

KINETICS OF HIGH TEMPERATURE CORROSION OF A LOW Cr-Mo STEEL IN AQUEOUS NaCl SOLUTION

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ABSTRACT

The kinetics of corrosion of a low Cr-Mo steel alloy were studied over the temperature range of 75-250°C in 1 M NaCl in absence and in presence of various levels of contamination with CuCl₂. We measured corrosion rates, weights of corrosion product (magnetite) film and total (integral) weight loss of the alloy over exposure times from 1 up to 480 hrs. The corrosion rate decreases rapidly with time, before it levels off at longer time, indicating the formation of a protective corrosion product film. The ability of the alloy to retain an adherent corrosion product (magnetite) film was expressed in terms of a retention coefficient. This was found to increase with temperature and exposure time and to decrease with the level of contamination with CuCl₂. This effect of temperature was attributed to the improvement of the crystallinity of the corrosion product. On the other hand, the effect of CuCl₂ was attributed to the electrodeposition of Cu and its impregnation within the corrosion product, which becomes less adherent. The free corrosion potential was found to be affected by the presence of the CuCl₂, in a fashion compatible with the Wagner-Traud theory of mixed potential.

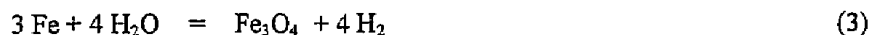
Key Words: Kinetics - Corrosion - Steel - High temperature - Sodium chloride solution - Copper chloride.

INTRODUCTION

The corrosion of steel in high temperature aqueous environments is encountered in many industrial applications, e.g. boiling water reactors [1], desalination plants [2], high temperature aqueous fuel cells [3], steam generators [4] etc. In such environments, contaminants, which are present in the aqueous media at trace levels, are concentrated by orders of magnitude to form highly corrosive solutions [5]. Due to the active nature of iron, it corrodes in high temperature deaerated water and steam giving rise to the formation of ferrous, Fe²⁺, species which change to ferrous hydroxide, Fe(OH)₂, and to magnetite, Fe₃O₄ [6-10] i.e.



The overall reaction is represented by:



Some of the resulting magnetite adheres onto the surface in the form of a film which affects the kinetics of subsequent corrosion of the steel. On the other hand, the rest of the resulting magnetite spalls off the surface into the electrolyte. The qualities of the adherent magnetite film depend on the temperature, composition of the environment and exposure time.

The objectives of this paper are to study the kinetics of corrosion of a low Cr-Mo steel in high temperature NaCl solution, and the mechanism of protective film formation during this process. Particular attention is given to the effect of contamination of the electrolyte with CuCl_2 on the integrity of the protective film and hence on the subsequent corrosion. The effect of CuCl_2 concentration, temperature and exposure time on the extent of adherence of the magnetite film was also determined.

EXPERIMENTAL

All measurements were performed in an autoclave fabricated from 316 Type stainless steel. It consisted of two parts. A (Teflon) PTFE cell was machined to fit tightly into the autoclave, to accommodate the electrolyte. Further details are given elsewhere [11]. The cell was preheated for about 5 hrs to obtain thermal stabilities [12,13]. The autoclave was placed in a furnace, connected with the temperature regulator to the heating source. A Ni-Cr thermocouple was used to regulate the temperature. It was inserted into a stainless steel tube coated with a layer of PTFE. The corrosion rate measurements were performed on coupons (2 x 5 x 0.2 cm) made of a low Cr-Mo steel of the following composition (wt%): Cr, 2.3; Mo, 1.0; Mn, 0.46; Si, 0.2; C, 0.13; P, 0.015; S, 0.007; Fe balance. They were annealed at 900°C for 1 hr in argon atmosphere and furnace cooled. Their microstructure revealed fine dispersed carbide in a matrix of ferrite. Before use, they were polished successively down to 600 grit using silicon carbide paper, rinsed with ethyl alcohol, distilled water and dried in air. Three electrolytes were used: (I) 1 molal(m) NaCl, (II) 0.999 m NaCl + 5×10^{-4} m CuCl_2 and (III) 0.9 m NaCl + 5×10^{-2} m CuCl_2 . They were deaerated by boiling the electrolyte under reflux for 15 min to give an oxygen content of less than 0.1 ppm (as estimated polarographically). The volume of the electrolyte in each test was 200 ml. The tests lasted for various durations i.e. 1, 3, 6, 12, 24, 48, 96 and 480 hrs and were performed in triplicates. Two of the three specimens were subjected to successive de-scaling by immersing for 20 min. in a 20% ammonium citrate solution at 80°C [14] to dissolve the corrosion products, rinsed with distilled water, dried and weighed until a constant weight was obtained. We calculated the integral weight (ΔW_i) i.e. the weight of the alloy which dissolved up to the particular time, and the weight of the corrosion product film (ΔW_f) which remained adherent per 1 cm² of the area after a particular time. After each test, the solution was found to contain some solid (spalled) corrosion products.

The working electrode consisted of a rectangular sheet of a bout 9 cm in length, 0.5 cm in width and 0.2 cm thickness. It was insulated with PTFE in such a way as to expose an area of 1 cm² at its end. The other end was threaded and connected to a stainless steel rod of 0.3 cm diameter through a stainless steel connector. A graphite rod of 0.5 cm diameter and about 10 cm length was used as a counter electrode and an Ag/AgCl was used as reference electrode [12,15].

RESULTS AND DISCUSSION

Corrosion rate

Figures 1 (a-c) illustrate the variation of the corrosion rate with the time of immersion at various temperatures in: (a) electrolyte I, (b) electrolyte II and (c) electrolyte III. Figure 3d compares the behaviour in the three electrolyte at 250°C. They clearly reveal same significant features; (i) At short times, the corrosion rate decreases rapidly with the time of immersion before it tends to level off at longer times. This behaviour is characteristic of protective film formation [16]. (ii) There is a strong detrimental effect of CuCl₂ on the ability of the magnetite film to protect the substrate alloy, (iii) As the temperature and / or exposure time increase, the corrosion rate decreases.

The present work reveals that the mechanism of corrosion changes after a transition time, τ , the magnitude of which, generally, decreases as the temperature of the test 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 [11,17], hence reducing the rate of corrosion. Before this transition time, the alloy corrodes more freely with higher rate of corrosion. It was found that, at a given temperature, increasing the concentration of CuCl₂ the transition time, τ , increases [17].

Retention coefficient

The retention coefficient is introduced here to give a quantitative expression for the ability of the alloy to retain an adherent corrosion product film on its surface under the corrosive environment. It is defined as the ratio of the weight of the adherent (magnetite) film $\Delta W_{f(adh.)}$ at a particular time of immersion to the total weight of the (magnetite) film which would form if the integral weight loss of the alloy were to be totally consumed in forming the film material (magnetite) i.e. $\Delta W_{f(total)}$. The later value is related to the integral weight loss ΔW_i by a chemical factor (C.F), which in the present case is given by the ratio of the molecular weights of Fe₃O₄ and 3 Fe i.e. C.F. = 232/168 = 1.38. Thus the retention coefficient is given by:

$$\text{Retention coefficient } \varphi = \Delta W_{f(adh.)} / \Delta W_{f(total)} \quad (3)$$

The retention coefficient was determined at various temperatures, CuCl₂ concentrations and at intervals of time. Figures 2 (a-d) illustrate the variation of the retention coefficient, φ , with the time of immersion for the three electrolytes at various temperatures. The curves clearly reveal that φ increases as the temperature increases and decreases as the concentration of CuCl₂ increases. Reaction (2) which is called the Schikorr reaction [18] has been extensively studied [19,20]. Ferrous hydroxide, Fe(OH)₂, decomposes rapidly above 100°C [21], but relatively slowly at lower temperatures. Robertson [22] stated that the corrosion of steel in hot water is controlled by the dehydration of the hydroxide phase (equation 2), which proceeds when the metal / solution interface becomes saturated with Fe(OH)₂. Consequently, we have two factors affecting reaction 2,

- i. The saturation with Fe(OH)₂ at the metal / solution interface which is time dependent, and

- ii. The temperature, which enhances the reaction in the forward direction and also affects the solubility [23] and crystallinity of the magnetite film [17].

This explains the higher ϕ values obtained at higher temperatures and longer exposure times and hence the increased efficiency of the film in retarding corrosion. On the other hand, it is seen that the presence of CuCl_2 in the electrolyte decreases ϕ . This has previously been shown [17] by x-ray diffraction and SEM to be due to the electrodeposition of Cu and its impregnation within the magnetite film which becomes less adherent.

Comparing the results of Figs. 1 and 2, it can be concluded that, in most cases, as the retention coefficient decreases, the corrosion rate increases. In other cases, both the retention coefficient and the corrosion rate increase in the same direction. This result indicates that the film formed, though is retained on the alloy surface, it is unable to protect it from subsequent corrosion.

Potential-time curves

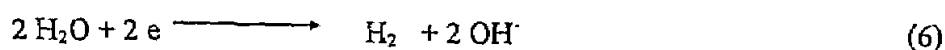
Figure 3 illustrates the time variation of the free corrosion potential, E_{cor} , of the alloy at different temperatures in electrolytes I, II and III. It is seen that E_{cor} shifts toward the noble direction as the concentration of CuCl_2 increases. This is in agreement with the results of Lin et al [24]. The increase in temperature, above 75°C , shifts the values of E_{cor} in electrolytes I and II closer to each other than they are at 75°C . 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 ($\text{H}_2\text{O}/\text{H}_2$) and copper reduction (Cu/Cu^{++}) reactions is in order to identify the cathodic half reactions. Table 1 lists the values of the equilibrium potentials of both systems at various temperatures in electrolytes I, II and III. Note that these values of E_{cor} are considerably negative (cathodic) with respect to the reversible equilibrium potentials of the Cu/Cu^{++} or the $\text{H}_2\text{O}/\text{H}_2$ electrode systems [6]. The approximate values for Cu/Cu^{++} system in electrolytes II and III are calculated at various temperatures using Nernst equation, i.e.



$$E = E^0_{\text{Cu}/\text{CuCl}_2} + 2.303 RT/2F \log [\text{Cu}^{2+}] \quad (5)$$

The values of E^0 were obtained from Latimer [25], the activity of the Cu^{2+} species was taken equal to its concentration. The values of E ($\text{H}_2\text{O}/\text{H}_2$) at different temperatures were taken from Pourbaix diagrams [6, 26,27].

Consequently, under the potentials shown in Fig. 6, the cathodic half cell reaction involves the reduction of both water i.e. reaction 6



and the electrodeposition of Cu according to reaction 4, while the anodic reaction involves the dissolution of the iron i.e. reaction 7

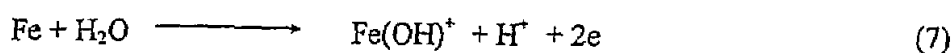


Table 1 Approximate values of electrode potential, V (NHE) of the Cu/Cu²⁺ calculated at various temperatures using Nernst equation in electrolytes II and III and of the H₂O/H₂ systems in electrolytes I, II and III [6, 26,27].

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

Since the concentration of Cu²⁺ is rather small in electrolyte II, the time behaviour of E_{cor} is not significantly different from that in electrolyte I at the higher temperatures i.e. 125, 175 and 250^oC. Alternatively, in presence of higher concentration of CuCl₂, the rate of reaction 4 is greatly enhanced leading to an increase in the corrosion rate.

The results of Figure 3 can be explained within the domain of the Wagner-Traud theory of mixed potential [28,29], shown schematically in Fig. 4, which illustrates the effect of a significant increase in the rate of the cathodic reaction on the corrosion rate (I_{cor}) and the corrosion potential (E_{cor}). For the sake of simplicity, we neglect the changes in the anodic polarization curves of reaction 4 brought about by adding CuCl₂. Upon changing the cathodic half cell reaction from reaction 6 to reaction 4, Fig. 4 shows a significant increase in the corrosion current, I_{cor} and a significant shift in the mixed (free corrosion) potential towards more noble values. Both phenomena we confirmed by the experimental measurements of Figs. 1 and 3.

CONCLUSIONS

Inspection of the above results reveals the following conclusions:

1. At short times, the corrosion rate decreases rapidly with the time of immersion before it tends to level off at longer times. This behaviour is characteristic of protective film formation
2. The retention coefficient is introduced here to give a quantitative expression for the ability of the alloy to produce an adherent corrosion product film under the corrosive environment. It was found that increasing the temperature enhances the ability of the alloy surface to retain the film. The concentration of CuCl₂ has an opposite effect.
3. The results of potential-time curves measured in different electrolytes reveal that E_{cor} shifts towards the noble direction to an extent which increases with the concentration of the CuCl₂. This is shown to be compatible with the Wagner-Traud theory of mixed potential. The increase in temperature, above 75^oC, shifts the values of E_{cor} in electrolyte I and II closer to each other than they are at 75^oC.

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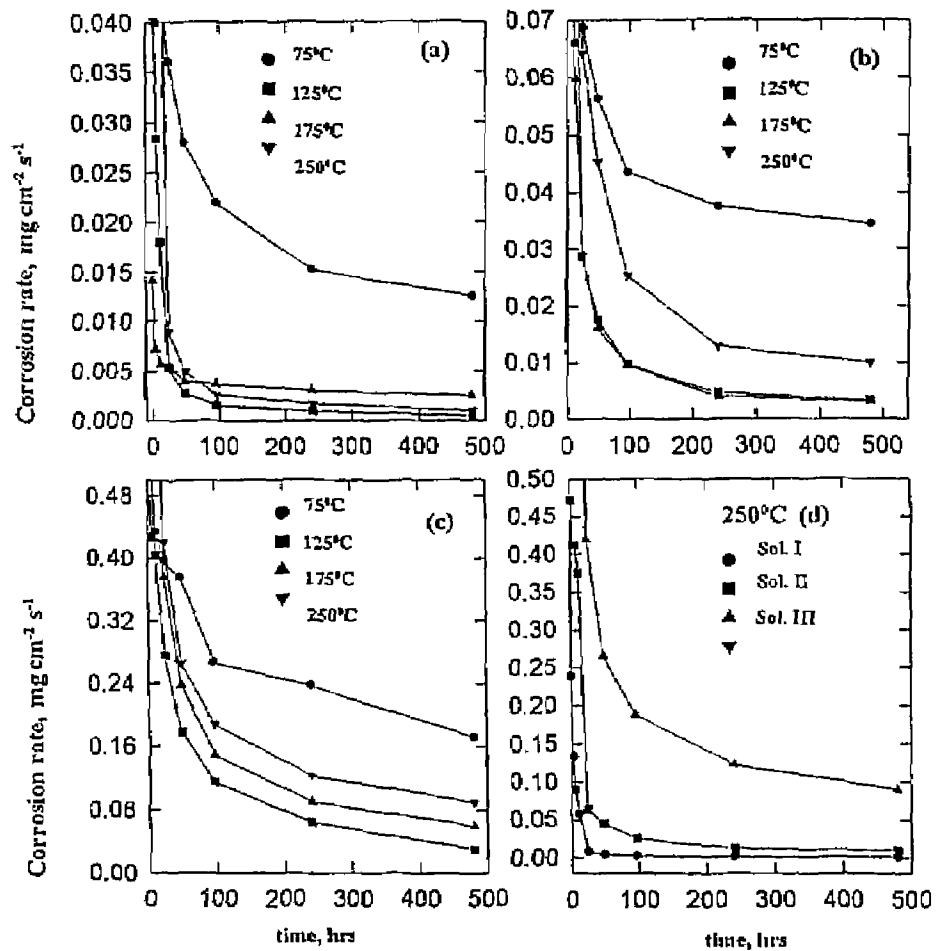


Fig. 1 Variation of the corrosion rate with the time of immersion
 * at different temperatures in (a) sol. I, 1 m NaCl; (b) sol. II,
 0.999 m NaCl + 0.0005 m CuCl₂; (c) sol. III, 0.9 m NaCl +
 0.05 m CuCl₂.

** at 250°C in different solutions (d)

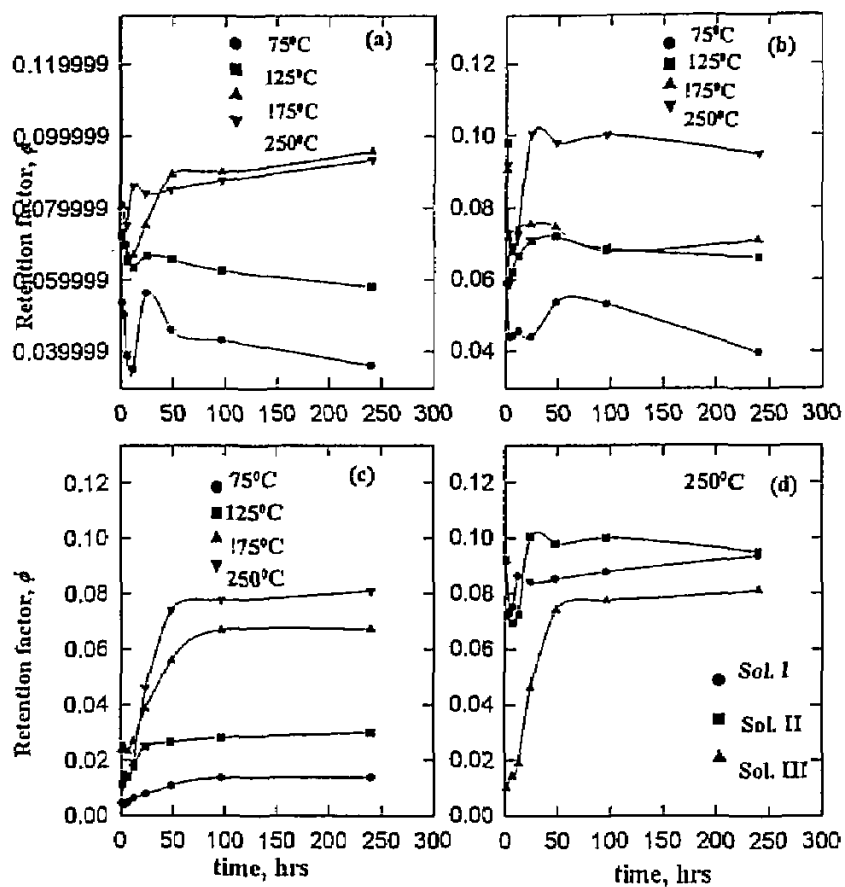


Fig. 2 Variation of the retention coefficient, ϕ , with the time of immersion

* at different temperatures in (a) sol. I, 1 m NaCl;

(b) sol. II, 0.999 m NaCl + 0.0005 m CuCl₂ ; .

(c) sol. III, 0.9 m NaCl + 0.05 m CuCl₂

** at 250°C in different solutions (d)

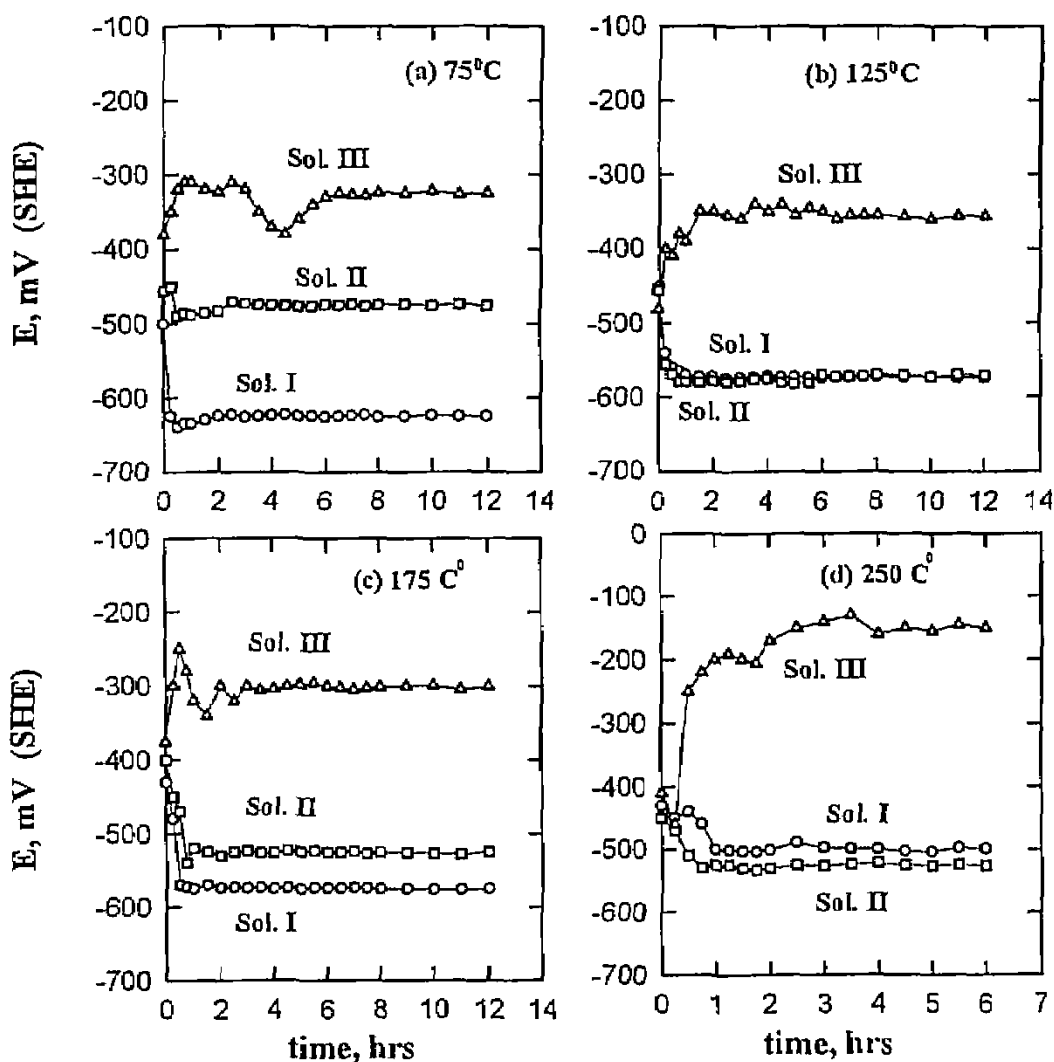


Fig. 3 Time variation of the free corrosion potential for the alloy at different temperatures in electrolyte I (1 m NaCl), II (0.999 m NaCl + 0.00005 m CuCl₂) and III (0.9 m NaCl + 0.05 m CuCl₂).

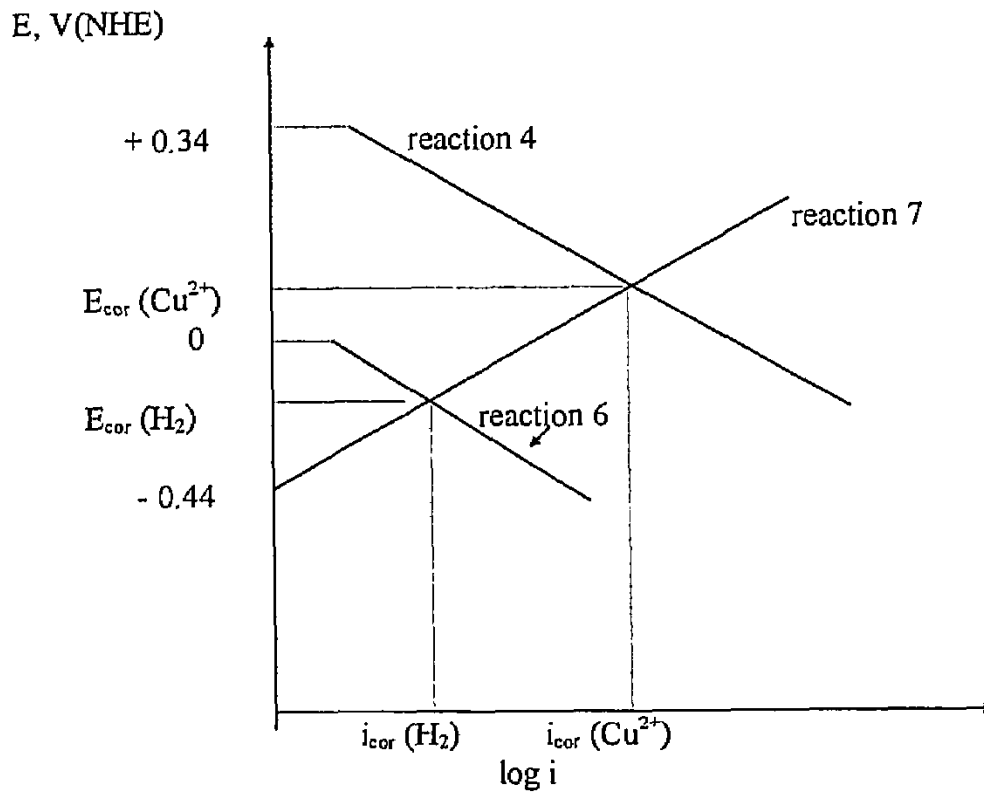


Fig.4 Schematic representation of the effect of $CuCl_2$ on the mixed potential of iron in the corrosive medium.