EFFECT OF APPLICATION OF CORROSION INHIBITOR ON PROPERTIES OF CONCRETE

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ABSTRACT

Reinforced concrete is the most widely used construction material but its durability issues still exist. Apart from structural design failures, the most significant cause of deterioration and premature failure of RC structures is the corrosion of the steel reinforcement. In last quarter century, many methods have been developed to reduce or prevent corrosion of steel in concrete. From all the methods available for corrosion protection, corrosion inhibitors sound very promising. In last two decades, corrosion inhibitors have been extensively used to protect steel reinforcement in RC structures. Most of the commercially available corrosion inhibitors are used for chloride (Cl^-) induced corrosion and are not effective for carbonation induced corrosion.

In this study, effectiveness of three corrosion inhibitors on the properties of concrete is evaluated. The three corrosion inhibitors used in this study are Aminoethanol, para-Aminobenzoic Acid and Sika ® FerroGard ®-903+. Sika ® FerroGard ®-903+ is a commercially available corrosion inhibitor, whereas, Aminoethanol and para-Aminobenzoic Acid are organic chemicals. Corrosion inhibition property on Ordinary Portland Cement - 43 Grade and Pozzolanic Portland Cement was studied. For this study, carbonation depth tests and compressive strength tests were conducted on concrete specimens. For carbonation depth test 100mm cubes were used. Whereas, for compressive strength test 150mm cubes were used. Compressive strength tests were conducted for 28 day and 56 day, from the day of casting. Carbonation depth was measured on specimens for 7 day, 14 day, 21 day, 28 day, 35 day, 42 day carbonation from the day, they were cured in carbonation chamber.

It was observed that all the corrosion inhibitors presented positive results for carbonation depth tests. It was noted that Aminoethanol and para-Aminobenzoic Acid gave best results but corrosion inhibition was also shown by Sika ® FerroGard ®-903+. For compressive strength test, no adverse effect on the strength of concrete was noted on applying corrosion inhibitors.

CONTENT

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 GENERAL

The most abundant man made material available is concrete, with consumption of dozens of billions of tons. Construction and durability of reinforced concrete (RC) structures play an important role in development of any country. Apart from structural design failures, the most significant cause of deterioration and premature failure of RC structures is the corrosion of the steel reinforcement.

Usually the alkalinity of concrete maintains the passivity of embedded steel and prevents corrosion from occurring. This passive layer may be disrupted by carbonation or the ingress of chlorides which thereby allow corrosion to occur in the presence of moisture and oxygen.

1.2 CORROSION

Corrosion is a natural process, which converts refined metal to their more stable oxide. It is the gradual destruction of materials by chemical reaction with their environment. In the most common use of the word, this means electrochemical oxidation of metal in reaction with an oxidant such as oxygen. Rusting, the formation of iron oxides, is a well-known example of electrochemical corrosion.

Many structural alloys corrode merely from exposure to moisture in air, but the process can be strongly affected by exposure to certain substances. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion-controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate conversion, can increase a material's corrosion resistance.

Corrosion of RC structures is actually corrosion of steel embedded as reinforcement in concrete. Corrosion of reinforcement in concrete is an electrochemical process. In a good quality concrete, the risk of corrosion is minimal as concrete itself provides good chemical and physical protection to the embedded reinforcement. Corrosion of steel reinforcement is

generally restricted in an alkaline environment within concrete (pH 13-14) with a chemically stable thin oxide film protecting the steel surface from contact with moisture and oxygen. Initiation of corrosion can be mainly due to the attack of chlorides on the steel (seawater, de-icing salt, unwashed sea sand, admixtures etc.) or by carbonation of the cover concrete due the reaction with carbon dioxide, which causes reduction in the alkalinity of concrete.

The failure of structures due to corrosion does not necessarily results in total structural collapse but in most of the cases, it is demonstrated by loss of structural serviceability, due to cracking and delamination of concrete. The repair work due to cracking and delamination includes high costs, sometimes, much more than initial cost. It is estimated that the cost of corrosion related maintenance and repairs for concrete infrastructure in the world is around $100 billion per year (Li et al. 2007). The cost of corrosion in India is estimated to be around 3, 60,000 million rupees ($8 billion) as published in Financial Express (financialexpress.com).

1.2.1 Corrosion Process

Corrosion can be defined as the degradation of a material due to a reaction with its environment. Degradation implies deterioration of physical properties of the material. This can be a weakening of the material due to a loss of cross-sectional area, it can be the shattering of a metal due to hydrogen embrittlement, or it can be the cracking of a polymer due to sunlight exposure.

Corrosion produces a new and less desirable material from the original metal and can result in a loss of function of the component or system. The three main reasons for the importance of corrosion are: economics, safety and conservation. Corrosion of reinforcement steel, being an electrochemical process, involves few electrochemical reactions. The process of corrosion of steel in accordance with these reactions is discussed below:

(Anode)

$$Fe \rightarrow Fe^{n+} + n \text{ electrons} \qquad (1.1)$$

The iron atom loses some electrons and becomes a positively charged ion allowing it to bond to atoms that are negatively charged. Other half of the reaction involves water (H_2O)

and oxygen (O_2). Pictorial representation of corrosion process of reinforcement steel is shown in Figure 1.1

(Cathode)

$$O_2 + 2H_2O + 4^{e-} \rightarrow 4OH^- \quad (1.2)$$

Now,

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2 \quad (1.3)$$

Iron + Water with oxygen → Iron Hydroxide

dissolved in it excess of oxygen present in water reacts with the iron hydroxide.

$$4Fe(OH)_2 + O_2 \rightarrow 2H_2O + 2Fe_2O_3.H_2O \quad (1.4)$$

Iron hydroxide + oxygen → water + Hydrated iron oxide

(brown rust)

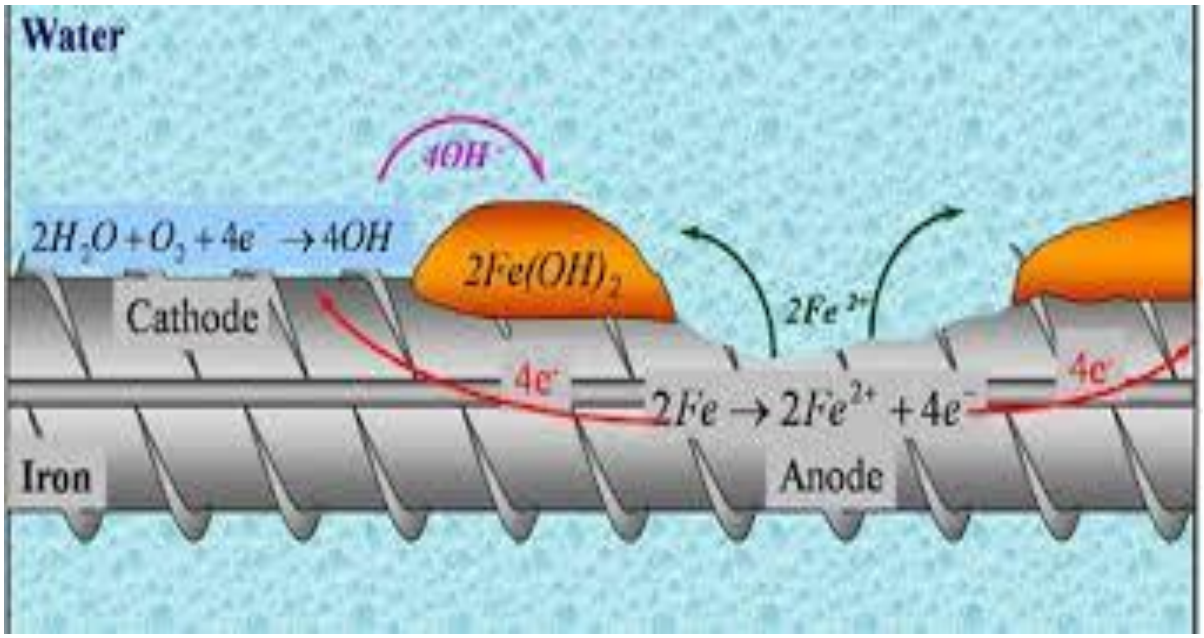

Figure 1.1: Pictorial representation of Corrosion Process of Reinforcement Steel

As discussed above, reinforcement steel resists corrosion because of high alkaline (pH 12-13) environment provided by concrete which in fact provides passivation to steel in the form

of a thin oxide layer. Therefore, initiation of intense corrosion takes place due to loss of alkalinity of concrete. Loss of alkalinity of concrete occurs mainly due to two causes:

- Carbonation

  It is a result of the interaction of carbon dioxide gas from atmosphere with the concrete. Carbon dioxide gas diffused from atmosphere can neutralize the alkalinity of concrete. It can reduce the pH of concrete to approximately 8 or 9 due to which the thin oxide layer is no longer stable. In presence of sufficient moisture and oxygen, corrosion will start.
- Chloride contamination

  It can occur due to application of de-icing salts to concrete surface or from the sea-water. Chloride ions can also enter concrete from salts present in mixing water or aggregates. Chlorides present in sufficient quantity can easily disrupt the passive film.

1.2.2 Methods of Reduction of Corrosion

Many methods have been developed with the intent of preventing corrosion from occurring. These methods include concrete removal and surface preparation, surface coatings to concrete surface, coatings to the reinforcement, cathodic protection, chloride removal and corrosion inhibitors. Some of them are listed below

1. Concrete removal and Surface preparation
2. Barrier Method
3. Sacrificial Anode System
4. Impressed Current System
5. Corrosion Inhibitors

1.3 CARBONATION

Carbonation is one of the two main causes of corrosion of steel in concrete, the other is chloride attack. The result of the interaction of carbon dioxide gas in the atmosphere with the alkaline hydroxides in the concrete, the carbonation process effectively drops the pH of the concrete to a level where the steel will corrode. The carbon dioxide dissolves in water to

form carbonic acid, which can migrate to the reinforcing steel if the concrete cover is low or if the concrete is of poor quality (open pore structure, low cement content, high water cement ratio, or poor curing of the concrete). Carbonation is more common in old structures, particularly buildings.

1.3.1 Introduction

Carbonation of concrete is associated with the corrosion of steel reinforcement and with shrinkage. However, it also increases both the compressive and tensile strength of concrete, so not all of its effects on concrete are bad. Carbonation is the result of the dissolution of CO_2 in the concrete pore fluid and this reacts with calcium from calcium hydroxide and calcium silicate hydrate to form calcite ($CaCO_3$). Aragonite may form in hot conditions.

Within a few hours, or a day or two at most, the surface of fresh concrete will have reacted with CO_2 from the air. Gradually, the process penetrates deeper into the concrete at a rate proportional to the square root of time. After a year or so it may typically have reached a depth of perhaps 1 mm for dense concrete of low permeability made with a low water/cement ratio, or up to 5 mm or more for more porous and permeable concrete made using a high water/cement ratio.

The microstructure of concrete is such that it has capillary pores. The extent of pores varies according to quality of concrete and also depends on water present at time of mixing of concrete. By using low w/c ratios, more dense concrete can be produced and amount of pores can be reduced. These pores are created because the excess free water gets evaporated during strengthening of concrete mass.

Carbonation of concrete is a process in which carbon dioxide from the atmosphere penetrates into concrete through the pores. This carbon dioxide reacts with calcium hydroxide to form calcium carbonate. The carbonation process will reduce the pH to approximately 8 or 9 in which the oxide film is no longer stable. With the presence of moisture and oxygen in sufficient amount, corrosion will start. The chemical reaction involved in carbonation of concrete is as follows:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \qquad (1.5)$$

Carbonation of concrete does not cause any harm to concrete itself indeed it may reduce its porosity and lead to more strength. However, carbonation can greatly affects the steel embedded as reinforcement. It may lead to corrosion of steel if the CO_2 penetrated in concrete reaches the surface of steel.

The pH value of pore water in the hardened concrete is generally 12 to 13. The high alkalinity forms a thin passivating layer around steel and protects it from action of oxygen and water. CO_2 present in atmosphere permeates into concrete and carbonates it and reduces the alkalinity of concrete. The pH value of pore water will be reduced to around 9.0. When the excess of carbonation occurs, the pH may reduce upto 8.

Due to reduction in alkalinity of concrete, the passive oxide layer is destroyed and the steel is prone to corrosion in presence of moisture and oxygen. Carbonation is one of the main reasons for corrosion of reinforcement steel. Cement paste contains 25-50 wt% calcium hydroxide ($Ca(OH)_2$), which mean that the pH of the fresh cement paste is at least 12.5. The pH of a fully carbonated paste is about 7.

The concrete will carbonate if CO_2 from air or from water enters the concrete according to:

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

When $Ca(OH)_2$ is removed from the paste hydrated CSH will liberate CaO which will also carbonate. The rate of carbonation depends on porosity & moisture content of the concrete.

The carbonation process requires the presence of water because CO_2 dissolves in water forming H_2CO_3. If the concrete is too dry (RH <40%) CO_2 cannot dissolve and no carbonation occurs. If on the other hand it is too wet (RH >90%) CO_2 cannot enter the concrete and the concrete will not carbonate. Optimal conditions for carbonation occur at a RH of 50% (range 40-90%).

Normal carbonation results in a decrease of the porosity making the carbonated paste stronger. Carbonation is therefore an advantage in non-reinforced concrete. However, it is a disadvantage in reinforced concrete, as pH of carbonated concrete drops to about 7; a value below the passivation threshold of steel.

1.3.2 Factors Affecting Carbonation

Process of carbonation starts from the surface of concrete and slowly ingresses further in the depth of concrete. The rate of carbonation is high in starting but reduces with the further increase in depth of carbonation. The factors affecting the rate of carbonation are discussed below:

Relative humidity: The rate of carbonation varies greatly with variation of relative humidity of concrete. In very humid environment, rate of diffusion of CO_2 will be very slow because the pores will be filled with water and diffusion of CO_2 is very slow in water as compared to air. Also, in very dry environment, carbonation is negligible because presence of moisture or water is must to start carbonation reaction (Lopez et al. 2003).

The rate of diffusion of CO2 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, CO2 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. Therefore, most critical carbonation occurs at relative humidity of 50-70 %.

Quality of concrete: The carbonation rate also depends on quality of concrete. The less permeable concrete will restrict ingress of CO2 thus will reduce the rate of carbonation. Depth of carbonation can be related to strength or grade of concrete. Carbonation depth with respect to strength of concrete is shown in Figure 1.2.

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.

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.

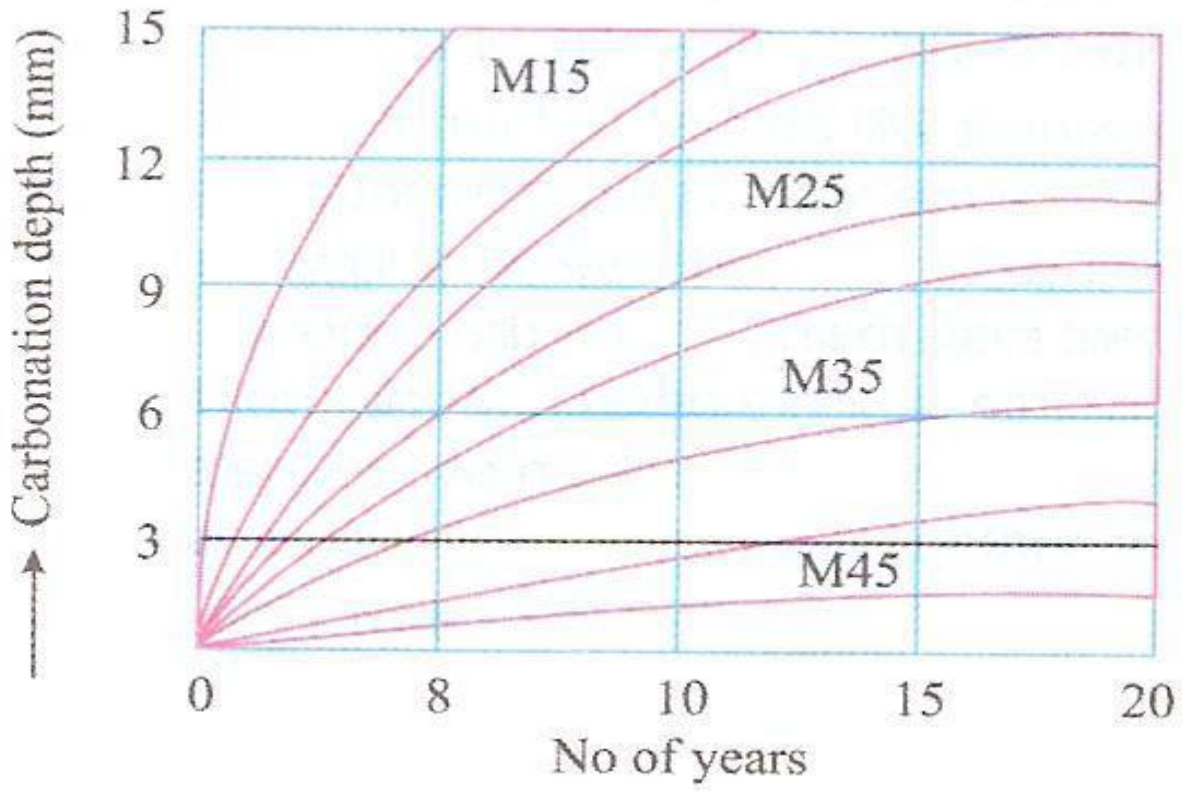

Figure 1.2: Carbonation Depth with respect to Strength of Concrete

Concrete cover: Depth of cover plays important role in rate of carbonation induced corrosion. More is the concrete cover, more time it will take carbonation to reach steel surface.

1.3.3 Carbonation Depth

Carbonation occurs progressively from the outside of concrete exposed to co_2,but does at decreasing rate. the rate is slow because co_2 has to diffuse through the pore system, including the already carbonated surface zone of concrete. the diffusion will be much faster in case of water as co_2 can diffuse4 times faster in it in magnitude as compared to air. this shows that the rate of carbonation depends on moisture content of concrete which varies with the distance from its surface.

Carbonation depth is the depth up to which CO_2 has penetrated. The measurement of the depth of carbonation is generally 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 colour, typical of phenolphthalein in a basic environment, while the colour of carbonated areas remains unchanged. The depth of carbonation increases in proportion to the square root of time, which is characteristic of sorption rather than the diffusion, but the carbonation involves an interaction between CO_2 and the pore system.

The highest rate of carbonation occurs at a relative humidity of between 50 and 70 percent.

In the presence of steady hygrometric conditions, the depth of carbonation increases in proportion to the square root of time, thus the following relation can be derived;

$$D=kt^{0.5}$$

Where k=carbonation coefficient in mm/year$^{0.5}$,

T=time of exposure in years,

The values of K are often more than 3 or 4 mm/year for low – strength concrete. In concrete with water –cement ratio of 0.6, a depth of carbonation of 15 mm would be reached after 15 years, but at water – cement of 0.45 only after 100 years.

1.4 CARBONATION INDUCED CORROSION

Carbonation of concrete does not causes much damage to concrete but it has adverse effects on reinforcement steel. Due to carbonation a weak carbonic acid is formed with dilution of CO_2 in water.

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (1.7)$$

(Weak acid)

Then, formation of bicarbonate ion takes place due to partial dissociation of carbonic acid (H_2CO_3).

$$H_2CO_3 \rightarrow H^+ + HCO^{3-} \qquad (1.8)$$

Now, the bicarbonate ion further dissociates to yield carbonate ion.

$$HCO^{3-} \rightarrow H^{+} + CO^{4-} \quad (1.9)$$

Solutions containing weak carbonic acid (H_2CO_3) are more corrosive to mild steel as compared to solutions containing strong acids. Carbonation-induced corrosion causes harms aesthetically and structurally due to expansive corrosion products that cause cracking, delamination, and spalling of the surrounding concrete.

1.5 CORROSION INHIBITORS

Corrosion inhibitors are chemicals that cause changes at the steel/concrete interface which can result in a reduction of the overall corrosion rate of steel in concrete.

1.5.1 General

In last quarter century, many methods have been developed to reduce or prevent corrosion of steel in concrete. From all the methods available for corrosion protection, corrosion inhibitors sound very promising.

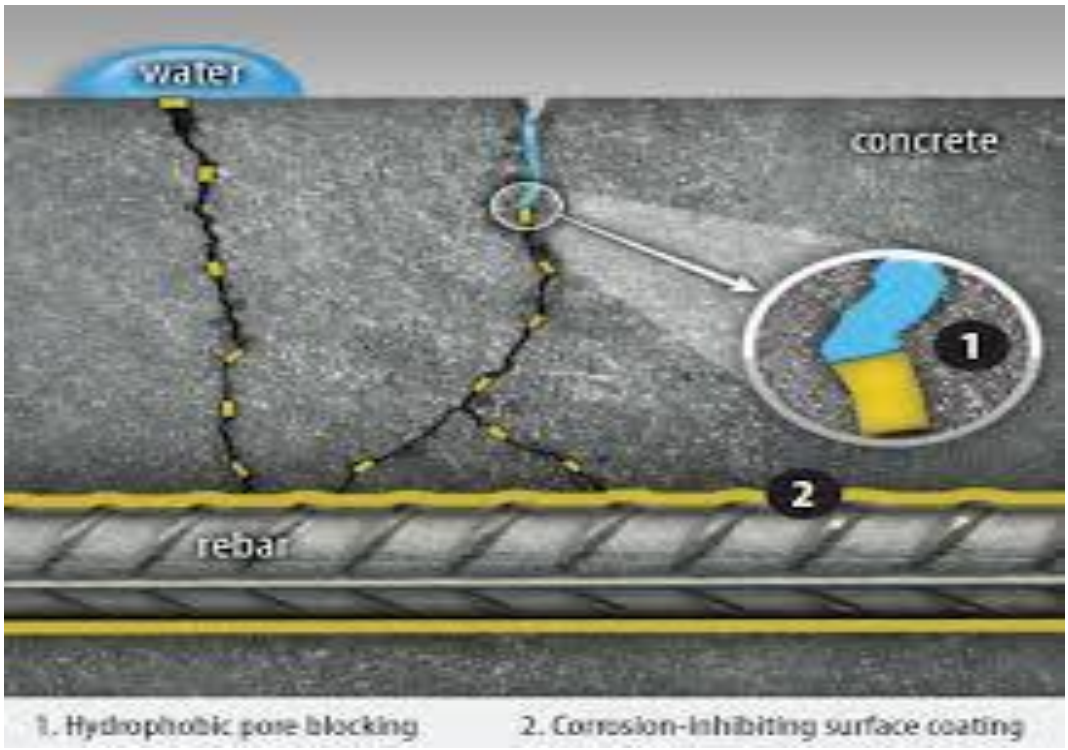

Figure 1.3: Representation of Corrosion Inhibition

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. 2003). A past study indicates that inhibitors can extend the service life through delay of depassivation and/or reduction of corrosion rate once propagated. Figure 1.3 represents corrosion inhibition.

There are mainly two types of corrosion inhibitors based on the application, some of them are to be added at the time of concrete mixing while other can be applied to surface of concrete. In recent years, surface applicable corrosion inhibitors have been developed for rehabilitation of existing RC structures. Several amine/alkanolamine based corrosion inhibitors have been applied for rehabilitation of reinforced concrete structures suffering from corrosion in past few years. These types of inhibitors have ability to diffuse considerable distance into concrete due to their high vapour pressure.

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.

Among various methods available to diminish corrosion, inhibitors seem to be attractive because of their easy handling and low cost, compared with other protective methods.

1.5.2 Classification of Corrosion Inhibitors

There are a number of corrosion inhibitors available at present day. Some of inhibitors are to be mixed in fresh concrete at the time of mixing only while; others can be applied on surface of concrete. Some of corrosion inhibitors interfere with anodic reaction and the others could hinder the cathodic reaction and few could affect anodic as well as cathodic reaction. Classification of corrosion inhibitors based on their action and based on their application is discussed below:

A. Based upon the physical mode of application:

The corrosion inhibitors can be classified into two groups depending on mode of application as:

- Admixed inhibitor

  Inhibitors which are added to the fresh concrete at the time of mixing for new structures are known as admixed inhibitors. These inhibitors are added immediately after the addition of water to cement at the time of mixing. Admixed inhibitor influence initial set, later strength gain and other properties like hydration processes of cement. To overcome this, retarders can be added to concrete mix which balances the acceleration of the inhibitors and provide 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 admixed inhibitors.

- Migrating inhibitors

  These are inhibitors which are applied on the hardened concrete surface and are capable of diffusing through concrete to the underlying reinforcement 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 [MFP](Ormellee 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 adsorption on the steel surface(Gaidis 2004).

They are supposed to be simple alternatives to other available rehabilitation methods such as patch repair or impressed current cathodic protection, but there are still several aspects to be clarified concerned with the effectiveness of surface-applied corrosion inhibitors .

B. Based upon the mechanisms of protection:

Various inhibitors have different mechanism for protection from corrosion. On the basis of their mechanisms, corrosion inhibitors can be classified as follows:

- Anodic inhibitor:

  Anodic inhibitors decrease the rate of reaction at the anode by accepting electrons. They generally react with the corrosion products to form a protective coating on the metal surface. At low dosage there is concern that they will suppress generalized corrosion but may fail to abolish all anodic sites. The most commonly used anodic corrosion inhibitor is calcium nitrite ($Ca(NO_2)_2$). The typical dosage is of the order of 10-30 litres per m^3 of concrete depending on chloride levels in concrete. Most of the admixtures in this category are effective only when present in adequately high concentrations.

  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. 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.

  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. Figure 1.4 shows both anodic and cathodic inhibition.

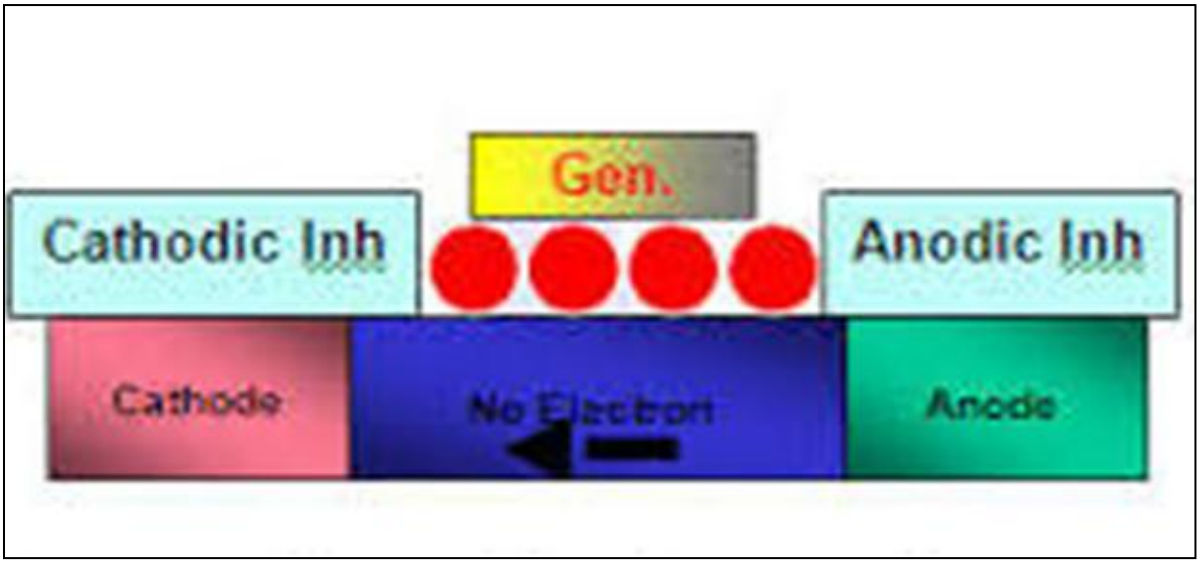

Figure 1.4: Anodic and Cathodic Inhibition

- Cathodic inhibitor:

  Inhibitors which retard the reaction at cathode are called cathodic corrosion inhibitors. These inhibitors prevent oxygen from reaching the reinforcement steel. Cathodic inhibitors act either by slowing the cathodic reaction or by selectively precipitating cathodic sites. Compounds in this category are strong proton acceptors and their action in contrast to anodic inhibitors is usually indirect. Cathodic inhibitors adsorb on the steel surface and act as a barrier to the reduction of oxygen. 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 .

- Mixed inhibitors:

  Mixed inhibitors influence both the anodic and cathodic regions. They retard the corrosion process both at the anode and the cathode. These combine the benefits of both anodic and cathodic inhibitors at relatively low dosages. 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. In these category organic migratory mixed corrosion inhibitors are the most widely used.

Migratory mixed corrosion inhibitors are organic inhibitors. They protect the steel at both the anodic and the cathodic sites. The mixed corrosion inhibitor chemistry involves migration of its molecules by electron density distribution to both the anodic and cathodic sites of the steel. They form a monomolecular layer on the reinforcing steel, which strongly adsorbs to the metal surface and interferes with the anodic and cathodic reactions in the area of adsorption. Studies have proved that addition of these types of corrosion inhibitors has no deleterious effect on the properties of concrete.

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.

1.6 APPLICATION OF CORROSION INHIBITORS

Corrosion inhibitor can be used for various purposes. It can be used as following

- Can be added to fresh concrete as an admixture .
- Applied on the hardened concrete surface, so called penetrating corrosion inhibitor (also migrating corrosion inhibitor and surface-applied corrosion inhibitor).
- Be added to repair mortars.
- Used as a surface treatment on the reinforcement bars before concreting.
- Volatile amines are used in boilers to minimize the effects of acid. In some cases, the amines form a protective film on the steel surface and, at the same time, act as an anodic inhibitor. An inhibitor that acts both in a cathodic and anodic manner is termed as mixed inhibitor. Figure 1.5 shows application of corrosion inhibitors.
- Benzotriazole inhibits the corrosion and staining of copper surfaces.
- Corrosion inhibitors are often added to paints. A pigment with anticorrosive properties is zinc phosphate. Compounds derived fromtannic acid or zinc salts of organonitrogens (e.g. Alcophor 827) can be used together with anticorrosive

pigments. Other corrosion inhibitors are Anticor 70, Albaex, Ferrophos, and Molywhite MZAP.

- Antiseptics are used to counter microbial corrosion. Benzalkonium chloride is commonly used in oil field industry.
- In oil refineries, hydrogen sulfide can corrode steels so it is removed often using air and amines by conversion to polysulfides. Figure 1.6 shows corrosion inhibitor being sprayed.

Inhibitors used in cases of pitting corrosion can act:

- By film forming prior to the ingress of chlorides.
- By buffering the pH in the local pit environment.
- By competitive surface adsorption process between inhibitor and chloride ions.
- By competitive migration of inhibitor and chloride ions into the pit.

Figure 1.5: Surface Application of Corrosion Inhibitor

Figure 1.6: Spraying of Corrosion Inhibitors

1.7 ORIENTATION OF THESIS

The objective of this testing was to understand the effect of application of corrosion inhibitor on the properties of concrete. The thesis has been divided into five chapters:

- 1st chapter is about General introduction, corrosion mechanism, introduction to carbonation, carbonation induced corrosion, general introduction to corrosion inhibitors, their classification and their application.
- 2nd chapter is about the thorough literature review of use of corrosion inhibitors against corrosion.
- 3rd chapter deals with the experimental program where all tests, procedures that were followed during experiments are explained in detail.
- 4th chapter deals with the results and discussions where findings of experimental program are discussed.
- 5th chapter is a concluding chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL

The premature deterioration of reinforced concrete structures is a serious problem for the global economy. The damages are induced by the corrosion of reinforcing steel, which otherwise passive in an alkaline concrete, becomes de-passivated by chloride ion contamination and/or concrete carbonation. One of the practiced methods for the control of steel corrosion in concrete is the use of corrosion inhibitors. Research has led to numerous numbers of inhibitors which can be used for the prevention and subsequent control of corrosion. in this chapter literature available has been discussed.

2.2 PROTECTION MECHANISM OF CORROSION INHIBITORS

Jang et al. (1995) investigated corrosion of reinforcing steel (rebar) samples in concrete-saturated solutions containing corrosion-inhibitor-added deicing salts and salt substitutes as well as in plain sodium chloride solutions. Galvanic cells were used to determine the effects of corrosion-inhibitor-added deicing salts and salt substitutes on rebar corrosion. The reinforcing steel samples were galvanically coupled and were recovered after 240 days. Pit depths and area percentages of corrosion were determined on the reinforcing steels with an optical microscope. Optimum concentrations were found to exist for the corrosion-inhibitor-added deicing salts and salt substitutes in reducing the rebar corrosion. Dramatic changes of pH values were noted in the concrete-saturated solutions containing corrosion-inhibitor-added deicing salts and salt substitutes. The formation of precipitates caused by chemical reactions between a concrete- saturated solution and corrosion-inhibitor-added deicing salts and salt substitutes was observed, also there is an optimum concentration of the corrosion-inhibitor-added deicing salts and salt substitutes for effective reduction of rebar corrosion. And was also noted that rebar corrosion due to corrosion-inhibitor-added deicing salts and salt substitutes is generally less than 50% of that resulting from plain NaCI solutions.

Fedrizzi et al (2005) studied the effectiveness of migrating corrosion inhibitors (MCIs) and repair mortars against rebar corrosion in concrete specimens made by ordinary Portland

cement with w/c ratio equal to 0.6 and containing 1 wt.% of chlorides. An alkanolamine-based inhibitor was tested in addition with a common mortar and two repair mortars. Electrochemical techniques, measurements of corrosion potential and electrochemical impedance spectroscopy (EIS) were used to determine the corrosion behavior of the specimens when a cell containing a 3.5% NaCl solution was applied on the rehabilitation mortar. Mercury intrusion porosimetry (MIP) was also used for the characterization of repair mortars total porosity and a chemical analysis was made to determine the amount of chlorides penetrated in the mortar layers and in the concrete substrate. Results demonstrate that the simultaneous use of the alkanolamine-based inhibitor with a good barrier coating offers protection against rebar corrosion and allows rehabilitation of deteriorated concrete structures.

On the basis of the performance recorded from the investigations undertaken with different kinds of repair mortars and, in case, with an additional alkanolamine inhibitor based treatment for corroding reinforced concrete it appears that it is important to rehabilitate deteriorated concrete structures using a good barrier effect coating. Thus, the repair mortar must have low porosity, low conductivity and low permeability to aggressive substances to prevent corrosion from chloride ingress in the cover. Moreover, it appears that inhibitor, when applied at the interface between concrete and repair grout, can cause some reduction in the corrosion rate of precorroding steel in concrete with high levels of chloride contamination.

Wombacher et al. (2004) studied the behavior of amino alcohol based (AMA) inhibitors on fresh and hard concrete by electrochemical measurements. The interaction mechanism of the inhibitors with a steel surface has been studied by using sophisticated surface analytical methods. The mode of action was shown by investigating its interaction with the steel surface and the subsequent formation of a protective layer. Concerning the transport of the surface applied inhibitor it could be shown that the penetration of inhibitors into the concrete dependent the concrete quality, the porosity and the humidity.

Sideris and Savva (2005) experimentally investigated the influence of calcium nitrite based corrosion inhibitor on the corrosion of reinforcing steel embedded in 14 different mortars. Two Portland cements, NPC and SR (type I and V according to ASTM Standards) and 12

blended cements were used. The pozzolanic materials used were three lignite fly ashes, silica fume and one natural pozzolan (Milos' Earth). All blended cements were produced in the laboratory by grinding Portland clinker, gypsum and the appropriate pozzolanic material. One commercially available blended cement (CEM II/A-M 32.5N) was also used in this research. Mortar specimens (cylinders 100 * 40 mm) were prepared with and without calcium nitrite and used for measurements of carbonation and chloride-induced corrosion for a time period of 2 years. Chloride resistance was monitored according to ASTM C876 on specimens immersed in a 5% NaCl solution after an initial curing of 28 days. Half Cell Potential, Gravimetric Weight Loss were also done. Figure 2.1 shows gravimetric weight loss of steel rebars after 2 years of immersion in 5% NaCl solution (Sideris et al. ,2005).

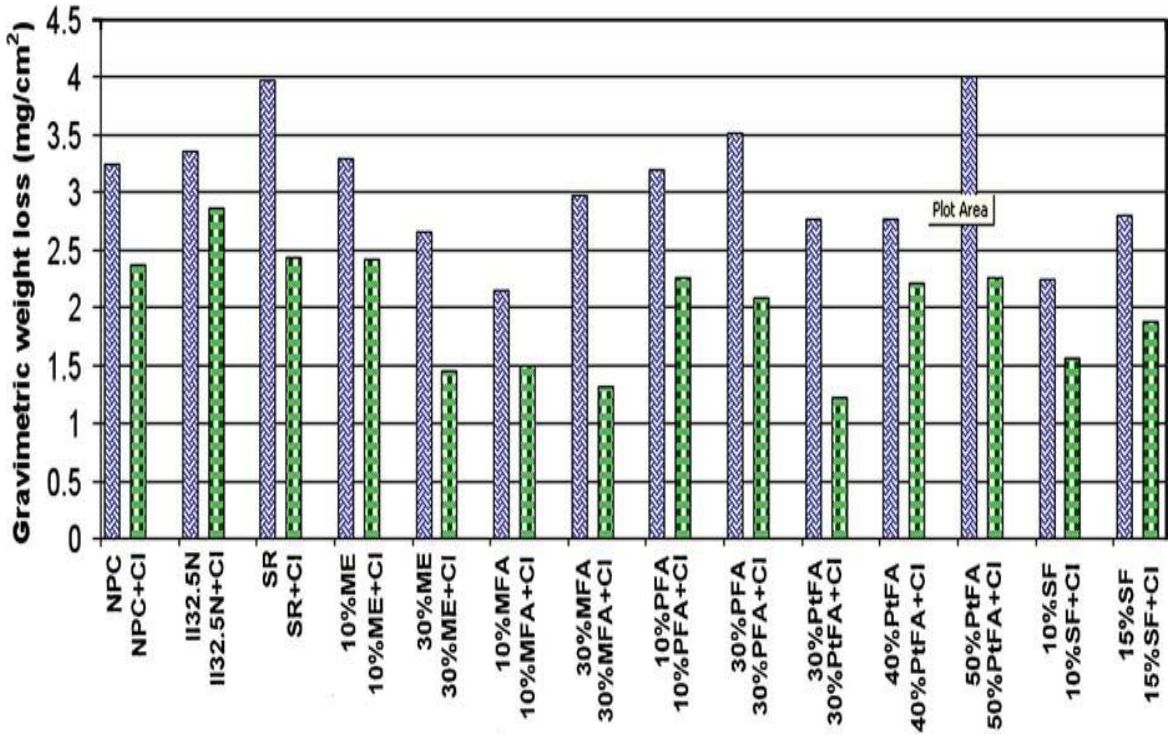

Figure 2.1: Gravimetric weight loss of steel rebars after 2 years of immersion in 5% NaCl solution (Sideris and Savva ,2005)

The carbonation depth was measured on cylinders cured in a severe environment using a spray indicator enabling the estimation of different pH values. Results show that calcium nitrite has a beneficial effect in shifting the corrosion potential towards electropositive direction especially in the case of NPC and SR cements. The corrosion potential of blended

mixtures was also shifted towards electropositive direction, but since the pozzolanic materials had a beneficial effect by themselves, the reduction was comparative smaller.

The beneficial effect of calcium nitrite was also confirmed by the gravimetric weight loss measurements performed after 2 years of immersion in the 5% NaCl solution. Carbonation depth of all mixtures was reduced or remained the same when calcium nitrite was used. Chloride permeability was not seriously influenced by the addition of calcium nitrite, as it is indicated by the total chloride measurements performed after 2 years of immersion in the 5% NaCl solution.

Tommaselli et al (2009) studied the effectiveness of corrosion inhibitors in saturated calcium hydroxide solutions acidified by acid rain components. They analysed the effect of sodium nitrite and sodium molybdate as corrosion inhibitors in a saturated calcium hydroxide solution polluted with sulfuric and nitric acids (acid atmosphere) using Anodic Polarization curve and Impedence test. Both compounds showed significant inhibitory effects depending on the concentration. sodium molybdate showed an efficiency of approximately 67% whereas sodium nitrite showed an efficiency of 52% at low concentrations that is 0.013% total solution mass, but at 0.040% total solution mass (at high concentrations) their inhibitory effect was found to be similar.

Zheng et al. (2012) studied the effect of a surface-applied corrosion inhibitor on the durability of concrete by using capillary water absorption test, chloride penetration test, and accelerated carbonation test. Here they took 3 water-cement ratios of 0.4, 0.5 and 0.6. Results showed that the inhibitor applied on the surface of hardened concrete improved the properties of water resistance, chloride resistance, carbonation resistance and therefore increasing the durability of concrete. However, the effectiveness of the applied inhibitor gradually decreased as water/cement ratio increased and as concrete density decreased. The improvement in the durability of concrete further protects the reinforcement. Unlike surface coatings, the surface-applied corrosion inhibitor cannot form a protective layer on the surface of concrete and its effect on the microstructure of concrete is limited to the surface. Therefore, the surface-applied corrosion inhibitor can improve the durability of concrete but this effect may weaken with time.

2.3 EFFECT OF CORROSION INHIBITOR ON CORROSION IN REBAR

Batis et al. (2003) evaluated the corrosion protection of reinforcement by inorganic coating in the presence of alkanolamine-based inhibitor. Here the specimens were cast using a cement type II-35 (pozzolanic), sand (BS 4550:P6) for the SG technique specimens and pumice 0–5 mm maximum grain dimension from Yali Island in Southeastern Greece for the corrosion testing specimens. Chemical analysis of cement and pumice are shown . Steel bars from steel type S400 and tap water were used. The mixture proportions are shown (SG-test specimens w/c:0.5/1; corrosion-test specimens w/c:0.7/1). A solution of alkanolamine-based corrosion inhibitor was used as an admixture (1 wt.% of cement) in the concrete mass. The SG-test specimens were in the form of 80X80 X 100 mm prisms as described in previous work with one steel bar of diameter 12 mm and length 100 mm machined on a lathe to a final diameter of 10 mm and prepared according to ISO/DIS 8407.3. The bar was embedded 85 mm into the mould. Thus, the exposed area equals to 2750 mm2. The mortar specimens were stored in the curing room (20 ºC, 100% humidity) for 24h in the mould.

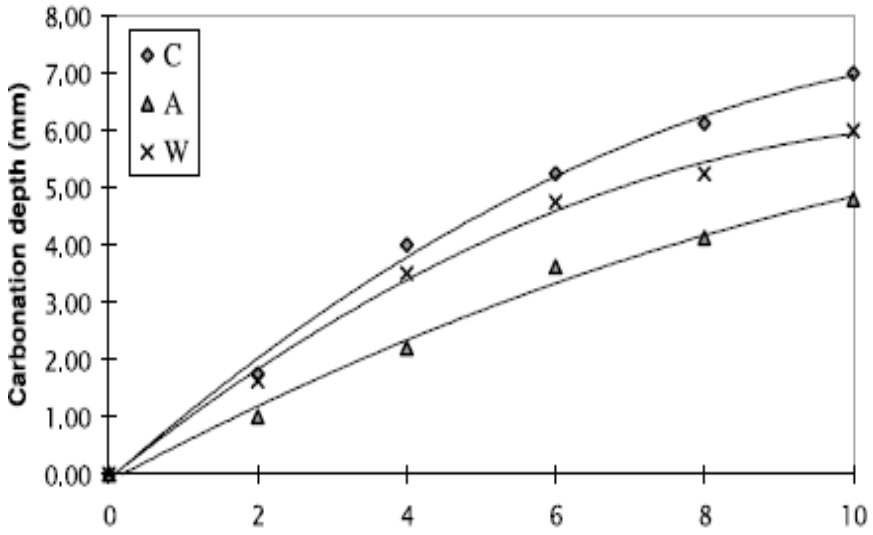

Figure 2.2: Carbonation depth versus time (Batis et al., 2003)

The specimens, after being demoulded, were cured immersed in tap water at 20 ºC for 7 days and then left dry for 24 h. A copper wire cable was connected to each steel bar and the specimens were covered with epoxy resin to protect the connection of steel with copper

cable against corrosion. Each corrosion-test specimen was cast to the form of 80 X80 X100 mm prisms with four steel bars, cylindrical diameter 12 mm and length 100 mm were embedded in it. Here 6 tests were done by them namely Impedence measurement, SG Technique, Carbonation Depth, Half Cell Potential versus Time, Reinforcing Bar Mass Loss and Chloride Diffusion Rate. Figure 2.2 shows carbonation depth versus time and Figure 2.3 shows mass loss of reinforcing steel bars.

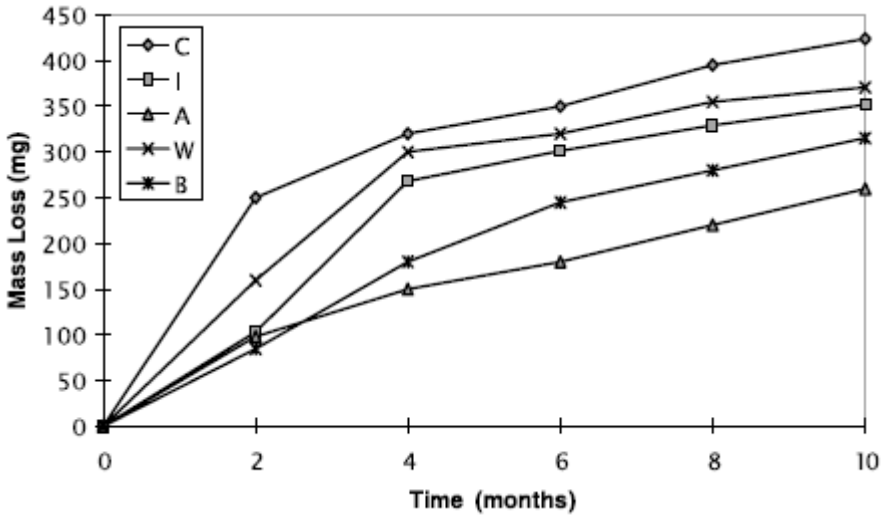

Figure 2.3: Mass loss of reinforcing steel bars (Batis et al., 2003)

They found out that the uncoated specimens exhibit the worst properties having the higher corrosion rate of the reinforcing steel bars, the acrylic dispersion coating provides adequate protection of reinforced concrete under aggressive corrosion environment, the inorganic coating alone results in poor protection and that the simultaneous use of alkanolamine-based corrosion inhibitor and inorganic coating almost equals the protection offered by the acrylic dispersion.

Nmai (2004) studied the mechanism of organic corrosion inhibitor consisting of amines and fatty acid esters. Multi-functional water-based organic inhibitor (MFOI) inhibits the corrosion of steel in concrete by a twofold mechanism that involves the formation of a protective film on the steel surface and a reduction in the susceptibility of concrete to chloride ion penetration, or simply stated, by chloride screening.

When the MFOI is first added to concrete, the esters become hydrolyzed by the alkaline mix water to form the carboxylic acid and its corresponding alcohol. This reaction, under alkaline conditions, is favorable and is not easily reversed. The reaction proceeds as shown in Eq. (2.1), where R and R‘ represent different hydrocarbon molecules:

$$RCOOR' + OH \rightarrow RO^{2-} + R'OH \qquad (2.1)$$

(ester) (base) (acid anion) (alcohol)

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. Film-forming mechanism the MFOI inhibits corrosion by adsorption on the metal surface. It is generally accepted that organic corrosion inhibitors bond to metals by adsorption, which can be physical and/or chemical in nature due to the polar or weakly-polar characteristic of the organic compounds typically used in their formulation.

The non polar tail of the inhibitor molecule is oriented in a direction generally vertical to the metal surface. It is believed that the hydrocarbon tails mesh with each other in a sort of "zipper" effect to form a tight film which repels aqueous fluids, establishing a barrier to the chemical and electrochemical attack of fluids on the base metal. A secondary effect is the physical sorption of hydrocarbon molecules from the process fluids by the hydrocarbon tails of the adsorbed inhibitor molecules. This increases both the thickness and effectiveness of the hydrophobic barrier to corrosion.

Huet et al. (2005) aimed to investigate the transition from passive to active corrosion of mild steel rebars in carbonated concrete. For this purpose electrochemical techniques (polarization curves, free corrosion potential measurements) and surface analyses (EDS, XRD, XPS) were used. Five different electrolytes, with pH ranging from 13 to 8.3, were chosen to simulate the interstitial concrete pore water at various degrees of carbonation. The results indicate that the transition pH is between 10 and 9.4. XPS results indicate a passivation of mild steel for pH values ranging from 13 to 10 due to the formation of a thin iron III oxide layer. Immersion tests highlight the importance of the buffering effect of the

carbonate content. At the free corrosion potential in an aerated solution, a decrease of the carbonate content increases the corrosion rate. On the opposite, at low electrode potential, the kinetics of oxidation increases with the carbonate content.

Passivation of FeE500 steel from pH 13 to 10 is confirmed by an increase of Ecor during corrosion test. After immersion, XPS analyses have shown that the oxide layer formed is very thin (<10 nm) and is mainly composed of iron III oxides. Decreasing the pH and/or decreasing the carbonate content of the electrolyte promotes the active corrosion of mild steel sample leading to the formation of a large amount of iron oxides that do not protect the steel substrate from further corrosion.

Królikowski and Kuziak (2011) took steel electrodes that were made of structural carbon steel rods with 8 mm diameter and about 19 cm^2 surface area exposed to the solution. The steel surface was polished with emery paper from 120 to 220 grit and then degreased with acetone and rinsed with methanol. Here inhibition effect of calcium nitrite was performed in a solution that represented the pore liquid in chloride contaminated concrete. The test protocol was adjusted to follow the performance of penetrating corrosion inhibitors in real reinforced concrete structure.

First the steel samples were pre-passivated by exposure to saturated solution of $Ca(OH)_2$ for 3 days. It was noted that at least 2 days exposure in alkaline solution was necessary to reach a good passive state of carbon steel. Then the steel was exposed to the solution as chloride contaminated concrete that is saturated solution of $Ca(OH)_2$ with addition of 1% NaCl. The steel samples were kept in this solution for 7 days to initiate corrosion. Subsequently, doses of calcium nitrite were added to simulate a gradual increase in the inhibitor concentration thus corresponding decrease in the chloride to nitrite ratio. All solutions were prepared from analytical grade reagents using double-distilled water. Calcium nitrite was supplied as 30% aqueous solution. Solutions were open to air and kept at room temperature(20±2 ◦C) during the test.

Two series of test were performed with different manner of calcium nitrite addition. Larger doses of inhibitor were given in the series CA I, so the final value of this ratio equal 0.33 was reached after 4 weeks from the initiation of steel corrosion. In contrary, lower additions

were applied in the series CA II, and the same value of the $[Cl^-]/[NO^{2-}]$ ratio was approached after 11 weeks from the initiation of steel corrosion.

They compared Impedance spectra (in Bode format) taken after these treatments. The capacitive response (a broad, asymmetrical peak of the phase angle) and large values of low frequency impedance for steel after the pre-passivation confirmed the development of passive film on steel surface. Dramatic change in impedance data was observed after subsequent exposure of pre-passivated steel in the chloride containing solution. Figure 2.4 shows images of steel.

Figure 2.4: Images of steel samples: (a) after the corrosion initiation and (b) after the last addition of inhibitor for CA I and CA II tests (Królikowskia et al, 2011)

They found out that in early stages of the corrosion process calcium nitrite can be effective as a penetrating corrosion inhibitor when present in enough quantity and that the ability of calcium nitrite to inhibit the initiated corrosion of steel depends not only on the chloride to nitrite ratio, but also on the time passing from the corrosion initiation. Also that the

polarization resistance or related parameters taken from impedance data can serve directly as an indicator of the corrosion behaviour of steel in concrete or concrete simulating solutions, without need of their conversion into corrosion current density.

Miyazato and Otsuki (2012) experimentally investigated the pattern of corrosion cell formation (macrocell and microcell) as well as the corrosion rate using mortar specimens with defects simulating cracks and/or joints. The three important factors are listed as follows: 1) supply position of chloride ions or carbon dioxide, 2) environmental conditions, and 3) water-cement ratio of mortar. The results indicated that in the case of chloride induced corrosion, decreasing the water-cement ratio (0.3) increased the activity of macrocell prominent corrosion. On the other hand, increasing the water-cement ratio (0.7) increased the activity of microcell prominent corrosion. Therefore, in the presence of defects, a high corrosion rate might be promoted even at a low water-cement ratio. They also found that in the case of carbonation induced corrosion macrocell prominent corrosion occurred regardless of the water-cement ratio, and the lower the water-cement ratio, the lower the corrosion rate. Finally, they proved that the corrosion rate induced by chloride was higher than that induced by carbonation.

Rankata et al. (2013) studied about the corrosion protection of steel with DMEA-based organic inhibitor. The test specimens considered for this study were cylinders 100 mm in height and 40 mm in diameter. One steel rebar was axially embedded in each cement mortar Cement, sand and water were mixed in a mortar mixer for approximately 5 min until a uniform consistency was achieved. The molds 100 mm in height and 40 mm in diameter were filled with mortar and vibrated for consolidation using a vibrating table. Copper wire cables were connected to the steel bar in order to receive electrochemical measurements.

Steel rebars were cleaned prior to their installation into the mortars according to ISO/DIS 8407.3 Standard . In particular the surface of the steel bars was washed with water and then immersed in strong solution of HCl (500 ml HCl, density q = 1.19 g/ml3 in 1000 ml distilled water) with organic corrosion inhibitor (3.5 g hexamethylene tetramine in 1000 ml distilled water) for 15 min, washed with water and washed thoroughly with distilled water to eliminate traces of the corrosion inhibitor and chloride ions. Following that, the surface was cleaned with alcohol and acetone and finally weighed to accuracy of 0.1 mg. Thereafter the

bars were placed in cylindrical molds, where the mortar was cast and stored at ambient conditions in the laboratory for 24 h.

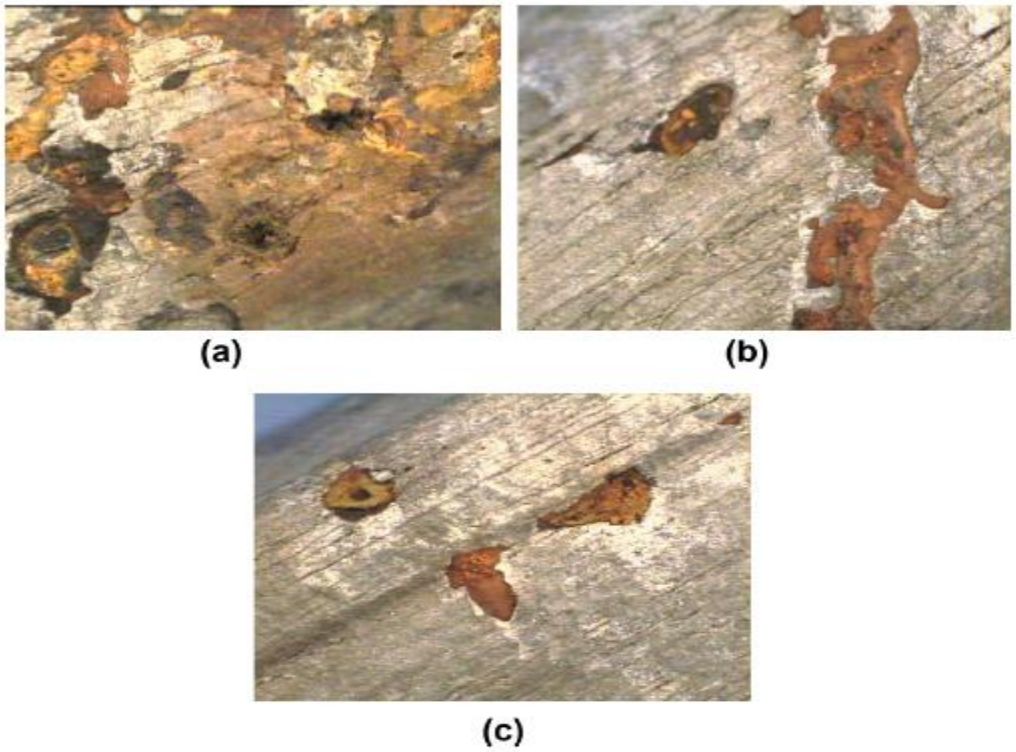

Figure 2.5: Fiber optical microscope images after 7 months partially immersion in 3.5 wt.% NaCl solution. Surface morphology of (a) steel reinforcement embedded in contaminated mortar with chloride ions (2 wt.% of cement), (b) steel reinforcement embedded in contaminated mortar with chloride ions (2 wt.% of cement) treated with corrosion inhibitor (DMEA 1 wt.% of cement) and (c) steel reinforcement embedded in contaminated mortar with chloride ions (2 wt.% of cement) treated with corrosion inhibitor (DMEA 2 wt.% of cement). For all the steel reinforcements the magnification used was 50 (Rankata et al., 2013)

After being demolded the specimens were placed in water in curing room (RH > 98%, T = 20 ± 1.5 ºC) for 24 h and then kept for an additional 7 days at ambient temperature in a laboratory environment to stabilize internal humidity. Epoxy resin was placed in the region in order to avoid atmospheric corrosion. Finally the specimens were partially immersed in 3.5 wt.% NaCl solution up to 20 mm from the bottom. The objective of partially immersing

the cement mortar specimens was to provide an increase of required moisture and oxygen for the initiation and acceleration of reinforcement corrosion. The chloride concentrations of the exposure solutions were selected to avoid leaching of chloride ions casted into cement mortar as contamination. The experimental duration of this study was 7 months.

Methods used to assess cement mortar specimens performance included the measurement of corrosion potential, corrosion rate and mass loss. The corrosion potentials for each of the test specimens were recorded at regular intervals versus a saturated calomel reference electrode (SCE). The measurements were initially recorded on an everyday basis until equilibrium conditions were established and then they were recorded on a weekly basis. Fiber optical microscopic images were also taken.

The corrosion potentials in cement mortar specimens contaminated with chloride ions shift to more negative values as the chloride concentration increases. On the other hand, when corrosion inhibitor is added, the corrosion potentials shift towards more positive values. The addition of 2 wt.% of cement DMEA inhibitor decreases the mass loss of the steel rebar about 43%. The corrosion rate of steel reinforcement increases as chloride concentration increases. However, the corrosion rate of the rebars decreases as the concentration of the corrosion inhibitor increases. Figure 2.5 shows fiber optical microscopic images.

2.4 CORROSION INHIBITORS AND CARBONATION INDUCED CORROSION

Parrott (1994) studied the measurements of corrosion in steel rods embedded at 4, 8, 12 and 20 mm from the exposed surface of concrete dried and carbonated uniaxially for 04, l .5 and 4 years. Corrosion was stimulated by exposing all specimens tao moist environment for a prescribed period prior to extraction and cleaning of the rods for gravimetric corrosion measurements. Corrosion was mainly controlled by the unneutralized remainder, i.e. the depth of reinforcement cover minus the depth of carbonation. Corrosion increased as the unneutralized remainder reduced from about +5 mm to - 10 mm. The relationship between corrosion and the unneutralized remainder was not signi3cantly affected by the depth of cover, the water/cement ratio, the period of curing or the exposure conditions during carbonation. However, corrosion seemed to be increased when there was 50% ground

granulated blast-furnace slug in the cement; in contrast 30% pulverized fuel ash or 5% ground limestone had little effect.

Monticelli et al. (2000) studied the inhibiting behavior of many organic and inorganic substances against steel corrosion 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 β-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 30®, which is a commercial corrosion inhibitive filming product. Chloridepolluted 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 30® coating. 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.

Gaidis (2004) used secondary ion mass spectroscopy to identify the surface layer of protection to be composed of the parent amino alcohol and the associated radicals, which completely cover all the anodic and cathodic sites. The results showed that amino alcohols form a continuous inhibitive layer and displace chloride and other ions from the surface. The investigations revealed that dimethylethanolamine, a model compound in such inhibitors, absorbs on mild steel in layers of roughly 20 Å and neutralized amino alcohols form layers of roughly 100 Å thickness. The XPS (X-ray photoelectron spectroscopy) spectra reveals that hydroxide groups and anions, normally strongly adsorbed on the steel surface, are replaced by amino alcohol. The amino alcohols can displace chlorides, other ionic species and carbon from mild steel in a chloride environment, with chloride/ amino alcohol ratios varying from 1 to 20.

Gaidis reported that the formation of chelate complexes with the iron ions at the steel surface has therefore to be considered. Amino alcohols such as ethanolamine (H_2N-CH_2-CH_2-OH) and dimethyl ethanolamine (($(CH_3)_2N$-CH_2-CH_2-OH) control corrosion by attacking cathodic activity, blocking sites where oxygen picks up electrons and is reduced to hydroxyl ion. These are also adsorbed at anodic sites as well.

Bertolini et al (2008) used electrochemical realkalisation which is a technique aimed at stopping rebar corrosion in carbonated concrete. The alkalinity of the concrete around the rebars is restored, and an environment favourable to the passivation of steel is re-created. The technique is based on the application of a DC current from an anode, placed on the external surface of the concrete, and the rebar. The anode is usually embedded in cellulose pulp soaked with a solution of sodium or potassium carbonate. The rebar and the anode are connected to a DC current feeder, the rebar to the negative terminal and the anode to the positive terminal.

The applied current produces alkalinity at the surface of the rebar, while the alkaline electrolyte in which the anode is immersed penetrates from the external surface. In this way the concrete is realkalised, its protective characteristics towards the steel are restored and rebars can return to passive conditions. The treatment is temporary: this feature makes it very attractive in the field of historical buildings and cultural heritage, where the conservation of the original materials and surfaces is often a stringent requirement in the design of the repair. This paper shows the advantages of this technique applied to historical structures by describing the application to a bell tower built in the 1920s.

The electrochemical realkalisation treatment was applied to eight columns on the bell tower where a traditional repair (based on the substitution of carbonated concrete with a repair mortar) would have been practically impossible. The application of the treatment followed two steps: initially a trial was made on two sections of two columns so as to calibrate the process parameters such as current density, time length and type of anode. After that the treatment was applied to all the columns. The analyses carried out on the concrete after the application of the treatment showed that the protection to the reinforcement was mainly connected to the alkaline layer produced around the steel, which is expected to prevent

further corrosion of the steel. Figure 2.6 shows progress of electrochemical realkalisation of concrete cover.

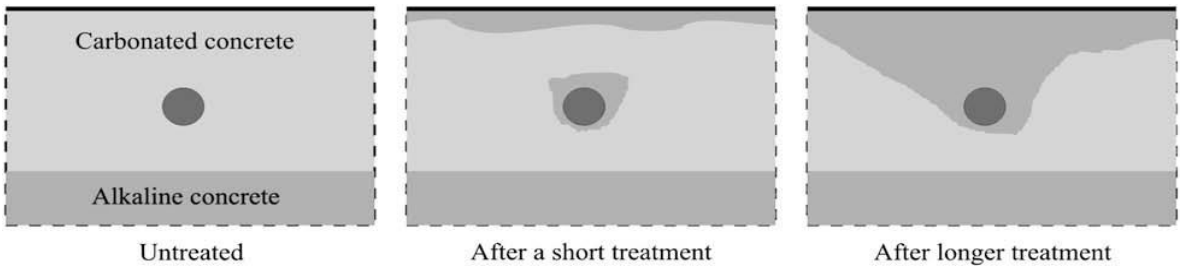

Figure 2.6: Progress of electrochemical realkalisation of the concrete cover (Bertolini et al, 2008)

Kubo et al. (2013) studied the application of electrochemical organic corrosion inhibitor injection to a carbonated reinforced concrete railway viaduct. The target structure selected for trial application of electrochemical corrosion inhibitor injection was a viaduct that has been in service carrying high-speed rail train cars for almost 40 years in Tokyo. The designed concrete cover is 40 mm for a slab and a cantilever, 50 mm for the bottom of a beam and 60 mm for the side of a beam. The viaduct's total surface of 56 m2 was used for the site trial. Based on the survey record prior to the electrochemical treatment, the reinforcing steel bars were found to be almost exactly where they were expected to be located and the average carbonation depth measured was 19 mm for cantilevers, 36 mm for slabs and 40 mm for bottom and side beams.

Before the current application, the concrete surface was inspected visually and by sounding with hammers to confirm that there were no significantly large cracks or regions of cover de-lamination. Small cracks with widths of <0.2 mm found during the inspection of the concrete surface were sealed with silicone sealant to avoid short circuits. To establish electric circuits, the cover concrete was first chipped to expose the steel bars. One end of a wire was then connected to the embedded steel (13 mm) that would act as the cathode and a cementitious mortar patch was applied to reinstate the concrete that had been removed.

The other end of the wire was connected to a stainless steel anode mesh (13 mm and 100 mm grid), fixed at a 20 mm distance from the concrete surface, via a DC power supply (galvanostats and convertors) that was able to provide a constant current to the circuit (max

capacity: 150 V and 100 A). Independent electrical circuits were carefully prepared for three sections surrounding each different part respectively (cantilever, beam, and slab).Appearance of concrete after treatment, carbonation depth, efficiency of electrochemical injection, pore solution pH near cathode and evolution of inhibitor concentration profiles after treatment were noted .

From the site trial described above, the electrochemical injection of the organic base corrosion inhibitor, ethanolamine, into an existing aged carbonated concrete railway viaduct was found to allow penetration of an adequate concentration of the inhibitor in the vicinity of the steel for passivation of the steel under the conditions studied. The moderate pH change near the steel cathode during the electrochemical treatment, which is presumably attributable to the buffering action of significant concentrations of ethanolamine injected to this region, would be likely to mitigate the risk of alkali-silica reaction in concrete with certain types of potentially reactive siliceous aggregate. It was also found that variability in concrete cover, as is usually the case in real concrete structures, significantly affects the current density distribution in the medium, resulting in an uneven injection treatment if the individual anode zones are made too extensive.

2.5 IMPORTANCE OF PRESENT RESEARCH WORK

In this research work, the effect of application of three different type of corrosion inhibitors has been seen on properties of concrete. Here carbonation depth and compressive strength of concrete has been noticed. Corrosion inhibitors have been in use now for some time so it was desired to know what it effects were on the strength and carbonation depth of concrete. It was important to know whether it has some harmful effect on the strength of concrete what is extent to which it helps us in control of carbonation depth.

CHAPTER 3

EXPERIMENTAL PROGRAM

3.1 GENERAL

The aim of the study is to note the effect of application of corrosion inhibitors on the properties of concrete. An effort has been made to understand the efficiency of corrosion inhibitor when they are applied on the surface of concrete as migratory inhibitor. The effect is studied in terms of development of compressive strength and carbonation depth after the inhibitor is applied. Effort has been also to understand the trend of carbonation depth in concrete.

3.2 MATERIAL PROPERTIES

Cement, fine aggregates, coarse aggregates, water and three different kind of inhibitors are used for present investigation. The properties of material used for designing concrete mix were determined in laboratory as per relevant code of practice. The aim of studying of various properties of materials was to check the appearance with codal requirements and to enable an engineer to design a concrete mix for a particular required strength. The properties of these materials are discussed in the following sections.

3.2.1 Cement

Cement is a fine, grey powder. All materials that go into concrete mix are essential, but the cement is very often the most important because it is usually the delicate link in the chain. The function of cement is first of all to bind the sand and stone together and second to fill up the voids in between sand and stone particles to form a compact mass. It constitutes only about 20 percent of the volume of concrete mix, it is the active portion of binding medium and is the only scientifically controlled ingredient of concrete. Any variation in its quantity affects the compressive strength of the concrete mix. It is mixed with water and materials such as sand, gravel, and crushed stone to make concrete. The cement and water form a paste that binds the other materials together as the concrete hardens. The ordinary cement contains two basic ingredients namely argillaceous and calcareous. In argillaceous materials,

clay predominates and in calcareous materials calcium carbonate predominates. In this study two types of cements have been used, that is OPC and PPC.

Table 3.1: Physical Properties of OPC-43 Grade Cement

Property	Value	Value as per IS 8112:1989
Grade	OPC-43	
Standard Consistency	28%	-
Specific Gravity	3.12	-
Initial Setting time	100 min	Not less than 30 minutes
Final Setting time	280 min	Not more than 600 minutes
28-Day Compressive Strength	48.01MPa	43MPa

Table 3.2: Chemical Composition of OPC-43 Grade

Constituents	Cement Used (%)
CaO	63.49
SiO_2	21.25
Al_2O_3	4.74
Fe_2O_3	4.30
SO_3	2.92
MgO	1.02
K_2O	0.78
TiO_2	0.36
BaO	0.32
Na_2O	0.30
P_2O_5	0.21
Cl	0.09
MnO	0.08
SrO	0.04
Ratio of aluminia to iron oxide	1.12

Ordinary Portland cement of grade – 43 (J.K. cement) conforming to Indian standard IS:8112-1989 has been used in the present study. The OPC is classified into three grades, namely 33 Grade, 43 Grade, 53 Grade depending upon the strength of 28 days. It has been possible to upgrade the qualities of cement by using high quality limestone, modern equipments, maintaining better particle size distribution, finer grinding and better packing. Generally use of high grade cement offers many advantages for making stronger concrete.

Although they are little costlier than low grade cement, they offer 10-20% saving in cement consumption and also they offer many hidden benefits. One of the most important benefits is the faster rate of development of strength. Ordinary Portland Cement from a single lot was used throughout the course of the investigation. It was fresh and without any lumps. The results of the various tests on cement properties are given in Table 3.1. The chemical composition is given in Table 3.2.

Portland Pozzolana Cement is a kind of blended cement which is produced by either inter-grinding of OPC clinker along with gypsum and pozzolanic materials in certain proportions or grinding the OPC clinker, gypsum and Pozzolanic materials separately and thoroughly blending them in certain proportions. Pozzolana is a natural or artificial material containing silica in a reactive form. It may be further discussed as siliceous or siliceous and aluminous material which in itself possesses little, or no cementitious properties but will in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cement properties. It is essential that Pozzolana be in a finely divided state as it is only then that silica can combine with calcium hydroxide (liberated by the hydrating Portland Cement) in the presence of water to form stable calcium silicates which have cement properties. PPC in concrete helps to reduce drying shrinkage and plastic shrinkage. Drying shrinkage is reduced because of lower internal concrete stresses and slower heat generation. Plastic shrinkage is also reduced considerably because concrete bleeds less at a given slump or workability by using PPC.

Table 3.3: Physical Properties of PPC(Fly Ash based)

Property	**Value**	**Values as per IS 1489(part 1):1991**
Grade	PPC	
Standard Consistency	35%	-
Specific Gravity	3.05	-
Initial Setting time	129 min	Not less than 60 minutes
Final Setting time	430 min	Not more than 600 minutes
28-Day Compressive Strength	45.3MPa	Not less than 33MPa

PPC(Fly Ash based) of ACC was used. For PPC the code referred is IS 1489 (Part 1):1991, the values obtained are checked with reference to the code. The results of the various tests on cement properties are given in Table 3.3. The major chemical components are given in Table 3.4.

Table 3.4: Major Components of PPC

Constituents	Cement Used (%)
CaO	47
SiO_2	23.7
Al_2O_3	12.9
Fe_2O_3	2.04
SO_3	2.21
MgO	1.74
K_2O and Na_2O	0.6
Cl	0.01
Insoluble Residue	20

3.2.2 Fine Aggregates

The material which passes through 4.75 mm sieve is termed as fine aggregate. Usually natural sand is used as a fine aggregate. At places, where natural sand is not available, crushed stone is used as a fine aggregate. The sand used for the experimental works is locally procured and conformed to grading zone II. The sieve analysis of fine aggregates is shown in Table 3.6 . The physical properties are provided in Table 3.5.

Table 3.5: Physical Properties of Fine Aggregate

Property	Value
Specific Gravity	2.59
Water Absorption	1.52%

3.2.3 Coarse Aggregate

The broken stone is generally used as a coarse aggregate. The nature of work decides the maximum size of the coarse aggregate. Locally available coarse aggregate having the maximum size of 10mm and 20 mm was used in the present work. The properties of natural aggregate are presented Table 3.7. Sieve analysis is given in Table 3.8 and Table 3.9.

Table 3.6: Sieve Analysis of Fine Aggregate

Sr. No.	IS-Sieve (mm)	Wt. Retained (gm)	Retained (%)	Passing (%)	Cumulative retained (%)
1	4.75	26	2.6	97.4	2.6
2	2.36	107	10.7	86.7	13.3
3	1.18	164	16.4	70.3	29.7
4	600 µ	146	14.6	55.7	44.3
5	300 µ	198	19.8	35.9	64.1
6	150 µ	272	27.2	8.7	91.3
7	Pan	87	8.7		
TOTAL		1000		SUM	245.3
Zone II			FM= 2.45		

Table 3.7: Physical Properties of Coarse Aggregate

Characteristics	Value	
Color	Grey	
Shape	Angular	
Maximum size	20mm	10mm
Specific Gravity	2.69	2.657
Water Absorption	0.5%	0.46%

Table 3.8: Sieve Analysis of Coarse Aggregate 20 mm

Sr. No.	IS-Sieve (mm)	Wt. Retained (gm)	Retained (%)	Passing (%)	Cumulative retained (%)
1	80	0.00	0.00	100	0
2	40	0.00	0.00	100	0
3	20	37	0.37	99.63	0.37
4	10	9601	96.01	3.62	96.38
5	4.75	337	3.37	0.25	99.75
6	2.36	24	0.24	0.01	99.99
7	1.18	0	0	0	100
8	600	0	0	0	100
9	300	0	0	0	100
10	150	0	0	0	100
11	Pan	1	0.01	0	
Total		10000			696.49
FM = 6.97					

Table 3.9: Sieve Analysis of Coarse Aggregate 10mm

Sr. No.	IS-Sieve (mm)	Wt. Retained (gm)	%age Retained	%age passing	Cumulative % retained
1	80	0.00	0.00	100.00	0.00
2	40	0.00	0.00	100.00	0.00
3	20	0.00	0.00	100.00	0.00
4	10	4373	43.73	56.27	43.73
5	4.75	4355	43.55	12.72	87.28
6	2.36	980	9.8	2.92	97.08
7	1.18	261	2.61	0.31	99.69
8	600	27	.27	0.04	99.96
9	300	0	0	0	100
10	150	0	0	0	100
11	Pan	4	0.04	0	
Total		10000			627.74
F.M. = 6.28					

3.2.4 Water

Water is an important ingredient of concrete as it actively participates in the chemical reaction with cement. Since it helps to form the strength giving cement gel, the quantity and quality of water is required to be looked into very carefully. Potable water is generally considered satisfactory. In the present investigation, tap water was used for both mixing and curing purposes.

3.2.5 Corrosion Inhibitor

‘‘A chemical substance that decreases the corrosion rate when present in the corrosion system at suitable concentration, without significantly changing the concentration of any other corrosion agent.’’ (ISO 8044:1989) This definition excludes other corrosion protection methods such as coatings, pore blockers and other materials, which change the water, oxygen and chloride concentrations. However, some inhibitors also behave as pore blockers, which is a secondary property. The use of organic corrosion inhibiting admixtures has grown over the last 15-20 years(Ormellese et al. 2006) because they provide a level of protection and longevity that would be too difficult (essentially too expensive) to achieve otherwise.

For the present study para-Aminobenzoic Acid, Aminoethanol and Sika ® FerroGard ®-903+ were tested. The properties of these corrosion inhibitors are discussed here:

A. Sika ® FerroGard ®-903+

Sika ® FerroGard ®-903+ is a surface applied mixed corrosion inhibitor, designed for impregnation of steel reinforced concrete and is an improved formulation of the original Sika ® FerroGard ®-903. It is based on organic compounds. It penetrates the concrete and forms a protective monomolecular layer on the surface of the reinforcing steel. The company claims that it is effective in Cl^- induced corrosion, so for this study its effect on concrete for carbonation is noted. Physical properties of Sika ® FerroGard ®-903+ are provided in Table 3.10.

Table 3.10: Physical Properties of Sika ® FerroGard ®-903+

Form	
Appearance / Colour	Transparent liquid
Packaging	25 kg pail 220 kg drum
Storage	
Storage Conditions / Shelf life	24 months from date of production if stored properly in undamaged and unopened, original sealed packaging. Store in a cool environment. In case of - frost (< -5°C), - reversible crystallisation may occur. If this happens, let the product warm up at room temperature (+15 to +25 °C), then stir well to re-dissolve the crystals
Technical Data	
Chemical Base	Aqueous solution of amino alcohols & salts of amino alcohols
Density	~ 1.04 (at +20°C)
pH Value	~ 10
Viscosity	~ 24 mPa .s

B. para-Aminobenzoic Acid (PABA)

In this study para-Aminobenzoic Acid is used as an migratory corrosion inhibitor. It is an organic substance where NH_2^- is present on para position with the $COOH^-$ ion. This when mixed with methanol and DMSO gives liquid solution which is thick and when applied as

corrosion inhibitor it blocks the pores of concrete to some extent and further prevents the concrete from corrosion.

para-Aminobenzoic Acid is an organic substance which is available in solid form and to be able to apply to concrete it needs to be converted into solution form. It was done by mixing it with Ethanol and DMSO (Dimethyl sulfoxide). For every 6ml of para-Aminobenzoic Acid, 6ml of DMSO and 1.5 ml of Methanol is added. Physical properties are given in Table 3.11. Molecular structure is shown in Figure 3.1.

Dimethyl Sulfoxide (DMSO) is an organosulfur compound with the formula $(CH_3)_2SO$. This colorless liquid is an important polaraprotic solvent that dissolves both polar and nonpolar compounds and is miscible in a wide range of organic solvents as well as water. It has a relatively high melting point. DMSO has the unusual property that many individuals perceive a garlic-like taste in the mouth after contact with the skin. Physical properties are given in Table 3.12. Molecular structure is shown in Figure 3.2.

Methanol, also known as methyl alcohol, wood alcohol, wood naphtha or wood spirits, is a chemical with the formula CH_3OH(often abbreviated MeOH). Methanol acquired the name "wood alcohol" because it was once produced chiefly as a byproduct of thedestructive distillation of wood. Modern-day methanol production occurs in a catalytic industrial process directly from carbon monoxide, carbon dioxide, and hydrogen.

Methanol is the simplest alcohol, and is a light, volatile, colorless, flammable liquid with a distinctive odour. Physical properties are given in Table 3.13. Molecular structure is shown in Figure 3.3.

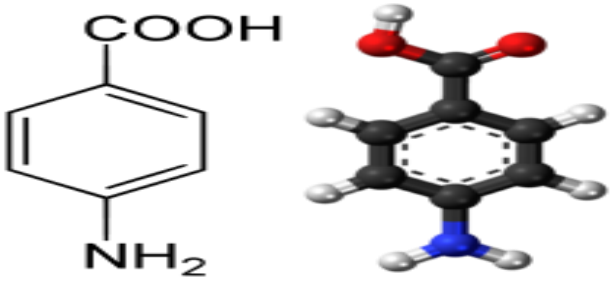

Figure 3.1: Molecular Structure of PABA

Table 3.11: Physical Properties of PABA

Chemical formula	$C_7H_7NO_2$
Molar mass	137.14 g·mol^{-1}
Appearance	White-grey crystals
Density	1.374 g/mL
Melting point	187 to 189 °C (369 to 372 °F; 460 to 462 K)
Boiling point	340 °C (644 °F; 613 K)
Solubility in water	1 gm /170 mL(25°C) 1 gm /90 mL(90 °C)
Price (INR/Kg)	5000

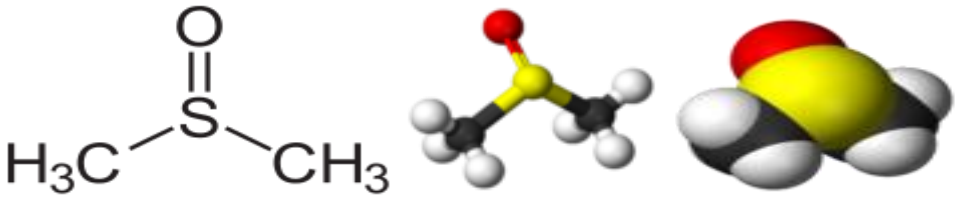

Figure 3.2: Molecular Structure of Dimethyl Sulfoxide (DMSO)

Table 3.12: Physical Properties of Dimethyl Sulfoxide (DMSO)

Chemical formula	C_2H_6OS
Molar mass	78.13 g·mol^{-1}
Appearance	Colourless liquid
Density	1.1004 g cm^{-3}
Melting point	19 °C (66 °F; 292 K)
Boiling point	189 °C (372 °F; 462 K)
Solubility in water	Miscible
Solubility in diethyl ether	very soluble
Acidity (pK_a)	35
Refractive index(n_D)	1.479 ε_r = 48
Viscosity	1.996 cP at 20 °C
Price (INR/Kg)	1050

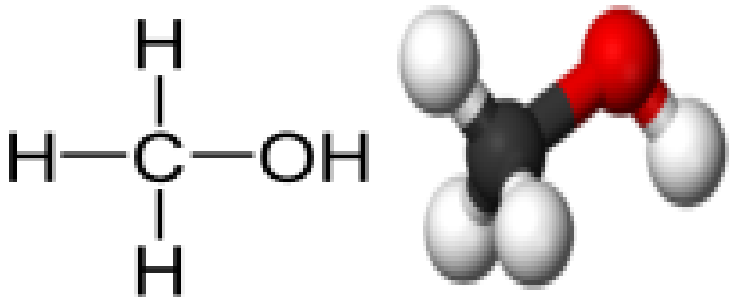

Figure 3.3: Molecular Structure of Methanol

Table 3.13: Physical Properties of Methanol

Chemical formula	CH_3 OH
Molar mass	32.04 g mol^{-1}
Appearance	Colorless liquid
Density	0.792 g·cm^{-3}
Melting point	−97.6 °C (−143.7 °F; 175.6 K)
Boiling point	64.7 °C (148.5 °F; 337.8 K)
log P	-0.69
Vapor pressure	13.02 kPa (at 20 °C)
Acidity (pK_a)	15.5
Refractive index(n_D)	1.33141
Viscosity	0.545 mPa×s (at 25 °C)
Price (INR/Kg)	460

C. Ethanolamine

Ethanolamine, also called 2-aminoethanol or monoethanolamine (often abbreviated as ETA or MEA) , is an organic chemical compound that is both a primary amine and a primary alcohol (due to a hydroxyl group). Like other amines, monoethanolamine acts as a weak base. Ethanolamine is a toxic, flammable, corrosive, colorless, viscous liquid with an odour similar to that of ammonia.

As it is an organic compound and it has presence of amines in it which is used to impart some corrosion inhibition property, it can be taken as an effective amine based organic corrosion inhibitor. This substance is used as corrosion inhibitor due to its presence in cationic form in solution. Which is why it was one of the corrosion inhibitor used by Kubo

et al. (2013) but was applied by the process of electrochemical injection. Physical properties are given in Table 3.14. Molecular structure is shown in Figure 3.4.

Figure 3.4: Molecular Structure of Ethanolamine

Table 3.14: Physical Properties of Ethanolamine

Chemical formula	C_2H_7NO
Molar mass	61.08 g·mol^{-1}
Appearance	Viscous colourless liquid
Odor	unpleasant ammonia-like odour
Density	1.012 g/cm^3
Melting point	10.3 °C (50.5 °F; 283.4 K)
Boiling point	170 °C (338 °F; 443 K)
Solubility in water	Miscible
Vapor pressure	64 Pa (20 °C)
Acidity (pK_a)	9.50
Refractive index(n_D)	1.4539 (20 °C)
Price (INR/Kg)	1150

3.2.6 Phenolphthalein Solution

Phenolphthalein is a chemical compound with the formula $C_{20}H_{14}O_4$ and is often written as "HIn" or "phph" in shorthand notation. Phenolphthalein is often used as an indicator in acid–base titrations. For this application, it turns colorless in acidic solutions and pink in basic solutions.

Phenolphthalein is slightly soluble in water and usually is dissolved in alcohols for use in experiments. It is a weak acid, which can lose H^+ ions in solution. The phenolphthalein molecule is colorless, and the phenolphthalein ion is pink. When a base is added to the phenolphthalein, the molecule ⇌ ions equilibrium shifts to the right, leading to more ionization as H^+ ions are removed. Physical properties are explained in Table 3.15.

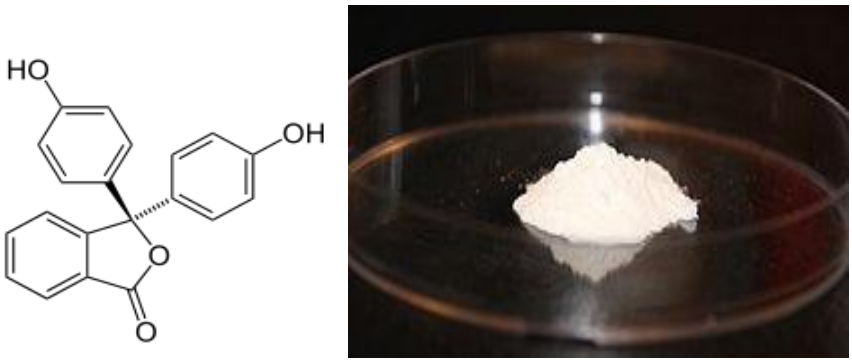

Figure 3.5: Phenolphthalein

Table 3.15: Physical Properties of Phenolphthalein

Chemical formula	$C_{20}H_{14}O_4$
Molar mass	318.33 g·mol^{-1}
Appearance	White powder
Density	1.277 g/cm^3 (32 °C (90 °F))
Melting point	258–263 °C (496–505 °F; 531–536 K)
Boiling point	N/A
Solubility in water	Soluble
Solubility in other solvents	Insoluble in benzene or hexane, very soluble in ethanol and ether, slightly soluble in DMSO
Price (INR/Kg)	620

The phenolphthalein indicator in solution form is available, it can be procured from Savraj Traders.

3.3 MIX DESIGN

Concrete mix has been designed using the provisions under the IS code specification of IS 10262:2009 for OPC 43. The mix proportion is explained in Table 3.16. Both OPC and PPC both were used. For mixes with PPC, OPC was directly replaced by PPC(by weight). In all the rest of the mixes, the mix proportion was kept same. Water content in both was kept same.

In concrete batching, first the natural coarse aggregates was added in the mixer, subsequently, fine aggregates and cement were added to the mixer the ingredients were dry mixed in the mixer for 2 minutes. Then half of water was added and again mixed for 1 minute. After this, the rest of the water was mixed for another 2 minutes. The mixture was

then ready to be poured in the moulds. The 28 day strength of both the mixes was 46 MPa and 44 MPa respectively for OPC and PPC when cured in water for 28 days.

Table 3.16: Mix Design

Substance	Value(Kg/m^3)
Cement	489
Water	186
Fine Aggregate	502
Coarse Aggregate	1152
Water/Cement Ratio	0.38

3.4. CASTING OF SPECIMENS

In this section, casting procedure for compressive strength test and carbonation depth test are discussed. In this test program, 2 types of tests were conducted that is compressive strength and carbonation depth. For both test cube specimen were required. For compressive strength study 150mm cube were for four sets(1 for control and 3 for each of the corrosion inhibitors). These were casted for both PPC and OPC, therefore in total 8 sets were made. For each of these 8 sets, 3 cubes were casted that was to be tested for compressive strength at 28 days from the day of casting. Same number of specimen were casted, so as to test their strength at 56 days from casting day. Some of the cubes casted for compressive strength are shown in Figure 3.6.

For carbonation depth tests 100mm cubes were casted, also in four sets(1 for control and 3 for each of the corrosion inhibitor). Casting was done for both PPC and OPC, giving us in total of 8 sets. All these sets were casted each for 7 day, 14 day, 21 day, 28 day, 35 day, 42 day testing for carbonation depth from the day they were kept in carbonation chamber.

3.5 CURING AND APPLICATION OF CORROSION INHIBITOR

The procedure adopted for curing for both compressive strength test and carbonation depth test was similar. All specimens were water cured for first 7 days and after that they all were further air cured for 7 days. After curing was completed respective corrosion inhibitors were applied to the specimen.

All the corrosion inhibitors were applied at the rate of 0.3Kg/m^2 on all the surfaces of the cubes. Corrosion inhibitor applied to specimen in three coats. after each coat the specimens were left undisturbed to dry for about 1-2 hours. Further after the application of corrosion inhibitors to their respective samples, the specimen for compressive strength test were left at room temperature whereas the specimens for carbonation depth test were kept in carbonation chamber filled with CO_2 for carbonation to take place. The application of corrosion inhibitor on cubes is shown in Figure 3.8.

Aminoethanol and SIKA Ferrogard 903 were applied as they were available in liquid form but para-Aminobenzoic acid was available in salt form so it was first converted in to solution form by mixing it with methanol and DMSO. For every 6gm of para-Aminobenzoic acid 6ml of DMSO and 1.5 ml of methanol was added to make the solution. After the application of corrosion inhibitors the specimens for compressive strength testing were left for air curing at room temperature. And the specimen for carbonation depth were kept in carbonation chamber for carbonation. The environment in the carbonation chamber was kept constant with very little variation. The temperature in carbonation chamber was kept at 28ºC-30ºC with humidity of 60%-70% and CO_2 content of 5%.

Figure 3.6: Cubes after casting for Compressive Strength Test

Fig 3.7: Cubes kept in Carbonation Chamber for Carbonation Depth Test

Figure 3.8: Application of chemicals

3.6 TESTING OF SPECIMENS

In this section, test setup for compressive strength test and carbonation depth test are discussed.

3.6.1 Test Setup for Compressive Strength Test

After application of corrosion inhibitors to the specimens the cubes were kept in air so that they could be tested for their 28 day and 56 day strength from the day of their casting. The compressive strength was calculated by dividing the failure load by average cross sectional area. The compressive strength testing machine of capacity 5000 KN was used for determining the maximum compressive loads carried by concrete cubes. The test was then carried out at the loading rate of 5 KN/s as specified in IS: 516– 1959 for which the specimen was kept perpendicular to the casting position. Average of 3 cubes in compressive strength tests was taken, both for 28 day as well as 56 day strengths. The test setup for compressive strength test is shown in Figure 3.9.

3.6.2 Test Setup for Carbonation Depth Test

For carbonation depth test after, the application of corrosion inhibitor the specimens were kept in the carbonation chamber which shown in Figure 3.10. The carbonation chamber conditions were kept constant for which the CO_2 concentration was kept at 5% with temperature of 28ºC-30ºC. The humidity in the chamber was kept at 60%-70%, though minute but some variation was noted which was due to the variation in temperature. After that they were tested for their 7day, 14day, 21day, 28dy, 35day and 42 day carbonation depth.

To measure carbonation depth, the specimens were broken diagonally so that we get two rectangular faces. The test setup to break the specimens diagonally into 2 is shown in Figure 3.11. After that both these faces were sprayed with phenolphthalein solution. Change in colour of the surface was observed to red or purple. Readings were taken using vernier scale and carbonation depth was measured at 16 locations(8 on each face). Average of these 16 values is taken as the mean value to depict the carbonation dept of the specimen. Specimen after the application of phenolphthalein solution is shown in Figure 3.12.

Figure 3.9: Set Up for Compressive Strength Test

Figure 3.10: Carbonation Chamber

Figure 3.11: Set Up for Carbonation Depth Test

Figure 3.12: Cubes after the application of Phenolphthalein Solution

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 GENERAL

In this chapter, the effect of application of corrosion inhibitor on strength and carbonation depth are discussed. Different types of corrosion inhibitors were used in this study. One of the corrosion inhibitor applied was commercially available corrosion inhibitor. Other inhibitors used for this study were chemicals that are available commercially. The inhibitors used in this study were applied as migratory corrosion inhibitors. These chemicals were applied after seven days of water curing and seven days of air curing for PPC and OPC. the specimen were then left room temperature for compressive strength test and for carbonation depth they were kept inside carbonation chamber. The details of the tests and their corresponding results are discussed here.

4.2 CARBONATION DEPTH

Carbonation depth was measured on cubes of size 100mmX100mmX100mm. Two types of cements were used for studying the effect of corrosion inhibitor on carbonation depth. For each mix, 3 types of corrosion inhibitors were applied on the surface of concrete. Out of the three inhibitors, one was commercially available, while the other two were organic chemicals. Therefore for one type of cement, 4 sets were cast. Out of these 4 mixes, one was control mix and 3 mixes were applied with inhibitors. Therefore in all 8 sets were studied.

These cubes were then cured in water for seven days and after that it was air cured for further seven days. Casting and curing regime for all the sets were kept same. After this curing regime, the corrosion inhibitors were applied on the specimens in three coats. After every coat, a time gap of 1-2 hours was given so that the surface dries for the next coat. The specimens were than kept in the carbonation chamber in which CO_2 was passed at certain environmental conditions. The temperature in the chamber was kept at 28ºC-30ºC with CO_2 content of 5% and humidity of 60%-70%.

The specimens were then tested for carbonation depth at 7 day, 14 day, 21 day, 28 day, 35 day and 42 day from the day they were kept in the carbonation chamber. They were tested by breaking them diagonally, which provided two faces. Each of these specimens was than sprayed by phenolphthalein solution. It is an acid-base indicator and the changes the colour of concrete surface to purple indicating that the absence of $CaCO_3$ at that level. Readings for the carbonation depth tests were than taken using a vernier scale at 8 location on each face. Average of these 16 readings were taken and it was considered to represent the carbonation depth of their corresponding specimen. The carbonation depth was measured at the exposure time of 7 days, 14 days, 21 days, 28 days, 35 days and 42 days. The values of which are represented in Figure 4.1- 4.6.

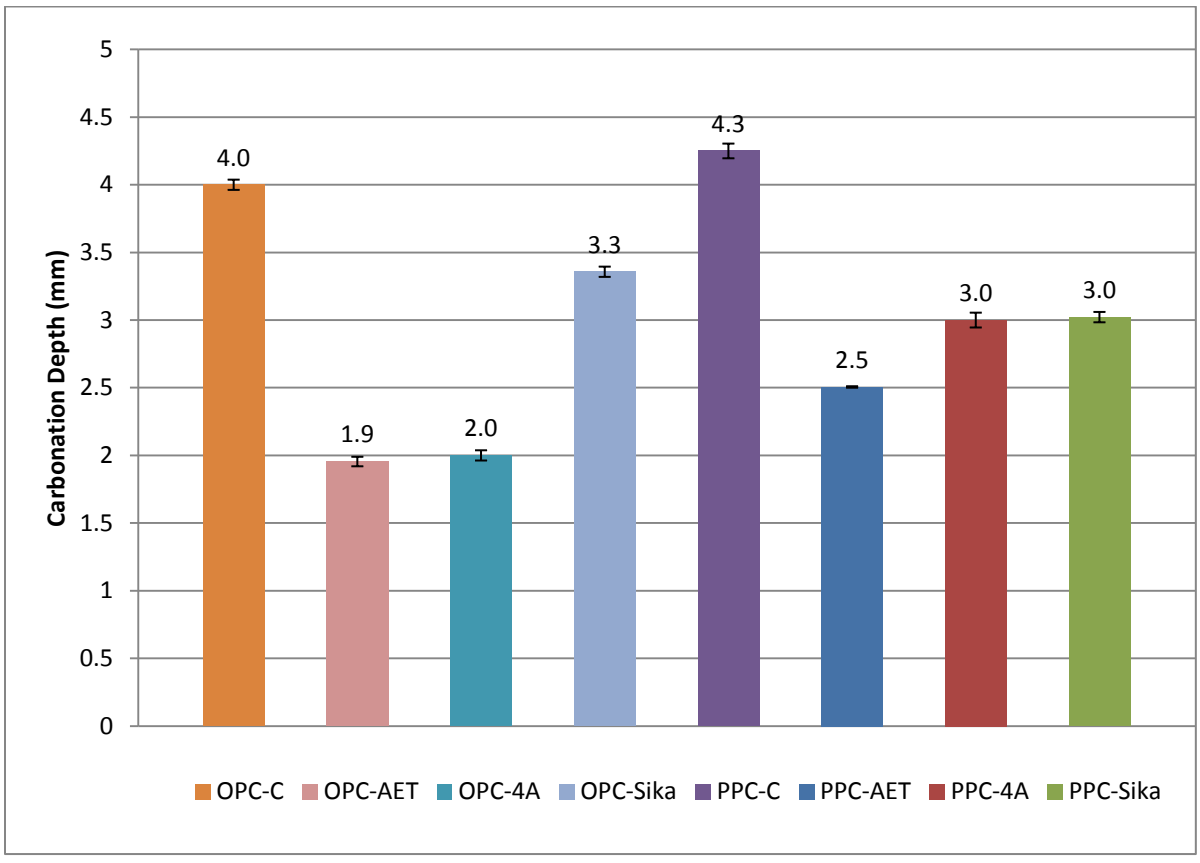

Figure 4.1: Carbonation Depth at 7 Day

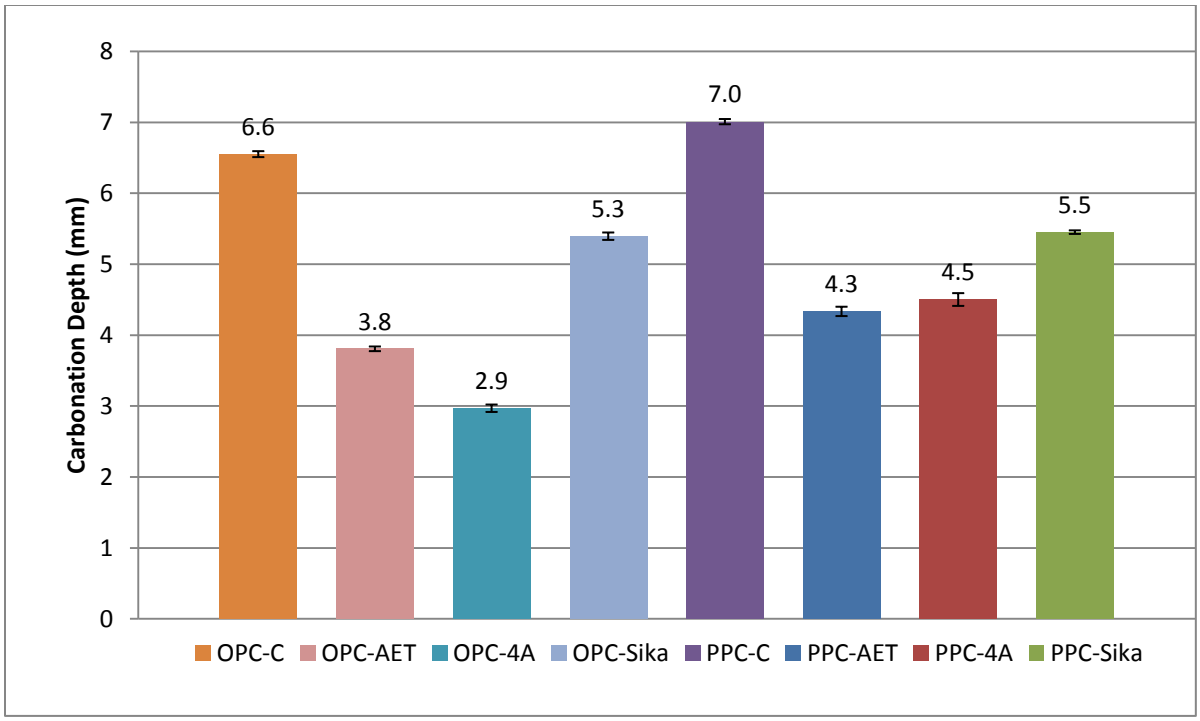

Figure 4.2: Carbonation Depth at 14 Day

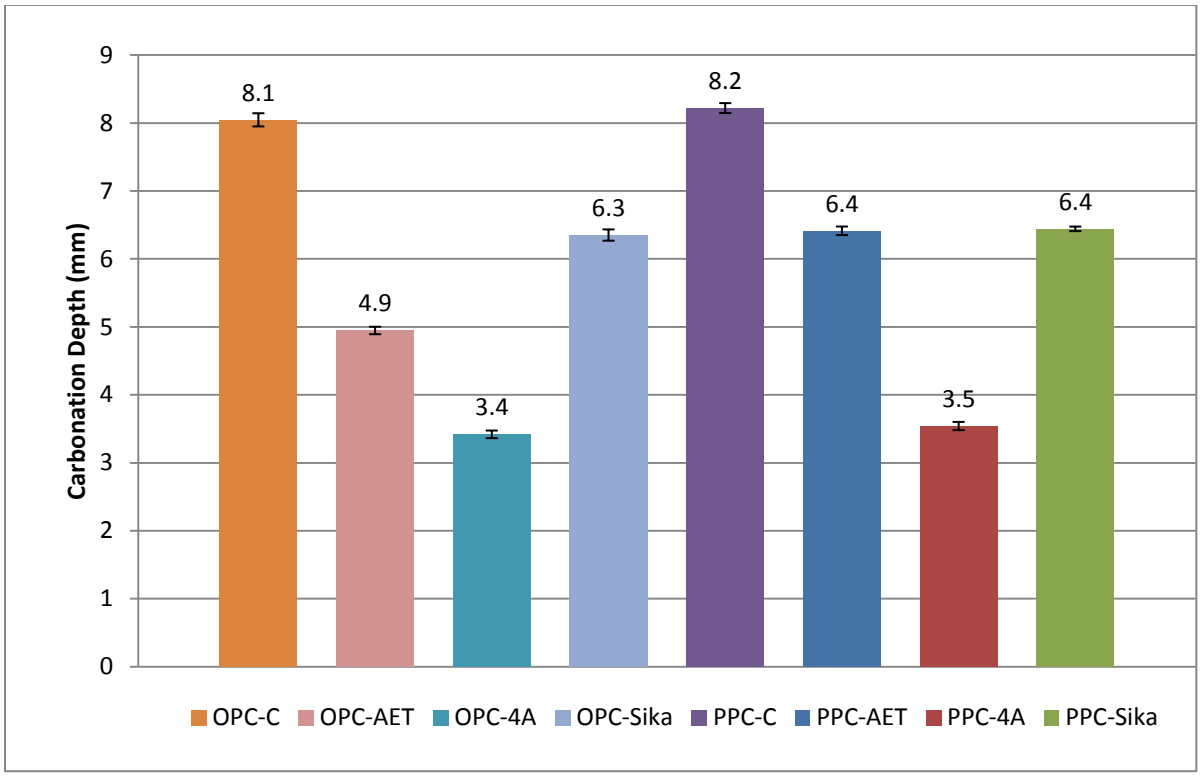

Figure 4.3: Carbonation Depth at 21 Day

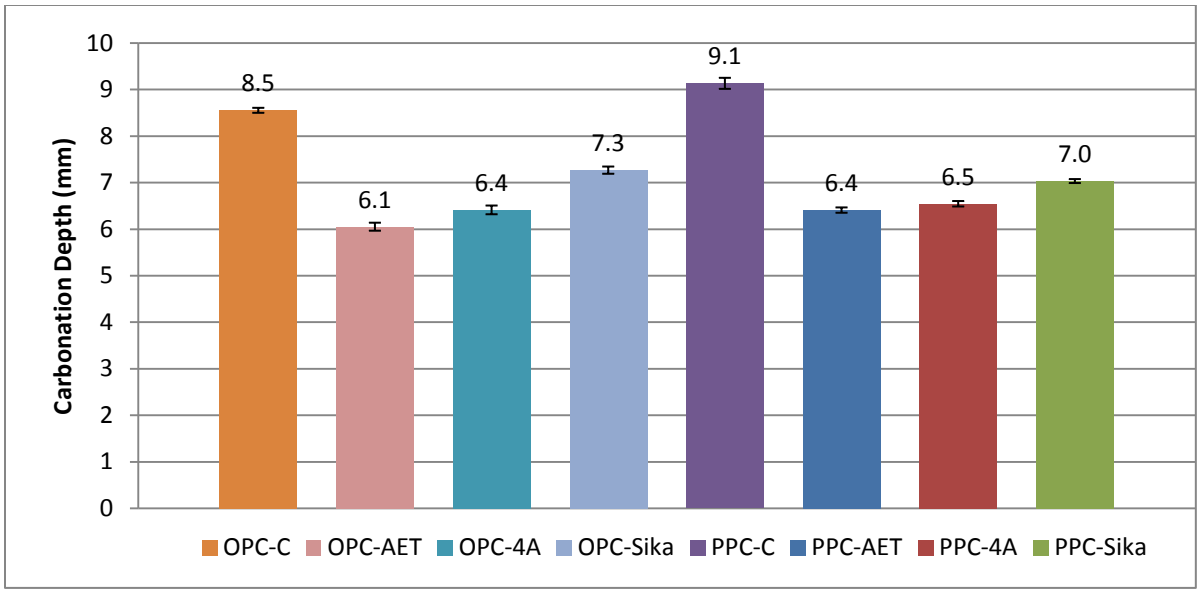

Figure 4.4: Carbonation Depth at 28 Day

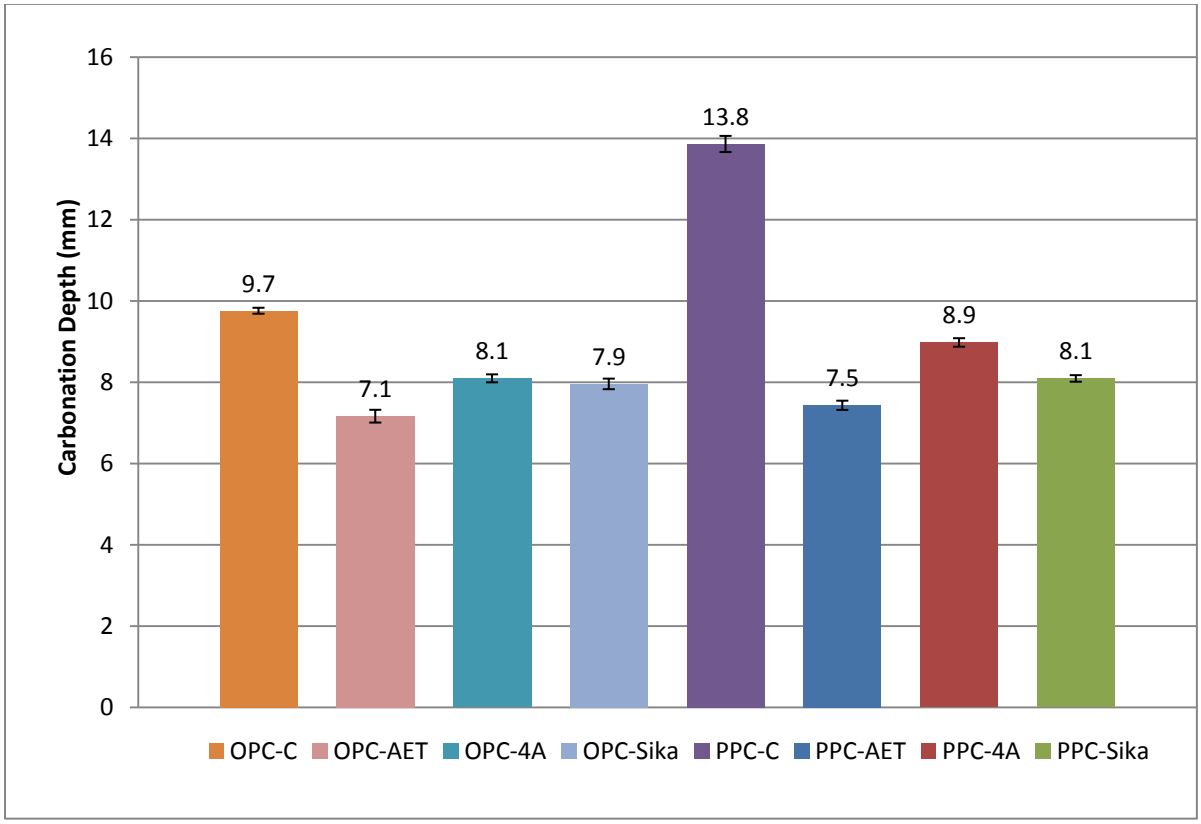

Figure 4.5: Carbonation Depth at 35 Day

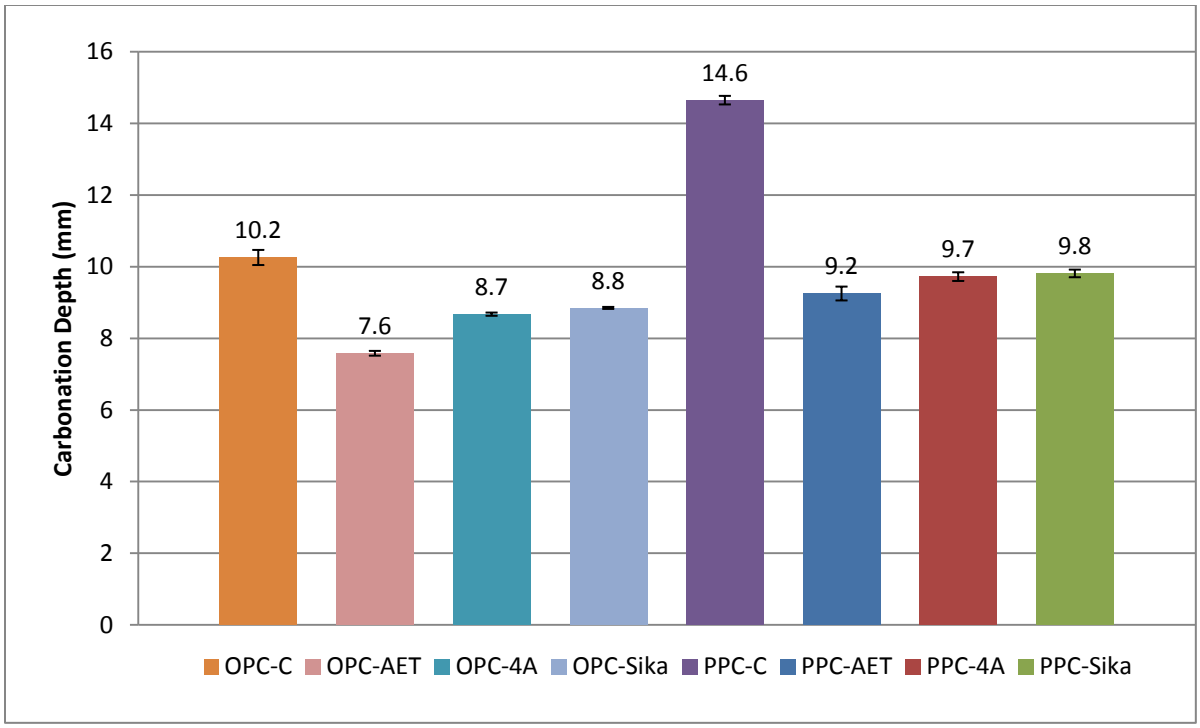

Figure 4.6: Carbonation Depth at 42 Day

4.2.1 Effect of Type of Cement on Carbonation Depth

From the figures it can be observed that irrespective of the duration for which the specimens were kept in the carbonation chamber, it can be seen that the carbonation depth of specimens of OPC were less than that of PPC. It can also be seen that for all the corrosion inhibitors also, the carbonation depth of specimens of OPC were less than that of PPC respectively. For the control specimen where there was no hindrances as no corrosion inhibitor was applied, it was seen that the carbonation depth was quite high. Still it can be seen that the carbonation depth of PPC was higher than OPC. When we compare carbonation depth at 7 day of carbonation it can be seen that OPC was approximately 7% less than PPC. When specimen applied with corrosion inhibitor were considered, a similar trend was observed. It can be seen in Figure 4.1 that the value of carbonation depth at 7 day was 2.0 mm and 3.0 mm for OPC and PPC respectively for para-Aminobenzoic Acid. From Figure 4.3 it was observed that value of carbonation depth is 4.9 mm and 6.4 mm for OPC and PPC respectively for Aminoethanol.

It indicates that PPC is more vulnerable to carbonation induced corrosion than OPC. There can be 2 reasons for this, firstly the curing time given to all the specimen was 7 days. This time of curing is not sufficient for PPC as the pozzolanic reaction normally starts after some days. Secondly, in the pozzolanic reaction, $Ca(OH)_2$ is consumed and is converted to C-S-H gel. Lesser amount of $Ca(OH)_2$ proves to be detrimental for carbonation induced corrosion.

4.2.2 Effect of Duration of CO_2 Exposure

In this research work the specimen were kept in the carbonation chamber and then tested for carbonation depth for durations of 7 days, 14 days, 21 days, 28 days, 35 days and 42 days. It can be seen that whether or not corrosion inhibitor was applied, there was an increase in the carbonation depth of the specimens when their exposure to CO_2 was increased. The specimens were exposed to CO_2 by keeping them in the carbonation chamber. As the duration of exposure of Control specimen to CO_2 was increased by keeping them in the carbonation chamber it was observed that there was an increase in the carbonation depth of the specimens. When we consider carbonation depth specimen of OPC-Sika for 7 day carbonation and 14 day carbonation, it can see that there is an increase of 40% in carbonation with respect to 7 day carbonation. Similarly when carbonation depth for 7 day carbonation (OPC) and 35 day carbonation(OPC) was considered, it was seen that the value of carbonation depth had risen from 4.0 mm for 7 day carbonation to 9.7 mm for 35 day carbonation. This can be seen from Figure 4.5.

As for the specimens coated with corrosion inhibitors, a similar trend is noted as the exposure period was increased. It can be noted that for specimens coated with Aminoethanol as corrosion inhibitor that, as the specimens were kept in the carbonation chamber for a long period of time their carbonation depth increased. It can be seen from Figure 4.2 and 4.4, that the value of carbonation depth for PPC for 14 day carbonation is 5.5 mm which increases to 7.0 mm for 28 day carbonation. Similar trends were observed for OPC as the carbonation depth value of carbonation depth increased with time, which can be seen in Figure 4.1 and 4.2. Similarly, an increase in the value of carbonation depth with increase in the exposure time is also noted for para-Aminobenzoic Acid. It can be seen from Figure 4.5 and 4.6, that there is an increase of approximately 9% in the value of carbonation depth for 42 day carbonation with respect to 35 day carbonation for PPC.

As shown in Figure 4.1-4.6, it was observed that as the time of exposure of the specimen to CO_2 increases the carbonation depth of any specimen, whether it was control specimen or specimen applied with corrosion inhibitors. This was also observed by Roy et al. (1996). It is seen that the rate of carbonation depends on many factors namely temperature, quality of concrete, CO_2 concentration, relative humidity and duration of exposure. Cement used in the casting of specimen were of the same batch, so the quality of cement was same all throughout. After casting, the specimen were water cured for 7 days and then air cured for further 7days. After this curing regime the specimens were then put in carbonation chamber which was supplied with CO_2. The temperature of the chamber was kept at 28ºC-30ºC with humidity of 60%-70% and CO_2 concentration of 5%. As the specimens were kept in carbonation chamber, the environmental conditions were monitored and kept same for the duration of this study. So when environmental conditions and quality of concrete are kept same, the only variable left is exposure time for carbonation depth 'd'.

$$d = k(t)^{0.5}$$

4.2.3 Effect of Corrosion Inhibitors

Irrespective of the type of corrosion inhibitor used, all were showing inhibition property even when applied on outer surface instead of being used as a admixture. But we can see that among all the corrosion inhibitors used Aminoethanol gave us the best results that were consistent.

Sika is a commercially available corrosion inhibitor and when it was taken into account, it can be seen that Sika shows corrosion inhibition property as the value of carbonation depth of specimens coated with Sika were less than that of Control specimen in every case. For PPC as well as OPC, it was seen that there was a decrease in the carbonation depth of the specimens. It can be noted that for carbonation depth for 14 day carbonation (OPC), a decrease of approximately 20% in the carbonation depth of specimen coated with Sika was observed when compared with control specimen. This can also be seen for carbonation depth for 35 day carbonation for PPC, the value of specimen coated with Sika was approximately 41% less than that of Control.

It can be seen that the carbonation depth was affected on addition of corrosion inhibitors. A decrease in carbonation depth is also noted when para-Aminobenzoic Acid was considered as a corrosion inhibitor. It is an organic substance which was applied as a migratory corrosion inhibitor for both type of cements (PPC and OPC) and decreases carbonation depth for both of them. It can be noted for carbonation depth test for 7 day carbonation that there is 50% decrease in carbonation depth for OPC when compared with OPC-Control and that there is a decrement of 30% with respect to Control when specimens for PPC were considered. When consideration was done for carbonation depth results for 21 day carbonation, it was observed that there was a decrease of 57.5% for OPC with respect to Control specimen.

When the specimens coated with Aminoethanol were considered, it can seen that they show good corrosion inhibition property all throughout the tests. It can observed that there is a decrease in the carbonation depth of concrete for both, OPC as well as PPC. When carbonation depth for 7 day carbonation was taken into account, it can be observed that there was a decrease of approximately 52% when compared to Control specimen for OPC and for PPC, a decrease of 42% with respect to the Control specimen was observed. Whereas for 42 day carbonation these values changes to 16% and 37% respectively when compared with control specimens.

As it was also seen in Zheng et al. (2012) the carbonation depth of Control specimen was more than that of specimens with inhibitor. This is due to the pore blocking property of these corrosion inhibitors that the CO_2 applied in the carbonation chamber does not spread as fast as in case of Control specimen. Carbonation takes place when CO_2 reacts with concrete. For the carbonation to take place at certain depth, CO_2 needs to reach there. Which is possible as CO_2 passes through the pores present in concrete. By the application of corrosion inhibitor, the pores get blocked and CO_2 is not able to travel through concrete pores. This leads to lesser carbonation depth in case of corrosion inhibitors.

4.3 EFFECT OF CORROSION INHIBITOR ON COMPRESSIVE STRENGTH

Compressive strength was measured on cubes of size 150mmX150mmX150mm. Two types of cements were used for studying the effect of corrosion inhibitor on compressive strength.

For each mix, 3 types of corrosion inhibitors were applied on the surface of concrete. Out of the three inhibitors, one was commercially available, while the other two were organic chemicals. Therefore for one type of cement, 4 sets were cast. Out of these 4 mixes, one was control mix and 3 mixes were applied with inhibitors. Therefore in all 8 sets were studied. Further, three cubes were casted for each set.

After this the specimens were water cured for 7 days. After water curing the specimens were air cured for further 7 days, corrosion inhibitors were then applied on the specimens. The inhibitors were applied in 3 coats, with a gap of 1-2 hour after each coat to allow it to dry. After the application of corrosion inhibitors the specimen were left at room temperature. The specimens were then tested for their 28 day and 56 day compressive strength on compressive strength testing machine of capacity 5000 KN. Three cubes were tested for each set and the average these results is taken as the value to depict the compressive strength of the set. The results for 28 day and 56 day compressive strengths are shown in Figure 4.7 and 4.8.

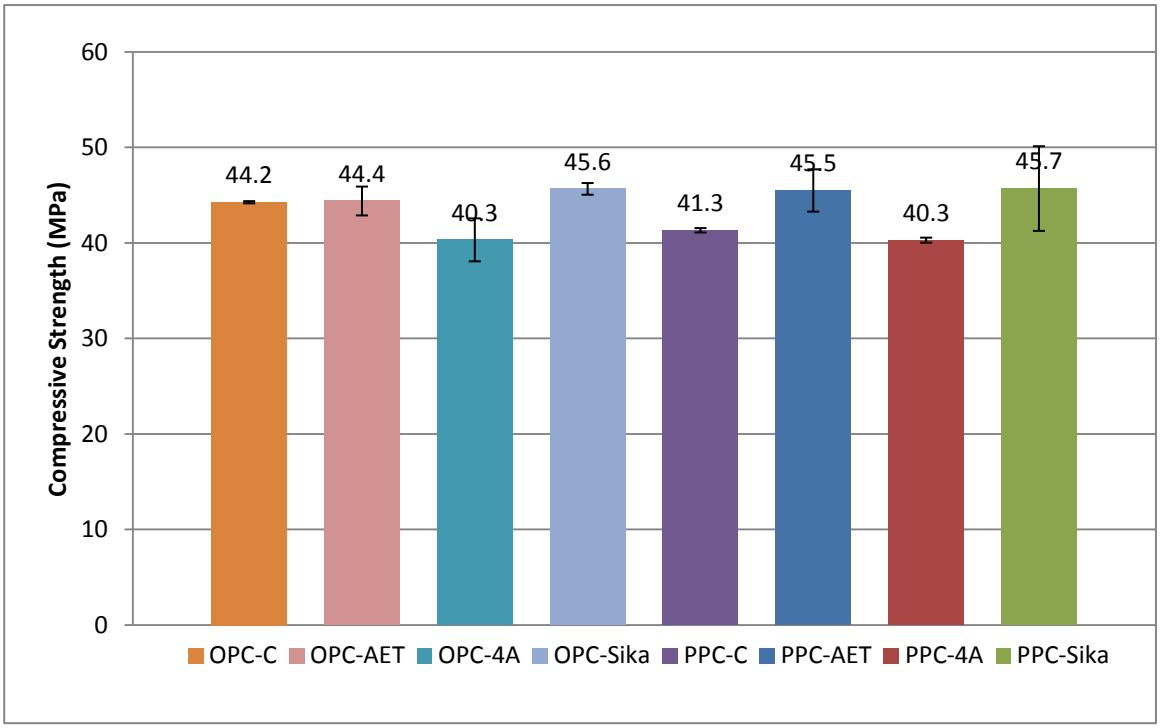

Figure 4.7: Compressive Strength Test at 28 Day

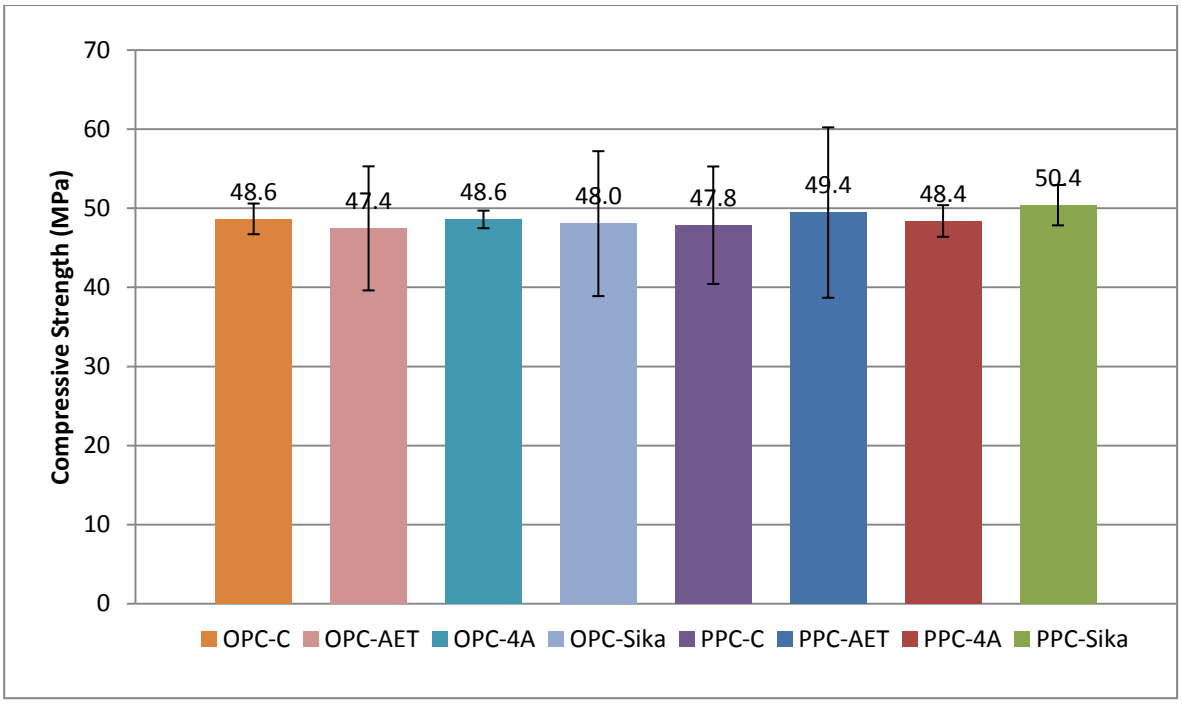

Figure 4.8: Compressive Strength Test at 56 Day

The testing of the specimens was done for 28 day and 56 day from the day of casting. As is known, that the strength of PPC is less than that of OPC, this can also be seen from the Control specimens for PPC and OPC. Now it can be seen that there was an increase in the strength of concrete as the time passed. This can be observed from Figure 4.7 and 4.8 that the strength of OPC-Control specimen increases from 44.267 for 28 day compressive strength to 48.66 for 56 day compressive strength. Similarly for PPC-Sika we can see that there is an increase of approximately 11% in strength for 56 day compressive strength when compared with 28 day compressive strength.

For 28 day compressive strength test it was seen that the compressive strength of OPC-Control was 44.267MPa whereas the compressive strength for OPC-Sika was 45.667MPa. When compressive strength of 56 day was taken into account, there too, negligible difference in the compressive strength was observed as the compressive strength for PPC-4A is 48.4MPa and PPC-AET is 49.4MPa. Wombacher et al.(2004) also proves our results, that the strength increases with time in specimen with and without corrosion inhibitors. He also shows that there is not much variation in strength of concrete for the specimens with or without corrosion inhibitor.

CHAPTER 5

CONCLUSION

From the research done for the effect of the application of corrosion inhibitor on properties of concrete, results were obtained from those result we derived the conclusions given below:

- All throughout the duration of examination it was noticed that the carbonation depth of specimens for Pozzolanic Portland Cement was always greater than that of the specimens for Ordinary Portland Cement. Even for the specimens covered with corrosion inhibitors, similar trend was observed.
- It was observed that as the duration of exposure to CO_2 increased, the carbonation depth also increased for Ordinary Portland Cement as well as for Pozzolanic Portland Cement. A similar trend was observed for specimens covered with corrosion inhibitors. There also, carbonation depth increased on increasing the duration of CO_2 exposure for the specimens.
- For specimens coated with corrosion inhibitors, there was a decrease in the carbonation depth when compared to the control specimens. For specimens coated with Sika ® FerroGard ®-903+, a decrease in carbonation depth was noted, though it was not that high. Better results were observed by specimens coated with para-Aminobenzoic Acid. As the decrease in carbonation depth in those specimens was greater when compared to the specimens covered with Sika ® FerroGard ®-903+.
- Best results were obtained for specimens coated with Aminoethanol as corrosion inhibitor, as the carbonation depth reduced drastically with its application, also the measured carbonation depth remained constant all throughout. The decrease in the carbonation depth for specimens coated with Aminoethanol was highest for most of the testing days
- From 28 day and 56 day Compressive Strength Test it was evident that there was not much difference in the compressive strength of Control specimen and specimens sprayed with corrosion inhibitors.

SCOPE OF FUTURE WORK

In this experimental research work, study of effect of application of corrosion inhibitors on properties of concrete was studied. Following the results of this research work, further investigations in this field can be performed in future. Some of which can be as following:

- Corrosion inhibition of these chemicals for various types of steel bars can be studied.
- Probability of any reaction of these chemicals with other admixtures like superplasticisers and air entraining agents can be studied.
- Effect of these chemicals can be seen for concrete of different strengths.
- Research can be conducted on effect of these corrosion inhibitors on other properties of concrete like flexural strength, absorption can be studied.
- these chemicals can be used as admixtures and then their effect on properties of concrete can be studied.

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