MIGRATORY TYPE CORROSION INHIBITOR FOR PREVENTING CORROSION IN REINFORCED CONCRETE

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CERTIFICATE

This is to certify that the work presented in thesis entitled "Migratory inhibitors for preventing corrosion of reinforced concrete" submitted by, **PRASHANT KUMAR, Roll No. 801022013** in partial fulfilment of the requirements for the award of **Masters of Engineering in Civil (Structures) at Thapar University, Patiala**, is an authentic record of student's own work carried out under our supervision and guidance. The work embodied in this thesis has not been submitted anywhere for award of any other degree.

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ABSTRACT

In general, reinforced concrete has proved to be successful in terms of both structural performance and durability. However, there are instances of premature failure of reinforced concrete components due to corrosion of the reinforcement. The two factors provoking corrosion are the ingress of chloride ions from deicing salts or sea water or the reaction of the alkaline pore solution with carbon dioxide from the atmosphere, a process known as carbonation.

A number of techniques are available for the prevention of corrosion. Despite of the huge demand, a simple, cheap, and reliable technique which either protects the steel from corrosion or at least lowers its corrosion rate is still lacking. Over the past decade, however, concrete repair industry has developed novel techniques that are claimed to prevent or at least reduce corrosion of steel in concrete. The use of the "corrosion inhibitors" is of increasing interest as they can be used in reinforced concrete either as preventive measure for new structures (addition to the mixing water) or as surface applied inhibitors for preventive and restorative purpose. Addition to the mixing water does not require any additional working steps and allows a simple handling of the inhibitor, unless it affects the properties of the cement paste adversely. Application from the concrete surface could be a promising technique to protect already existing structures from corrosion or increase the lifetime of structures that already show corrosion attack.

The application of inhibitors on the concrete surface requires the transport of the substance to the rebar where it has to reach a sufficiently high concentration to protect steel against corrosion or reduce the rate of the ongoing corrosion. This thesis investigates the effectiveness of migrating type corrosion inhibitors on the concrete slabs made with different water-cement ratios. Therefore effectiveness of corrosion inhibitor, when applied on concrete surface, will depend upon the factors like quality of concrete etc because the inhibitor have to pass through concrete cover to reach the rebar. The effect of Corrosion Inhibitor on the half cell potential measurements and corrosion current has been studied.

From the experiments, it has been observed that i.e. corrosion current obtained is similar for all water-cement ratios indicating that corrosion inhibitor protect all types of concrete by the same proportion. It is also concluded that only two coats of corrosion inhibitor are sufficient in reducing corrosion rate.

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CHAPTER 1 INTRODUCTION

1.1 GENERAL

Reinforced concrete is a versatile, economical and successful construction material. It can be moulded to a variety of shapes and finishes. Usually it is durable performing well throughout its service life. However, sometimes it does not perform adequately as a result of poor design, poor construction, inadequate materials selection, a more severe environment than anticipated or a combination of these factors. A large portion of concrete production is used in residential, commercial and public buildings.

Corrosion of steel reinforcement is normally inhibited because the protective oxide film on the surface of the steel is chemically stable in the usual, alkaline environment within concrete. However, the protective oxide film can be destroyed if the concrete becomes less alkaline as a result of carbonation or if chloride ions are present in the surrounding concrete.

Whatever the source of deterioration and the mechanism of its development, corrosion of embedded reinforcement is recognized as the major problem affecting the durability of concrete structures. It has been found that 40% failure of structures is on account of corrosion of embedded steel in concrete (*Sethy,2005*). Therefore corrosion control of steel reinforcement is a subject of paramount importance. Corrosion is a form of damage which is often insidious and hidden until striking at the worst moment of a system operation. The reason of these phenomena is explainable with the mechanism of corrosion. When reinforcement corrodes, the corrosion products generally occupy considerably more volume than the steel. The magnitude of this increase in volume varies approximately 2 or 3 times the volume of the original material. As a result, the corrosion products produce an internal stress that destroys the neighbouring concrete under tensile stress.

The prevention and treatment of rebar corrosion can be addressed by several techniques which include, increased cover over the rebars, reduced water cement ratios, denser concretes, latex or polymer modified concrete overlays, waterproofing membrane with asphalt overlays, epoxy coated rebars and cathodic protection are used. Use of epoxy coated rebars was initially believed to be the “ideal” solution to prevent corrosion of rebars, but its long-term effectiveness is being questioned. Cathodic protection systems protect steel reinforcement in concrete contaminated with high levels of chloride but are rather expensive and a source of electricity must be available. To conclude, a number of rebar protection

systems are available for the customer today, each having certain drawbacks and with varying degree of cost.

One of these methods is the use of corrosion inhibitors, which provide simple and cost effective techniques. Inhibitors are materials that are able to reduce corrosion rate. They are used in relatively small quantities. Many different types of inhibitor are available today, but in many cases the mechanism of inhibitor is not fully understood. The use of these corrosion inhibitors is of increasing interest as they can be used in reinforced concrete either as preventive measure for new structures (addition to the mixing water) or as surface applied inhibitors for preventive and restorative purpose. Addition to the mixing water does not require any additional working steps and allows a simple handling of the inhibitor, unless it affects the properties of the cement paste adversely. Application of corrosion inhibitor onto concrete surface could be a promising technique to protect already existing structures from corrosion or increase the lifetime of structures that already show corrosion attack. The application of inhibitors on the concrete surface requires the transport of the substance to the rebar where it has to reach a sufficiently high concentration to protect steel against corrosion or reduce the rate of the ongoing corrosion.

1.2 THE CORROSION PROCESS – MECHANISM

Corrosion is the deterioration of a material, usually a metal that results from a reaction with environment. The corrosion of steel in concrete is considered as an electrochemical process with anodes and cathodes formed adjacently on the rebar and are surrounded by the concrete pore solution which acts as the electrolyte allowing the movement of ions between anodic and cathodic sites. This electrochemical process involves following reactions;

The anodic reaction: $Fe \rightarrow Fe^{2+} + 2e^-$ (1.1)

The two electrons ($2e^-$) created in the anodic reaction must be consumed elsewhere on the steel surface to preserve electrical neutrality. In other words, it is not possible for large amounts of electrical charge to build up at one place on the steel; another chemical reaction must consume the electrons. This is a reaction that consumes water and oxygen:

The cathodic reaction : $2e^- + H_2O + 1/2O_2 \rightarrow 2OH^-$ (1.2)

Hydroxyl ions ($2OH^-$) are generated in the cathodic reaction increase the local alkalinity and will therefore strength the passive layer, warding off the effects of carbonation and chloride ions at the cathode.

The anodic and cathodic reaction are only the first steps in the process of creating rust.

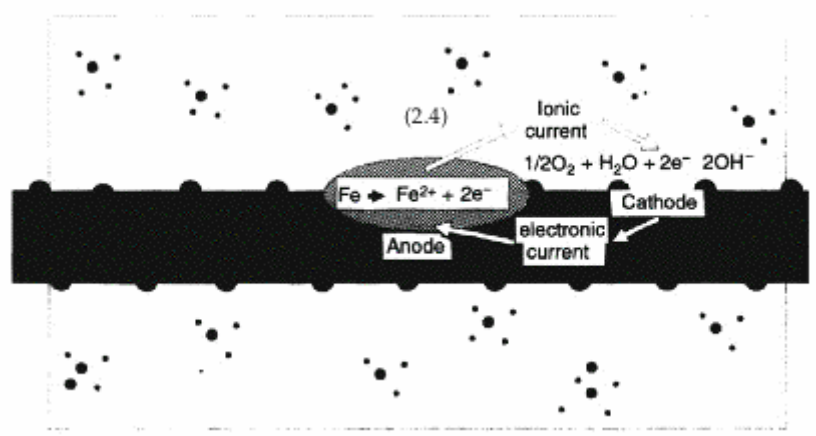

Fig. 1.1 The anodic and cathodic reactions. ***(Broomfield, 2006)***

If the iron were just to dissolve in the pore water (the ferrous ion Fe^{2+} in equation 1.1 is soluble) we would not see cracking and spalling of the concrete. Several more stages must occur for 'rust" to form. This can be expressed in several ways; one is shown below where ferrous hydroxide becomes ferric hydroxide and then hydrated ferric oxide or rust:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad \text{(Ferrous hydroxide)} \qquad (1.3)$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \quad \text{(Ferric hydroxide)} \qquad (1.4)$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3.H_2O + 2H_2O \quad \text{(Hydrated ferric oxide)} \qquad (1.5)$$

The full corrosion process is illustrated in Figure 1.2. Unhydrated ferric oxide Fe_2O_3 has a volume of about twice that of the steel it replaced when fully dense. When it becomes hydrated, it swells even more and becomes porous. This means that the volume increase at the steel/concrete interface is two to ten times. This leads to the cracking and spalling that we

observe as the usual consequence of corrosion of steel in concrete and the red/brown rust in the bar and the rust stains seen at cracks in the concrete.

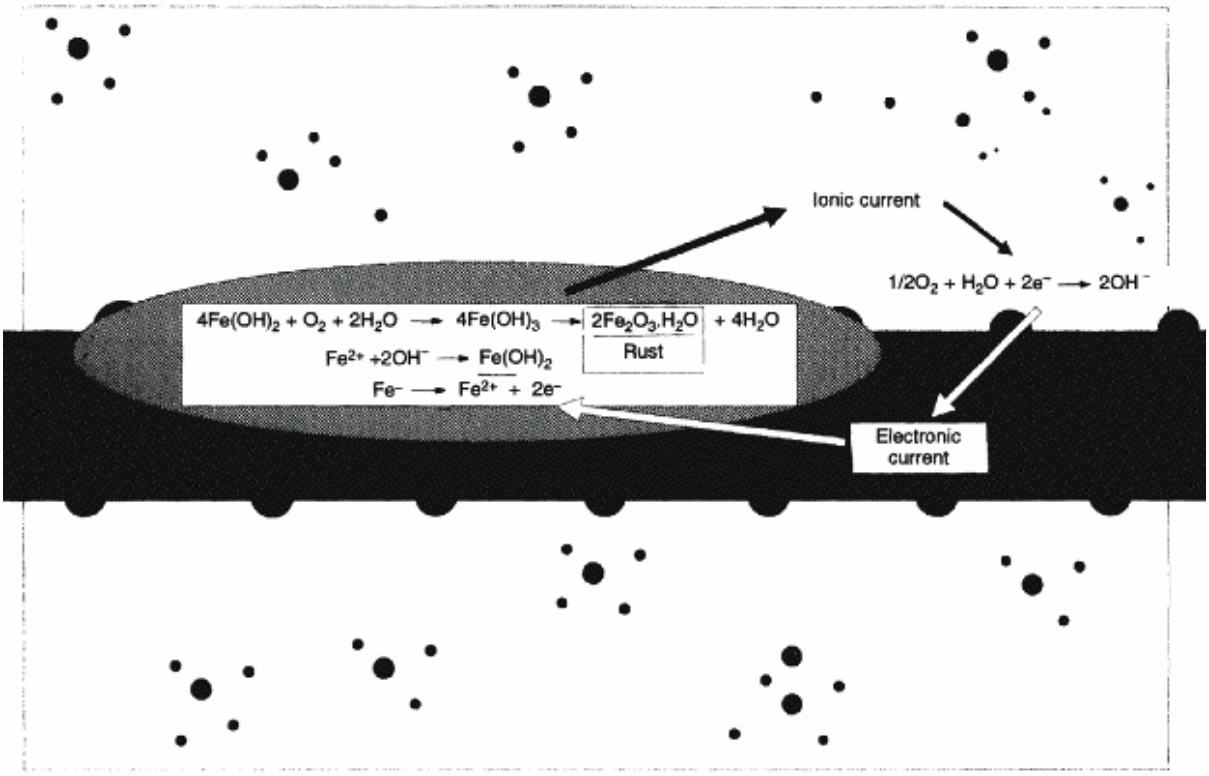

Fig. 1.2. The corrosion reactions on steel. ***(Broomfield, 2006)***

1.3 REBAR CORROSION AND ITS CAUSES

The concrete provides the steel with a physical barrier against agents that promote corrosion, such as water, oxygen and chlorides. The chemical effect of concrete is attributed to its alkalinity, which causes an oxide layer to form on the steel surface. This phenomenon is called passivation, as the oxide layer prevents propagation of corrosion. In normal outdoor concrete structures, corrosion of reinforcement takes place only if changes occur in the concrete surrounding the steel. The changes may be physical, such as cracking and disintegration, exposing part of the steel surface to open air and leaving it without the physical and chemical protection of concrete.

Sound concrete is an ideal environment for steel but the increased use of deicing salts and the increased concentration of carbon dioxide in modern environments principally due to industrial pollution, has resulted in corrosion of the rebar becoming the primary cause of failure of this material. The scale of this problem has reached alarming proportions in various parts of the world.

Carbonation of concrete or penetration of chlorides into the concrete, are the major causes of reinforcement corrosion. Chlorides in concrete either penetrate from the surrounding chloride-bearing environment (such as moisture, oxygen, humidity, temperature, bacterial attack, stray currents, etc.) or is contributed from the concrete ingredients (such as concrete quality, w/c ratio, cement content, impurities in the concrete ingredients, presence of surface cracks, etc).

The assessment of the causes and extent of corrosion is carried out using various electrochemical techniques (*Broomfield, 2006*). Prediction of the remaining service life of a corroding reinforced concrete infrastructure is done with the help of empirical models and experimental methods (*Weyers, 1998*).

Following are the two most common contributing factors leading to reinforcement corrosion:

(i) General breakdown of passivity by neutralization of the concrete, predominantly by reaction with atmospheric carbon dioxide called carbonation.

(ii) Localized breakdown of the passive film on the steel by chloride ions called chloride attack.

The following section discuss the two major causes of corrosion, i.e, chlorides and carbonation along with some minor causes of corrosion.

1.3.1 Carbonation

Carbonation is a result of the interaction of carbon dioxide gas in the atmosphere with the alkaline hydroxides in the concrete. Due to the high alkalinity of the concrete pore water, the steel reinforcing bars are passivated by an iron oxide film (Fe_2O_3) that protects the steel. At this pH value a passive film forms on the steel that reduces the rate of corrosion to a very low and harmless value.

Concrete is permeable and allows the slow ingress of the atmosphere; the acidic gases react with the alkalis (usually calcium, sodium and potassium hydroxides), neutralizing them by forming carbonates and sulphates, and at the same time reducing the pH value. If the carbonated front penetrates sufficiently deeply into the concrete to intersect with the concrete reinforcement interface, protection is lost and, since both oxygen and moisture are available, the steel is likely to corrode. The extent of the advance of the carbonation front depends, to a considerable extent, on the porosity and permeability of the concrete and on the conditions of the exposure.

In the case of carbonation, atmospheric carbon dioxide (CO_2) reacts with pore water alkali according to the generalized reaction,

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (1.6)$$

It consumes alkalinity and reduces pore water pH to the 8–9 range, where steel is no longer passive.

The depth of carbonation (d) can be reasonably described by a square root of the time (t) relationship:

$$d = kt^{1/2} \tag{1.7}$$

Where,

d=the depth of carbonation at time *t*,

k=the carbonation coefficient and

t=time or age

The initiation time of corrosion can be determined as follows:

$$t_0 = \left[\frac{d}{k}\right]^2 \tag{1.8}$$

Carbonation coefficient k depends on environmental factors and on concrete properties. Carbonation depends upon the degree of porosity of the structure. The moisture content of concrete has a major role. The carbonation rate is negligible in water saturated concrete as the diffusion of carbon dioxide is hindered in the water-filled pores. The carbonation rate is also negligible in dry concrete, as the reaction of carbon dioxide with the alkalinity of the concrete is prevented due to lack of water. The value of k is higher for intermediate moisture contents (*Tuutt, 1982, Parrott 1992, Alonso and Andrade 1994*)

Once the carbonation front has reached the reinforcement, and thus the steel is depassivated, the availability of oxygen and water at the steel surface are the controlling factors for the corrosion rate (*Alonso and Andrade, 1994*). Oxygen depletion may only occur under complete and permanent saturation of concrete with water. In other exposure conditions, the corrosion rate of steel in carbonated concrete is governed by the electrical resistivity of concrete. Various researchers observed that the corrosion rate of steel in carbonated concrete decreases as the electrical resistivity increase (*Alonso et al., 1988, Glass et al., 1991*). However , (*Bertolini and polder, 1997*) emphasised that a universal correlation between the corrosion rate of steel and the electrical resistivity of concrete cannot be found, as this may change according to concrete composition and the chloride contamination.

1.3.2 Chloride Ingress

Conditions for Chloride Initiated Reinforcement Corrosion :

For chloride – initiated Reinforcement Corrosion to occur the following conditions must be fulfilled :

(i) The chloride concentration in the pore solution must exceed a critical value known as the threshold value.

(ii) The concrete must be moist, in other words it contains an electrolyte which permits ion transport.

(iii) Oxygen must be present (this is necessary if the electrochemical corrosion process is to proceed).

Ways of Chloride Intrusion :

The following are the most common causes of chloride intrusion :

(i) Chlorides have been added, in the form of accelerating admixtures or contaminated constituents when mixing the concrete.

(ii) Chlorides have been transported into concrete which have been exposed to sea water.

(iii) Chlorides have been transported into concrete which has been exposed to deicing salts.

In the case of (i), the presence of chlorides will set up immediate corrosion reactions, while in cases (ii) and (iii), the chloride content of the concrete will build up with time, possibly leading to conditions of depassivation.

States in which Chlorides are Present :

Chlorides are often present in concrete in a number of states:

(i) BOUND :

(a) Chemically bound with the hydration products of the cement such as C_3A and C_4AF phases ;

(b) Loosly bound with the C-S-H gel ; and

(ii) FREE ions within the pore solution (*Wee et al.,1997*)

It is generally recognised that only the free chloride ions influence the corrosion process. The total Cl^- concentration by weight of cement (C_T) can be expressed as :

$C_T = C_F + C_B = C_F + (C_{BC} + C_{BP})$

Where C_F is the Cl^- concentration ;

C_B is the bound Cl^- concentration;

C_{BC} is the chemically bound Cl^- concentration;

C_{BP} is the physically bound Cl^- concentration;

All of which are defined by weight of cement.

C_{BC} is the Cl^- which reacts chemically with the hydration compounds of cement, particularly with C_3A to form calcium chloro aluminate (also known as Friedel's salt). C_{BP} is Cl^- which is attracted to the positively charged cement hydrates at the pore surface. This phenomenon results in the formation of an electrical double layer at the solid liquid interface within the cement pastes *Welle et al. (1997*).

The corrosion rate is not only influenced by these factors but also there are some other factors which may lead to the rate of corrosion and hence may affect the service life.

1.3.3 Cracks due to Mechanical Loading

Cracks in concrete formed as a result of tensile loading, shrinkage, frost attack or other factors allows the ingress of water and oxygen from atmosphere and provide a zone from which the carbonation front can develop. If the crack reaches the surface of rebar the protection can be lost. Due to formation of cracks, debonding of steel and concrete occurs to some extent on each side of the crack, thus removing the alkaline environment and so destroying the protection in the vicinity of the debonding.

1.3.4 Corrosion of Rebar due to Atmospheric Pollution

Most of the times steel reinforcement is exposed to the atmosphere during transportation and storage in the building sites for a long period before their installation in the concrete structures. At any of those stages, steel rebars can be contaminated by chloride ions from windblown salt. This fact leads to the formation of corrosion products on their surface.

1.3.5 Moisture Pathways

If the surface of the concrete is subjected to long-term wetting, the water will eventually reach the level of the reinforcement, either through diffusion through the porous structure of the concrete, or by travelling along cracks in the concrete. Concretes structures, by their nature, are meant to be protected from moisture. However, the presence of moisture on roofing systems may result from

failure of the roofing membrane, poor detailing of drainage facilities, or lack of maintenance of drainage facilities.

1.3.6 Water-Cement Ratio

Concrete placed with a high water-cement ratio, is more porous due to the presence of excess water in the plastic concrete. The porosity increases the rate of diffusion of water and electrolytes through the concrete and makes the concrete more susceptible to corrosion.

1.3.7 Corrosion due to difference in environments

Corrosion occurs when two different metals, or metals in different environments, are electrically connected in a moist or damp concrete. This will occur when:

1. Steel reinforcement is in contact with an aluminium conduit.
2. Concrete pore water composition varies between adjacent or along reinforcing bars.
3. There is a variation in alloy composition between or along reinforcing bars.
4. There is a variation in residual/applied stress along or between reinforcing bars.

The aggressiveness of environmental conditions is exacerbated by deicing salts spread on roads and pavements. Deicing salts not only increase pressures within the concrete, but also diminish its ability to withstand them. The application of de-icing agents to a concrete surface covered with ice will cause a substantial drop in temperature at the concrete surface during thawing of the ice. The difference in temperature between the surface area and the interior of the concrete gives rise to a state of internal stresses likely to induce cracking in the region of the outer layer of the concrete.

1.3.8 Low Concrete Tensile Strength

Concrete with low tensile strength facilitates corrosion damage in two ways. First, the concrete develops tension or shrinkage cracks more easily, admitting moisture and oxygen, and in some cases chlorides to the level of the reinforcement. Second, the concrete is more susceptible to developing cracks at the point when the reinforcement begins to corrode.

1.3.9 Electrical contact with dissimilar metals

Dissimilar metals in contact initiate a flow of electrons that promotes the corrosion of one or the other, by a process known as galvanic corrosion. When two dissimilar metals are in contact with

each other, the more active metal will induce corrosion on the less active metal. Such corrosion may induce cracking and damage in the concrete.

1.4 METHODS TO REDUCE CORROSION

Various Physical, Chemical and Electrochemical repair techniques are available today, to arrest rebar corrosion and hence extend the service life of reinforced concrete structures. Physical techniques are generally used for the repair works, while the chemical techniques can be used in the new structures. Electrochemical Techniques work by applying an external anode and passing current from it to the steel so that all of the steel is made into a cathode. Table 1.1 gives the details of various physical, chemical and electrochemical techniques used for the repair of the corrosion damaged structures.

Table 1.1: Physical, Chemical and electrochemical repair techniques

Techniques	Types
Concrete Removal and Surface preparation by Pneumatic hammer, Hydrojetting	Physical
Patches by incipient anodes	Physical
Coatings against chlorides, Penetrating Sealers	Physical
Waterproofing Membranes and Barriers	Physical
Corrosion Inhibitors	Chemical
Cathodic Protection by impressed current system	Electrochemical
Cathodic protection by sacrificial anode system	Electrochemical

The problem with physical techniques is that they have a 10 to 12 year life time, after this period they must be replaced and causes the problem called severe pitting and black rust. However, Electrochemical techniques require constant supply of current to make the system fully effective. Chemical protection techniques like application of corrosion inhibitor work by development of chemical layer, usually one or two molecules thick, on the steel surface that inhibit the corrosion. Among various methods available to mitigate corrosion, corrosion inhibitors seem to be attractive because of their low cost and easy handling, compared with other preventive methods.

1.5 CORROSION INHIBITOR

The principle of inhibitors is to develop a thin layer, usually one or two molecules thick, on the steel surface, which inhibits corrosion either by forming a protective film on the substrate, or by immobilizing the corrosive species and preventing them from reaching the steel. They act like negative catalysts and have become indispensable in a variety of applications. The use of corrosion inhibiting admixtures has grown over the last 25 years because they provide a level of protection and longevity that would be too difficult (essentially too expensive) to achieve otherwise. Corrosion inhibitors interfere with the corrosion process without detrimental effects on concrete quality but this is not to say that corrosion inhibitors have no effect except on corrosion. The mechanisms by which the corrosion inhibitors are able to protect reinforcing steel include:

- A decrease on the diffusion rate of the chloride ion.
- An increase on the amount of bound chloride.
- An increase on the chloride ion threshold value.
- The inhibition of the anodic, cathodic or both reactions.

1.6 OBJECTIVE OF PRESENT RESEARCH WORK

There are various Physical, Chemical and Electrochemical repair techniques that are available today to extend the service life of reinforced concrete structures. Among various methods available to mitigate corrosion, corrosion inhibitors seem to be attractive because of their low cost and easy handling, compared with other preventive methods. The objective of the present research work for preventing corrosion in reinforced concrete is to study the effectiveness of migrating type corrosion inhibitors on concrete prepared with various water-cement ratios with regard to reduction in rebar corrosion.

1.7 FORMAT OF THESIS REPORT

The thesis presentation has been organized in five chapters.

- In the first chapter, Mechanism and Causes of Rebar Corrosion are presented.
- Second chapter deals with the Corrosion inhibitors , classification of corrosion inhibitor and some commonly used corrosion inhibitors
- Third chapter deals with the Literature Review justifying the objectives of the research work which is presented.
- In fourth chapter, the experimental investigation carried out for measurement of half-cell potential, Linear Polarization resistance on prism specimens subjected to external chloride exposure to establish its suitability as a stable indicator of rebar corrosion initiation and application of penetrating type corrosion inhibitor on concrete samples.
- Chapter five deals with the results and discussions of the experiment.
- In Chapter six, conclusions are presented

CHAPTER 2 CORROSION INHIBITOR

2.1 INTRODUCTION

Corrosion Inhibitor is define as ‘‘a chemical substance that decreases the corrosion rate when present in the corrosion system at suitable concentration, without significantly changing the concentration of any other corrosion agent.’’ (ISO 8044 1989). This definition excludes other corrosion protection methods such as coatings, pore blockers and other materials, which change the water, oxygen and chloride concentrations . However, some inhibitors also behave as pore blockers, which is a secondary property**.**

Corrosion inhibitors may be a good alternative to other protection methods or classical repair methods due to its lower cost and easy application.

2.2 USE OF CORROSION INHIBITOR IN CONCRETE

The use of corrosion inhibitors in metal industry is wide-spread and well established. For example inhibitor-based protection systems are used to protect metal equipment and components during transport and storage, or to limit the corrosion of process equipment such as cooling systems, pipelines, or central heating systems. Very often the long experience with chemicals operating as corrosion inhibitors e.g. in the oil field, gas or petroleum industry is taken as an example for the successful use of corrosion inhibitors, and is further thought that this technique can be transferred with success into applications for protection of reinforced concrete structures. This is a however, not correct because the mechanism of inhibitor action are completely different:

- in the application of oil and gas industry (and most others) the steel to be protected is uniformly corroding in slightly acidic or neutral media. Thus the inhibitors have to protect the bare metal surface, e.g. as adsorption inhibitors acting specifically on the anodic or on the cathodic partial reaction of the corrosion process or as film forming inhibitors blocking the surface more or less completely. Usually a reduction in corrosion rate of 95 to 99 % is achieved with a very small inhibitor concentration in the order of 10^{-3}– 10^{-2} mol/l. (*Nurnberger, 1996*).
- Steel in concrete instead is in a highly alkaline environment, the high concentration of hydroxyl ions acts as passivation promoting inhibitor and indeed, steel in concrete is

passive, thus protected by a thin oxy-hydroxide layer. This is the starting point for any mechanistic action of inhibitors in concrete.

- Inhibitors for chloride induced pitting corrosion are by far less studied. Inhibitors for pitting corrosion can act by film forming prior to the ingress of chlorides, by buffering the pH in the local pit environment, by competitive surface adsorption processes between inhibitor and chloride ions or by competitive migration of inhibitor and chloride ions into the pit.

2.3 TYPES OF CORROSION INHIBITOR

Many different types of inhibitors are available today, but in many cases the mechanism of inhibition is not fully understood. It is, however, possible to identify groups of inhibitors based on their chemical structure and their physical, chemical and electrochemical behaviour. Corrosion inhibitors may be a good alternative to other protection methods or classical repair methods due to its lower cost and easy application. The corrosion inhibitors can be classified in different ways**:**

1. Based on the physical mode of application
2. Based on their mechanism of protection

The classification of corrosion inhibitor is further studied in detail in the following sections :-

2.3.1 Based Upon the Physical Mode of Application :

1. Admixed Inhibitor :

Those compounds which are added to the fresh concrete at the time of mixing for new structures are known as admixed inhibitors. Admixed inhibitors are commercially available since 1960's. The inorganic compounds which are based upon calcium nitrite, sodium benzoate and sodium chromate are used as admixed inhibitors. Organic compounds based upon mixtures of alkanolamines, amines or amino-acids, or based on an emulsion of unsaturated fatty acid ester of an aliphatic carboxylic acid and a saturated fatty acid are also proposed to be used as admixed inhibitors.

2. Migrating Inhibitor:

These are the chemicals which are applied on the hardened concrete surface and are able to diffuse through concrete to the underlying rebar where they act to suppress both the anodic and cathodic corrosion reactions by forming a monolayer film at the steel-concrete interface. Concrete penetrating corrosion inhibitors (CPO) based on bipolar inhibition mechanism is a

new generation corrosion inhibition. Upon penetration, Concrete penetrating corrosion inhibitors based on bipolar inhibition mechanism (both cathodic and anodic inhibition) inhibit the corrosion even at high chloride levels. This differs from conventional corrosion inhibitors based on calcium nitrite which are only anodic inhibitors in mechanism. Calcium nitrite inhibitors are effective at low chloride concentrations but may actually accelerate corrosion at higher chloride levels in concrete. Further, the new generation corrosion inhibitor (CPCI) is eco-friendly and non-toxic. These inhibitors are typically based on mixtures of alkanolamines and amines or on inorganic compounds based upon Monoflurophosphate [MFP]. The means by which the inhibitor migrates is first by diffusion through the moisture that is normally available in concrete, then by its high vapor pressure and finally by following hairlines and microcracks. This mechanism allows a greater amount to be applied where it is most needed. The diffusion process requires time to migrate through the concrete pores to reach the rebar's surface and form a protective layer.

2.3.2 Based Upon the Mechanism of Protection:

1. Anodic Inhibitor:

Anodic inhibitors act on the dissolution of the steel and they reduce the corrosion rate by an increase in the corrosion potential of the steel. Passivating inhibitors like nitrites represent special types of anodic inhibitors and they are generally very effective inhibitors if present in sufficient concentrations The most commonly used anodic inhibitor is calcium nitrite, Sodium nitrite, sodium benzoate and sodium chromate have also been used.

2. Cathodic Inhibitor:

Cathodic inhibitors act on the oxygen reaction on the steel surface and they reduce the corrosion rate by a decrease in corrosion potential. The most commonly used cathodic inhibitors are sodium hydroxide and sodium carbonate, which are supposed to increase the pH near the steel, and reduce the oxygen transport by covering the steel surface. Phosphates, silicate and polyphosphates are also used.

3. Mixed Inhibitor:

Mixed inhibitors act on both anodic and cathodic sites and they reduce the corrosion rate without a significant change in the corrosion potential, generally by surface adsorption over the surface of the steel in contact with the inhibitor and consequently forming a thin protective layer. In mixed type inhibitors, material with the hydrophobic group that have

polar groups such as N, S, OH is effective. Organic polymer compounds such as amine and aminoalcohol (AMA) are also used.

2.4 COMMONLY USED CORROSION INHIBITOR:

Some of the commonly used corrosion inhibitor and their mechanism of action is described in the following section.

2.4.1 Calcium Nitrite:

Nitrites (calcium or sodium salt) are anodic inhibitors *Dhouibi et al. (2003)*, they compete with chloride ions for the ferrous ions at the anode to form a film of ferric oxide, Fe_2O_3 as indicated in the equations below:

$$2Fe^{2+} + 2OH^- + 3NO_2^- \longrightarrow 2NO + Fe_2O_3 + H_2O \quad (2.1)$$

$$Fe^{2+} + OH^- + NO_2^- \longrightarrow NO\uparrow + \gamma\text{-}FeOOH \quad (2.2)$$

These reactions are much more rapid than the transport of ferrous ions via chloride ion complex formation. Thus nitrite ions aid the formation of a stable passive layer even in the presence of chloride ions (with γ-FeOOH being the more stable oxide in presence of chlorides) *Soeda et al. (2003)*. However, full protection depends greatly on the concentration of aggressive ions such as the chloride ion *Rincon et al. (2002*), and severe pitting may occur when insufficient quantity of inhibitor is used compared to the level of chloride in the concrete .

Calcium nitrite is the first corrosion inhibitor admixture commercialized on a large scale for reinforced concrete. It first saw use in Japan, where it was used at relatively small doses to counter the salt present in sea sand used in construction of reinforced concrete. Sodium nitrite had been used for corrosion inhibition in non-concrete applications previously and was commercially available (and has been investigated in Europe), but the addition of such an alkali salt was not advantageous in concrete. The disadvantage of an alkali-metal salt admixture is even more pronounced now, as alkali levels in cements drift higher and as alkali-aggregate reactions become more prominent.

The first study of commercial calcium nitrite to be published detailed its ability to increase 28-day strength by over 6% for each per cent of calcium nitrite added (by weight of cement), starting with a large increase at the 24 h test. Its acceleration of initial set was more than 2 h at 2% addition, and final set was accelerated by more than 3 h. These accelerations could be controlled by minor amounts of retarder to give set times as long as or longer than unadmixed concrete with due attention paid to timing of admixture addition.

Calcium nitrite is an effective corrosion inhibitor which always improves corrosion resistance, and gives especially good performance at water-cement ratios below 0.5.

2.4.2 Calcium Nitrate:

Recent work indicates that calcium nitrate may have some corrosion inhibiting properties of its own. A good reason for continuing the investigation of calcium nitrate as a corrosion inhibitor is its lower cost. Nitrates do not have the extensive history of corrosion inhibition in concrete that nitrites have. Part of the reasoning behind looking into calcium nitrate is that the electrochemical relation between nitrite and nitrate is so energy-neutral.

$$2NO_3^- + 2H_2O + 4e^- = 2NO_2^- + 4OH^- \quad (2.3)$$

$$E_0 = +0.01V$$

The electrochemical potential strongly favors nitrite oxidation to nitrate

$$2NO_2^- + O_2 = 2NO_3^- \quad E_0 = +0.39\ V \quad (2.4)$$

Its widespread use as an accelerator suggests at least that it is not harmful to concrete (except in very concentrated form). The acceleration in set may be

accompanied by a temporary compressive strength loss at 1 day, but the strength gain is quickly regained. In spite of a superficial chemical resemblance to calcium nitrite, corrosion inhibition by calcium nitrate could occur by an entirely different process, perhaps one dependent more on the improved properties of the concrete. Concrete grade calcium nitrate contains no ammonium nitrate, and is much preferred to the fertilizer grade, which contains more than 8% ammonium nitrate on a dry basis.

2.4.3 Amines and alkanolamines (AMA):

The movement of a AMA-based surface applied inhibitor (SACI or MCI) through the concrete shows the following characteristics:

- When applied, the active agent is absorbed by the substrate by capillary suction.
- The material is then carried along by permeating moisture and is also distributed by its tendency to level out the concentration gradient.
- MCI achieves deep penetration because it is also conveyed in gas form.

This surface-applied organic inhibitors have two parts: volatile part (alkanolamine – main component) and non-volatile part (an acid – secondary compound). When the concrete is very dry, its penetration is quicker by capillary absorption. In carbonated, and chloride-contaminated concrete the AMA had hardly been absorbed by concrete by capillary suction,

but at first remained close to the concrete surface and the aminoalcohol is transported mainly via diffusion into the concrete.

According to some researchers the penetration rate of the AMA inhibitors is about 2–20 mm/day (70 mm depth in 28 days). Also some researchers concluded that there is almost even distribution of the inhibitor within the concrete matrix 28 days after its application. Also the transport rate does not dependent on the transport direction. Thus gravitation does not seem to have a significant influence on the transport properties of the inhibitors. The penetration of AMA depends on w/c, degree of hydration.

2.4.4 Monofluorophosphates (MFP):

Monofluorophosphate is chemically represented as Na_2PO_3F. This compound hydrolyses in aqueous and neutral media to form orthophosphate and fluoride through a process like that indicated in the following equation:

$$Na_2PO_3F + H_2O \leftrightarrows F^- + H_2PO_4^- + HPO_4^{-2} \quad (2.5)$$

The inhibition mechanism of the MFP is not clear, it may be anodic, cathodic or mixed. The inhibiting action of Na_2PO_3F may be attributed to the formation of phosphates, and so the anodic formation of a passive layer of Fe_3O_4, γFe_2O_3 and $FePO_4 . H_2O$.

However, as PO_3F^{2-} , PO_4^{3-} and OH^- are all potential corrosion inhibitors, it is difficult to say which, if any, of these ions may be responsible for corrosion inhibition effects induced by $Na2PO_3F$ *Ngala et al.(2003)*.

The finding of another research study confirms this dual effect of the phosphates: at low values of inhibitor to chloride ion ratio, phosphate (sodium phosphate) acts as a cathodic inhibitor, whereas at higher ratios, it becomes a mixed inhibitor *Dhouibi et al. (2003)*.

2.4.5 Aminoalcohols:

$H_2N\text{-}CH_2\text{-}CH_2\text{-}OH$	$(CH_3)_2N\text{-}CH_2\text{-}CH_2\text{-}OH$
Ethanolamine	Dimethylethanolamine

Aminoalcohols such as ethanolamine and dimethylethanolamine control corrosion by attacking cathodic activity, blocking sites where oxygen picks up electrons and is reduced to hydroxyl ion. They may adsorb at anodic sites as well. One study examined the inhibition effect of a commercially available complex inhibitor containing 15% nitrite and an aminoalcohol on Type 304 stainless steel electrodes immersed in limewater solutions for up to 72 h using a potentiostat (Munteanu and Kinney,2000). A synergistic effect was observed,

combining the effect of nitrite on ferric ion precipitation with the known filmforming properties of hydroxyalkylamines. The corrosion current in the presence of 3% NaCl was reduced at pH 12.67 by a factor of 2.5 and at pH 9.37 by a factor of 5.4. N,N-dimethylethanolamine (DMEA) is used to protect rebar in concrete in commercial corrosion inhibitors. X-ray photoelectron spectroscopy was used to examine steel surfaces which were first cut, polished and oxidized and then immersed in solutions of sodium chloride and DMEA.

CHAPTER 3 LITERATURE REVIEW

Corrosion inhibiting admixtures has been used in the industry since 1970s. Many chemical have been investigated in the past for use as concrete corrosion inhibitor. Some showed promise as an inhibitor, but had detrimental effects on certain concrete properties or were expensive. The "ideal" corrosion inhibitor system would prevent the initiation of corrosion for the service life of the structure. To date, only a few corrosion inhibitor exist that do not have adverse effects on concrete properties and delay corrosion initiation. The research is generally on the effectiveness of migratory type corrosion inhibitors on corrosion initiation, mechanism of action and its effect on mechanical properties of concrete. The following section discusses the observation by various researchers.

Soylev et al. (2007) studied the effect of two amino alcohol based surface applied corrosion inhibitor (SACI) on the initiation and propagation stages of corrosion in chloride environment. Concrete prisms of size 280×280×75 mm, which were reinforced by two horizontally placed and fixed reinforcing bars were used for corrosion testing. The concrete cover was 18 mm. The cement used was an Irish Portland cement. The inhibitors used were two new-generation amino alcohol-based surface-applied organic corrosion inhibitors. For Group 1 specimens, chloride cycles involve four-day ponding (70 g/l NaCl solution) followed by three-day air drying in the laboratory. Both of the inhibitors were applied in the same way, on the ponding-surface by a brush as recommended by its manufacturer and at the recommended dosage (500 g/m^2). The inhibitors were applied: a) before chloride application, b) after first chloride cycle, and their effect on corrosion were compared to control samples. The specimens are named accordingly as ORG1a, ORG1b, ORG2a and ORG2b. Group 2 specimens consist of control, ORG1 and ORG2 specimens exposed only to one ponding cycle but a higher concentration (5MNaCl solution). For this group of specimens, the inhibitor was applied after the chloride ponding and the results are compared with control specimens until the end of the testing period without adding any other chloride. The specimens were wetted before corrosion measurement to obtain lower resistivity for concrete during the measurement.

After the chloride application, there was a sharp drop in E_{CORR} values for all specimens, varying between approx. −350 and −395 mV. The E_{CORR} value of the control specimens decreased gradually with increasing chloride ponding cycles from −393 mV up to −522 mV,

and fluctuated between approx. −500 mV and −420 mV. The higher E_{CORR} was measured for ORG2b specimens, remaining almost stable at first cycles and then increasing despite increasing chloride ponding cycles. ORG1(a,b) specimens displayed lower (more negative) Ecorr, the drop for ORG1b being slightly lower. However, there is no significant difference between ORG1(a,b) and control specimens. I_{CORR} of control continued a sharp increase from 1.14 to 2.69 μA/cm^2 and fluctuated between 2.69 μA/cm^2 and 1.59 μA/cm^2. ORG2(a,b) specimens, which had the highest E_{CORR} (less negative) had the lowest I_{CORR} values. I_{CORR} of ORG2a decreased from 1.17 to 0.90 μA/cm^2 after the first sharp increase and remained stable around this value. ORG2b had very similar behaviour and the values are very close to those of ORG2a. The I_{CORR} values for ORG1(a,b) are not very different from the control as in the case of E_{CORR}. Fig. 3.1 and Fig. 3.2 shows the results of E_{CORR}, I_{CORR}.

It was found that the new-generation amino alcohol-based inhibitor was effective against corrosion when it is applied before the chloride application or just after the first chloride ponding cycle. It kept the I_{CORR} at 1 μA/cm^2, which can be accepted as a threshold value for corrosion initiation, despite high chloride content at the level of the embedded steel. It was also found that once concrete is contaminated with chloride and when the inhibitor was applied after a high corrosion rate (2 μA/cm^2) both of the inhibitors are ineffective. The new-generation amino alcohol-based inhibitor appeared to be a good repair strategy when it is applied before the initiation of corrosion or the corrosion rate is relatively low.

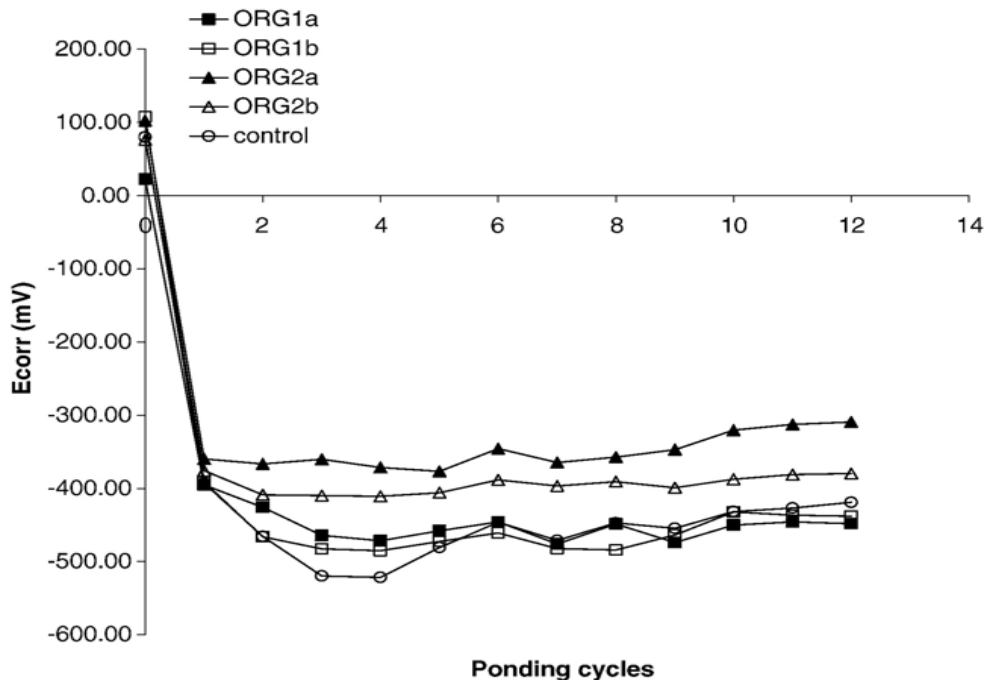

Fig. 3.1. Corrosion potential–time curves for Group 1 specimen *(Soylev et al., 2007)*

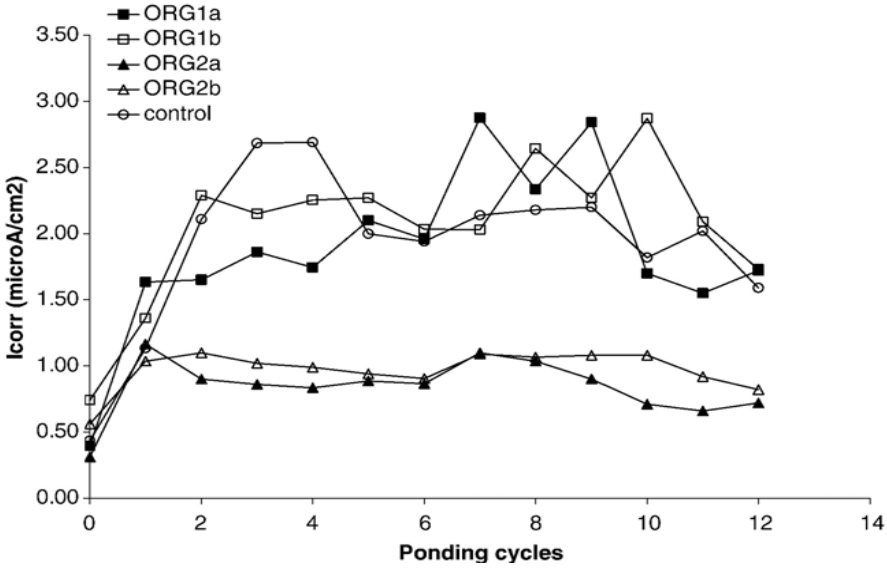

Fig. 3.2. Corrosion current density–time curves for Group 1 specimens *(Soylev et al., 2007)*

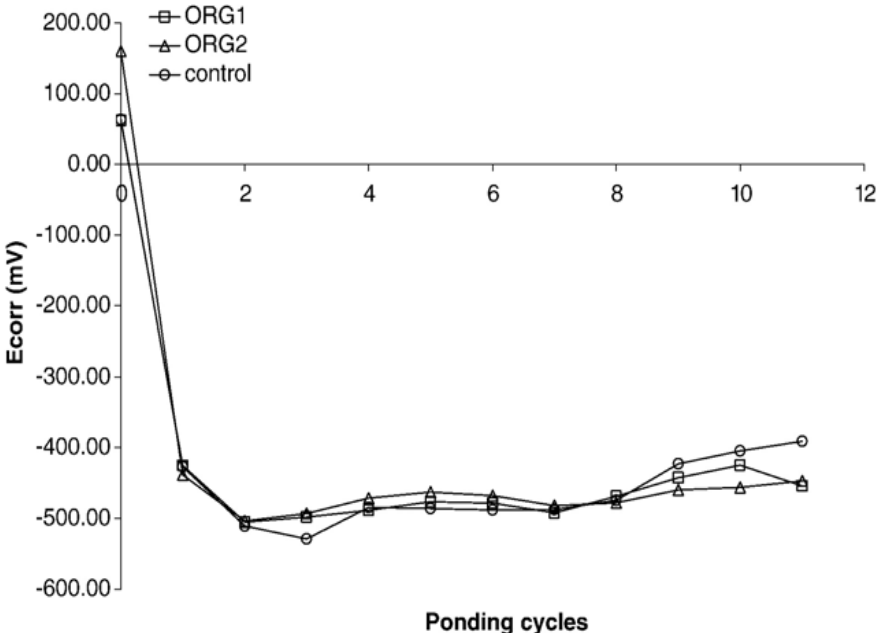

Fig. 3.3. Corrosion potential–time curves for Group 2 Specimens *(Soylev et al., 2007)*

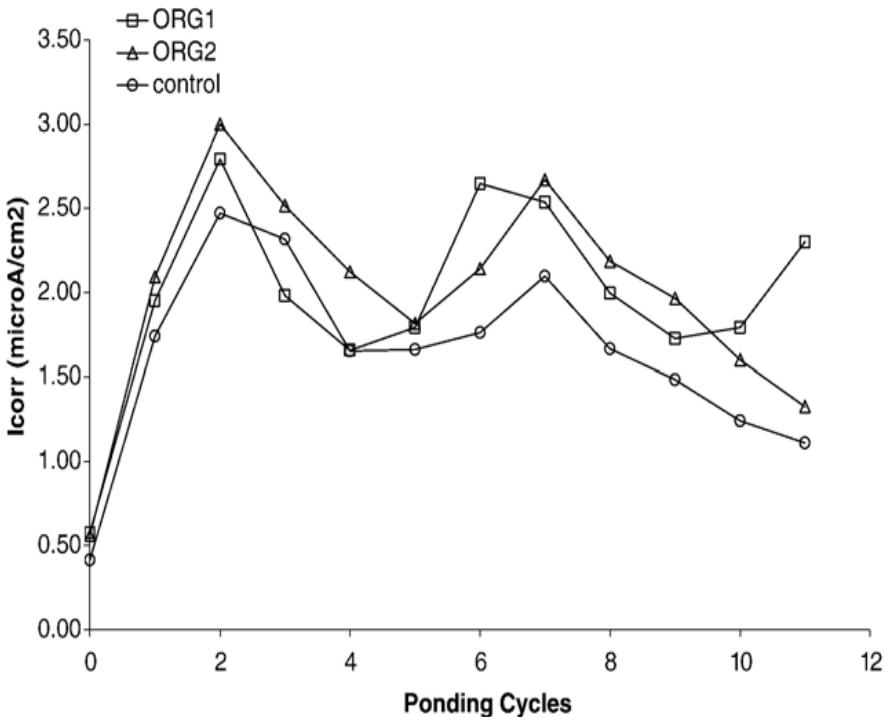

Fig.3.4. Corrosion current density–time curves for Group 2 specimens *(Soylev et al., 2007)*

Soylev et al. (2007) investigated the influence of organic surface applied corrosion inhibitor on common mechanical properties and durability properties after its application on the hardened concrete surface: The study included the influence on compressive strength, tensile strength, steel–concrete bond strength, permeability, drying shrinkage, freeze–thaw resistance. The emphasis was given to the permeability as the pore-blocking effect by the inhibitors as this property is prone to affect the other properties. For each test programme two concrete mixes (A & B) were used. The Amino alcohol based corrosion inhibitors were applied on the concrete surfaces 42 days after casting and the inhibitor-applied specimens were compared with control samples.

Compressive strength : The samples were tested before the inhibitor application at the end of curing period and after 14 days in controlled environment (20 ^{0}C and 70%) and 7, 28, 49 and 70 days after inhibitor application. Three cubes were tested at each test-age (3 control + 3 inhibitor-applied concrete). It was found that the inhibitors do not have any effect on the strength and strength development. AMA or amine-based inhibitors did not have any deleterious effect on compressive strength. Compressive strength values for mix A and mix B specimens are shown in Figs.3.5 and 3.6

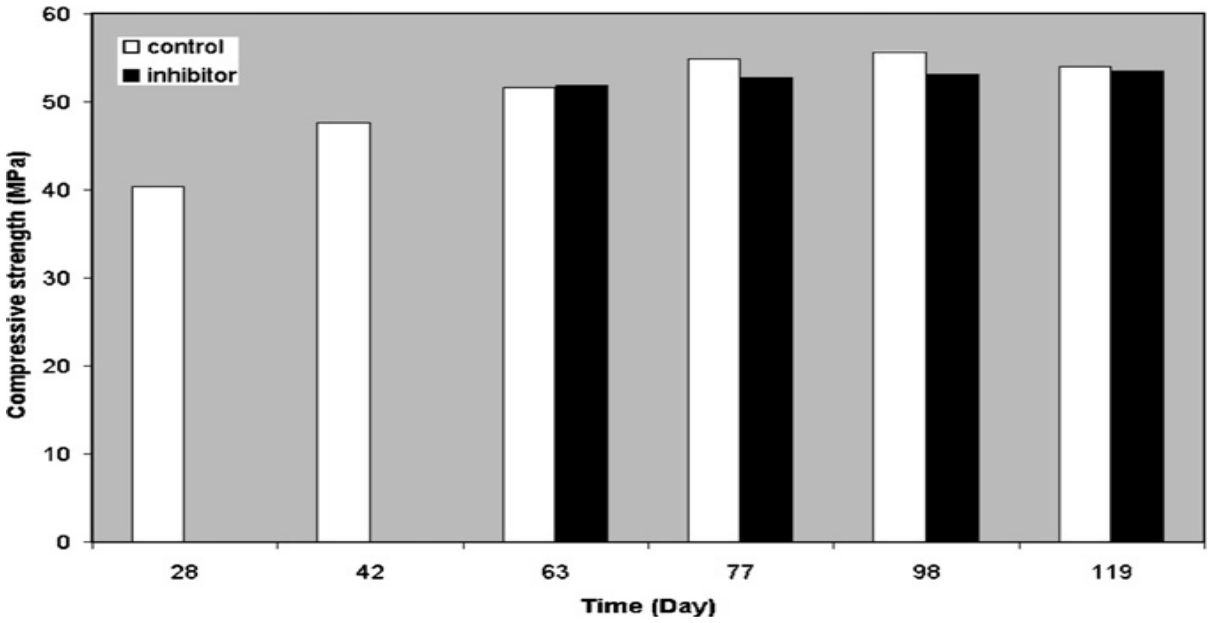

Fig. 3.5. Compressive strength of mix A specimens. ***(Soylev et al., 2007)***

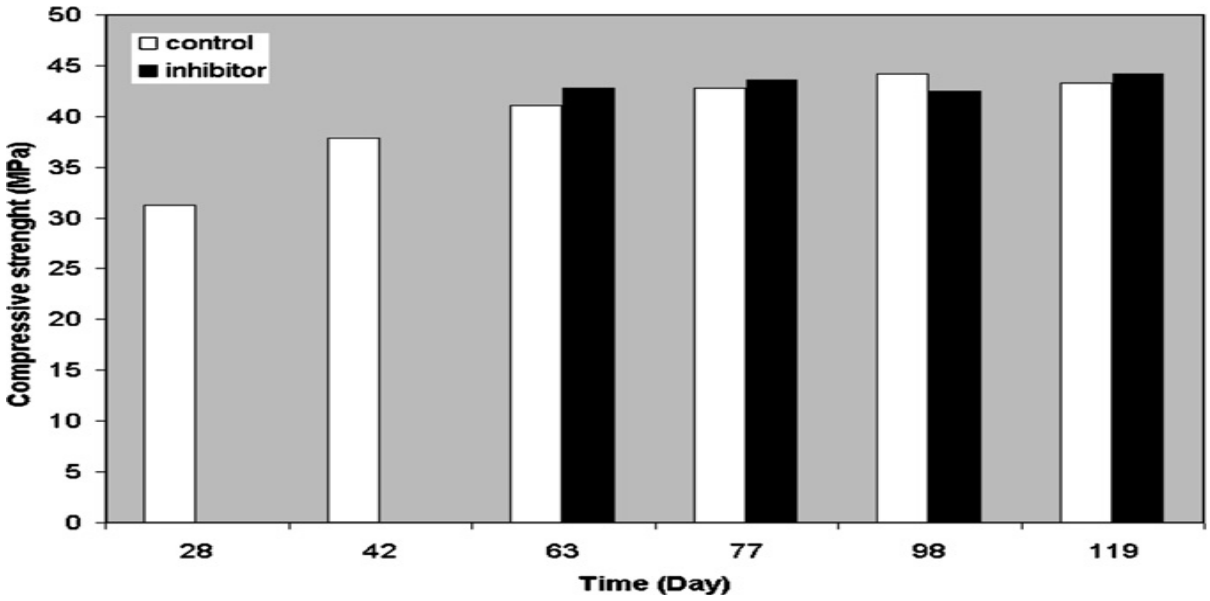

Fig. 3.6. Compressive strength of mix B specimens. ***(Soylev et al., 2007)***

Tensile strength : Similar trend was observed for the tensile strength of concrete.

Steel–concrete bond strength: Pull-out specimens were prepared (only mix A) as 200 mm cubes with 20 mm diameter either ribbed or plain steel bar at the centre of the cube. The pull-out tests were performed at 70 days after inhibitor application. They concluded that Pull-out resistance results were not affected by the use of the inhibitor. However, it was very difficult

to comment on the ribbed bar results due to the high scatter. The scatter with pull-out test was expected as the resistance of these type of bars are obtained by mechanical interlocking rather than the adhesion between concrete and steel. The results for pull-out tests with plain and ribbed bars are shown in Fig.3.7 and Fig. 3.8.

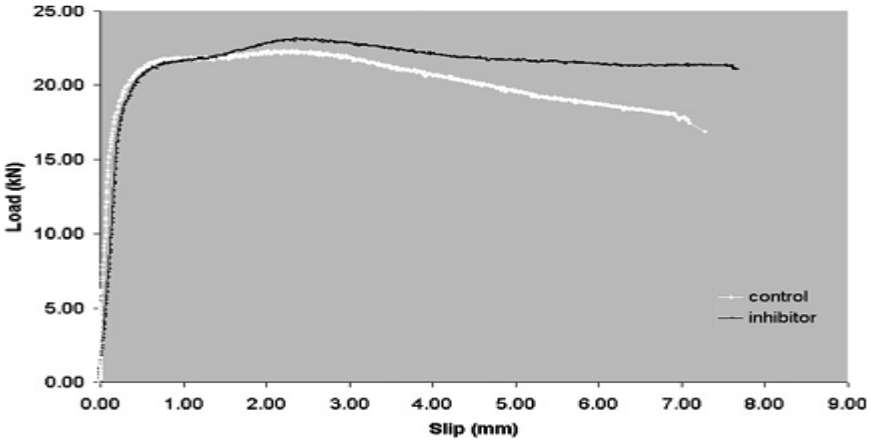

Fig. 3.7. Pull-out resistance of the plain bars. ***(Soylev et al., 2007)***

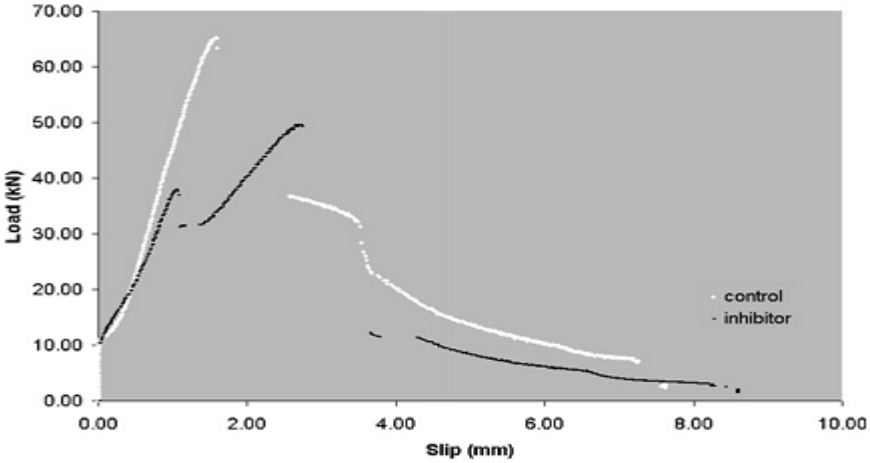

Fig. 3.8. Pull-out resistance of the ribbed bars. ***(Soylev et al., 2007)***

Permeability: The Initial surface absorption test (ISAT) results showed more clearly the effect of the inhibitor on concrete permeability for both mixes (Fig.3.9)). For mix B, the average of the 10 min-absorption values were approximately one third for inhibitor-applied specimens. For mix A, the difference between inhibitor-applied (lower absorption) and control specimens was more than double and decreasing with time as expected. It was concluded that the application of corrosion inhibitor lowered the permeability of all mixes.

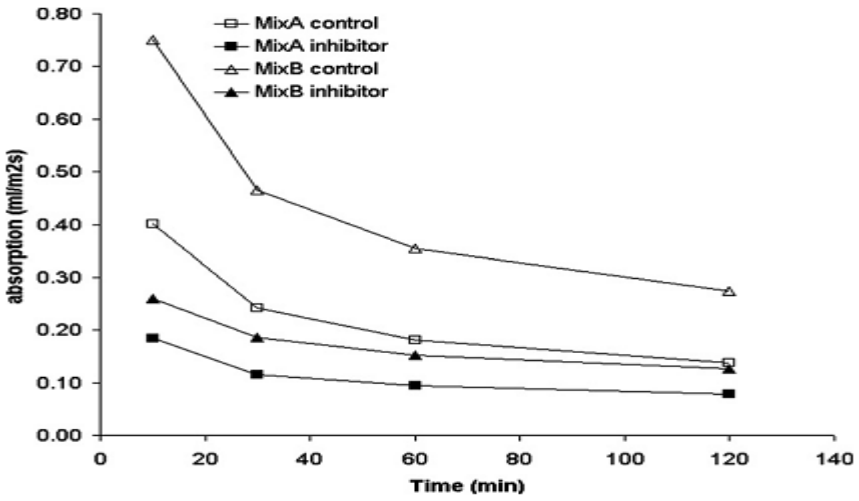

Fig. 3.9. Initial surface absorption of mix A and mix B specimens. ***(Soylev et al., 2007)***

Freeze–thaw surface scaling resistance : The freeze–thaw surface scaling resistance results are shown in Fig. 3.10. A very significant (five to six times) difference was found for both mix A and mix B: for the inhibitor applied specimens the freeze–thaw resistance increased significantly. This result can be interpreted by the pore-blocking effect, which does not allow the water to fill the pore of the concrete with freezable water. Surface-applied AMA-based inhibitors were found to increase concrete freeze–thaw scaling resistance.

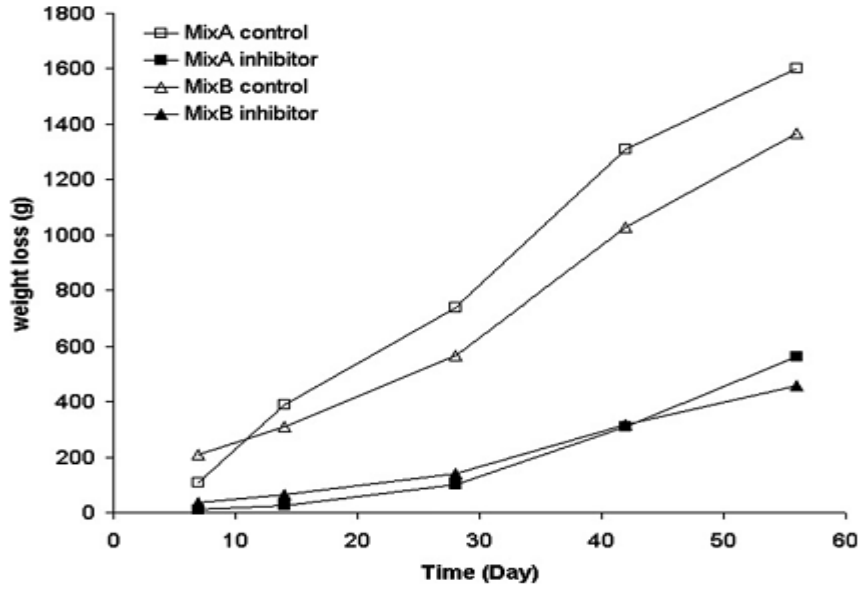

Fig. 3.10 Freeze–thaw surface scaling resistance of mix A and mix B specimens. ***(Soylev et al., 2007)***

Heiyantuduwa et al. (2006) studied the performance of an organic, penetrating corrosion inhibitor in reducing the rate of corrosion and delaying the onset of corrosion in carbonated concrete. The objective was to improve understanding of the use of such materials, as well as limitations in this approach. The 30 MPa concrete mix was selected for corrosion test specimens, since it was most typical of structural concrete and was well penetrated by the corrosion inhibitor. Concrete test specimens were blocks of size 120 mm×120 mm×380 mm, with each specimen containing a 16 mm high tensile ribbed steel reinforcing bar longitudinally at the center, at nominal covers of 10 or 20 mm. Twelve concrete blocks were cast using the Grade 30 CEM I mix, six blocks for each reinforcement cover depth(i.e., 10 or 20 mm cover). Each group of six had two control specimens, two specimens that were treated with the penetrating inhibitor before the carbonation process (BC), and two specimens that were treated with the penetrating inhibitor after the carbonation process (AC).

The corrosion inhibitor was applied to BC and AC specimens by brush at a rate of 0.1 L/m^2 on each of the test specimens over three consecutive days, to give a total of 0.3 L/m^2. The inhibitor used was a mixed water-based impregnation for reinforced concrete, incorporating an organic film-forming amino compound (amino alcohol) and an inorganic component (*Burge 1997*). Each coat of the penetrating inhibitor was allowed to dry for 24 h before application of the next coat. Twenty-four hours after the application of the final coat the concrete surface was wetted with tap water, this procedure being repeated for two consecutive days. The application of water saturated the surface layer of the concrete, thereby aiding the penetration of the inhibitor through diffusion and preventing evaporation of the inhibitor from the surface.

For AC specimens accelerated carbonation was done using a chamber maintained at 10% carbon dioxide, 30^0C, and a relative humidity of 85 ± 5%. Twelve corrosion test specimens and concrete cubes were placed in the carbonation chamber for accelerated carbonation 56 days after casting (28 days after treatment for BC specimens). Specimens were kept in the chamber until sufficient carbonation had occurred to activate corrosion (roughly two or four months for 10 and 20 mm cover, respectively.

In the 10 mm cover specimens, controls with no inhibitor maintained the highest corrosion rates (and the most negative potentials). Average measured corrosion rates in this case ranged from about 0.1 to 0.9 $\mu A/cm^2$ corresponding to active corrosion. Average corrosion rates of the blocks where the inhibitor was applied before the carbonation process and after the carbonation process, showed much lower values in comparison with the con-

trol samples: the ranges were between 0.05 and 0.4 μA/cm^2, and 0.07 and 0.4 μA/cm^2, respectively. Trends similar to those in the 10 mm cover specimens were also displayed in the 20 mm cover specimens. Average corrosion rates for these specimens ranged from about 0.1–0.5 μA/cm^2. Corrosion rates of the samples that were treated with the inhibitor before carbonation and after carbonation showed much lower corrosion rates of between 0.09 and 0.02 μA/cm^2 and 0.1 and 0.22 μA/cm^2 for BC and AC, respectively. Results indicate that penetrating corrosion inhibitors can be effective, when applied to the surface of existing or new structures, in extending the useful life of reinforced concrete exposed to carbonation.

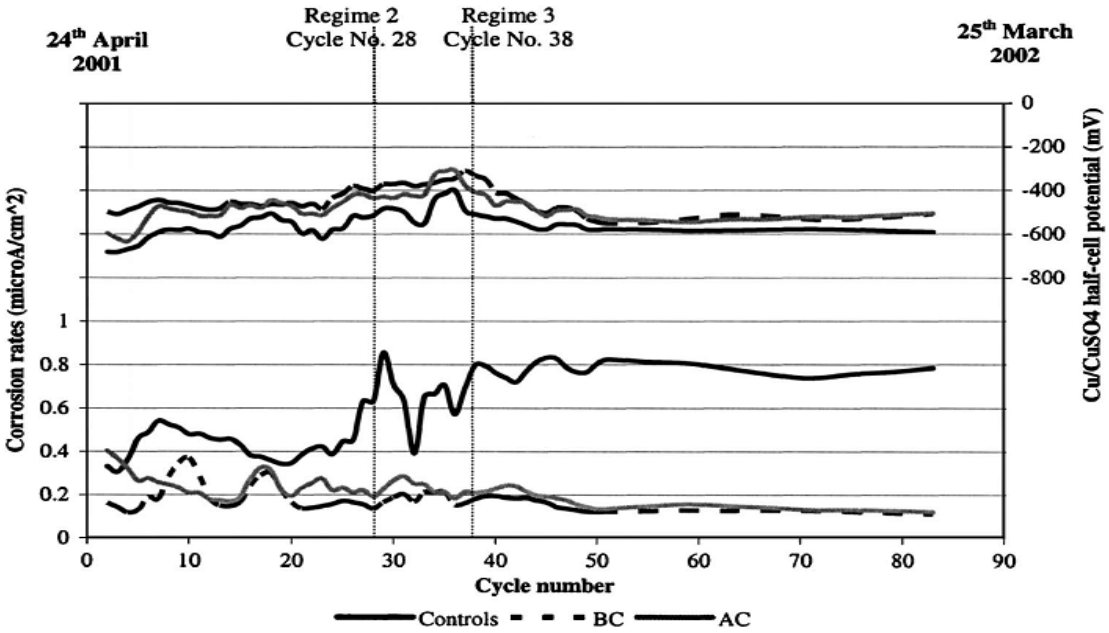

Fig. 3.11. Corrosion rates and half-cell potentials for 10 mm cover samples.
(Heiyantuduwa et al., 2006)

Malik et al. (2004) studied on the performance of migratory corrosion inhibitors in protection of rebar concrete in Gulf seawater environment. The results of a study concerning with the corrosion behavior of reinforced concrete in presence of MCI in marine environment have been described. Corrosion inhibitors MCI-A and MCI-B and volatile corrosion inhibitor VCI-C were used during the experiments. MCI-A and MCI-B were dimethyl ethanol amine and triethanol amine based inhibitors, respectively, VCI-C was tolyltriazole based vapor based inhibitor. Concrete mixes were prepared using OPC cement with and without inhibitor coating. The inhibitors MCI-A and MCI-B (in liquid form) were applied as a coat on the concrete sample using a brush. Another inhibitor, belonging to vapor phase type, VCI-C was

used as a coating on a group of rebars in concrete casting of a number of specimens. The electrochemical parameters including polarization resistance (R_P), corrosion current (I_{CORR}), CR, Tafel-C, Tafel-A and corrosion potential (E_{CORR}) were computed.

The immersion tests were of 26 months duration. Fig.3.12 shows plots of time vs. corrosion parameters (CR, I_{CORR} and R_P) for uncoated (control) specimens immersed in seawater. The corrosion current, I_{CORR} increases with time till a maxima is observed at 9.3 months then there is a decrease in current value till 17.4 months when a minima is obtained, the current again increases up to 22.9 months when it drops down sharply up to 26 months. The alternate cycles of increase and decrease in corrosion current values can be attributed to breaking up of the protective film on rebar followed by passivation and then again depassivation due to the permeation of chloride through the pores of the concrete. Considering the electrochemical behavior of MCI-A coated concrete specimens when compared to the control ones, i.e., un-coated; the CR and I_{CORR} show identical behavior (Fig. 3.13) and R_P shows quite opposite behavior.

Fig. 3.14 shows comparison of the corrosion rates of concrete under different coatings immersed in seawater for various periods of time. It was observed that :

(1) There is an irregular relationship between corrosion rate and immersion time for uncoated and coated specimens in seawater.

(2) Corrosion rates of coated specimens are always lower than uncoated one (control).

(3) MCI-B has always higher corrosion rate and corrosion current density than MCI-A in seawater.

(4) Although the coating of VCI-C on rebar decreases the corrosion rates but it is not much effective while comparing to MCI-A and MCI-B.

Fig. 3.15 represents bar diagrams for CR of uncoated and coated concrete samples in 5% NaCl at different time intervals. The diagram shows that whilst the corrosion rate of concrete are decreased on addition of MCI-A, the addition of MCI-B increases the corrosion rate considerably indicating the negative effect of MCI-B inhibitor. The presence of VCI-C rebar in concrete enhances the corrosion rate but the corrosion rate is slightly lower than MCI-B coated concrete specimen.

Fig. 3.16 shows plots of immersion time vs. Open circuit potential (OCP) for coated and uncoated concrete samples in seawater. It was found that the negative potential increases

steeply in the first 6 months then it becomes almost constant with variation within ±50 mV. MCI-A coated specimen exhibits more positive OCP values than MCI-B and controlled samples. The controlled sample appears to be more noble than MCI-B sample.

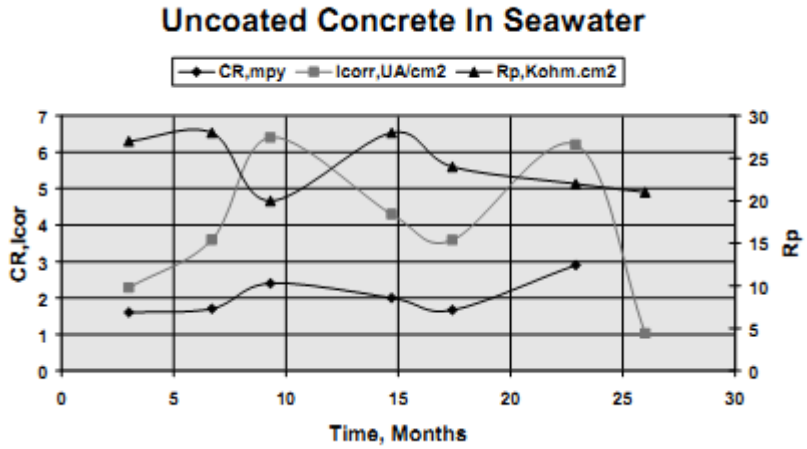

Fig. 3.12. Time vs. CR, Icorr and Rp plot for uncoated (controlled) samples in seawater. ***(Malik et al., 2004)***

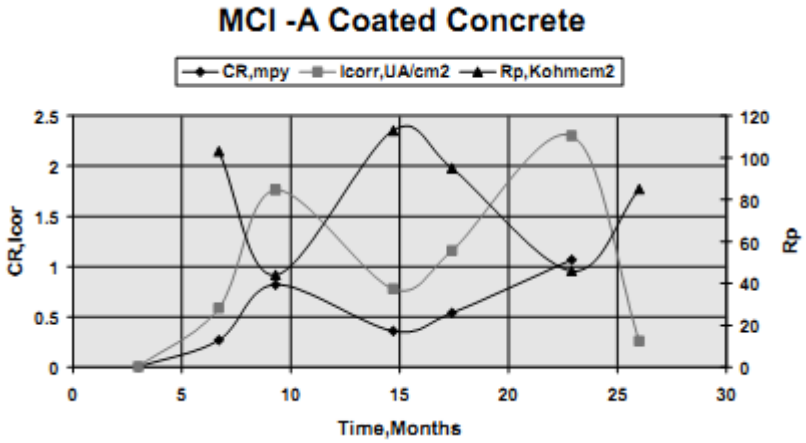

Fig. 3.13. Time vs. CR, Icorr and Rp plot for uncoated (controlled) samples in seawater. ***(Malik et al., 2004)***

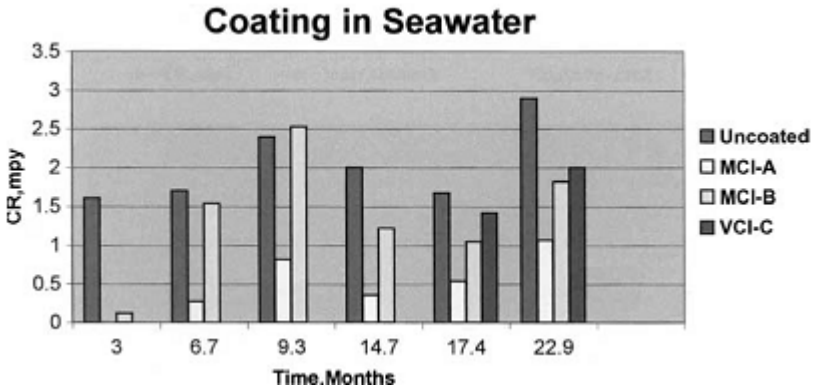

Fig. 3.14. Bar diagram representing CR for different coatings immersed in seawater for various periods of time. ***(Malik et al., 2004)***

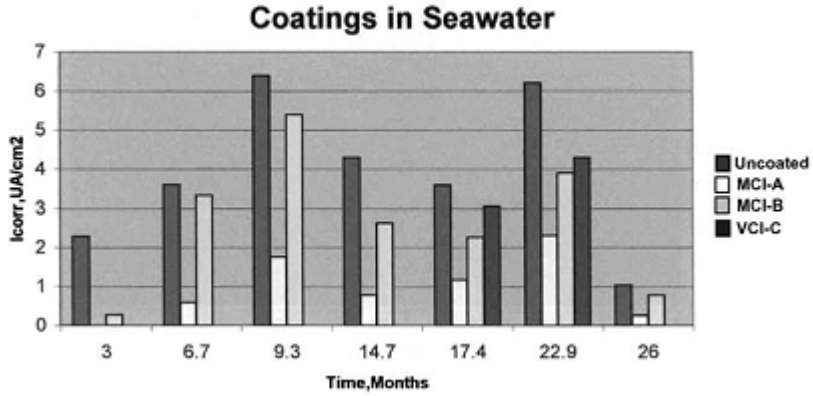

Fig. 3.15. Bar diagram representing Icorr for different coatings immersed in seawater for various periods of time. ***(Malik et al., 2004)***

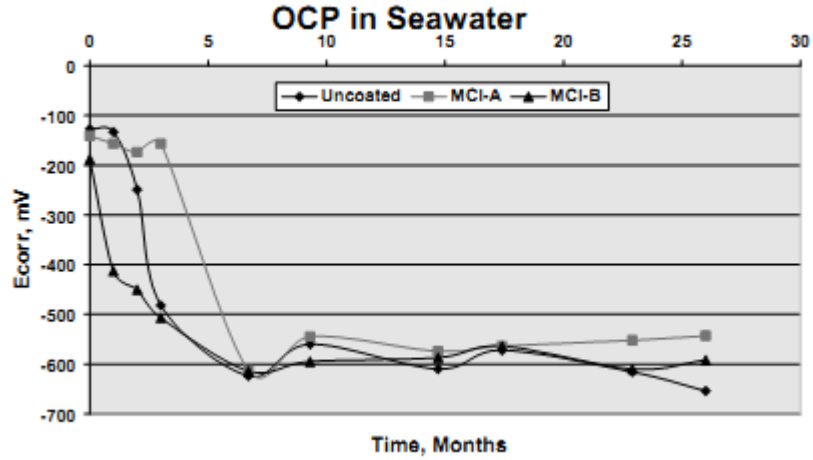

Fig. 3.16. OCP vs. immersion time plot for uncoated and coated concretesamples in seawater. ***(Malik et al., 2004)***

Chaussadent et al. (2005) studied effectiveness conditions of sodium monofluorophosphate as a corrosion inhibitor for concrete reinforcements and focuses on the knowledge of MFP, in particular in terms of its potential penetration into concrete materials. Cylindrical mortar specimens (35 mm diameter and 40 mm long) containing a centred mild steel (6 mm diameter) were cast with ordinary Portland cement. Cement paste specimens were also produced using Portland cement and a water-cement ratio of 0.5. All specimens were wrapped in an adhesive aluminium sheet, in order to reduce moisture loss, and then conserved one year at 20^0C before the experimental campaign.

MFP penetration profiles in carbonated or non-carbonated hardened cement pastes were determined. These profiles were obtained 7 and 28 days after application of MFP aqueous solution on the surface of cement paste specimens. A 5-mL volume of an aqueous MFP solution (20% by mass) was applied to one of the surfaces perpendicular to the axis of cylindrical cement paste specimens (3 cm diameter, 6 cm high), either carbonated or not.

The MFP penetration profiles in hardened cement pastes, both carbonated and not, are shown in Fig. 3.17. In the non-carbonated cement pastes, the MFP remains mainly within the first centimetre from the surface of application. It was observed that MFP penetration has been slowed due to the fact that this compound reacted with portlandite to form fluoroapatite. However, MFP at low content levels (only 0% to 10% of MFP applied) was found at greater depths as a result of initial capillary penetration. In carbonated cement pastes, MFP was distributed uniformly throughout the depth. The presence of $CaCO_3$ (instead of $Ca(OH)_2$) has made it possible for MFP to penetrate, with no interaction being observed between calcite and MFP.

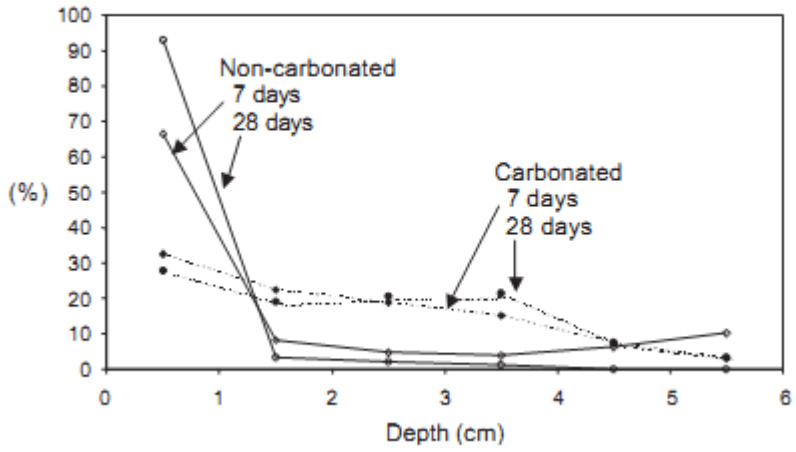

Fig. 3.17. MFP penetration profiles (determined MFP / total applied MFP in %) in carbonated or not carbonated hardened cement pastes. ***(Chaussadent et al., 2005)***

The monitoring of steel corrosion potential in the mortar specimens was performed upon application of the MFP solution for a period of 48 h. Fig. 3.18. showed that potential was constant over a certain time and then a rapid decrease (100 to 150 mV SCE) appeared. At the end of this decrease, the potential once again remained constant. No effect ascribable to the action of MFP was observed on the steel corrosion, although the inhibitor was found quite near to the steel surface (2% to 9% of the applied MFP was identified after total dissolution of the mortar in nitric acid). This finding was simply due to the absence of free MFP ions, resulting from their reactivity with portlandite in a non-carbonated mortar.

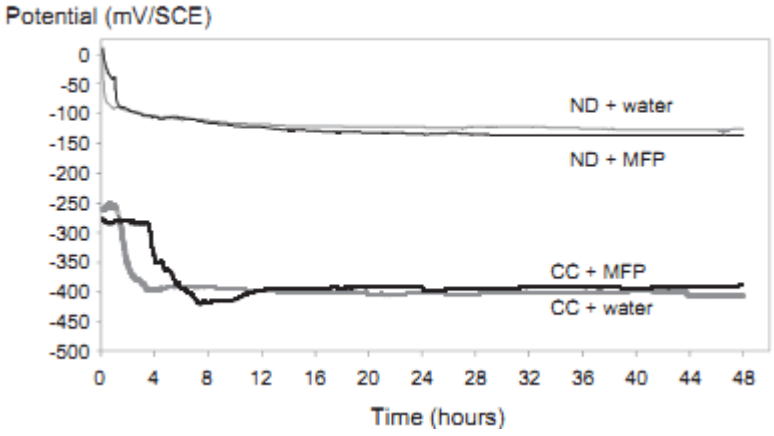

Fig. 3.18. Evolution of the steel corrosion potential after applying MFP solution or water onto reinforced mortar surface (non-carbonated mortars) (ND: non-degraded – CC: chloride contaminated). ***(Chaussadent et al., 2005)***

Bavarian et al. (2002) studied the effectiveness of two commercially available migrating corrosion inhibitors (MCI 2021 and 2022) for steel rebar in concrete and the results compared with untreated concrete. The objective of this investigation was to study the corrosion inhibition of commercially available migrating corrosion inhibitors on steel rebar in three concrete densities. Theoretically, high density concrete impedes corrosive species from reaching the surface of the rebar. It may also prevent the inhibitor from reaching the surface of the concrete. Concrete samples with dimensions 8” x 4” x 4” were prepared, and their densities were adjusted to achieve 130, 140, and 150 lb/ft3. Each sample consisted of one 8 inch steel (class 60) rebar (1/2” diameter) and one 8-inch Inconel metal strip (counter electrode). The rebar prior to being placed in concrete were exposed to 100% RH (relative humidity) to initiate corrosion. MCI 2022 and MCI 2021 were applied to all but two of the concrete samples (used as a control). The samples were then immersed in 3.5 % NaCl solution (roughly 7 inches of each sample was immersed in the solution continuously). EIS

(Electrochemical AC Impedance Spectroscopy) testing started 24 hours after immersing the samples.

Throughout this investigation, changes in the resistance polarization and the corrosion potential of the rebar were monitored to determine the degree of effectiveness for Cortec MCI 2021 & 2022 products. Figure 1 shows that corrosion potentials for all of the high density samples (HD2022-1, HD2022-2, HD untreated, HD2021-1, HD2021-2) were between the range of -400 mV to -600 mV after 128 days of immersion in NaCl. For the untreated control sample (L untreated), the corrosion potential was –295 mV at the end of testing. The corrosion potentials for MCI treated concrete samples (L2022-1, L2022-2, L2021-1) were between –120 to -145 mV. One of the samples (L2021-2) treated with MCI 2021 had a corrosion potential of -350 mV. They concluded that the low density samples had significantly higher corrosion potentials, which translates to a greater likelihood of corrosion protection.

It was found that MCI treated concrete samples are increasing in their R_P (resistance polarization) values compared with the control samples that seem to have a decreasing trend. The high density concrete samples results were an exception. They showed rapid chemical deterioration; the MCI product did not have any effect on them. The resistance polarization values at the end of testing were between 13,000 and 22,000 ohms for the low density concrete samples with MCI. The high density concrete showed much less corrosion inhibition with R_P values in the 1000 to 2000 ohm range. For non-treated samples (controls), the R_P value ended at 3170 ohms for low density samples and 1200 ohms for high density concrete. Changes in the R_P value were not immediately observed, indicating that corrosive species and/or Migrating Corrosion Inhibitors (MCIs) require an induction period for diffusion into the concrete.

Jamil et al. (2005) studied Corrosion behaviour of reinforcing steel exposed to an amino alcohol based corrosion inhibitor. The ability of an amino alcohol-based inhibitor to penetrate through mortar specimens and at assessing the corrosion behaviour of steel samples immersed in chloride contaminated solutions is investigated. Two different electrochemical cells were used to study the penetration of the inhibitor into mortar. The mortar disks were prepared using a mixture of cement, water and sand. The water/cement ratio was 0.6. The amount of sand was three times that of cement. The mortar disks were then cured for 3 days in a high humidity environment (100% relative humidity) at room temperature.

Fig. 3.19. shows the evolution of open circuit potential of steel samples in solutions with and without inhibitor addition. It was found that the potential evolution is different in the presence and in the absence of inhibitor. The potential values for the system without inhibitor decreases with time and stabilises around -300 mV (SCE) after approximately 24h of immersion. In the presence of inhibitor the potential also shows some fluctuations during the first 24h, but thereafter it slowly increases with time, reaching values around -160 mV (SCE). The number and amplitude of the potential fluctuations is much lower than that observed in the absence of inhibitor.

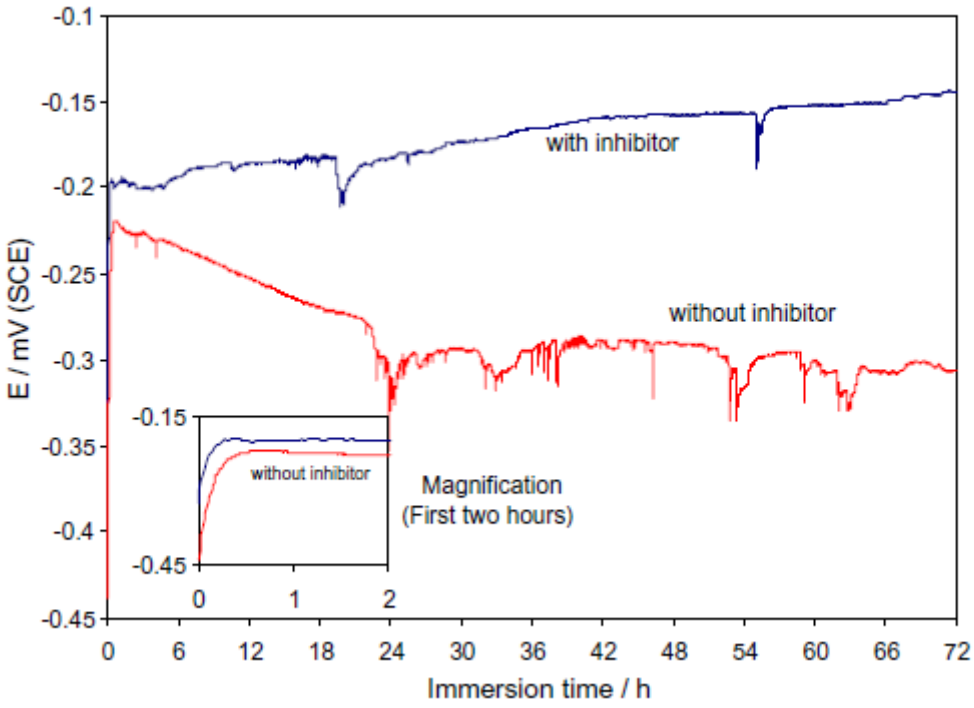

Fig. 3.19. Open circuit potential for the systems with and without inhibitor. ***(Jamil et al., 2005)***

The evolution of the charge transfer resistance, which is an indicator of the corrosion rate, was also determined for the different systems as shown in Fig. 3.20. In the absence of inhibitor the charge transfer resistance increased during the first day of immersion, but later on it started to decrease as expected due to passive film breakdown induced by the chloride ions.

Andrade et al. found that after 48h of immersion the charge transfer resistance is around 20000 ohmcm^2, corresponding to a corrosion rate above 1μA/cm^2, which can be considered critical. However in the presence of inhibitor, the charge transfer resistance increased

gradually and consequently the corrosion rate decreases by more than one order of magnitude, attaining values around 0.1μA/cm^2. When the inhibitor is applied by spray the initial values of the charge transfer resistance are identical to those calculated in the absence of inhibitor. after 72h of exposure the charge transfer resistance starts to increase, revealing a decrease in the corrosion rate.

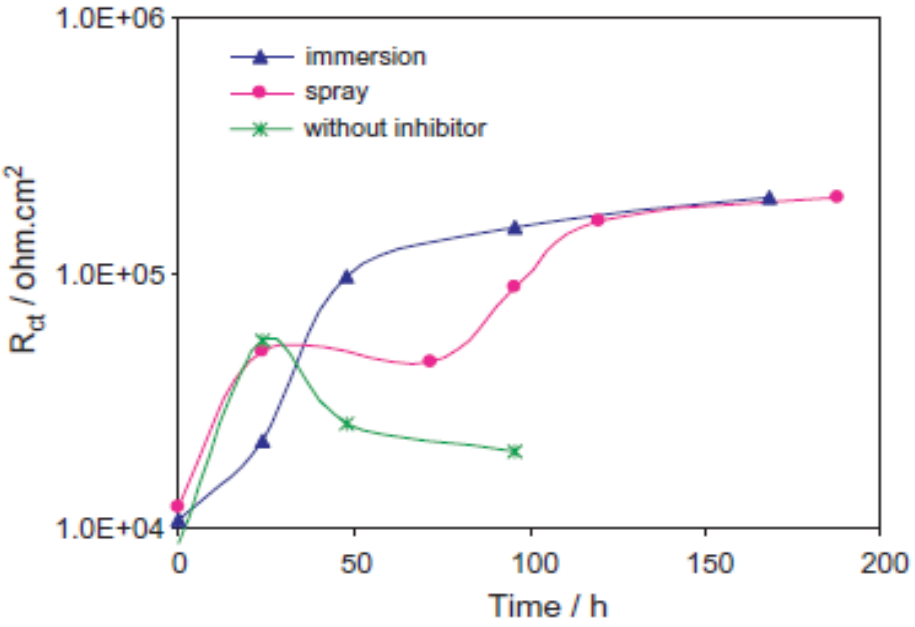

Fig. 3.20. Charge transfer resistance for steel samples. Different application procedure using mortar specimens with 1cm. ***(Jamil et al., 2005)***

Limaye et al. (2000) presents experimental studies on a new generation of corrosion inhibitor, which is based on bipolar mechanism and which can penetrate even dense concrete by virtue of its vapour pressure and affinity for the embedded steel in concrete. The inhibitor is used both as an admixture in fresh concrete and as a coating on hardened concrete. The concrete specimens chosen were of two types: weak and strong grades namely mix 8 (Fc : 12 N/mm^2) and mix 4 (Fc : 30 N/mm^2). Tests on fresh and hardened concrete were carried out first to rule out any deleterious effect of corrosion inhibiting admixture. Further electrochemical tests were carried out to assess their effectiveness in corrosion protection.

There was no significant variation in the values of initial as well as final setting time with or without corrosion inhibiting admixture. Mixes were chosen with the criteria that they have the same workability; but when corrosion inhibitor in the form of admixture was used, it did not change the workability either. No accelerating or retarding effect was observed. it was

observed that the admixture does not exhibit any adverse effect on compressive strength. On the contrary, it shows slight increase in the compressive strength values. Due to corrosion of rebar; bond strength is affected most and hence performance of RC. From Tables 3.1 and 3.2 it is seen that bond strength of control specimens was reduced to 10-15 percent of original strength after corrosion tests. This is a clear indication of a bond failure. It is however restricted between 40-50 percent in the corrosion inhibitor admixtured samples. The potentials were measured at the interval of 150 hours. From this electrochemical study it was evident that the coulombs consumed in corrosion inhibitor admixture sample was 60 percent in both weak and strong concrete as compared to control. However, in the coated specimens it was between 68 to 70 percent.

The application of penetrating corrosion inhibitor coating has reduced the corrosion rate, though it is less as compared to the one containing corrosion inhibiting admixture. However, it is significant to note that there is certainly migration of inhibitor to steel since it is reflected in reduction of coulombs and increase in bond strength

Table 3.1: Electrochemical and pull out test results. ***(Limaye et al., 2000)***

Specimen	Pull out force required initial, N	Coulombs consumed, mA-hrs	Pull out force required final, N
Mx-8/P	5600.20	6628	846.80
Mx-8/C	5600.20	4820	1648.09
Mx-8/A	5860.00	4226	2008.80
Mx-4/P	8900.00	2640	5110.00
Mx-4/C	8900.00	1608	6345.17
Mx-4/A	9233.33	1333	7020.23

Notes:

i. Samples cured for 28 days and connected in circuit

ii. Mx-8: Fc = 12 N/mm^2 , Mx-4: Fc = 30 N/mm^2

iii. P – Plain mix, A – Mix with corrosion inhibiting admixture, C- Plain mix with corrosion inhibiting coating

iv. Initial – before the electrochemical tests started

v. Final – at the end of electrochemical tests

Table 3.2: Electrochemical and pull out test results. ***(Limaye et al., 2000)***

Specimen	Pull out force required Initial, N	Coulombs consumed, mA-hrs	Pull out force required Final, N
Mx-8/P	5610.00	6872	588.00
Mx-8/C	5884.13	5182	1469.00
Mx-8/A	5884.13	4420	2104.20
Mx-4/P	8980.20	2824	4840.00
Mx-4/C	8980.20	1820	6405.30
Mx-4/A	9242.33	1530	7156.33

Morris et al. (2002) studied a migrating corrosion inhibitor evaluated in concrete containing various contents of admixed chlorides. The performance of a surface-applied migrating corrosion inhibitor based on an alkyl-aminoalcohol on concrete specimens containing rebar segments was investigated. Two blank specimens (with no inhibitor) and two treated with the inhibitor were exposed to a so-called ‘‘marine’’ environment. These specimens were placed in a metallic cage located at the top terrace of a forty-floor building. Fig. 3.21a and b shows the variation of the rebar corrosion potential in time for the specimens (blank and treated with inhibitor) exposed to the marine environment. The blank and the treated specimens showed no significant difference between the rebar corrosion potential trends obtained on each of the three mixes containing admixed chlorides (A, B and C). The difference in the rebar corrosion potential trend of mix D (w/c = 0.6 and no admixed chlorides) became evident after approximately 400 days of exposure. After this period, the E_{CORR} values of the blank specimens start shifting towards more negative potentials. On the other hand, the rebar corrosion potential values of the treated specimens show an increasing trend in time, reaching values characteristic of passive steel. Therefore, even when blank and treated specimens present similar chloride concentrations at the rebar surface, the presence of the inhibitor in mix DI seems to maintain the passive state of steel.

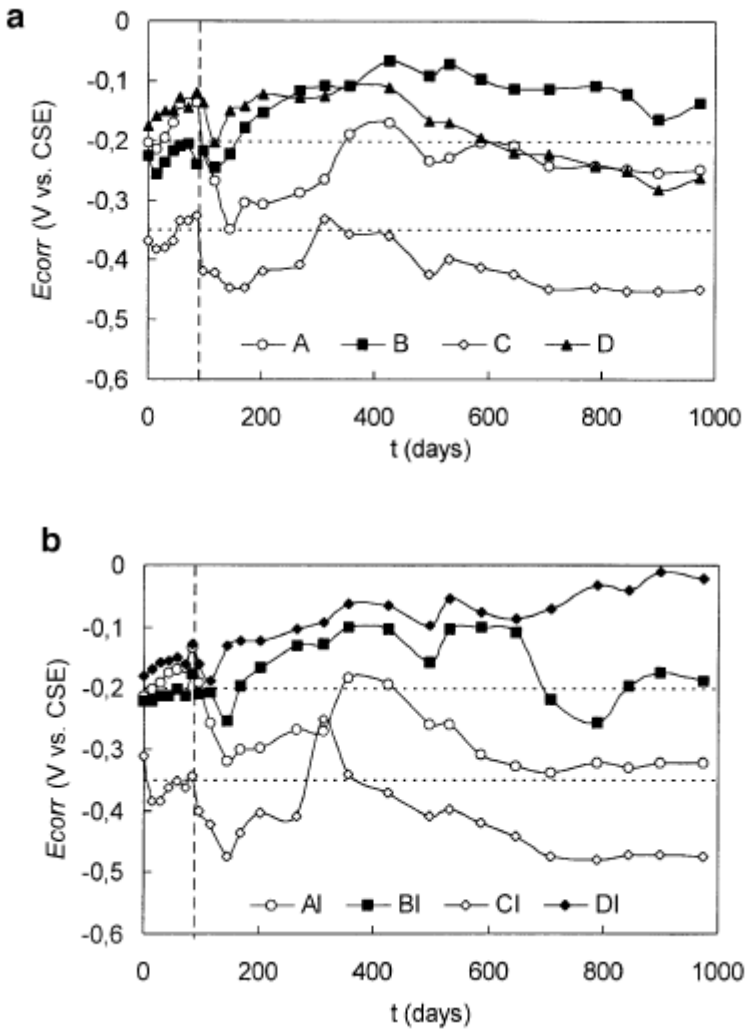

Fig. 3.21. Variation of the rebar corrosion potential (E_{CORR}) with time for the four mix designs under study. Samples were exposed to the marine environment. (a) Blank specimens. (b) Treated with inhibitor. ***(Morris et al., 2002)***

Fig. 3.22a and b present the rebar CR evolution in time for the blank and treated specimens exposed to marine environment. No significant difference was observed between the CR values measured on blank and treated specimens prepared with admixed chlorides (A, B and C). As could be expected, the rebar CR of both blank and treated specimens increased as the initial chloride content in these mixes increased. In the case of mix D (no admixed chlorides, w/c = 0.6), the treated specimens presented CR values that were almost one order of magnitude lower than the values measured on the blank specimens.

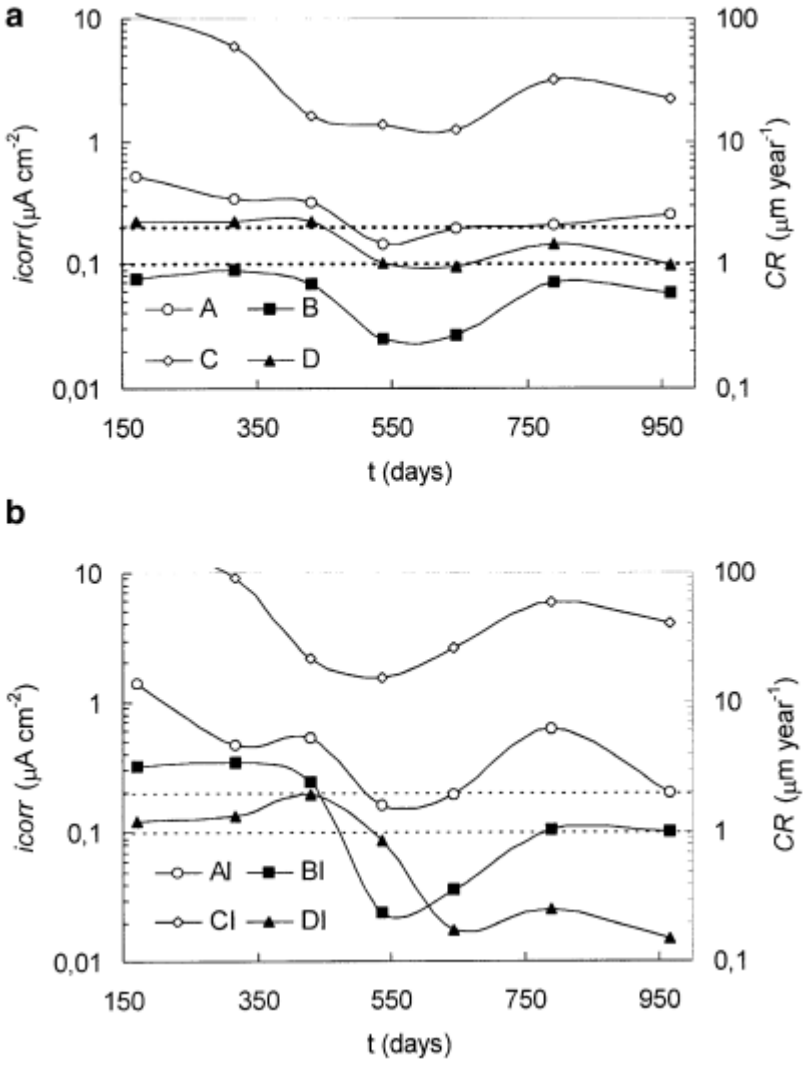

Fig. 3.22. Variation of the rebar corrosion current density (I_{CORR}) and corrosion rate. ***(Morris et al., 2002)***

The efficiency of the inhibitor strongly depends on the initial chloride ions concentration in concrete. The inhibitor was able to reduce the CR of steel in concrete only when the initial chloride concentration was approximately 0.2 wt.% referred to the content of cement in concrete. In this case, the inhibitor was applied to concrete having no admixed chlorides and even when samples had w/c = 0.6 and were exposed to a marine condition for 1000 days, the CR decreased almost one order of magnitude to values typical of steel in passive state (CR <1 mm $year^{-1}$). After this period of exposure, the concentration of total chlorides raised up to approximately 1% at the rebar surface due to the incorporation of chlorides coming from the environment.

Fedrizzi et al. (2005) studied the use of migrating corrosion inhibitors to repair motorways' concrete structures contaminated by chlorides. In the present study, the efficiency of the repair mortars barrier effect and of the MCI has been tested using corrosion potential (E_{CORR}) versus time measurements, electrochemical impedance spectroscopy (EIS) and, at the end of the monitoring period (from 220 to 420 days), chloride penetration analysis. The concrete specimens were cast in parallelepiped blocks (30×30×9 cm^3) using an ordinary Portland cement. Six rust-free steel rods (dia 10 mm, 400 mm length) were embedded into the concrete and used as rebars. At the end of the curing period (at least 28 days), the superior surface of each specimen was coated with one of three different types of mortar of 1 cm thickness, with or without the addition of an MCI at the interface between the concrete substrate and the coating. A quantity from 60 to 70 g per specimen of the alkanolamine-based inhibitor was applied by brush on the surface of the concrete before applying the repair mortars.

Corrosion potentials of the six rebars of each specimen have been measured during the exposure time. An average between the three upper bars and the three lower bars has been made to obtain a statistical value of the potential versus time trend. The graphs (Fig. 3.23) also show the effect of inhibitor treatment on the potential of the reinforcing bars of the specimens, which were subjected to ponding by a sodium chloride solution besides the already present amount of chlorides added in the concrete mix. The mean potential values of the upper and lower steel bars show that the repair mortars A and B offer a better barrier effect compared to the Standard Mortar of reference (Fig. 3.23a and c). With control specimen (covered with Standard Mortar and free from inhibitor), the potential was very and permanently negative, especially for the upper rebars (Fig. 3.23a). It is interesting to note that the samples with the alkanol-amine-based inhibitor applied at the concrete–mortar interface have corrosion potential values (Fig. 3.23b and d) less negative or similar to those of control specimens, covered with the different coatings but without the MCI (Fig. 3.23a and c).

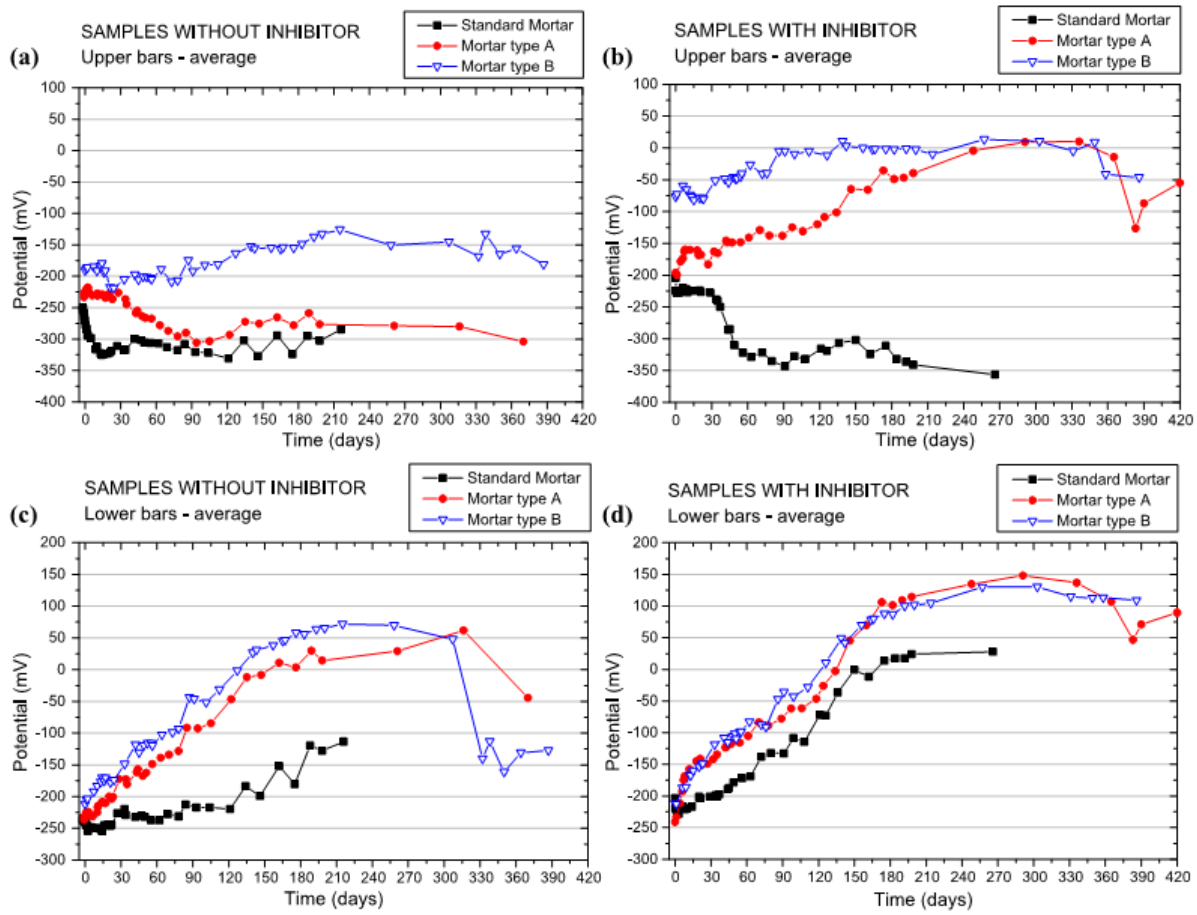

Fig. 3.23. Corrosion potential (versus Ag/AgCl) versus time diagrams. ***(Fedrizzi et al., 2005)***

The comparison among the corrosion rates of the upper bars (Fig. 3.24a) shows that the Standard Mortar alone cannot offer a sufficient barrier action against rebar corrosion in these severe conditions. I_{CORR} increases with the exposure time for the upper rebars of the reference specimen, which means high corrosion levels reached, while its average value is low for the deeper reinforcements (Fig. 3.24c) and has the tendency to decrease in time. A similar trend in upper rebars corrosion rates (Fig. 3.24a) is evident for Mortar type A, with increasing values of I_{CORR} versus time, but delayed 20 days and always at lower values than Standard Mortar. Very different is the behaviour of Mortar type B, whose average upper rebars I_{CORR} remains stable and low during the first 200 days. The addition of the migrating inhibitor shows its effect on standard mortar sample in the first days of the monitoring period, delaying the onset of the severe corrosion on the upper rebars (Fig. 3.24b). There are no significant differences between the lower rebars with or without inhibitor addition (Fig. 3.24d versus 3.24c); in both conditions, the tendency is to diminish the corrosion rate. The

comparison between the upper bars (Fig. 3.24b versus 3.24a) shows the long-term efficacy of the MCI when associated to repair mortars, such as Mortar type A and Mortar type B.

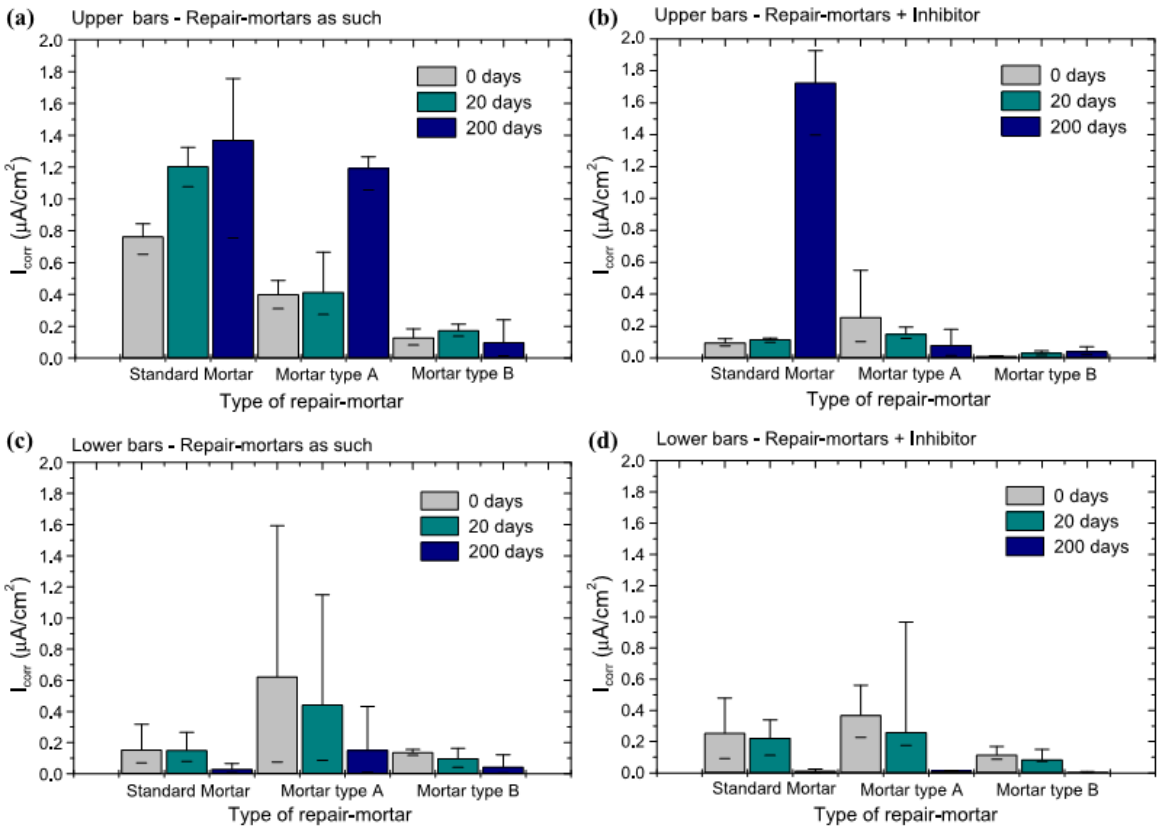

Fig. 3.24. Corrosion rates (I_{CORR}) calculated at three different monitoring periods (beginning of ponding, and after 20 and 200 days) ***(Fedrizzi et al., 2005)***

Portanguen et al. (2005) studied detection or quantitative analysis of a corrosion inhibitor, the sodium monofluorophosphate, in concrete. They present two methods to analyse quantitatively the inorganic inhibitor sodium monofluorophosphate in concrete. The first method using ion chromatography and permits the determination of the ionic compounds of MFP (PO_4^{3-}, F^- or PO_3^{2-}). The second method proposes the analysis of fluoride using an ion specific electrode. The first method consists of extracting the MFP from concrete using a cation exchanger and then analysing it with an ion chromatograph in an eluant phase made of Na_2CO_3 and $NaHCO_3$. In this process, the MFP peak is clearly identifiable and can be easily distinguished from the peaks of $F^-$and HPO_4^{2-} , which can be due to the hydrolyse of the MFP. From a practical point of view, this method permits observation of the evolution of MFP in the cement matrix and its possible hydrolyse. This method also allows the identification of the ingredient actually active in the inhibition of corrosion. Second method is

an alternative method to analyse the MFP using a specific electrode has been proposed. The MFP is hydrolysed with nitric acid and quantified by fluoride analysis.
It was found that

- When the MFP is extracted using a nitric acid solution, 50% of the fluoride introduced under MFP form is detected with a significant uncertainty of 25% because of the loss during extraction.
- The cation exchanger, amberlite IR 120, allows the detection of 91% of the initial fluoride with a low uncertainty of 3.5%.

They observed that ion chromatography and specific electrode are two complementary tools that can be used to evaluate the MFP present in concrete after anticorrosive treatment. If accurate information on the MFP forms at different depths are needed, then ion chromatography will be used. In case of a need to assess the presence of MFP in concrete without requiring more particular information, then the specific electrode method will give the answer.

Tritthart, (2003) studied transport of a surface-applied corrosion inhibitor in cement paste and concrete. He focused on the transport of the ingredients of an inhibitor in cement paste and concrete, which contained an aminoalcohol and a phosphorous compound.
The study on the binding of the ingredients of the investigated inhibitor by cement showed that the aminoalcohol had not been bound by cement but remained completely dissolved in the pore solution, thus providing optimal conditions for high mobility. However, the phosphorus component forming a salt with the aminoalcohol was insoluble in the alkaline environment of cement paste and precipitated quantitatively from the liquid phase. It was thus unable to penetrate from the outside into the alkaline concrete zone and could not develop its inhibiting effect there.
Elsener et al. (*1999*) found that the salt-forming component of the product of other manufacturers precipitated in contact with cement as well, it seems that this is not restricted to the investigated product because the products of other manufacturers contain comparable ingredients. It was also observed that the salt-forming component of the investigated product hardly penetrated, not even into carbonated concrete, and was poorly soluble therein only.
From this, it can be inferred that this component is hardly effective as an inhibitor, even if the product is applied according to the manufacturer's instructions. Diffusion process has turned out to be by far the most effective one, while basically transport of aminoalcohol via the

gaseous phase is possible, the latter plays an inferior role only. The aminoalcohol, however, penetrates much more slowly than expected at the beginning, with a speed comparable to that of chloride ions.

CHAPTER 4 EXPERIMENTAL PROGRAM

4.1 GENERAL

In this chapter, the experimental setup is presented to find out the effect of migrating inhibitors for preventing corrosion of reinforced concrete prisms. The procedure for monitoring the progression of corrosion of steel in concrete is done namely by electrochemical tests i.e. LPR measurement and half cell measurement. The following sections describe the test procedure in detail.

4.2 TEST PROGRAMME

The objective of test programme is to study the effectiveness of migrating type corrosion inhibitors with regard to reduction in rebar corrosion. Reinforced concrete prisms having different water-cement ratio were cast to study the effect of corrosion inhibitor. The test programme involved

1. Determinations of basic properties of constituent materials namely cement, fine aggregates, coarse aggregates and steel bars as per relevant Indian standard specifications.
2. Casting of prisms of plan size 300 x 300 mm^2 with 25 mm diameter TMT steel bar using different water cement ratio and depth of 65 mm with the clear cover of 20 mm.
3. Subjecting the prism specimens to accelerated corrosion by providing initial voltage of 5V and monitoring the prisms till the specimen is severely corroded.
5. Application of Migratory type Corrosion Inhibitor on hardened concrete surface after severe corrosion and monitoring the specimen thereafter.

4.3 MATERIALS USED

Cement, fine aggregates, coarse aggregates, water and TMT bars are used in casting of prisms. The specifications and properties of these materials are as under:

4.3.1 Cement

43 grade Ordinay Portland cement is used for the present investigation. Ultra Tech cement from a single lot is taken for the study. The cement is of uniform colour i.e. grey with a light greenish shade and is free from any hard lumps. Summary of the various tests conducted on cement are given in Table 4.1. All the tests are carried out in accordance with procedure laid down in IS: 8112-1989.

4.3.2 Fine Aggregates

The fine aggregates used for the experimental work is locally procured and conformed to grading zone III. Sieve Analysis of the fine aggregate is carried out in the laboratory as per IS 383-1870. The sand is first sieved through 4.75 mm sieve to remove any particle greater than 4.75 mm sieve and then washed to remove the dust. The physical properties and sieve analysis of fine aggregates are shown in Table 4.2 and 4.3.

Table 4.1: Physical Properties of Cement

S. No.	Characteristics	Values Obtained	Standard Values
1.	Normal Consistency	33%	-
2.	Initial Setting Time	48 min	Not be less than 30 minutes
3.	Final setting time	240 min	Not be greater then 600 minutes
4.	Fineness	4.8 %	<10
5.	Specific Gravity	3.09	-
Compressive strength	:- Cement : Sand	(1:3)	
1.	3 days	24.5 MPa	22 MPa
2.	7 days	38 MPa	33 MPa
3.	28 days	45 MPa	43 MPa

Table 4.2: Physical Properties of Fine Aggregates

S.No.	Characteristics	Value
1.	Specific Gravity	2.46
2.	Bulk Density	1.4
3.	Fineness modulus	2.56
4.	Water absorption	0.85
5.	Grading Zone (Based on percentage passing through 600 μ sieve)	Zone III

Table 4.3: Sieve Analysis of Fine Aggregate

S.No.	Sieve Size	Mass Retained	Percentage Retained	Cumulative Percentage Retained	Percent Passing
1	4.75 mm	4.0	0.4	0.4	99.6
2	2.36 mm	75.0	7.50	7.90	92.1
3	1.18 mm	178.0	17.8	25.70	74.3
4	600 µm	220.0	22.0	47.70	52.3
5	300 µm	274.0	27.4	75.10	24.9
6	150 µm	246.5	24.65	99.75	0.25
7	2.50	0.25	0.25	Σ = 256.55	

Total weight taken = 1000 gm

Fineness Modulus of fine aggregates = 2.56

4.3.3 Coarse Aggregates

Crushed stone aggregate (locally available) of nominal size 20 mm is used throughout the experimental study. The aggregates are washed to remove dust and dirt and are dried to surface dry condition. The aggregates are tested as per IS: 383-1970. The results of various tests conducted on coarse aggregate are given in Table 4.4 and Table 4.5 shows the sieve analysis results.

Table 4.4: Physical Properties of Coarse Aggregates

S.No.	Characteristics	Value
1	Type	Crushed
2	Specific Gravity	2.66
3	Total Water Absorption	0.56
4	Fineness Modulus	6.83

Table 4.5 Sieve Analysis of Coarse Aggregates

S.No.	Sieve Size	Mass Retained (gm)	Percentage retained	Cumulative percentage retained	Percent passing
1	20 mm	0	0	0	100
2	10 mm	2516	83.89	83.87	16.13
3	4.75 mm	474	15.8	99.67	0.33
4	PAN	10	0.33	Σ = 183.54	

Total weight taken = 3Kg

FM of Coarse aggregate = (183.54+500) /100 = 6.83

4.3.4 Water

Fresh and clean tap water is used for casting the specimens in the present study. The water is relatively free from organic matter, silt, oil, sugar, chloride and acidic material as per Indian standard.

4.3.5 Steel Reinforcement

TMT steel bars of 25 mm diameter and 550 mm length are used as longitudinal reinforcement.

4.3.6 Corrosion Inhibitor (Dura Corobit- 60)

Dura Corobit- 60 is used as a corrosion inhibitor in present research work. It is organic modified liquid amine admixture for concrete. As claimed by the manufacturer, it is efficient in preventing corrosion anodically and cathodically, thus effectively blocking corrosion at both anodic and cathodic sites for improved corrosion protection of concrete steel reinforced structures exposed to high chloride and certain chemical environments. It is a liquid inhibitor and is added in small quantities to mixes of Portland cement. It can be introduced to the concrete batch after adding water or it may be applied on concrete hardened surface as migratory type corrosion inhibitor. It is soluble in water and may be added to water before the water is incorporated. Dura Corobit-60 is recommended to be used at the rate of 0.6 Ltr per m^3. The technical data supplied by the manufacturers is summerized in Table 4.6

Table 4.6: Technical Data for Corrosion Inhibitor

Active Ingredients	100%
Colour	Clean (amber)
Dot/Flash Point	Flammable Liquid (39^0 C)
Shelf Life	12 months if unopened
Mixing and Use	All equipment should be clean and flushed with water. Stir thoroughly. Do not very proportions. Add DURA COROBIT -60 Corrosion inhibitor to the concrete batch after adding the water or brush it on concrete hardened surface.

4.4 DESIGN OF CONCRETE MIX

Concrete mix is prepared using 43 grade Portland pozzolana cement, fine aggregate (medium sized natural river sand) and crushed stone coarse aggregate with nominal size of 10 mm. The mix is designed as per Indian Standard Guidelines. Different water ratios are used 0.51, 0.48, 0.45, 0.42. The mixes are designed for constant water content and the mix proportions obtained for various water-cement ratios are summarized in Table 4.7.

Table 4.7 Various mix proportions

S.No.	W/C Ratio	Water Kg/m^3	Cement Kg/m^3	Fine Aggregates Kg/m^3	Coarse Aggregates Kg/m^3	Mix proportions
1	0.51	197	386	551	1176	1:1.42:3.04
2	0.48	197	410	532	1175	1:1.29:2.86
3	0.45	197	437	516	1167	1:1.18:2.67
4	0.42	197	469	500	1162	1:1.06:2.47

4.5 CASTING OF SPECIMENS

4.5.1 Preparation and Preconditioning of Steel Bars

Steel bars are cut to the required length of 550 mm. Each bar is then wire brushed to remove any surface scale. These are then cleaned by soaking in analytical reagent grade hexane and allowed to air dry. This steel specimen preparation is similar as specified in ASTM G 109. The central 300 mm length of rebar is embedded in concrete and 250 mm is exposed on one side in order to make electrical connections. For preventing the 250 mm of bar exposed to environment, an anti-corrosive protective coating system known as epoxy-based interpenetrating polymer network (IPN) was used. For, the anti corrosive paint was applied to this portion of the bar. However, some portion (about 10 mm) of bar at the end was not coated so as to make electric connections.

4.5.2 Preparation of Prism Specimen

In the present program, a special moulding system is fabricated for casting the specimens. The prisms are cast in mould of plan size 300 x 300 mm^2 having depth of 65 mm. First of all the interior of prism mould is oiled, so that the prisms can be easily removed from the mould after 24 hours. While embedding these bars in concrete, they are kept in such a way that 250 mm lengths of these bars is protruded outside of the concrete specimen from one side. The bar is positioned in the centre so that a cover of 20 mm is maintained on both sides. When the bars have been placed in position, concrete mix is poured and vibrations are given so that the mix gets compacted. The vibration is done until the mould is completely filled and there is no gap left. The prisms are then removed from the mould after 24 hours. After demoulding the prisms are cured for 28 days using jute bags. The concrete surface of the prisms is then cleaned and all dirt and loose materials are removed before initiation of corrosion work. In all, three prisms are cast for each water-cement ratio.

4.5.3 Preparation of Concrete Cubes

For doing testing of water impermeability and compressive strength, cubes of sizes 150 mm × 150 mm are cast along with the prisms. For each water-cement ratio, three cubes are cast for water impermeability measurements and three are cast for compressive strength measurements.

4.6 CORROSION ACCELERATION

The objective of inducing corrosion to the reinforcing bar is to simulate the corrosion damaged concrete. The commonly used methods of inducing corrosion in RC specimens can be recalled as salt spray, Chloride diffusion, alternate drying and wetting in salt water and impressing anodic current. Previous studies have shown that test specimens kept in a salt spray chamber for more than 100 days did not show any visible signs of corrosion. This method was not found suitable considering the time constraint. Method of adding chlorides artificially to the concrete during casting is an effective method of initiating corrosion in an steel rebar. This method was not considered because it did not simulate the present condition of interest. Alternate immersion into NaCl (Sodium Chloride) solution and drying of the specimens also induces corrosion. However, the quickest method of inducing corrosion is by impressing anodic current. In this method, NaCl solution is supplied to the specimens and a direct current is passed making the reinforcement bar as an anode and another metal nobler than steel in electro-chemical series as cathode. Incidentally, this method has been used by a number of previous investigators

4.6.1 Present method of inducing accelerated corrosion

In this investigation, the specimens are kept fully saturated by continuously dripping with 5% NaCl solution. Mats are placed over the tops to provide even distribution of NaCl solution. The rebar is used as anode. A stainless steel (SS) mesh is rolled around 300 mm length of specimen and tied together with metal ties in order to assure electrical continuity and is used as cathode (Fig. 4.1). The reinforcement extended 250 mm on one side of the concrete to allow easy access for making electrical connections to the steel. The constant voltage of 5V is impressed in order to accelerate corrosion. The DC regulated power supplier (DCRPS) used in the present study could supply 1000mA DC at 30V. The rebar is connected to the positive terminal of the external DC source and negative terminal is connected to the SS mesh. The test set up is shown in Fig.4.2. Half-Cell potential and linear polarization measurements are obtained daily for all the specimens throughout the duration of accelerated corrosion.

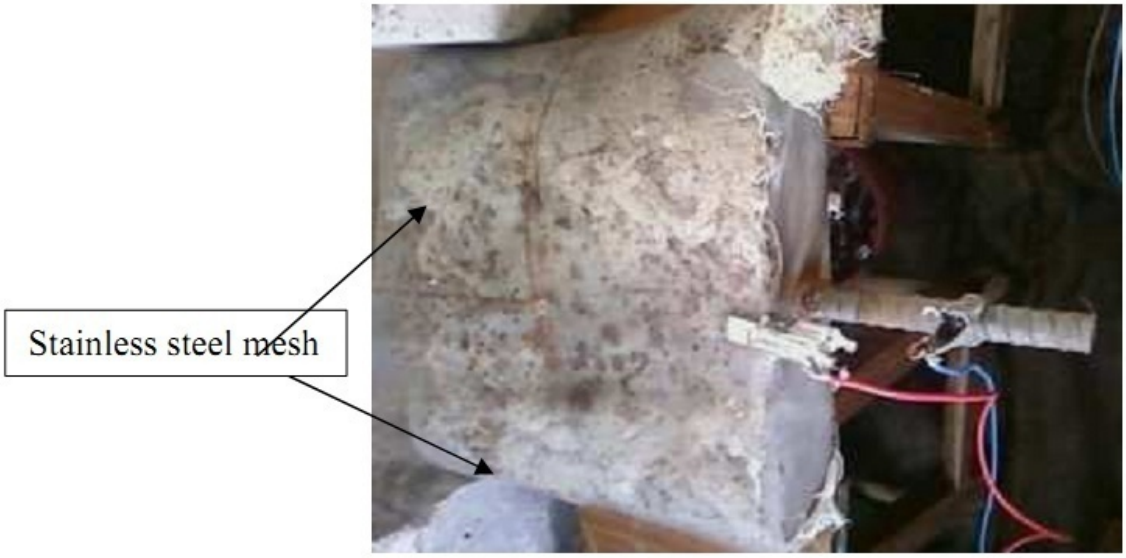

Fig. 4.1 View of Stainless steel mesh

Fig 4.2 Specimens and the Power Supplies used to accelerate corrosion

4.7 APPLICATION OF CORROSION INHIBITOR

For corrosion inhibiting admixtures to be viable, they should not only prevent or delay the onset of corrosion, but also must not have any detrimental effects on the properties of the concrete itself, such as strength, setting time, workability or durability. For the present study, a penetrating corrosion inhibitor was used as corrosion inhibitor. Migratory type corrosion

inhibitor is a concrete-surface applied penetrating corrosion inhibitor and is not in direct contact with the reinforcement. It is brush applied after the specimen is subjected to severe corrosion at the rate of 0.1 L/m^2 on each of the test specimens over six consecutive weeks. The inhibitor is applied at the top surface of the specimen. After the application of inhibitor, a sponge dipped in inhibitor is kept at the top surface to avoid inhibitor loss due to evaporation.

4.8 FURTHER CORROSION

For further corrosion the concrete specimens are sealed on all sides except the testing surface in order to ensure unidirectional chloride penetration into the specimen. On the testing surface, a 30 mm dyke is made with cut out pieces of glass to allow for ponding. 5% sodium chloride is used for ponding. In order intensify the degradation process, the specimens are subjected to wetting and drying cycle for three days i.e. two days wetting and one day drying

4.9 TESTS CONDUCTED ON CONCRETE CUBES

Some basic tests are conducted on concrete cubes to define the basic parameters of concrete mix. It includes measurement of compressive strength and water impermeability tests. These test are used to define the quality of concrete obtained at each water-cement ratio. The test procedures are described in the following section

4.9.1 Water Impermeability Test

Deterioration of concrete structures has been the subject of major concern and research for the past few years. The main factors for deterioration of RC concrete structures are corrosion of reinforcement, sulfate attack and salt weathering and cracking due to environmental effects and potential aggregate-cement reactivity. These factors are visible manifestation of excessive salt inclusions in concrete mostly due to ingress of aggressive through cracks and pores. Therefore, these factors are mostly permeability oriented. The permeability of concrete is the most important property determining its long term durability in aggressive environment. The permeability test gives a measure of the resistance of concrete against the penetration of external agents into cover concrete. In the present study, permeability of various mixes is measured by water impermeability test.

Most deterioration processes have two stages. Initially, aggressive fluids (water, solution etc.) penetrate through the capillary pore structure of the concrete to reaction sites. This penetration is followed by the actual chemical or physical deterioration reactions. To access concrete durability during the first stage, tests that measure transport rates in concrete are

required. The transport rate, normally called permeability of concrete, is measured in terms of flow of water through the concrete specimen. However, there is a problem with the permeability test: in good quality concrete, there is no flow of water through concrete even after some days also. It is expected that the water permeability tests might not give any data for comparison of mixes. Therefore, water impermeability test is performed instead of water permeability test. The test is performed as per the German Standard DIN 1048 (Part 5). For performing the test, 150 mm cubical specimens are cast similar to the procedure adopted for casting specimens for strength tests. The specimens are subjected to all the five curing regimes and the test is carried out at the age of 28 days. For conducting the test, the concrete specimens are exposed to a water pressure of 0.5 N/mm^2 acting normal to the mould filling direction, for a period of three days. Three cell apparatus is used for performing the test, i.e. three specimens are subjected to the said pressure at the same time. The pressure is kept constant throughout the test. At the end of three days, the pressure is released and the specimens are split down the center with the face which was exposed to water facing down. After about ten minutes, the maximum depth of penetration in the direction of cube thickness is measured on each of the split halves in mm. The mean of the maximum depth of penetration obtained from the three specimens tested is taken as the test result. In high water heads, a concrete specimen measuring 150x150x150 mm^3 is casted and after 28 days of curing, it is exposed from above to a water pressure of 0.5 N/mm^2 acting to the normal mould filling direction, for a period of three days. This pressure is kept constant throughout the test. Before start of the experiment it is checked that the specimen placed under pressure should not leak. If it leaks, then epoxy is applied around it. Immediately after the pressure has been released, the specimen shall be removed and split down the centre, with the face which is exposed to water facing down. When the split faces shows signs of drying (after about 5 to 10 minutes), the maximum depth of penetration in the direction of prism thickness, shall be measured in mm.

Fig.4.3 Water permeability Apparatus

4.9.3 Compressive Strength Test

This test is performed on the 150 mm cubical specimens as per IS 516:1959. At the required age of testing, the cubes are taken out from the curing tank and cleaned with cloth to wipe out excess water from the surface in order to bring them to saturated surface dry condition. If, according to the curing condition, the cubes are already in the dry condition, they are tested as such. These specimens are then placed on the automatic compression-testing machine (3000 KN Capacity) in such a way that it is tested at right angles to the as cast position. The compressive load is applied through the hydraulic jack at a constant rate of 140 kg/cm^2/min till failure. The average failure stress of three cubes is considered as the representative compressive strength of the mix.

4.10 CORROSION MONITORING ON PRISM SPECIMENS

Corrosion of steel embedded in concrete is not visually evident until the damage reaches to the external signs of deterioration as rust spots, cracks or spalling. In order to predict the corrosion service life of reinforced concrete structures and to determine the need of repair or rehabilitation, it is necessary to use non-destructive techniques for assessing the corrosion

activity and measuring the corrosion rate of the reinforcements. In the present study, the corrosion rate of rebar is monitored by electrochemical methods.

Electrochemical Techniques

The electrochemical measurements are carried out using a versatile instrument (ACM model: serial no.1463 field machine) that is capable of performing various electrochemical tests such as potential measurement, AC impedance technique, potentiostatic cyclic sweep test, LPR measurements etc.

Fig 4.4 shows ACM setup used for electrochemical monitoring. The instrument is capable of processing the data and plotting the outputs automatically. The half cell potential measurement gives only an indication of the corrosion risk of the steel and is linked by empirical comparisons to the probability of corrosion. Therefore along with half cell, linear polarisation (corrosion rate) measurements are taken which provides a valuable insight into the instantaneous corrosion rate of the steel reinforcement, giving more detailed information than a simple potential survey. The LPR data enables a more detailed assessment of the structural condition and is a major tool in deciding upon the optimum remedial strategy to be adopted.

Hence the two important electrochemical techniques that are used for the studying the corrosion activity are corrosion potential (E_{CORR}) and corrosion current /current density (I_{CORR}). These determining parameters indicate the corrosion initiation. The following section describes the procedure in details:

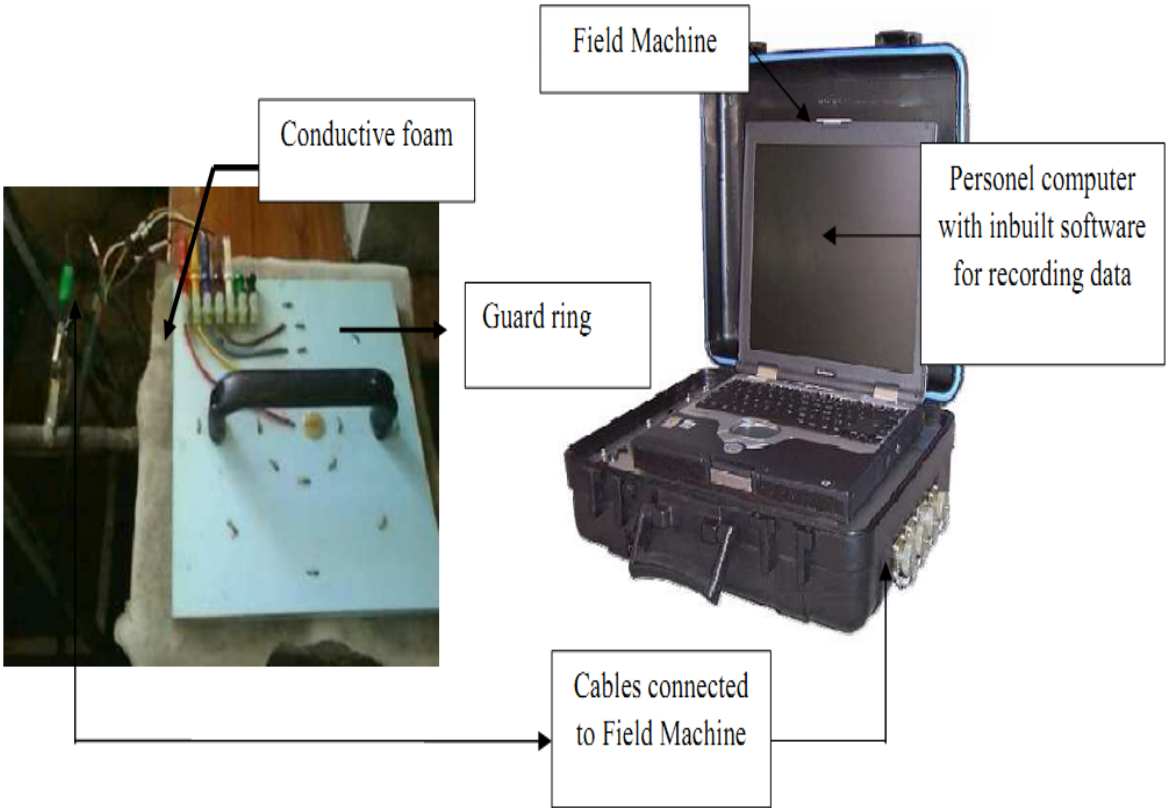

Fig 4.4 ACM Setup Used for Electrochemical Monitoring

4.10.1 Half cell potential measurements

In the present study, all the specimens are monitored daily by half-cell potential using a saturated calomel reference electrode by placing the electrode on top surface of the concrete. The procedure followed is ASTM Standard C 876. The power supply is switched off one hour before taking the half cell readings in order to completely depolarize it. To maintain a consistent testing environment over the experimental test period, the dripping salt water is replaced daily, electrodes are cleaned daily and the wiring and electrical connections checked twice a day. If the corrosion potential reading is more positive than -200 mV, probability is that no reinforcing steel corrosion is occurring in the area at the time of measurement and if the potential reading is more negative than -426 mV, probability is that the reinforcing steel corrosion is occurring. The ASTM interpretation of half-cell potential (SCE) is summarized in Table 4.8. The experimental arrangement for half cell measurement is shown in Fig. 4.5.

Table 4.8 The ASTM Interpretation of Half-Cell Potential Readings

Open circuit potential (OCP) values	Corrosion condition
< -426 mV	Severe corrosion, corrosion induced cracking may occur
< -276 mV	High risk, 90% probability of corrosion
-126 to -275 mV	Intermediate risk, corrosion activity in uncertain
0 to -125 mV	Low risk, 10% probability of corrosion

Fig 4.5 Half Cell Arrangement

4.10.2 Linear polarization resistance (LPR) measurements

Electrochemical LPR technique is especially good at measuring the localized corrosion. LPR measurements on concrete surfaces are performed using guard ring that is supplied with the field machine for precise location of rebar areas. The Guard Ring simply connects to the front panel via the supplied cables. Incorporated into the Guard Ring are a $Cu/CuSO_4$ reference electrode. Before performing the test, conducting sponge is wetted with NaCl solution and placed on the surface of the prism specimen to have proper electrical contact with the guard ring. Guard ring assembly is then placed above the wetted sponge. The electrical connections

are made to the steel rebar. For linear polarization resistance measurement, the working electrode i.e. the steel rebar is polarized to ± 20 mV from the equilibrium potential at a scan rate of 0.1 mV per second. The experimental arrangement for LPR measurement with guard ring arrangement is shown in Fig. 4.6. The polarized surface area of the steel rebar is taken to be that lying under a circle intersecting the midpoint between the two sensor electrodes and only the top half surface area of the steel reinforcement is assumed to be polarized.

Fig. 4.6 Guard Ring Arrangement

For calculation of the corrosion current density I_{CORR}, Stern-Geary equation is used;

$$I_{CORR} = \frac{B}{R_P}$$

Where B is the Stern-Geary constant and is given by B = (βa ×βc) /2.3(βa +βc). βa and βc are anodic and cathodic Tafel constants respectively. The value of B is taken as 26mV considering steel in active condition. Rp is the polarization resistance.

$$B = \frac{\beta_a \times \beta_c}{2.3\ (\ \beta_a\ +\ \beta c\ )}$$

CHAPTER 5 RESULTS AND DISCUSSION

5.1 INTRODUCTION

This chapter deals with the effect of water cement ratio on permeability and compressive strength of concrete specimens, effect of corrosion inhibitor on the half cell potential measurements and linear polarization resistance and the chemistry between corrosion inhibitor and concrete specimen.

5.2 EFFECT OF WATER CEMENT RATIO ON PERMEABILITY AND COMPRESSIVE STRENGTH OF CONCRETE

Permeability of concrete is the most important property determining its long term durability in aggressive environment. Four different water cement ratios were taken of 0.51, 0.48, 0.45, and 0.42 and its effect on permeability is monitored. From the graphs given in figure 5.1, it is clear that with decrease in water-cement ratio, the permeability of concrete decreases.

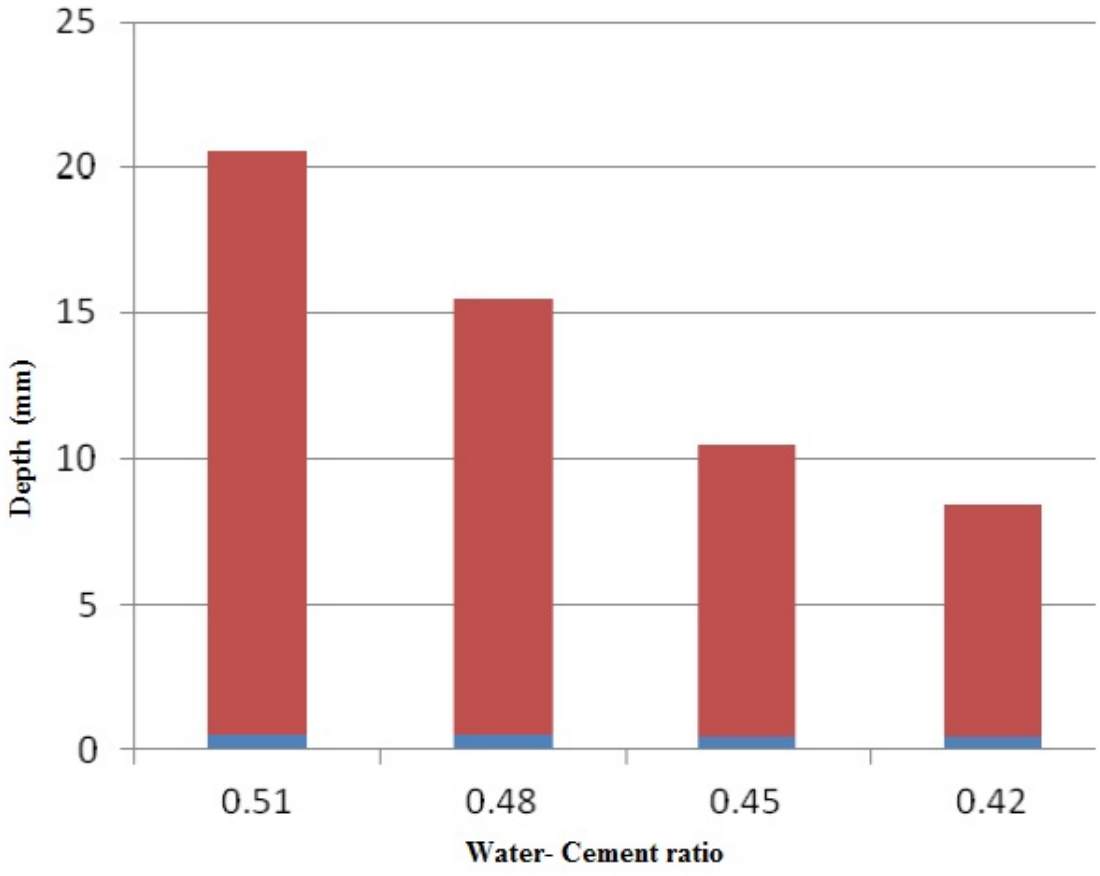

Fig. 5.1 Variation of Water Cement Ratio on Water Permeability Test

Table 5.1 shows the effect of water cement ratio on compressive strength. It is clear that as water cement ratio increases compressive strength of the concrete samples decreases.

Table 5.1 Variation of Water Cement Ratio on Compressive Strength

Water Cement Ratio	28 days Compressive Strength (N/mm^2)
0.42	39.92
0.45	36.82
0.48	31.5
0.51	29.81

5.3 HALF CELL POTENTIAL MEASUREMENTS

Half -cell potentials is measured on the reinforcing steel bars embedded in the concrete with different water cement ratios. Half cell potential readings are taken with respect to Saturated Calomel electrode as reference electrode. The value of half cell potential obtained gives an indication of depassivation of steel and hence the possibility of corrosion. ASTM C876 suggests that the corrosion possibility of rebar embedded in concrete is higher than 90% when the open circuit potential is lower than -270 mV (SCE). In addition, the corrosion possibility is lower than 10% when the open circuit potential is higher than -120 mV (SCE).

In the present work, half cell potential readings are measured on prism specimens with plan size of 300 x 300 mm^2 and with 20 mm cover to rebar. The readings are taken daily when the corrosion process is accelerated and are taken at variable intervals after corrosion inhibitor is applied.

5.3.1 Half Cell Potential During Induced Corrosion

For accelerating the corrosion process, in this investigation, the specimens are kept fully saturated by continuously dripping with 5% NaCl solution. The rebar is used as anode and a stainless steel (SS) mesh is used as cathode. The constant voltage of 5V is impressed in order to accelerate corrosion. The DC regulated power supplier (DCRPS) used in the present study

could supply 1000mA DC at 30V. The rebar is connected to the positive terminal of the external DC source and negative terminal is connected to the SS mesh. Half-Cell potential and linear polarization measurements are obtained daily for all the specimens throughout the duration of experiment. The half cell potential readings for all 4 water cement ratios are presented in Fig.5.2

It is observed from the figure, drop in half cell potential value occurred at different periods depending upon the water cement ratio. For all water cement rations, the half cell measurements keep on increasing with time but within a certain defined range. In the first few days, the potential is less than -250 mV, which indicates that corrosion has not yet initiated and further the value falls and becomes more negative and reaches the range of -250 mV to -600 mV, which indicates that there is possibility of corrosion initiation.

When 5V of voltage supply on the samples is applied having different water cement ratios 0.51, 0.48, 0.45 and 0.42 , it is observed that the time taken by the lower water cement ratio to reach the threshold value is more. Time taken by the chlorides to reach the threshold value increases with decrease in the water cement ratio.

It is observed from the figure 5.2, the time required to reach the threshold corrosion potential increase with the decrease in water cement ratio. It is because of the decrease in permeability with decrease in water cement ratio.

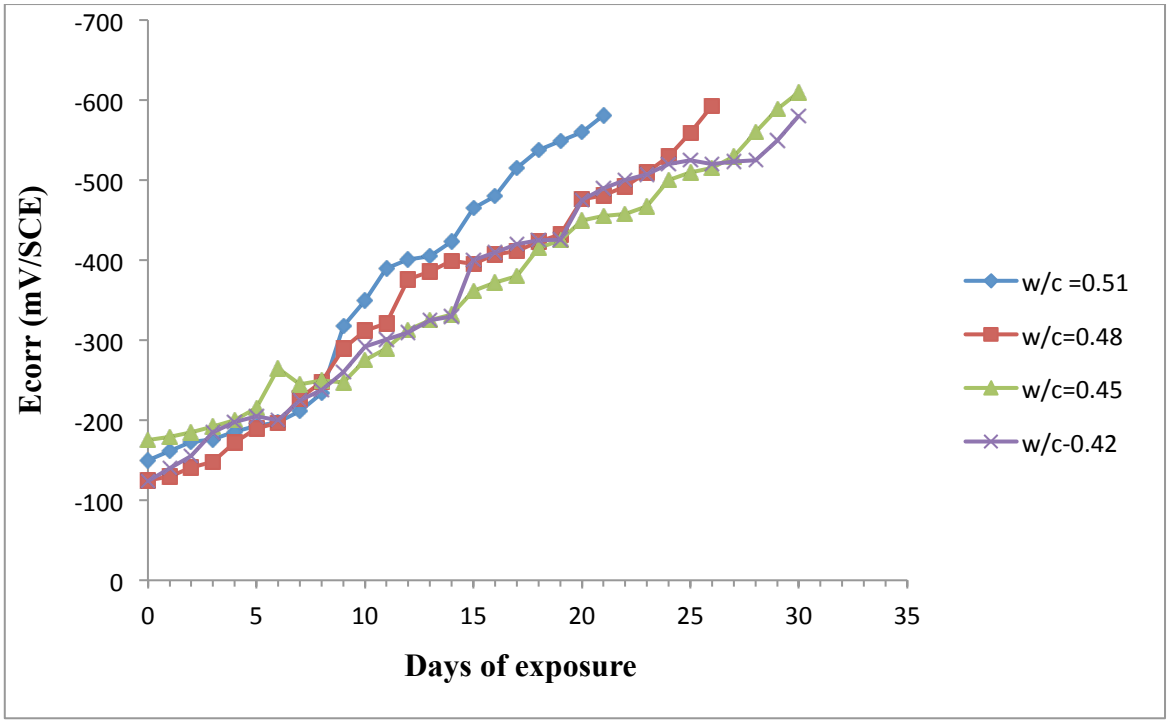

Fig. 5.2 Half cell Potential with different water cement ratio

5.3.2 Effect of Corrosion Inhibitor on Half Cell Potential

After the values of corrosion potential become active, the penetrating corrosion inhibitor is applied to each specimen by brush at a rate of 0.1 L/m^2 over six consecutive weeks, to give a total of 0.6 L/m^2 . In addition, a sponge wetted with the corrosion inhibitor solution is kept on top of the sample to avoid inhibitor loss due to evaporation. The half cell potential readings are taken daily before application of the next coat. Once, the six coats are applied, the specimens are ponded with 5% NaCl solution and the readings are noted after every 3 days thereafter.

From the experimental results, it is observed that when six coats of MCI were applied on concrete surface, half cell potential value decreased with time. After the application of 1st coat, the decreased in potential is drastic in almost all the specimens. Also, the potential readings lowered till the application of three coats of corrosion inhibitor, after which the potential values remained more or less same with the application of further coats on the surface. It indicated that the three coats of corrosion inhibitor are sufficient to arrest corrosion and any further application of inhibitor does not have any positive effect on resisting corrosion. The drastic reduction in potential after the application of 1st coat might be due the penetration of inhibitor onto the steel surface through the cracks that are formed during accelerated corrosion process.

For most of the mixes, the half cell potential values at 80 days is in the intermediate corrosion range, that is, the corrosion risk shifts from severe corrosion to intermediate corrosion.

After the six coats are applied and the specimens are subjected to chlorides for a period of nearly 45 days, the half cell potential values kept on decreasing, although on the lower pace. It indicates, the corrosion inhibitor helps in resisting any further corrosion to occur. Similar observations are obtained by *Fedrizzi et al. (2005)* and it was observed that repair coating by corrosion inhibitor can be effective for a long period of time and the rebar corrosion potential values of treated specimens ultimately reach the passive stage in 1 year. *Jamil et al. (2004)* concluded that amine based inhibitors allow the formation of protective film on the steel which is stable and provide protection even when the inhibitor concentration is reduced to zero.

Looking at the effect of water-cement ratio on the protection achieved by corrosion inhibitors, it can be observed from the figure, that the corrosion inhibitor is effective in all water cement ratios. The value of rebar potential is reducing with the application of inhibitor at, more or less, the same rate. The rebar potential at the end of 84 days is slightly higher for water cement ratio of 0.51.

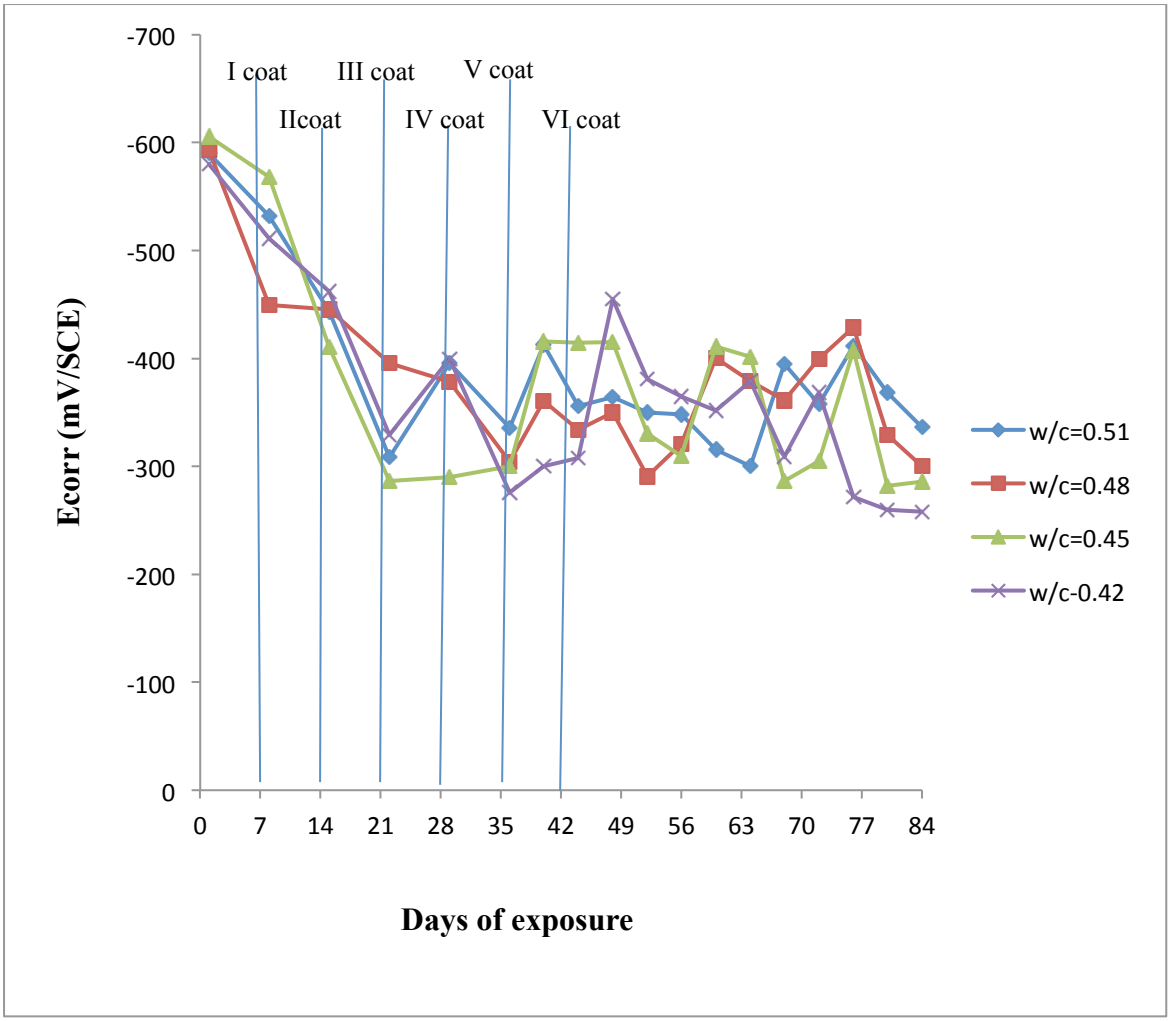

Fig. 5.3 Effect of Corrosion Inhibitor on half cell Potential with different water cement ratio

5.4 LINEAR POLARIZATION RESISTANCE

Corrosion initiation described as the process by which chloride ions permeate into the cover concrete and accumulate around the reinforcing steel, thereby breaking down passivity of the reinforcing steel and allowing corrosion to initiate. Corrosion propagation is described as the process by which the rate of corrosion is accelerated by the electric current at a constant voltage. Half cell potential is effective only in monitoring the corrosion initiation. Therefore, LPR measurements are necessary as the values obtained from corrosion current density indicates the progression of corrosion in the propagation phase.

In the present investigation, the corrosion current density is obtained daily during the accelerated corrosion phase and then at variable intervals during the protection phase, similar to potential measurements.

5.4.1 Corrosion Current Density During the Accelerated Corrosion Phase

From the determined corrosion current density values by LPR method, it is observed that the corrosion current rises as the corrosion progresses through the prism specimens. It is because of the depassivation of layer formed around the rebar due to the increase in concentration of chlorides.

When 5V of voltage supply on the samples was applied having different water cement ratios 0.51, 0.48, 0.45, and 0.42 , it is observed that the time taken by the lower water cement ratio to reach the threshold value is more. Time taken by the chlorides to reach the threshold value increases with decrease in the water cement ratio. It can be attributed to more dense concrete and hence lower permeability. As can be seen in fig. 5.1, it is clear that as the water cement ratio increases, permeability keeps on increasing. Since the cover depth provided in the prisms are same but still the time taken by the chlorides to reach the threshold value depends on water cement ratio only. With decrease in water cement ratio, the permeability decreases. Hence, more time will be required by the chlorides to reach threshold value on rebar surface.

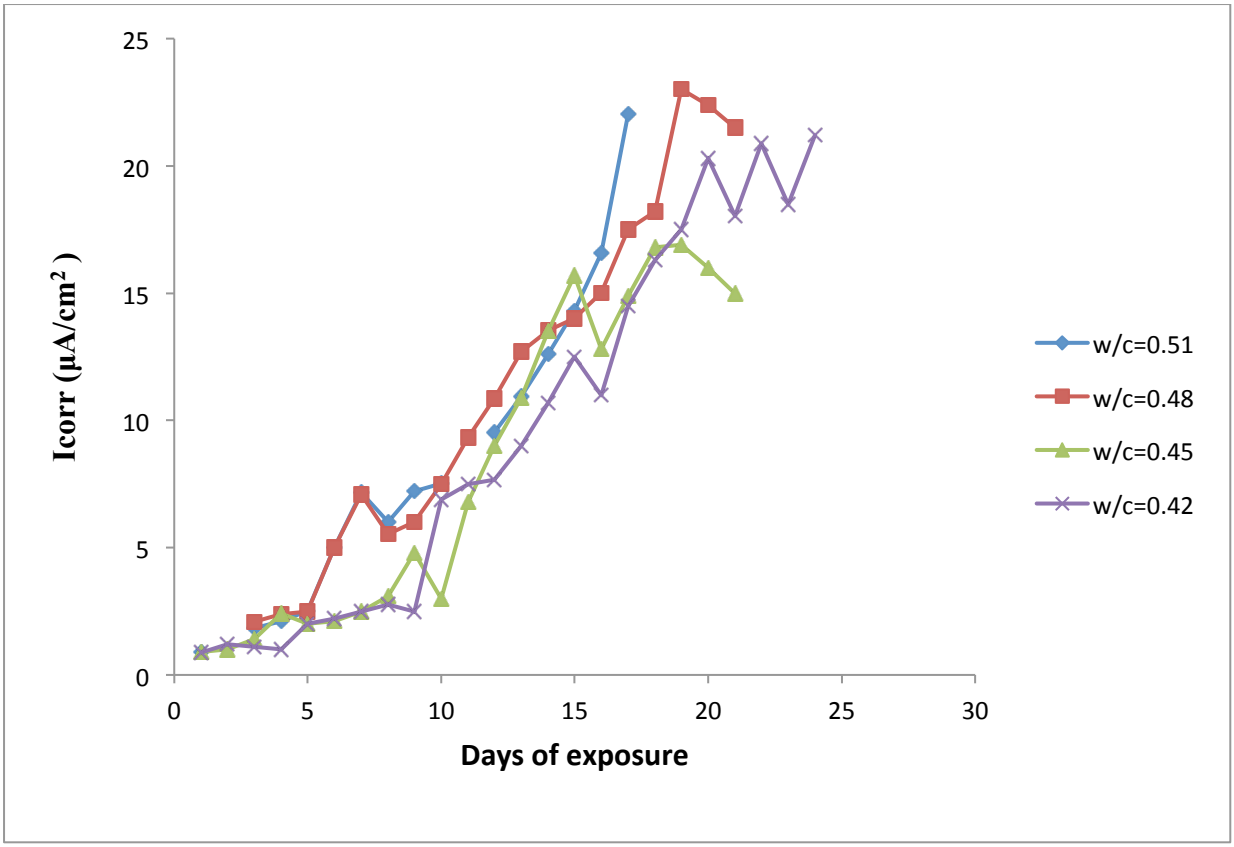

Fig.5.4 Linear Polarization Resistance with different water cement ratio

(Stewart and Vu, 2002), on the basis of the measured values of corrosion current density, have given criteria for corrosion activity. Corrosion current density values less than 0.1µA/cm^2 correspond to passive condition and corrosion current density values ranging between 0.1µA/cm^2 and 1µA/cm^2 correspond to moderate corrosion rate. Similarly corrosion current density values ranging between 1µA/cm^2 and 10µA/cm^2 and between 10µA/cm^2 and 100µA/cm^2 correspond to high and very high corrosion rate respectively. As can be seen from Fig. 5.4**,** all the specimens have reached the same level of corrosion current so that, for applying corrosion inhibitor, a common platform is obtained for all specimens for comparative studies.

5.4.2 Effect of Corrosion Inhibitor on LPR Measurements

The effect on application of corrosion inhibitors on corrosion current is presented in Fig.5.5. From the experimental results, it is observed that when six coats of MCI are applied on concrete surface, corrosion current readings keep on decreasing with time. It is observed from fig. 5.5 that the value of corrosion current shift drastically after the application of first coat and second coat, thereafter any further application of coats decrease the values by lower

order. It can, therefore, be concluded that only two coats of corrosion inhibitor are sufficient in reducing corrosion rate. There is sudden reduction in the value of corrosion current after the application of two coats while no significant difference is observed after that. Similar observations was also made by *Limaye et al. (2006)*. Only two coats of MCI were brushed with a gap of 4 hours. The findings of electrochemical studies reveal that two coatings of corrosion inhibitor dramatically reduce the rate of corrosion.

It is also observed that reduction in corrosion current achieved for all the specimens after 80 days of monitoring is same, irrespective of water-cement ratio of the mix. It suggests that the working of corrosion inhibitor does not depend upon the permeability of the mix only. It also makes the use of corrosion inhibitor a promising solution for protection of low grade concrete structures. Similar observation was made by *Morris et al. (2002),* They, however, observed that the performance of inhibitor, measured in terms of rebar corrosion resistance, is better in the specimens with higher water-cement ratio as compared to lower water-cement ratio mixes.

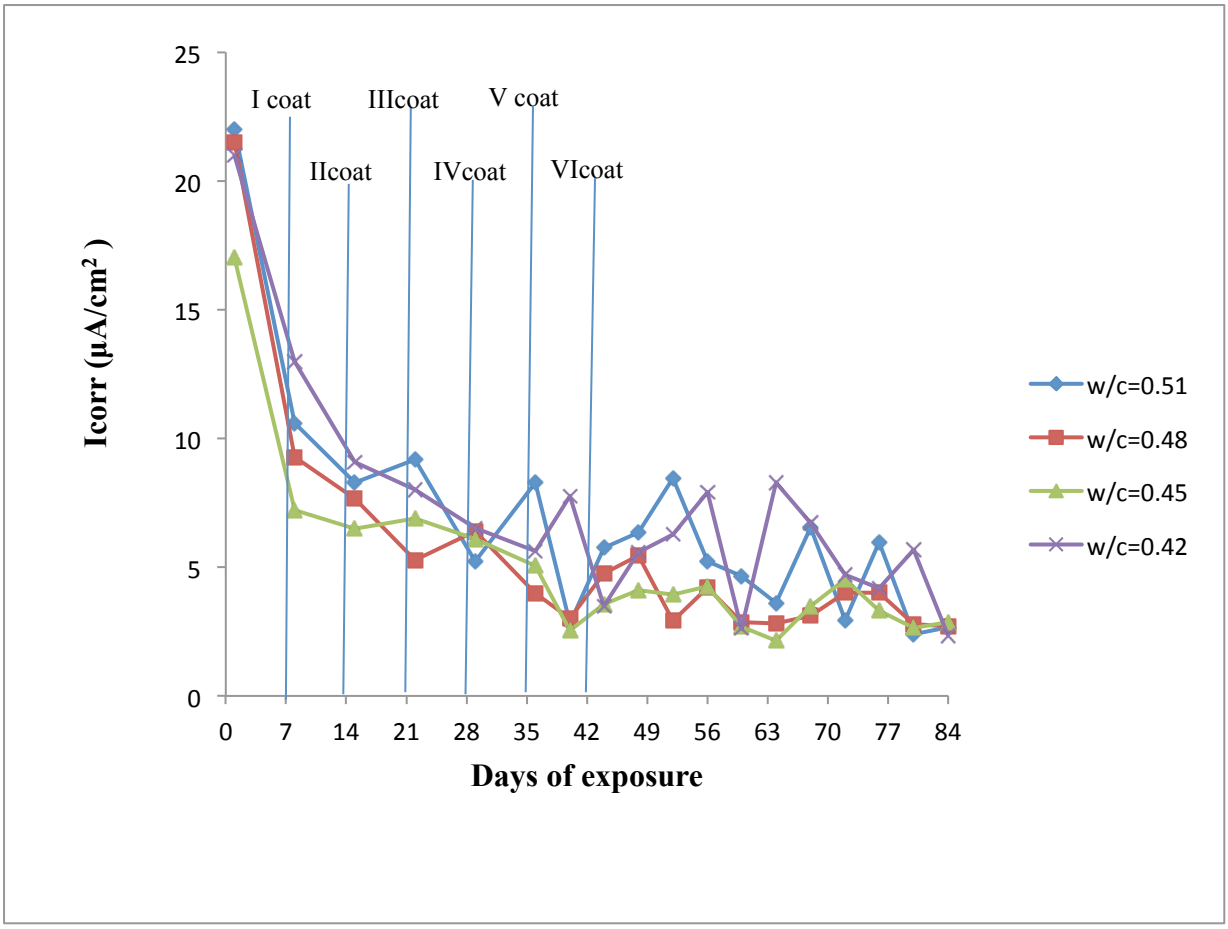

Fig. 5.5 Effect of Corrosion Inhibitor on Corrosion Current with different water cement ratio

5.5 CHEMISTRY BETWEEN CORROSION INHIBITOR AND CONCRETE

The similar performance of corrosion inhibitor for all water-cement ratios can be explained considering the chemistry between corrosion inhibitor and concrete. Amine based corrosion inhibitor is said to be chelating agent, which can form five or six membered chelate rings (groups which function as two associating units and fasten on to the central metallic atom so as to produce heterocyclic rings). These rings are formed as a result of bonding between two or more functional groups from the inhibitor ($-NH_2$) and the cation metal. Due to the presence of rings, Amine organic inhibitors have both film-forming and pore-blocking effects. The film-forming component is an amine group. They get adsorbed on metals and oxides because of an unshared electron pair of the nitrogen atom. *Welle et al. (1997)* and *Nmai (2004)* report that amines and the associated radicals form a layer on the steel surface which completely cover all the anodic and cathodic sites. The film forming effect, therefore depends on the property of corrosion inhibitor and does not depend upon the quality of concrete. *Jamil et al. (2003)* further observed that the thickness and composition of the protective film depends on the concentration of inhibitor. The limit concentration of inhibitor to form the protective film is reported to be 0.5 – 1%. Further, it is observed that higher concentration of inhibitor (2% to 4%) does not have any effect on the protective film *Jamil et al. (2005).* It explains the reason that beyond the application of two coats on corrosion inhibitor, any further application did not result in further drastic reduction in corrosion current.

CHAPTER 6 CONCLUSIONS

A corrosion inhibitor is a chemical substance that decreases the corrosion rate when present in the corrosion system at suitable concentration, without significantly changing the concentration of any other corrosion agent. The principle of inhibitors is to develop a thin layer, usually one or two molecules thick, on the steel surface, which inhibits corrosion either by forming a protective film on the substrate, or by immobilizing the corrosive species and preventing them from reaching the steel. After applying corrosion inhibitor on the severely corroded specimens and monitoring it, the following observations can be made :

1. For most of the mixes after applying corrosion inhibitor, the half cell potential values shifts from severe corrosion to intermediate corrosion range. This shift is visible at all water-cement ratios.

2. Similar to potential measurements, I_{CORR} values also shifts after the application of corrosion inhibitor. The final I_{CORR} obtained is similar for all water-cement ratios, indicating that corrosion inhibitor protect all types of concrete by the same proportion.

3. Both electrochemical techniques are good for measurement of corrosion rate. Linear polarization method gives better results than half cell potential measurement because half cell potential gives only the indication of depassivation. From the determined corrosion current density values by LPR method, it is concluded that effect of significant reduction in corrosion risk is observed effectively by linear polarization resistance measurements.

4. The half cell potential decreases with decrease in water cement ratio. As a decrease in water cement ratio, results in decreased permeability, thus more time will be required by the chlorides to reach threshold value on rebar surface.

5. The reduction in corrosion current achieved for all the specimens after 80 days of monitoring is same, irrespective of water-cement ratio of the mix indicating that the working of corrosion inhibitor does not depend upon the permeability of the mix only.

6. Only two coats of corrosion inhibitor are sufficient in reducing corrosion rate. There is sudden reduction in the value of corrosion current after the application of two coats while no significant difference is observed after that.

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