

## SODIUM NITRITE AS INHIBITORS FOR PROTECTION OF REBAR AGAINST CORROSION

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### Abstract:

Corrosion inhibitors studies were carried out on carbon steel rebar samples under different pH conditions and in the presence and absence of chloride ions in solution. A known amount of sodium nitrite was added as an inhibitor and the mechanism of inhibition was studied by tracking both the thermodynamic and kinetic properties of the system. The studies indicate that inhibition efficiency decreases with increase of temperature, and there is a competition between the corrosion and passivation reactions, and the resulting open-circuit potential depends on the relative strength of the corroding and passivating environments. The corrosion rate depends to a great extent on the pH of the solution. Nitrite ions act as anodic inhibitors by increasing the rate of formation of a barrier oxide film. The protective action of the nitrite ions seems to be more pronounced in highly corroding environment. This is due to the mechanism of inhibition, which uses the product of the unwanted corrosion reaction and converts it into a favorable passivating one. For a given amount of chloride, a minimum threshold concentration of nitrite is essential for protecting the steel.

**Keyword :** Corrosion Inhibitors, Corrosion of rebar, Sodium Nitride.

استعمال نتريدات الصوديوم كمادة مثبطة في حماية حديد التسليح من التآكل

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الخلاصة :

في هذه الدراسة تم اختبار عينات من حديد التسليح Rebar تحت ظروف PH مختلفة ودرجات حرارة مختلفة وبوجود نسب مختلفة من مثبطات التآكل. إذ أضيفت كميات او نسب مختلفة من نترينات الصوديوم Sodium Nitrite كمادة مثبطة للتآكل بعدها درست ميكانيكية عمل هذه المثبطات ، ومن خلال هذه الدراسة وجد أن كفاءة التنشيط للمثبط تقل بارتفاع درجة الحرارة ، وعند جميع درجات الحرارة فإن كفاءة التنشيط تزداد بأزدياد تركيز المثبط. كما وجد أن آلية التنشيط لهذا المثبط هي عبارة عن تكثيف Adsorption جزيئات النترينات على سطح المعدن ( حديد التسليح ) بالإضافة الى تكوين طبقة خاملة على

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سطحه ( يوجد تنافس بين تكوين طبقة رقيقة خاملة على سطح المعدن او ميله إلى التآكل ). ووجد أيضاً أن معدل التآكل يعتمد على مقدار PH للمحلول.

كلمات مفتاحية : مثبطات التآكل ، تآكل حديد التسليح ، نتريدات الصوديوم

## 1. Introduction:

ASTM terminology (G15) defines corrosion as “the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties.” For steel embedded in concrete, corrosion results in the formation of rust which has two to four times the volume of the original steel and none of its good mechanical properties. Corrosion also produces pits or holes in the surface of reinforcing steel, reducing strength capacity as a result of the reduced cross-sectional area. Reinforced concrete uses steel to provide the tensile properties that are needed in structural concrete. It prevents the failure of concrete structures which are subjected to tensile and flexural stresses due to traffic, winds, dead loads, and thermal cycling. However, when reinforcement corrodes, the formation of rust leads to a loss of bond between the steel and the concrete and subsequent delamination and spalling. If left unchecked, the integrity of the structure can be affected. Reduction in the cross-sectional area of steel reduces its strength capacity. This is especially detrimental to the performance of tensioned strands in prestressed concrete (American Concrete Institute).

Steel in concrete is usually in a noncorroding, passive condition. However, steel-reinforced concrete is often used in severe environments where sea water or deicing salts are present. When chloride moves into the concrete, it disrupts the passive layer protecting the steel, causing it to rust and pit.

Carbonation of concrete is another cause of steel corrosion. When concrete carbonates to the level of the steel rebar, the normally alkaline environment, which protects steel from corrosion, is replaced by a more neutral environment. Under these conditions the steel is not passive and rapid corrosion begins. The rate of corrosion due to carbonated concrete cover is slower than chloride-induced corrosion. Occasionally, a lack of oxygen surrounding the steel rebar will cause the metal to dissolve, leaving a low pH liquid (Perenchio, 1994).

Corrosion inhibitors are a class of protective products that are added to the concrete mix to delay and prevent corrosion. As such, they are considered admixtures. Both organic and inorganic inhibitors are commercially available (Perenchio, 1994).

A lot of work has been done in identifying the causes, monitoring the corrosion and suggesting and implementing various remedial measures (Tonini and Gaidis 1980; Page et al. 1990). The highly alkaline nature of concrete causes the formation of a natural passive oxide film on the surface of the rebar that would ideally prevent further dissolution of iron. However, the presence of impurities such as chloride ions in the concrete matrix causes the passive film to break down.

(Leek 1991), thereby aiding the corrosion of the rebars. The addition of certain compounds to these systems in regulated quantities has been shown as an effective method to decrease the corrosion rate of steel in concrete (Berke 1989). Organic compounds (Collins et al. 1993), in general, inhibit the corrosion rate by adsorbing onto the surface and hence prevent the passive film breakdown. Inorganic inhibitors like calcium nitrite and molybdates have been added to the

concrete in order to inhibit corrosion (Berke and Stark 1985; Berke 1989; Hope and Ip 1989; Berke et al.1993).

The electrochemical aspect of steel passivation has been studied in more detail in the presence of organic inhibitors (Stratmann et al. 1995) than the inorganic ones.

The objective of this work is attempt to better understand the mechanism by which sodium nitrite aids in the reduction of corrosion rate in a fresh carbon steel surface, as a function of the pH and the availability of chlorides in the system. Long-term studies have been done to study the stability of the passive film formed by sodium ions

## **2. Experimental Study:**

Carbon steel reinforcing bars were machined and polished to provide a cylindrical electrode of area 0.5 cm<sup>2</sup>, that chemical composition is:

Element	C	Mn	Si	P	S	Fe
Weight %	<b>0.2</b>	<b>0.25</b>	<b>0.04</b>	<b>0.009</b>	<b>0.06</b>	<b>Rem.</b>

The passive oxide film along the length of the rebar was covered with Teflon tapes in order to ensure that only the polished surface was exposed to the solution. The electrode was mechanically polished with different grades of silicon carbide papers (240–60 grit size) and alumina to provide a mirror finish. These electrodes were then washed, treated with ethanol, rinsed with ultrapure water, and air dried.

These prepared rebar rods were immersed in a three electrode electrochemical cell containing solutions of two different levels of pH (9.0 and 12.5) and different concentrations of sodium nitrite inhibitors.

The pH levels of the solutions were adjusted by analytical grade NaOH.

A standard saturated calomel electrode (SCE) and a platinum mesh electrode were used as the reference and counter electrode, respectively. A par model 273A potentiostat interfaced to a personal computer was used for data acquisition.

The variation of the corrosion potential ( $E_{corr}$ ) was tracked with time until the sample reached a stable corrosion potential. The variation of  $E_{corr}$  can be used as an indicative test for the formation of a passive film. Linear polarization (Stern-Geary technique) and Tafel measurements were used as the chief experimental techniques in order to determine the instantaneous corrosion rates. The corrosion current can be calculated from the Stern-Geary equation (Fontana 1986)

$$i_{corr} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \frac{1}{R_p} \dots\dots\dots(1)$$

Where  $\beta_a$  and  $\beta_c$  = anodic and cathodic Tafel slopes, respectively; and  $R_p$  = polarization resistance. The Tafel extrapolation technique was carried out by polarizing the electrode system from +250 mV to -250 mV versus open circuit (corrosion) potential.

Apart from the above studies, long-duration experiments were performed on carbon steel samples. The studies were performed in both low (pH = 9.5) and highly alkaline (pH = 12.5) solutions. The

pH solution was prepared by dissolving sodium hydroxide in deionized water until the required pH was reached. For both pH values, a separate set of solutions with 3.5%  $\text{Cl}_2$  by weight was prepared. The two different substrates were then immersed completely in the stock solutions. Linear polarization and corrosion potential measurements were performed on these samples at regular intervals.

Linear polarization was done by polarizing the carbon steel sample 20 mV above and below the equilibrium corrosion potential at a scan rate of 1 mV/s.

### 3. Results and Discussion:

#### 3.1. Effect of temperatures on inhibitors efficiency

Fig. 1 illustrates the variation of the inhibition efficiency (%) versus the concentration of Sodium nitrite at different temperatures.

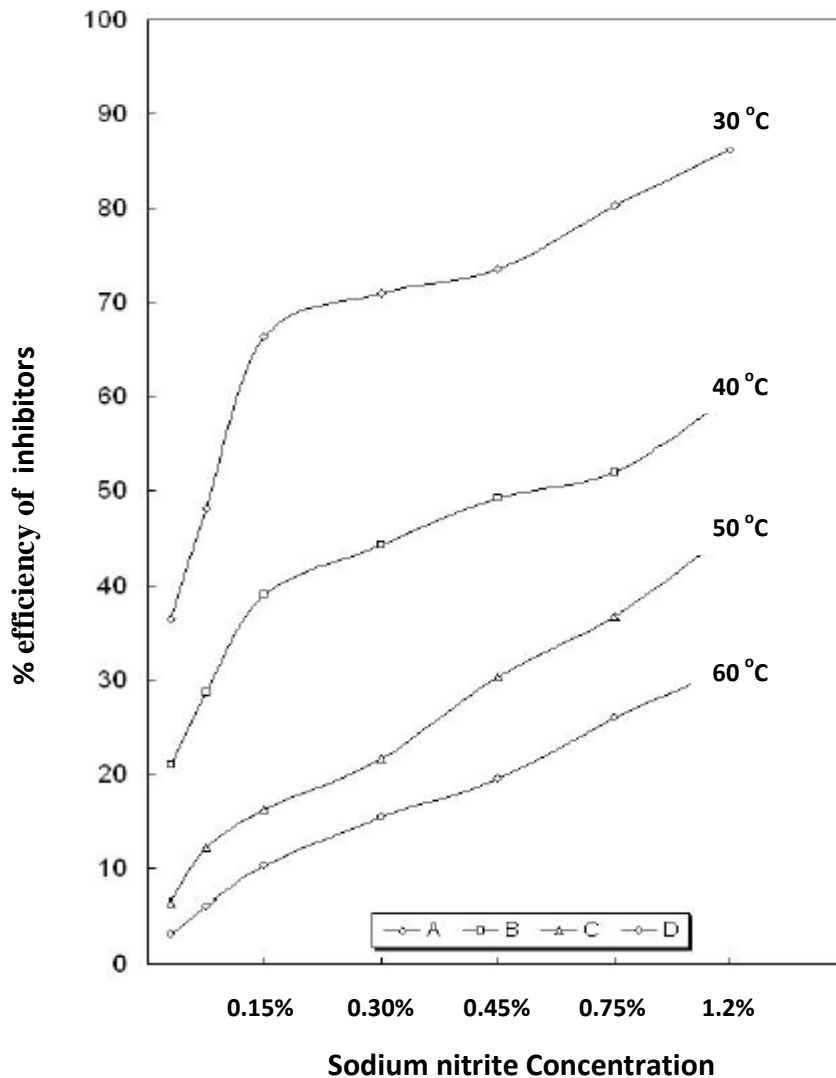


Fig 1: Inhibition efficiency against concentration for rebar in 0.5M HCl at different temperature.

It was observed that inhibition efficiency increases with increased inhibitor concentration with the maximum inhibition for each temperature at Sodium nitrite concentration of 0.005M. Increase in temperature was observed to lower the inhibition efficiency of Sodium nitrite and this behaviour can be explained on the basis that an increase in temperature resulted in the desorption of some adsorbed Sodium nitrite from the steel surface. This makes us predict the mechanism of physisorption of Sodium nitrite on the metal surface. Since physical adsorption is proposed, we expect to have the formation of a multi-layer protective coverage on the surface of the rebar by the inhibitor.

### 3.2. Studies Nitrite Inhibition Mechanism

Fig. 2 gives the  $E_{corr}$  versus time plot obtained for rebar samples immersed in NaOH solutions in pH 9.0 and 12.5 with and without chloride ions in the system.

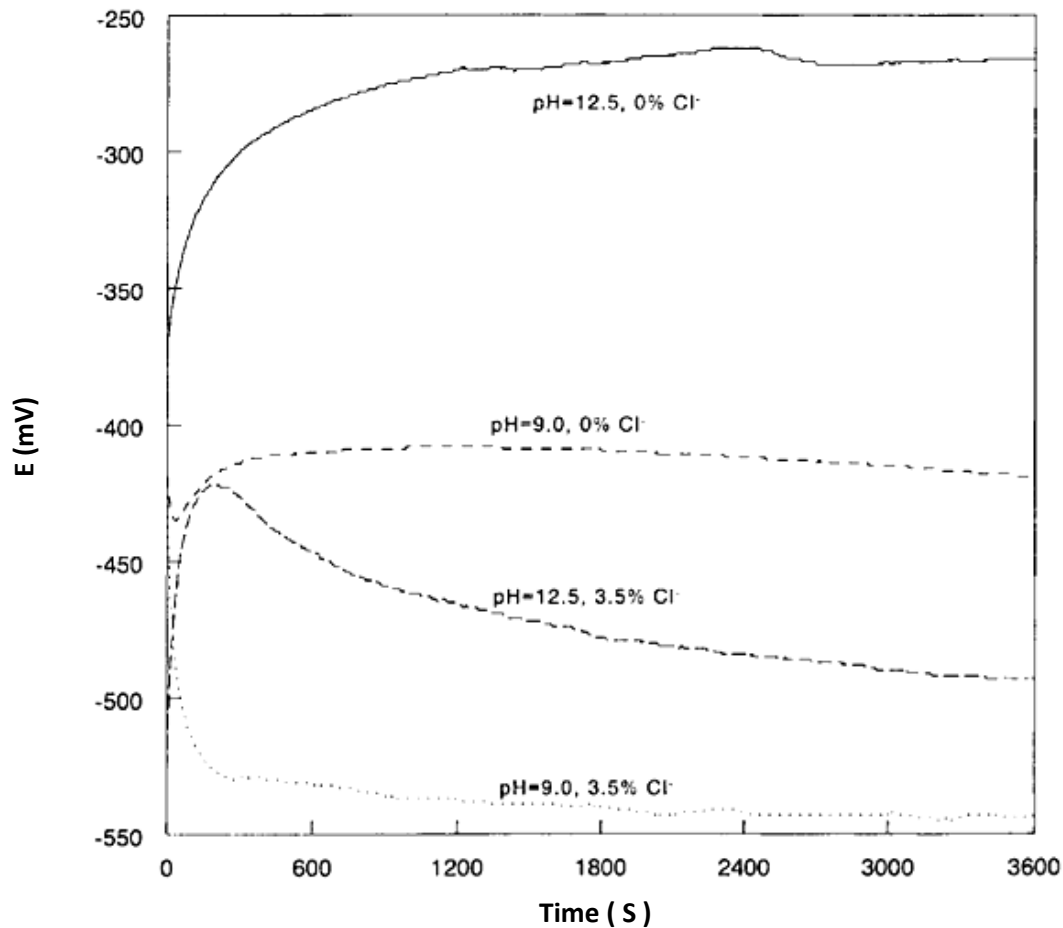


Fig. 2:  $E_{corr}$  versus Time Plots for Rebar Sample Immersed in Solution of Different pH with and without Cl.

The response of the potential at a pH of 12.5 in the absence of chloride indicates that the open circuit (or corrosion) potential starts from around -400 mV. The potential then exponentially

increases in the positive direction and finally stabilizes at a more anodic value at about -270 mV . At a pH of 9.0 in the absence of chlorides, the electrode potential starts at about -420 mV, goes more cathodic and subsequently goes in the anodic direction and stabilizes at about -410 mV. Before an explanation of this behavior is attempted, it must be understood that even though Fig. 2 has a time component in it, the data obtained in this figure does not give any information on the kinetics of the system. The plot of  $E_{corr}$  versus time gives information on the thermodynamics of the process only. An explanation for such a response can be found from the principles of the mixed potential theory (Fontana 1986).

Fig. 3 gives a representative E-log(I) plot for a system, which has rebar, immersed in water. The cathodic reaction is assumed to be oxygen reduction alone.

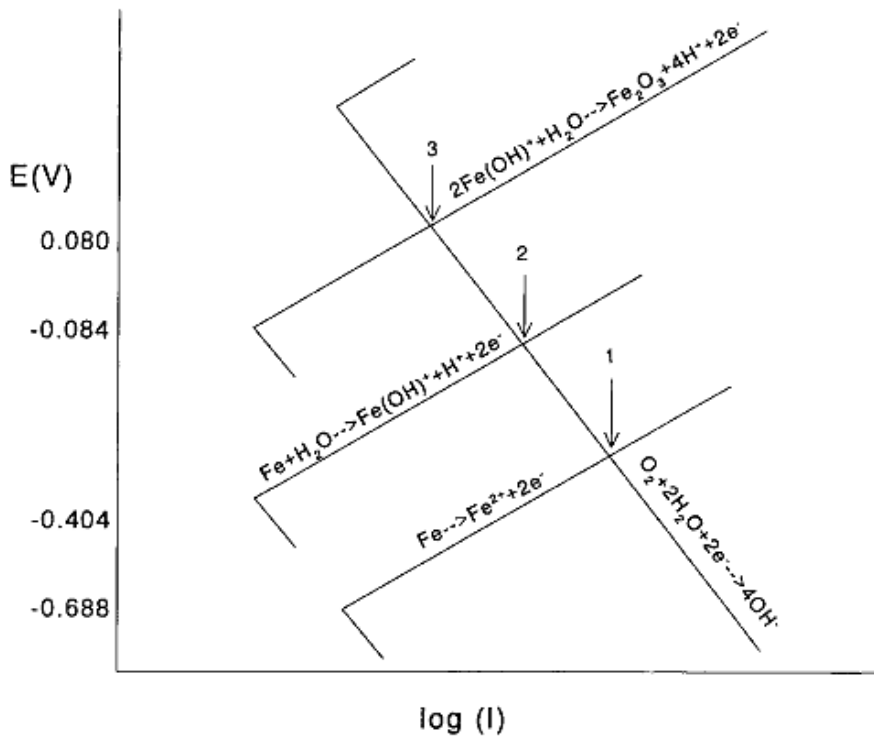
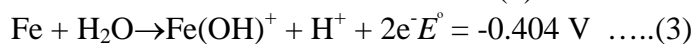
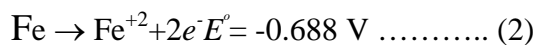


Fig. 3: Evans Diagrams for Rebar.

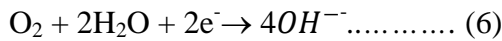
The cathodic reaction is assumed to be oxygen reduction alone. As soon as the iron sample is immersed in the solution, it can react in either of these two predominant ways.



The values for  $E_0$  are the ones obtained for the metal under unit activity (Wagman et al. 1981). The reaction pathway for (3) is given as follows (Bockris and Yang 1991):

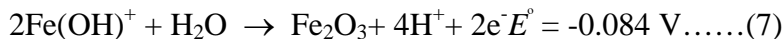


This mechanism indicates that the formation of the hydroxide,  $\text{Fe}(\text{OH})^+$ , depends on the pH of the solution, i.e., availability of  $\text{OH}^-$  ions. At a high pH, the probability of this reaction to occur over in equ. (2) is higher than at low pH. As soon as the metal is immersed in the electrolyte, the corrosion reaction, equ. (2), has a higher possibility to occur due to the unavailability of  $\text{OH}_2$  ions at the electrode surface. As bivalent  $\text{Fe}^{+2}$  ions are formed as a result of (2), in order to maintain electroneutrality,  $\text{OH}^-$  ions are transported from the bulk to the surface. Hydroxide ions are also produced as a result of the cathodic oxygen reduction reaction:



Which causes an increase in the pH at the surface. This prompts the reaction forming  $\text{Fe}(\text{OH})^+$ , equ. 3, to occur over the formation of bivalent  $\text{Fe}^{+2}$  ions, (2).

Hence, in order to accommodate this reaction, the electrode potential tends to shift into a more anodic direction. As the time for which the electrode is immersed increases, the concentration of  $\text{Fe}(\text{OH})^+$  at the surface increases and the surface is covered by these ions. Thus, in order to provide an anodic component for the oxygen evolution reaction,  $\text{Fe}(\text{OH})^+$  undergoes the following reaction:

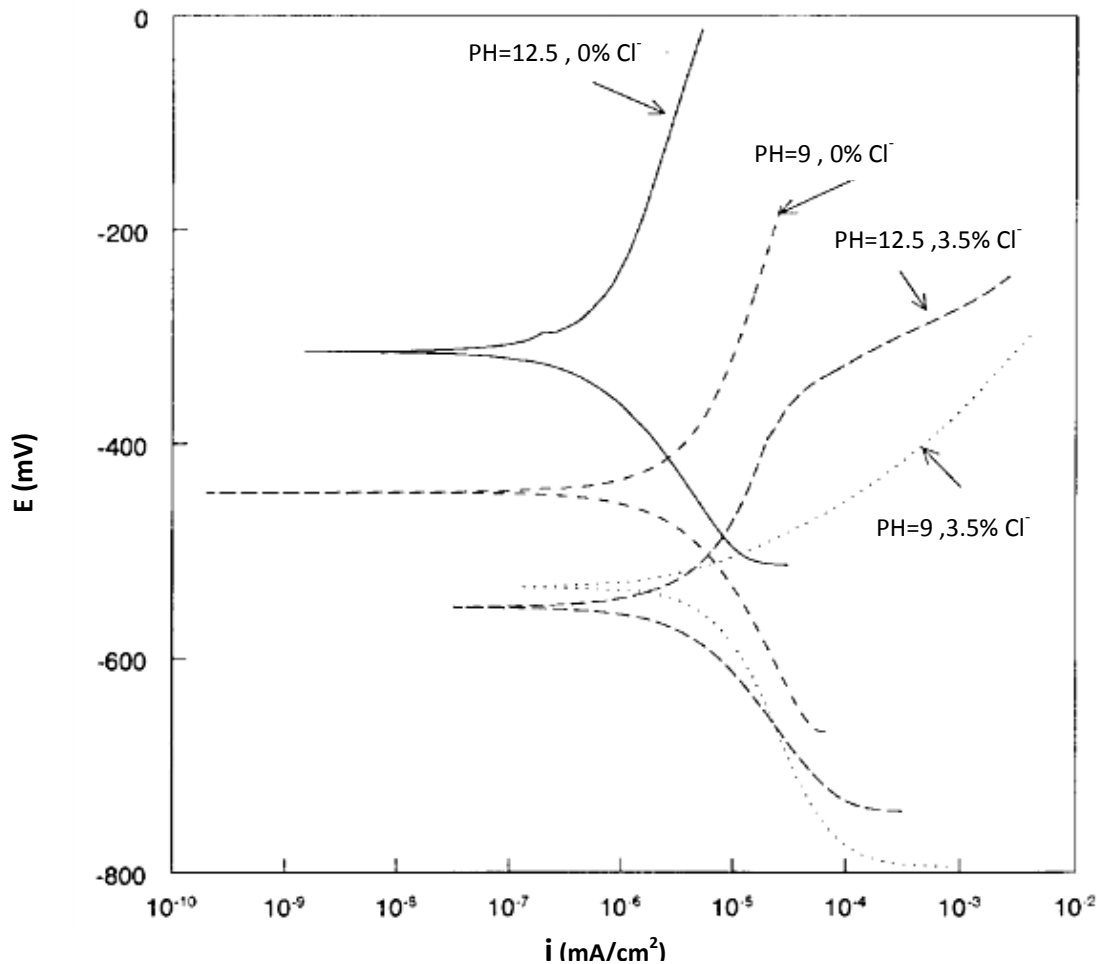


This reaction results in the formation of a barrier oxide layer. This oxide layer can also hydrolyze to form hydroxides on the surface. The potential shifts again to a more anodic direction and, once the barrier film forms on the surface, stabilizes. Thus, thermodynamically, the change in the equilibrium (corrosion) potential can be explained as being due to the occurrence of different electrochemical reactions. In Fig. 2 it can be seen that at a lower pH of 9.0, the stable open circuit potential is more cathodic than at pH = 12.5. This is due to the lesser availability of free hydroxide ions at a lower pH.

Fig. 2 also shows the corrosion potential as a function of time for a system consisting of chloride ions. At a pH of 12.5, the electrode potential starts at about -500 mV and proceeds in the anodic direction. It then goes through a maximum and shifts to a more cathodic direction and stabilizes at about -490 mV. The initial increase of the potential can be explained along the lines of the behavior in the solution without chlorides. In addition to the reaction of  $\text{Fe}(\text{OH})^+$  being formed, the introduction of chloride in the system causes pitting corrosion behavior. The anodic corrosion current for iron is a function of anion in solution, in this case chloride ions (Foley 1975). The chloride pitting reaction is of the autocatalytic nature (Fontana 1986). As mentioned before, when the corrosion reaction, (2), occurs, it produces an excess of positive charges near the surface of the rebar. Now, to conserve electroneutrality, the negatively charged hydroxide ions and chloride ions, move to the surface. Since chloride ions are more mobile than hydroxide ions, the concentration of chlorides increases near the surface. In the interfacial region, adjacent to the metal surface, specific cation ( $\text{Fe}^{+2}$ )-anion ( $\text{Cl}^-$ ) species will exist (Foley 1975). As the chloride ions

replacethe amount of hydroxide ions present at the surface to a largeextent, the occurrence of the formation reaction of the metalmonohydroxide, (3) is reduced. The iron-chloride complexescan be preferentially adsorbed to the surface. These complexeswill be transitory and will dissolve in the test solution leadingto a shift in the potential to a more cathodic direction (Foley 1975). Thus the presence of chlorides induces a competitionbetween the two reactions (2) and (3). The competing natureof these two reactions cause the electrode potential to gothrough a maxima, and the resulting stable potential is an indicatorof the relative driving force for these two reactions. Inthe case of a solution with a pH of 9.0 in the presence ofchlorides, the predominance of (2) is much higher due to thelesser availability of the hydroxide ions, and hence, the potentialgoes into the cathodic direction as soon as it is immersed.Even though the thermodynamic data does not give much informationon the rate of deterioration of the metal, it servesas an indicator to the reactions that might be occurring on theelectrode surface.

Fig. 4gives a plot of the corresponding Tafel plots obtained for conditions described in Fig. 2.Their corresponding anodic andcathodicTafel slopes are given in Table 1.



**Fig. 4: Tafel Plots for rebar Samples Immersed in Solutions of pH 9.0 and 12.5 with and without Cl<sup>-</sup>.**



Table 1. Corrosion Rates for Different Solutions

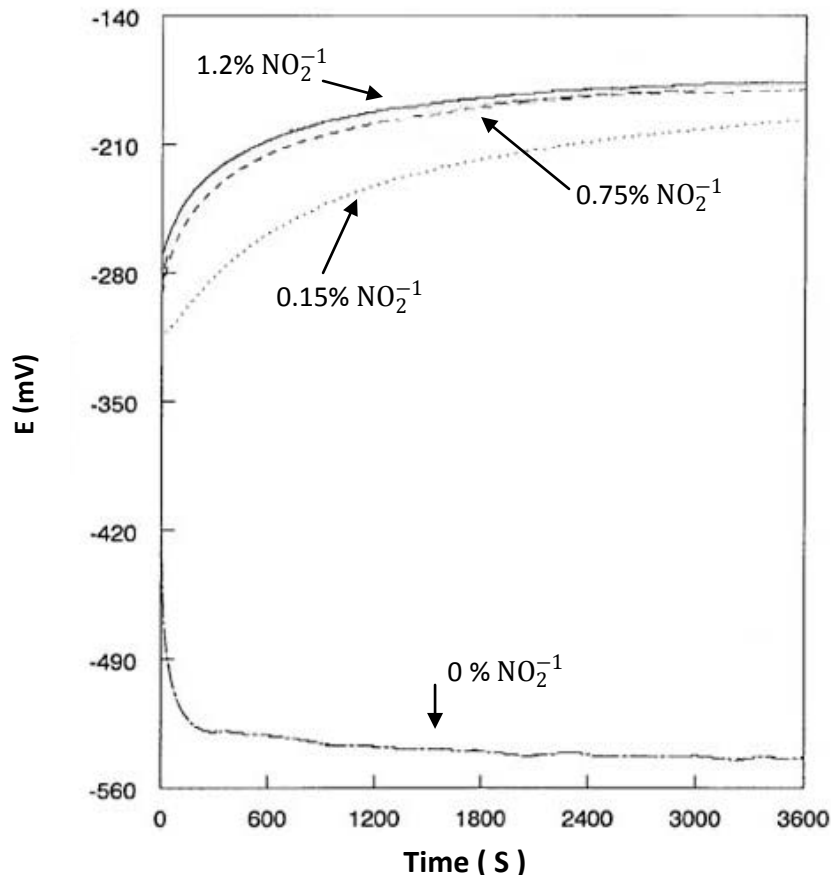
Solution type	$R_o$ ( $K\Omega$ )	$\beta_a$ ( $V^{-1}$ )	$\beta_c$ ( $V^{-1}$ )	$i_{corr}$ ( $\mu A/cm^2$ )	Corrosion rate ( mpy )
pH=12.5, 0%NaCl	44.9	0.360	0.162	0.736	0.34
pH=12.5, 3.5%NaCl	4.57	0.202	0.140	4.276	1.95
pH=9, 0%NaCl	8.46	0.394	0.232	5.481	2.50
pH=9, 3.5%NaCl	1.19	0.081	0.252	7.739	3.53

As expected, the corrosion rate is the least for a solution with a pH of 12.5 in the absence of chlorides and the greatest for a solution of pH = 9.0 in the presence of chlorides. There is a striking difference in the anodic slopes ( $\beta_a$ ) for the samples in the presence and the absence of chlorides. The anodic slopes in the presence of chlorides are much less than those in their absence.

The slope of the E-log(I) curve gives an indication of the extent of the difficulty in overcoming the activation energy barrier associated with the reaction. Thus, the presence of chlorides increases the ease of the anodic reaction. This is consistent with the autocatalytic mechanism of pitting mentioned above. The presence of chloride ions acts as a catalyst for the reduction of iron into its bivalent ferrous ion. Thus the anodic slope decreases as can be seen from Fig. 4.

One of the ways an anodic inhibitor can reduce the corrosion rate is by aiding the passivation reaction by acting as a catalyst, or by increasing the activation energy barrier for the metal reduction reaction. In other words, it can reduce the corrosion rate by either increasing the anodic Tafel slope or by increasing the rest potential, or both. The action of the inhibitor can be explained based on the electrode potential and Tafel plots obtained for the representative case of the solution with a pH of 9.0 in the presence of chlorides, which is the one with the highest corrosion rate.

Fig. 5 gives the  $E_{corr}$  versus time plots for rebar samples immersed in the above solution with and without different concentrations of sodium nitrite [0.15, 0.75, and 1.2 M  $[NaNO_3 \cdot H_2O]$ ].



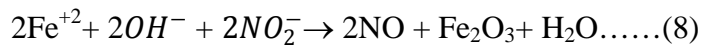
**Fig.5: Ecorr versus Time Plots for rebar Samples Immersed in pH = 9.0, 3.5% NaCl Solution for Various Inhibitor Concentrations.**

Solution type	Corrosion rate ( mpy )	Efficiency
pH=9, 3.5%NaCl + 0% $NO_3^{-1}$	3.53	-
pH=9, 3.5%NaCl + 0.15 % $NO_3^{-1}$	1.77	50%
pH=9, 3.5%NaCl + 0.75 % $NO_3^{-1}$	0.93	74%
pH=9, 3.5%NaCl + 1.20 % $NO_3^{-1}$	0.56	84%

The stable electrode potential obtained for the substrate in the absence of nitrite is around -545 mV, whereas those in the presence of inhibitors are in the range of -170 to -200 mV . This indicates

that there is some sort of mechanistic change in the presence of the inhibitor. The electrode potential observed starts in the range of -300 mV and goes in a more anodic direction and stabilizes at a more anodic value.

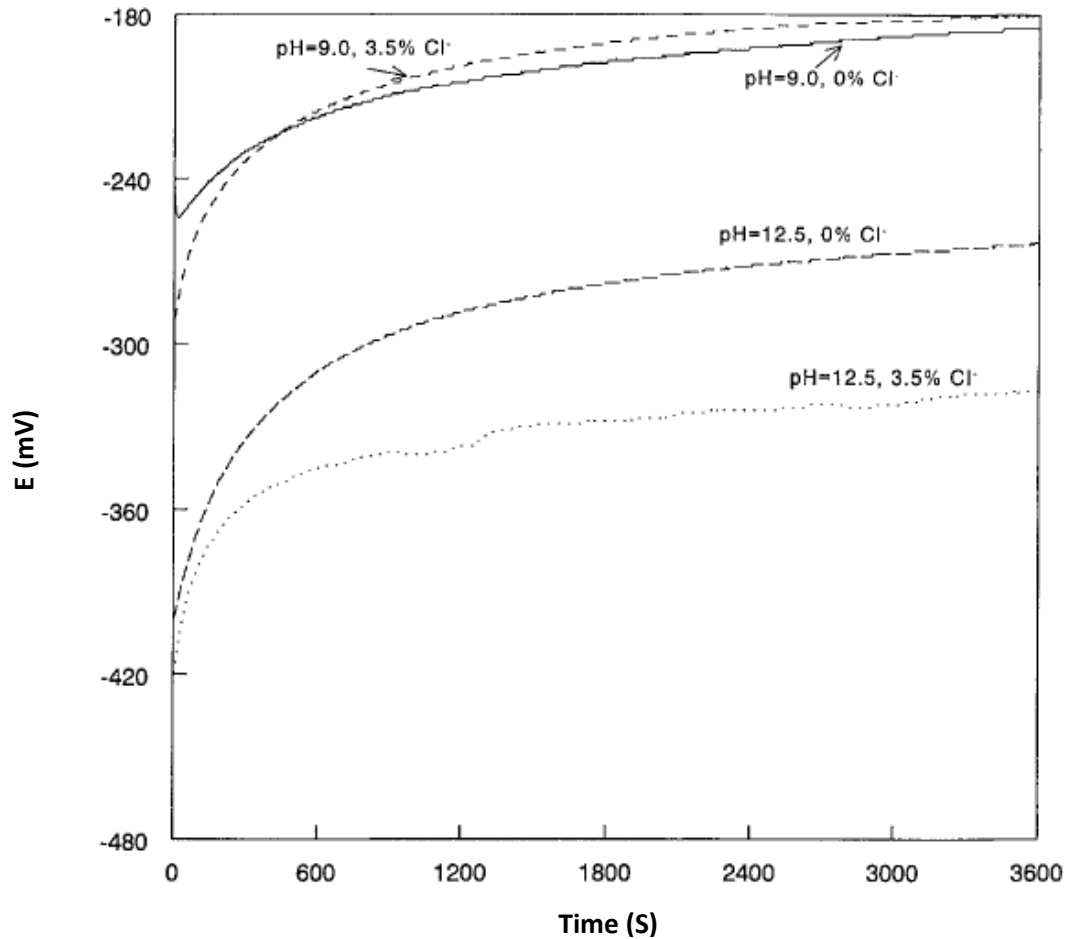
This can be explained by looking at the thermodynamics of the reaction of iron in the presence of an oxidizing agent like nitrite. It has been suggested in the literature (Rosenberg and Gaidis 1979) that nitrite undergoes a chemical reaction with the ferrous iron.



This reaction would cause the products of the corrosion reaction, (2), to be subdued in order to form a barrier oxide film of  $\text{Fe}_2\text{O}_3$ . The resulting potential would then be the potential of  $\text{Fe}_2\text{O}_3$  in water. As soon as the substrate is immersed in the solution, the corrosion reaction takes place. The product of the corrosion reaction reacts with nitrite immediately to form the barrier oxide. The potential shift in the anodic direction would result as the electrode surface is progressively covered by the barrier oxide film. When the surface is completely covered by the oxide film, the potential would stabilize. The presence of chlorides in the system causes a competition between the chloride and the nitrite ions to reach the electrode surface in order to maintain electroneutrality.

Fig. 6 gives the  $E_{\text{corr}}$  versus time plots for 0.75 M  $\text{NaNO}_2$  in the solution at pH of 9.0 and 12.5 in the presence and absence of chloride ions. The most interesting feature of this plot is, contrary to what one would expect, that the stable potential goes to a more anodic value at a pH of 9.0 than at 12.5. This apparent contradiction can be resolved by going over the suggested mechanism of protection against corrosion.

It can be seen from (8) that if a higher amount of  $\text{Fe}^{+2}$  is present in the solution, there is more formation of  $\text{Fe}_2\text{O}_3$ . At a lower pH the amount of  $\text{Fe}^{+2}$  formed is higher as noted before. This would cause more of the oxide to be formed than at a higher pH where the monohydroxide reaction is predominant. Again, it would be in order to stress that this is not an indicative of the corrosion rate.



**Fig.6:  $E_{corr}$  versus Time Plots for Rebar Samples Immersed in Different Solutions for 0.75 M Inhibitor Concentration.**

The more positive potential might lead to a lesser corrosion rate. But this can be ascertained only by examining the kinetic plot for this set of experiments, which are given in Fig. 7. The Tafel plots show a higher anodic Tafel slope than the ones obtained for the substrates without the inhibitors in all the cases. The slopes obtained for all the four cases are similar, which suggests that there is the formation of a layer of oxide that acts as a barrier, irrespective of the presence of chloride (Whiting 1990).

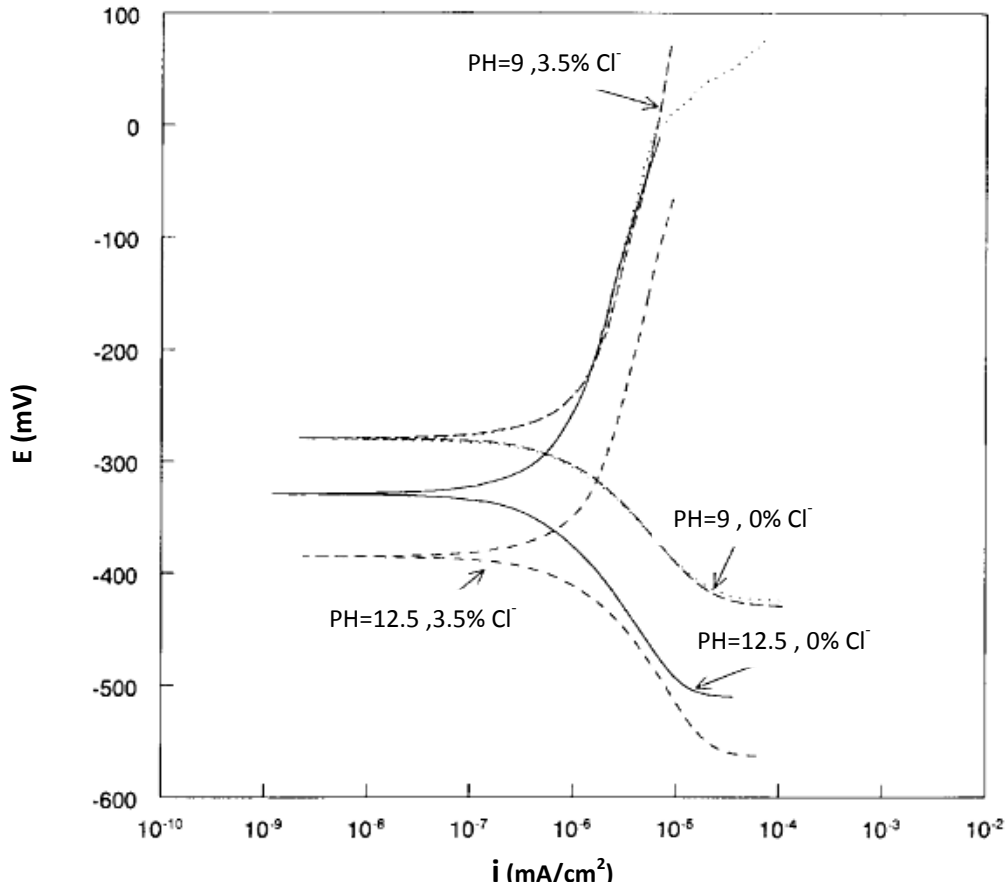


Fig.7: Tafel Plots for rebar Samples Immersed in Different Solutions for 0.75 M Inhibitor Concentration

#### 4. Conclusions:

1-Inhibition of rebar in hydrochloric acid (HCl) solution is attributed to adsorption of the inhibitor onto rebar surface.

2- Inhibition efficiency increases with increased inhibitor concentration with the maximum inhibition for each temperature, while Inhibition efficiency decreases with Increase of Temperature.

3- The open circuit potential data can give valuable information on the thermodynamics of the system and the state that one would expect the metal to be in.

4-The corrosion rate depends to a great extent on the pH of the solution. The presence of chlorides, however increase the rate of the corrosion reaction by acting as a catalyst for the corroding reaction.

5- Nitrite ions act as anodic inhibitors by increasing the rate of formation of a barrier oxide film.

6-The protective action of the nitrite ions seems to be more pronounced in highly corroding environment. This is due to the mechanism of inhibition, which uses the product of the unwanted corrosion reaction and converts it into a favorable passivating one.

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