+} species was taken equal to its concentration. The values of E (H_2O/H^+) at different temperatures were taken from Pourbaix diagrams [26, 27]. Consequently, under the potentials shown in Fig. 2, the cathodic half reaction involves the reduction of both water and Cu^{2+}, while the anodic half reaction involves the dissolution of the alloy. Since the concentration of Cu^{2+} is rather small in electrolyte II, the time behavior of E_{corr} is not significantly different from that in electrolyte I at the higher temperatures i.e. 125, 175 and 250°C. This indicates that the reduction of copper becomes less significant in electrolyte II.

Table 1. Approximate values of electrode potential (V) for Cu/Cu^{2+} calculated at various temperatures using Nernst equation in electrolytes II and III and H_2O/H^+ systems in electrolytes I, II and III [11-13].

Med. / Temp.	Electrolyte I	Electrolyte II		Electrolyte III	
	H_2O/H^+	Cu/Cu^{2+}	H_2O/H^+	Cu/Cu^{2+}	H_2O/H^+
75°C	- 0.442	+ 0.312	- 0.405	+ 0.329	- 0.361
125°C	-	+ 0.309	-	+ 0.327	-
175°C	-	+ 0.305	-	+ 0.326	-
250°C	- 0.551	+ 0.299	- 0.484	+ 0.325	- 0.415

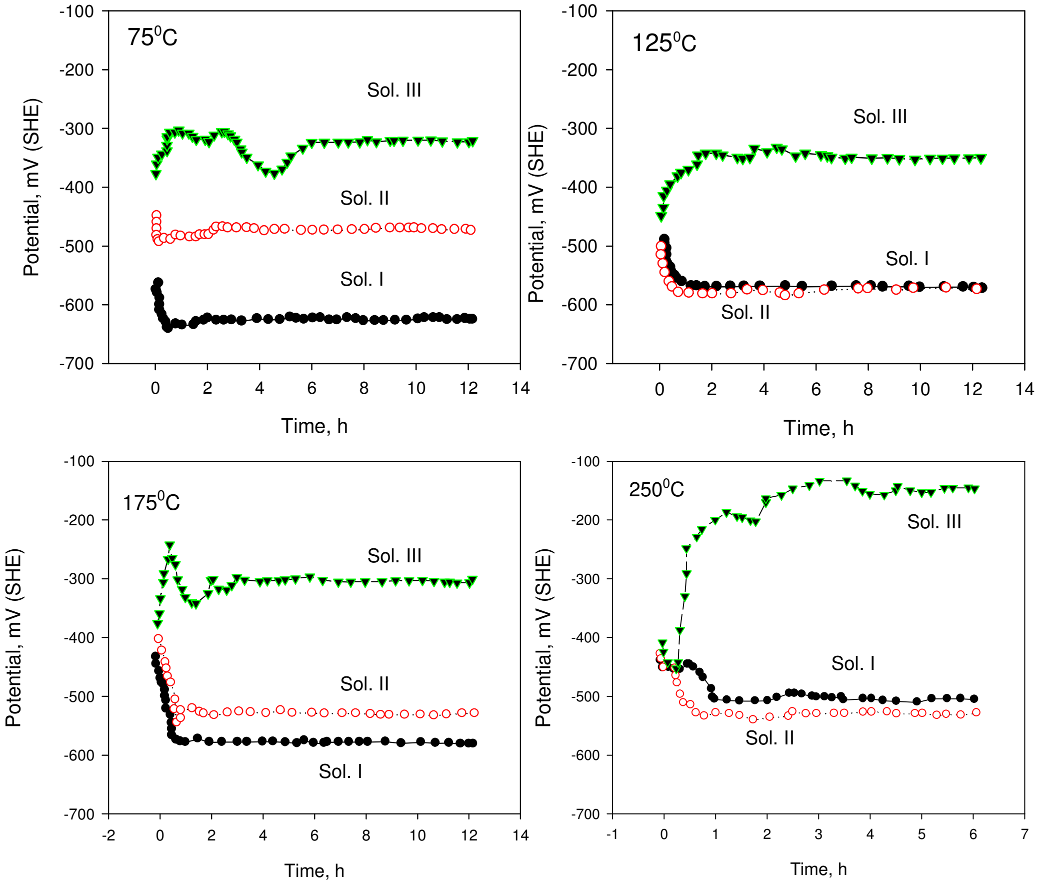

Figure 2. Time variation of the free corrosion potential of the alloy in different solutions at different temperatures; Sol. I (1 m NaCl), Sol. II (0.999 m NaCl + 0.0005 m $CuCl_2$) and Sol. III (0.9 m NaCl + 0.05 m $CuCl_2$).

3.2 Polarization Curves

Figure 3 shows the potentiodynamic current-potential curves for the alloy at different temperatures in electrolytes I, II and III obtained at a scan rate of 1.6 mV s^{-1}. The free corrosion potential is quite sensitive to the level of $CuCl_2$ in the electrolyte. The results reveal the following features, upon increasing the concentration of $CuCl_2$ at 75^0C.

i. The free corrosion potential shifts towards more noble values, to an extent which increases with the concentration of $CuCl_2$. These results are in accordance with that obtained in Fig. 2 which shows the variation of the free corrosion potential with time.

ii. The cathodic current density increases. The cathodic limiting current increases by about 3 orders of magnitude upon addition of 5 x 10^{-2} m $CuCl_2$.

iii. The anodic limiting current is not significantly affected.

iv. The effect on the anodic current (below the limiting current) is more complex. While the presence of 5 x 10^{-4} m $CuCl_2$ appears to promote the anodic reaction (by decreasing the potential by several tens of mVs), the presence of 5 x 10^{-2} m $CuCl_2$ retards the anodic reaction considerably (by increasing the potential by up to about 200 mV). Both phenomena are attributed to the presence of Cu^{2+} ions in solution. Thus in the case of high $CuCl_2$ concentration, the reduction of Cu^{2+} ions leads to the formation of solid Cu metal on the corroding metal surface. This explains the increase in the cathodic limiting current with the increase in the concentration of $CuCl_2$.

The corresponding current-potential results obtained at 125, 175 and 250°C are presented in Figs. 3 b, c and d, respectively. These bear similar features to those shown in Fig 3a. It is clearly seen at all temperatures that as the concentration of $CuCl_2$ increases, the corrosion potential shifts towards more noble values. Furthermore, as the temperature increases, the limiting currents of both the anodic and cathodic half reactions increase.

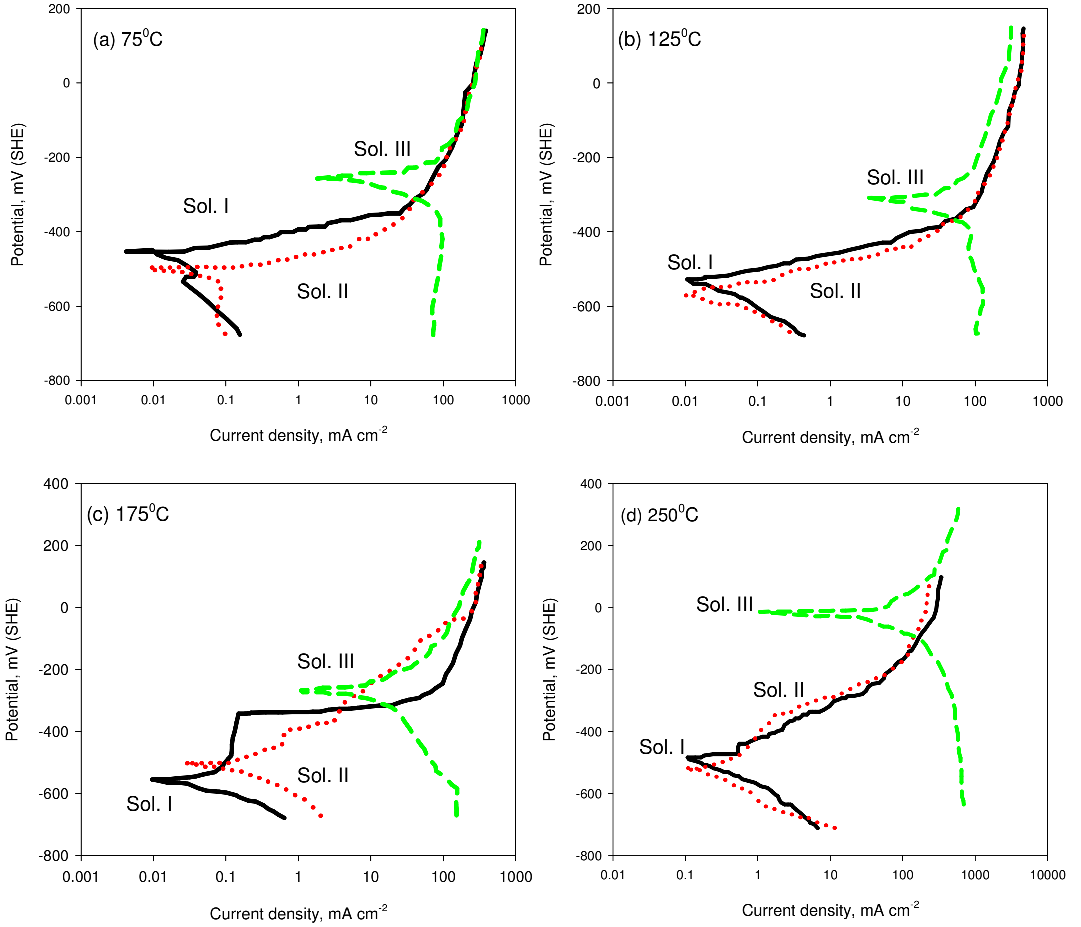

Figure 3. Current-potential curves for the alloy at different temperatures; Sol. I (1 m NaCl), Sol. II (0.999 m NaCl + 0.0005 m $CuCl_2$) and Sol. III (0.9 m NaCl + 0.05 m $CuCl_2$).

3.3 Effect of precorrosion on polarization

A set of cyclic potentiodynamic polarization curves were obtained using precorroded electrodes for different times (7 and 72hrs) in sol. I and sol. III either by using the same precorroding solution or a fresh solution.

Inspection of the results of polarization in the same solution I in Fig.4 (a and b) revealed that, as the time of the precorrosion increases, the free corrosion potential is shifted to more noble values. These were -560, -400 and -390 mV at 0, 7 and 72 hrs precorrosion time, respectively. During the backward direction of scanning E_{corr} was shown to be more noble. The above results indicate that the corrosion product which formed protects the alloy surface. The protective effect of the corrosion product is illustrated by the decrease in the anodic limiting current upon increasing the precorrosion time (~ 200, 150 and 90 mA at 0, 7 and 72 hrs, respectively). The cathodic limiting current in the forward scanning direction disappeared. While in the backward scanning direction the presence of Fe^{2+} ions , due to the anodic dissolution, is responsible for the observation of cathodic limiting current of about 5 and 10 mA at 7 and 72 hrs precorrosion time, respectively.

Figure 4 (c and d) shows also cyclic potentiodynamic polarization curves in solution I using a fresh solution. A shift in the free corrosion potential to more noble values was observed which points to the protective effect of the corrosion product. The anodic limiting current decreases as the time increased then it increases again (200, 150 and 190 mA at 0, 7 and 72 hrs, respectively), this is due to increasing the Fe^{2+} ions concentration due to the anodic dissolution. As the concentration of these reducible cations reaches a pronounced level it accelerates the dissolution.

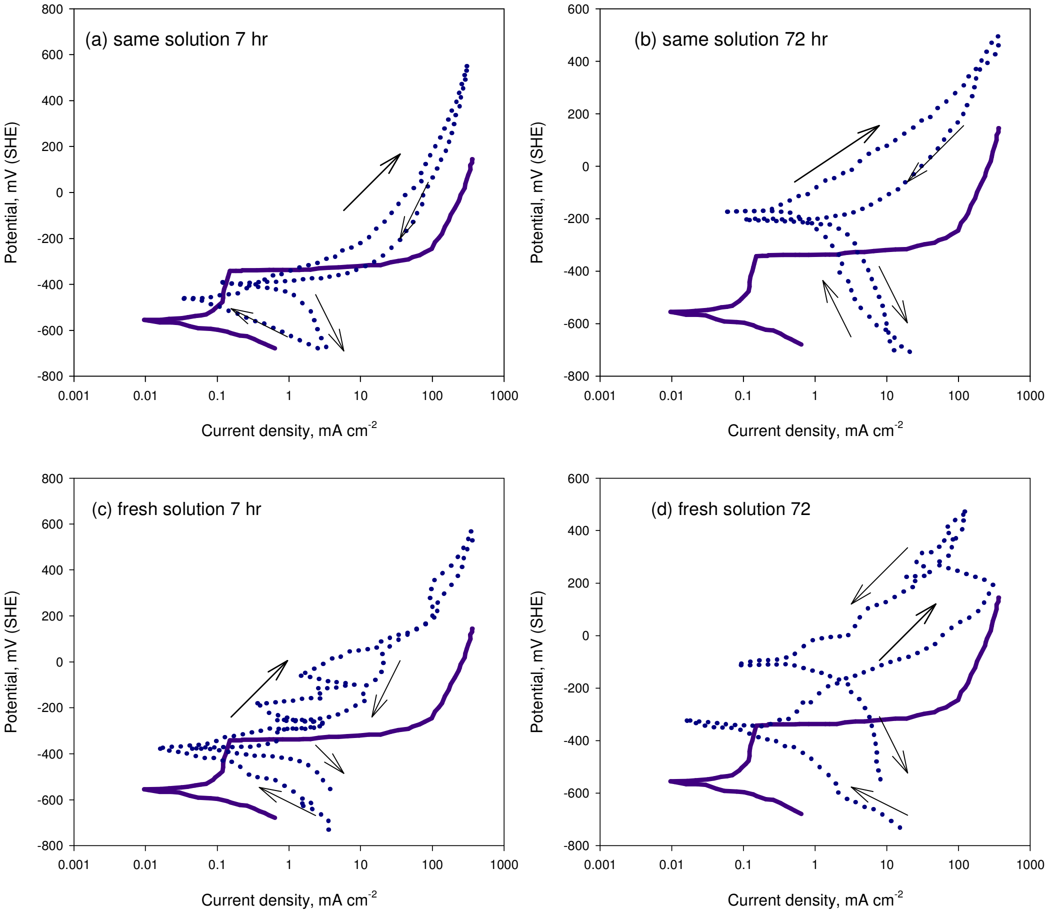

Figure 4. Current-potential curves for the alloy precorroded in 1 m NaCl at 175^{0}C for 7 hrs and 72 hrs. Solid line represents polarization using blank electrode surface.

Figure 5 shows the cyclic potentiodynamic polarization in solution III after different precorrosion times using the same and fresh solutions. According to the discussion presented above, the presence of Cu^{2+} ions in solution was shown to shift the corrosion potential to more noble values (about 200 mV). This may interpreted in terms of reaction 1. Applying the theory of mixed potential [28], it is assumed that reaction 1 shifts the overall mixed potential to more noble values. This tendency increases as the concentration of Cu^{++} increases according to Nernest equation (eqn. 6) this is shown schematically in the following Fig. 6.

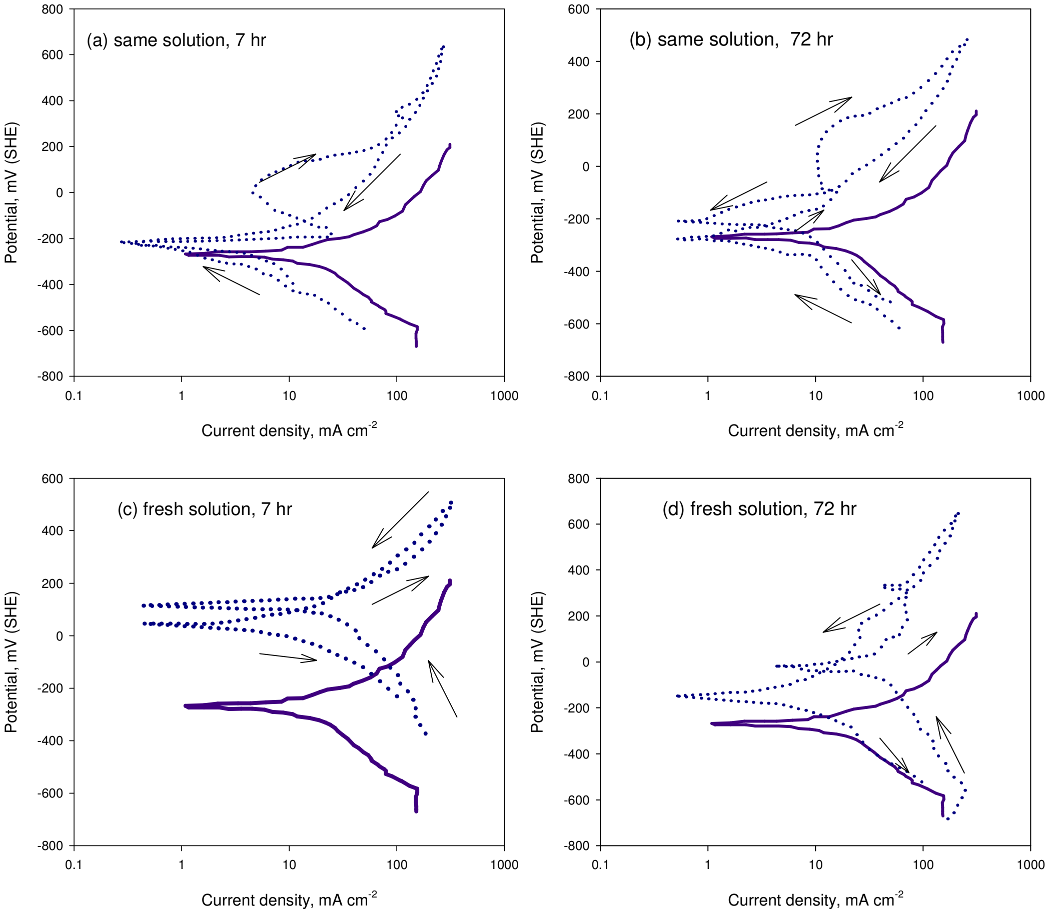

Figure 5. Current-potential curves for the alloy precorroded in sol. III at 175^0C, using the same and fresh solution for 7 and 72 hrs. Solid line represents the polarization using blank electrode surface.

Thus, the corrosion potential is shifted to more noble values in fresh solution III , Fig. 5 (c) at 0 and 7 hrs precorrosion time. It is noteworthy that the effect of addition of Cu^{2+} ions no longer affect the precorroded electrode (at and beyond 72 hrs) . This may be due to the low electronic conductance of the loosely adherent film. Cathodic limiting current (i_{Lc}) was observed in the polarization curve on the fresh electrode surface in electrolyte III as a result of Cu^{2+} ions deposition. Using a fresh solution, we expected that the limiting current increases as the concentration of $CuCl_2$ increases. However, the results in Fig. 5 revealed that, after 7 hrs of precorrosion, i_{Lc} was found to increase but after 72 hrs of precorrosion the value of i_{Lc} remains unchanged. This may be attributed to the hindrance effect of the corrosion product film or to the high electronic resistivity of the loosely adherent film which retards the electron transfer reaction. When the polarization experiment was conducted in the same solution, i_{Lc} was clearly disappeared, this is due to Cu^{2+} depletion from the solution i.e. Cu^{2+} was deposited on the electrode surface during precorrosion, some of them spall off the corroding surface in metallic state. The deposition of metallic copper was evidenced previously at open circuit condition by XRD [16]. The anodic limiting current seems to be the same, regardless of whether the solution used was fresh or the same solution in which the precorrosion test was performed. This means that Cu^{2+} ions have no role on the anodic limiting current. Although the polarization in fresh solution reveals lowering the corrosion rate by shifting the potential towards more noble values, it was found that the absence of further addition of Cu^{2+} (i.e. using the same solution) passivates the alloy surface. This is shown in Fig. 5 , in the same solution. The passive region was continued for 200 mV at current density 9 mA after 7 hrs and 15 mA after 72 hrs.

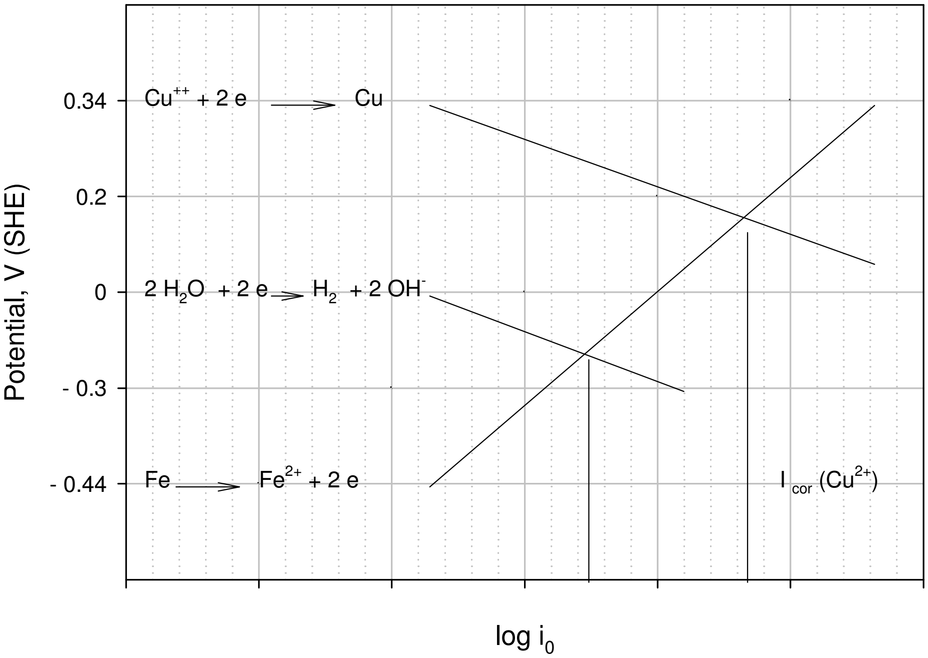

Figure 6. Schematic representation of the electrode kinetics behavior of iron and copper in aqueous solution.

4. CONCLUSIONS

- Contamination of salt water with a fairly high concentration of Cu^{2+} ions results in a shift in corrosion potential, at all temperatures, towards more noble values and to an increase in the cathodic current density.

- Cu^{2+} ions undergo electrodeposition of Cu metal onto the corrosion products, which becomes less adherent and less protective. Most of this Cu metal falls off the alloy surface along with the spalled corrosion products. Passivation occurs after the effect of copper is diminished.
- In absence of Cu^{2+} ions the shift in the corrosion potential towards more noble values, with the increase in the precorrosion time, indicates that the corrosion product which forms protects the surface against further attack.

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