We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Introduction of Inhibitors, Mechanism and Application for Protection of Steel Reinforcement Corrosion in Concrete

Anil Kumar

Abstract

The corrosion of steel reinforcement in concrete due to environmental factors has been studied through numerous approaches and the reduction of corrosion has been managed by various methods; however, among the protection techniques, the use of corrosion inhibitors has gained encouragement. In this chapter, nitrites and nitrates of sodium and calcium and sodium molybdates and sodium tungstates (oxyanions of group VI) were studied and have gained sufficient scientific coverage. However, their exact role of inhibition was studied by simple polarization technique. In this chapter, we compare the inhibitive efficiency of nitrites and nitrates of sodium and calcium and also that of molybdates and tungstates. The results, however, indicate that among nitrites and nitrates, the calcium salts are more efficient and molybdates and tungstates are comparable in their inhibitive efficacy.

Keywords: corrosion, steel reinforcement, inhibitors, polarization, mechanism, I_{corr}

1. Introduction

Corrosion is the destructive attack upon a metal by its environment and it is an electrochemical phenomenon. Most common examples of corrosion include the rusting of iron and steel, tarnishing of silver and copper, blistering and bubbling of chromium plating and paintwork on cars, discharge of rust-coloured water from domestic taps and seizure of nuts and bolts. Corrosion leads to weakening of metal structures, failure of plant and pollution of process liquors. It is necessary to understand the basic principles of corrosion before taking appropriate preventative or protective measures. The various efforts towards reducing corrosion of metals can be grouped into the following: modification of bulk alloys, modification of environments and surface modifications. Here, in this chapter, we discuss the modification of environments by adding small concentration of inhibitors. An inhibitor is a chemical substance that inhibits or effectively decreases the corrosion rate. It can be understand by **Figure 1**, I_{corr} decreases with inhibitors in comparison to without inhibitors.
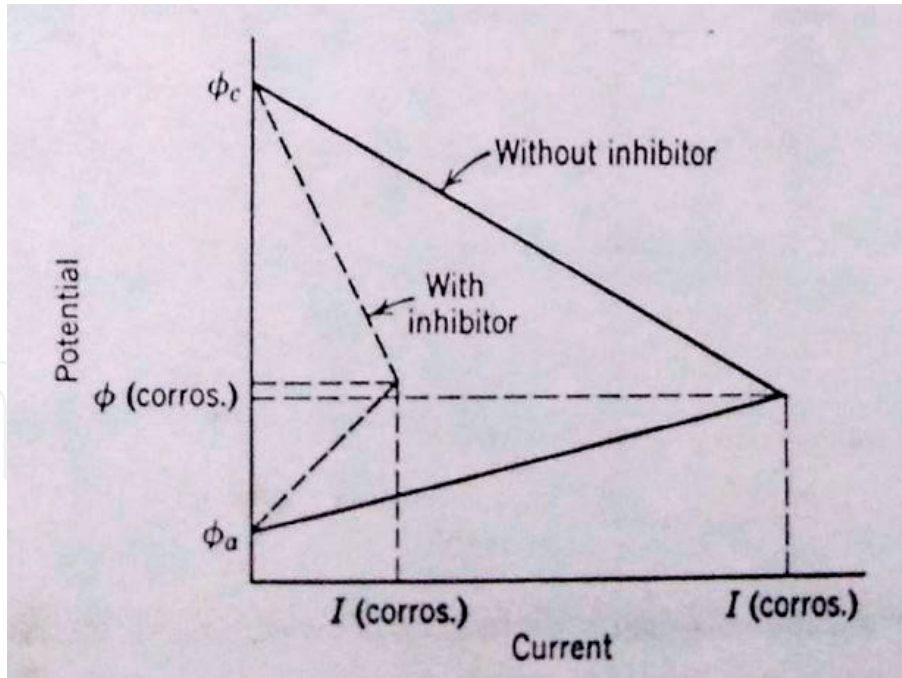
Figure 1.
Polarization diagram for steel corroding in pickling acid with and without inhibitor.

2. Types of inhibitors

There are several classes of inhibitors designated as follows:

2.1 Passivators

Passivators are usually inorganic oxidizing substances that passivate the metal and shift the corrosion potential several tenths of a volts in the noble direction, in which the metal reacts with inhibitors to form inhibiting layer or film on the metal surface. The following inhibitors act as passivators: chromates, nitrates, molybdates etc.

2.2 Non-passivating inhibitors

These include inhibitors such as the pickling inhibitors, which are usually organic substances that have only slight effect on the corrosion potential, changing it either in the noble or active direction usually by not more than a few milli or centivolts. They form an absorbed monolayer thickness on the metal surface, which essentially blocks the discharge of H^+ and dissolution of metals ions. Some inhibitors block the cathodic reaction (raise hydrogen overvoltage) more than the anodic reaction or vice versa; but adsorption appears to be generally over the whole surface rather than at specific anodic or cathodic sites, and both reactions tend to be retarded. Hence, on addition of an inhibitor to an acid, the corrosion potential of steel is not greatly altered (<0.1 V), although the corrosion rate may be appreciably reduced as shown in **Figure 1**. Generally, polar group compounds serve as pickling inhibitors. These include the organic nitrogen, amine, S and OH groups' compound. The size, orientation, shape and electric charge of the molecule play a part in the effectiveness of inhibition. Whether a compound adsorbs on a given metal and the relative strength of the adsorbed bond often depend on factors such as surface charge of metal. For inhibitors that adsorb better at increasingly active potentials as measured from the point of so-called zero surface charge (potential of minimum ionic adsorption), cathodic polarization in the presence of the inhibitor provides better protection than either the equivalent

cathodic protection or use of an inhibitor alone. This was demonstrated by Antropov for iron and zinc in sulphuric acid containing various organic inhibitors. In general the passive-type inhibitors reduce corrosion rate to very low values, being more efficient in this regard than most of the non-passivating types. They represent, therefore, the best inhibitors available for certain metal-environment combinations.

2.3 Slushing compounds inhibitors

Slushing compounds are used to protect steel surface temporarily from rusting during shipment or storage. They consist of oil, greases or waxes that contain small amounts of organic additives. The additives are polar compounds that absorb on the metal surface in the form of a closely packed oriented layer. Organic amines, zinc naphthenate, various oxidation products of petroleum, alkali and alkaline earth metal salts of sulphonate oils, and various other compounds were used as additive for slushing compound.

2.4 Vapour-phase inhibitors

Vapour phase inhibitors are basically soluble film-forming inhibitors, such as nitrites, benzoates or carbonates, which are attached to a large organic cation. The large organic cation functions as a parachute or umbrella for the organic cation and the inorganic anion will provide the molecule with a vapour pressure that will lie within the range of 0.1–1.0 mm mercury (at ambient temperatures). Through this, the inhibitor will slowly evaporate and provide an adequate supply of inhibitor at the metal surface for protection if required, but the evaporation rate will not be so fast that the inhibitor is lost in too short a time. It moisture condenses on the metal surface, the vapour phase inhibitor will dissolve and the concentration of inhibitive anions will be sufficient to ensure passivation of the metal. It is possible, however, that there is conjoint action between the passivating anion inhibitor and some form of adsorption inhibition by the organic cation, the latter being assisted by anions such as chloride or sulphate shifting the corrosion potential to move negative values. They are used to protect critical machine parts (e.g., ball bearing or other manufactured steel articles) temporarily against rusting by moisture during shipping or storage. It appears to be one of adsorbed film formation on the metal surface that provides protection against water or oxygen, or both. In the case of volatile nitrites, the inhibitor may also supply a certain amount of NO_2^-, which passivates the surface. Examples of vapour-phase inhibitors are dicyclohexylammonium nitrite, cyclohexylamine and ethanolamine carbonate. Dicyclohexylammonium nitrite has been one of the most effective of the vapour-phase inhibitors for corrosion of steel for a period of years. This substance is white crystalline, almost odorless and relatively non-toxic. It has a vapour pressure of 0.0001 mm of Hg at 21° C (70° F), which is about one-tenth the vapour pressure of mercury itself. One gram saturates about 550 m^3 of air, rendering the air relatively noncorrosive to steel. However, it should be used with caution in contact with non-ferrous metals. In particular, corrosion of zinc, magnesium and cadmium is accelerated. Cyclohexylamine carbonate has a somewhat higher vapour pressure of 0.4 mm Hg at 25°C and its vapour also effectively inhibits steel. The higher vapour pressure provides more rapid inhibition of steel surfaces either during packaging or on opening and again closing a package, during which time concentration of vapour may fall below that required for protection. The vapour reduces the corrosion of aluminium, solder and zinc but it has no inhibition effect on cadmium and it increases corrosion of copper, brass and magnesium. Copper dipped in 0.25%

benzotriazole in water at 60°C for 2 min forms a thin adsorbed film that protects the metal against subsequent tarnish in the atmosphere, which acts as a diffusion barrier known as inhibitor to tarnishing of copper. It is also effective for brasses and for nickel-silver (zinc-nickel alloys).

The overall inhibitors may be classified on their nature as follows:

1. Type A: Substances that form an inhibiting layer or film on the metal, that is passivation of metal. Type A inhibitors may be subdivided as follows:

   i. Type IA: Inhibitors that that reduce the corrosion rate but do not completely prevent corrosion, for example pickling inhibitors (**Figure 2**).

   ii. Type IIA: Inhibitors that delay the onset of corrosion for long periods so that the metal has a temporary immunity to corrosion, for example, benzotriazole for copper (**Figure 3**).

   iii. Type IIIA: Passivating inhibitors, which result in the formation of passive films on the metal surface, the films generally being an oxide or an insoluble salt of the metal, for example, NaNO2, phosphates and chromates for steel, sulphates for lead (**Figure 4**).

2. Type B: Substances that reduce the aggressiveness of the environment, which may be subdivided as follows:

   i. Type IB: Inhibitors that retard the corrosion process but do not completely prevent it.

   ii. Type IIB: Inhibitors that incubate corrosion by reacting with substances that produce corrosion in a given environment, for example, organic amines, which 'neutralize' organic acid in oils and emulsion. In another way, it may be divided into two types of corrosion inhibitors:

      a. Organic inhibitors: Inhibitors of Type IA, IIA and IIB are organic compounds and

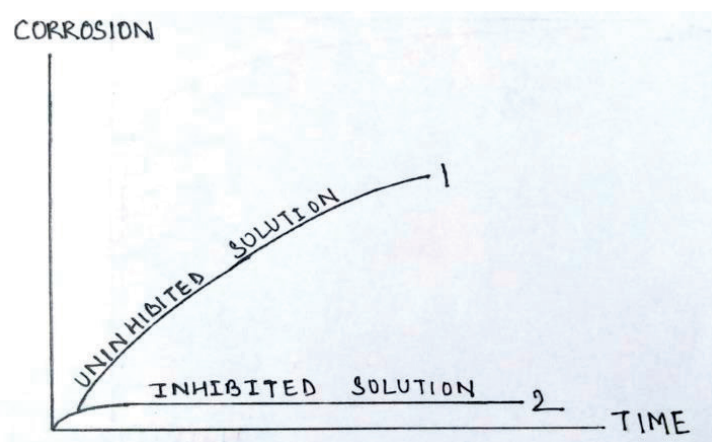   b. Inorganic inhibitors: Inhibitors of Type IIIA and IB are inorganic compounds.
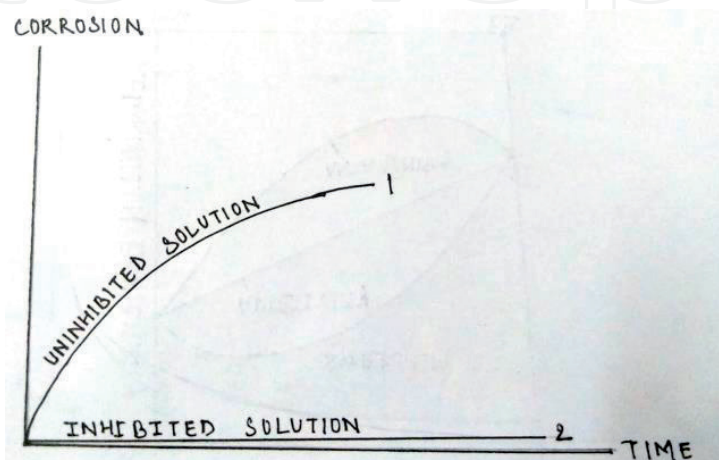
Figure 2.
Effect of type IA inhibitors on corrosion.
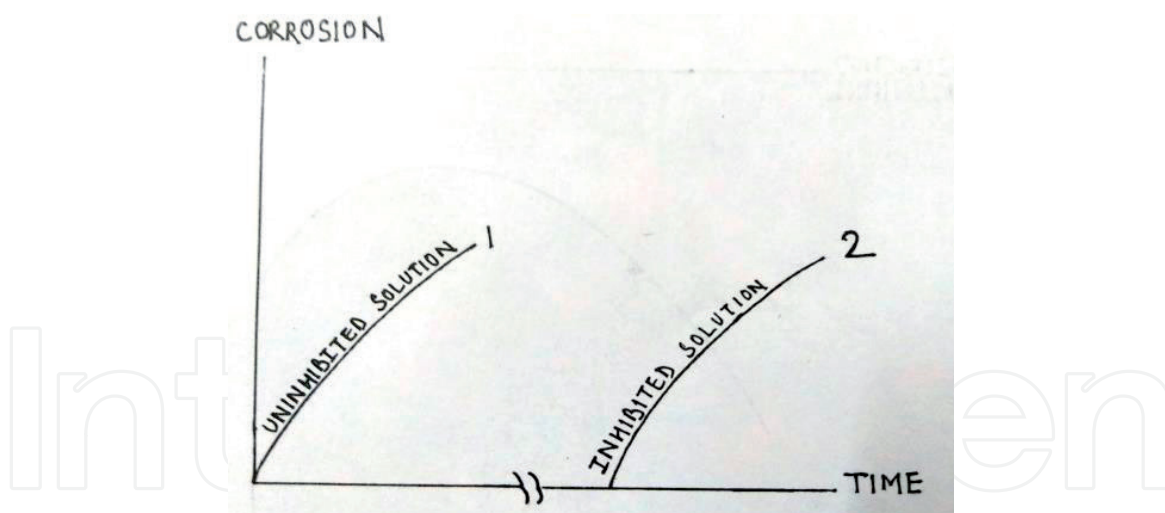
Figure 3.
*Incubation of corrosion by type IIA inhibitors.*

Figure 4.
Effect of passivating type IIIA inhibitors on corrosion.

2.5 Mechanism of inhibitors

Inhibitors act as depolarizers, when metal surface comes in contact with passivators. In this case, they initiate high current densities at residual anodic areas, which exceed i_{critical} for passivation as shown in **Figure 2**. Generally, those substances are oxidizing agents with redox potentials that are nobler than that of the metal and they are readily reduced, resulting in a very high cathodic current density and consequently a high anodic current density, which is greater than the critical current density. Consequently, the metal will passivate after a short initial period of dissolution. Ions such as sulphates and chlorides do not passivate iron since they are not easily reduced and nitrates are poor passivating agents since they, too, are only sluggishly reduced (**Figure 2**).

Only those ions can serve as passivators that have both an oxidizing capacity in the thermodynamic sensor (noble oxidation reduction potential) and that are readily reduced with shallow cathodic polarization curve (**Figure 5**). Passivating agents are reduced at cathodic areas at a current density equivalent to that at the anodic areas, which is itself greater than the critical current density of the metal such that passivation of the metal occurs. For the optimum inhibition of corrosion, that is complete passivation of the metal surface, the inhibitor concentration must be greater than a critical concentration. This critical concentration varies with the type of inhibitor but it is generally within the range of 10^{-4} to 10^{-3} M; but it will
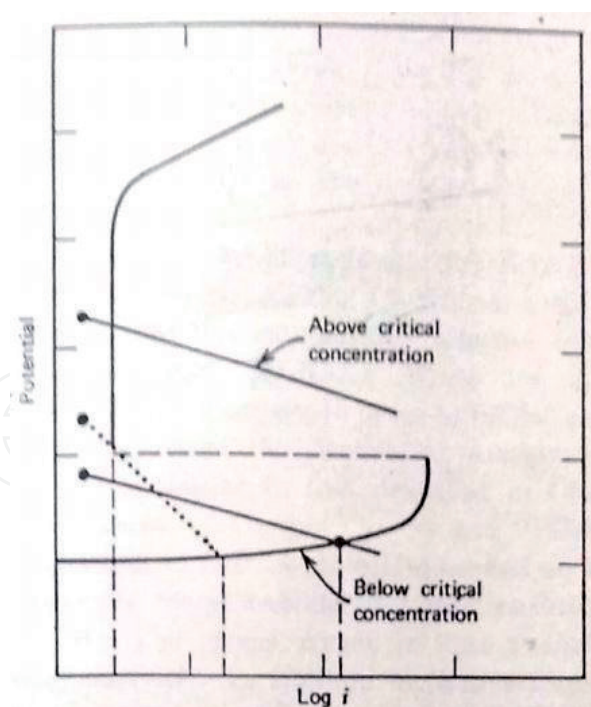
Figure 5.
Polarization curves that show the effect of passivator concentration on corrosion of iron. An oxidizing substance that reduces sluggishly does not induce passivity (dotted cathodic polarization curve).

be greater in the presence of high hydrogen ion or chloride ion concentrations and at elevation temperatures. If the inhibitor concentration lies below the critical level, incomplete passivation is found and the passivator can function as an active depolarizer at other (unpassivated) areas such that increased corrosion rates are observed in localized areas, that is, pitting occurs. Thus, as the inhibitor falls below the critical concentration, either through consumption of the inhibitor or through inadequate or though inadequate dosing in stagnant areas, the more active redox potential of the inhibitor results in cathodic polarization curves that intersect the anodic polarization curve within the active region (**Figure 5**). Generally, the cathodic areas are larger than the anodic areas so that passivity becomes established on the metal surface. The passive areas become noble to adjacent areas and passivity spreads over the entire metal surface. Once passivity of the entire metal surface is established, the whole surface functions as a cathode and further reduction of the passivator is very slow and only a small or residual passive current flow is found. This low current flow is that required for passivator reduction corresponding to slow chemical dissolution of the passive film by its environment. Indirect passivators or the so-called cathodic inhibitors have a different mechanism for inhibition. These substances, for example, sodium hydroxide, phosphate, silicate or borate, result in passivation of metals such as iron by facilitating the adsorption of oxygen. With these inhibitors, there is both anion adsorption and reaction with the inhibitor such that a film covering the metal surface is formed. In general, the corrosion (or open-circuit) potential falls to more active or base values (as opposed to the more noble E_{corr} values found with true passivators). These substances are, however, less efficient as inhibitors and the protective power is rarely greater than 80–90%. Hence, there is no single mechanism of inhibitors. Passivators form film on the metal surface or selectively adsorbed on to a active anodic or cathodic sites on the surface. This adsorption, even in the absence of metal-inhibitor chemical interactions, results in polarization of the anodic and/or cathodic reaction so that corrosion is retarded or inhibited. Benzotriazole inhibitors incubate corrosion by forming a chelate-type of reaction product with the copper metal. Then corrosion is

retarded or even prevented as long as the chelate was present on the metal. Pickling inhibitors are those that are adsorbed on to the metal and ultimately form a layer of chemisorbed material by interaction with the metal. The effectiveness of inhibitor depends on the nature of the film, rather than its thickness. Non-specific adsorption of ions or molecules that can form ions, on a metal surface, is dependent upon the surface charge on the metal. At the point of zero charge (ZPC), which for mercury is the point at which it exhibits maximum surface tension or shows an electro capillary maximum, the metal is uncharged. Clearly, at the ZPC, adsorption of both ions and molecules on to the metal surface can occur. When adsorption occurs, the electro capillary maximum is reduced or depressed and ions or molecules that are absorbed and depress the capillary are known as capillary-active agents. Capillary-active anions are adsorbed at potentials positive to (i.e., cathodic to) the ZPC while cations are adsorbed at potentials negative to (or anodic to) the ZPC. When such adsorption occurs, the ZPC is shifted, in the case of anions, to slightly more negative values, and the potential shift is known as a theta potential. For inhibition by anions to occur, the potential of a metal surface must be held positive to the ZPC, that is the metal is positively charged, and this generally occurs during corrosion of the metal in acid solutions. In neutral or basic media, an additional agent such as oxygen is generally required to maintain the metal corrosion potential positive to the ZPC. Organic amines and heterocyclic compounds will be able to absorb on to the corroding iron surface in hydrochloric acid solutions since the corrosion potential is positive or cathodic to the ZPC. Steric effects, for example, the size and shape of the molecule forming the anion as well as the shift in ZPC produced by the absorption process, will determine the effectiveness of the inhibitor on the corrosion rate. Cation-forming molecules, for example, many organic sulphur compounds, as well as the surface-active or wetting agent will have no effect on corrosion because they are not adsorbed at potentials cathodic to ZPC. In sulphuric acid solutions, however, sulphur compounds are effective inhibitors because iron becomes negatively charged in H_2SO_4, that is, its corrosion potential is negative (on anodic) to ZPC. Many inhibitive anions, even those that 'passivate' the metal surface, must be absorbed on to the metal surface before metal passivation can occur. Benzoates will not passivate iron unless the corrosion potential is cathodic to ZPC; for this to occur, oxygen must be present in solution and, in fact, benzoates are poor inhibitors for iron in deaerated solution. In alkaline solutions, the presence of OH ions (pH 6.5 or higher) assists adsorption of benzoate and it is possible that the so-called synergistic effect of nitrite ions with benzoate ions with may be due to the capillary-active behavior of the nitrile ion. Benzoates do not inhibit iron corrosion in acid solutions since the cathodic reaction is predominantly hydrogen evolution and no hydroxyl ions are released at the cathodic sites to assist benzoate adsorption.

2.6 Effect of inhibitor concentration

In general, corrosion rates decrease by increase in inhibitor concentration. Their plot is a mirror image of adsorption isotherms for the most organic inhibitors. It is shown in **Figure 6**. But in specific conditions, there appears to be a limiting corrosion rate even in the presence of large amount of inhibitor (**Figure 7**). This effect is most common with pickling inhibitors and the increase in corrosion rate often occurs at levels above 1–2% inhibitor. The cause of this phenomenon may be is ascribed to the ability of many organic substances, when present at relatively high concentration in solution, to function as hydrogen acceptors and so depolarize the cathodic reaction, for example, aliphatic aldehydes in acid solution. This increase in attack is found with substances that cannot accept hydrogen, that is, there is no overt depolarizing action.
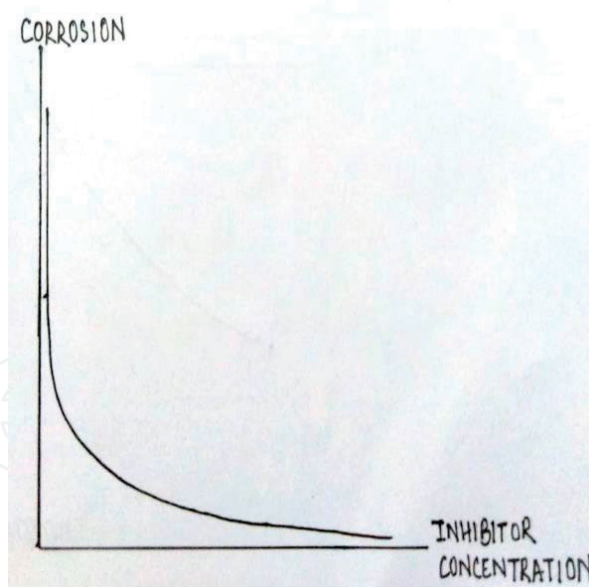
Figure 6.
Effect of inhibitor conc^n. On corrosion.
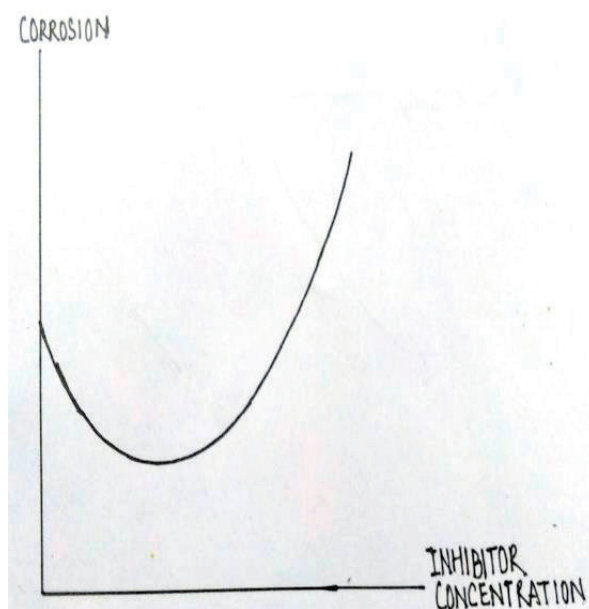
Figure 7.
*Effect of depolarizing inhibitors on corrosion.*

When two inhibitors are present in solution, it is rare that there is a simple additive effect of the combined protection power. In fact, three different effects can be observed when inhibitors are mixed (**Figure 8**).

Additive effect was found with similar structures and chemical properties of substance, for example, formaldehyde and acetaldehyde when used for steel in acid solution. It should also be noted that only very rarely do two inhibitors have the same retarding efficiency, R, for the same corrosion reaction.

$$\text{Retardation efficiency (or coefficient) } R = P_o/P.$$

$$\text{And protective power } P = P_o - P/P \times 100\,\%.$$

where P and P_o are the corrosion rates of the metal in the given medium with and without inhibitor respectively.
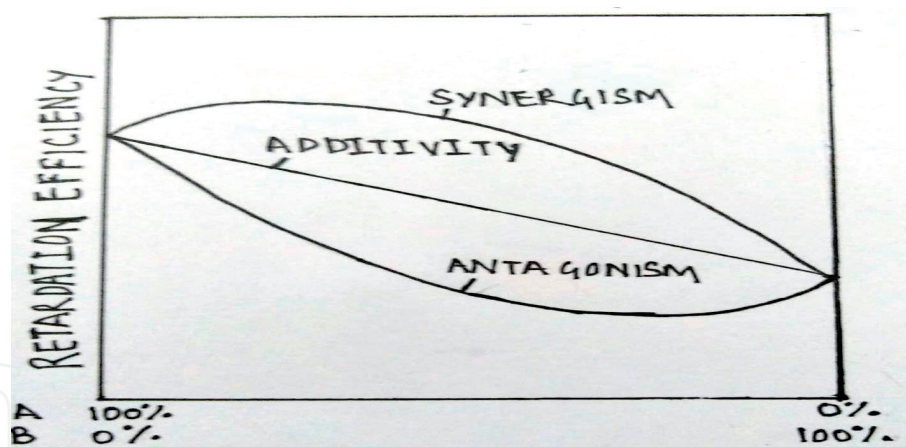
Figure 8.
Effect of mixtures of inhibitors on the retardation efficiency R of a corrosion reaction.

Clearly, R = 100/100 – P.

Synergism is the term applied to the marked reinforcement of the inhibiting action of one inhibitor by the addition of small amount of a second inhibitor, even though the second inhibitor is less effective when used alone. The retardation efficiency of the combination of inhibitors is considerably greater than a simple additive effect of the separate R value. An example is the effect of small addition of furfuralimine to formaldehyde for steel in sulphuric acid. The third effect that may be found for mixtures of inhibitors is antagonism or the mutual weakening of the inhibitive efficiency so that the retardation efficiency is lower (i.e., the corrosion rate is greater) for the mixture than for either substance alone. This effect is most common when there appears to be some form of chemical interaction between the two inhibitors. A typical example is the reduced efficiency of inhibition of steel in hydrochloric acid in the combined presence of antinomy chloride and aniline.

3. Application of inhibitors

3.1 Role of sodium nitrite inhibitor in rebar corrosion

In ideal situation, reinforcement concrete rebar corrosion was not happening but in actual situation the pore water may always be contaminated with different amounts of aggressive ions. This situation can be reproduced by the addition of 3.5% NaCl in the test solution (pore solution), with $NaNO_2$ (1, 2, 3, 4 and 5%) as inhibitor. **Figure 9** shows the polarization of rebar in pore solution +3.5% NaCl and various amounts (1, 2, 3, 4 and 5%) of $NaNO_2$. This figure shows the shift of potential of rebar in the positive direction in test solution (pore solution +3.5% NaCl) with addition of $NaNO_2$ (1–5%). This positive trend is due to rebuilding of rebar surface (rebuilding after local failure of oxide film by Cl^-) with the addition of $NaNO_2$. This is also indicative in **Figure 10**, where the corrosion current decreases with the addition of $NaNO_2$, and in **Figure 11** where the corrosion potential moves towards positive direction with the incremental addition of $NaNO_2$.

The addition of $NaNO_2$ in the experimental solution (PS + 3.5% NaCl) caused shift of both the anodic and cathodic curves towards positive direction as shown in **Figure 11**. Movement of polarization curves towards positive direction is indicative of the fact that the addition of $NaNO_2$ causes reduction in the rate of corrosion [1].
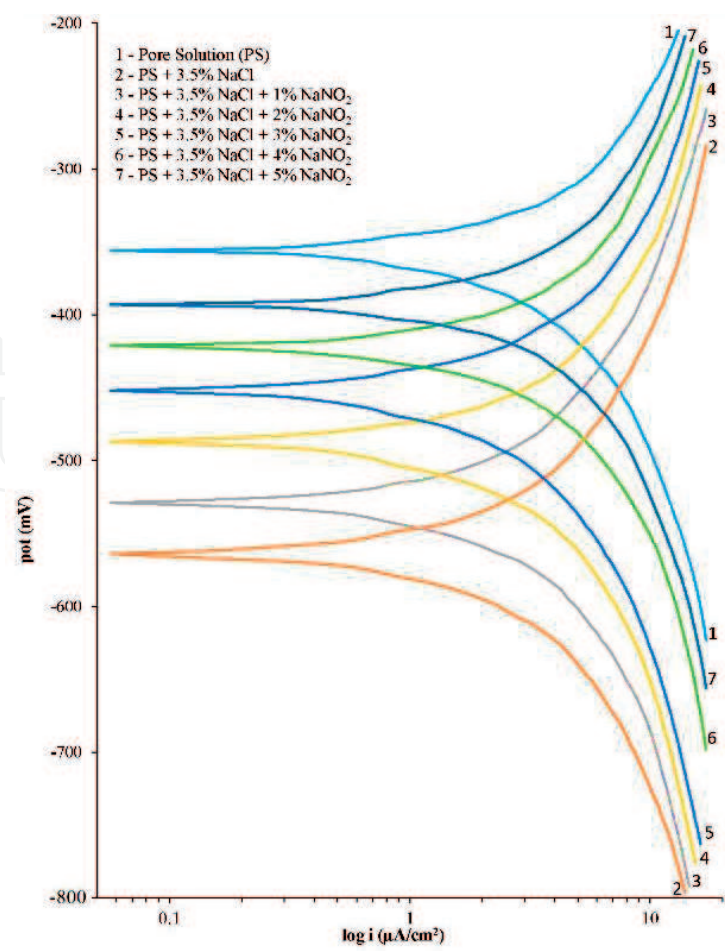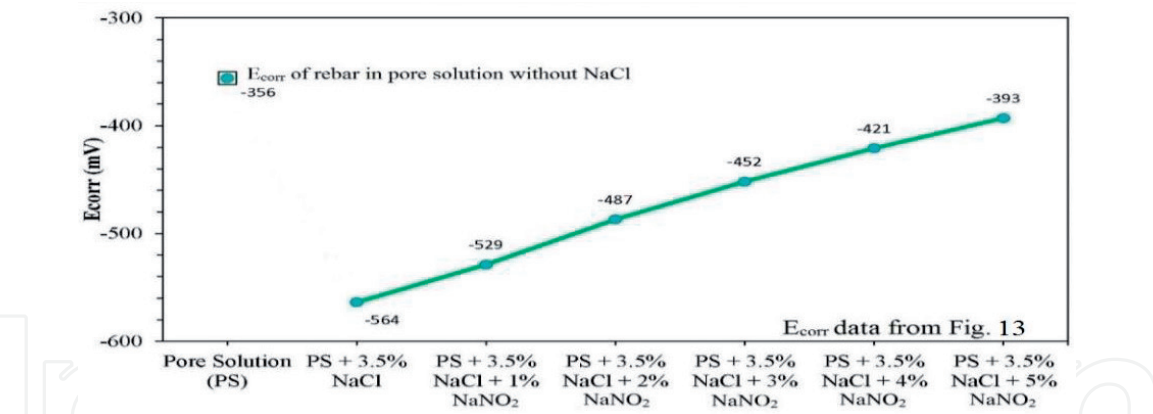
Figure 9.
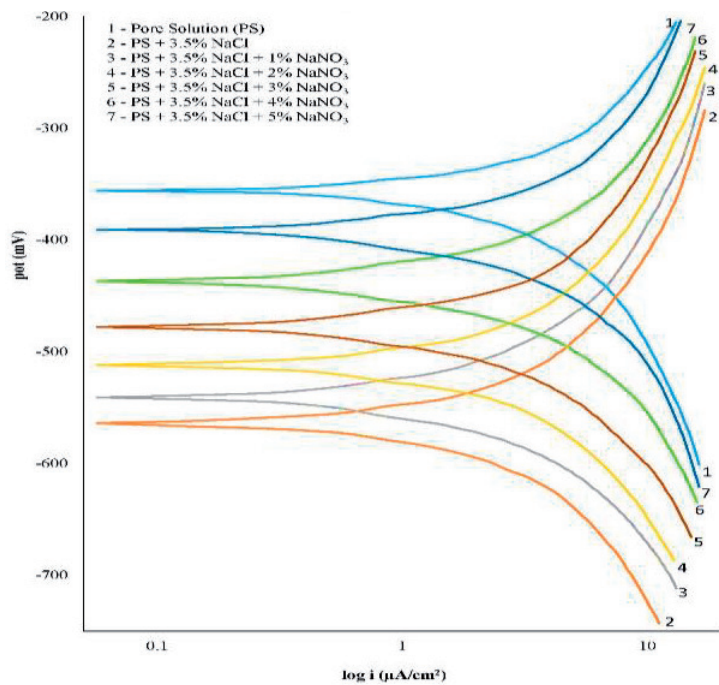*Polarization of rebar in pore solution containing 3.5% NaCl and various NaNO₂ concentrations.*
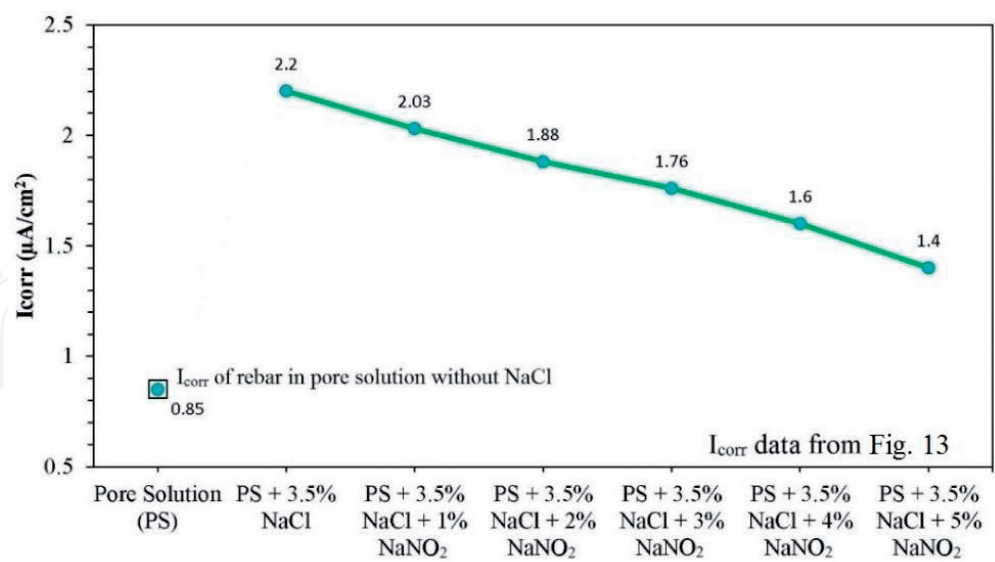
Figure 10.
I_{corr} for rebar (steel) in pore solution containing 3.5% NaCl and various NaNO₂.

## 3.2 Role of sodium nitrate (NaNO₃) inhibitor in rebar corrosion

Use of sodium nitrate ($NaNO_3$) as corrosion inhibitor has been in practice since recent past. In the present study, the rebar sample was exposed to pore solution containing 3.5% NaCl with further addition of 1–5% $NaNO_3$. The polarization diagram has been shown in **Figures 12** and **13**.

Figure 11.
E_{corr} for rebar (steel) in pore solution containing 3.5% NaCl and various $NaNO_2$ concentrations.

Figure 12.
Polarization of rebar in pore solution containing 3.5% NaCl and various $NaNO_3$ concentrations.
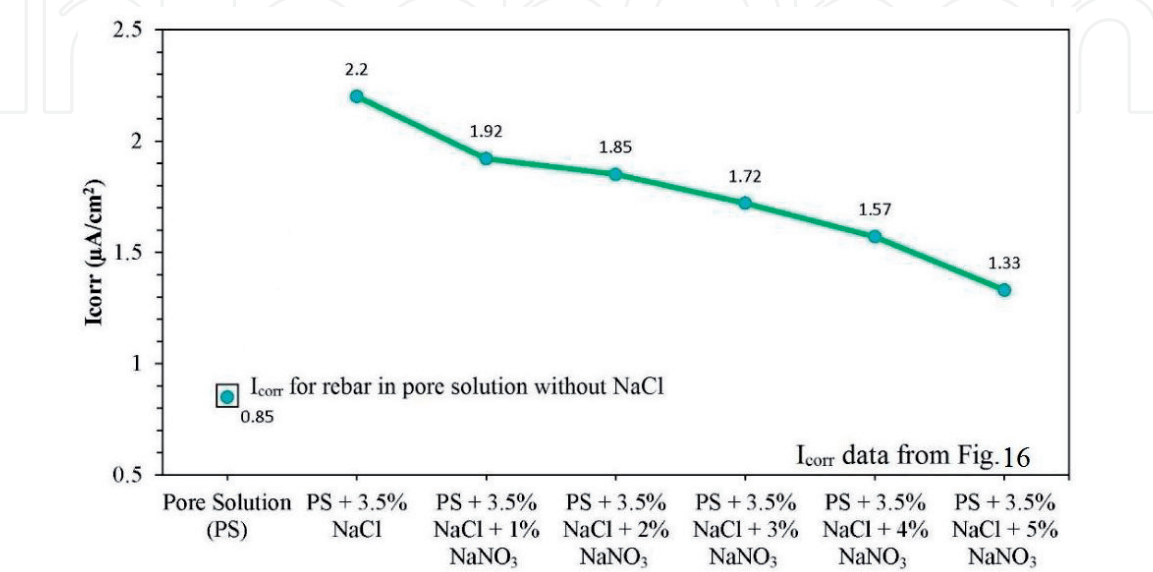
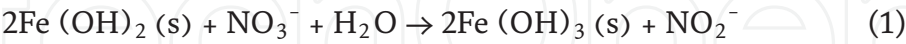**Figure 13.**
I_{corr} for rebar in pore solution containing 3.5% NaCl and various $NaNO_3$ concentrations.

The I_{corr} and E_{corr} values of polarization are shown separately in **Figures 14** and **15**. The E_{corr} value with the addition of $NaNO_3$ increases in the positive direction and I_{corr} decreases continuously. A comparison of I_{corr} values obtained in $NaNO_2$ and $NaNO_3$ are given in **Table 1**, which indicates better performance of $NaNO_3$ (i.e., continuous decrease in I_{corr} values) in the ranges studied.

The I_{corr} values for rebar in pore solution containing various % of $NaNO_2$ and $NaNO_3$ as shown in **Table 1** indicate that $NaNO_3$ shows better inhibitive efficiency than $NaNO_2$ [1]. This can be attributed to the fact that three moles of ferrous ion is oxidized to ferric ion per mole of nitrate as shown in Eqs. (1) and (2).

$$2Fe\,(OH)_2\,(s) + NO_3^- + H_2O \rightarrow 2Fe\,(OH)_3\,(s) + NO_2^- \qquad (1)$$

$$Fe\,(OH)_2\,(s) + NO_2^- + H_2O \rightarrow Fe\,(OH)_3\,(s) + NO + OH^- \qquad (2)$$

3.3 Role of calcium nitrite inhibitor in rebar corrosion

Calcium nitrite is most widely used corrosion inhibitor for the protection of steel reinforcement corrosion in concrete. Here, similar conditions were used by addition of 3.5% NaCl in the test solution (pore solution), with $Ca\,(NaNO_2)_2$ (1, 2, 3, 4 and 5%) as inhibitor. **Figure 15** shows the polarization of rebar in pore solution containing 3.5% NaCl and various amounts of $Ca\,(NO_2)_2$.

From the above results, the I_{corr} and E_{corr} values have been calculated. The value of I_{corr} decreases continuously with the increase in the % of $Ca\,(NO_2)_2$ and the value of E_{corr} moves towards positive direction with the increase in $Ca\,(NO_2)_2$ content [1]. Both the above data are suggestive of continuous inhibition by increase in $Ca\,(NO_2)_2$ content because of the formation of passive oxide file on the metal surface. Actually in presence of chlorides, the nitrite 'competes' with both the chloride and hydroxide ion for the free Fe^{2+} ions. Over time, nitrite and/or an alkaline environment free of chlorides will reduce the number of flaws in the protective film and thus decrease the number of available sites from which chloride complexes may formed [2, 3].

3.4 Role of calcium nitrate inhibitor in rebar corrosion

Polarization diagram for rebar dipped in pore solution +3.5% NaCl + varying amounts (1–5%) of calcium nitrate $Ca\,(NO_3)_2$ is shown in **Figure 16**.
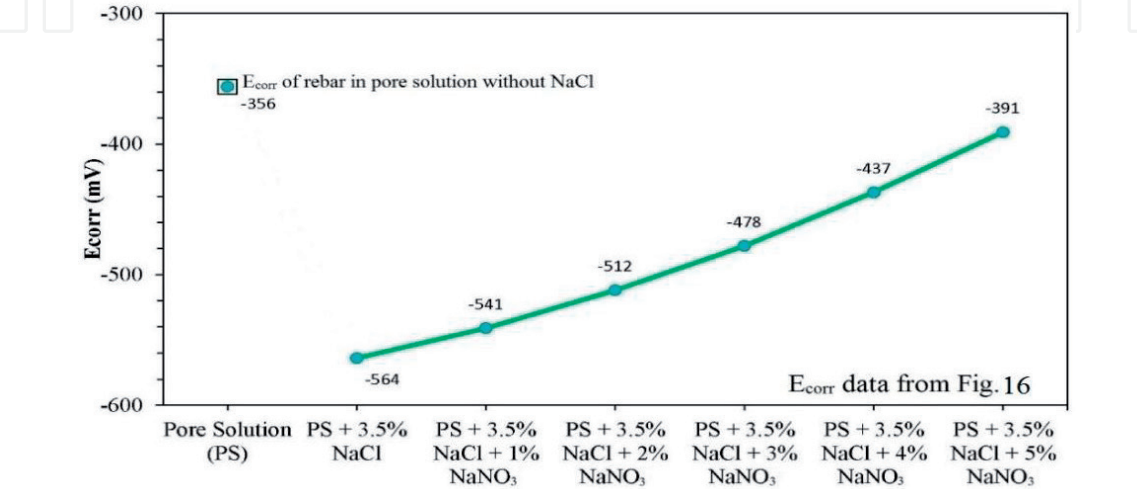
Figure 14.
E_{corr} for rebar in pore solution containing 3.5% NaCl and various $NaNO_3$ concentrations.
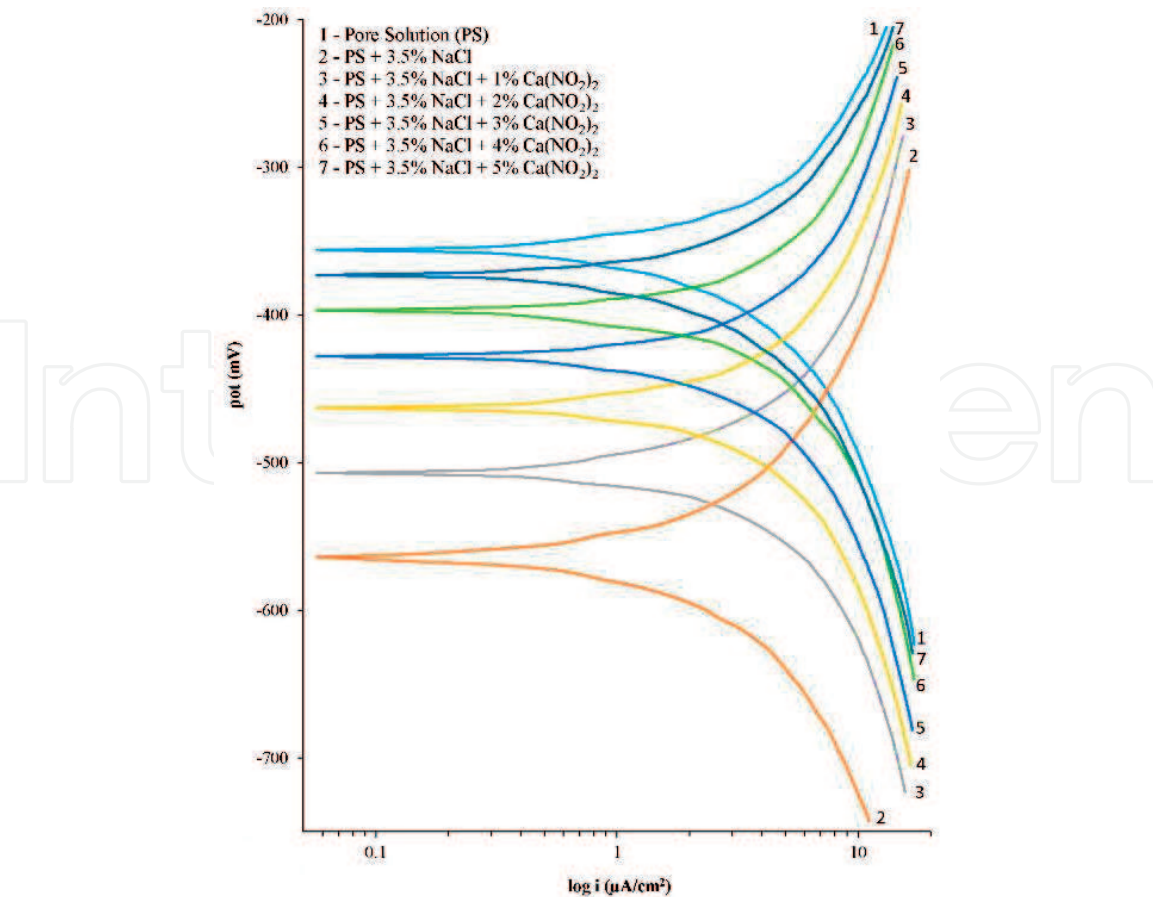
Figure 15.
Polarization of rebar in pore solution containing 3.5% NaCl and various Ca $(NO_2)_2$ concentrations.

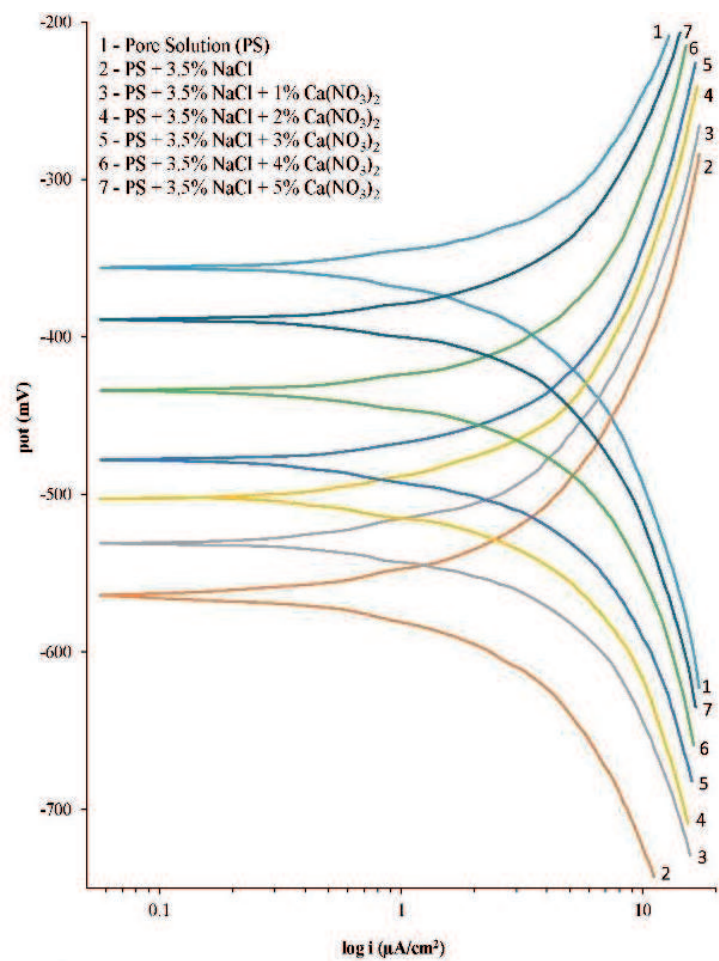| Inhibitor	I_{corr} ($\mu A/cm^2$)				
	1%	2%	3%	4%	5%
$NaNO_2$	2.03	1.88	1.76	1.60	1.40
$NaNO_3$	1.92	1.85	1.72	1.57	1.33

Table 1.
I_{corr} values of rebar in PS containing 3.5% NaCl and various % of $NaNO_2$ and $NaNO_3$.

Figure 16 shows that the nature of protection of the calcium nitrate is comparable to that of calcium nitrite. A comparison of I_{corr} values of calcium nitrite and calcium nitrate as shown in **Table 2** indicates that calcium nitrate offers better inhibition within the range studied [1].

3.5 Role of sodium molybdate inhibitor in rebar corrosion

Sodium molybdate is a non-toxic [4], environment-friendly anodic corrosion inhibitor [5, 6]. It is highly effective in protecting steel reinforcement corrosion in concrete [7] and steel corrosion in saturated calcium hydroxide [8]. In actual situation the pore water in concrete may always be contaminated with different amounts of aggressive ions such as chloride. This situation can be represented by addition of 3.5% NaCl in the test solution (pore solution), with Na_2MoO_4 ($10^{-1.0}$, $10^{-1.5}$, $10^{-2.0}$, $10^{-2.5}$, $10^{-3.0}$, $10^{-3.5}$ and $10^{-4.0}$ M) as inhibitor. **Figure 17** shows the polarization of rebar in pore solution containing 3.5% NaCl and different concentrations of Na_2MoO_4.
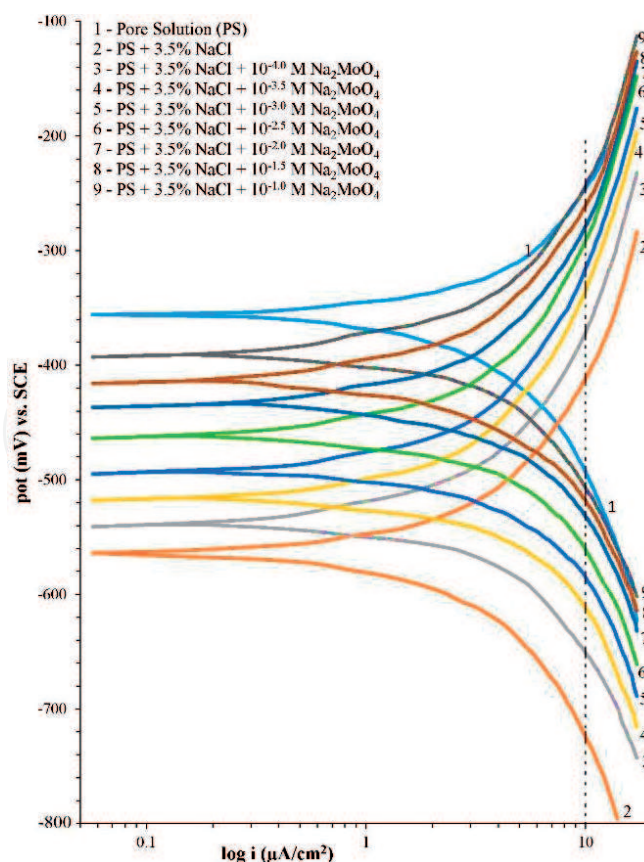
Figure 16.
Polarization of rebar in pore solution containing 3.5% NaCl and different Ca (NO$_3$)$_2$ concentrations.

Inhibitor	I_{corr} (μA/cm^2)				
	1%	**2%**	**3%**	**4%**	**5%**
Ca(NO$_2$)$_2$	1.93	1.81	1.71	1.58	1.31
Ca(NO$_3$)$_2$	1.88	1.79	1.66	1.51	1.24

Table 2.
I_{corr} values of rebar in PS containing 3.5% NaCl and different % of CaNO$_2$ and CaNO$_3$.

From the above results, the I_{corr} and E_{corr} values have been calculated. The I_{corr} decreases continuously with the increase in the molar concentration of Na$_2$MoO$_4$ and the value of E_{corr} moved towards positive direction with the increase in Na$_2$MoO$_4$ content [9]. Both the above data are suggestive of continuous inhibition by increase in Na$_2$MoO$_4$ content. This can be attributed to the formation of a hydrated mixed oxide film, which provides a barrier for anodic dissolution [10, 11]. In fact a non-protective ferrous (Fe^{2+})-molybdate complex is initially formed and is subsequently oxidized in the presence of oxygen [12]. The resulting ferric (Fe^{3+})-molybdate complex is insoluble and increases the stability of the Fe$_2$O$_3$ films that develop over the active corroding sites [13]. Further, the MoO$_4^{2-}$ ions adsorb on the outermost part of the hydrated oxide layer (by ion exchange mechanism), thereby imparting a negative charge on the surface [14]. This leads to a barrier effect that impedes both the ingress of Cl$^-$ ion to the underlying substrate and the transport of Fe^{2+} away from the surface [13].

Figure 17.
Polarization of rebar (steel) in pore solution containing 3.5% NaCl and different concentrations of Na₂MoO₄.

### 3.6 Role of sodium tungstate inhibitor in rebar corrosion

Tungstates are very efficient corrosion inhibitor in more realistic environments such as neutral or alkaline solutions containing chlorides, sulphates and some other ions [15, 16]. Sodium tungstate has been extensively studied in the protection of iron as an environmentally-friendly anodic-type inorganic corrosion inhibitor [17–20] and is one of the effective corrosion inhibitors. The situation where pore water may always be contaminated with different amounts of aggressive ions such as chloride can be represented by addition of 3.5% NaCl in the test solution (pore solution), with Na_2WO_4 ($10^{-1.0}$, $10^{-1.5}$, $10^{-2.0}$, $10^{-2.5}$, $10^{-3.0}$, $10^{-3.5}$ and $10^{-4.0}$ M) as inhibitor. **Figure 18** shows the polarization of rebar in pore solution containing 3.5% NaCl and different concentrations of Na_2WO_4, which is almost similar to that in case of Na_2MoO_4 (**Figure 17**).

From the above results, the I_{corr} and E_{corr} values have been calculated. The value of I_{corr} decreases continuously with the increase in the molar concentration of Na_2WO_4 and the value of E_{corr} moves towards positive direction with the increase in Na_2WO_4 content [9]. Both the above data are suggestive of continuous inhibition by increase in Na_2WO_4 content. This may be attributed to the formation of a hydrated oxide film that acts a passive layer and provides a barrier for anodic dissolution [21, 22]. In fact the oxyanions (WO_4^{2-} ion) adsorb on the outermost part of the hydrated oxide layer, which leads to a barrier effect that inhibits both the ingress of Cl^- ion to the underlying substrate and the transport of Fe^{2+} away from the surface [23].

3.7 Comparative analysis of the inhibition by molybdate and tungstate

Inhibitors, molybdate and tungstate are oxygen-dependent anodic inhibitors [10–13, 24] in alkaline environment where these oxyanions remain stable and do
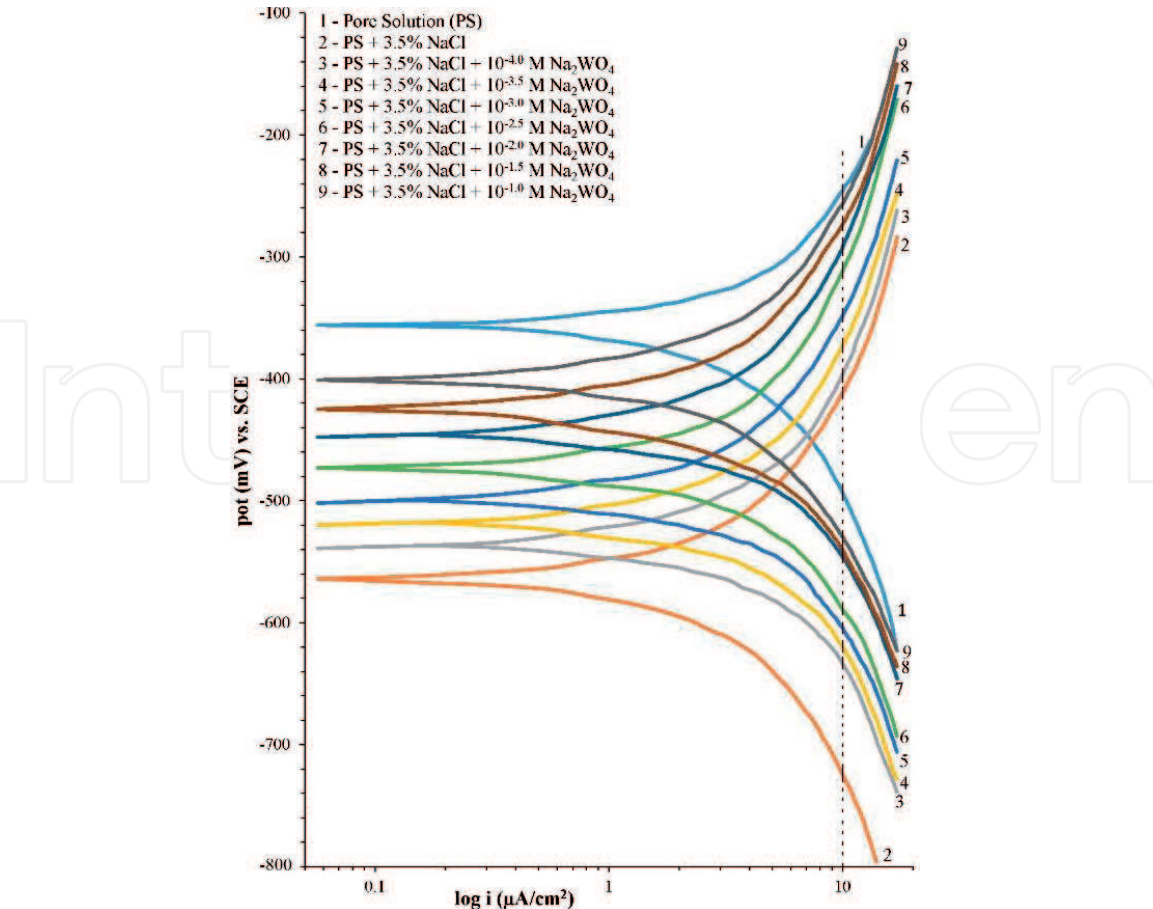
Figure 18.
Polarization of rebar (steel) in pore solution containing 3.5% NaCl and different concentrations of Na_2WO_4.

Inhibitor	I_{corr} ($\mu A/cm^2$)						
	$10^{-1.0}$ M	$10^{1.5}$ M	$10^{-2.0}$ M	$10^{2.5}$ M	$10^{3.0}$ M	$10^{3.5}$ M	$10^{-4.0}$ M
Na_2MoO_4	1.99	1.91	1.83	1.78	1.61	1.48	1.43
Na_2WO_4	1.98	1.92	1.82	1.77	1.60	1.51	1.41

Table 3.
I_{corr} values of rebar (steel) in pore solution containing 3.5% NaCl and different molar concentrations of Na_2MoO_4 and Na_2WO_4.

not promote spontaneous passivation in absence of dissolved oxygen [9]. The mechanism of inhibition involves the formation of a mixed oxide film, which acts as a barrier for anodic dissolution [13]. This has been reported that both molybdate and tungstate are comparable in their inhibitive efficiencies in alkaline environment [24] as obtained in the **Figures 17** and **18**.

However, the actual comparative performance of the sodium molybdate and sodium tungstate can be realized better from the I_{corr} values as given in **Table 3**. The I_{corr} values indicate that sodium molybdate and sodium tungstate are comparable in their inhibitive efficiencies; however, the inhibitive performance of sodium tungstate is slightly better [9].

4. Comparative analysis of the inhibition by nitrites (NO_2^-) and nitrates (NO_3)

Further to the discussion regarding inhibitive role of nitrite [Eqs. (1) and (2)], many other [25–27] theories have been put forward, some [28] even claimed that

nitrite ions readily form complexing agents with Fe^{2+}, which are competitive with Cl^- complexation, thereby preventing formation of chlorocomplexes (these complexes appeared to be essential components of anodic corrosion processes [29]). Another proposal [27] explains sacrificial reduction of nitrite to nitrogen with simultaneous oxidation of ferrous to ferric ion. The formation of FeOOH (or similar product) has been indicated to decrease ion migration as ferrous/ferric chlorocomplexes and thereby stifle iron dissolution. It has been noted [25] that the reduction mechanism of NO_2^- inhibitor does not proceed further to nitric oxide (NO).

The inhibition process of NO_3^- may be summarized as: nitrate is reduced to nitrite [25] by ferrous ion in alkaline environment [pore solution].

$$2 \, Fe(OH)_2 \, (s) + NO_3^- + H_2O = 2Fe(OH)_3 \, (s) + NO_2^- \tag{3}$$

To explain the comparative performance of nitrite and nitrate, it me be summed up that one mole of NO_3^- inhibitor can offer protection equivalent to three moles of NO_2^- inhibitor.

The above strong inhibitive effect of NO_3^- has been noted in the present experiments with sodium and calcium salts, both in terms of potential and polarization studies.

5. Comparison of effectiveness of calcium and sodium inhibitors

Figure 19 below gives the assorted values of the I_{corr} vs. wt % data of sodium nitrite $NaNO_2$, sodium nitrate $NaNO_3$, calcium nitrite $Ca(NO_2)_2$ and calcium nitrate
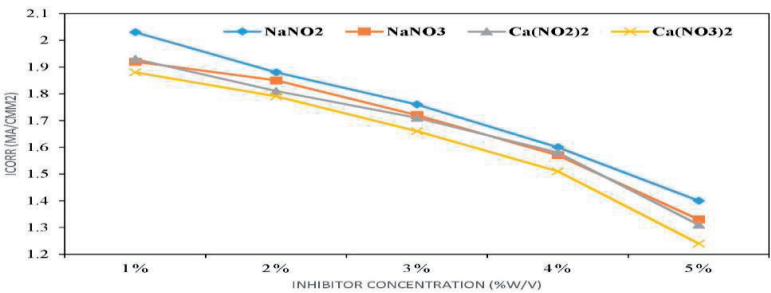

Figure 19.
Comparison of I_{corr} in terms of % m/v of inhibitors.

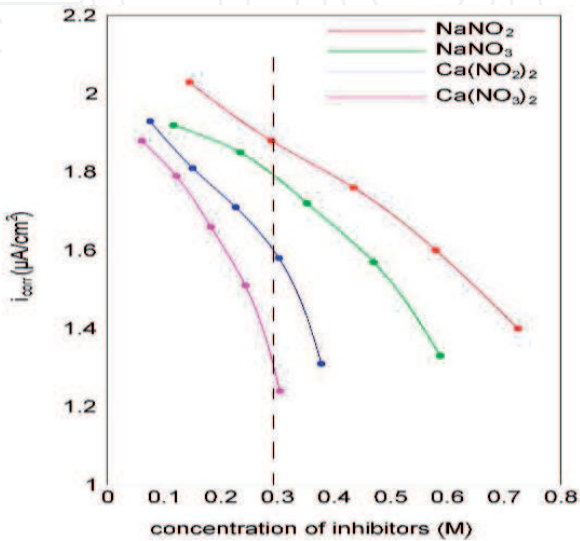**Figure 20.**
Comparison of I_{corr} in terms of molar concentration of inhibitors.

Ca(NO$_3$)$_2$, which gives a comparative performance of sodium and calcium inhibitors. However, the actual comparative performance of the calcium and sodium inhibitors can be realized better if the molar concentrations are considered as in **Figure 20**, which indicates that for inhibition purpose, increasing the molar content, the calcium inhibitors become more effective (as marked in vertical dotted line).

6. Conclusion

The present investigation tried to explore types of inhibitors, nature of inhibitors, their mechanism and also to explore whether the simple polarization technique can be used to compare the efficiency of most prevalent inhibitors, for example, NaNO$_2$ and NaNO$_3$ as compared to the corresponding calcium salts and that of oxyanions of group VI (molybdate and tungstate) for the inhibition of rebar in concrete. The findings indicate that performance wise (a) nitrate salts are more efficient than nitrite salts (sodium and calcium); (b) calcium salts are more effective; (c) further, it was observed that molar concentration wise calcium salts offer greater efficiency; and (d) molybdates and tungstates are almost comparable in their inhibitive efficiency in terms of I$_{corr}$ values, however, tungstates show comparably better inhibitive efficiency in protecting steel reinforcement corrosion in concrete.

Acknowledgements

Author details

Anil Kumar
Department of Applied Sciences and Humanities, National Institute of Foundry and Forge Technology, Ranchi, India

*Address all correspondence to: akiitk_70@rediffmail.com

IntechOpen

References

[1] Ahamad A, Kumar A. Comparative behaviour of nitrite and nitrate for the protection of rebar corrosion. Journal of the Institution of Engineers (India): Series D. 2017;**98**(2):177-187

[2] El-Jazairi B, Berke NS. The use of calcium nitrite as a corrosion inhibiting admixture to steel reinforcement in concrete. In: Page CL, Treadaway KW, Bamforth PB, editors. Corrosion of Reinforcement in Concrete. London: Elsevier Science Publishers; 2002. pp. 571-585

[3] Berke NS, Weil TG. World-wide review of corrosion inhibitors in concrete. In: Malhotra VM, editor. Advances in Concrete Technology. 2nd ed. Ottawa: CANMET; 1992. pp. 891-914

[4] Vukasovich MS, Farr JPG. Molybdate in corrosion inhibitor –a review. Polyhedron. 1986;**5**(1/2):551-559

[5] Armour AW, Robitaille DR. Corrosion inhibition by sodium molybdate. Journal of Chemical Technology and Biotechnology. 1979;**29**: 619-628

[6] Weber TR, Stranick MA, Vukasovich MS. Molybdate corrosion inhibition in deaerated and low-oxygen waters. Corrosion. 1986;**42**:542-545

[7] Hope BB, Ip AKC. Effect of calcium nitrite and sodium molybdate on corrosion inhibition of steel in simulated concrete environment. Admixtures for Concrete— Improvement of Properties. Proceedings of the International Symposium Held by RILEM. New York, London: Chapman & Hall; 1990. ISBN: 0 412 37410 2 (Print edition)

[8] Tommaselli MAG, Mariano NA, Kuri SE. Effectiveness of corrosion inhibitors in saturated calcium hydroxide solutions acidified by acid rain components. Construction and Building Materials. 2009;**23**:328-333

[9] Ahmad A, Kumar R, Kumar A. Effect of sodium molybdate and sodium tungstate in concrete rebar corrosion. Anti-Corrosion Methods and Materials. 2019;**63**(3):253-263

[10] Pryor MJ, Cohen M. The inhibition of the corrosion of iron by some anodic inhibitors. Journal of the Electrochemical Society. 1953;**100**(5):203-215

[11] Vukasovich MS, Robitaille DR. Corrosion inhibition by sodium molybdate. Journal of the Less Common Metals. 1977;**54**(2):437-448

[12] Lizlovs EA. Molybdates as corrosion inhibitors in presence of chlorides. Corrosion NACE. 1976;**32**(7):263-266

[13] Kodama T, Ambrose JR. Effect of molybdate ion on the repassovation kinetics of iron in solutions containing chloride ions. Corrosion. 1977;**33**:155-161

[14] Al-Saffar AH, Ashworth V, Bairamov AKO, Chivers DJ, Grant WA, Procter RPM. The effect of moly-bdenum ion implantation on the general and pitting corrosion behaviour of pure aluminium and a high strength aluminium alloy. Corrosion Science. 1980;**20**:127-144

[15] Mammoloti L, Hansson CM, Hope BB. Corrosion admixtures in concrete part II: Effect on chloride threshold values for corrosion of steel in synthetic pore solutions. Cement and Concrete Research. 1999;**29**(10):1583-1589

[16] Cisse MB, Zergar B, El Kalai F, EbnTouhami M, Sfaira M, Taleb M, et al. Two dipodal pyridine-pyrazol derivatives as efficient inhibitors of mild steel corrosion inHCl solution—part I: Electrochemical study. Surface Review and Letters. 2011;**18**(6):303-313

[17] Shibli SMA, Saji VS. Co-inhibition characteristics of sodium tungstate with potassium iodate on mild steel corrosion. Corrosion Science. 2005;**47**: 2213-2224

[18] Boucherit MN, Amzert SA, Arbaoui F, Hanini S, Hammache A. Pitting corrosion in presence of inhibitors and oxidants. Anti-Corrosion Methods and Materials. 2008;**55**:115-122

[19] Rao BVA, Rao MV, Rao SS, Sreedhar B. Tungstate as a synergist to phosphonate-based formulation for corrosion control of carbon steel in nearly neutral aqueous environment. Journal of Chemical Sciences. 2010;**122**(4):639-649

[20] Alentejano CR, Aoki IV. Localized corrosion inhibition of 304 stainless steel in pure water by oxyanions tungstate and molybdate. Electrochimica Acta. 2004;**49**:2779-2785

[21] Celeste RA, Vieira VA. Localized corrosion inhibition of stainless steel in pure water by oxyanions tungstate and molybdate. Electrochimica Acta. 2004;**49**:2779-2785

[22] Song Q, Qui XQ. Study on the complex of sodium tungstate and urotropine as inhibitors against stainless steel corrosion in the NaCl solution. Materials Science. 2011;**689**:450-454

[23] Deepak VK, Jagadeesh B. Effect of sodium tungstate as a green corrosion inhibitor on the passivation behaviour of mild steel sheet in aggressive media. International Journal of Applied Sciences and Biotechnology. 2016;**4**(2):183-190

[24] Robertson WD. Molybdate and tungstate as corrosion inhibitors and the mechanism of inhibition. Journal of the Electrochemical Society. 1951;**98**(3):94-100

[25] Rosenberg AM, Gaidis JM. The mechanism of nitrite inhibition of chloride attack on reinforcing steel in alkaline aqueous environments. Materials Performance. 1979;**18**(11):45-48

[26] Gaidis JM, Rosenberg AM. The inhibition of chloride-induced corrosion in reinforced concrete by calcium nitrite. Cement, Concrete and Aggregates. 1987;**9**(1):30-33

[27] El-Jazairi B, Berke NS. The use of calcium nitrite as a corrosion inhbiting admixture to steel reinforcement. Corrosion of Reinforcement in concrete. In: Page CL, editor. Society of Chemical Industry; London. 1990. pp. 571-585

[28] Sagoe-Crentsil KK, Yilmaz VT, Glasser FP. Properties of inorganic corrosion inhibition admixtures in steel-containing OPC mortars. Part 1: Chemical properties. Advances in Cement Research. 1992;**4**:91-96

[29] Sagoe-Crentsil KK, Glasser FP. Green rust, iron solubility and the role of chloride in the corrosion of steel at high pH. Cement and Concrete Research. 1993;**23**:785-791