“EFFICIENCY OF CORROSION INHIBITOR TO MITIGATE CARBONATION INDUCED CORROSION”

A thesis submitted in partial fulfilment
of the requirement for the award of degree of

MASTER OF ENGINEERING
IN
STRUCTURES

Submitted by:

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DECLARATION

The author hereby declares that this thesis entitled **"Efficiency of Corrosion Inhibitor to Mitigate Carbonation Induced Corrosion"**, in whole or part, has not been used to obtain any degree in this, or any other, institute. Except where references have been given in text, it is entirely the authors own work.

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ABSTRACT

Reinforced concrete is one of the most commonly used construction materials in civil engineering but its durability problems have been obsessing people. The worst of these problems is caused by corrosion of steel in concrete, inducing the early deterioration of concrete infrastructures. Structural deterioration of reinforced Concrete structures affected by corrosion is a gradual process consisting of a few different phases during service life, including corrosion initiation, concrete cracking, excessive deflection and final collapse due to loss of structural strength. A number of corrosion mitigation techniques are now a days available. There efficiencies depends upon the reason behind the corrosion of rebar.

The purpose of this thesis is to study the effectiveness of corrosion inhibitor in reducing the rate of corrosion against carbonation induced corrosion. Commercial and chemical corrosion inhibitors are investigated for this purpose. This experiment conducted using the carbon hydroxide solution as the base solution. Two types of tests, i.e., Linear polarization Method and Open circuit potential are performed to find out the values of I_{corr} and OCP. These values further tell us about the performance of corrosion inhibitor on the steel bar. The corrosion monitoring is carried out for a period of 480 hours.

It is observed that that type of corrosion inhibitors and its concentration both play an important role in mitigation of corrosion activity

ACKNOWLEDGEMENTS

A dissertation cannot be completed without the help of many people who contribute directly or indirectly through there constructive criticism in the evolution and preparation of this work. It would not be fair on my part, if I don't say a word of thanks to all those whose sincere advice made this period a real educative, enlightening, pleasurable and memorable one.

First of all, a special debt of gratitude is owned to my supervisor, **Dr. Shweta Goyal** for her gracious efforts and keen pursuits, which has remained as a valuable asset for the successful completion of research work. Her dynamism and diligent enthusiasm has been highly instrumental in keeping my spirit high. The flawless and forthright suggestions blended with an innate intelligent application have crowned my task a success.

I also like to offer my sincere thanks to all faculty members, teaching and non-teaching staff of Civil Engineering Department (CED), and staff of central library, TU, Patiala for their assistance. I am extremely thankful to Mr. Ram Simran, and all other manpower for helping me carry out experimental work.

I would also like to thank to my parents, brothers, sisters and my friends for their constant encouragement during the entire course of my seminar work.

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CHAPTER 1 – INRODUCTION

1.1 GENERAL

Reinforced concrete is one of the most important construction material and is used for almost all types of construction purposes, for its proved durability and high structural performance. The whole process of its creation (for its ease), materials used in its preparation (for their availability in abundance),use in rehabilitation and regeneration of infrastructure system of any country, it plays an important role in improving the overall face of the country. Thus, any source that reduces the overall performance (durability and stability), it will pose a great threat to the country's overall performance and the sustainable growth of concrete and construction industries.

One of the major problems that RC faces is of corrosion of steel that is used as reinforcement in RC structures. This ultimately reduces the structural performance and durability of structure to such a great extent that the age of the structure reduces to its half, for which it is constructed. It has been estimated that 40 % of the structural failures in the whole world are attributed to corrosion *(Sethi 2005)*. Therefore, this matter of protecting the structures from corrosion is of prime importance. Corrosion is a like a CANCER, hidden and slow, but when it shows up, lots of damage has been done. Therefore, it is highly required to study and understand the whole process of corrosion, and, also research for various techniques that can be used before damage and also after damage, in order to have more stability and high performance.

1.2 CORROSION OF RC STRUCTURES

Corrosion of RC structures would literally mean the corrosion of steel embedded in concrete. Thus, we can say that it is the degradation or deterioration of metal Steel corrodes actively in oxygen rich environments due to its large content of iron. Chloride ions found in de- icing salt and seawater accelerates the corrosion of steel and therefore are a concern for reinforced concrete structures. When steel is embedded in concrete, a passive film develops and covers the steel surface. Cement paste is

alkaline (pH between 12 and 14) and enables the formation of this thin passive film coating on steel that protects the steel from corroding. After passing through the hardened concrete the chloride ions present in de-icing salts destroy this protective layer, thus making the steel liable to corrosion similar to chloride ions ingress.

1.3 FACTORS AFFECTING THE CORROSION

Sound concrete is an ideal environment for steel but the increased use of de-icing 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. Following are the major contributing factors leading to corrosion:

1.3.1 Loss of alkalinity due to carbonation

Alkalinity can be lost as a result of reaction with acidic gases such as carbon dioxide from the atmosphere and leaching of water from the surface of concrete. Therefore, the extent of advance of carbonation would depend on the porosity and permeability of concrete and also on the conditions of exposure.

1.3.2 Loss of alkalinity due to chlorides

The passivity provided by the alkaline conditions can also be destroyed by the presence of chloride ions, even though a high level of alkalinity remains in the concrete. The chloride ion can locally de-passivity the metal and promote active metal dissolution. At low levels of chloride in the aqueous phase, the rate of corrosion is very small, but higher concentration increases the risks of corrosion.

1.4 PROTECTION MEASURES

Several solutions to the problem of rebar corrosion have been proposed and tested, though to date no ideal solution has been found. Some of these methods involve increasing the concrete cover over the rebar (this will increase the material used,

higher cost and low stability), reducing water/cement ratios (it will affect the paste), using denser concrete, using latex or polymer modified concrete overlays (polymers are costly), adding waterproofing membrane with asphalt overlay (increase in technical labour), coating the rebar with epoxy or zinc, protecting the rebar cathodically, and using corrosion inhibiting admixtures. Ideally, a concrete corrosion prevention system would protect the reinforcing steel from the initiation of corrosion for the duration of the structure's service life. Initially, the use of epoxy coatings was thought to be the "ideal" solution for the prevention of rebars corrosion, but the long-term effectiveness of this method is being questioned. The high costs or lack of effectiveness for some of the other methods reveal several advantages for the using corrosion inhibiting admixtures.

1.5 FORMAT OF THESIS

The objective of this testing procedure will be to understand the effectiveness of the corrosion inhibitors when used against the Carbonation-induced corrosion. The thesis has been divided into six chapters:

- 1st chapter is about General introduction, corrosion in R.C. structures, factors affecting corrosion, and its protective measures.
- 2nd chapter explains in detail the causes and mechanism of rebar corrosion. Also a brief description on different types of corrosion is been given and followed by a brief description about corrosion inhibitors.
- 3rd chapter is about the thorough literature review of use of corrosion inhibitors against carbonation induced corrosion.
- 4th chapter deals with the experimental programme wherein all test, procedures and measures that are followed during experiments are explained in detail.
- 5th chapter deals with the results and discussions where findings of experimental programme are discussed.
- 6th chapter is a concluding chapter.

CHAPTER 2 - MECHANISM OF CORROSION

2.1 GENERAL

Corrosion is a process by virtue of which metals tend to achieve the least energy state i.e., the combined state. Corrosion is basically a combination of the oxidation and the reduction processes. Matter in the form of electrons move out of the surface (Reduction) and gets deposited at some other place on the same surface(Oxidation).This is attributed to difference in potential developed on the surface of metal.

$$M \rightarrow M^{2+} + 2e^{-} \text{(Anodic Reaction)} \quad (2.1)$$

$$N^{2-} + 2e \rightarrow N \text{ (Cathodic Reaction)} \quad (2.2)$$

Thus, corrosion is a process that returns the metal to its original form. Steel is primarily made of iron. The natural state of iron is iron oxide, as it exists in iron ore. Iron oxide is the natural state of iron because it is more thermodynamically stable in this form.

2.2 CORROSION

Steel is used in concrete principally as reinforcement. Concrete ordinarily provide an almost ideal environment for protecting steel from corrosion. Its high alkalinity causes the formation of a thin invisible protective passive film of Ferric Oxide (Fe_2O_3) on the steel (thickness approx. 10000 A^0) *(Ashwini K Sinha 2013).* It is expected that when the embedded steel is protected from air by an adequate thick cover of low permeability concrete, the corrosion of steel would not arise. This expectation is not fully met in practice, as is evident from the unusually high frequency with which the Reinforced Concrete & Pre Stressed Concrete structures suffer damage due to steel corrosion. The magnitude of damage is especially large in structures exposed to marine environments. The damage to concrete, resulting from corrosion of embedded

steel, manifests in the form of expansion, cracking and eventually spalling of the cover concrete.

2.2.1 Mechanism of corrosion

The corrosion process that takes place in concrete is electrochemical in nature. Corrosion will result in the flow of electrons between anodic and cathodic sites on the rebar. Concrete, when exposed to wet and dry cycles, has sufficient conductivity to serve as an electrolyte.

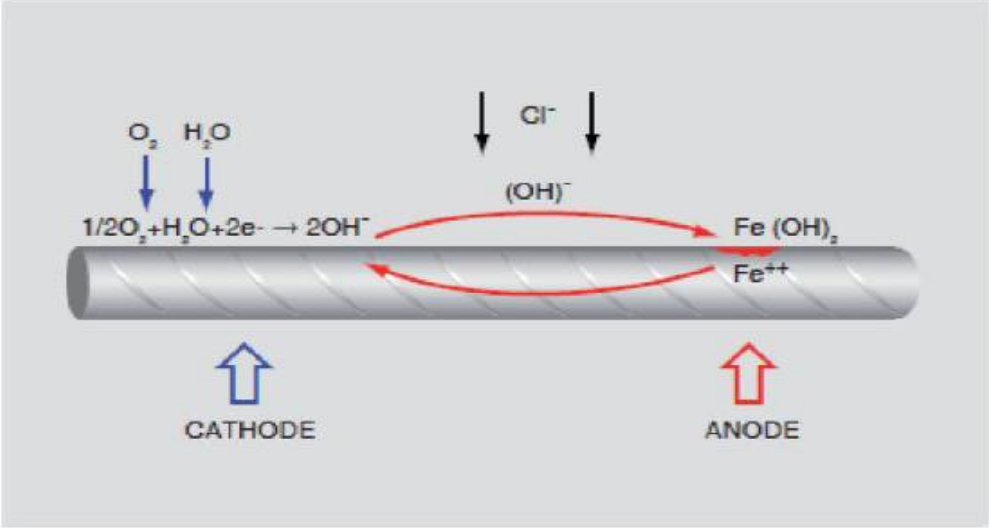

Fig. 2.1 Mechanism of corrosion *(Ashwini K Sinha 2013)*

The corrosion of steel in concrete in the presence of oxygen but without chlorides takes place in several steps:

1. **Corrosion in absence of chlorides**

At the anode, iron is oxidized to the ferrous state and releases electrons

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (2.3)$$

These electrons migrate to the cathode where they combine with water and oxygen to form hydroxyl ions

$$2e^{-} + H_2O + 1/2O_2 \rightarrow 2OH^{-} \qquad (2.4)$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad (2.5)$$

In the presence of water and oxygen, the ferrous hydroxide is further oxidized to form Fe_2O_3

$$4Fe(OH)_2 + O_2 + H_2O \rightarrow 4Fe(OH)_3 \quad (2.6)$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3.2H_2O \quad (2.7)$$

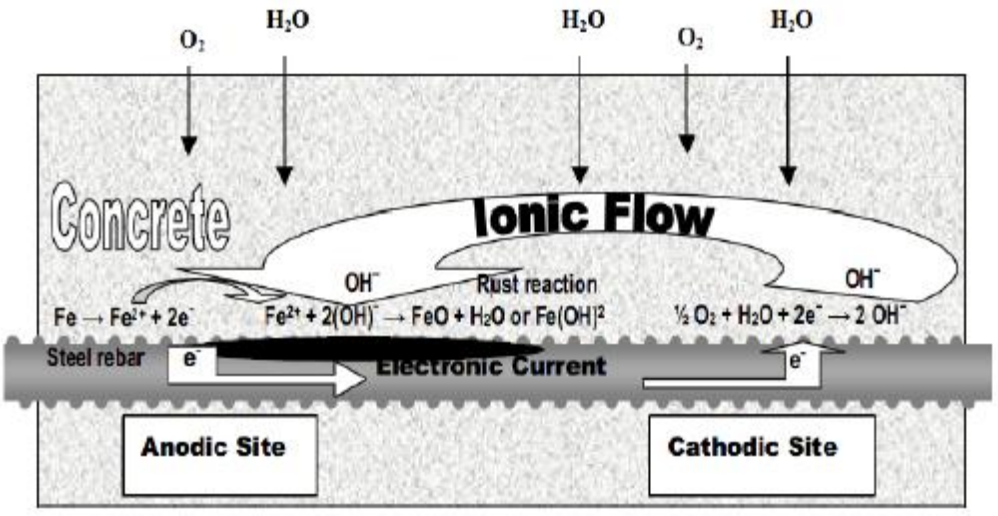

Fig. 2.2 Mechanism of corrosion in absence of chloride *(Ashwini K Sinha 2013)*

2. **Corrosion in presence of Chloride**

   At the anode, iron reacts with chloride ions to form an intermediate soluble iron chloride complex

$$Fe + 2Cl^- \rightarrow (Fe^{2+} + 2Cl^-) + 2e^- \quad (2.7)$$

When the iron–chloride complex diffuses away from the bar to an area with higher pH and concentration of oxygen, it reacts with hydroxyl ions to form $Fe(OH)_2$. This complex reacts with water to form ferrous hydroxide.

$$(Fe^{2+} + 2Cl^-) + 2H_2O + 2e^- \rightarrow Fe(OH)_2 + 2H^+ + 2Cl^- \quad (2.8)$$

The hydrogen ions then combine with electrons to form hydrogen gas

$$2H^+ + 2e^- \rightarrow H_2\uparrow \quad (2.9)$$

As in the case of corrosion of steel without chlorides, the ferrous hydroxide, in the presence of water and oxygen, is further oxidized to form Fe_2O_3

$$4Fe(OH)_2 + O_2 + H_2O \rightarrow 4Fe(OH)_3 \quad (2.10)$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3.2H_2O \quad (2.11)$$

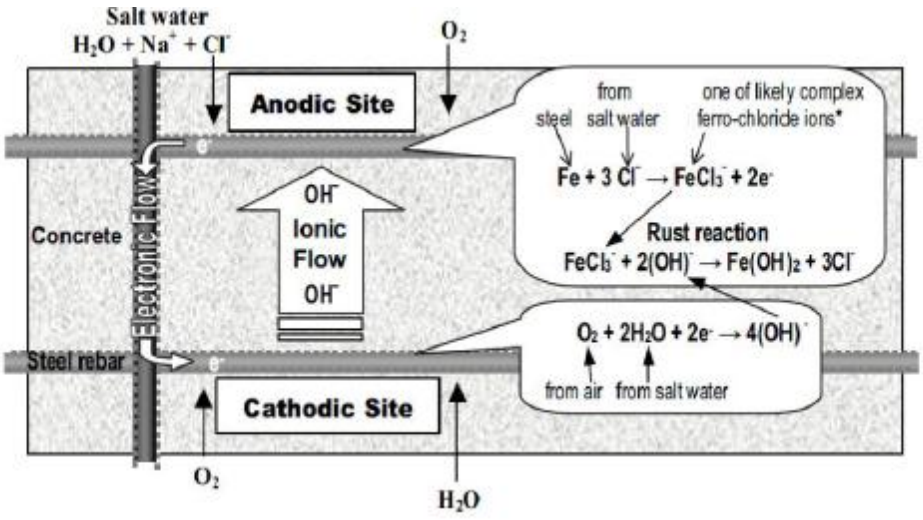

Fig. 2.3 Mechanism of corrosion in presence of chloride ***(Ashwini K Sinha 2013)***

3. Corrosion in presence of CO_2

The corrosion mechanisms of CO_2 and its effects on mild steel under varying conditions of pressure, temperature and pH. Carbon dioxide gas dissolves in water and forms a “weak” carbonic acid through hydration by water;

$$CO_2(g) \rightarrow CO_2 \quad (2.12)$$

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (2.13)$$

The carbonic acid (H_2CO_3) then partially dissociates to form the bicarbonate ion, which can further dissociate to yield the carbonate ion:

$$H_2CO_3 \rightarrow H^+ + HCO^{3-} \quad (2.14)$$

$$HCO^{3-} \rightarrow H^+ + CO^{3-} \quad (2.15)$$

It is widely known that solutions containing H_2CO_3 are more corrosive to mild steel than solutions of strong acids.

2.3 TYPES OF CORROSION

There are several types of corrosion that can occur. All the types of corrosion are identical as for the chemical process of corrosion is concerned. They differ in how and where they attack the metal. The various types of corrosion are enlisted as under.

2.3.1 Uniform Corrosion

Uniform corrosion is characterized by corrosive attack proceeding evenly over the entire surface area, or a large fraction of the area of the metal under attack. Uniform corrosion results in loss of material until failure. This is the most widespread form of corrosion that is observed. This form of corrosion occurs in RCC structures when it is subjected to carbonation induced corrosion due to ions of alkalinity of the whole surface of rebar. The corroded steel railing at the boundary near shore, in marine environment is shown Figure 2.4.

Fig. 2.4 Uniformly corroded steel railing (*Bertolini et al. 2004*)

2.3.2 Pitting Corrosion

Pitting corrosion is a localized form of corrosion by which pits or "pin holes" are produced in the material as shown in Fig. 2.5. Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to predict and design against. Corrosion products often cover the pits making the detection often very difficult. A small, narrow pit with minimal overall metal loss can lead to the

failure of an entire engineering system. This form of corrosion occurs in RCC structures when it is subjected to chloride induced corrosion.

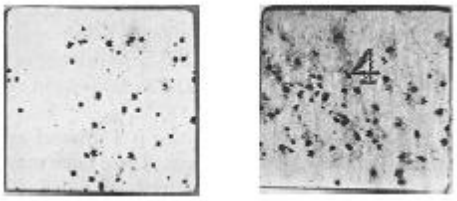

Fig. 2.5 Pin holes formed due Pitting Corrosion *(Goodwin P. D. 2000*)

2.3.3 Crevice corrosion

Crevice corrosion is a localized form of corrosion that occurs in the presence of stagnant solution in a small (micro) crevice. Local chemistry changes in crevices (shielded areas) such as those formed under gaskets, washers, insulation material, fastener heads, surface deposits, disbanded coatings, threads, lap joints and clamps, can result in crevice corrosion. A corroded bolt and screw which were used in a steel structure is shown in Fig. 2.6.

Fig. 2.6 Bolt and screw corroded due to Crevice corrosion *(Autolab application note 16)*

2.3.4 Galvanic Corrosion

Galvanic corrosion refers to corrosion damage induced when two dissimilar materials are coupled in a corrosive electrolyte. It occurs when two (or more) dissimilar metals are brought into electrical contact under water as seen in Fig. 2.7. When a galvanic couple forms, one of the metals in the couple becomes the anode and corrodes faster than it would all by itself, while the other becomes the cathode and corrodes slower than it would alone. Either (or both) metal in the couple may or may not corrode by itself (themselves) in seawater. Galvanic corrosion is more likely to play an important role in a large dimensioned concrete structure.

Fig. 2.7 Galvanic corrosion on a metal washer *(Autolab application note 16)*

2.3.5 Microbiologically Induced Corrosion (MIC)

Microbiologically Induced Corrosion or MIC refers to corrosion caused by biological organisms or microbes. These microbes are categorized by common characteristics such as their by products (i.e., sludge producing) or compounds they effect (i.e. sulfur oxidizing). They all fall into one of two groups based upon their oxygen requirements; one being aerobic (requires oxygen) such as sulfur oxidizing bacteria which is seen in fig. 2.8, and the other being anaerobic, (requires little or no oxygen), such as sulfate reducing bacteria. *(AUTOLAB APPLICATION NOTE 16)*

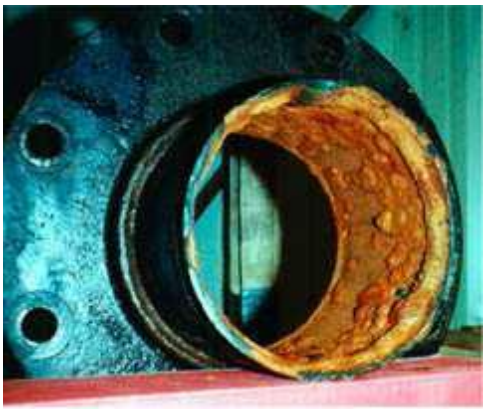

Fig. 2.8 Corrosion on a metal ring due to Sulfur Oxidizing bacteria

2.4 FACTORS AFFECTING CORROSION

The cement paste in concrete is alkaline with a pH typically between 12 and 14. This paste surrounds reinforcing steel in concrete. It is believed that this alkaline environment facilitates the protective passive film around the steel. The passive film is not invulnerable, though. It can be damaged both chemically and mechanically. Some examples of chemical damage of the protective passive film are carbonation and chloride ingress.

Carbonation is the result of the reaction of atmospheric carbon dioxide and hydroxides in the cement paste. Through this reaction, carbonates and water are formed. The carbonates that form from this reaction consume the hydroxides present and therefore can lower the pH of the concrete below the value of 8.0. This action causes the steel to depassivate, leaving it susceptible to attack from corrosives. The likelihood of this occurrence is relative to the impermeability characteristics of the concrete. Adequate depths of the concrete cover for the bars and the use of good quality concrete mixes have greatly reduced the concern for carbonation and its effect on corrosion.

Ingress of chlorides, on the other hand, is far more destructive to the steel. These damaging chlorides are common in concrete environments. They are mainly present in marine environments and in deicing salts, however they can also be due to admixtures containing chlorides and chloride contaminated cements, aggregates, and batch water. Following sectors discussed both forms of corrosion in details.

2.5 CARBONATION-INDUCED CORROSION

One of the major causes of rebar corrosion is due to concrete carbonation. Carbonation-induced corrosion tends to develop later, proceeds at slower rates than chloride-induced corrosion, and leads to uniform steel corrosion that would accelerate the crack formation and decrease the structure's remaining service life.

2.5.1 Carbonation of Concrete

In moist environments, carbon dioxide present in the air forms an acid aqueous solution that can react with the hydrated cement paste and tends to neutralize the alkalinity of concrete (this process is known as carbonation). Also other acid gases present in the atmosphere, such as SO_2, can neutralize the concrete's alkalinity, but their effect is normally limited to the surface of concrete.

The alkaline constituents of concrete are present in the pore liquid mainly as sodium and potassium hydroxides or as solid hydration products, e.g. $Ca(OH)_2$ or C–S–H. Calcium hydroxide is the hydrate in the cement paste that reacts most readily with CO_2. The reaction, that takes place in aqueous solution, can be written schematically as:

$$CO_2 + Ca(OH)_2 \xrightarrow{H2O,NaOH} CaCO_3 + H_2O \qquad (2.12)$$

This is the reaction of main interest, especially for concrete made of Portland cement, even though the carbonation of C–S–H is also possible when $Ca(OH)_2$ becomes depleted, for instance by pozzolanic reaction in concrete made of blended cement .

Carbonation does not cause any damage to the concrete itself, although it may cause the concrete to shrink. Indeed, in the case of concrete obtained with Portland cement, it may even reduce the porosity and lead to an increased strength. *(Lopez et al.2003)*

However, carbonation has important effects on corrosion of embedded steel. The first consequence is that the pH of the pore solution drops from its normal values of pH 13 to 14, to values approaching neutrality. If chlorides are not present in concrete initially, the pore solution following carbonation is composed of almost pure water.

This means that the steel in humid carbonated concrete corrodes as if it was in contact with water. A second consequence of carbonation is that chlorides bound in the form of calcium chloroaluminate hydrates and otherwise bound to hydrated phases may be liberated, making the pore solution even more aggressive. *(Bertolini et al. 2004)*

2.5.2 Penetration of Carbonation

The carbonation reaction starts at the external surface and penetrates into the concrete producing a low pH front. The measurement of the depth of carbonation is normally carried out by spraying an alcoholic solution of phenolphthalein on a freshly broken face. The areas where pH is greater than 9 take on a pinkish color typical of phenolphthalein in a basic environment, while the colour of carbonated areas remains unchanged. *(Tesfamariam et al.2008)*

The rate of carbonation decreases in time, as CO_2 has to diffuse through the pores of the already carbonated outer layer. The penetration in time of carbonation can be described by:

$$d = kt^{1/2} \tag{2.13}$$

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:

$$t_0 = \left[\frac{d}{k}\right]^2 \tag{2.14}$$

The carbonation coefficient K ($mm/y^{1/2}$) can then be assumed as a measure of the rate of penetration of carbonation for given concrete and environmental conditions.

In dense and/or wet concrete, however, the reduction of the carbonation rate with time is stronger than that described by the parabolic formula, so that n > 2; in very impervious concrete the carbonation rate even tends to become negligible after a certain time. *(Tesfamariam et al.2008)*

2.5.3 Factors that Influence the Carbonation Rate

The rate of carbonation depends on both environmental factors (humidity, temperature, concentration of carbon dioxide) and factors related to the concrete (mainly its alkalinity and permeability). Some of the major factors that affect carbonation are:

- **Humidity:** The rate of carbonation varies with humidity of concrete for two reasons. First, as diffusion of carbon dioxide within concrete is facilitated through the aerated pores, but it is very slow through those filled with water (the diffusion of CO_2 in water is four orders of magnitude slower than in air) *(Lopez et al. 2003)*.

The rate of diffusion of CO_2 consequently decreases with an increase in humidity of the concrete until it becomes zero in water-saturated concrete. This means that when the concrete is wet, CO_2 does not penetrate it. On the other hand, the carbonation reaction occurs only in the presence of water so that it becomes negligible in dry concrete.

The carbonation rate, and thus the value of K, will change passing from a wet or humid climate to a dry one. Under conditions of equilibrium with an environment of constant relative humidity, the carbonation rate may be correlated to the humidity of the environment as shown in Figure 2.6. The interval of relative humidity most critical for promoting carbonation is from 60 to 70 %.

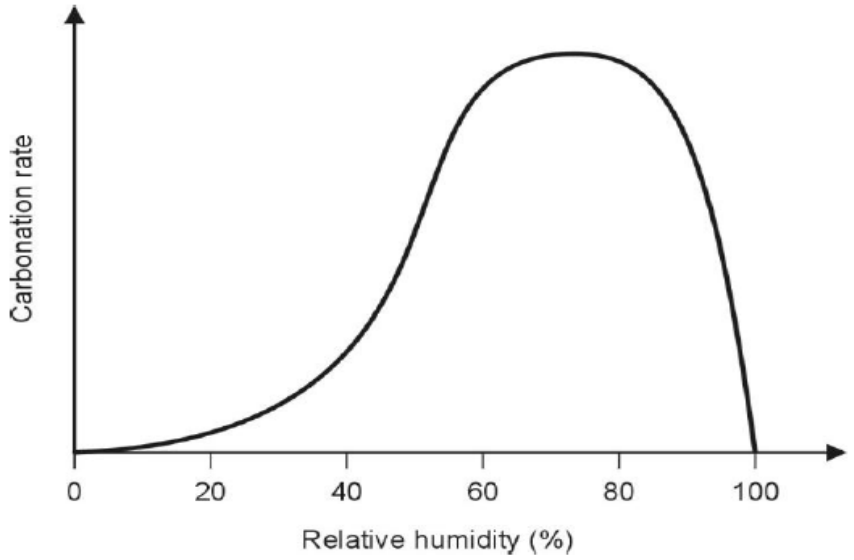

Fig. 2.9 Schematic representation of the rate of carbonation of concrete as a function of the relative humidity of the environment, under equilibrium conditions *(Bertolini et al. 2004)*

- **CO_2 Concentration:** The concentration of carbon dioxide in the atmosphere may vary from 0.03% in rural environments to more than 0.1% in urban environments. Comparatively, high concentrations can be reached under specific exposure conditions, such as inside motor vehicle tunnels. As the CO_2 content in the air increases, the carbonation rate increases. Accelerated tests carried out in the laboratory to compare the resistance to carbonation in different types of concrete show that, indicatively, one week of exposure to an atmosphere containing 4% CO_2 will cause the same penetration of carbonation as a year of exposure to a normal atmosphere *(Bertolini et al. 2004)*. Some researchers suggest that with a high concentration of CO_2 the porosity of carbonated concrete is higher than that obtained by exposure to a natural atmosphere, particularly if the concrete has been made with blended cement or has high cement content.
- **Temperature:** All other conditions being equal, especially that of humidity, which is, in general, the most important single parameter, an increase in temperature will raise the rate of carbonation**.** *(V. S. Ramachandran)*

- **Concrete composition:** The permeability of concrete has a remarkable influence on the diffusion of carbon dioxide and thus on the carbonation rate. A decrease in the w/c ratio, by decreasing the capillary porosity of the hydrated cement paste, slows down the penetration of carbonation. Nevertheless, the advantages of a lower w/c ratio can only be achieved if concrete is properly cured, since poor curing hinders the hydration of the cement paste and leads to a more porous cement matrix. It should be stressed that poor curing will mainly affect the concrete cover, i. e. the part that is aimed at protecting the reinforcement. In fact, the outer layer of concrete is the part most susceptible to evaporation of water (resulting in poor curing).

2.6 Chloride induced corrosion

Steel embedded in hydrating concrete reacts with oxygen to form a thin (~10 nm thick) layer of insoluble ferrous oxide on its surface (so called passivity layer). This layer strongly adheres to the underlying steel and prevents it from any further corrosion as long as the alkalinity of environment remains high (pH>12). Chloride ions, however, react with the ferrous oxide and form a soluble complex which dissolves in the surrounding solution and does not provide any longer protection. The chemical reactions involved are as follows *(Bentur et al. 1997, and Callister 2000).*

Decomposition of passivity layer:

$$Fe^{2+} + 2Cl^- \longrightarrow FeCl_2 \quad \text{(soluble in pore solution)}$$

Corrosion of steel:

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad \text{(oxidation)}$$

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^- \quad \text{(reduction)}$$

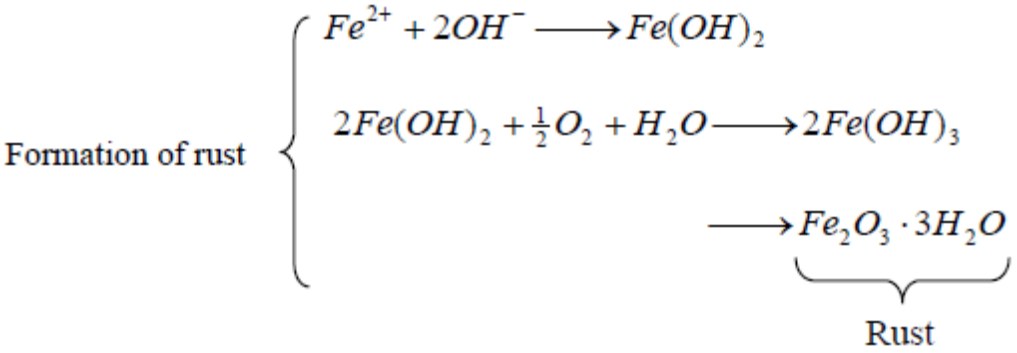

Fig. 2.4 illustrates the process of chloride induced corrosion in reinforced concrete. For corrosion process to continue, the presence of oxygen and moisture are necessary. There will be limited corrosion in dry concrete (i.e., when the relative humidity inside concrete is less than 60 percent), and also in concrete fully immersed in water (due to the lack of oxygen). The relative humidity that is most susceptible for corrosion is between 70 and 80 percent *(Neville 1996)*.

Chlorides in concrete originate from two main sources. Chlorides can be incorporated at the time of mixing, through the use of contaminated aggregate, seawater, or admixtures containing chlorides. In order to restrict the chloride content from this source, standards generally prescribe limits on the use of materials containing chlorides in concrete mixtures. For example ACI 201.2R (2001) limits the total chloride ion content in an exposed reinforced concrete member to 0.1% of the weight of concrete. Chloride ions can also ingress from outside into concrete. There are several situations in which concrete surfaces are in contact with a material containing large amount of chlorides. Examples of such materials are de-icing salt, seawater, and brackish groundwater.

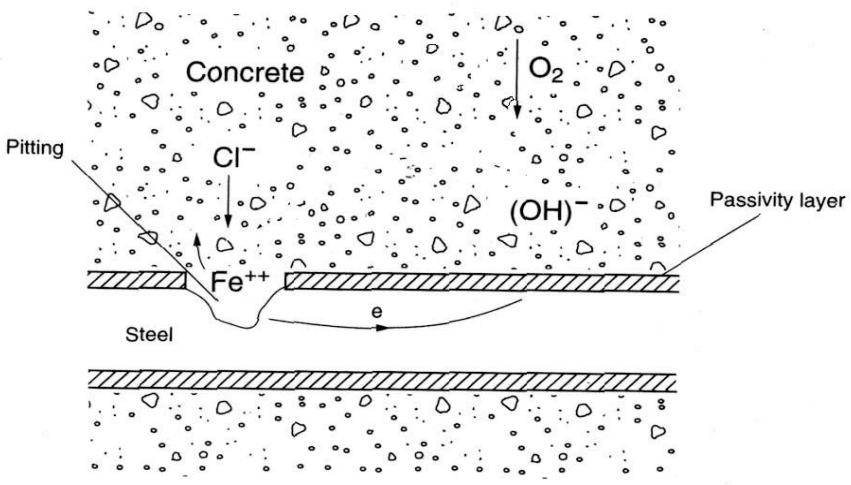

Fig. 2.10 Schematic representation of electro-chemical corrosion in the presence of chlorides (Neville 1996)

2.6.1 Concrete Properties that Influences Its Chloride Penetrability

Concrete is a porous material composed of solid, liquid, and gaseous phases. However, the penetration of chloride ions into concrete can take place only through the liquid phase. As a result, the volume and the geometry of the liquid phase (porosity, size distribution and connectivity of the pores) have strong influence on the rate of chloride penetration. Factors changing the volume and geometry of the pores influence the penetration rate. As an example, high water to cement ratios (w/c) results in a matrix with high porosity which is more susceptible to chloride penetration. During hydration, the liquid phase reacts with cement particles and forms a large volume of solid products. As a result, porosity is consumed through the hydration process and consequently chloride penetrability reduces.

Temperature at the time of casting influences the rate of chloride penetration. High temperatures at very early ages accelerate the process of hydration, resulting in reduced porosity at early ages compared to an identical mixture, which has been cured at a normal temperature. However, high-early temperatures develop internal micro-cracks in concrete and consequently increase penetrability at later ages.

Another important issue is chloride binding capacity of the matrix. All chloride ions do not participate equally in corrosion reactions. A part of these ions react with C_3A to form calcium chloroaluminate and are chemically bound in the cement paste. A number of chloride ions become physically bound, being adsorbed on the surface of capillary pores. Thus only a part of chloride ions are free to react with the passivation layer coating the steel. The C_3A content of the cement influences the binding capacity of the matrix -with increased C_3A content leading to increased binding capacity.

The cement type and cement content of the mixture determine the rate of hydration and the total C_3A content of the mixture and consequently affect penetrability of the matrix.

Air content also alters the resistance against penetration. If air bubbles get filled with pore solution they become conductive paths for chloride ions. However, only entrapped air content can influence the chloride penetration, since entrained bubbles are somewhat stabilized and will rarely get filled with solution.

Pozzolanic materials such as fly ash, blast furnace slag, and silica fume also influence the penetration rate through improvement of the porous microstructure *(Stanish et al.2006)*

2.7 CLOSING REMARKS

This chapter discusses the theory of corrosion mechanism and causes of rebar. The various factors and effect of corrosion process are well discussed. It is concluded that the two most important causes of rebar are the ingress of chloride ions and carbon dioxide to the steel surface.

CHAPTER 3 - CORROSION INHIBITORS

3.1 GENERAL

To minimise the corrosion processes a number of procedures can be assessed. The literature reports several ways to decrease or to prevent reinforcement corrosion. Among them, the use of corrosion inhibitors has been an envisaged solution. An ideal corrosion inhibitor is a chemical which, when added to concrete, can prevent corrosion onset without adverse effects on the mechanical properties of the concrete *(Jamil et al. (2004)*. It is accepted that inhibitors may influence the kinetics of the electrochemical reactions involved in the corrosion process occurring in steel.

3.2 CORROSION INHIBITORS

Corrosion inhibiting admixtures has been used in the industry since 1970's. They provide a level of protection and longevity that would be too difficult to achieve otherwise. Corrosion inhibitors are the materials that are able to reduce the corrosion rate. They are used in relatively small amounts. 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. In general, the effects of an inhibitor are to raise the level of chloride ion necessary to initiate corrosion and to decrease the rate of corrosion even if it starts. Additives which reduce the ingress of chloride ion are not categorized as corrosion inhibitors, yet they may have a corrosion-reducing effect.

The literature review indicated that inhibitors can extend the service life under certain conditions through delay of depassivation and/or reduction of corrosion rate once propagated. The beneficial inhibitor action is thought to be due to a number of factors including the formation of a protective layer on the reinforcement; an increase in the chloride ion threshold necessary to initiate corrosion by binding chloride to the quaternary salt; displacement of chloride ions and other potentially deleterious ions on the reinforcement surface; and gel formation leading to a pore blocking effect. Circumstances of particular relevance to the effectiveness of surface-applied corrosion inhibitors are chloride ion content at the reinforcement; degree of carbonation in chloride-contaminated concrete; the inhibitor to chloride concentration ratio; concrete permeability; and environmental conditions, especially the moisture state, prior to and during application, especially the moisture state.

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.

Thus, there is some controversy regarding the inhibition mechanism. Furthermore, literature is contradictory in what concerns protection efficiency. Some authors *(Elsener (2002)* report that they are not effective when concrete is under immersion conditions, whereas others report that these inhibitors are effective in reducing corrosion rate in concrete contaminated with chlorides *(Maeder (1989).*

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.

3.3 CLASSIFICATION OF INHIBITORS

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. The available inhibitors can be classified into various categories based upon mechanism of protection and mode of application.

3.3.1 Based upon the physical mode of application:

The corrosion inhibitors can be classified into two groups depending on its physical mode of protection as:

I. Admixed inhibitor

II. Migrating inhibitor

I. Admixed inhibitors: Those compounds which are added to the fresh concrete at the time of mixing for new structures are known as admixed inhibitors *(Jamil et al. (2005)*. Admixed inhibitors are commercially available since 1960's *(Soylev et al. (2008).* These compounds are added immediately after the addition of water to cement. Admixed inhibitor influence initial set, later strength gain or other properties i.e. hydration processes of cement. To overcome this, retarder was added to concrete mix which balances the acceleration of the inhibitors and provided a little more retardation.

The inorganic compounds which are based upon calcium nitrite *(Berke et al. (2004)*, sodium 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 also proposed as a admixed inhibitors.

II. Migrating inhibitors: These are the chemical 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 *(Soylev et al. (2008).* According to physical mode of application these types of inhibitors are also known as Surface applied corrosion inhibitors or Penetrating corrosion inhibitors. Use of migrating corrosion inhibitors are proposed in the last 15-20 years and are generally proposed for the repair works.

These inhibitors are typically based either on mixtures of alkanolamines and amines or on inorganic compounds based upon Monofluro-phosphate [MEP] *(Ormellase et al.(2006)*. In addition, nitrite ions can penetrate into concrete by absorption and diffusion if applied to the surface by spraying or ponding with aqueous solutions. Alkanolamines and amines have relatively high vapour pressure under atmospheric conditions, assisting diffusion and migration into concrete. Amino alcohols, such as ethanolamine and dimethylethanolamine, can act at the cathode and prevent oxygen reduction to hydroxyl ion by a blocking mechanism, following adsorbtion on the steel surface *(Gaidis (2004)*.

3.3.2 Based upon the mechanisms of protection:

The corrosion inhibitors based upon protection mechanisms can be classified into three groups as:

I. Anodic inhibitor
II. Cathodic inhibitor
III. Mixed inhibitor

I. Anodic inhibitor: Anodic inhibitors are materials which function as inhibitors due to their ability to accept electrons. They exert their action by stifling the reaction at the anode. Most of the admixtures in this group are effective only when present in sufficiently high concentrations. The concentration required is often determined by the level of chloride to which the steel will be exposed.

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 *(Soylev et al. (2007)*. It functions by oxidizing corrosion product - ferrous ions - to ferric ions that precipitate in the alkaline solution of the concrete and form a protective layer on the reinforcement. The precipitate functions as a film repair because the ferric ions are insoluble in aqueous alkaline solutions and block the transfer of ferrous ions into the electrolyte.

The most commonly used anodic inhibitor is calcium nitrite ($Ca(NO_2)_2$). Sodium nitrite, sodium benzoate and sodium chromate have also been used *(Soylev et al. (2008)*. But when insufficient

quantities of corrosion inhibitors are used, then intensity is localized and causing severe pitting *(Vaysburd et al. (2004).*

II. Cathodic inhibitor: Cathodic inhibitors act either by slowing the cathodic reaction or by selectively precipitating cathodic sites. Materials in this group are strong proton acceptors and their action in contrast to anodic inhibitors is usually indirect. 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 *(Soeda et al. (2003).*

III. Mixed inhibitor: Mixed inhibitors may simultaneously affect both anodic and cathodic processes. A mixed inhibitor is usually more desirable because its effect is all encompassing, covering corrosion resulting from chloride attack as well as that due to microcells on the metal surface. Since microcell corrosion is characterized by microscopic distances separating anodic and cathodic areas, it is impossible to locate either the anodic or cathodic sites on the reinforcement.

It 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 has polar groups such as N, S, OH is effective. Organic polymer compounds such as amine and aminoalcohol (AMA) are also used *(Soeda et al. (2003).*

3.4 MECHANISM OF SOME COMMONLY USED COMMERCIALLY AVAILABLE INHIBITORS:

3.4.1 Calcium nitrites: Nitrites (calcium or sodium salt) are identified as an anodic inhibitors because 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 *(Gaidis J.M (2004)*:

$$2Fe^{2+} + 2OH^- + 2NO^-_2 \rightarrow 2NO + Fe_2O_3 + H_2O \quad (3.1)$$

$$Fe^{2+} + OH^- + NO^-_2 \rightarrow NO + \gamma\text{-}FeOOH \quad (3.2)$$

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). However, full protection depends greatly on the concentration of aggressive ions such as the chloride ion, and severe pitting may occur when insufficient quantity of inhibitor is used compared to the level of chloride in the concrete.

3.4.2 Monofluorophosphate (MFP): The inhibition mechanism of the MFP (Na_2PO_3F) is not clear, it may be anodic, cathodic or mixed *(Alonso et al. (2000).* Na_2PO_3F hydrolyses in aqueous and neutral media to form orthophosphate and fluoride through a process like that indicated in the following equation:

$$Na_2PO_3F + H_2O \rightarrow F^- + H_2PO^-_4 + HPO_4^{-2} \quad (3.3)$$

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, γ Fe_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 Na_2PO_3F. The finding of various research studies confirms this dual effect of the phosphates. *Soylev et al. (2008)* confirm that 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

3.4.3 Amino alcohol based (AMA) inhibitor: In AMA-based organic inhibitor the main component is aminoalcohol, which is the volatile component and aminoalcohol is transported mainly by gas diffusion. The second component is in general an acid component. This acid component is reported to react with hydration products *(Tritthart J. (2003)*. The reaction with calcium hydroxide results in a gel formation that blocks the pores of the concrete *(Soylev et al. (2007).*

3.4.4 Amine ester based: Amine- and ester-based inhibitors have dual actions in concrete as the amine compound acts as an inhibitor whereas the carboxylate ester compound has pore-blocking effect, which blocks the ingress of the chlorides *(Gaidis (2004)*. For Surface applied type amino carboxylates-based inhibitors the pore-blocking effect as a secondary protection mechanism against reinforcement corrosion *(Soylev et al. (2007)*. The esters become hydrolysed by the alkaline mix water to form the carboxylic acid and its corresponding alcohol. The reaction proceeds as shown in Eq. (3.4), where R and R` represent different hydrocarbon molecules:

$$RCOOR`(ester) + OH^- (base) \rightarrow RO_2^- (acid\ anion) + R`OH(alcohol) \quad (3.4)$$

The carboxylic anion is quickly converted in concrete to the insoluble calcium salt of the fatty acid. The created fatty acids and their calcium salts provide a hydrophobic coating within the pores *(Nmai (2004).*

3.4.5 Mixed inhibitor: An organic corrosion inhibitor comprising an aqueous emulsion of ester and amino alcohol is a mixed inhibitor, affecting corrosion through a combination of active and passive mechanisms *(Wombacher et al. (2004)*. A study extending over a decade investigated the active part, a layer-forming amino alcohol which is generally taken to be a cathodic inhibitor. The passive part of the inhibitor mechanism reduces permeability by hydrolysis of an organic ester and deposition of insoluble calcium salts of fatty acid which hydrophobe the concrete pores to reduce ingress of chloride ions.

3.5 CLOSING REMARKS

This chapter has studies the mechanism of working of corrosion inhibitors, various types of corrosion inhibitors and their effectiveness in delaying the rate of corrosion.

CHAPTER 4 - LITERATURE REVIEW

4.1 GENERAL

The problems of corrosion of steel in concrete still exist despite the extensive research conducted over the last 20 years. The numerous factors involved in this type of corrosion instigate a number of studies to help understand the phenomenon and an equal number to bring about its prevention.

4.2 LITERATURE REVIEW ON CORROSION INHIBITOR FOR CARBONATION INDUCED CORROSION

Gulbrandsen et al. (2000) studied the influence of pre-corrosion on the performance of inhibitors for CO_2 corrosion of carbon steel. The tests were performed at 20-50ºC, pH 5, 1 bar CO_2, and 1-3 wt. % NaCl solution. They used generic inhibitor compounds and the test specimens were pre-corroded for six days in the corrosive media prior to the inhibitor addition. They reported results from four different commercial inhibitors and three different steels: X65, St52 and Cr0.5. They concluded that the negative effect of pre-corrosion in ferritic-pearlitic steels could be related to differences in the cathodic reaction inhibition efficiency on cementite and on ferrite.

Nmai (2004) discussed the multi-functional benefits of water-based organic corrosion inhibitor in context to the corrosion protection of embedded steel and resistance to chemical attack; specifically, the resistance of concrete to sulphate attack and deterioration due to sulphuric acid exposure. The multi-functional organic corrosion inhibitor (MFOI) consists of amines and fatty-acid esters and the mechanism by which it functions were presented and substantiated. In addition to a 30% of calcium nitrite inhibitor, this amine-ester based organic corrosion inhibitor was found to be a commonly used corrosion inhibitor in new construction. Time-to-corrosion evaluations in moderate and high quality concrete materials with w/c ratio of 0.50 and 0.40 respectively showed that the inhibitor was effective regardless of concrete quality, and significantly reduced chloride ingress. The permeability reducing

property of the amine ester based organic corrosion inhibitor showed effectiveness in reducing deterioration due to the ingress of other aggressive species such as sulfate and sulfuric acid. For comparison purposes, the corrosion inhibiting performance of the amine-ester based organic inhibitor was compared to that of calcium nitrite, while its effect in mitigating sulfate attack and reducing deterioration due to sulfuric acid exposure was compared to that of silica fume.

Trabanelli et al. (2005) made a synthetic solution (SS) by bubbling pure CO_2 in a saturated $Ca(OH)_2$ solution till obtaining pH 7 and then filtering it for electrochemical study on inhibitors of rebar corrosion in carbonated concrete. And concrete carbonation has been obtained by maintaining the concrete specimens in CO_2 atmosphere for 80 days, at 68% RH and room temperature. In SS, benzoate, its amino-derivatives and dicarboxylates were able to form a long-lasting passive layer on the steel surface. Their efficiency improved with time.

Then he find that after 1 h immersion, specimen omitting the very high frequency arc due to the low solution conductance, EIS spectrum of steel exhibited a single capacitive semicircle in the 10^3– 10^2 frequency range (Fig. 4.1), showing that the corrosion process was mainly charge-transfer controlled at short immersion times.

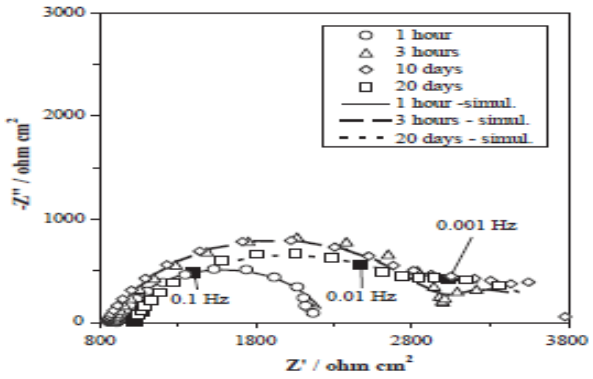

Fig. 4.1 Experimental and simulated EIS spectra recorded in uninhibited SS at different immersion times. The frequencies indicated refer to the 20 day spectrum. ***(Trabanelli et al. 2005)***

Among the additives tested as admixed inhibitors in carbonated concrete, only BEN (benzoic acid) and 2AMB (2-amino benzoic acid) exhibited some inhibitive effect

towards the rebar corrosion process. However, in BEN-containing concrete specimens no inhibitive action was maintained till 400 days of exposure, while in the presence of 2AMB inhibiting efficiencies around 60% were still measured at the end of the test. The inhibitor leakage is reputed responsible of the decrease with time in the inhibiting efficiency of both additives.

Heiyantuduwa et al. (2006) study of a penetrating corrosion inhibitor in terms of its effectiveness in controlling 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. Specimens were demoulded after 24 h and wet cured at 23°C for six days, followed by 21 days curing in air at 23°C and 68% relative humidity .Concrete test specimens were blocks of size 120 mm X120 mm X 380 mm, with each specimen containing a 16 mm high tensile ribbed steel reinforcing bar longitudinally at the centre, at nominal covers of 10 or 20 mm. A single reinforcing bar was used in each block to simplify casting, processing, and measurement. Each group of six had two control specimens, two specimens that were treated with the penetrating inhibitor before the carbonation process, and two specimens that were treated with the penetrating inhibitor after the carbonation process.

Three different wet and dry cycles were used in an attempt to get steady corrosion rates. The first regime was found to be too wet and stifled corrosion by limiting the availability of oxygen at the cathode. It was discontinued after 28 and 13 cycles for covers of 10 and 20 mm, respectively. The second regime was discontinued after a further 10 cycles. The third regime provided relatively stable corrosion conditions and was continued to the end of corrosion monitoring. Corrosion rate measurement was done using a linear polarization resistance technique with a guard ring sensor. Corrosion rate measurements were taken at three points on each of the two areas on the site. At each of these points maximum negative potentials were occurring, indicating that corrosion was likely to be highest at these points. Testing was carried out twice a week, on consecutive days, in order to obtain consistent results. The corrosion inhibitor penetrated into carbonated and uncarbonated concrete to at least 30

mm depth within 28 days. The results, however, indicate that the penetration and retention are dependent on the grade and, hence, the pore structure of concrete. Penetration was most effective in Grade 30 concrete where sufficient amounts of inhibitor were present at all depths up to 60 mm; for the higher Grades 40 and 50 concretes the penetration rate or the inhibitor was not as high as in the Grade 30 concrete due to their denser microstructure. Penetration of the inhibitor may, therefore, be slow in higher grades of concrete and concrete with low porosity. The penetrating corrosion inhibitor was effective in delaying the onset of corrosion as shown by specimens treated with inhibitor before carbonation. Laboratory findings indicate that the application of the penetrating corrosion inhibitor prior to carbonation delayed the onset of carbonation-induced corrosion, and after 50 wetting and drying cycles, corrosion rates were at passive.

Lopez et al. (2003) studied the influence of microstructure on inhibitor performance. Using electrochemical measurements, they evaluated the effect of the addition of 100 ppm of benzimidazole on the corrosion layers for two different microstructures. The presence of the inhibitor improved the corrosion resistance for the annealed samples, while for the Q and T samples, the opposite effect is observed, despite benzimidazole not being particularly efficient in the experimental conditions studied.

The author concluded that the microstructure of steel influences inhibitor efficiency, the properties of the corrosion layers, such as morphology, and the quantity of the various chemical compounds that are present. Having studied two steel compositions with the same microstructures and keeping the experimental conditions constant, *Lopez* demonstrated that not only the molecular structure of the inhibitor molecule is important when determining its performance in chloride media containing deoxygenated CO_2, but also the microstructure of the steel to be used as the working material. Also in his study, he concluded that the presence of a long hydrocarbon chain with hydrophobic properties could be linked with the formation of a protective, yet porous, film that reduces thoroughly the corrosion process.

Monticelli et al. (2011) have studied about two corrosion inhibitors, that is sodium 2-amino-benzoate (2AMB) and sodium glycero-phosphate (GPH), in a synthetic solution

simulating the composition of the pore solution in a carbonated concrete, containing chlorides. Tests have been performed to verify if the simultaneous use of the two substances is compatible and if their addition can efficiently hinder the corrosion attack in the presence of both chlorides and carbonation. The synthetic solution has been prepared by bubbling carbon dioxide through a saturated (and filtered) solution of $Ca(OH)_2$, containing 0.1M NaCl, in order to reach pH 7. He prepared ribbed AISI 1033 type steel bars of 10mm diameter, commercialized as concrete reinforcement (composition: C=0.31%; Mn=0.94%; Cr=0.26%; Ni=0.19%; Cu=0.50%; Si=0.14%; Co=0.02%; Al=0.04%; S=0.03%; balance iron) with exposed surface area of 4.5 cm^2. These electrodes are exposed to the test solutions after grinding by emery papers up to grade 600, washing with double distilled water and degreasing with acetone.

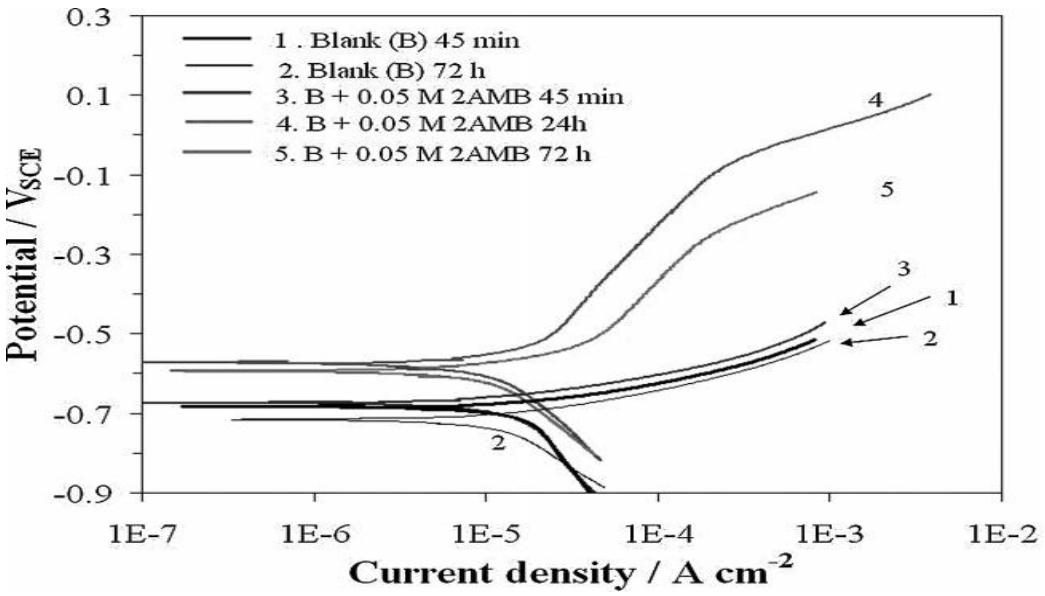

Fig. 4.2. Polarization curves recorded on steel in carbonated chloride solution, both in the absence and in the presence of 0.05M 2AMB*(Monticelli et al. (2011)*

From this experiment he conclude that in carbonated chloride-containing solution (from here on the blank solution) no significant variation of steel corrosion behaviour is achieved by prolonging the immersion period from 45 min up to 72 h. This suggests that the corrosion product film growing on the metal surface is not protective. At the end of the immersion period, I_{CORR} is close to 1.2 x 10^{-5} A/cm^2, as estimated by the Tafel method by extrapolation of the cathodic polarization curve.

The addition of 0.05M 2AMB to the blank solution affords no inhibiting effect on the corrosion process after 45 min of immersion (Fig. 4.2). However, after 24 h of immersion E_{COR} is ennobled up to -0.58 VSCE, owing to the increase in the slope of the anodic polarization curve, likely due to the formation of a surface film. The protectiveness of this film is scarce (as suggested by the measured I_{COR} values which are only slightly lower than those measured in the blank solution) and diminishes with time, as the anodic curve shifts again towards higher current densities, at the end of 72 h immersion (Fig. 4.2).

Polarization curve recording and EIS technique have shown that the mixture inhibiting action develops slowly within 24 h, during which a surface porous film forms with a higher pore resistance and particularly a higher mass transport resistance with respect to those evaluated in the blank solution. The polarization curve analysis suggests that diffusion of Fe_2^+ cations from the metal surface to the aggressive solution may be the mass transport process controlling the steel corrosion rate in inhibited solutions.

4.3 LITERATURE REVIEW ON EFFICIENCY OF CORROSION INHIBITOR

Trepanier (1994) used 2-inch diameter lollipop mortar specimens and also ASTM G-109 concrete slab specimens for evaluating four commercial concrete inhibitors. The lollipops were constantly submerged in 3.5% NaCl solution to approximately mid-height of the specimens, and the slabs were treated per ASTM G-109 procedures. Half cell potentials, linear polarization, and AC impedance methods were used to monitor the lollipops whereas the slabs were monitored using macro-cell current measurements. All four of the corrosion inhibitors delayed the initiation of corrosion to some degree. However, none of them completely prevented the corrosion from occurring. The performance of the inhibitors was indirectly proportional to the water/cement ratio. The effectiveness of the inhibitors increased as the w/c ratio decreased. The results from both the AC impedance and linear polarization measurements were comparable. After nearly one year of cyclic ponding only the control specimens of the ASTM G-109 slabs were actively corroding, which had

initiated after 271 days. From this it was evident that a considerable amount of time was needed in order to obtain any results from this type of test.

Though this form of testing is not quick to produce results, it is felt that the evaluation of corrosion inhibitors should be conducted using concrete specimens representative of real world conditions.

Chaussadent et al. (2005) presented some key aspects on the use of monofluorophosphate (MFP) as a corrosion inhibitor for concrete reinforcements. The corrosion inhibitor applied to the concrete surface, was intended to diffuse into the concrete in order to reach the reinforcement and stop or delay corrosion. The experimental work involved studying the chemical interactions taking place between MFP and calcium ions, when the portlandite $Ca(OH)_2$ is present but not in the presence of other Ca-containing compounds such as calcium carbonate $CaCO_3$. When portlandite was present, the interaction led to the formation of fluoroapatite, which then limited penetration of MFP into the concrete. The difficulty of penetration of MFP into non-carbonated concrete and thus inhibiting the corrosion process was confirmed by corrosion potential measurements on steel in mortars during the 48 h following MFP application on the mortar surface. In the case of a carbonated cementitious material, MFP was able to penetrate. Under laboratory conditions, chemical analyses on carbonated cement pastes showed that MFP ions could reach a depth of 40 mm. Electrochemical measurements performed on steel in carbonated mortars confirmed this level of penetration and showed that when MFP ions reach the steel surface, they become effective in improving steel protection.

Felhosi et al. (1999) investigated the influence of calcium and zinc ions on the corrosion inhibition of 1-hydroxyethane-1,1-diphosphonic acid (HEDP) on carbon steel. They related the increasing in the inhibition efficiency of HEDP to the formation of different complexes species with the cation additives. They found that the molar ratio play an important role in the formation of protective complexes and reported that zinc ions have a better effect on the inhibition efficiency of HEDP. *Turgoose et al. (1997)* supported the results obtained by *Felhozi et.al (1996)* they studied the effect of calcium and zinc ions on the effectiveness of 1-

hydroxyethylidene-1,1-diphosphonic acid (HEDP) on the inhibition of mild steel corrosion. They reported that zinc-HEDP mixture give effective inhibition, at a molar ratio 2:1 of zinc- HEDP. Addition of calcium showed some inhibition for the corrosion of mild steel, but it is much lower than that for zinc. This is attributed by the authors to the low stability of calcium complexes compared with ferrous complexes, which facilitates the displacement of calcium ions from their complexes by ferrous ions forming soluble un-protective ferrous complexes. *Gomma (1993)* suggested that addition of copper cations to the benzotriazole reduced the corrosion rate of steel in 0.1 M H_2SO_4, due to the co-adsorption process. *Gaur et al. (1995)* investigated the effect of the cations (Cu^{2+} As^{3+} Sb^{3+} and Sn^{2+}) on the inhibition of steel by hexamine in hydrochloric acid solution. They attributed the positive role of the cations on the inhibitive performance of hexamine to the formation of anion complexes with chloride ions of acid solution. These anions replace the adsorbed chloride ions from the metal-electrolyte interface owing to their higher affinity toward the interface and help the protonized molecules of hexamine to be adsorbed more strongly at the interface. *Telegdi et al. (1989)* demonstrated that bivalent cations (Ba^{2+}, Sr^{2+}, Ca^{2+} and Zn^{2+}) synergically improved the inhibition efficiency of amino-phosphoric acid. They found that the addition of zinc ions influenced both anodic and cathodic process, while the rest of cations hindered the anodic iron dissolution. *Pech-caul (1990)* reported that the N-phosphono-methyl-glycine/ Zn^{2+} mixture inhibited steel corrosion in neutral chloride solutions by retardation of both the anodic dissolution and oxygen reduction reactions. *Venkatachari (1997)* related the enhanced inhibition performance of polyaniline in the presence of cerium ions to the formation of metal-amine complexes, with more quinoid moiety which facilitate strong adsorption and higher coverage on iron surface. *Gomma et al (1992)* attributed the corrosion inhibition of oxalic to the adsorption of a stable Fe/oxalate complex having the formula FeL2, where L is an acid ligand.

Monticelli et al. (2000) have studied the inhibiting behavior of many organic and inorganic substances against steel corrosion was evaluated in an alkaline chloride solution, constituted by a saturated calcium hydroxide solution containing 0.1 M chloride ions. Besides 0.05 M sodium nitrite (SN), among the tested substances, only

0.005 M 5-hexyl-benzotriazole (C6BTA), 0.05 M sodium b-glycerophosphate (GPH), and saturated dicyclohexylammonium nitrite (DCHAMN) were able to prevent pitting corrosion over 30-day exposures to the aggressive electrolyte. Moreover, very good results were obtained with steel specimens coated by DINITROL AV 301, which is a commercial corrosion inhibitive filming product. Chloride polluted mortars embedding steel rods were also prepared to assess the influence of the most promising inhibitors, added either as admixtures or as impregnation agents, under conditions closer to those experienced in concrete. The inhibiting efficiencies (IE) were tested by Electrochemical Impedance Spectroscopy (EIS). Good results were obtained with admixed tungstosilicic acid (TSAH), with GPH or DCHAMN penetrated from the outside or in the presence of DINITROL AV 301 coating.

Specimens were cut from AISI 1033 rods (chemical composition: C=0.3%; S=0.03%; P<0.01%; Si=0.04%; Mn=0.96%; Ni=0.2%; Cu=0.02%; Al=0.07%; balance Fe), used as concrete reinforcement. Cylinders with exposed area about 4.5 cm^2, for electrochemical tests in simulated concrete pore solutions. Preliminary tests were carried out in a saturated calcium hydroxide solution containing a chloride concentration of 0.1 M. The solution was filtered to avoid solid suspension and showed a pH value of about 13.

A rapid screening test based on anodic polarization curverecording is a useful tool to select candidate inhibitors of steel corrosion during 30-day immersions in alkaline chloride solutions.

Among the promising substances, only 0.05 M SN, 0.005 M C6BTA, 0.05 M GPH, and sat. DCHAMN are able to keep the inhibiting action throughout the exposure. Very good results are also obtained with steel specimens coated by DINITROL AV 301. Tests carried out in chloride-polluted mortars after 1 year of curing show that a good inhibiting action is achieved with admixed TSAH (IE% 62) or in the presence of the protective coating DINITROL AV 301 (IE%>74). Preliminary results obtained after 6 months of exposure to chloridepolluted mortars give IE% of 88 or 90 with GPH- or DCHAMN-impregnated mortars, respectively.

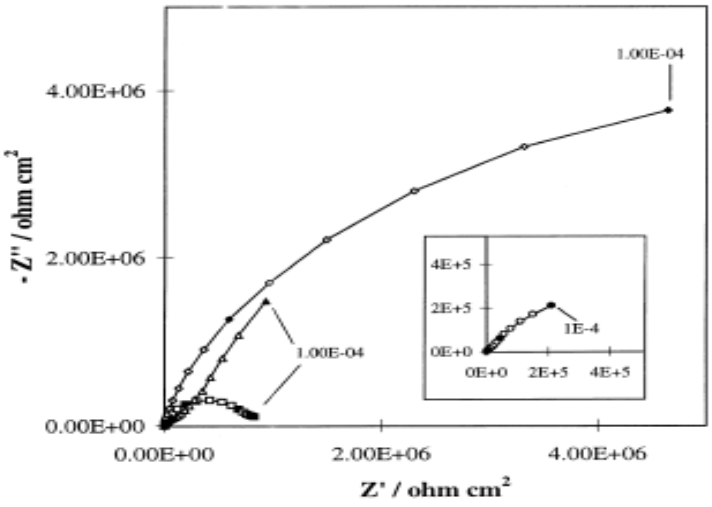

Fig. 4.3 Impedance spectra obtained in m.t. 10 (dots, in the insert), 11 (diamonds), 12 (triangles), and 13 (squares). The solid symbols refer to integer frequency decades. ***(Monticelli et.al 2000)***

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. 4.4 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.

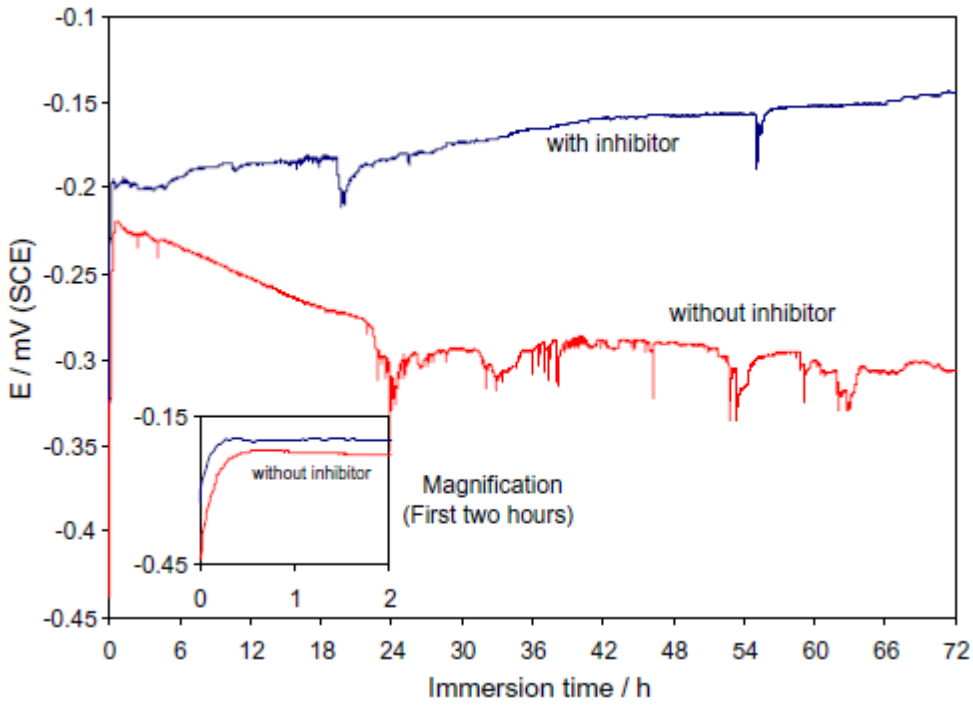

Fig. 4.4 Open circuit potential for the systems with and without inhibitor. ***(Jamil et al., 2005)***

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. 4.5. 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.

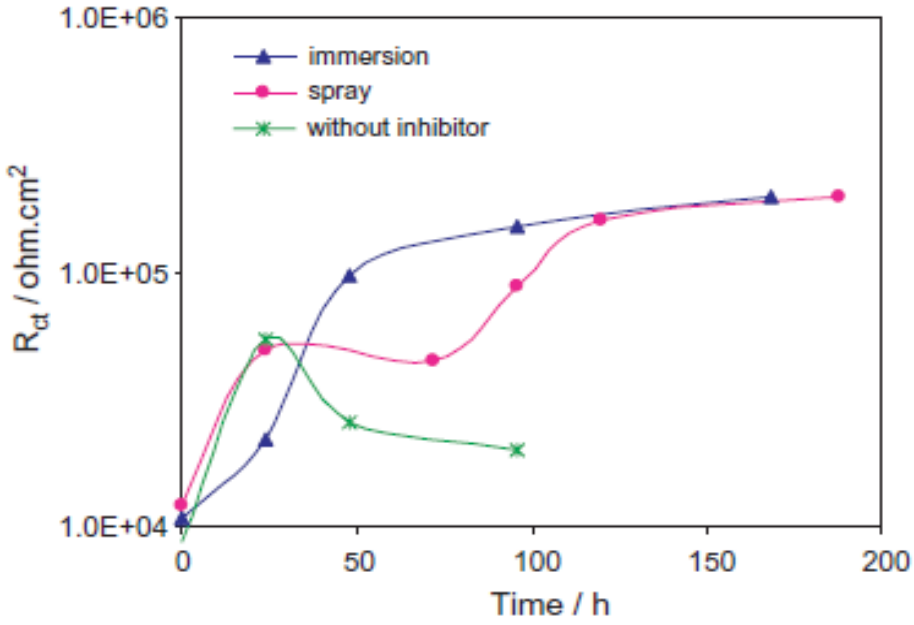

Fig. 4.5 Charge transfer resistance for steel samples. Different application procedure using mortar specimens with 1cm. ***(Jamil et al., 2005)***

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 RP (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 RP values in the 1000 to 2000 ohm range. For non-treated samples (controls), the RP value ended at 3170 ohms for low density samples and 1200 ohms for high density concrete. Changes in the RP 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. (2004) used an extract solution that was obtained from a cement mix having a water/cement ratio of 0.5. The composition of the extract solution is depicted in Table 4.1. The pH of the solution was between 12.5 and 13.

Table 4.1 Composition of the extract solution

Composition	CaO	SO_4^{2-}	Na_2O	K_2O	Fe_2O_3	$PO4^{3-}$	Cl^-	F^-	Mg^{2+}
Content (ppm)	841	6642	1022	8586	806	6.62	330	3.44	<2

Sodium chloride in the concentration of 2 g/l was added to the extract solutions. The corrosion inhibitors (Ferrogard 901®—preventive inhibitor and Ferrogard 903®—curative inhibitor) were added to the solution in the concentration of 4% (v/v).

On that specimen he performed Electrochemical impedance spectroscopy using a three electrodes arrangement, a frequency response analyser and an electrochemical interface from Solartron. The frequency range was swept between 50 kHz and 0.05 mHz. All the experiments were conducted at the corrosion potential. For presentation purposes the values of the phase angle were corrected to positive values.

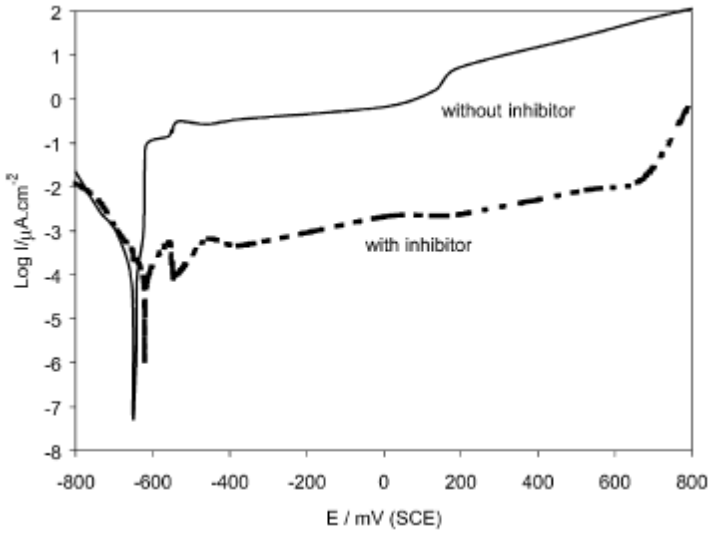

Fig 4.6 Potentiodynamic polarisation curves for samples immersed in the working solution contaminated with 2 g/l of NaCl with and without preventive inhibitor addition. ***(Jamil et al. 2004)***

The electrochemical behaviour of the surface was studied by potentiodynamic polarisation. Figure 1 depicts the polarization curves obtained in the working solution

contaminated with chlorides with and without preventive inhibitor addition. The presence of inhibitor decreases the anodic currents by about four orders of magnitude, revealing that the anodic reactions are strongly hindered. The observation of the cathodic branch does not show evidence of cathodic inhibition. This result shows that the preventive inhibitor acts essentially as an anodic inhibitor.

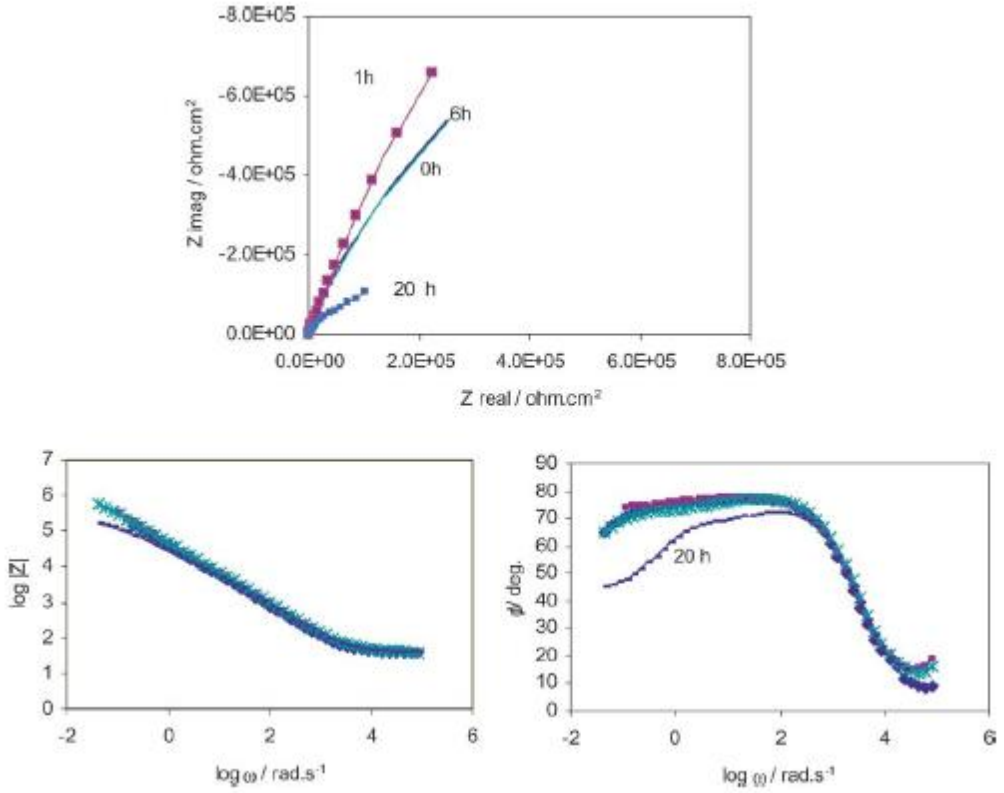

Fig. 4.7 Impedance spectra obtained for the control samples immersed in the working solution contaminated with 2 g/l of NaCl. ***(Jamil et al. 2004)***

The inhibition effect of the preventive inhibitor was also investigated by the use of electrochemical impedance spectroscopy (EIS). Figure 2 depicts the impedance spectra obtained on a sample immersed in a solution containing 2 g/l of NaCl without inhibitor addition after different immersion times. Initially there is a slight increase of the impedance values, probably due to the presence of a passive film, which spontaneously forms on the iron surface as consequence of the alkaline pH of the solution. However, later there is a decrease of about one order of magnitude in the total impedance values, revealing an increase of the corrosion rate.

Dhouibi et al. (2001) studied about the application of electrochemical impedance spectroscopy to determine the long-term effectiveness of corrosion inhibitors for steel in concrete. For this experiment he used prisms specimen of dimension 40 x 40 x 160 mm^3. Reinforcement with a cylindrical plain carbon steel (C = 0:22%) bar, 6.5 mm in diameter and 120 mm long. Brushing, before being placed in concrete mould cleaned it. A copper wire was welded in its middle for connecting it to the electric circuit. This weld and the sides of the rebar were protected with epoxy resin. Concrete cover was about 20 mm.

After the experiment he find that 1 year immersed specimen in calcium nitrate based inhibitor decreases the solubility of some cement components in the vicinity of reinforcing steel. Then the resistivity of concrete cover is increased and the corrosion rate is lowered. When the immersion exceeds 1 year, the effect of this inhibitor vanished, and steel corrosion rate increased in chloride solution.

Alkanolamine based inhibitor increases the resistivity of concrete cover but it seems to be aged or to flow out of the concrete after a long time immersion. This inhibitor forms an unstable interfacial layer on steel surface which is able to keep the interface under a passive state and consequently the corrosion intensity decreases. However, when concrete is contaminated by chloride, the efficiency of this layer is lowered and corrosion occurs.

Loto et al. (2012) performed a test on Type 316 austenitic stainless steel with the different concentrations (the intermediate and the concentrated) of sulphuric acid, H_2SO_4, and phosphoric acid, H_3PO_4. Similar tests were also performed by the addition of 2% (20g/l) sodium chloride, NaCl, to each of the specified acid concentrations to form their acid chlorides. Potentiostatic polarization method was used for the corrosion investigation on the specimen of Austenitic stainless steel –SS316 in cylindrical form (10mm dia and 10mm long) with mounted in araldite resin and connected with a flexible wire connection, ground and polished to fine diamond (1μm), cleaned and rinsed/degreased in an ultrasonic bath using acetone. The samples were immediately kept in a desiccator for subsequent corrosion experimental studies.

The electrochemical corrosion reactions exhibited both the passive and active corrosion reactions characteristics.

In the test of 9.1M H_2SO_4 observe that the corrosion rate is 2.09 x 10-5 mm/yr and the corrosion polarization resistance (Rρ) is -3.8 x $10^{-7}\Omega$. The corrosion current density of 5 x 10^{-6} A/cm^2 was low and the corrosion current is 3.56 x 10^{-7}A which was also very low. All these results data confirmed the corrosion of the test specimen in H_2SO_4 to be very low. But with the addition of 20g/l NaCl to the acid environment. The results obtained here were quite different from H_2SO_4. There was increased corrosion rate 4.84 x 10^{-2} (mm/yr) and the E_{corr} (OCP) of -0.380V. The polarization resistance value was -2.3 x 10^{-5} and with a corrosion density of 1.2 x10^{-4} A/cm^2. The corrosion current recorded was 8.25 x 10^{-5} A. Comparatively these corrosion reactions data indicated more corrosion occurrence than in the environment without NaCl.

The corrosion polarization behaviour for the tests performed in phosphoric acid, H_3PO_4, also showed active corrosion reactions behaviour at all the used concentrations (7.4M; 42.5% and 14.8M; 85%). The addition of NaCl gave less corrosion resistance of the test electrode as indicated by the obtained results data

4.4 CLOSING REMARKS

This chapter presents the literature survey on corrosion inhibitors used to delay the rate of carbonated induced corrosion in reinforcement. It is observed that lots of work needs to be done on corrosion inhibitors since their full mechanism is yet to be understood.

CHAPTER 5 - EXPERIMENTAL PROGRAM

5.1 GENERAL

In this chapter, the experimental setup is presented to evaluate the performance of various corrosion inhibitors to mitigate the carbonation induced corrosion in steel. Various corrosion monitoring devices used are OCP, Long term LPR sweep test. The experimental setup and the corrosion monitoring devices are discussed in the following sections.

5.2 MATERIALS

In order to conduct the experiment, the only materials used were HYSD steel, inhibitors and Epoxy. The various properties of the materials used in the study are as follows.

5.2.1 Steel rebar

HYSD steel bars of 12mm diameter and 60 mm in length are used for studying the efficiency of various corrosion inhibitors. The various properties of steel bar used are:

Table 5.1 Properties of steel bar

Type and size of bar	Ultimate tensile stress(MPa)	Yield stress (MPa)	Youngs modulus	Percentage elogation
HYSD,12mm	443.23	238.2	415	20

5.2.2 Inhibitors

Corrosion inhibitor is basically a chemical compound, which when added to a liquid or a gas, decreases the rate of corrosion in the metals. Here, various types of corrosion inhibitors are used in order to decrease the rate of corrosion in HYSD steel. Some of the corrosion inhibitors are available in the market with their brand names. Their chemical properties are provided by the company. However the chemical composition

is not disclosed. Along with the commercially available corrosion inhibitors, some of the chemicals which have potential to be used as corrosion inhibitor (based on previous studies for Cl^- induced corrosion) are also selected. The list of the corrosion inhibitors is shown in the Table 5.2.

Table 5.2 – Physical properties of Inhibitors

Inhibitor	Colour	Specific Gravity	Active content	flash point	Shelf life
Duracorobit – 60	Clean (amber)	0.96	100%	39^0C	12 month
Duracorobit –750	Colourless	0.88 ± 0.02	100%	39^0C	15 month
Kem corpro 710	Light	0.85	98%	43^0C	12 month
Kem corpro M810	Colourless	0.98 ± 0.02	100%	41^0C	18 month
Sikko	Light yellow	1.08	100%	49^0C	12 month

5.2.3 Epoxy

Fevilite Rapid is a two component multipurpose epoxy adhesive. It contains resin and hardner which are mixed in the ratio of 1:1 few seconds before its used. In this experiment, it is used to prevent some **portion** of steel from chemical reaction with the corrosion inhibitor.

5.3 PREPARATION AND PRECONDITIONING OF STEEL SPECIMENS

Steel specimens were cut to the required length of 60mm were drilled and threaded at one end according to the requirement of the electrochemical cell and the test. The diameter of drill was 2.5mm for Type 1 test and 3mm for Type 2 test. The line diagram of the specimen is shown in Fig. 5.1. Each specimen was then rubbed by wire brush to remove any rust present on the surface. They were then cleaned by soaking in analytical reagent grade hexane and allowed to air dry. The specimen in Type 1 was coated with one layer of epoxy (A-1, pidilite), leaving the 4mm height at the bottom that was exposed to corrosion later. Similarly the specimens for Type 2 test were coated with two layers of epoxy. The resulting specimens after epoxy coating are kept

for 24 hours. Plate 5.1 shows the specimens ready for experiment after coating. By this process total 8 numbers of steel specimens were prepared for Type 1 test and 7 specimens prepared for Type 2 test. For Type 2 test, a nut was screwed with two bolts for attaching the working electrode with the help of copper wire.

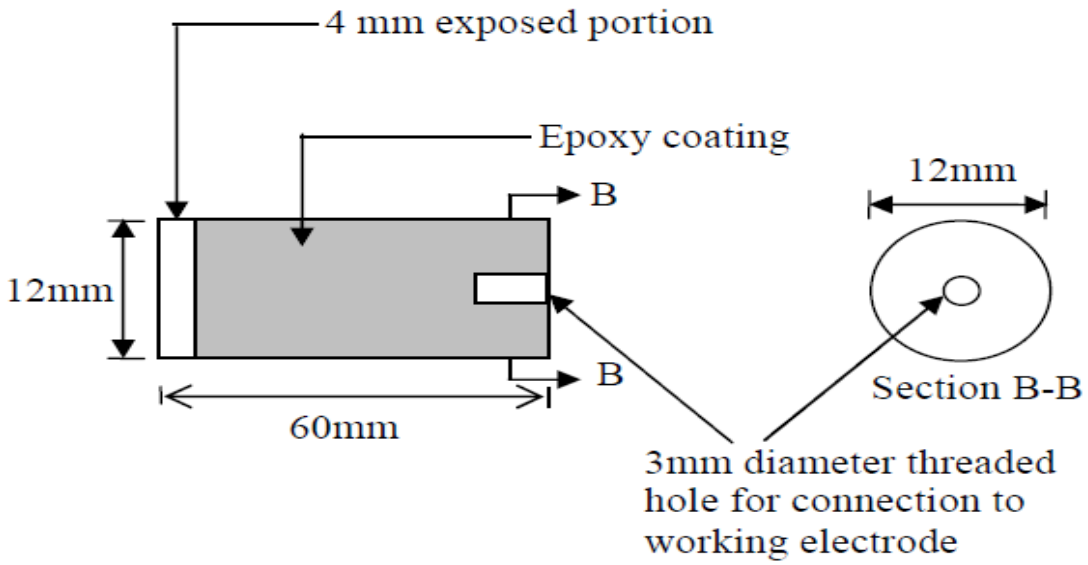

Fig. 5.1 - Line diagram of bare steel specimen

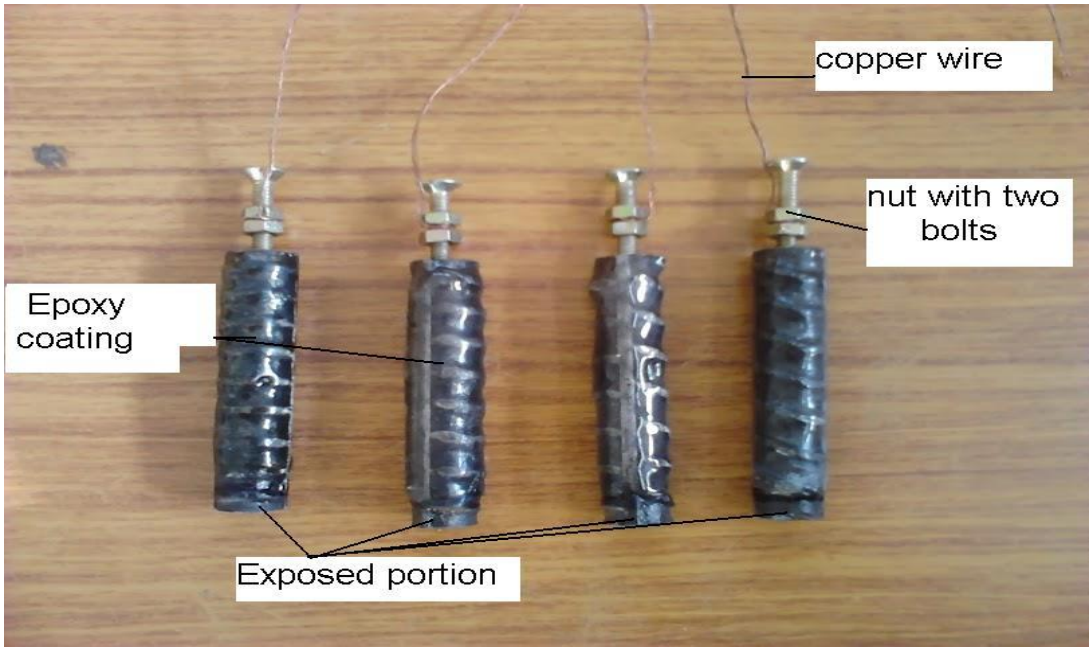

Plate 5.1 – Steel specimens with epoxy coating

5.4 PREPARATION OF $Ca(OH)_2$ SOLUTION.

To simulate an environment of concentrated pore solution with pH range from 12-13, saturated solution of $Ca(OH)_2$ is used.. Calcium hydroxide solution is also known as lime water. It is prepared by taking 1 teaspoon of calcium hydroxide in a clean glass jar, up to 1 liter in size (Limewater is a saturated solution, which means there will be some extra chemical that doesn't dissolve. A teaspoon will result in a fully saturated solution whether you use a liter jar or smaller one). The jar is shaken vigorously for 1-2 minutes. After this, the jar is allowed to stand for 24 hours. After 24 hrs the clearer solution is poured off from the top of the jar through a clean filter paper and collected in a beaker.

5.5 PREPARATION OF CARBONATED SOLUTION

The purpose of making a carbonated solution is to decrease the pH value of the saturated calcium hydroxide solution from 12 to a value of 7 this is done to simulate a condition of concentration during carbonation process. To prepare the carbonated solution, carbon dioxide is bubbled into the lime water. Actually, CO_2 then reacts with calcium hydroxide present in lime water to produce calcium carbonate precipitates out as a white suspended solid, making the solution appear milky**.** This so is monitored from time to time to check the pH. If pH value increases CO_2 is again bubbled.

5.6 MIXING OF CORROSION INHIBITORS

After preparing the carbonated solution, different corrosion inhibitors, in the required quantities in various forms are mixed. After mixing the corrosion inhibitors in the prepared solution, the pH value of the solution again increased beyond 7, for which carbon dioxide is bubbled again, in order to make it stable at 7. The final solutions are then used for the experimental purpose.

5.7 DETAILS OF TYPE 1 TEST

For the Type 1 test, eight different steel bars are used. These steel bars are coated with one layer of epoxy along the length leaving a length of 4mm from the bottom as discussed in the previous sections. The bottom uncoated length of the six different

steel bars were submerged in six different corrosion inhibitors solution understand their effectiveness to prevent corrosion. Along with this, two test specimens were submersed in control solutions of calcium hydroxide and carbonated solution to compare the results with uncarbonated and carbonated stages respectively. The details of the different samples with specimen designations with their solutions pH are shown in the Table 5.3.

Table 5.3 – Detail of Type 1 test samples

Sr. No.	Sample	Solution	pH value
1	S1-C-CH	Saturated $Ca(OH)_2$	12.46
2	S1-C-CC	Carbonated saturated $Ca(OH)_2$	7.80
3	S1-CI-EA	Ethanol amine 0.07M	7.00
4	S1-CI-D7	DURACOROBIT 750 (0.3% v/v)	7.03
5	S1-CI-K8	Kem corpro M810 (0.3% v/v)	7.11
6	S1-CI-D6	DURACOROBIT 60 (0.3% v/v)	6.98
7	S1-CI-S9	Sica Ferrogard 903 (0.3% v/v)	7.00
8	S1-CI-ED	EDTA 0.07M	6.90

In this the specimen was monitored for a period of 480 hours. However, in all these tests, same working electrode was used. Due to this the solution was disturbed when the reading was taken. In order to avoid any error due to this, the system was kept untouched for 45 minutes prior LPR and OPC readings. This was suggested by *kujur jitu*.

Plate 5.2 - Type 1 test solutions after experiment

5.8 DETAIL OF TYPE 2 TEST

For Type 2 test, Seven different steel specimens were used which were coated with two layer of epoxy along the length leaving a length of 4mm from the bottom. The bottom uncoated length of the seven different steel specimens was submerged in seven different solutions with or without corrosion inhibitors. The solutions details along with corresponding specimen designation are shown in Table 5.4. In order to avoid the disturbance to specimen while inserting working electrode for these set of tests, the working electrode was made using one nut and two bolts attached with copper wire and was fixed in 3mm groove made in the steel bar. The specimens were monitored for any corrosion activity for a period of 480 hours.

Table 5.4 – Detail of Type 2 test samples

Sr. no.	Sample	Solution	pH value
1	S2-C-CH	Saturated $Ca(OH)_2$	12.46
2	S2-C-CS	Carbonated saturated $Ca(OH)_2$	7.80
3	S2-C-EA	Ethanol amine 0.07M	7.00
4	S2-CI-K8	Kem corpro M810 (0.5% v/v)	7.01
5	S2-CI-K'8	Kem corpro M810 (1% v/v)	7.00
6	S2-CI-S9	Sica Ferrogard 903 (0.5% v/v)	7.13
7	S2-CI-S'9	Sica Ferrogard 903 (1% v/v)	7.09

Plate 5.3 - Arrangement for Type 2 test samples

5.9 CORROSION MONITORING

After preparing the solutions, steel specimens were placed in them and then monitored for corrosion and two electrochemical tests were conducted to monitor corrosion activity i.e. open circuit potential measurement, corrosion current density measurement. These tests are explained in detail in the following sections.

5.9.1 Current and Voltage per time

In the present study, all the specimens are monitored time to time by half-cell potential using a saturated calomel reference electrode by placing the electrode in the solutions. The procedure followed by ASTM Standard. The half-cell potential measurement is the most common method used in the bridge deck corrosion surveys. An indication of the relative probability of corrosion activity can be empirically obtained through measurement of the potential difference between a standard portable half-cell placed on the surface of the steel rebar underneath. The ASTM interpretation of half-cell potential (SCE) is summarized inn Table 5.5.

Table 5.5 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

This test was performed to stabilize the system. Current & Voltage permits the continuous measurement of potential and galvanic readings. The maximum read rate for Current & Voltage is limited by the mains frequency, 0.02 for 50Hz and .0166667 for 60Hz. The Long Term test was performed with Potential measurement in which the read rate was very frequent i.e. One point every 1 minute.

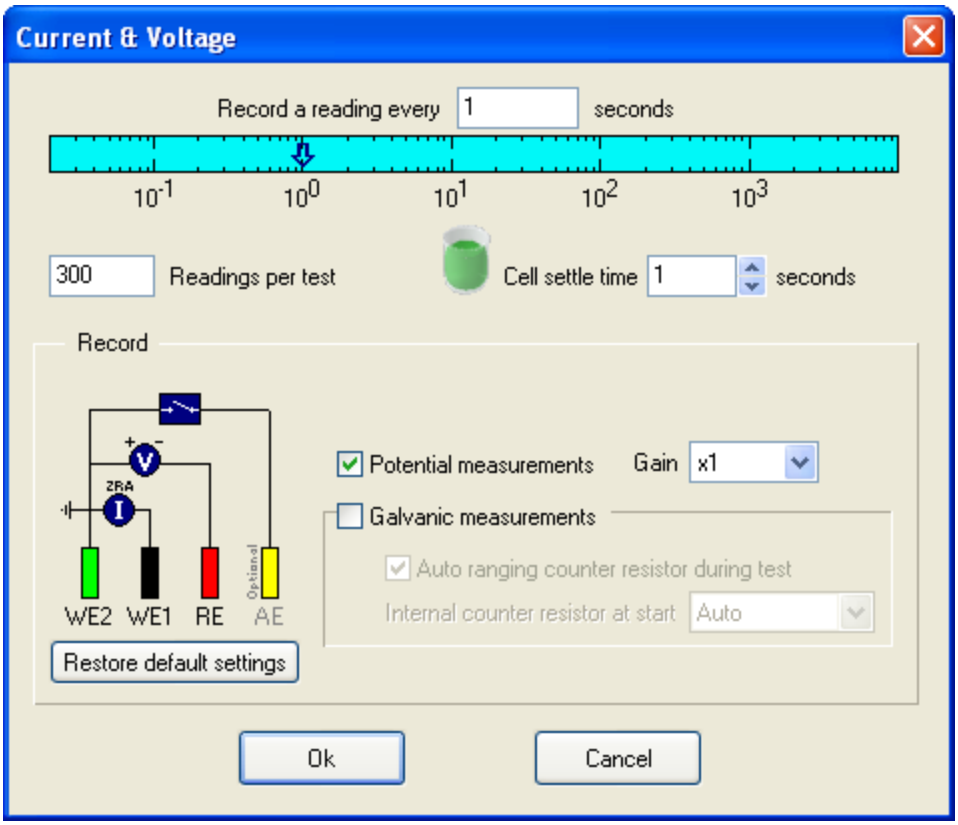

Fig. 5.2 Input readings for OCP test

5.9.2 Long Term – LPR Sweep

Long term LPR sweep or potentiodynamic polarization is done to find corrosion current density. Polarisation resistance determinations have been used for more than 50 years for the rapid and relatively accurate determination of corrosion rates or general corrosion trends in single and multiphase fluids. The use of polarisation resistance for the determination of corrosion rates for simple systems has been reviewed by Callow et al.

For a simple and symmetrical anodic and cathodic charge transfer controlled process, the small section of the polarisation curve approximately ≤ 20 mV either side of the corrosion potential, E_{corr}, the current vs potential response is expected to be linear. The slope of such direct current (d.c.) steady state curves can be measured directly and the instantaneous corrosion rate (presented here as corrosion current density I_{corr}) can be derived. This simple case can be described by the Stern-Geary equation :

$$I_{corr} = \frac{\beta_A \beta_C}{2.3 R_p (\beta_A + \beta_C)} = \frac{B}{R_p}$$

β_A and β_C are the anodic and cathodic Tafel slopes (potential vs log10 current, typically iunits of V decade-1 of current) respectively and B is the proportionality constant between I_{corr} and Rp for the reaction conditions under study. Rp is termed the polarisation resistance (the slope of the potential vs current curve with units of the Ohm). This relationship assumes uniform current distributions which have received compensation for the electrolyte Ohmic/IR drop between the galvanised steel working electrode and the tip of the reference electrode.

To obtain a value of estimated corrosion rate, B must be determined from Tafel slope data or, as is usually the case under most practical circumstances, guessed from prior experience, published data or from a manual accompanying the instrumentation. Callow et al. observed that many workers quote Rp values rather than absolute corrosion rates in an effort to compare relative corrosion resistance with traditional weight loss studies. It was stressed that in the majority of cases, for any values of β_C and β_A between 60 and 120 mV decade-1, a maximum error of only 20% can be expected. Moreover, if one of the β values is assumed to be infinite, the resulting error is generally only as much as 200%.

This electrochemical technique is commonly incorrectly referred to as LPR, although theoretically non-linearity of the polarization curve is expected to dominate in the majority of cases. In practice, the anodic and cathodic mechanisms and polarization behaviour is not usually identical. Moreover a number of reactions which can occur simultaneously during either cathodic or anodic polarization and mass transfer effects and which can influence the rate of reactant and product movement are not considered by given equation. The resistance measurement, however, is capable of providing a broad indication of relative corrosion rate via Rp, regardless of non-linearities. Thus, states of surface condition, such as ‘passivity’ and ‘activity’, can be distinguished within reasonable limits.

With the application of polarization resistance within poorly conducting electrolytes (such as soil) and complicated geometries (such as buried grillages and other support structures), Ohmic drop and the potential/current distribution reaching the object will become significant factors. From the fundamentals of electrochemical theory, it is clear that these complications must be included in any accurate discussion of the polarization resistance analysis technique. It is essential to consider how far an applied current has to travel through a soil of a given resistance and how tortuous this path would be. In general terms, if the cell electrode design is not symmetrical there will not be uniform current distribution. In many cases the geometry of the buried structure will not be known, or cannot be defined within reasonable limits.

Environmental factors will also affect soil conditions and the IR drop behaviour. Such conditions will usually vary locally, nationally and seasonally. Thus, the introduction of a practical, reliable and simple polarization resistance model is required. Flexibility and simplicity in application would be a huge asset, where relatively unskilled technicians can determine corrosion rates in reproducible manner at any time of the year.

In this experiment potentiostatic linear sweep test was carried out on bare steel specimens using the ACM Field Machine. The electrochemical cell consists of a cylindrical jar with a polypropylene lid. It is provided with fittings for connecting the auxiliary electrode, noise reduction probe, reference electrode, thermometer and the specimen. Throughout the test, the reference electrode used was saturated calomel electrode (SCE). The test set-up is shown in Plate 5.4. For testing, the bare steel specimen screwed to the working electrode, the reference electrode, auxiliary electrode, and noise reduction probe were attached to the electrochemical cell. The potentiostatic linear sweep test was carried out from -250 mV to 1500 mV with offset from corrosion potential at a sweep rate of 60 mV per minute. The input readings as shown on ACM field machine while performing this test are shown in Figure 5.3.

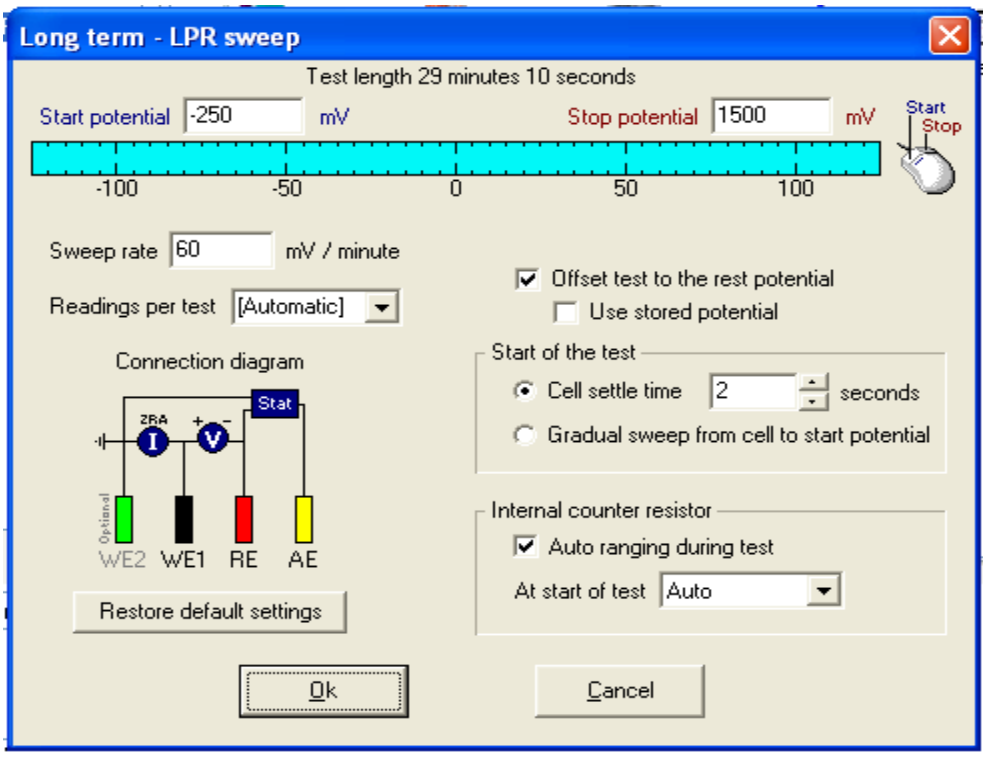

Fig. 5.3 Input readings for Long term LPR-sweep test

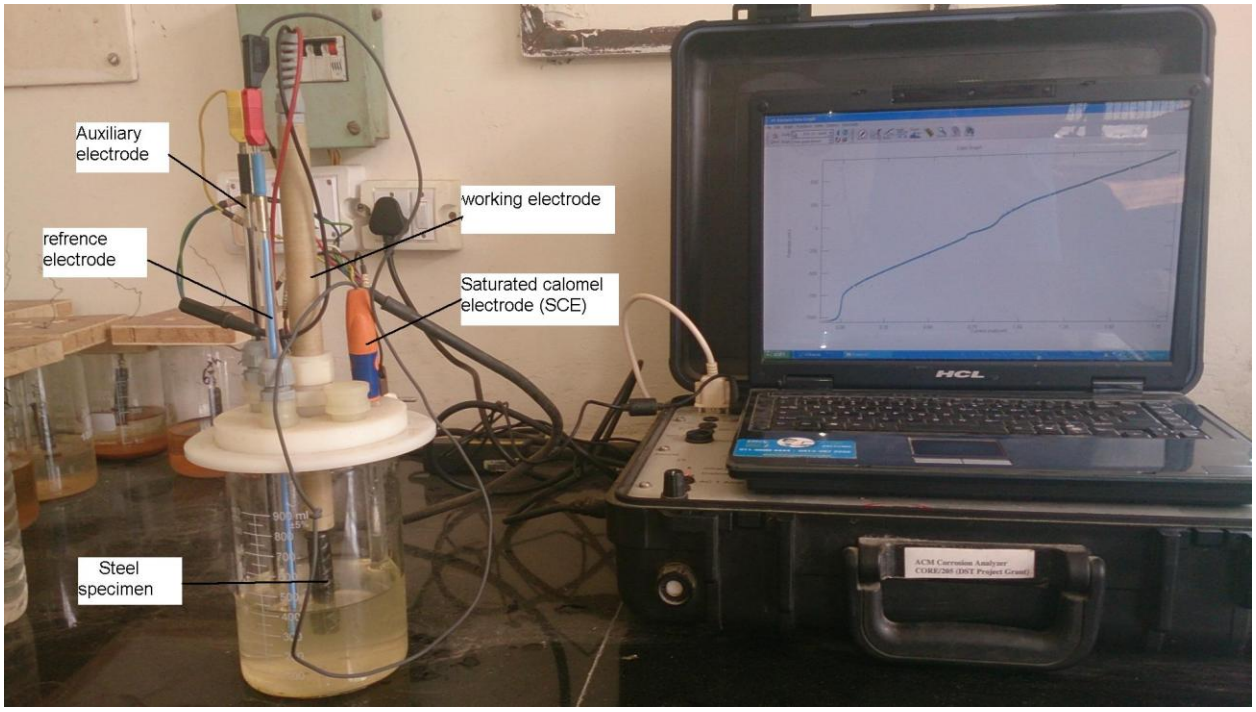

Plate 5.4 - Experimental arrangement for potentiostatic linear sweep

The readings of these tests were recorded on specific time intervals. For the Type 1 test series, total five readings were recorded at 1, 24, 72, 240, 480 hours from the start of the test. And for the Type 2 test series, six readings were recorded at 1, 24, 48, 130, 240, 480 hours from the initialization of the test. These readings at specific time interval were recorded to understand, when the corrosion inhibitors become effective and form layer around the steel specimen to protect it from corrosion.

Plate 5.5 and 5.6 show the conditions of test specimens at the end of the experiment for the Type 1 test series and for Type 2 test series experiments.

Plate 5.5 – Condition of steel rebars of Type 1 test series at the end of test

Plate 5.6 – Condition of steel rebars of Type 2 test series at the end of test

5.10 CLOSING REMARKS

In this chapter, the procedure of using corrosion inhibitors and the various parameters that needs to be kept in mind while using them are discussed in detail.

CHAPTER 6 - RESULTS AND DISCUSSIONS

6.1 GENERAL

The major objective of the test program was to understand the effectiveness of the various corrosion inhibitors in protecting the Steel from corrosion in carbon dioxide rich environment. The following sections discuss the results based on the data from OCP and LPR sweep tests.

6.2 PERFORMANCE OF REBAR WITH ONE LAYER OF EPOXY COATING

Type 1 test series, had one layer of epoxy coating on the steel rebar and the corrosion inhibitors used is of 0.3% by volume of solution. The various corrosion inhibitors were used out of which four were commercial inhibitors from the market and two were self prepared with the chemicals in the lab. Along with these corrosion inhibitor solutions, the steel rebar was also tested in calcium hydroxide saturated solution and carbonated solution (basic solutions) so that the results could be compared to understand the effectiveness of corrosion inhibitors used. The calcium hydroxide solution corresponds to the pre solution of concrete and the carbonated solution corresponds to the pre solution of carbonated concrete.

For the Type 1 test series, various tests were conducted which includes OCP test and Long Term – LPR Sweep test for measuring corrosion current densities. The readings from these were recorded at the intervals 1, 24, 72, 240 and 480 hours from the initiation of the test. There were eight samples for Type 1 test series and were tested simultaneously and the setup was completed in 20 days. The results for I_{corr} and open circuit potential for all the samples are shown in Table 6.1. The test results are discussed as under.

Table 6.1 – OCP and I_{corr} results for Type 1 test series

S.No.	Sample	Tests	1hr	24 hrs	72 hrs	240 hrs	480 hrs
1	S1-C-CH	OCP (-) (mV)	407.04	488.48	651.54	588.28	654.96
		I_{corr} (mA/cm^2)	0.05752	0.06473	0.06672	0.07991	0.08009
2	S1-C-CC	OCP (-) (mV)	535.08	556.75	642.80	660.45	826.99
		I_{corr} (mA/cm^2)	0.0589	0.06951	0.06995	0.07019	0.08324
3	S1-CI-EA	OCP (-) (mV)	722.57	675.15	659.7	635.3	525.4
		I_{corr} (mA/cm^2)	1.1895	2.2113	2.1626	2.0098	1.0952
4	S1-CI-D7	OCP (-) (mV)	636.49	809.91	650.24	526.68	509.71
		I_{corr} (mA/cm^2)	1.1522	0.8144	0.7682	0.6632	0.5913
5	S1-CI-K8	OCP (-) (mV)	472.34	607.9	696.58	688.39	654.45
		I_{corr} (mA/cm^2)	0.1855	0.2099	0.2450	0.2230	0.1605
6	S1-CI-D6	OCP (-) (mV)	567.51	658.11	645.47	625.32	603.23
		I_{corr} (mA/cm^2)	0.7100	0.5977	0.4653	0.3995	0.3017
7	S1-CI-S9	OCP (-) (mV)	260.62	404.22	452.9	402.61	353.86
		I_{corr} (mA/cm^2)	0.5242	0.5455	0.3666	0.2052	0.1165
8	S1-CI-ED	OCP (-) (mV)	695.95	725.5	760.15	680.0	680.4
		I_{corr} (mA/cm^2)	4.6018	2.8098	2.0872	2.8842	3.00002

6.2.1 Open Circuit Potential

The open circuit potential (also referred as the equilibrium potential, the rest potential, or the corrosion potential) is the potential at which there is no current; that is, experiments based on the measurement of the open circuit potential are potentiometric experiments.

The results obtained of open Circuit potential are shown in Table 5.1.The values are again plotted as bar charts in Fig. 6.1 and Fig. 6.2 for OCP and I_{corr} respectively For control specimens, which were free from inhibitor (S.no. 1and 2), the potential was permanently negative when specimen was in saturated calcium hydroxide and

carbonated solution. On comparing the readings of specimen 1 and 2, it is observed that OCP of carbonated solution is more negative then the corresponding value for uncarbonated solution. Similar trend is shown by corrosion current density records, however, the difference is not as pronominal as given of OCP results.

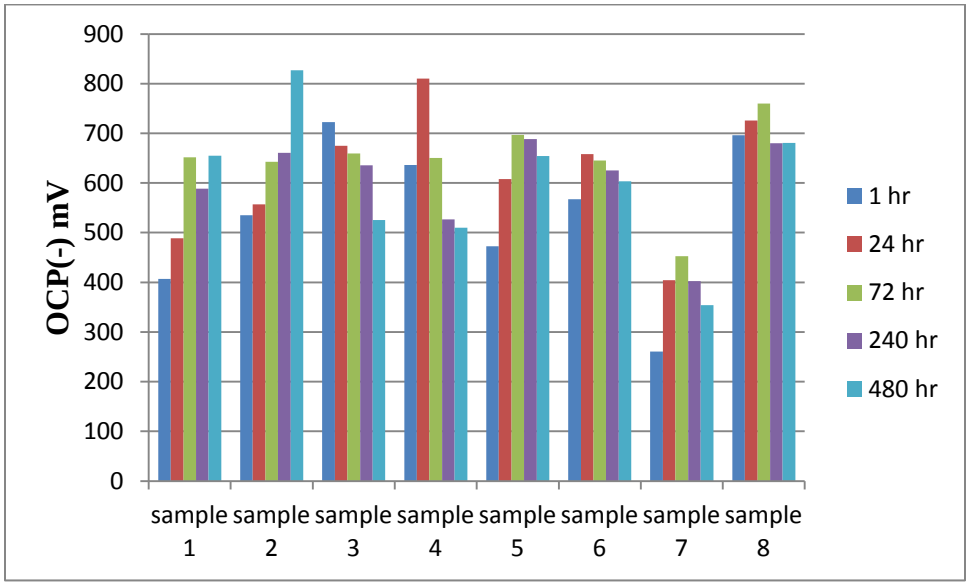

Fig. 6.1 Open circuit potential of specimens in Type 1 test series

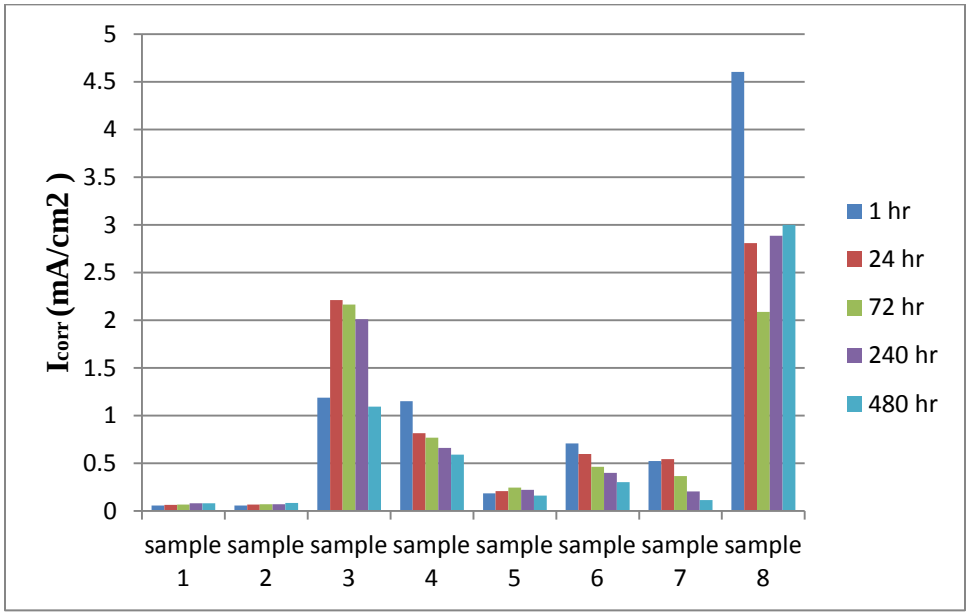

Fig. 6.2 – Corrosion current density of specimens in Type 1 test series

However, the readings of OCP and corrosion current density were very high for all specimens having corrosion inhibitor‘s. So, initially it was thought that these set of corrosion inhibitor’s are not effective in carbonation induced corrosion. However, the base steel specimen was monitored very closely it was observed that corrosion pits were formed on the surface where epoxy was applied. Therefore, it led to the conclusion that corrosion happened on epoxy coated surface also. And the test results were error nous due to the epoxy used. The following conclusion were drawn from this set up:

- One layer of epoxy coating is not sufficient therefore; it was decided to put two layers of epoxy before putting the specimens in test solution. This procedure was followed in Type1 test series and no pitting was observed in that series at the end of the test.
- Out of 6 corrosion inhibitors, three were chosen. Out of the six , two were chemicals and only one was chosen. And from the remaining four commercial corrosion inhibitors, two were chosen. The results of sample 8 were so poor that it cannot be used as a corrosion inhibitor. In the plate 6.1, the corroded material is clearly shown in the beaker for sample 8.
- Due to the disturbance of working electrode, their readings were affected .TO overcome this, we created a setup with which the disturbance can be reduced to max.

Plate 6.1 - 8th solution after experiment

6.2.2 Linear Polarization Resistance (LPR)

Linear Polarization Resistance monitoring is an effective electrochemical method of measuring corrosion. Monitoring the relationship between electrochemical potential and current generated between electrically charged electrodes in a process stream that allows the calculation of the corrosion rate. LPR is most effective in aqueous solutions, and has proven to be a rapid response technique. This measurement of the actual corrosion rate allows almost instant feedback to operators.

The linear sweep test conducted on bar steel specimen. Anodic polarization curve were obtained for different types of corrosion inhibitors, with and without carbonation, are shown in the figure 6.3 this graph shows different zones of corrosion for the steel reinforcement which is indicated:

- **Active zone** It is the zone where the increase in current density is significantly high with a very little change in potential.
- **Passive zone** The zone where the change in current density is relatively small with significant increase in potential lies above the active zone.
- **Pitting zone** The pitting zone with oxygen evolution lies above the passive zone.

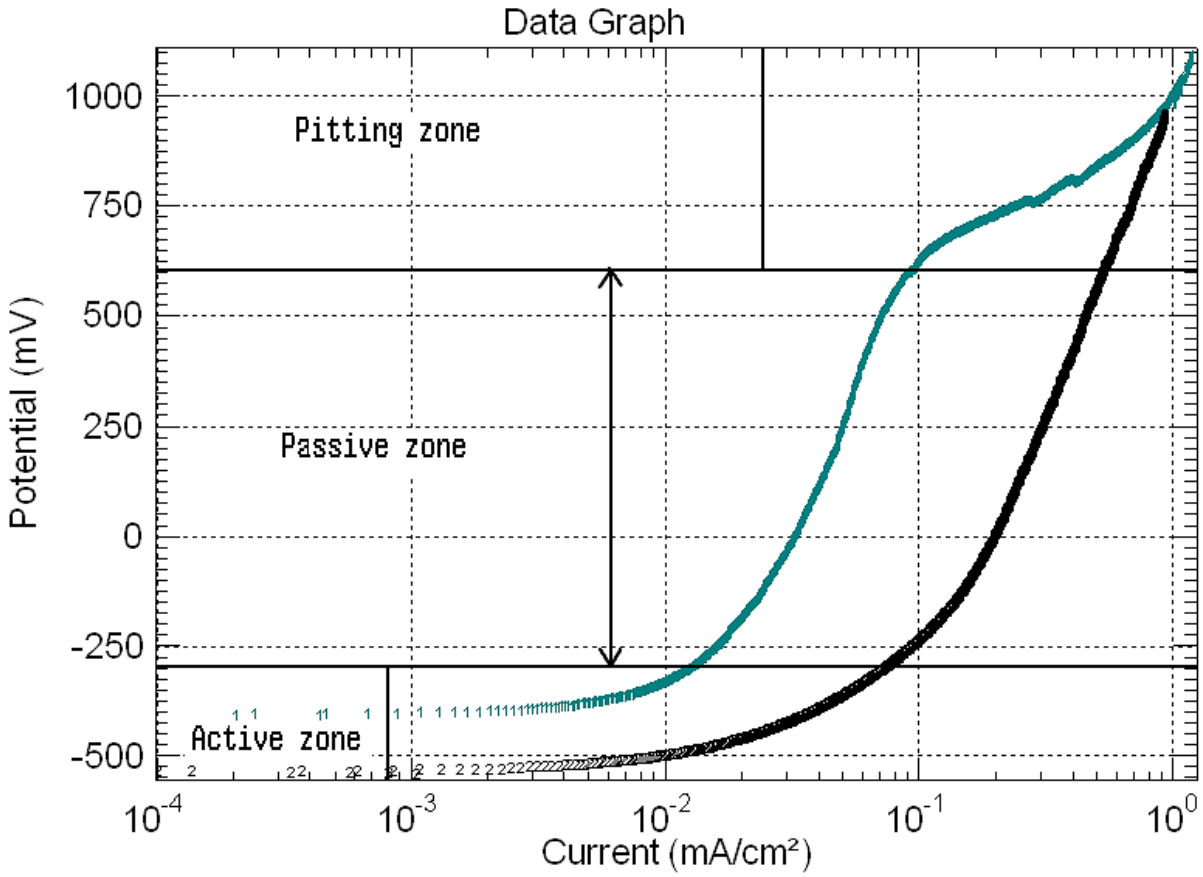

Fig. 6.3 – Anodic polarization curve for with and without passing CO_2

The Fig. 6.3 shows the anodic polarization curve for sample 1 in calcium hydroxide saturated solution for 1hr and sample 2, after passing CO_2 gas. From the graph it can be seen that for sample 1 all the zones are well defined unlike sample 2. For sample 1 the active zone is which the steel bar is very resistant to the current density, which means there no effect on the passive layer around the steel. The passive zone is well defined as the steel bar starts to resist the corrosion from current density of 10^{-2} mA/cm^2 and the passive layer starts to deplete from 10^{-1} mA/cm^2 of current density and does enter into the pitting zone afterwards. For sample 2 as CO_2 gas is passed through calcium hydroxide, the graph did not showed any defined zones. In the initiation period or active zone for sample 2, starts to flow a very low potential when compared to sample 1. The passive zone which is the propagation period is small or does not exist as the passive layer is now deplete at very low potential or we can say

steel did not prepare any passive layer as there is reduction in the pH of the solution. From comparing the both samples it can be said that CO_2 in the solution causes rapid deterioration of the steel bar due to carbonation induced corrosion. In the future samples different corrosion inhibitor will added to the sample 2 solution to prevent corrosion and even understand their effectiveness.

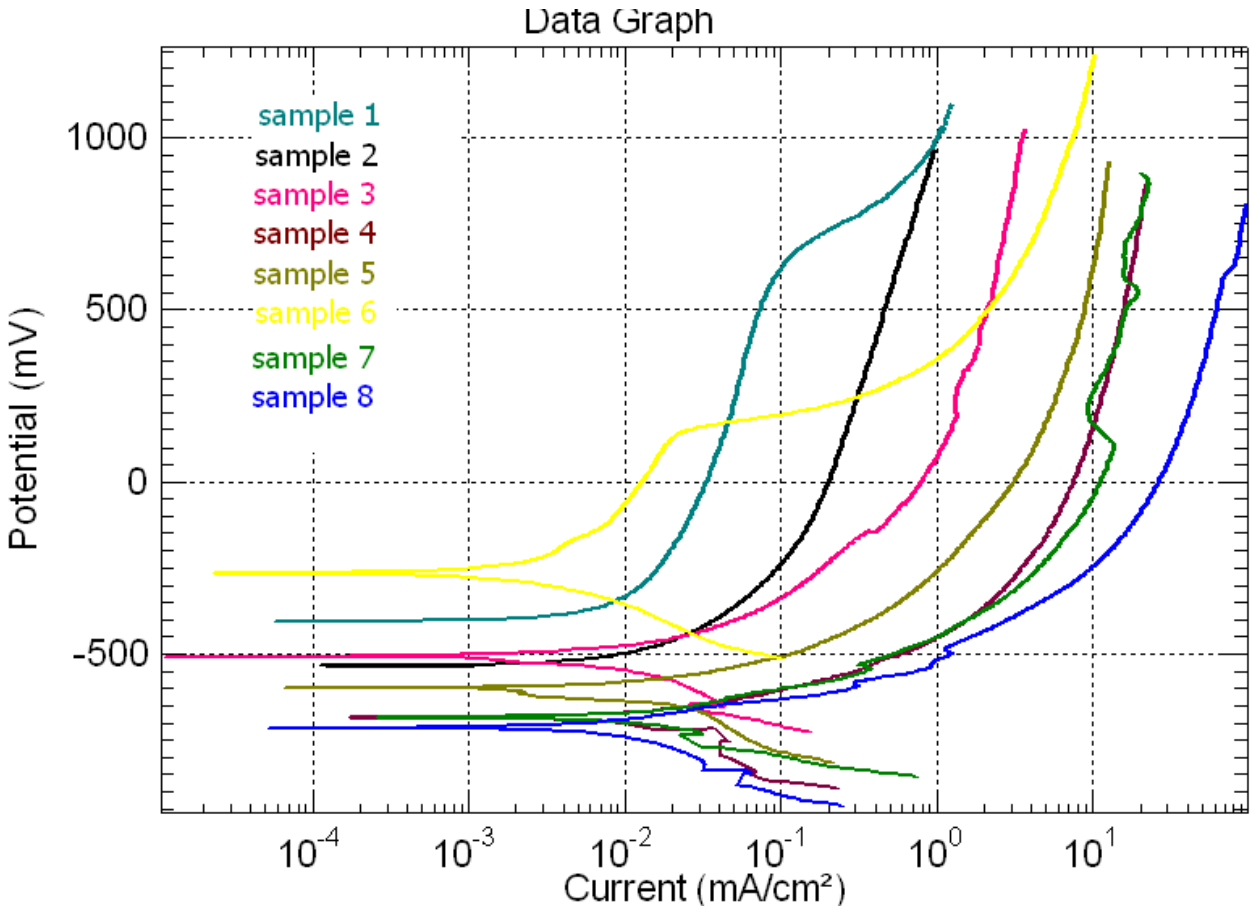

Fig. 6.4 – Polarization curves for all samples at 1 hour

6.3 PERFORMANCE OF REBAR WITH TWO LAYER OF EPOXY COATING

Table 6.2 - Rp and Icorr results for type 2 samples

S.No	Sample	Test	1hr	24 hrs	48 hrs	130 hrs	240 hrs
1	S2-C-CH	OCP (-) (mV)	350.68	379.66	530.3	686.44	686.76
		I_{corr} (mA/cm^2)	0.00375	0.00501	0.01274	0.02542	0.03458
2	S2-C-CS	OCP (-) (mV)	599.03	656.85	674.01	680.53	687.28
		I_{corr} (mA/cm^2)	0.01294	0.01632	0.02572	0.02881	0.03700
3	S2-C-EA	OCP (-) (mV)	706.97	720.49	701.32	685.79	589.87
		I_{corr} (mA/cm^2)	0.80070	0.80019	0.79142	0.78532	0.70168
4	S2-CI-K8	OCP (-) (mV)	618.15	715.01	732.45	773.55	602.19
		I_{corr} (mA/cm^2)	0.05126	0.05170	0.05931	0.06015	0.02458
5	S2-CI-K'8	OCP (-) (mV)	603.75	724.88	726.92	785.63	589.23
		I_{corr} (mA/cm^2)	0.04460	0.05885	0.06286	0.04289	0.03510
6	S2-CI-S9	OCP (-) (mV)	338.5	574.17	710.24	705.23	537.29
		I_{corr} (mA/cm^2)	0.01369	0.05585	0.06114	0.02259	0.01857
7	S2-CI-S'9	OCP (-) (mV)	273.28	445.77	469.58	250.45	219.27
		I_{corr} (mA/cm^2)	0.00838	0.01433	0.01069	0.00497	0.00385

The reason for conducting the experiment again with TYPE 2 samples is that the previous experiment failed because the portion of steel which was covered with epoxy, also started getting corroded .Therefore, in this experiment two layers of epoxy on the bare steel specimens were provided. In this experiment, in all 7 specimens are taken with following description.

- Specimen 1 and 2 are controlled specimen in which sample is saturated carbon hydroxide and sample 2 is carbonated solution.
- Solution 3 is the chemical corrosion inhibitor named "Ethanolamine". It is also used in TYPE 1 test.

- Sample 4-7 are various commercial corrosion inhibitors, performing well in TYPE 1 Test are used in different concentrations.

6.3.1 Observation w.r.t. control specimen

It indicates that two layers of epoxy has controlled any corrosion to happen in coated zone. It is shown in the plate 6.1 that depicts the final condition of bare steel specimens in these 2 solutions.

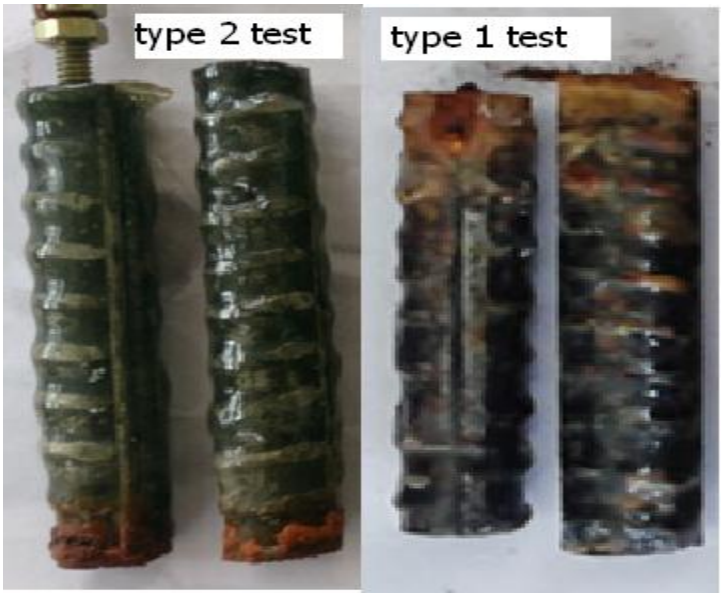

Plate 6.2 Steel specimens at the end of experiment

The values of Icorr and OCP are increasing regularly from beginning to end and this is being observed through Bar chart. But in comparison toType1 sample, the values of Icorr and OCP are less because of two layers of epoxy coating and the sample is not disturbed even.

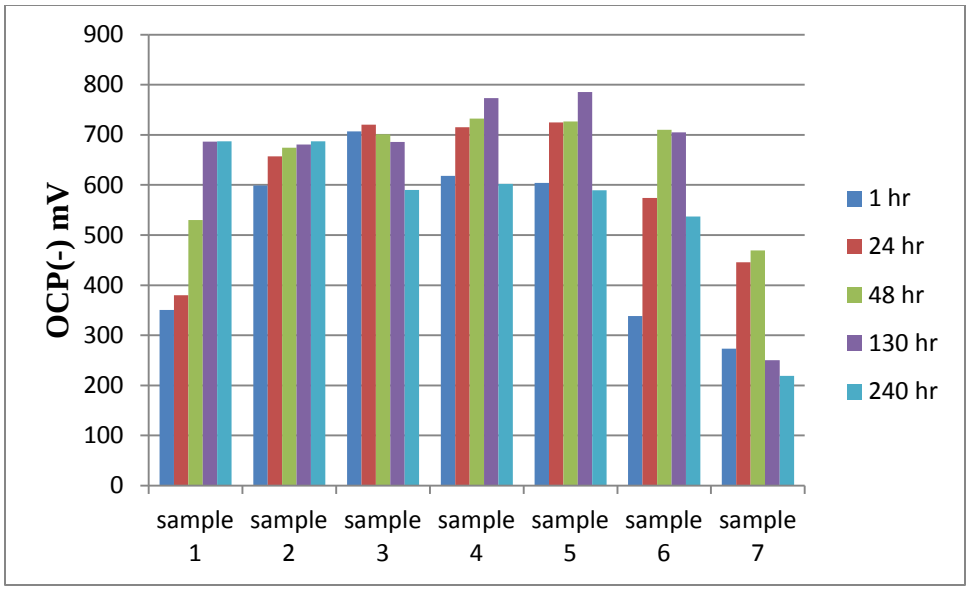

Fig. 6.5 Open circuit potential of specimens in Type 2 test series

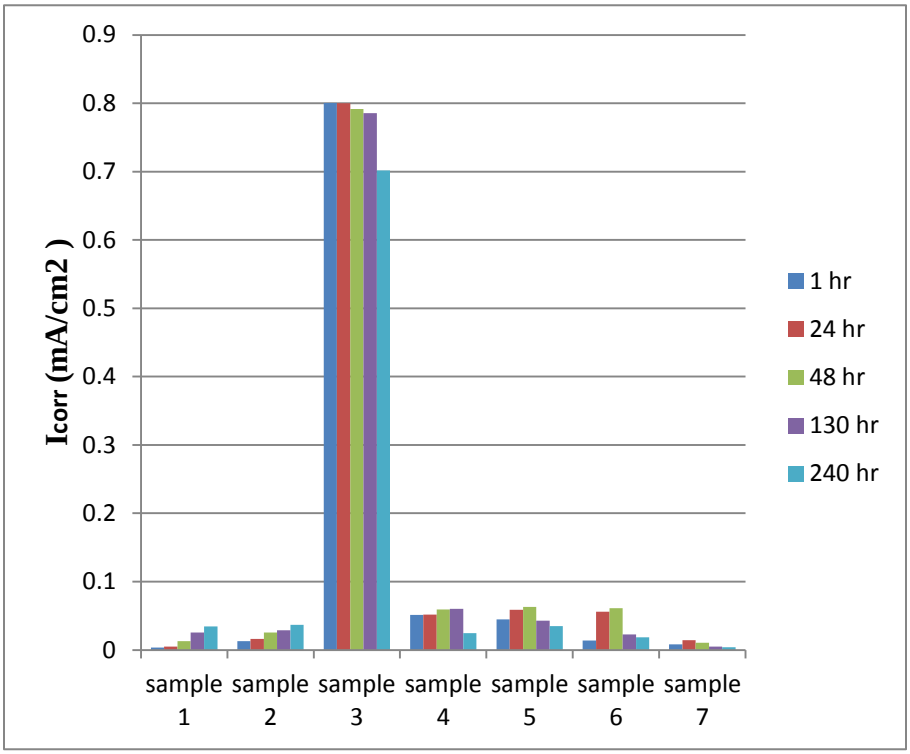

Fig. 6.6 Corrosion current density of specimens in Type 2 test series

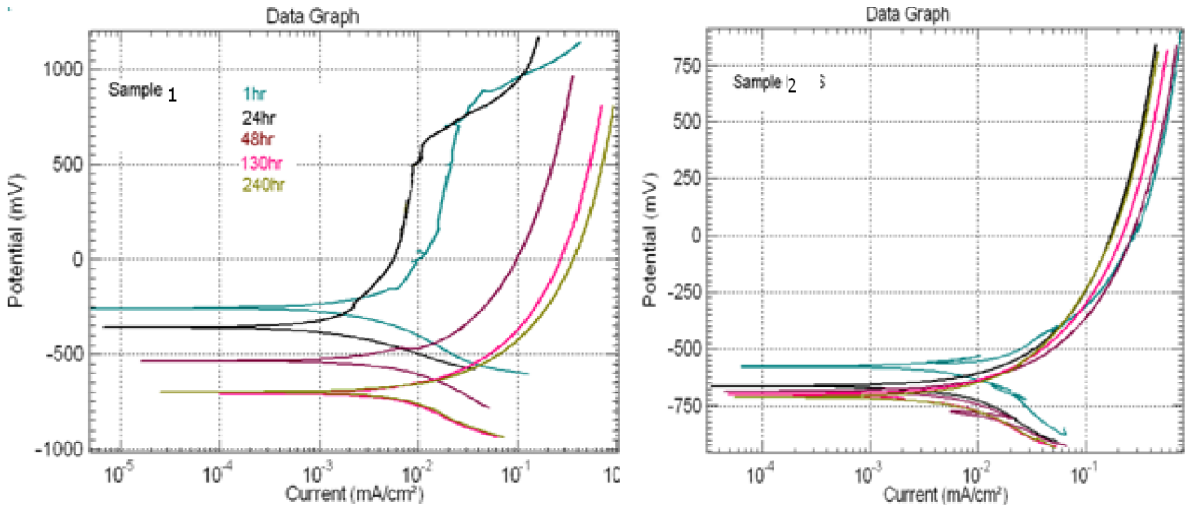

Fig. 6.7 Polarization curves for sample 1 and 2

6.3.2 Observation w.r.t. Ethanolamine

The values of OCP and I_{corr} are very high in this case than those of controlled samples. The rate of corrosion is still in high risk zone. Although the trend of the values of OCP and I_{corr} is in decreasing order but this chemical is not effective as a corrosion inhibitor. A chemical is effective as a corrosion inhibitor only when it is used as salt.

6.3.3 Observation w.r.t. commercial corrosion inhibitors

Two types of commercial available corrosion inhibitors are taken at two different concentration levels. These are discussed separately

1. **Chemcorpro M 810:** OCP and I_{corr} values are almost similar to control specimens and in high risk zone only, as per Table 6.2. This is a chloride induced inhibitor for corrosion due to the ingress of chloride. This shows that the corrosion inhibitors available for Chloride induced corrosion are not effective in case of carbonation induced corrosion .This cannot be used prior testing.

   If we increase its concentration from 0.5 to 1, then the difference between the values I_{corr} and OCP is not very high, i.e, the decrease in this case is very less.

Even at high concentrations, corresponding lower values of I_{corr} and OCP, this does not lie in the corrosion safety zone.

2. **Sica ferrogard 903**: We are using this corrosion inhibitor in sample 5 and 6 in two different concentrations. At both the concentrations, the values of OCP and Icorr are less than that of the controlled samples and this being observed from the Table 6.2

   In both these sample, from their Tafel plots Fig. 6.10, we can say that the passive zone is not at all decreasing. i.e. the steel specimens did not reach the pitting zone.

   In this sample even, the inhibitor in which low concentration was used is at intermediate risk and the corrosion activity is uncertain where the one in which the high concentration is used, low risk factor is involved and there is 10% probability of corrosion.

   This shows that this corrosion inhibitor is effective in carbonated induced corrosion but in high concentration.

   This implies that, these corrosion inhibitors they start becoming effective and taken some time to be most effective. Also from the plate 6.3, it can be seen that the corrosion inhibitor sicaa ferragard has made a wide layer which is ultimately preventing steel from corrosion.

Plate 6.3 – Type 2 steel specimens from 1-7 after corrosion

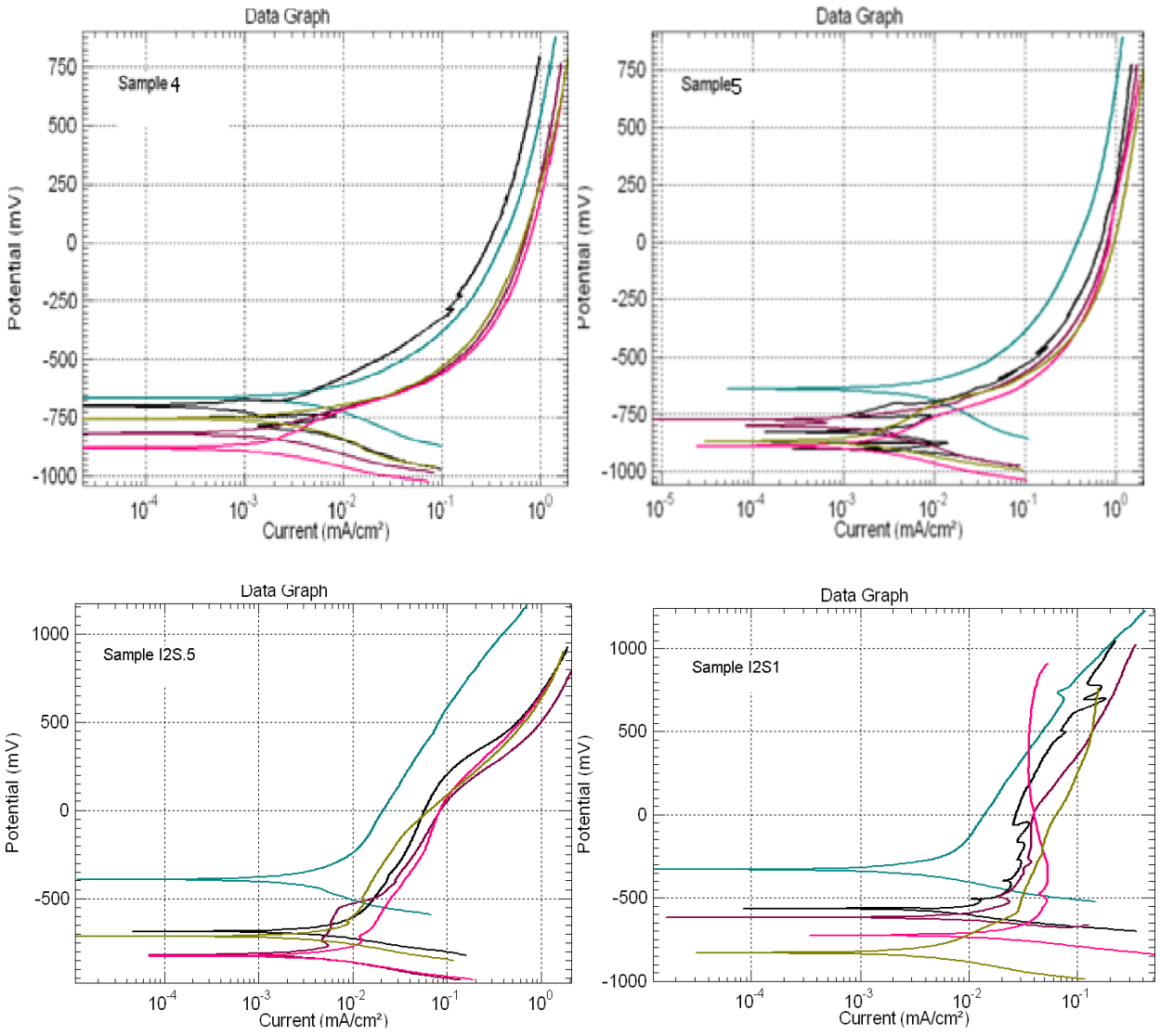

Fig. 6.8 Polarization curves for sample 4, 5, 6, and 7

6.4 CLOSING REMARKS

Corrosion inhibitors are very effective in delaying the rate of corrosion in steel. There are certain parameters on which their effectiveness depends i.e. concentration and

time. It should also be noted that while using corrosion inhibitors, two layers of epoxy gives better results.

CHAPTER 7 - CONCLUSION

From the research done, for the study of efficiency of corrosion inhibitor in carbonation induced corrosion, following conclusions can be drawn:

- The one layer of epoxy coating is not sufficient for protecting the required area of rebar from the effects of corrosion. The steel specimen got corroded and pitting occurred even the length of steel specimen that were coated with one layer of epoxy. However two layers of the same epoxy gave reliable results.
- The commercially available inhibitors for chloride induced corrosion cannot be used to decrease the rate of carbonation induced corrosion without prior investigation.
- Effectiveness of corrosion inhibitors is time dependent. Even in pore water solution they became effective after 72 hours of their use.
- The efficiency of corrosion inhibitor depends on their concentration, that is higher the concentrations higher will be their effectiveness.
- Chemicals only, cannot be taken as corrosion inhibitors .Since when used alone, the alkalinity increases and the pH decreases and thus the passive layer does not get formed on the steel. Therefore, the chemicals cannot be taken as corrosion inhibitor unless they form any compound with any salt.
- Sica ferrgard has come out to be an effective corrosion inhibitor.

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