

**MIGRATING INHIBITORS FOR PREVENTING CARBONATION
INDUCED CORROSION OF REINFORCED CONCRETE**

A thesis submitted in fulfillment of the requirement for the award of the degree of

DOCTOR OF PHILOSOPHY
in
Civil Engineering

Submitted by

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DECLARATION

I, Kulwinder Kaur, hereby declare that the thesis entitled, "**Migrating Inhibitors for Preventing Carbonation Induced Corrosion of Reinforced Concrete**" submitted to **Thapar Institute of Engineering and Technology (Deemed University), Patiala**, in fulfillment of the requirements for the award of degree of "**Doctor of Philosophy**" in Civil Engineering is a record of an original and independent research work done by me during the period 2012-2017, under the supervision and guidance of Dr. Shweta Goyal, Associate Professor, Department of Civil Engineering, Thapar Institute of Engineering and Technology, Patiala; Dr. Maneek Kumar, Professor and Dean of Student Affairs, Department of Civil Engineering, Thapar Institute of Engineering and Technology, Patiala and Dr. Bishwajit Bhattacharjee, Professor, Department of Civil Engineering, Indian Institute of Technology Delhi, New Delhi. The work contained in this thesis has not been previously submitted to meet the requirements for a degree or diploma at this or any other higher education institution.


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CERTIFICATE

Certified that the work presented in this thesis entitled “**Migrating Inhibitors for Preventing Carbonation Induced Corrosion of Reinforced Concrete**” which is being submitted by **Mrs. Kulwinder Kaur (Regd. No. 951002007)** in fulfillment of the requirements for the award of degree of “**Doctor of Philosophy**” in the **Department of Civil Engineering, Thapar Institute of Engineering and Technology, Patiala, India**, is an authentic record of the research work carried out by her under our supervision and guidance. The contents of this thesis, in full or in part, have not been submitted to any other Institute or University for the award of any degree or diploma.



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ABSTRACT

Since its inception in the mid 19th century, Reinforced Concrete (RC) has become the most widely used construction material in the world. However, deterioration of RC structures, due to exposure of rebar to aggressive environment, has become a major concern all around the world. De-icing salts and carbonation are the two major factors responsible for the deterioration of RC structures. During the 20th century, extension in industrial emissions have raised the CO₂ levels in air drastically, which has further led to increase in the carbonation rate of concrete and carbonation related distress of RC structures. Rebar corrosion ultimately affects the service life of the RC structures and rehabilitation of such structures has become a great challenge both technically as well as financially.

The prevention of rebar corrosion can be handled using several techniques such as denser concrete, latex or polymer modified concrete overlays, waterproofing membrane with asphalt overlays and cathodic protection to the rebar etc. One amongst these methods involves the use of corrosion inhibitors, which provide a simple and cost effective solution for prevention of corrosion of RC structures. Corrosion inhibitors are chemicals that are able to reduce corrosion rate and are generally used in relatively small quantities.

Based upon the mode of application, corrosion inhibitors are generally classified into two categories: (a) admixed corrosion inhibitors which are mixed during casting of concrete and (b) migrating corrosion inhibitors, which are applied on the surface of concrete during rehabilitation procedures and they subsequently diffuse into the hardened concrete to reach the rebar level thereby developing their inhibiting action at the rebar surface. Migrating inhibitors have an advantage over admixed corrosion inhibitors in terms of their negligible effect on cement hydration and properties of the resultant concrete. Present study explores the effectiveness of the migrating type organic based corrosion inhibitors in controlling carbonation induced corrosion in reinforced concrete.

The initial choice of chemicals to be used as corrosion inhibitors was based on the preliminary investigations carried out on the simulated pore solution in the form of saturated solution of calcium hydroxide bubbled with pure CO₂ to reach a pH value of 8.1. In the preliminary investigation, eight types of corrosion inhibitors were tested for their effectiveness in carbonated conditions. The effectiveness of the bare steel specimens immersed in different solutions was assessed through the Potentiodynamic Polarization technique at a sweep rate of 60 mV per minute over a potential range of -250 mV/SCE to 1500 mV/SCE, with an offset from the rest potential. Each time the measurement was performed on an undisturbed sample because the adopted high potential range during testing was considered to disturb the actual corrosion activity of the specimens. The testing was carried out till the exposure duration of 240 hours. Recorded polarization curves indicated that out of all the tested inhibitors, generic inhibitor 2-Aminobenzoic acid and amino alcohols based commercially available inhibitor C.I4 performed most efficiently, with an inhibitor efficiency of 61% and 71%, respectively. Also, both these inhibitors were able to keep the inhibiting action throughout the exposure period of 240 h. These two inhibitors were further investigated for their effectiveness as migrating type inhibitors in carbonated reinforced concrete specimens.

The performance of commercially available inhibitor C.I4 (SFG) and generic inhibitor 2-Aminobenzoic acid (ABA) applied as migrating type inhibitors was assessed for concrete mixture made at two different w/c ratios. The investigation was carried out by using both OPC and PPC cements in concrete. The carbonation acceleration of the specimens was achieved in carbonation chamber maintained at a relative humidity of 60-70%, a temperature of 30±2°C and having 5±0.5% CO₂ concentration by volume. The progress in carbonation front was monitored by the carbonation depth measurements made on 100 mm cube specimens. The experimental results indicated that the carbonation depth increases with an increase in w/c ratio. On making a comparison based upon the cement type, higher carbonation depth was reported in concrete made with PPC as compared to OPC cement because of lower content of portlandite present in PPC cement. Further, the treatment of concrete surface with inhibitors namely, SFG and ABA decreased the carbonation rate coefficient as compared to corresponding control specimens. With the application of inhibitor SFG the decrease in carbonation coefficient was 18-36% while a 29-46% decrease was observed in ABA treated specimens. This reduction in carbonation

coefficient is attributed to the pore blockage effect of corrosion inhibitors. The 150 mm cube specimens tested under compression did not show any detrimental effect of applied corrosion inhibitors on the compressive strength of resultant concrete.

The effect of inhibitor application on rebar behaviour under accelerated carbonation conditions was studied by using electrochemical techniques viz. Half Cell Potential measurement (HCP), Tafel Extrapolation and Electrochemical Impedance Spectroscopy (EIS). For electrochemical measurements, prism specimens of size $300 \times 300 \times 150$ mm were prepared with three steel rebars embedded into it; two steel rebars were embedded at the bottom with cover of 25 mm and one rebar was placed at the top with clear cover of 5 mm. The carbonation acceleration exposure conditions were kept same for carbonation depth measurement. HCP and Tafel extrapolation measurement were performed on prism specimens made with two different types of cement (OPC and PPC), two w/c ratios (0.43 and 0.52) and two inhibitor applications (SFG and ABA), while EIS was performed on concrete specimens made with two different types of cement, two inhibitor applications for concrete mixture designed for a w/c ratio of 0.43. All electrochemical measurements were made with the help of Advanced Corrosion Monitoring (ACM) field machine provided with the guard ring arrangement.

HCP results demonstrate higher corrosion risk in PPC concrete as compared to OPC concrete. HCP values for mixes made with PPC lie in the range corresponding to 90% corrosion risk; while in OPC concrete intermediate corrosion risk was observed till the exposure duration. Similar with the HCP value, corrosion current density (i_{corr}) values also indicate less resistance of PPC concrete as compared to OPC concrete towards the carbonation induced corrosion. The application of inhibitors proved to be effective in retarding corrosion risk, for all concretes. However, the surface applied inhibitors took some time to migrate through the concrete pores to reach the rebar level. Once the inhibitors reached the rebar surface, they were able to form a protective layer around the rebar. It was demonstrated by HCP values which shifted towards more negative potential side till 30 days of exposure, followed by shift towards nobler potential side. Observed lower i_{corr} value with the inhibitor application shows that inhibitors had reached the rebar surface and formed a protective layer around the rebar surface.

The physical interpretation of the various processes involved during rebar corrosion in carbonated environment could be studied through EIS measurement. In the present study, EIS was used as a non destructive technique (NDT) for studying the carbonation behavior of the concrete specimens treated with migrating type organic corrosion inhibitors. During the EIS measurements, an AC signal was supplied with a 25 mV RMS for a frequency range of 100 kHz to 10 mHz with five points obtained per decade. The interpretation of the obtained impedance plots were done by using equivalent electrical circuit in ZMAN software. It was observed that the two capacitive arcs obtained at high frequency and low frequency during EIS measurements could be correlated to the bulk properties of concrete and the rebar, respectively. Increase in the first capacitive arc of the Nyquist plot obtained at high frequency represented decrease in porosity of concrete with progressive carbonation resulting in denser microstructure, while decrease in second capacitive arc obtained at low frequency corresponded to the breakdown of protective oxide layer on the rebar surface. The concrete surface treated with inhibitors exhibited behaviour different from the control specimens. Both of the tested migrating type inhibitors were able to form a passive layer around the rebar surface and their efficiencies improved with time. Inhibition efficiency of 72% and 80% respectively, was achieved in OPC and PPC concrete with inhibitor SFG at the end of exposure duration of 90 days. Similarly, the inhibitor efficiency of 78% and 91% was observed with inhibitor ABA in OPC and PPC concrete, respectively.

Impedance results indicate that carbonation depth can be predicted by analyzing the high frequency arc of Nyquist plot. The developed model shows a strong correlation between the impedance difference measured between 10 Hz to 10 kHz frequency range, fitted resistive parameter R_1 and carbonation depth measured by phenolphthalein indicator, with a very high regression coefficient of 0.9. The variation in the predicted carbonation depths by using developed relations and measured carbonation depths is below 15% for most of the exposure durations. Thus, all these relationships can be used effectively for predicting the carbonation depth from EIS, which is a popular NDT used for in-situ health monitoring of RC structures.

LIST OF PUBLICATIONS

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ABBREVIATIONS

Abbreviation	Word(s)
RC	Reinforced Concrete
CO ₂	Carbon dioxide
C-S-H	Calcium silicate hydrate
Ca(OH) ₂	Calcium hydroxide
CaCO ₃	Calcium carbonate
k	Carbonation coefficient
w/c ratio	Water-cement ratio
OPC	Ordinary Portland cement
PPC	Pozzolana Portland cement
RH	Relative humidity
EIS	Electrochemical Impedance Spectroscopy
NDT	Non-Destructive Techniques
HCP	Half-Cell Potential
GCP	Galvanic Coupling Potential
SCE	Saturated Calomel Electrode
LPR	Linear Polarization Resistance
R _p	Polarization resistance
B	Stern-Geary constant
i_{corr}	Corrosion current density
E _{corr}	Corrosion potential
AC	Alternating Current
EEC	Equivalent Electrical Circuit
CPE	Constant Phase Element
ABA	2-Aminobenzoic acid

Z	Impedance
OH ⁻	Hydroxyl ions
Z _{DH}	Impedance difference between 10Hz-10kHz frequency
Z _{DL}	Impedance difference between 10mHz-10Hz frequency
IE	Inhibition Efficiency

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CHAPTER 1

INTRODUCTION

1.1 GENERAL

Since its inception in mid 19th century, Reinforced Concrete (RC) has developed into one of the most widely used construction materials in the world. Dense and good quality concrete often provides long-term durability to RC structures (*Kujur and Bhattacharjee, 2011*). However, sometimes due to inadequate material selection, poor design, poor construction and a more severe environment than expected or due to a combination of these factors, RC structures fail to perform adequately (*Heiyantuduwa, 2002; Kujur, 2012*).

Deterioration of RC structures, due to exposure of rebar to aggressive environment, has become a major concern all around the world (*Kujur, 2012*). De-icing salts and carbonation are the factors responsible for deterioration of reinforced structures situated in temperate climatic regions such as North America and European countries. Thousands of bridges and other RC structures needed repair world-wide before the actual service life due to corrosion of the embedded rebar (*Wombacher et al., 2004*). It was recognized that majority of the RC structures situated in U.S.A, Italy and South Africa got deteriorated in a relatively short duration because of intrusion of chloride from de-icing salts into the concrete (*Pradhan, 2007*). Corrosion of rebar is found to be the major factor for failure of reinforced concrete structures in coastal areas of Arabian Gulf (*Dehwah et al., 2002; Saricimen et al., 2002*). India also has a large coastal belt where corrosion is extremely severe. In India, the sites exposed to coastal, marine and industrial atmosphere show premature failure signs in RC structures.

Rebar corrosion ultimately affects the service life of the RC structures and rehabilitation of such structures has become a great challenge both technically as well as financially. It is estimated that requisite cost for repair, rehabilitation and demolition of damaged RC structures are in trillions of dollars around the world (*Azad et al., 2010; Nepal and Chen, 2015; Talakokula et al., 2014*). Worldwide direct cost due to corrosion damage is between € 1.3 -1.4 trillion i.e 3% of the GDP (*Landolfo et al., 2010*). In Europe, around 40-60% of the construction budget is devoted for the repair and maintenance of the existing corroded structures. Out of this, every

year around £ 550 million is spent on maintenance and repair of RC structures in UK alone. In North America, total corrosion cost is around \$276 billion, which is distributed amongst the various sectors as shown in Fig.1.1. In India alone, the direct cost of corrosion was estimated in 2014 to be around \$67 billion (over Rs. 4 lakh crore) (www.naceindia.org).

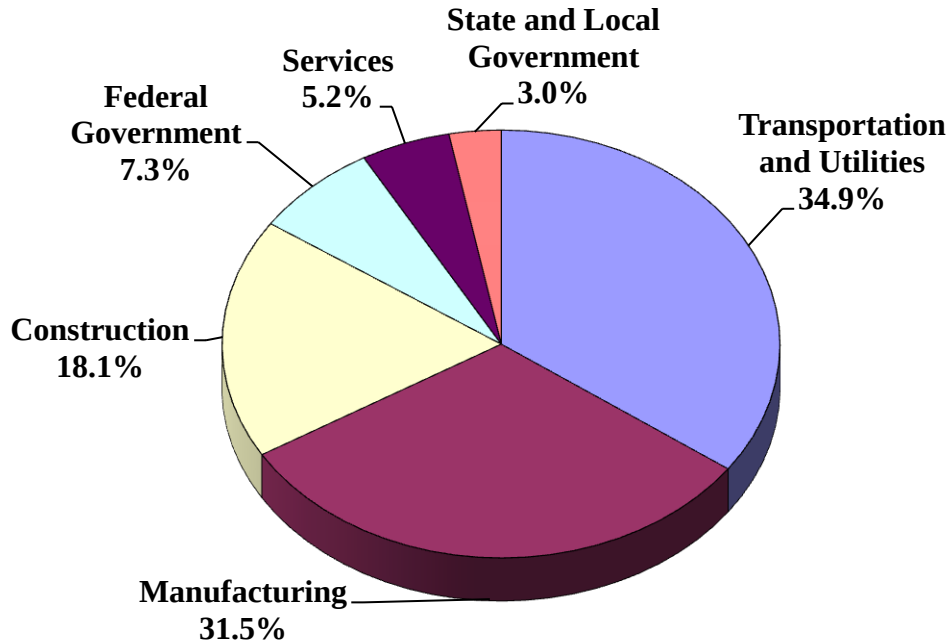


Fig.1.1. Corrosion cost extrapolated by NACE international: \$276 billion, 3.1% of GDP (www.corrosioncost.com)

The mechanism of rebar corrosion in reinforced concrete is a combined function of the properties of concrete and of reinforcing steel. Concrete provides protection to the rebar firstly, by acting as a physical barrier (presence of cover concrete) against the external aggressive environment and secondly, by developing a passive layer on the rebar surface because of high pH of concrete (*Riberio and Abrantes, 2016; Shen, 2017*). The constituents of concrete provide high alkalinity to the pore solution, with the pH of pore solution ranging from 12.5 to 13.5 (*Shi and Sun, 2012; Heiyantuduwa et al., 2006; Montemor et al., 2000; Montemor et al., 2002; Pu et al., 2012*), which leads to formation of a thin passive layer around the rebar, thus protecting it from corrosion. However, the passive layer becomes de-passivated due to the ingress of aggressive acidic compounds from the environment or due to the presence of significant quantity

of chloride ions at the reinforcement level. Overall, chloride ions and carbonation are the major factors responsible for the corrosion of steel rebar embedded in concrete

1.2 SCOPE AND OBJECTIVES OF THE PRESENT RESEARCH WORK

There are several techniques available for prevention and treatment of rebar corrosion, which include increased cover to the rebars, reduced w/c ratio, denser concrete, latex or polymer modified concrete overlays, waterproofing membrane with asphalt overlays (*Bertolini et al., 2004*) and enamel-coated dowel bars etc. Each of the available techniques has certain drawbacks with varying degree of cost implications. For instance, use of epoxy coated rebars was initially believed to be the “ideal” solution to prevent corrosion of rebars, but its long-term effectiveness is being questioned. Cathodic protection systems protect steel embedded in concrete contaminated with high levels of chloride but they are rather expensive and need a constant source of electricity. One amongst these methods involves the use of corrosion inhibitors, which provide a simple and cost effective prevention technique. Inhibitors are chemicals that are able to reduce corrosion rate and are generally used in relatively small quantities.

Many chemicals have been investigated in the past for use as corrosion inhibitors. The inhibitors available in market are usually classified into two categories: (i) admixed corrosion inhibitors which are mixed during the casting of concrete and (ii) migrating corrosion inhibitor (MCI) which are applied on the surface of concrete during rehabilitation procedures and they diffuse into the hardened concrete to reach the rebar level (*Griffin, 1975; Gaidis, 2004*). The admixed inhibitors are commercially available since 1970's, but the use of migrating type inhibitors in concrete has gained momentum over the last decade (*Gaidis, 2004*). The surface applied migrating inhibitors have advantages over admixed corrosion inhibitors in terms of their negligible effect on cement hydration and properties of the resultant concrete (*Soylev et al., 2007b*).

Calcium nitrite is the first traditional inhibitor used for providing protection against chloride induced corrosion in RC structures (*Rosenberg and Gaidis, 1979; Monticelli et al., 2011*). Several studies have been conducted to evaluate the effectiveness of admixed inhibitors in chloride enrich environment (*Andrade, 1992; Sideris and Savva, 2005; Montes et al., 2004*;

Saraswathy and Song, 2007; Monticelli et al., 2000; Ormellase et al., 2006; Nmai, 2004). Apart from admixed inhibitors, some researchers (*Wombacher et al., 2004; Malik et al., 2004; Holloway et al., 2004; Soylev et al., 2007a,b; Jamil et al., 2004*) have also investigated the effectiveness of surface applied inhibitors in chloride induced corrosion.

In carbonation induced corrosion in concrete, almost all studies are based on use of admixed corrosion inhibitors (*Trabanelli et al., 2005; Criado et al., 2012; Monticelli et al., 2011*). The studies on prevention of carbonation induced corrosion by using surface applied inhibitor are limited (*Heiyantuduwa et al., 2006*). Therefore, the present investigation had been planned to assess the effectiveness of migrating type corrosion inhibitor in a carbonation contaminated environment. In addition, previous researchers observed that ingress of carbonation front varies with cement type and grade of concrete. Thus, the present study has been carried out by considering two separate grades of concrete involving two different types of cements.

The following are the objectives of the present study;

1. To study the effect of two types of organic based migrating corrosion inhibitors on carbonation depth for variation in concrete strength using different types of cement (OPC and PPC).
2. To study the effectiveness of migrating type corrosion inhibitors with regard to reduction in rebar corrosion.
3. To study the effect of migrating type corrosion inhibitors on strength related properties of resulting concrete.

1.3 ORIENTATION OF THESIS

The thesis presentation has been organized in seven chapters. In the first chapter, in addition to introducing the topic, the objectives of the present study have been laid out.

In the second chapter, basic concepts of carbonation induced corrosion in reinforced concrete and critical literature review on prevention of corrosion by means of corrosion inhibitors are presented. A review of the various electrochemical techniques has also been presented.

In the third chapter, preliminary investigations conducted on the bare steel specimens immersed in synthetic pore solution containing various corrosion inhibitors and its corresponding outcomes are detailed.

The fourth chapter is dedicated to highlighting changes in the properties of concrete due to application of corrosion inhibitors. In this chapter, the effect of cement type, w/c ratio and type of inhibitor on carbonation depth and compressive strength is discussed.

In the fifth chapter, the experimental investigations carried out on prism specimens reinforced with 12 mm diameter rebars, for studying the role of inhibitor treatment on corrosion current density are discussed. The experimental outcomes in the form of the Half Cell Potential measurements and corrosion current density measured from Tafel Extrapolation technique forms the basis of comparison.

In the sixth chapter, the results of Electrochemical Impedance Spectroscopy (EIS), used as a non destructive technique (NDT) for studying the carbonation behavior of the concrete specimens treated with migrating type of organic corrosion inhibitors are presented. A mathematical relationship between measured carbonation depth with phenolphthalein indicator and predicted carbonation depth from fitted values of high frequency arc of Nyquist plot is presented.

Seventh chapter deals with the relevant conclusions drawn from the present study and suggestions for the future work. At the end, appendix and references cited in the entire work are presented.

CHAPTER 2

INTRODUCTION TO REBAR CORROSION AND LITERATURE REVIEW ON CORROSION INHIBITORS

2.1 INTRODUCTION

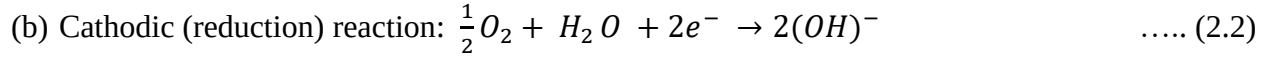
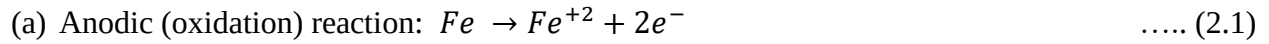
Corrosion is a naturally occurring process, in which deterioration of metal or its properties take place because of its reaction with the environment. The corrosion process can be classified into two categories depending upon the surrounding environment under which the corrosion process takes place, viz. wet corrosion and dry corrosion. Wet corrosion process occurs in the presence of water or an aqueous solution; while dry corrosion process occurs in the absence of aqueous solution or water. Corrosion process occur in reinforced concrete comes under the category of wet corrosion because the metal dissolution occur in the aqueous media i.e. electrolyte (*Pradhan, 2007*). It was recognized that rebar corrosion involves an electrochemical phenomena. The present chapter deals with the basics of rebar corrosion and the literature review on the effectiveness of corrosion inhibitors to mitigate rebar corrosion.

2.2 REBAR CORROSION: AN ELECTROCHEMICAL PHENOMENON

In dense and good quality concrete, the constituents of concrete provide high alkalinity to the concrete pore solution with pH of the pore solution ranging from 12.5 to 13.5 (*Shi and Sun, 2012; Heiyantuduwa et al., 2006; Montemor et al., 2000; Montemor et al., 2002; Pu et al., 2012*). When a rebar is embedded in highly alkaline concrete, a protective oxide layer of thickness in nanometers (also known as passive layer) is formed around the rebar spontaneously. This passive layer is composed of hydrated iron oxides with varying degree of ferrous ions (Fe^{+2}) and ferric ions (Fe^{+3}) which protect the rebar from corrosion (*Bertolini et al., 2004*).

However, the passive layer becomes de-passivated due to the ingress of aggressive acidic compounds from the environment or due to the presence of significant quantity of chloride ions at the reinforcement level. Once the depassivation of rebar has occurred, chemical reactions start at the rebar surface, which are responsible for the initiation of corrosion. In the corrosion process, one part of the rebar act as an anode and the other part of the same rebar behave as a

cathode in the presence of concrete pore solution which act as a electrolyte. The basic reactions involved in this electrochemical process are as follows:



(c) Flow of negatively charged electrons (liberated during oxidation reaction) within the rebar form anodic region to cathodic region and are consumed during reduction reaction. Transport of negatively charged electrons within rebar results in the flow of electrical current in opposite direction i.e. from cathodic region to anodic region within the rebar.

(d) Finally, to complete the circuit, the current flow inside the concrete pore solution from anodic side to cathodic side by liberating the ions in the concrete pore solution.

All these reactions are mandatory to complete the electrochemical process and occur at the same rate (Pradhan, 2007). The electrochemical reaction occur at the rebar surface are schematically shown in Fig. 2.1.

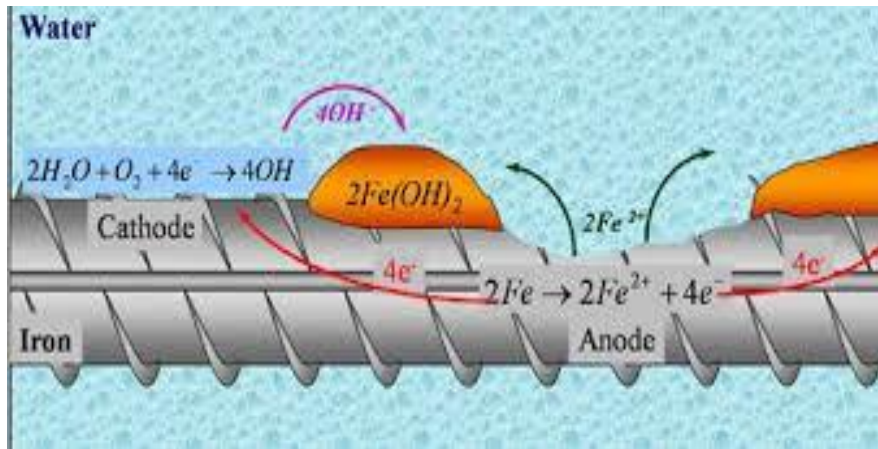
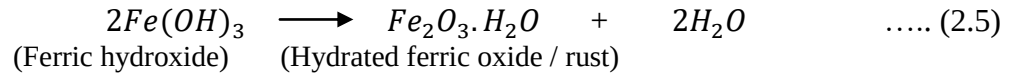
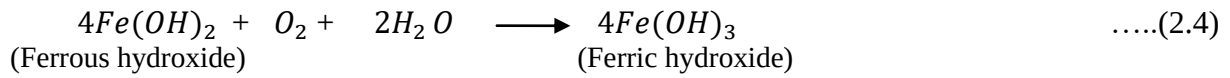
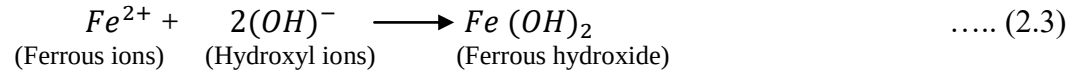


Fig.2.1. Electrochemical behaviour inside the reinforced concrete

([www.cement.org/learn/concrete-technology/durability/corrosion-of-embedded materials](http://www.cement.org/learn/concrete-technology/durability/corrosion-of-embedded-materials))

It is reported that $(OH)^{-}$ generated during the reduction reaction increases the alkalinity of the pore solution and thus strengthen the passive layer on the rebar surface. On the other hand, ferrous ions (Fe^{2+}) liberated during the oxidation reaction are soluble and does not produce any cracking and spelling of concrete. Thus, several more reactions mandatory for the formation of rust are as (Broomfield, 2007):



The hydrated ferric oxide has a volume six to ten times larger than the original volume of the steel at the steel/concrete interface as shown in Fig. 2.2. This increase in volume ultimately results in cracking and spelling of the concrete cover.

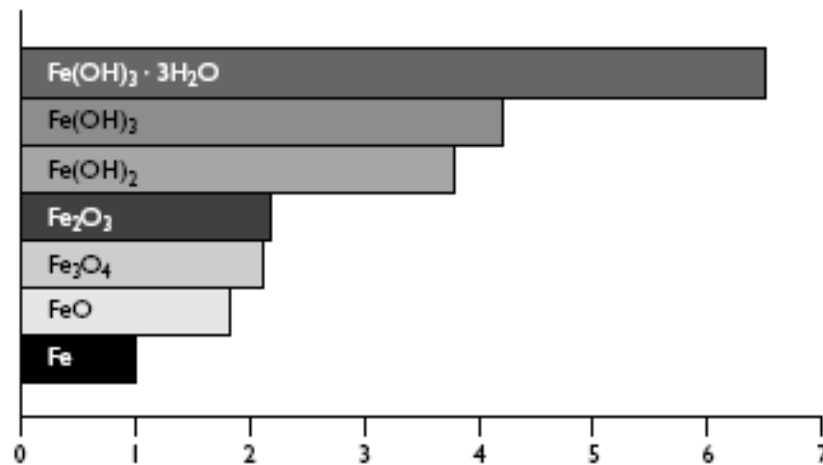


Fig.2.2. Relative volume of iron and its oxides (*Broomfield, 2007*)

2.3 CAUSES OF CORROSION

A number of causes are responsible for the de-passivation of rebar embedded in concrete. These include insufficient thickness of concrete cover, grade of concrete, stray current, presence of bacteria, water, oxygen, the advancement of carbonation front and presence of aggressive ions such as chlorides, sulphate etc. Out of these, chloride attack and carbonation are the two major factors responsible for the corrosion of rebar embedded in concrete.

The ingress of chloride ions from the environment into the concrete is the major cause for deterioration of concrete structures situated in marine and de-icing salt

environment (*Heiyantuduwa, 2002*). Chloride ions de-passivate the passive layer only when concentration of chloride ions at rebar level exceeds the threshold chloride ion concentration. Once sufficient amount of chloride ions reach the rebar level, then chloride ions act as a catalyst for the oxidation of iron and allow the corrosion process to proceed quickly (*Broomfield, 2007*).

However, carbonation induced corrosion occur only when CO_2 from the atmosphere diffuses through the capillary pores of concrete and reduces alkalinity of the concrete. In industrial areas and metropolitan cities, the concentration of CO_2 in air is much higher than the rural area concentration of CO_2 which is approximately 0.03% by volume (*Singh and Singh, 2016*). Higher concentration of CO_2 in air increases the possibility of carbonation induced corrosion in RC structures.

Carbonation induced corrosion leads to complete dissolution of the protective layer (general corrosion) while chloride ions induce localized corrosion by forming small pits surrounded by non corroded areas. Fig. 2.3 provides the schematic representation of both general and pitting corrosion processes. Since the present study is focused on the prevention of carbonation induced corrosion of RC, the carbonation process is explained in more detail in the succeeding sections.

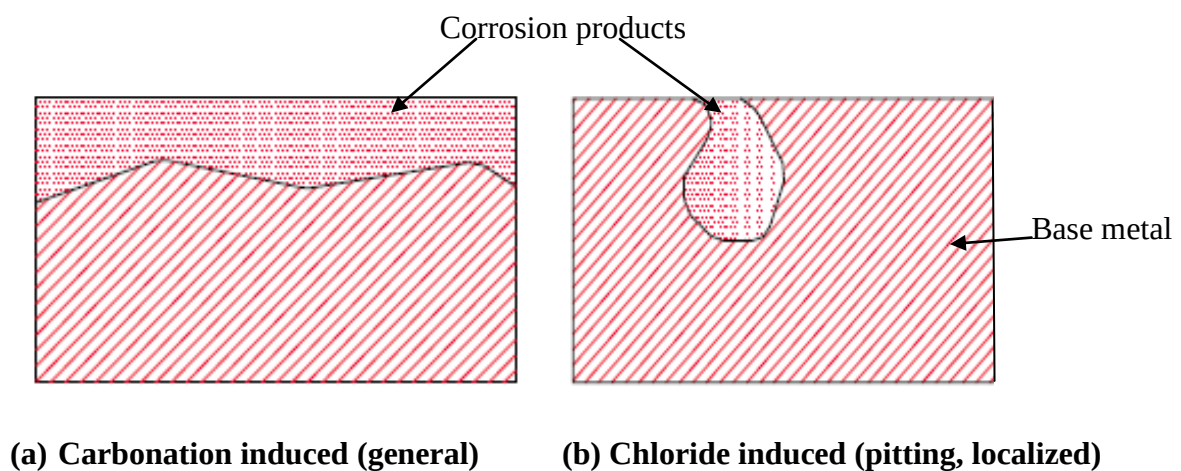
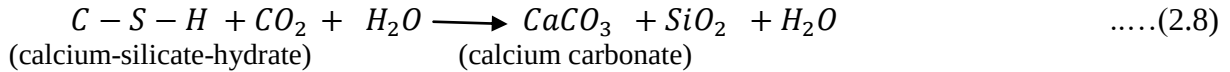
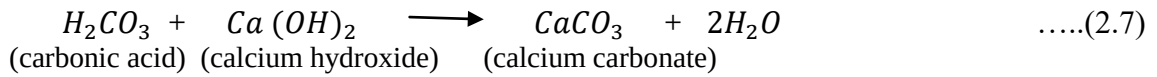
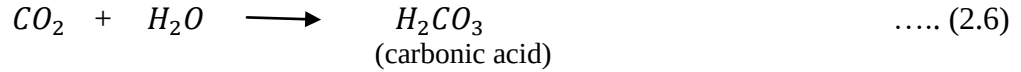


Fig.2.3. Schematic representation of corrosion process in reinforced concrete
(theconcreteportal.com/pillai.pdf)

2.4 CARBONATION PROCESS

Carbonation involves a gradual interaction between acidic CO₂ gas from the air and the alkaline solid cement hydration components i.e. calcium hydroxide (Ca(OH)₂) and calcium silicate hydrate (C-S-H) to form calcium carbonate (CaCO₃) (Singh and Singh, 2016) which consequently results in depression of the pore solution pH to a value below 10. It was further established that CO₂ itself is not reactive but in the presence of water, CO₂ gas gets converted into dilute carbonic acid which reacts with the Ca(OH)₂ and reduces the alkalinity of concrete. The decomposition of calcium compounds continue until the full consumption of Ca(OH)₂ (Bertolini *et al.*, 2004; Broomfield, 2007).

The basic chemical reactions involved in the carbonation process are (Broomfield, 2007):



Carbonation has dual effect on the properties of RC structures. CaCO₃ gets deposited in the concrete pores, thereby decreasing the porosity of concrete. With respect to durability, the importance of carbonation lies in the fact that it reduces the pH of the pore water in hardened Portland cement paste from 12 - 13.5 to a value of 9. When all Ca(OH)₂ has become carbonated, the value of pH gets reduced to nearly 8.3. At this low pH carbonation front reaches the vicinity of the reinforcing steel and break down the protective passive layer that protects the rebar from corrosion (Bertolini *et al.*, 2004; Sisomphon and Franke, 2007; Dong *et al.*, 2014; Aguiar and Junior, 2013).

2.4.1 Rate of carbonation

CO₂ ingress occurs progressively from the surface of RC structure into the concrete through pores. CO₂ penetrates inside the concrete at decreasing rate because CO₂ has to diffuse through the pore system, including the already carbonated surface zone of concrete. Such diffusion is a slow process if the pores in hydrated cement paste are filled with water because the diffusion of CO₂ in water is four orders lower than its diffusion in air (Bertolini *et al.*, 2004). On

the other hand, if there is insufficient water in the pores, CO₂ remains in the gaseous forms and does not react with the hydrated cement. Thus the carbonation rate depends upon the moisture content of the concrete, which varies with its distance from the surface (*Kujur, 2012*).

Under steady hygrometric conditions, the depth of carbonation increases in proportion to the square root of time, which is a characteristic of sorption rather than diffusion. Thus the penetration of carbonation can be described as (*Bertolini et al., 2004; Khunthongkeaw et al., 2006; Sisomphon and Franke, 2007; Neves et al., 2012*):

$$D \rightarrow k.t^{1/n} \quad \dots\dots(2.9)$$

where, D refers to the depth of carbonation (mm),

t refers to exposure time in years,

k refers to carbonation coefficient in mm/year. Carbonation coefficient indicates the penetration rate of carbonation against the given concrete and environment conditions.

Exponent ‘n’ is approximately taken as two, thereby indicating that a parabolic trend is generally observed in carbonation front progress.

2.4.2 Factors influencing carbonation

The rate of carbonation depends on the both environmental factors and factors related to concrete. The major factors affecting rate of carbonation are:

(a) Relative Humidity and Temperature: The diffusion rate of CO₂ decreases with an increase in relative humidity of concrete. In water-saturated and in wet concrete conditions CO₂ does not penetrate inside the concrete. However, water is mandatory for the occurrence of carbonation reaction so it becomes negligible in dry concrete conditions. Under equilibrium conditions, the carbonation rate can be correlated with the relative humidity of the environment as shown in Fig. 2.4 (*Bertolini et al., 2004*). The favourable conditions for advancement of the carbonation front are when atmospheric relative humidity lies between 50 – 75% and temperature ranges between 20-30°C (*Ulloa et al., 2013; Aperador et al., 2012; Montemor et al., 2002*).

(b) CO₂ Concentration: During the 20th Century, the levels of CO₂ in air have risen drastically because of industrial emission. As CO₂ concentration is an important factor for the advancement

of carbonation front, increase in CO₂ content in the air increases the carbonation rate. Based upon the experimental results obtained from natural and accelerated conditions, the researchers suggest that 100% CO₂ acceleration gives carbonation rate equivalent to 40 times the carbonation occurring in natural atmospheric conditions (*Sanjuan et al., 2003*), while 5% CO₂ acceleration gives the carbonation rate equivalent to 5 times the natural atmospheric conditions (*Montemor et al., 2002; Aperador et al., 2012*).

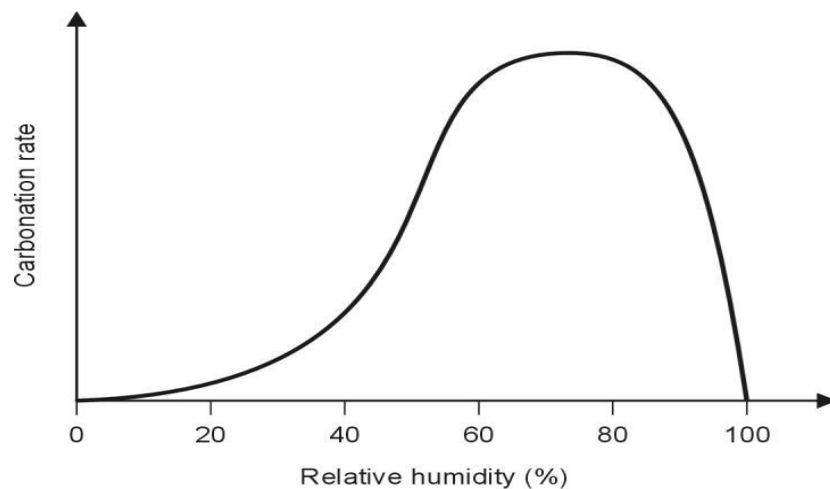


Fig.2.4. Carbonation rate variation with relative humidity of the environment
(*Bertolini et al., 2004*)

(c) Effect of water-cement ratio and curing: The various physical properties like density, porosity, permeability, diffusivity etc. depends upon the w/c ratio of the mix. *Dong et al. (2014)* found that the internal porosity of concrete increases with the increase in w/c ratio, resulting in more remarkable carbonation. Advantages of a lower w/c ratio can only be achieved if the concrete is properly cured, since the poor curing hinders the hydration of the cement paste and leads to a more porous cement matrix. *Kulakowski et al. (2009)* examined the effect of silica fume addition in concrete on carbonation induced corrosion with water/binder (w/b) ratio ranging between 0.3 to 0.8. They reported that effect of pozzolanic reaction were negligible at w/b ratio lower than 0.5; while after this ratio, Ca(OH)₂ consumption play an important role. *Aguiar and Junior (2013)* tried to improve the carbonation resistance of concrete by applying various types of coatings on the surface of concrete. Higher carbonation diffusion coefficient was observed in non protected concrete made with high w/c ratio. *Bogas et al. (2016)* observed increase in carbonation coefficient with the increase in w/c ratio and aggregates porosity.

(d) Cement Compositions: Type of the cement plays an important role for the advancement in carbonation front. *Montemor et al. (2002)* reported that concrete made with ordinary Portland cement (OPC) has higher carbonation resistance as compared to concrete made with cement having pozzolanic material. This is attributed to the whole consumption of Ca(OH)_2 during the formation of CaCO_3 in OPC but in concrete made with pozzolanic material some part of the Ca(OH)_2 is already involved in the pozzolanic reactions. *Rabehi et al. (2013)* established a relationship between initial absorption, carbonation depth of concrete and compressive strength made with different types of cements viz. OPC (CEM I) and Compound cement (CEM II). They observed that the concrete made with CEM II carbonated at faster rate than concrete made with CEM I because of lower content of Ca(OH)_2 in the former concrete.

(e) Supplementary cementitious addition: Cement replacement with supplementary cementitious material like silica fume and fly ash had a great impact on the carbonation behaviour of the concrete. *Atis (2003)* investigated the accelerated carbonation behaviour of concrete by replacing the cement with 50 and 70% of fly ash at 0.28 to 0.55 w/c ratio. Author observed that larger replacement of cement with fly ash had an adverse effect on carbonation behaviour. *Badar et al. (2014)* found that geopolymer concrete made with fly-ash containing low calcium content presents better resistance towards exposure to carbonating environment. *Leemann et al. (2015)* found that addition of mineral such as GGBS and silica fume into concrete decreased the carbonation resistance of mortar and concrete. They proposed a novel parameter to evaluate the carbonation resistance of concrete based upon the ratio of water added during mixing and amount of reactive CaO present in binder. *Dong et al. (2016)* found that fly ash blended cement materials exhibit higher carbonation depth as compared to the control specimens without fly ash. *Bogas et al. (2016)* also reported that cement replacement with mineral admixtures (silica fume, fly ash) leads to increase in carbonation coefficient.

(f) Exposure Conditions: The mechanism of rebar in carbonated concrete is likely to be the same, independent of whether carbonation was induced in an accelerated condition or occurred in a natural exposure condition (*Kujur, 2012*). *Khunthongkeaw et al. (2006)* predicted the carbonation depth of concrete made with fly ash having high and low lime content in natural and accelerated environment. They noticed a strong linear relationship in carbonation depth tested

under natural and accelerated exposure conditions. *Sisomphon and Franke (2007)* investigated the carbonation depth with phenolphthalein indicator on specimens maintained at 3% CO₂ concentration by volume and 65% RH. They proposed a Fick's diffusion equation to estimate the carbonation depth of fly ash and blast furnace slag concrete under both natural and accelerated conditions. *Badar et al. (2014)* achieved the accelerated carbonation by putting the specimens in a chamber maintained at 24±5°C temperature, 65±5% RH, and 5±0.3% CO₂ concentration.

2.5 METHODS TO MITIGATE CORROSION

Various physical, chemical and electrochemical repair techniques are available today, to extend the service life of RC structures. Physical and electrochemical techniques are generally used for the repair of existing structures, while the chemical techniques can be applied for the new structures. Electrochemical techniques work by applying an external anode and passing current from it to the rebar so that the rebar act as a cathode (*Broomfield, 2007*). Table 2.1 gives the details of various physical, chemical and electrochemical techniques used for the repair of the corrosion damaged structures.

Table 2.1 Physical, chemical and electrochemical repair techniques (*Broomfield, 2007*)

S. No.	Repair Techniques	Category
1.	Concrete Removal and Surface preparation by Pneumatic hammer, Hydro-jetting	Physical
2.	Patches by Incipient anodes	Physical
3.	Coatings against chlorides, Penetrating Sealers	Physical
4.	Waterproofing Membranes and Barriers	Physical
5.	Corrosion inhibitors	Chemical
6.	Cathodic protection by impressed current system	Electrochemical
7.	Cathodic protection by sacrificial anode system	Electrochemical

Each technique has its own merits and demerits. For instance, the problem with physical techniques is that they have a service life of 10 to 12 year, thereafter they must be replaced. Also,

any defect in the application can even cause severe pitting and black rust formation. Electro-chemical techniques require constant supply of current to make the system fully effective.

The use of corrosion inhibitor comes under the categories of chemical technique which inhibit the corrosion by developing a very thin chemical layer on the rebar surface (*Gaidis, 2004*). Among various methods available to mitigate corrosion, corrosion inhibitors seem to be attractive because of their low cost and easy handling, compared with other preventive methods (*Wombacher et al., 2004*). The detailed literature on the use of corrosion inhibitors in concrete is presented in subsequent sections.

2.6 CORROSION INHIBITORS

A number of definitions are used in the context of corrosion inhibitors. A well defined definition for corrosion inhibitor provided by *ISO 8044-1986 (1989)* is: “A chemical substance that decreases the corrosion rate when present in the corrosion system at suitable concentration, without significantly changing the concentration of any other corrosion agent.” Corrosion inhibitors are in use since 1940’s, but initially their use was limited to the water treatment, chemical processes, oil and gas industry. It was reported that 95 to 99% reduction in corrosion rate was observed in the oil and gas industry with the use of inhibitors (*Elsener, 2000*).

The use of corrosion inhibitors to control corrosion of rebar embedded in concrete was first investigated in 1960’s (*Heiyantuduwa, 2002*). There is a difference in mode of application of corrosion inhibitors in oil industry and in RC structures. In case of oil and gas industry, application of the inhibitors is directly on the surface of bare steel; while in RC structure, it is admixed with/applied on hardened concrete surface and inhibition is required on rebar embedded in concrete. Actually, in RC structures, inhibiting mechanism is based on the efficiency of corrosion inhibitor in forming a passivation layer around the rebar.

For the use of corrosion inhibitors in concrete industry, an ideal corrosion inhibitor is a chemical which, when added to concrete, can prevent corrosion onset without having any adverse effects on the mechanical properties of the concrete. It interferes with the corrosion process without having any detrimental effect on concrete quality (*Gaidis, 2004*). Corrosion

inhibitors do not totally stop the corrosion process but they increase the time to the inception of corrosion and eventually reduce the corrosion rate as shown in Fig. 2.5.

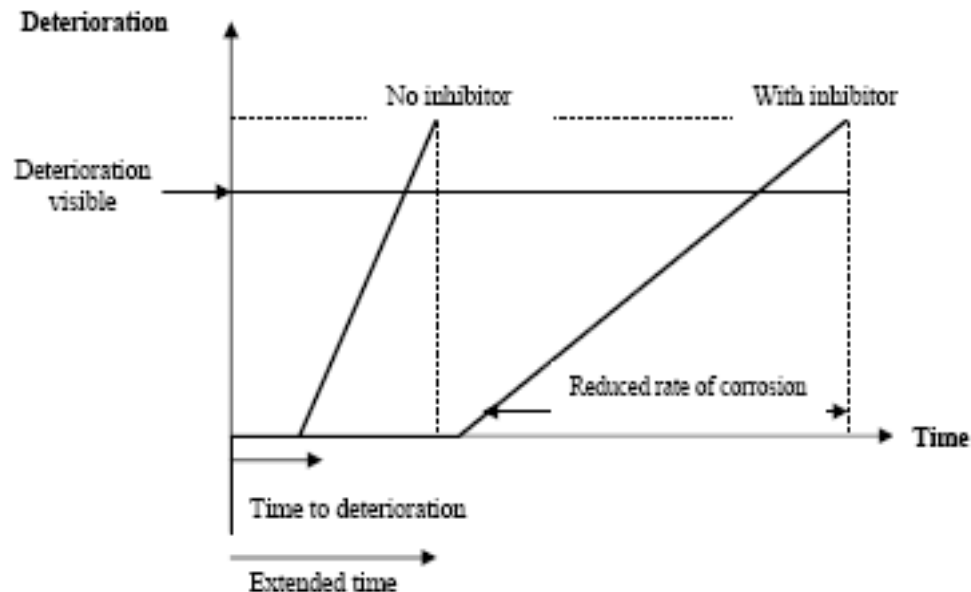


Fig.2.5. Extension in Service life of the concrete structures with corrosion inhibitors (Mackechnie et al., 2004)

2.7 CLASSIFICATION OF CORROSION INHIBITORS

Many different types of inhibitors are available today, but in most of the cases, the mechanism of inhibition is not fully understood. It is, however, possible to identify groups of inhibitors based upon their physical mode of application, mechanism of protection and chemical structure. All these classifications are discussed in detail in the succeeding sections:

2.7.1 Classification based upon the physical mode of application: Based upon the application mode of inhibitors, they are classified as admixed inhibitors and migrating or surface applied inhibitors.

(a) Admixed inhibitors: Those compounds which are added to the fresh concrete at the time of mixing and casting of concrete are known as admixed inhibitors. Admixed inhibitors are commercially available since 1960's. The inorganic compounds which are based upon calcium nitrite, sodium nitrite, sodium benzoate, zinc oxide and sodium chromate were initially used as admixed inhibitors (Rosenberg and Gaidis, 1979; Ann et al., 2006; Saraswathy and Song, 2007)

Organic compounds based upon mixtures of alkanolamines, amines or amino-acids, or based on an emulsion of unsaturated fatty acid ester of an aliphatic carboxylic acid and a saturated fatty acid are now being proposed for their use as admixed inhibitors (*Nmai and Krauss, 1994; DeSchutter and Luo, 2004; Jamil et al., 2003*).

(b) Migrating inhibitors: These are the chemical which are applied on the hardened concrete surface and are able to diffuse through concrete to the underlying rebar where they act to suppress both the anodic and cathodic corrosion reactions by forming a monolayer film at the steel-concrete interface (*Tritthart, 2003*). These inhibitors are typically based either on mixtures of alkanolamines and amines or on inorganic compounds based upon monofluoro-phosphate (*Wombacher et al., 2004; Jamil et al., 2003; Soylev et al., 2007a; Malik et al., 2004*).

2.7.2 Classification based upon the mechanism of protection: Based upon the protection mechanism of the inhibitors, they are classified into three categories as anodic inhibitors, cathodic inhibitors and mixed inhibitors.

(a) Anodic inhibitors: The anodic inhibitors act on anodic reaction of the rebar and they reduce the corrosion rate by 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. The precipitate functions as a film repair because the ferric ions are insoluble in aqueous alkaline solutions and block the transfer of ferrous ions into the electrolyte (*Gaidis, 2004; Saraswathy and Song, 2007*).

(b) Cathodic inhibitors: The cathodic inhibitors act on the oxygen reaction on the steel surface and they reduce the corrosion rate by a decrease in corrosion potential. The most commonly used cathodic inhibitors are sodium hydroxide and sodium carbonate, which are supposed to increase the pH near the steel, and reduce the oxygen transport by covering the steel surface (*Soylev and Richardson, 2008*).

(c) Mixed inhibitors: The mixed inhibitors may simultaneously affect on both anodic and cathodic processes. A mixed inhibitor is usually more desirable because its effect is all encompassing, covering corrosion resulting from chloride attack as well as that due to microcells

on the metal surface. In mixed type inhibitors, chemicals with the hydrophobic group and polar groups such as N, S, OH are found to be effective (Soylev and Richardson, 2008). Organic polymer compounds such as amine and aminoalcohol (AMA) are also used (Soeda and Ichimura, 2003).

2.7.3 Classification based upon the chemical structure: Based on the chemical structure, inhibitors are classified into following two types:

(a) Inorganic Inhibitors: Chemicals inorganic in nature like nitrites, phosphates, mono-fluorophosphate comes under the category of inorganic inhibitors. Calcium nitrite was the mostly used inorganic inhibitor (Rosenberg and Gaidis, 1979; Ann et al., 2006; Gaidis, 2004).

(b) Organic Inhibitors: Organic inhibitors generally consist of amines, fatty acid esters, alkanolamines and amino-alcohol etc. (Nmai, 2004, Ormellese et al., 2006).

Many chemical have been investigated in the past for their use as corrosion inhibitors in concrete industry. Some showed promise as an inhibitor, but had detrimental effects on certain properties of the concrete. The following section discusses the observation made by previous researchers on the effect of use of corrosion inhibitors in RC systems.

2.8 EFFECT OF CORROSION INHIBITORS ON MECHANICAL PROPERTIES OF CONCRETE

The effect of inorganic compounds on the fresh and hardened properties of concrete has been studied by many researchers. Ann et al. (2006) studied the effect of three calcium nitrite-based corrosion inhibitors on setting time and compressive strength of concrete at different inhibitor dosages. It was reported that inhibitor dosages upto 6 l/m^3 did not lead to variation in initial and final setting time; however the setting times got adversely affected by using inhibitor dosage beyond 6 l/m^3 . Further, it was observed that calcium nitrite based inhibitors increased the early age compressive strength of concrete but marginal decrease in strength was observed on long term basis. Saraswathy and Song (2007) studied the compressive and tensile strength of concrete with anodic inhibitors (sodium nitrite, zinc oxide), cathodic inhibitors (monoethanol amine, diethanolamine and tri ethanolamine) and mixed inhibitor at three concentration levels. They observed that sodium nitrite and mixed inhibitor at 2% inhibitor dosages gave the highest strength amongst the all other tested inhibitors as well as than the control specimens. Dharmaraj

and Malathy (2016) studied the effect of inorganic inhibitor sodium nitrite at varying dosages of 1-5% by weight of cementitious material. It was reported that addition of 3% inhibitor dosage presents the maximum strength properties and beyond this dosage level, decrease in strength was observed because of decrease in degree of hydration.

Apart from the inorganic compounds, some researcher investigated the effect of organic compound on the fresh and hardened properties of the concrete. Wombacher *et al.* (2004) studied the effect of amino alcohol based (AMA) inhibitors on fresh and hardened concrete properties like setting time, compressive strength, air content by using different dosages of inhibitors at different w/c ratios. It was found that the addition of inhibitor up to 4% in the concrete mix had no detrimental effect on setting time and increased the compressive strength. Devi (2012) studied the strength properties of concrete containing organic inhibitor namely, Triethylamine at 1-4% dosages level with quarry dust as fine aggregates. Experiment results show that concrete containing quarry dust with 2% inhibitor dosage was optimum with respect to the compressive, tensile, flexural and bond strength. DeSchutter and Luo (2004) studied the effect of four corrosion inhibiting admixtures namely calcium nitrite-based inhibitor, amino and ester-based organic inhibitor, aminoalcohol-based inhibitor and an organic based migrating corrosion inhibitor on fresh and hardened concrete properties. Based upon the experimental results, they concluded that calcium nitrite-based corrosion inhibitor increased the early age compressive strength, showing the accelerating properties, while migrating inhibitors improved the ultimate compressive strength. Soylev *et al.* (2007b) studied the effect of aminoalcohol based surface applied inhibitor on mechanical and durability properties of concrete. They reported no detrimental effect of the use of tested inhibitor on the mechanical properties of concrete. Reduction in durability properties like air permeability, water absorption and drying shrinkage was observed because of the pore-blocking effect of the surface applied inhibitor. Further, from density measurement, it was suggested that this pore blocking effect was limited to the surface of concrete.

2.9 EFFECTIVENESS OF CORROSION INHIBITORS IN CHLORIDE INDUCED CORROSION

Most of the previous studies on the use of corrosion inhibitors are based on their effectiveness under chloride induced corrosion. In these cases, the inhibitors were either admixed

in concrete at the time of casting or were applied on the surface of concrete as a repair strategy. The literature review is accordingly divided into two categories and is discussed in the succeeding sections.

2.9.1 Performance of admixed type corrosion inhibitors

Based upon the chemical composition, both inorganic and organic compounds were investigated as admixed inhibitors. *Rosenberg and Gaidis (1979)* investigated the effectiveness of inorganic inhibitor such as calcium nitrite in chloride contaminated reinforced concrete. They used polarization techniques for evaluated the performance of the tested inhibitor and reported that inhibitor admixed at 2% and 4% concentration shows relative corrosion rates 15 times lower than the control specimens. *Saraswathy et al. (2001)* investigated the effectiveness of inorganic compounds and mineral admixtures against chloride induced corrosion in reinforced concrete system. They found that combination of fly ash (25%) and sodium hydroxide, sodium stannate, sodium citrate (1% each) and calcium oxide (0.5%) presents the 10 fold decrease in corrosion rate of rebar on comparison with control concrete under accelerated corrosive environment. *Montes et al. (2004)* investigated the effect of calcium nitrate-based corrosion inhibitor (CNI) on reinforcement corrosion in high performance concrete. They concluded that CNI alone does not always provide corrosion protection to the rebar embedded in concrete. The combination of good quality concrete (w/c ratio 0.29 or 0.37) and the use of CNI at an addition rate of 12.5 L/m³ along with 20% fly ash reduced the corrosion rate caused by chlorides. *Sideris and Savva (2005)* studied the influence of CNI on the corrosion of reinforcing steel embedded in 14 different mortars. They concluded that the addition of calcium nitrite increased the chloride-induced corrosion resistance of all mixtures, but the protection offered strongly depended on the type of cement used. *Ann et al. (2006)* investigated the effect of calcium nitrite based inhibitor at three different concentration levels to prevent the corrosion of rebar. They found that increase in inhibitor dosage at a given chloride content decrease the corrosion rate by increasing the chloride threshold level. *Diamanti et al. (2015)* investigated the inhibition mechanism of sodium tartrate (Ta), sodium benzoate (Be), sodium glutamate (Glu), dimethylethanolamine (DMEA) and triethyenetetramine (TETA) in simulated concrete pore solution. On the basis of molecular modeling it was observed that Ta presents the excellent inhibitive behaviour because of its excellent surface coverage, adsorption strength and repulsive effect exerted on Cl⁻ ions.

Shen. (2017) investigated the effect of calcium nitrite at three concentrations (3, 6, 12%) in chloride contaminated concrete through EIS. It was concluded that calcium nitrite has excellent effectiveness to inhibit the corrosion when the ratio of $[Cl^-] / [NO_2^-]$ are equal.

Apart from inorganic compounds, numbers of organic compounds have been investigated for their performance against chloride induced corrosion. *Monticelli et al. (2000)* studied the inhibiting effect of 32 organic compounds against chloride polluted mortar as well as in synthetic solution of calcium hydroxide with 0.1M Cl^- concentration. Experimental results show that tungstosilicic acids with Sodium β -glycerophosphate have the inhibiting efficiency of approximately 90% to resist rebar corrosion. *Dhouibi et al. (2002)* studied the long term effectiveness of alkanolamine on concrete specimens immersed in 0.5M of NaCl solution for 3 years. Based upon the EIS results, they concluded that tested inhibitors increased the resistivity of the concrete during 1 year measurement but the effectiveness of inhibitors decreased with immersion time. *Jamil et al. (2004)* studied the effectiveness of amino alcohol based organic inhibitor in simulating concrete interstitial electrolyte solution contaminated with 2g/l of NaCl. They found that both of the tested inhibitor at 4% (v/v) concentration was able to reduce corrosion rate of the steel. *Ormellese et al. (2006)* investigated the effectiveness of three organic commercial inhibitors namely, amine-esters, amino-alcohols and alkanol-amines for preventing corrosion of reinforced concrete. Chlorides were added in the concrete mixture or penetrated from outside by ‘‘ponding’’ cycles with a 3.5% sodium chloride solution. Based on three years corrosion tests, they observed the tested inhibitors were able to delay the occurrence of chloride induced corrosion. *Fayala et al. (2013)* observed that inhibitor action of sodium nitrite (SN) and diethanolamine (DEA) on the galvanized coated steel rebar in mortar specimens exposed to 3% NaCl solution. The measured polarization resistance indicated that the presence of DEA improved the corrosion resistance of rebar but the use of SN accelerated the corrosion process. They further observed that DEA addition decreased the porosity, while SN increased the total porosity of the concrete. *Rakanta et al. (2013)* investigated the effectiveness of organic inhibitor such as N.N dimethylaminoethanol (DMEA) in concrete pore solution as well as in cement mortar specimens contaminated with chloride ions. Electrochemical results show that the addition of inhibitor into the cement mortar shifted the potential towards more positive side. *Akshatha et al. (2015)* investigated the effectiveness of organic inhibitors (*Azadirachta indica*,

Ruta graveolens plants) and inorganic inhibitors (sodium nitrite, ethylenediaminetetraacetic disodium dihydrate) in reinforced concrete specimens immersed in sodium chloride, hydrochloric acid and magnesium sulphate solution. Weight mass and Half Cell Potential measurements shows that Azadirachta indica had superior inhibition efficiency in chloride and acid solution while ethylene-diamine-tetra-acetic disodium dehydrate exhibited better performance in sulphate solution.

2.9.2 Protection mechanism of admixed type corrosion inhibitors

Some researchers investigated the protection mechanism provided by the corrosion inhibitors in reinforced concrete. *Andrade et al. (1992)* studied the mechanism by which organic-based corrosion-inhibiting admixtures provided protection to rebar. They observed that corrosion inhibitors function by providing a physical barrier to the ingress of aggressive agents or by chemically stabilizing the steel surface. *Nmai and Krauss (1994)* reported that water-based organic admixtures function by reducing chloride ion ingress into concrete and forming a coating on the surface of the embedded steel. *Dhouibi et al. (1998)* reported that organic inhibitors work by forming a monomolecular layer between the metal and the water. They further explained that in layer forming amines, one end of the molecule is hydrophilic and the other hydrophobic. These molecules will arrange themselves parallel to one another and perpendicular to the reinforcement forming a barrier. *Jamil et al. (2003)* studied the inhibition mechanism of an amino alcohol based inhibitor used as admixture to prevent corrosion of steel in concrete. They performed the investigation in the presence of chloride ions, using solutions simulating the concrete interstitial solution. They found that inhibitor film was formed around the rebar surface which suggests an initial increase of the anodic activity in some sites on the surface, probably due to displacement of the first hydrated monolayer of the iron oxide film. It is proposed that these anodic points can act as favorable anchorage points for the development of inhibitor monolayer. *Nmai (2004)* studied the mechanism of organic corrosion inhibitors consisting of amines and fatty-acid esters and suggested that the inhibitors decrease 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. *Gaidis (2004)* used secondary ion mass spectroscopy to identify the surface layer of protection and the

results showed that amino alcohols form a continuous inhibitive layer and displace chloride and other ions from the surface.

2.9.3 Performance of migrating type corrosion inhibitors

Most of the researchers used organic chemicals as migrating type inhibitors. *Holloway et al. (2004)* observed that the surface applied inhibitors were effective to resist rebar corrosion in the presence of high chloride ions. *Wombacher et al. (2004)* reported that penetration of the surface applied AMA based inhibitor depends upon the concrete porosity, grade of concrete and the humidity. Authors suggested that the inhibitor treatment can be provided to existing repairable structures that contain upto 1% chloride ions by weight of cement. *Jones (2000)* investigated the effect of migrating type corrosion inhibitor on high performance concrete. He observed a delayed action of inhibitor application on corrosion prevention, which was further related to the time the inhibitor takes to migrate through high quality, low permeability and concrete cover. *Malik et al. (2004)* investigated the performance of surface applied type dimethylethanol amine-based (MCI-A) and triethanol amine-based (MCI-B) inhibitors and vapor based inhibitor (VCI-C). RC specimens coated with migrating inhibitors were exposed to 5% NaCl solution and to the Arabian Gulf seawater for up to 12 months. They observed that the corrosion rate for inhibitor applied specimen was lesser than the control specimen. Further, they reported that VCI –C shows less effectiveness on comparison with MCI-A and MCI-B. *Jamil et al. (2004)* also observed that the presence of surface applied inhibitors led to continuous shift in potential reading toward positive value, suggesting that the inhibitor was able to penetrate through mortar disk to reach the point where steel was embedded. *Soylev et al. (2007a)* studied the effectiveness of commercially available surface applied organic based inhibitors, applied at different stages of chloride exposure. From the results, they observed that the amino alcohol-based inhibitor was effective against corrosion when applied before the chloride application or just after the first chloride ponding cycle. *Thangavel et al. (2009)* studied the migrating versus admixed inhibitor behaviour in three different cements concrete. The Portland slag cement concrete showed best performance under macro cell corrosion conditions amongst all tested cements. Further, 60% reduction in microcell current was observed in migrating type treated specimens whereas this reduction was limited upto 40% with admixed inhibitors.

2.9.4 Protection mechanism of migrating type corrosion inhibitors

Protection mechanism of migrating type inhibitor against chloride induced corrosion was studied by *Maeder (1989)* and *Zheng et al. (2012)*. *Maeder (1989)* found that amines and alkanolamines based inhibitors have the tendency to diffuse through the concrete due to their higher vapor pressure. Author claimed that these types of inhibitors are preferable over the inorganic inhibitors like nitrites because of their non toxic nature and these inhibitors provide protection to the reinforcing steel at both anodic and cathodic sites. *Zheng et al. (2012)* observed that amine based surface applied inhibitor inhibit the transportation of Cl^- ions, H_2O and CO_2 by blocking the pores on the surface of the concrete. However, these inhibitors became less effective with the increase in w/c ratio and with time.

2.10 EFFECTIVENESS OF CORROSION INHIBITORS IN CARBONATION INDUCED CORROSION

The detailed literature review on the effectiveness of both admixed inhibitors and migrating inhibitors in carbonation induced corrosion is presented in the succeeding sections.

2.10.1 Effectiveness of admixed type corrosion inhibitors

Most of the researchers used organic compounds as corrosion inhibitors in carbonation induced corrosion. *Trabanelli et al. (2005)* examined the effectiveness of benzoic acid (BEN) and its derivatives: 2-amino benzoic acid (2AMB), dicarboxylic acids and dicyclohexylammonium nitrite (DCHAMN) in synthetic solution and in carbonated concrete. EIS data represents that amino derivatives and dicarboxylates protect the steel in synthetic solution by forming a long lasting passive layer. In carbonated concrete the best inhibition effect was shown by BEN and 2AMB. However, BEN containing specimens lost its inhibitive action towards the end of exposure duration of 400 days, while 2AMB maintained their inhibition efficiencies around 60% even at the end of exposure duration. *Criado et al. (2012)* evaluated the combined action of organic inhibitors in carbonated and chloride contaminated mortars. The inhibitors used were combination of disodium β glycerol phosphate (GPH) with sodium 3aminobenzoate (3AMB) and GPH with sodium N- phenythantranilate (PhAMB). Out of the tested inhibitors, combination of GPH with PhAMB presented the best inhibition protection as measured by polarization curve and EIS analysis.

2.10.2 Effectiveness and protection mechanism of migrating type corrosion inhibitors

The performance of penetrating type corrosion inhibitors in terms of penetration of inhibitor and reduction in corrosion rate was investigated by *Heiyantuduwa et al. (2006)*. They observed that the penetration of inhibitors was most effective in M30 grade of concrete as compared to M20, M40 and M50 grade. Concrete specimens treated with inhibitors show corrosion rate in passive levels till 50 wetting and drying cycles indicating that application of inhibitors delayed the onset of carbonation induced corrosion.

The protection mechanism of the organic based (aminoalcohol and phosphorous compounds) surface applied inhibitors against carbonation induced corrosion were studied by *Tritthart (2003)*. The author reported that phosphorous components were unable to penetrate into deeper layers of concrete because of the segregation of this compound at the transition zone of carbonated and non carbonated concrete. On the other hand, aminoalcohol remained largely dissolved in the pore solution and thus provided conditions of high mobility and hence, higher level of protection.

From the referred literature, it can be concluded that extensive amount of work was oriented towards the use of corrosion inhibitors in preventing chloride induced corrosion. The use of corrosion inhibitor for prevention of carbonation induced corrosion is limited and needs further exploration.

2.11 CORROSION MONITORING TECHNIQUES

Electrochemical techniques are most widely used to assess the corrosion state of rebar embedded in concrete. Electrochemical techniques being Non-destructive techniques (NDT) have now become an important aspect of durability studies on RC. Amongst the various electrochemical techniques, Half cell potential, Linear Polarization Resistance and Tafel Extrapolation technique are widely used in laboratory as well as in field for corrosion assessment of embedded rebar (*Ahmad and Bhattacharjee, 1995; Criado et al., 2012; Talakokula et al. 2014; Song, 2000; Poursaei and Hansson, 2009; Song and Saraswathy, 2007; Vedalakshmi and Thangavel, 2011*). Along with these, Electrochemical Impedance Spectroscopy (EIS) is also becoming increasingly popular NDT technique for investigating the electrochemical behaviour

of complex heterogeneous systems, like reinforced concrete. EIS has been used by various researchers as an effective method to provide information regarding the microstructure of concrete, corrosion rate and reaction at the steel-concrete interface (*Dong et al., 2014; Dhouibi et al., 2002; Ismail and Ohtsu, 2006; Duarte et al., 2014; Montemor et al., 2002; Ribeiro and Abrantes, 2016; Braganca et al., 2014; Criado et al., 2012; Trabanelli et al., 2005*). The detailed information regarding these techniques is presented in the subsequent sections.

2.11.1 Half-Cell Potential measurements

Half Cell Potential measurements (HCP) are most widely used for assessment of corrosion risk of embedded rebar. This technique was introduced by Richard F. Stratfull in 1970 (*Stratfull, 1968; Stratfull, 1972*) and was later approved as ASTM C 876 (*ASTM, 1991*). Literature suggested that HCP is most commonly used technique for the routine inspection of corrosion activity in RC structures (*Elsener et al., 2003; Pradhan and Bhattacharjee, 2009; Kujur, 2012*). As suggested by name, HCP represents the potential difference between the electrode (steel) and the electrolyte (adjacent concrete). According to ASTM C 876 (*ASTM, 1991*), HCP of an electrode can be measured by coupling the electrode with the standard reference electrode. The various reference electrodes used for the potential measurement are copper-copper sulfate electrode (Cu/CuSO_4), silver-silver chloride electrode (Ag/AgCl), mercury–mercurous sulfate electrode (Hg/HgSO_4) and saturated calomel electrode (SCE). During the HCP measurements, the rebar is attached to the positive terminal of the high impedance voltmeter while the reference electrode is attached to the negative terminal as shown in Fig. 2.6. As per ASTM C876 (*ASTM, 1991*), the probability of corrosion risk in terms of potential with reference to Cu/CuSO_4 and SCE is assessed and is provided in Table 2.2.

The probability of corrosion presented in Table 2.2 corresponds to the chloride induced corrosion in RC. For carbonation induced corrosion, a different range for potential is given by the RILEM TC 154-EMC (*Elsener et al., 2003*) for different drying conditions. For humid and carbonated concrete, the potential of normal steel embedded in concrete varied between 100 mV to -400 mV with respect to Cu/CuSO_4 . For dry and carbonated concrete, this potential range varies from 200 mV to 0 mV with respect to Cu/CuSO_4 .

**Table 2.2 Corrosion interpretation related with HCP measurements
(ASTM C 876, 1991)**

Corrosion interpretation	HCP values (mV) w.r.t	
	SCE	Cu/CuSO ₄
High (90% risk of corrosion)	< -276	< -350
Intermediate (uncertain)	-126 to -275	-200 to -350
Low (10% risk of corrosion)	> -125	> -200

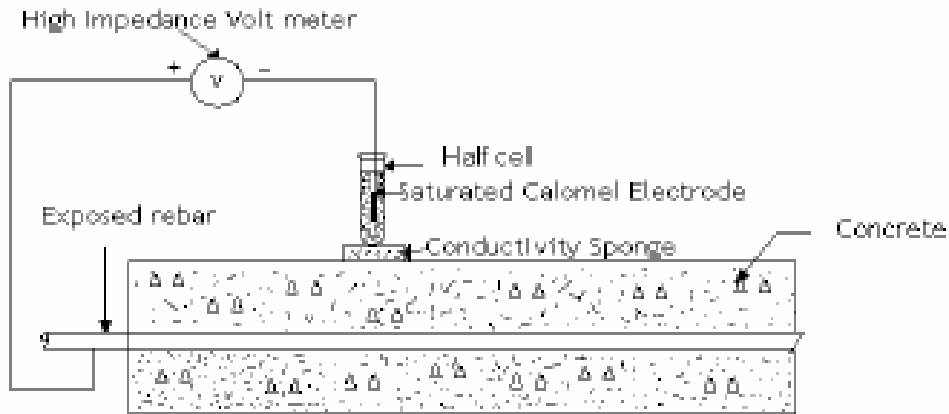


Fig.2.6. Schematic illustration of the HCP measurement (Song and Saraswathy, 2007)

2.11.2 Linear Polarization Resistance technique

Linear Polarization Resistance (LPR) technique is a rapid and non intrusive technique used to determine the instantaneous corrosion rate of the rebar embedded in concrete. This technique was introduced by Stern and Geary in 1957 and has now become most widely used technique for the evaluation of corrosion rate of the embedded rebar (Huang *et al.*, 1996; Andrade and Alonso, 2001; Broomfield *et al.*, 2002; Song and Saraswathy, 2007). During LPR measurement, the rebar is perturbed from its equilibrium potential by a small potential scan (0.167mV/s) through auxiliary electrode. This perturbation can be done either potentiostatically or galvanostatically. In potentiostatic perturbation, the potential of the rebar is varied between a fixed amount (ΔE) and the current decay (ΔI) is monitored after a fixed time. While in

galvanostatic perturbation, current is supplied to the rebar by a fixed amount (ΔI) and potential change (ΔE) is monitored after a fixed time (Song and Saraswathy, 2007). The polarization resistance (R_p) of the rebar is estimated by using the following Stern-Geary equations (Gu et al., 2000, Song and Saraswathy, 2007):

$$R_p = (\Delta E / \Delta I) \quad \text{..... (2.10)}$$

Corrosion current, I_{corr} is then calculated from the measured value of R_p and the relationship is provided in eq. (2.11)

$$I_{corr} = B / R_p \quad \text{.....(2.11)}$$

where, R_p refers to polarization resistance ($\Omega \text{ cm}^2$),

B refers to the Stern- Geary constant which depends upon the Tafel constant of the polarization curve and is calculated by using equation 2.12.

$$B = \frac{\beta_a \beta_c}{2.3 (\beta_a + \beta_c)} \quad \text{..... (2.12)}$$

where, β_a is the slope of the anodic curve of Tafel curve and β_c is the slope of the cathodic branch of the Tafel curve.

The value of B has been adopted as 26mV and 52mV for active and passive steel respectively, with little error (Gu et al., 2000).

In order to determine the corrosion current density (i_{corr}) from the calculated value of corrosion current (I_{corr}), the value of I_{corr} is divided by the polarized surface area of the rebar as shown in eq. (2.13)

$$i_{corr} = I_{corr} / A \quad \text{..... (2.13)}$$

The polarized surface area of the rebar is assumed to be that area which lies directly beneath the auxiliary electrode. However, literature suggested that the current flowing from the auxiliary electrode is unconfined and can spread laterally over an unknown larger surface area of the rebar (Law et al., 2000). Thus, there are chances of inaccuracies in taking the polarized surface area, which further leads to an error in the calculation of corrosion current density. In order to overcome the problem associated with the confinement of the current to a predetermined area on a rebar, the use of outer (second) auxiliary guard ring electrode surrounding the inner auxiliary electrode has been developed (Pradhan and Bhattacharjee, 2009). The purpose of this outer auxiliary guard ring is to confine the current to a predetermined area during the LPR measurements. In addition to the outer guard ring electrode, two sensor electrodes are also placed

between the inner and outer auxiliary guard ring electrode to obtain an appropriate level for the confinement current. Guard ring electrode with two sensors to monitor potential between the counter electrode and the ring is more successful in confinement of current, especially when cover thickness is not high (*Song and Saraswathy, 2007; Kujur, 2012; Gu et al., 2000*).

Now these days Guard ring technique has gained momentum during LPR measurement and test set up by using Guard ring is presented in Fig. 2.7. Generally, the Guard ring is placed parallel to the rebar on the concrete surface and reference electrode should be in contact with the concrete aligned over the rebar. Various researchers (*Song, 2000; Pradhan and Bhattacharjee, 2009; Andrade and Alonso, 2001; Vedalakshmi and Thangavel, 2011; Kujur, 2012*) have proposed the use of Guard ring technique for measurement of the corrosion rate of steel embedded in concrete. Based upon the field and laboratory investigation, *Andrade and Alonso (2001)* and *Song and Saraswathy (2007)* suggested the ranges of i_{corr} corresponding to different stages of corrosion, which are presented in Table 2.3.

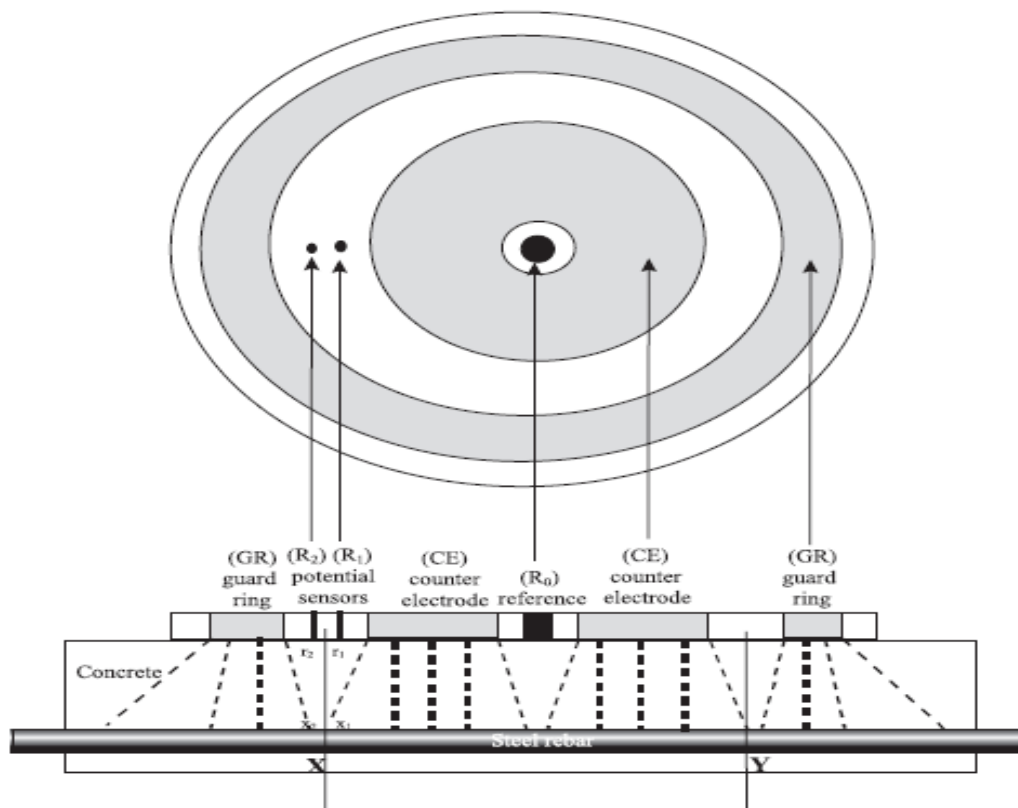


Fig.2.7. Schematic illustration of Guard ring set up (*Song, 2000*)

Table 2.3 Guidelines for rebar condition assessment using i_{corr} (Andrade and Alonso, 2001; Song and Saraswathy, 2007)

Corrosion current density ($\mu\text{A}/\text{cm}^2$)	Rebar Corrosion Condition
Applied to devices with guard ring arrangement	
$i_{corr} > 1.0$	High corrosion rate
$0.5 < i_{corr} < 1.0$	Moderate to high corrosion
$0.1 < i_{corr} < 0.5$	Low to moderate corrosion
$i_{corr} < 0.1$	Passive conditions
Applied to devices without guard ring arrangement	
$i_{corr} > 10$	Corrosion expected in 2 years or less
$1.0 < i_{corr} < 10$	Corrosion expected in 2-10 years
$0.2 < i_{corr} < 1.0$	Corrosion possible in 10-15 years
$i_{corr} < 0.2$	No corrosion expected

2.11.3 Tafel Extrapolation (Potentiodynamic Polarization) Technique

Tafel Extrapolation Technique is also an electrochemical technique used to calculate corrosion rate based upon the corrosion current density and the Tafel slopes. In this technique, a large range of anodic and cathodic potential polarization is applied to the working electrode starting from the open circuit potential. The fundamental principle of Tafel Extrapolation Technique is similar to the LPR technique. The major difference between the two techniques is the potential perturbation applied to the working electrode. In LPR technique, change in potential must be kept less than ± 25 mV but in Tafel Extrapolation technique the change in potential can go up to ± 250 mV (Song and Saraswathy, 2007).

The measured current on log scale is plotted against applied potential, and resulting plot is referred to as Tafel plot. The linear region of the plot describing a relatively high polarization potential follows the Tafel relationship ($\eta = a + b \log i$); and slope is referred to as Tafel slope (Gu et al., 2000). In order to obtain the corrosion current density (i_{corr}), Tafel extrapolation is performed on the polarization curves. The tafel slopes for the anodic and cathodic reactions are obtained by extrapolating linear regions of the polarization curve. The point observed by

extrapolating back both of the anodic and cathodic regions correspond to the corrosion current density (i_{corr}) and the potential at which it lies is referred as the corrosion potential (E_{corr}), as shown in Fig.2.8. Rebar condition can be interpreted on the basis of i_{corr} values and Table 2.3 guidelines have been suggested and are widely accepted for in-situ rebar corrosion condition assessment. In Tafel Extrapolation technique, the corrosion current density can also be determined by substituting the Tafel slopes in the Butler –Volmer equation as:

$$i = i_{corr} \{ \exp[S_1(E - E_{corr})] - \exp[-S_2(E - E_{corr})] \} \quad \dots (2.14)$$

where, S_1 = slope of the anodic branch = $2.303/\beta_a$,

S_2 = slope of the cathodic branch = $2.303/\beta_c$,

β_a = anodic Tafel constant,

β_c = cathodic Tafel constant,

E_{corr} = the corrosion potential,

E = the potential at any time,

i_{corr} = the corrosion current in Ampere,

This Technique has drawn significant importance because of following reasons (*Song and Saraswathy, 2007*):

- (i) Corrosion current can be directly measured from the Tafel slope.
- (ii) Can be used for regular monitoring of the corrosion rate.
- (iii) Extremely low corrosion rate can be measured with this technique.
- (iv) Performance of the inhibitors and alloys can be easily determined with the Tafel plots.

The main disadvantage of using Tafel Extrapolation technique is that it can damage the reinforcing steel-concrete interface because of large perturbation in applied potential. Therefore, this technique is sometimes considered as a relatively destructive electrochemical technique and is generally applied only for limited numbers of times or is applied on the fresh samples at each measurement time.

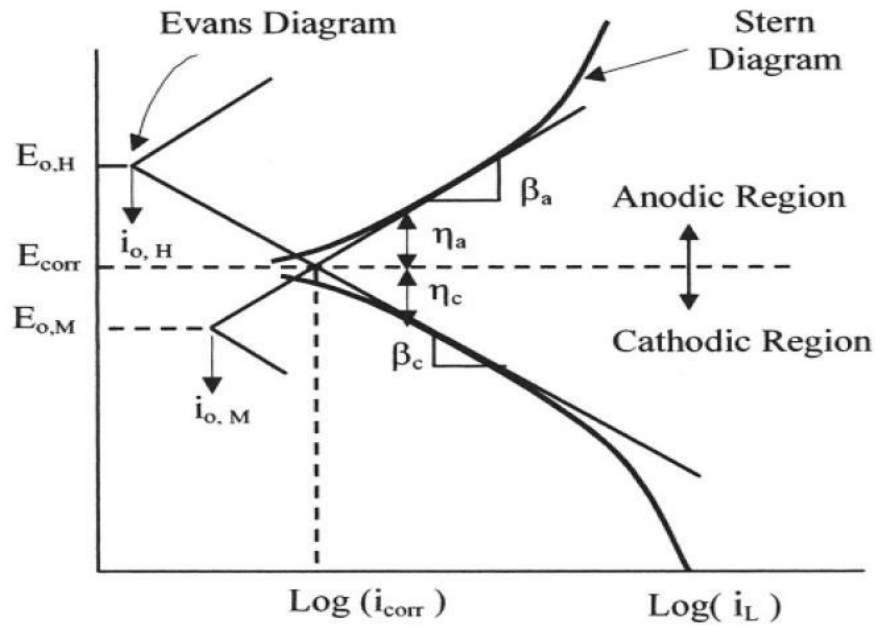


Fig.2.8. Polarization curve representing Tafel slopes (Kujur, 2012)

2.11.4 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is becoming increasingly popular as NDT for characterizing the electrochemical processes in materials that are inhomogeneous, like RC. EIS involves the analysis of the material by applying an alternating current signal to a sweep of frequencies (Braganca *et al.*, 2014). Since rebar corrosion is also an electrochemical process, this technique can be effectively used to monitor the behavior of steel embedded in concrete. EIS gives the information regarding the corrosion kinetics, corrosion mechanism, morphology of corrosion and conditions of the rebar due to corrosion (Ribeiro and Abrantes, 2016). EIS has the capability of studying the charge dynamics in the bulk and the interfacial regions of solids and liquids (Dong *et al.*, 2014). Electrochemical impedance spectroscopy has been used by various researchers as an effective method to provide information regarding microstructure of concrete, corrosion rate and reaction at the steel-concrete interface (Dong *et al.*, 2014; Dhouibi *et al.*, 2002; Ismail and Ohtsu, 2006; Duarte *et al.*, 2014; Montemor *et al.*, 2002; Ribeiro and Abrantes, 2016; Braganca *et al.*, 2014; Criado *et al.*, 2012; Trabanelli *et al.*, 2005).

EIS data can be represented in Nyquist plot or in Bode plot format, explained in detail in ASTM G3 (ASTM, 2004). Typical Nyquist and Bode plot corresponding to a single time constant

is represented by one semicircle, as shown in Fig. 2.9. Nyquist plot corresponds to graph of $Z = Z' + jZ''$ (where Z' is the real part and Z'' is the imaginary part) plotted at different frequencies (Fig. 2.9 a). Bode plot format further has two representations (i) Bode magnitude plot (ii) Bode phase angle plot. In Bode magnitude plot, the base-ten logarithm of frequency is plotted on abscissa and base-ten logarithm of impedance magnitude or modulus $|Z|$ is plotted on ordinate (upper graph of Fig. 2.9b) (Ismail and Ohtsu, 2006). In Bode phase angle plot, negative of phase angle is plotted against base-ten logarithm of frequency (lower graph of Fig. 2.9b).

From the Nyquist plot (Fig. 2.9a) it was observed that low frequency data lies on the right side of the plot and high frequencies lies on the left side of the plot. On the Nyquist plot, the impedance is represented as a vector of length $|Z|$ while phase angle (Φ) corresponds to the angle between $|Z|$ and x-axis. The major drawback of the Nyquist plot is that frequencies are not observed from any data point on the Nyquist plot. However, Bode plot in both formats are plotted against the frequency domains (Fig. 2.9b). Both Nyquist and Bode plots shown in Fig. 2.9 are the outcome from the equivalent electrical circuit (generally known as Randles circuit) shown in Fig. 2.10 i.e. the parallel combination of pure a resistor and a capacitor. However the solution resistance (R_s) are having zero value because the circle pass through the origin as presented in Fig. 2.9a.

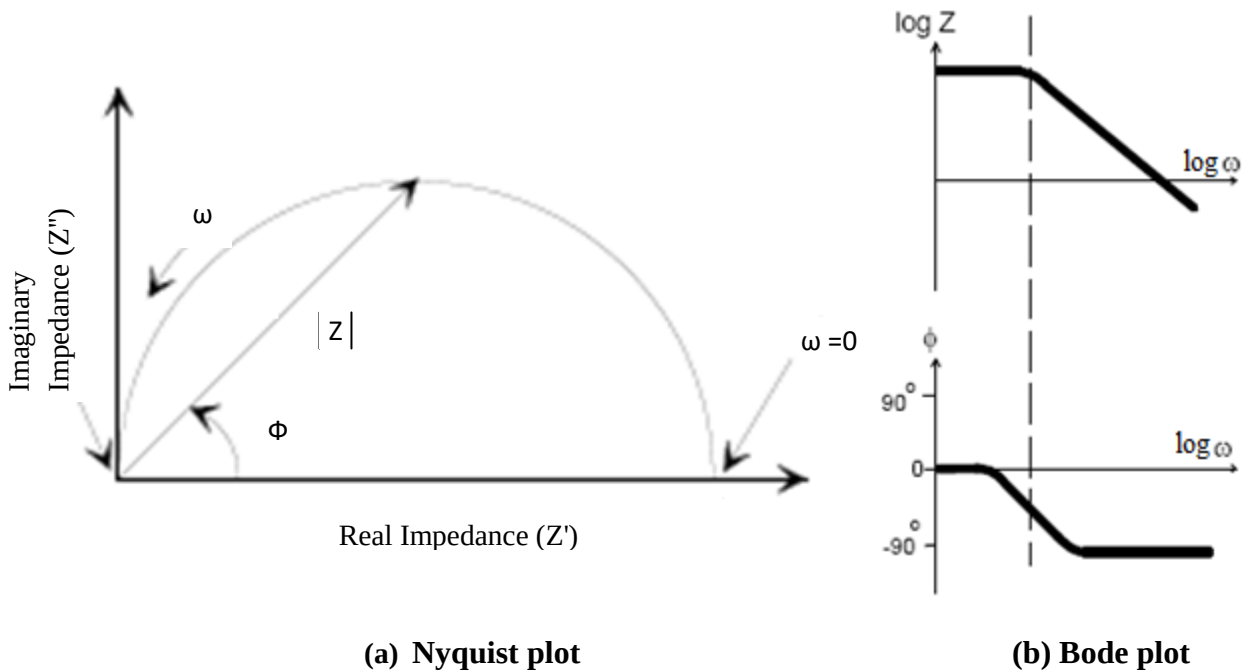


Fig.2.9. Typical EIS data representation with single time constant (www.gamry.com)

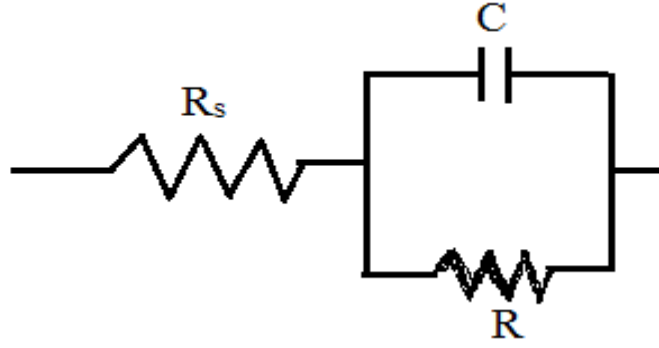


Fig.2.10. Equivalent electrical circuit consists of pure resistor and capacitor

The impedance of this circuit can be described by the following equation:

$$\frac{1}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2} \quad \text{..... (2.15)}$$

Impedance corresponding to the resistive and the capacitive element can be represented by eq. (2.16)

$$\frac{1}{Z} = \frac{1}{R} + \frac{j}{X_c} \quad \text{..... (2.16)}$$

where, Z is the interface impedance,

R is the resistance,

$$j = \sqrt{-1}$$

X_c is reactance of the capacitance and

$X_c = 1/\omega C$ and ω is angular frequency $= 2\pi f$

The frequency dependent $Z(\omega)$ of the equivalent circuit shown in Fig. 2.10 can be written as:

$$Z(\omega) = \frac{R}{1+(\omega CR)^2} - j \frac{\omega CR^2}{1+(\omega CR)^2} \quad \text{..... (2.17)}$$

Plot corresponding to eq. (2.17) is a perfect semicircle as shown earlier in Fig. 2.9a. Generally, an ideal semicircle is not observed practically in most of the materials. It is normally an inclined semicircle with its centre depressed below the x-axis by an angle θ . Also the circle does not pass through origin, due to the presence of pore solution resistance as depicted in Fig. 2.11a. Nyquist shown in Fig. 2.11a is an outcome from the equivalent electrical circuit shown in Fig. 2.11b.

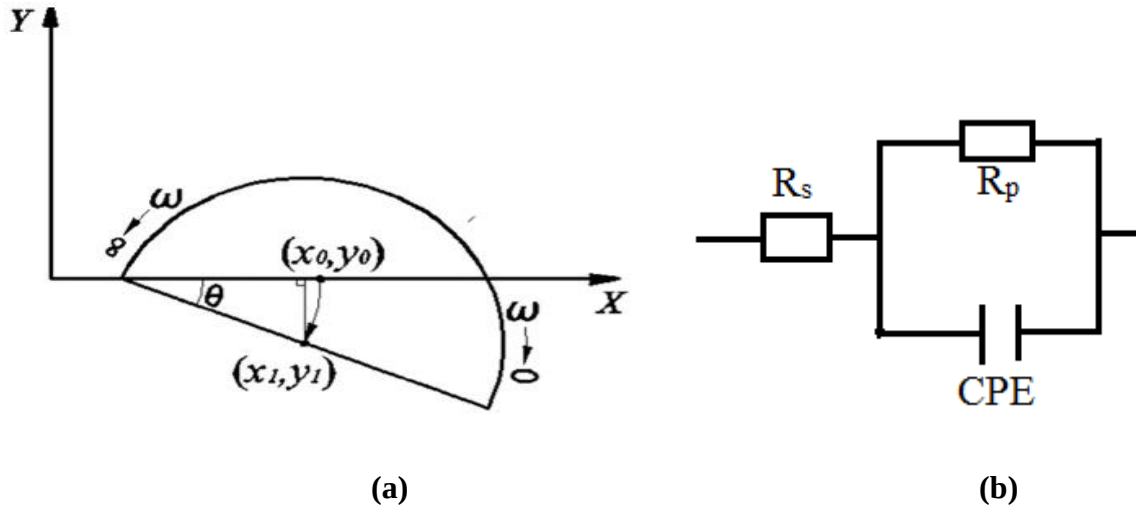


**Fig.2.11. (a) Nyquist plot with its centre depressed below the real axis by an angle θ
(b) Corresponding equivalent electrical circuit (He et al., 2017)**

This depressed semicircle is associated with the spread of the relaxation time and is observed by the constant phase element (CPE) instead of a pure capacitor in the equivalent circuit. Substitution of pure capacitor with the CPE modifies the impedance values, which can be expressed as:

$$Z(CPE) = \frac{R}{[1 + RC(j\omega)^\alpha]} \quad \dots (2.18)$$

where, α represents the degree of perfection of the capacitor and is a measure of the arc depressed below the real impedance axis. The value of α lies in the range of $0 < \alpha < 1$; CPE is a pure resistor when $\alpha = 0$, while CPE is a pure capacitor for $\alpha = 1$ (Fajardo et al., 2014; Criado et al., 2012).

The detailed literature review on the use of EIS technique in RC elements to assess the corrosion behaviour of the embedded rebar is presented in the succeeding section. Some researchers assessed the condition of the rebar in the simulated concrete pore solution, while others carried out the experiments on the actual RC specimens.

(a) Impedance spectra with distinct frequency regions: The detailed literature focused on the splitting of impedance spectra based upon the distinct frequency regions are presented here under:

Ford et al. (1998) studied the concrete and its simulated pore solution by dividing the impedance spectra into distinct regions related to specific frequency range. They performed the EIS measurements by applying an excitation signal of 25mV with a frequency ranged between 20MHz to 2mHz. They recommended that the impedance spectra can be typically divided into two distinct regions: low frequency arc and the high frequency arc. They further observed that the mechanism of low frequency arc (from 1mHz to 100Hz) corresponds to the interaction of concrete with the rebar and is independent of the bulk concrete behaviour. The high frequency arc (higher than 100Hz) mechanism was attributed to the resistance of the bulk concrete and increased with the enhancement in curing time. The behaviour of the material regarding diffusion of ions, blocking of pores, curing of cement and ions migration etc were also characterized in the high frequency region. *Braganca et al. (2014)* studied the electrochemical impedance behaviour of mortar subjected to chloride and sulfate exposure conditions by dividing the impedance spectra into three distinct frequency regions. They performed the EIS measurements by applying an 25mV alternating signal for a frequency ranged between 10^6 Hz - 5×10^{-2} Hz in open circuit potential. The analysis of high frequency region (higher than 100Hz) corresponds to the resistance of the mortar and tended to increase with the hydration process. The bar/mortar interface behaviour was described by the intermediate frequency region (100Hz – 10^{-2} Hz). The low frequency region (less than 10^{-2} Hz) was related to the corrosion process that tend to develop at the rebar surface.

(b) Simulation of impedance spectra with equivalent circuit:

In RC structure, due to complexity at the steel-concrete interface, the basic Randles circuit could not be applied to interpret the EIS spectra. Corrosion process in RC structures involves several physical processes and often composed of several different semicircles which could arise from film effects etc. Therefore the equivalent circuit used to interpret EIS data is generally composed of several circuit elements. Previous researchers have proposed different equivalent circuits corresponding to different frequency regions to model the different stages of

corrosion process occurring at the steel-concrete interface. All the used equivalent circuits by various researchers are schematically shown in Table 2.4.

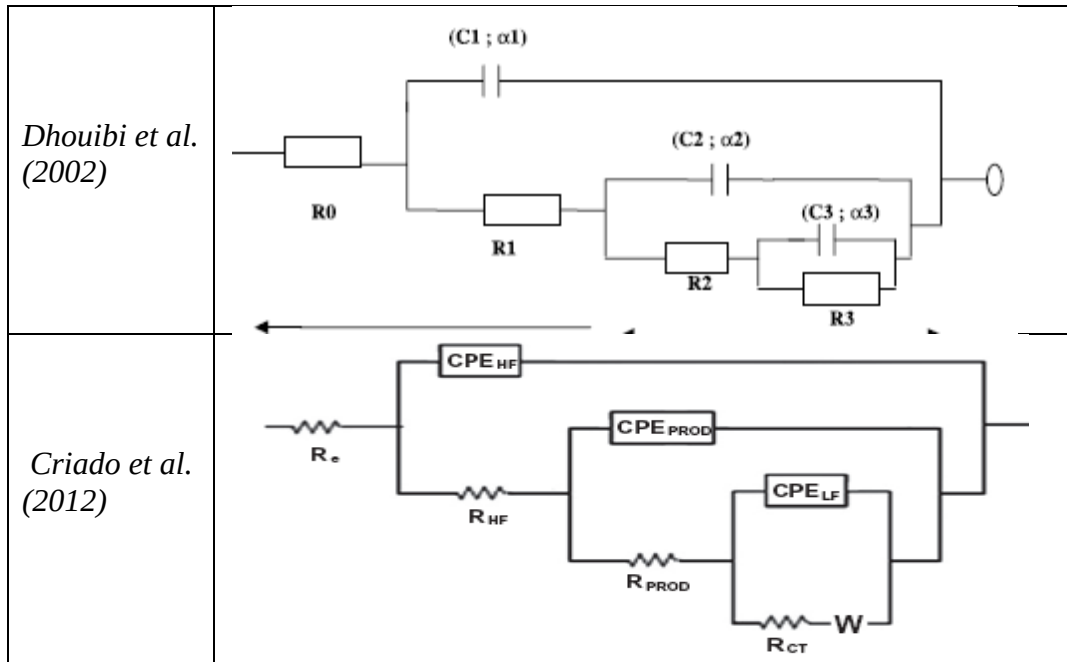
Montemor et al. (2002) monitor the corrosion behaviour of embedded rebar exposed to chloride and carbon dioxide with the help of open circuit potential and EIS. EIS measurements were performed between a frequency range of 50kHz to 1mHz with an 10mV RMS alternating current signal. The equivalent circuit used by them included resistance R_s in series with the high and low frequency parameters. To simulate the low frequency arc, double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) was used; while R_{HF} and C_{HF} were introduced to simulate the high frequency arcs. *Dong et al. (2014)* studied the carbonation behaviour of the concrete with the use of EIS and proposed an electrochemical model to study the carbonation related phenomenon. The equivalent circuit proposed by them included the parameters corresponding to the reaction at the surface of the electrode and the interaction at solid-liquid phase. Also, in the equivalent circuit, they considered the Warburg elements to account for the ion diffusion procedure inside the cement sample and at the surface of the electrode. *Duarte et al. (2014)* studied the electrochemical behaviour of the different stainless steel rebars with the help of EIS and open circuit potential (OCP). The embedded rebars were subjected to the chloride exposure conditions. EIS measurements were carried out by applying a r.m.s voltage of 10mV in a frequency range for 100kHz to 3.7mHz. The equivalent circuit used by them to simulate the electrochemical behaviour of the embedded rebar consisted of parameters; R_e , CPE_1 , R_1 and CPE_2 . R_e was associated with the ohmic resistance of concrete pores; CPE_1 , R_1 was attributed to the areas covered with the passive film and CPE_2 was associated to the double layer capacitance response. *Liu et al. (2017)* investigated the carbonation effect in cement extract solution with the electrochemical techniques such as potentiodynamic polarization and EIS measurement. EIS measurement was performed at open circuit potential with a frequency range of 100kHz to 10mHz at the amplitude of 10mV. Equivalent circuit considered by them was composed of solution resistance R_s , charge transfer resistance R_1 , passive film resistance R_2 , double layer membrane capacitance Q_1 and interface capacitance of passive film and solution Q_2 .

(c) Effectiveness of corrosion inhibitors studied by EIS: Some researchers investigated the effectiveness of corrosion inhibitors with the use of EIS technique.

Monticelli et al. (2000) investigated the inhibiting efficiencies of the corrosion inhibitor through EIS in chloride polluted mortars. The measurements were performed by applying a 10mV sinusoidal potential wave around the E_{corr} with frequency ranged between 10^6Hz to 10^{-3}Hz . The equivalent circuit adopted by them consisted of three parallel RC combinations in series with the solution resistance R_s . The first, second and third parallel RC combinations corresponds to dielectric properties of cover mortar, corrosion product film and electrochemical properties of the corroding rebar respectively. Similarly, *Dhouibi et al. (2002)* studied the long term effectiveness of corrosion inhibitors against chloride contaminated concrete specimens through EIS. The polarization of rebar was done at 10mV r.m.s between a frequency sweep of 65kHz down to 10mHz, with 5 frequency values per decade. It was suggested that the low frequency arc resistance can be used to estimate the polarization resistance of the rebar. Further, they reported that the decrease in intermediate frequency resistance with the corresponding increase in low frequency resistance indicates that inhibitors ions are present at the interfacial layer and have capability to decrease the corrosion rate. *Trabanelli et al. (2005)* used EIS technique to evaluate the inhibition action of corrosion inhibitors against rebar embedded in carbonated concrete. EIS technique was performed by imposing a $\pm 10\text{mV}$ r.m.s sinusoidal excitation at corrosion potential between a frequency range of 10^5Hz to 10^{-3}Hz . The equivalent circuit imposed by them consists of resistance of the electrolyte inside the concrete pores (R_o) + resistance of the concrete itself (R_c) in series with the two parallel RC combination. Similarly, *Criado et al. (2012)* investigated the effect of organic corrosion inhibitor for rebar embedded in carbonated alkali – activated fly ash mortar with the use of EIS. The two organic compound investigated were; (i) disodium β -glycerol phosphate (GPH) with sodium 3-aminobenzoate (3AMB) and (ii) GPH with sodium N-phenylanthranilate (PhAMB). EIS were performed at E_{corr} by imposing a 10mV r.m.s amplitude excitation voltage with 10^6Hz to 10^{-4}Hz frequency sweep. Based upon the low frequency charge transfer resistance R_{ct} values, it was reported that inhibitor treated fly ash mortars specimens have two orders higher resistance to corrosion than the control mortar specimens. Higher value of R_{ct} suggested that the inhibitor toughened the passive film on the rebar surface by adsorption. All the equivalent circuits used by various researchers without and with the use of corrosion inhibitor are schematically shown in Table 2.4.

Table 2.4 Equivalent Electrical Circuit (EEC) used by previous researchers

Researcher Description	Equivalent Electrical Circuit (EEC) Representation
Montemor et al. (2002)	
Dong et al. (2014)	
Duarte et al. (2014)	<i>Model 2</i> <i>Model 3</i>
Liu et al. (2017)	
Monticelli et al. (2000)	



2.12 CLOSING REMARKS

In this chapter, corrosion process in reinforced concrete specimens with two major causes of rebar corrosion (chloride induced and carbonation induced) is presented. Further, the detailed study on carbonation process is presented; which includes the carbonation front penetration deeper inside the concrete, factor influencing the carbonation process etc. Next to this, a detailed literature review focusing on the influence of variation in w/c ratio, cement type and the addition of mineral admixtures on carbonation behaviour of concrete is presented.

Apart from this, various physical, chemical and electrochemical repair strategies available to mitigate the rebar corrosion process are discussed. The detailed literature review suggested that the use of corrosion inhibitor is an effective technique that can be used to retard the corrosion process. Also, the low cost and easy handling of corrosion inhibitors make it a popular preventive measure.

Last section of the chapter is dedicated to the brief discussion on the corrosion monitoring techniques which include; Half-cell potential (HCP), Linear Polarization Resistance (LPR), Tafel Extrapolation and Electrochemical Impedance Spectroscopy (EIS). A brief

literature review regarding the use of EIS to obtain the information of corrosion mechanism, charge dynamics in bulk and interfacial region of solid-liquid phase are discussed.

Through the extensive review of literature carried out related to the proposed research, it is inferred that most of the previous studies investigating the performance of admixed and migrating type corrosion inhibitors were focused on chloride induced corrosion. The studies investigating the performance of inhibitors under carbonation induced corrosion are limited. Therefore, in the present research work, use of migrating type organic based inhibitors in carbonation induced corrosion is explored.

Although EIS is widely used for analyzing the corrosion rate and reaction at the steel-concrete interface, little research has been performed with regards to prediction of carbonation behavior of concrete by using EIS. There is a need to look into the potential of EIS in carbonation depth prediction. Besides, EIS may predict the onset of de-passivation of rebar as well. Consequently, present study was intended to investigate the effectiveness of EIS in evaluating carbonation behavior of reinforced concrete specimens. Based upon the extensive literature review, objectives purposed for the present research work have already been presented in Chapter 1.

CHAPTER 3

INVESTIGATIONS ON BARE STEEL SPECIMENS IN SYNTHETIC SOLUTION

3.1 GENERAL

The focus of the current study is to mitigate rebar corrosion through use of migrating type corrosion inhibitors. Corrosion inhibitors are chemical substances classified into inorganic and organic inhibitors based upon their chemical structures. Various researchers evaluated the effectiveness of inorganic chemicals such as calcium nitrite, sodium nitrite, sodium stannate, zinc oxide, monofluorophosphate-based chemicals etc. in inhibiting the rebar corrosion against chloride induced corrosion (*Saraswathy et al., 2001; Montes et al., 2004; Saraswathy and Song, 2007*). The organic substances which were explored as an effective inhibitor against chloride laden environment consisted of monoethanol amine, diethanol amine and triethanol amine, amino alcohol based chemical, amine-esters, aminoalcohols, alkanolamines etc. (*Andrade et al., 1992; Malik et al., 2004; Saraswathy and Song, 2007; Jamil et al., 2003; Nmai, 2004*). From the referred literature, it was seen that inorganic compounds were more effective for chloride induced corrosion; while for carbonation induced corrosion, organic-based corrosion inhibitors worked more efficiently (*Heiyantuduwa et al., 2006; Monticelli et al., 2011; Nmai, 2004; Montemor et al., 2002; Jamil et al., 2004*).

In this chapter, the effectiveness of some of the organic-based inhibitors against carbonation induced corrosion was explored. The tested inhibitors were either commercially available or were generic chemicals. In reinforced concrete, the occurrence of corrosion phenomena would take long time. Therefore, it is prudent to devise alternative ways to introduce corrosion in a relatively smaller duration to preliminary check the efficiencies of the tested inhibitors in a short period of time. So, effectiveness of these inhibitors was accessed in the saturated calcium hydroxide solution, which is considered to simulate the pore water chemistry of concrete that normally surround the rebar (*Monticelli et al., 2000; Saremi and Mahallati, 2002; Fei et al., 2014*). Although, this system does not represent the actual condition of rebar in concrete, it can be used for comparing the efficiencies of various tested chemicals in relatively shorter time span. The material used in pore solution tests, experimental setup, corrosion monitoring technique and the test results of pore solution tests are discussed in the succeeding sections.

3.2 MATERIAL SYSTEM

The major materials used for the preliminary pore solution tests were bare steel specimen, organic based inhibitors and calcium hydroxide. The details of all these materials are presented in the following sections:

3.2.1 Bare steel

Thermo – mechanically treated (TMT) bars are generally used in the construction of the reinforced concrete (RC) structures. Therefore, TMT bars of 12 mm diameter and 60 mm in length conforming to BIS: 1786-1985 (*BIS, 2004*) were tested for their performance under corrosive environment. The chemical composition of steel bars, as obtained from the manufacturer, is presented in Table 3.1.

Table 3.1 Chemical composition of steel

Compound (%)	Carbon (C)	Sulphur (S)	Phosphorus (P)	CE*	S+P
TMT steel	0.28	0.045	0.045	0.40	0.090

*CE: carbon equivalent

3.2.2 Organic based corrosion inhibitors

Corrosion inhibitors are chemical substances that decrease the corrosion rate when present in the corrosion system in a suitable concentration, without significantly changing the concentration of any other corrosion agent (*ISO-8044, 1989*). The details regarding the corrosion inhibitors have already been discussed in Chapter 2 under Sections 2.6 and 2.7. Briefly, based upon the application mode, corrosion inhibitors are categorized into two types; namely admixed corrosion inhibitors which are mixed during casting of concrete and migrating corrosion inhibitor which are applied on the surface of concrete during rehabilitation procedures. The migrating corrosion inhibitors after application, diffuse into the hardened concrete to reach rebar level (*Griffin, 1975; Gaidis, 2004*). The admixed inhibitors have been commercially available since 1970's, but the use of migrating type inhibitors in concrete has gained momentum over the last decade or so (*Gaidis, 2004*). The surface applied migrating inhibitors have advantage over admixed corrosion inhibitors in terms of their negligible effect on both the cement hydration process as well as on properties of resultant concrete (*Soylev et al., 2007b*). The objective of the

present study is to use the inhibitors as migrating type and study their effectiveness in corrosion inhibition.

Literature reviewed suggested that both inorganic and organic compounds could be used as corrosion inhibitors. Inorganic compounds such as nitrites and nitrates were found to be effective for chloride induced corrosion only whereas, for carbonation induced corrosion, organic-based corrosion inhibitors registered higher efficiency (*Heiyantuduwa et al., 2006; Monticelli et al., 2011; Nmai, 2004; Montemor et al., 2002; Jamil et al., 2004*). Since the present study focuses on carbonation induced corrosion, organic based inhibitors were investigated in the present work, which included both organic based commercially available and generic inhibitors.

Initial selection of inhibitors was based on the literature review conducted for studying the effectiveness of chemicals in chloride contaminated / carbonated concrete. From the referred literature, it was observed that aminoalcohol and amines were efficient in inhibiting both chloride and carbonation induced corrosion. Therefore, generic inhibitors consisting of aminoalcohol and amine groups were considered for investigation. Among the commercially available inhibitors, the inhibitors which were claimed to be effective in chloride induced corrosion were tested for their efficiency in carbonated induced corrosion. The commercially available inhibitors were proprietary materials and the manufacturer only disclosed the active ingredients of the inhibitor, while exact composition was kept undisclosed. Table 3.2 shows the details of the investigated generic type inhibitors and Table 3.3 enlists the physical properties of the commercially available inhibitors, as claimed by the manufacturer.

Table 3.2 Chemical and Physical properties of generic inhibitors

S. No	Inhibitor name	Chemical composition	Density (g/cm ³)	Molar Mass (g/mol)	Boiling Point (°C)
1.	Ethanolamine	C ₂ H ₇ NO	1.01	61.08	170
2.	Sodium gluonate	C ₆ H ₁₁ NaO ₇	1.80	218.14	196-198
3.	2 Aminobenzoic acid	C ₇ H ₇ NO ₂	1.40	137.14	200
4.	Di-cyclo-hexal-amine	C ₁₂ H ₂₃ N	0.91	181.32	256

Table 3.3 Chemical and Physical properties of commercially available inhibitors

S. No	Inhibitor Specification	Chemical Base	Colour	Flash Point	Specific Gravity	Shelf life (months)	Dosage
1.	Commercial Inhibitor 1	Aminoalcohol, aminocarboxylates	Pale yellow	43 °C	0.85	12	5.5 ltr/m ³
2.	Commercial Inhibitor 2	Organic based	Colourless	41 °C	0.98±0.02	18	-
3.	Commercial Inhibitor 3	Organic based	Colourless	39 °C	0.88±0.02	12	0.5 -0.6 kg/m ³
4.	Commercial Inhibitor 4	Amino alcohols based	Light yellow	49°C	1.04±0.02	24	0.50 kg/m ²

3.2.3 Epoxy

To ensure that the corrosion reaction occurs over a specific area, only a small portion of the bare steel specimen was exposed to corrosion process and the remaining area was sealed with epoxy. Epoxy used in the present study was available in market with the trade name “Fevilite Rapid”. It was a two component adhesive, consisting of resin and hardener. Both the components were required to be mixed in equal proportions before use.

3.2.4 Chemicals other than inhibitors

Besides the chemicals that were investigated for their use as corrosion inhibitors, some other chemicals were also used for preparation of the concrete pore solution. For this purpose, reagent grade calcium hydroxide ($\text{Ca}(\text{OH})_2$), hexane and sodium hydroxide (NaOH) were used.

3.3 PREPARATION PROCEDURES

The test set up required a prepared bare steel specimens and a synthetic mixture which could simulate the real concrete pore solution that surrounds the steel rebar. The details of preparation of both bare steel specimens and of synthetic pore solution are presented in the following sections.

3.3.1 Preparation of bare steel specimens

The bare steel specimens of length 60 mm were cut and cleaned by rubbing with emery papers so as to remove any rust present on the surface. They were further cleaned by soaking in analytical reagent grade hexane and finally allowed to air- dry. After cleaning, the surface of the steel specimens was coated with epoxy, leaving a 4 mm length at the bottom exposed to the

corrosion process. The exposed surface area was kept to be 350 mm². To ensure electrical connectivity, prior to cleaning, a 3 mm threaded hole was made on top of the steel specimens. Subsequently, a stainless steel screw and nut was inserted into the hole and a copper wire was connected to the nut. The details of the bare steel specimen are schematically shown in Fig. 3.1 and prepared steel specimens ready for investigation are shown in Fig. 3.2.

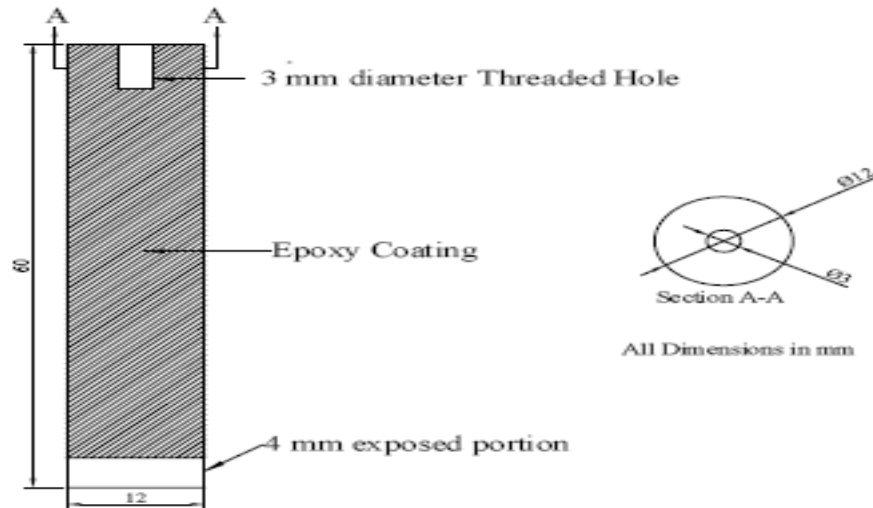


Fig.3.1. Detail of bare steel specimens used in synthetic solution



Fig.3.2. Prepared bare steel specimens ready for experimental investigation

3.3.2 Preparation of synthetic solution

To simulate the pore solution of concrete that normally surrounds the rebar, saturated solution of calcium hydroxide ($\text{Ca}(\text{OH})_2$) was prepared. The saturated $\text{Ca}(\text{OH})_2$ solution was

prepared by adding one tablespoon of reagent grade Ca(OH)_2 in 1 liter of distilled water. This solution was shaken vigorously for 2 minutes and was left undisturbed for 24 hours. After 24 hours, the saturated solution of Ca(OH)_2 was filtered with the help of a filter paper and pH value was measured as 12.5.

Further, in order to simulate the carbonated pore solution, prepared solution was bubbled with pure CO_2 to reach a pH value of 8.1. During the bubbling process, Ca(OH)_2 of synthetic solution usually react with CO_2 to form calcium carbonate (CaCO_3), which precipitates out as a suspended solid, making the solution to appear milky. The resultant solution was filtered again to remove the precipitated calcium carbonate. Further, pH value of the carbonated solution was monitored at regular interval; and if the pH value of the solution increased, CO_2 was bubbled again.

Table 3.4 Abbreviation and concentration of inhibitors for synthetic solution

Sol. No.	Description	Abbreviation	Chemical Base/ Composition	Concentration	pH value
1.	Saturated Ca(OH)_2	CH	-	-	12.5
2.	Carbonated	carb	-	-	8.10
3.	Ethanolamine	*G.I1	$\text{C}_2\text{H}_7\text{NO}$	0.07 M	8.00
4.	Sodium gluconate	G.I2	$\text{C}_6\text{H}_{11}\text{NaO}_7$	0.07 M	8.04
5.	2 Aminobenzoic acid	G.I3	$\text{C}_7\text{H}_7\text{NO}_2$	0.07 M	8.05
6.	Dicyclohexylamine	G.I4	$\text{C}_{12}\text{H}_{23}\text{N}$	0.07M	8.08
7.	Commercial Inhibitor 1	**C.I1	Aminocarboxylates	1%v/v	8.04
8.	Commercial Inhibitor 2	C.I2	Organic based	1%v/v	8.00
9.	Commercial Inhibitor 3	C.I3	Organic based	1%v/v	8.03
10.	Commercial Inhibitor 4	C.I4	Amino alcohols based	1%v/v	8.08

*G.I Generic Inhibitors

**C.I Commercially available Inhibitors

Once the carbonated solution was prepared, the desired inhibitor (as mentioned in section 3.2.2) was added to it. The abbreviation and concentration of various organic based inhibitors used in the present work are listed in Table 3.4. After mixing the corrosion inhibitors in the

carbonated solution, a slight change in the pH value of the resultant solution was observed. To maintain the pH value of the solution at 8.1, the solution was either bubbled with CO₂ (if the inhibitor addition increased the pH value) or sodium hydroxide was added (if the inhibitor addition lowered the pH value). In all, ten types of synthetic solutions were prepared by adding various kinds of organic chemicals. After having achieved the desired synthetic solution, the prepared bare steel specimens were placed into it as shown in Fig. 3.3.



Fig.3.3 Bare steel specimens positioned in different synthetic solutions

3.4 CORROSION MONITORING

The corrosion monitoring was done in an electrochemical cell, using an Advanced Corrosion Monitoring (ACM) field machine (serial number 1463). The electrochemical cell consisted of a cylindrical jar with a polypropylene lid. It was provided with necessary fittings to make connection with the reference electrode, noise reduction probe, auxiliary electrode, thermometer and the test specimen. Saturated Calomel Electrode (SCE) was used as a reference electrode throughout the investigation.

The various solutions required to be tested for corrosion activity were filled in the cylindrical jars. The amount of solution was taken to insure that the bottom uncoated length of the steel specimens remained submerged during the investigation as shown in Fig. 3.3. These specimens were periodically monitored for their corrosion activity by using ACM field machine. Fig.3.4 presents the connection arrangement of electrochemical cell made with the ACM field

machine. For testing, the bare steel specimen was screwed to the working electrode and all the other electrodes, viz. reference electrode, auxiliary electrode, and noise reduction probe were also attached to the electrochemical cell. The noise reduction electrode was used to reduce mains signal polarization and hence, minimizes the reference electrode measurement noise.

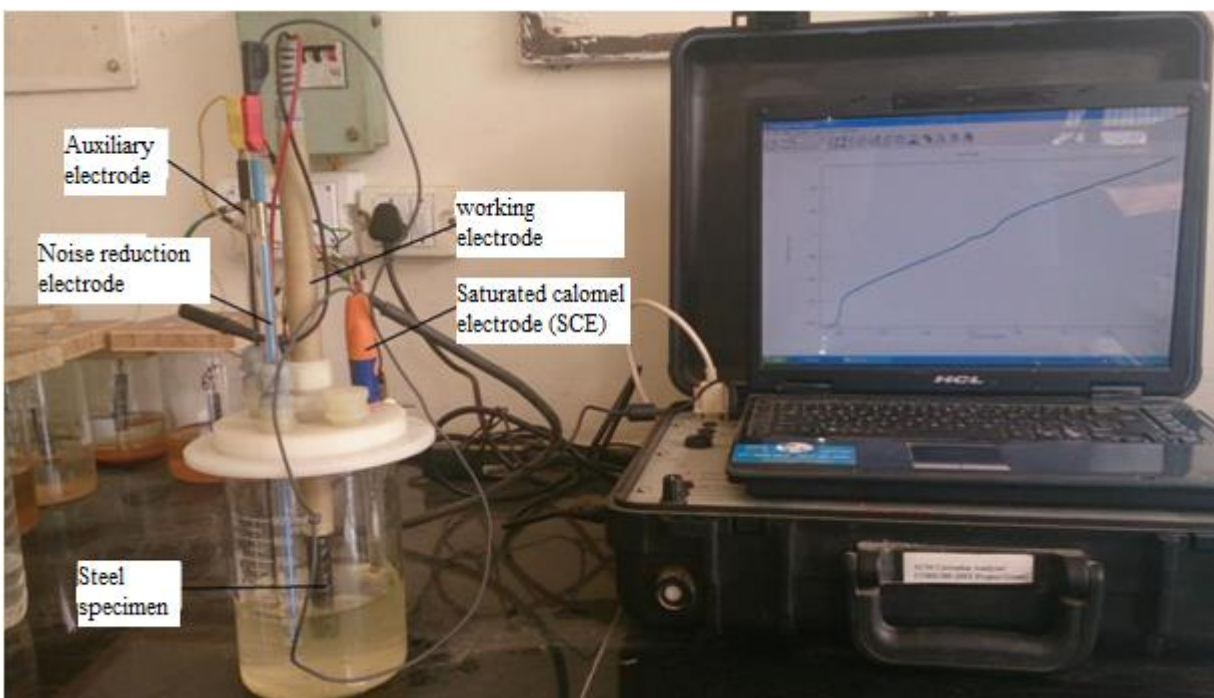


Fig.3.4. Connection arrangement of electrochemical cell with ACM machine

The potentiodynamic sweep test was undertaken to study the passivation behaviour of steel specimens immersed in different types of solutions. Corrosion activity was monitored by performing electrochemical measurement i.e. long term – LPR sweep or potentiodynamic polarization measurement at the age of 1h, 24h, 48h, 130h and 240h of immersion. However, the immersion period was prolonged to 480h for some solutions where the tested inhibitors started developing the inhibiting action at a slower rate. The measurements at 480h also helped in monitoring the stabilization tendency of the tested inhibitor. Potentiodynamic polarization curves were recorded at a sweep rate of 60mV per minute over a potential range of -250mV/SCE to 1500mV/SCE , with an offset from the rest potential. In order to cover all possible zones of corrosion, the upper range of polarization potential was kept high at 1500mV (Kapat *et al.*, 2006; Pradhan and Bhattacharjee, 2007). It is known that when specimen is subjected to very high potential testing the actual corrosion activity of the specimens gets disturbed. Keeping this in

mind, all measurements at each age were made on fresh specimens in undisturbed state. The visible conditions of steel specimens immersed in different solutions at end of testing period are shown in Fig. 3.5.



Fig.3.5. Conditions of steel specimens at the end of immersion duration in different solutions

3.5 RESULTS AND DISCUSSION

Fig.3.6 shows a typical polarization curve which consists of two distinct branches namely; anodic and cathodic. The anodic branch of the polarization curve is further split into three zones namely; active, passive and transpassive zone as marked in the Fig.3.6. The zone below mark A is termed as active zone, in which increase in the current density is significantly high with a very little change in potential. The zone between marks A and B is called the passive zone, in which change in the current density is relatively small with a significant increase in potential (*Pradhan and Bhattacharjee, 2007*). The transpassive zone, with oxygen evolution lies above the mark B i.e. above the passive zone. The Tafel slope for the anodic and cathodic reactions are obtained by the extrapolation of linear regions of the polarization curve. The point obtained by extrapolating back, both of the anodic and cathodic regions corresponds to the corrosion current density (i_{corr}) and the potential at which it lies is referred to as the corrosion potential (E_{corr}).

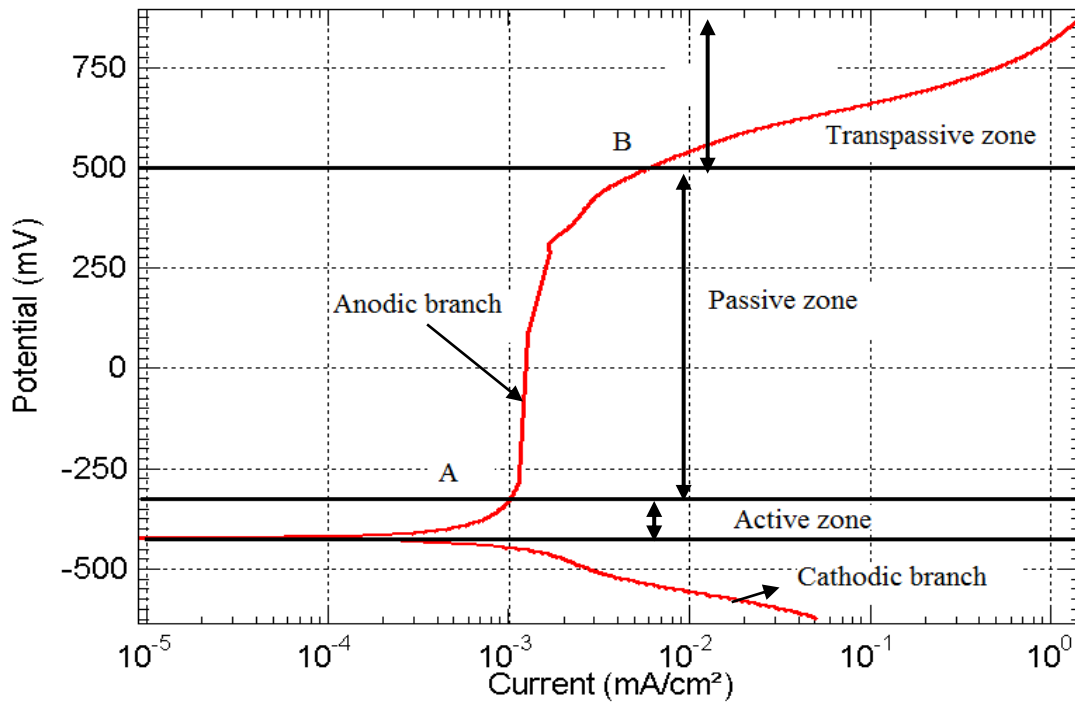


Fig.3.6. Typical polarization curve with anodic and cathodic branches

3.5.1 Polarization curves for different immersion durations

The polarization curves recorded for various solutions at different immersion durations are presented in Figs. 3.7 to 3.16. Further, in order to quantify the performance of tested inhibitors, polarization curves of carbonated and inhibitor treated specimens were compared. The polarization curves obtained at 240h of immersion for generic inhibitor are presented in Fig. 3.17, while the Fig. 3.18 shows the comparison between carbonated and commercially available inhibitor treated specimens at the same duration.

(a) Polarization curves for CH and carb. Solution

Anodic polarization curves obtained at 24h of immersion in uncarbonated (CH) and carbonated (carb.) solutions with different zones of corrosion are presented in Fig. 3.7. From the figure, it was observed that in the uncarbonated solution, all the zones were well defined while in the carbonated solution (with pH 8.1) no explicit passive zone was observed. In the uncarbonated solution; the passive zone (where steel rebar resist corrosion) was observed for the current density between 10⁻³ mA/cm² to 10⁻² mA/cm². However, in carbonated solution no explicit

passive behaviour was observed because the passive film, which consists of compounds of iron, is chemically stable at high pH (above 12) only. On comparing both the curves, it can be said that carbonation does increase the corrosion risk of steel rebar.

Along with the absence of distinct passive zone, a small decrease in rest potential was also observed in the carbonated solution in comparison to the uncarbonated solution. This decrease in rest potential may be associated with decrease in the anodic reaction i.e. decreased concentration of Fe^{++} in the solution. The additional supply of oxygen in carbonated solution leads to early depassivation of rebar at lower current density (Kujur, 2012).

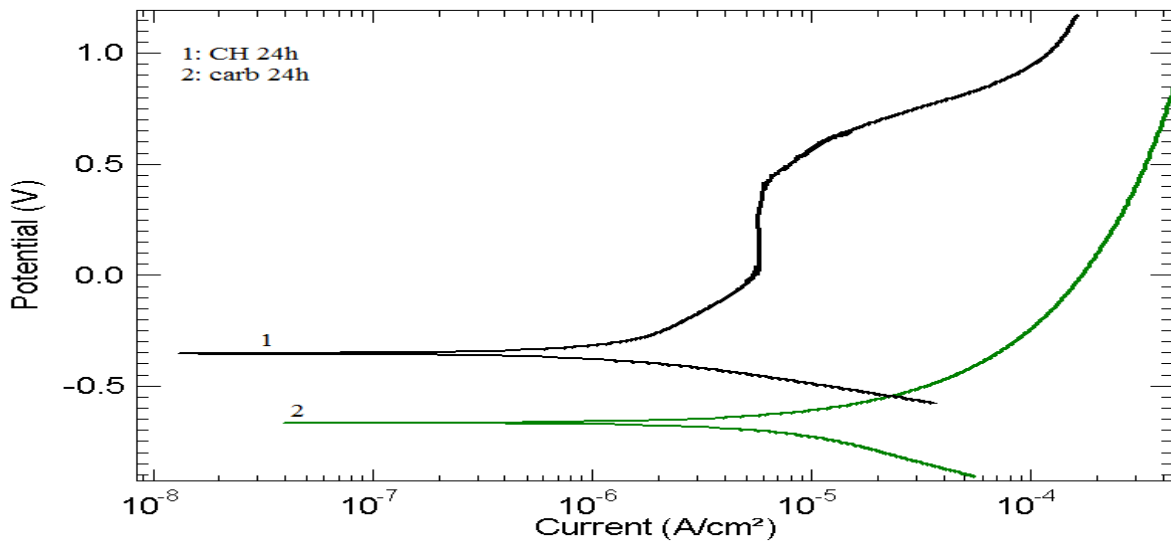


Fig.3.7. Anodic polarization curves recorded in uncarbonated (CH) and carbonated (carb) solution at 24h of immersion

Further, variation in the polarization curves with exposure duration in CH and carbonated solution is presented in Fig. 3.8. As can be observed from the figure, in CH solution at 1h of immersion, anodic branch of polarization curve started at $-0.252\text{V}_{\text{SCE}}$, followed by a passive region, and then at potential above $0.850\text{V}_{\text{SCE}}$ (breakdown potential) an abrupt increase in current density was observed. The current density for CH at 1h was observed to be a $0.48 \mu\text{A}/\text{cm}^2$. In the carbonated solution, anodic branch of the polarization curve exhibited a shift towards the active zone ($-0.576 \text{V}_{\text{SCE}}$) with current density close to a $5.5 \mu\text{A}/\text{cm}^2$ and no explicit passive behaviour was observed at 1h of immersion. By increasing the immersion time to 240h, steel specimen in CH solution showed stabilized passive behaviour upto $0.630\text{V}_{\text{SCE}}$ with a current density of $0.45 \mu\text{A}/\text{cm}^2$, while in carb. solution the rest potential further shifted towards the active zone

with a potential value of $-0.749V_{SCE}$ and a higher current density of $9.2 \mu A/cm^2$, where in, no explicit passive behaviour was observed.

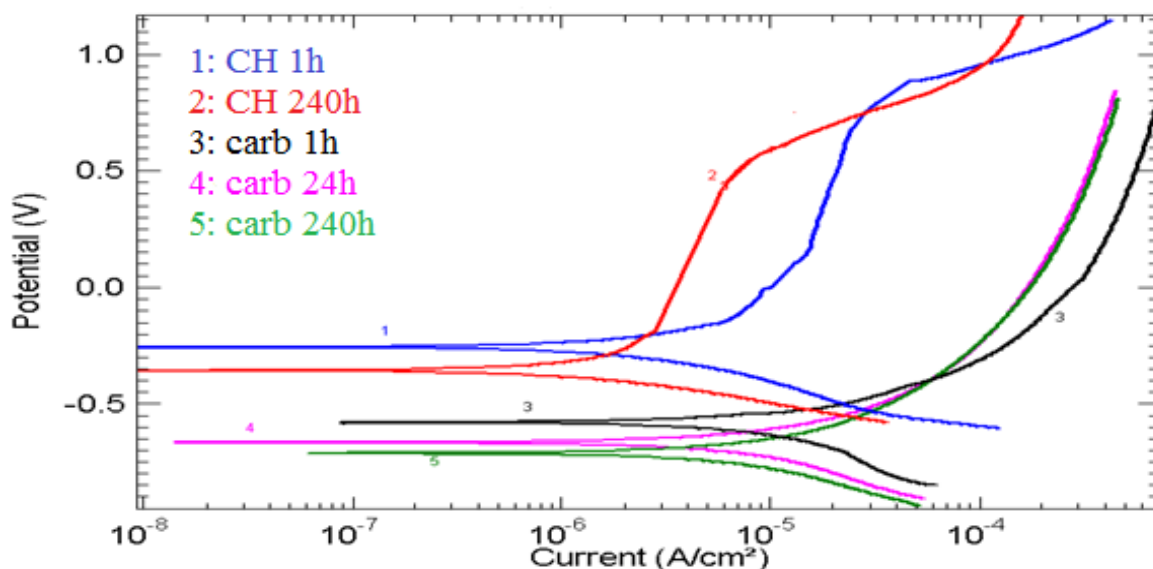


Fig.3.8. Polarization curves recorded in CH and carb solution for different immersion durations

(b) Polarization curves for solution containing inhibitor G.I1

The addition of inhibitor G.I1 to the carbonated solution provided no inhibiting effect on the corrosion process at all immersion times (Fig.3.9). In the presence of G.I1, steel underwent active corrosion but an active/passive transition occurred during 240h of immersion with small potential range (-0.8 to $-0.68 V_{SCE}$). At 240h of immersion, the solution containing G.I1 had current density of $15.8 \mu A/cm^2$ which was even higher than the corresponding value in carb. solution ($9.2 \mu A/cm^2$). It can, therefore, be concluded that inhibitor G.I1 is not an effective corrosion inhibitor for carbonated concrete.

(c) Polarization curves for solution containing inhibitor G.I2

Fig. 3.10 depicts the polarization curve recorded in solution having inhibitor G.I2. It shows an undulation type curve with no distinct passive range during 24h of immersion period. During this period, the corrosion current density measured was $21 \mu A/cm^2$ with an active corrosion potential of $-0.79 V_{SCE}$. With the enhancement in immersion time, solution containing inhibitor G.I2 started showing stabilized behaviour. At 240h of immersion duration, a decrease in corrosion current density ($11 \mu A/cm^2$) with a shift in potential towards nobler side ($-0.54 V_{SCE}$)

was observed. The trend remained constant upto 480h of immersion duration. Although this inhibitor gave an i_{corr} value comparable to the carbonated solution towards the end of exposure duration, but an active/passive transition zone was clearly marked for this inhibitor solution. From curves 4 and 5 of Fig. 3.10, it was observed that active/passive transition started from $-0.40V_{SCE}$ and remained passive upto $-0.10V_{SCE}$ (240h) and $0.01V_{SCE}$ (480h). Presence of this passive behaviour confirmed the efficiency of the tested inhibitor in forming the passive layer around the steel specimens.

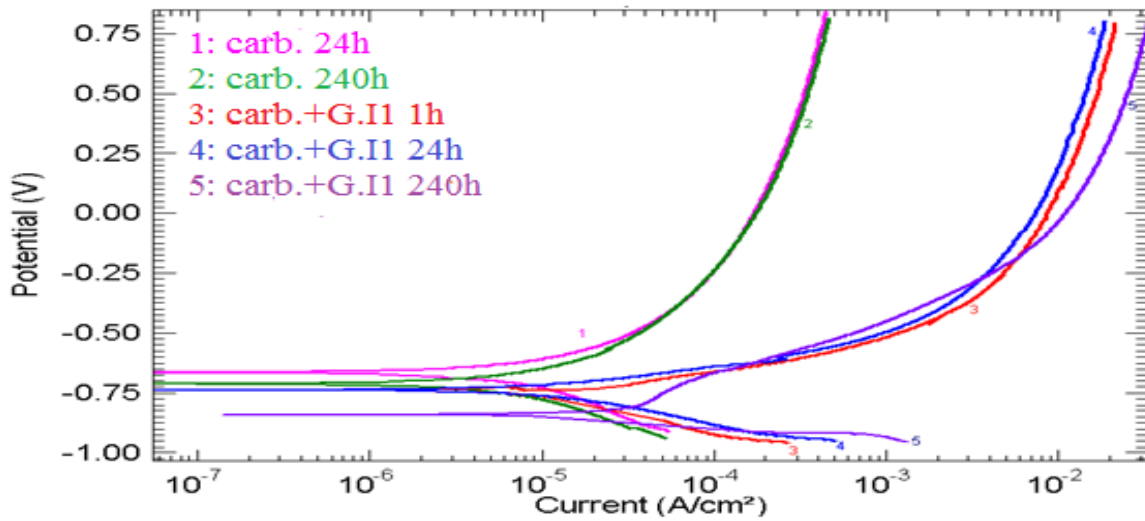


Fig.3.9. Polarization curves recorded in carbonated solution in the absence (1,2) and in presence of G.I1 (3,4,5) for different immersion durations

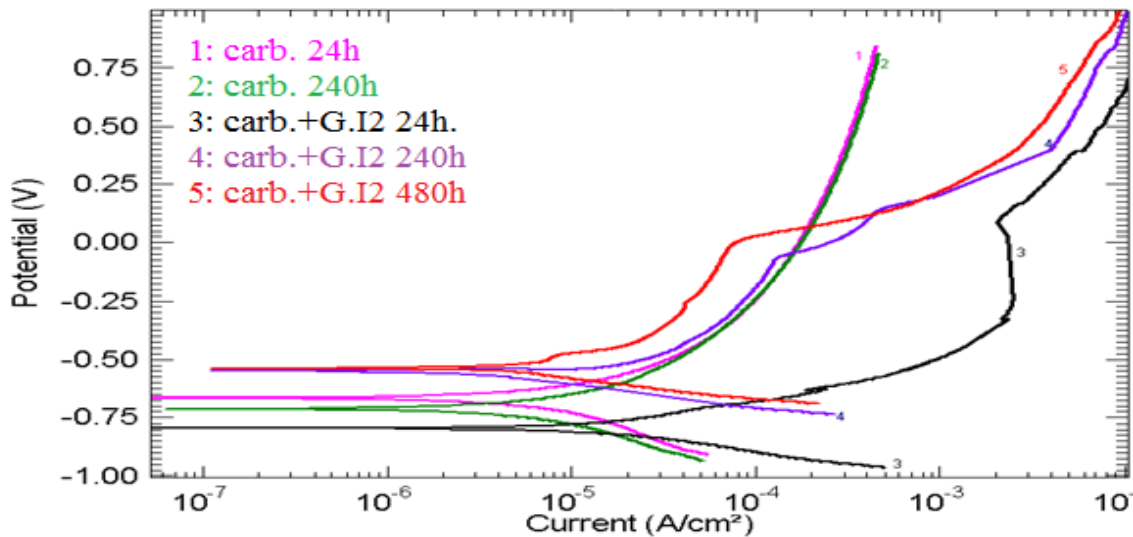


Fig.3.10. Polarization curves recorded in carbonated solution in the absence (1,2) and in presence of G.I2 (3,4,5) for different immersion durations

(d) Polarization curves for solution containing inhibitor G.I3

Fig. 3.11 presents the polarization curves obtained in carbonated solution with inhibitor G.I3 at different immersion times. All the polarization curves of solution having G.I3 inhibitor had a distinct passive zone. The passive zone tends to become more stable with passage of immersion duration. At 48 h of immersion, E_{corr} is ennobled to $-0.35V_{\text{SCE}}$, owing to an increase in the slope of anodic polarization curve, which is likely due to the formation of a surface film. The protectiveness of this film remained stable up to 240h of immersion as indicated by measured i_{corr} value which was slightly lower at 240h as compared to 48h and 130h of immersion. The value of corrosion current density observed at 240h of immersion was much lower ($3.9 \mu\text{A}/\text{cm}^2$) in G.I3 inhibitor as compared to the carbonated solution ($9.2 \mu\text{A}/\text{cm}^2$). Also, in the presence of G.I3 inhibitor, a marked shift of the potential towards the noble side was observed. The measured nobler potential and lower current densities confirmed the effectiveness of this inhibitor in carbonated environment.

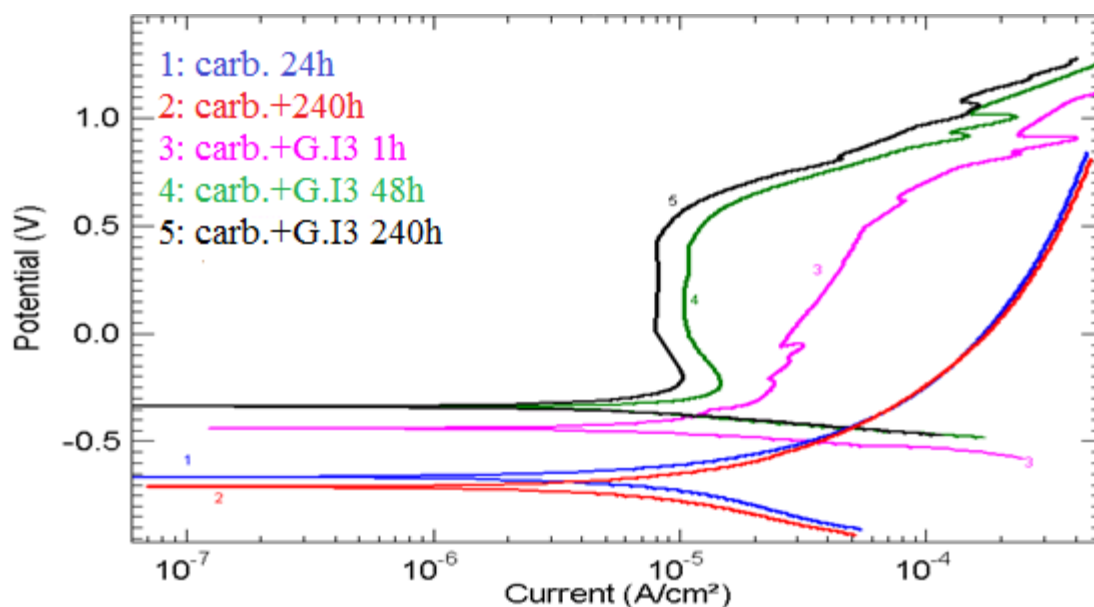


Fig.3.11. Polarization curves recorded in carbonated solution in the absence (1,2) and in presence of G.I3 (3,4,5) for different immersion durations

(e) Polarization curves for solution containing inhibitor G.I4

Fig.3.12 indicates that the solution containing G.I4 inhibitor had corrosion behaviour similar to that of the carbonated solution. Although solution containing G.I4 inhibitor exhibited a

shift of potential towards the nobler side at 240 h of immersion but the corrosion current density remained in the range of $7.2 \mu\text{A}/\text{cm}^2$ (1h of immersion) to $9.5 \mu\text{A}/\text{cm}^2$ (240h of immersion). Observed higher current density with no explicit passive behaviour indicates the ineffectiveness of this inhibitor.

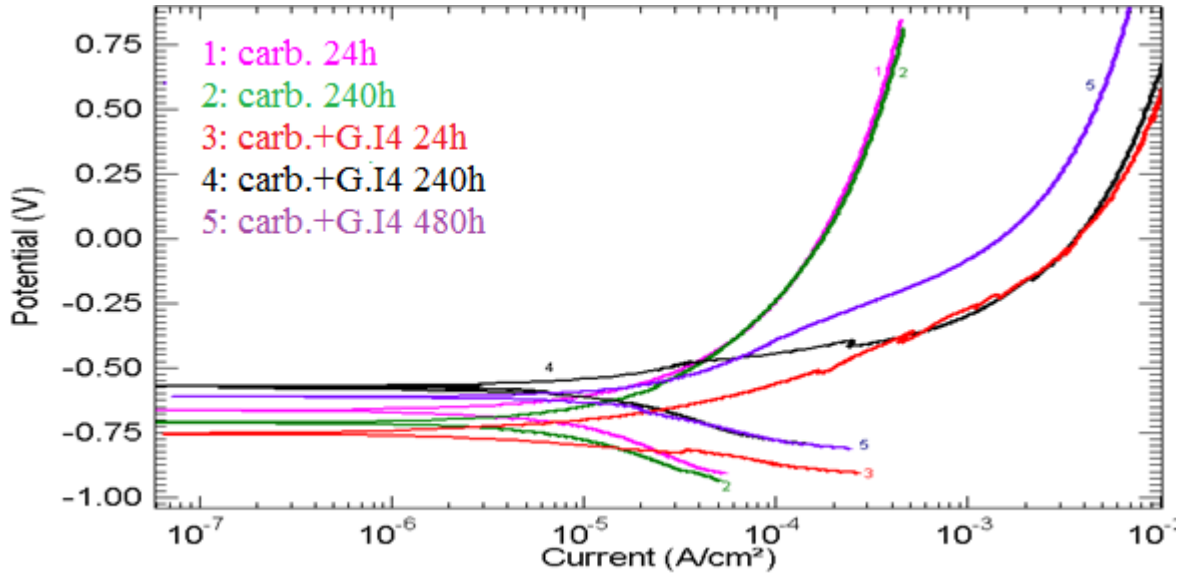


Fig.3.12. Polarization curves recorded in carbonated solution in the absence (1,2) and in presence of G.I4 (3,4,5) for different immersion durations

(f) Polarization curves for solution containing inhibitor C.I1

Fig. 3.13 clearly indicates that the inhibitor C.I1 ennobled the corrosion potential with the occurrence of active/passive transition zone from the beginning of immersion duration. It was observed that in solution containing C.I1 inhibitor, corrosion potential had a small variation in the range of $-0.57V_{\text{SCE}}$ (24h) to $-0.48V_{\text{SCE}}$ (240h). From curves 4 and 5 of Fig. 3.13, it was observed that active/passive transition started from a potential of approximately $-0.30V_{\text{SCE}}$ and remained passive till the potential of $0.20V_{\text{SCE}}$. However, with the use of this inhibitor the i_{corr} value of the steel specimens increased with increase in immersion period. The i_{corr} value increased from $16 \mu\text{A}/\text{cm}^2$ at 1h of immersion to $33 \mu\text{A}/\text{cm}^2$ at 240h of immersion.

(g) Polarization curves for solution containing inhibitor C.I2

Fig.3.14 illustrates that for solution containing inhibitor C.I2 no explicit passive zone was observed. At 240 hours of immersion, although corrosion current density ($4.5 \mu\text{A}/\text{cm}^2$)

decreased as compared to carbonated solution ($9.2 \mu\text{A}/\text{cm}^2$), the potential still remained within the active range ($-0.753\text{V}_{\text{SCE}}$). This behavior is typical for anodic inhibitors which reduce the corrosion rate and increase the corrosion potential (Shi and Sun, 2012).

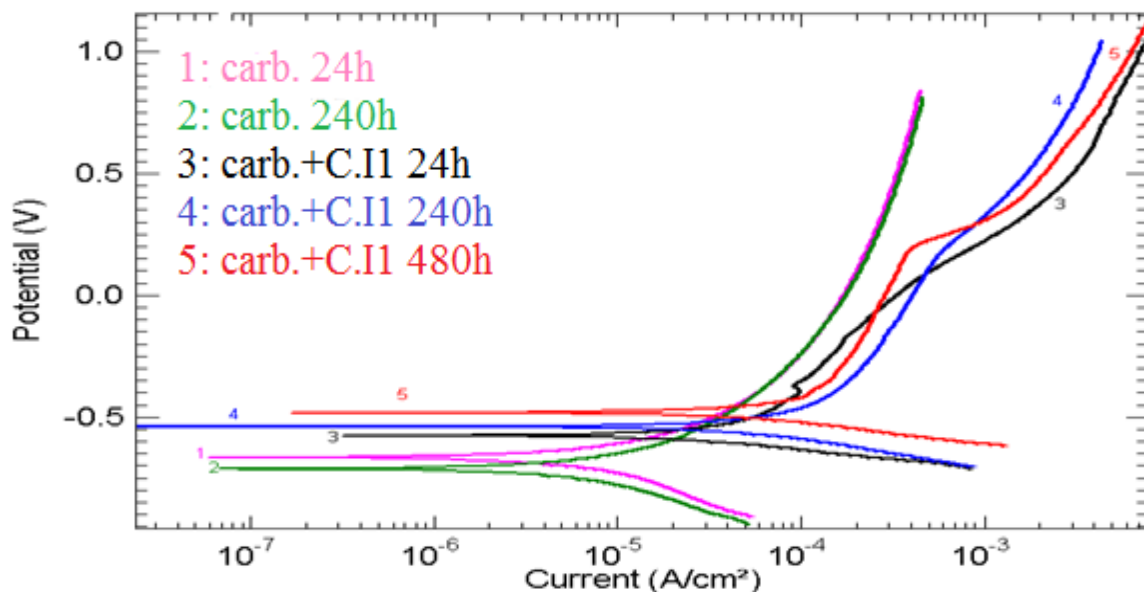


Fig.3.13. Polarization curves recorded in carbonated solution in the absence (1,2) and in presence of C.I.1 (3,4,5) for different immersion durations

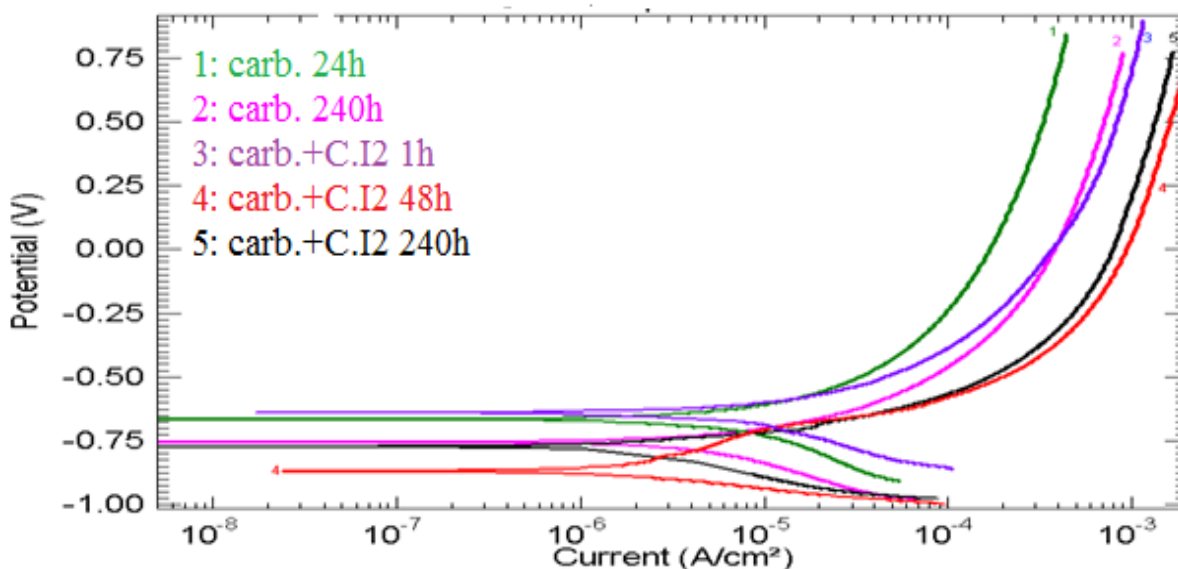


Fig.3.14. Polarization curves recorded in carbonated solution in the absence (1,2) and in presence of C.I.2 (3,4,5) for different immersion durations

(h) Polarization curves for solution containing inhibitor C.I3

Corrosion inhibitor C.I3 was found to be the least effective inhibitor as indicated by the polarization curves (Fig. 3.15). In the solution containing C.I3, with the increase in immersion duration, continuous increase in i_{corr} was observed. The highest corrosion current density of $35\mu\text{A}/\text{cm}^2$ was observed at the end of immersion duration of 240h. Higher current density with no passive behaviour confirmed the in-effectiveness of inhibitor C.I3 against carbonation induced corrosion.

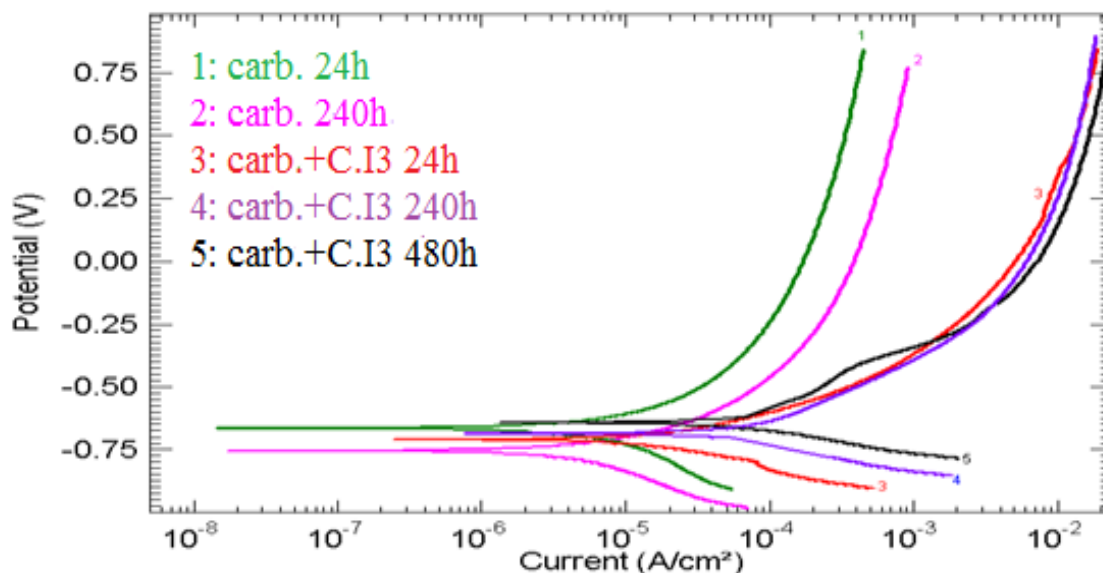


Fig.3.15. Polarization curves recorded in carbonated solution in the absence (1,2) and in presence of C.I3 (3,4,5) for different immersion durations

(i) Polarization curves for solution containing inhibitor C.I4

The polarization curves for inhibitor C.I4 at 1h, 48h, 240h and 480h of immersion are shown in Fig.3.16. In the presence of this inhibitor, although the corrosion potential shifted towards the active zone, however an active/passive transition phase could be seen in the anodic branch with passive behaviour up to $0.20V_{SCE}$ at 48h of immersion. After 48h of immersion, slow formation of protective passive film was observed, showing good inhibiting properties. At 240h of immersion, E_{corr} ennobled to $-0.58V_{SCE}$ with passive potential in the range of $-0.37V_{SCE}$ to $0.08V_{SCE}$ in the anodic branch of the polarization curve; while the cathodic branch of the polarization curve was quite similar to the polarization curve of the carbonated solution. By prolonging the immersion time to 480h, E_{corr} ennobled to $-0.37V_{SCE}$ with increased slope of

the anodic polarization curve. Progressive decrease in corrosion current density from $4.2 \mu\text{A}/\text{cm}^2$ to $3.5 \mu\text{A}/\text{cm}^2$ with increase in immersion duration from 24h to 240h further confirmed the effectiveness of this inhibitor.

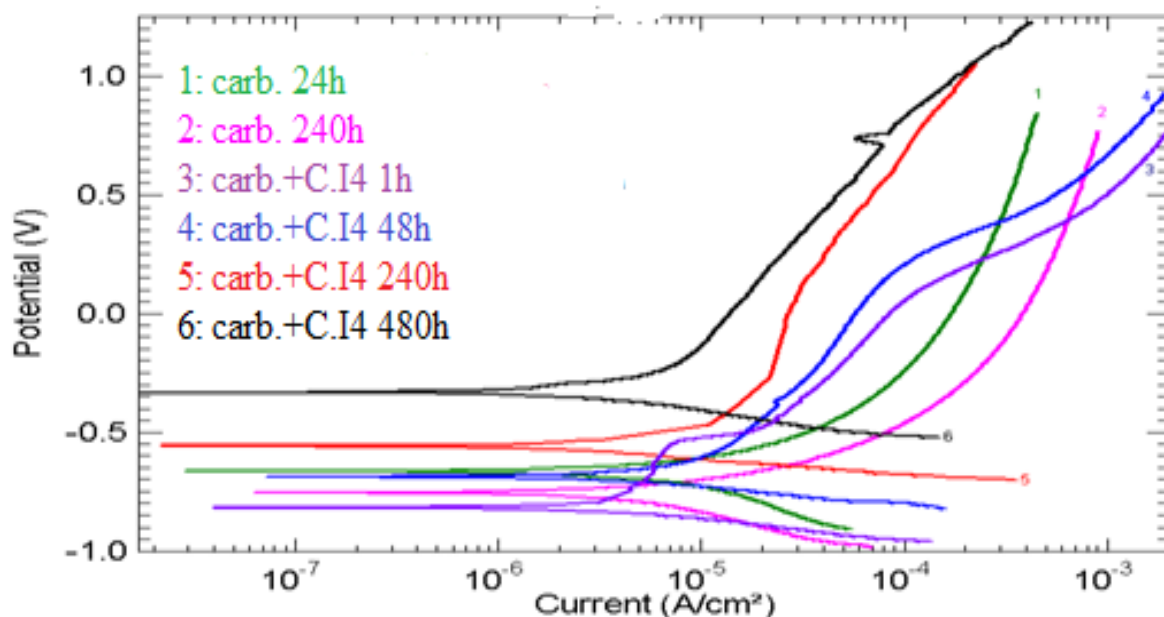


Fig.3.16. Polarization curves recorded in carbonated solution in the absence (1,2) and in presence of C.I4 (3,4,5,6) for different immersion durations

3.5.2 Comparison of polarization curves observed at 240h of immersion duration

In order to further evaluate the effectiveness of generic and commercially available inhibitors, comparison was made on the basis of polarization curves recorded at 240h of immersion and the same are presented in Figs. 3.17 and 3.18 respectively. Fig. 3.17 clearly indicates that inhibitor G.I3 was the most effective while inhibitor G.I1 was found to be the least effective amongst the generic type inhibitors. Thus on the basis of polarization curves, it can be concluded that the order of protectiveness of generic inhibitor is: $G.I3 > G.I2 > G.I4 > G.I1$. Similarly, on comparing the polarization curves of commercially available inhibitors, it can be concluded that C.I4 was the most effective inhibitor. Inhibitors C.I1 and C.I3 were ineffective in protecting bare steel specimens in carbonation induced corrosion conditions (Fig. 3.18). The order of effectiveness of commercially available inhibitors in carbonation induced corrosion is $C.I4 > C.I2 > C.I1 > C.I3$.

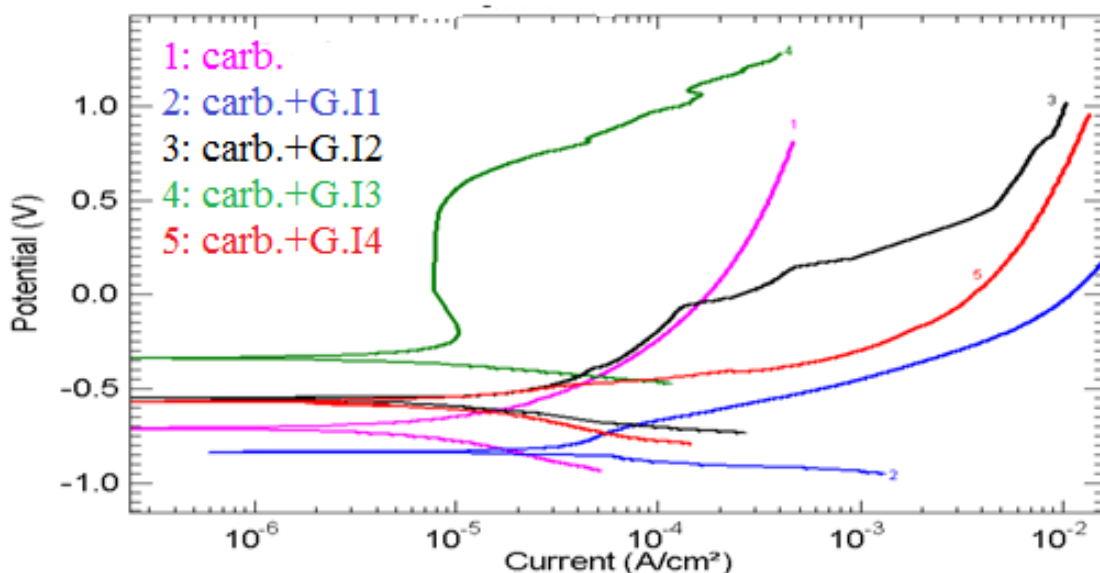


Fig.3.17. Polarization curves recorded in carbonated and generic inhibitors at 240h of immersion period

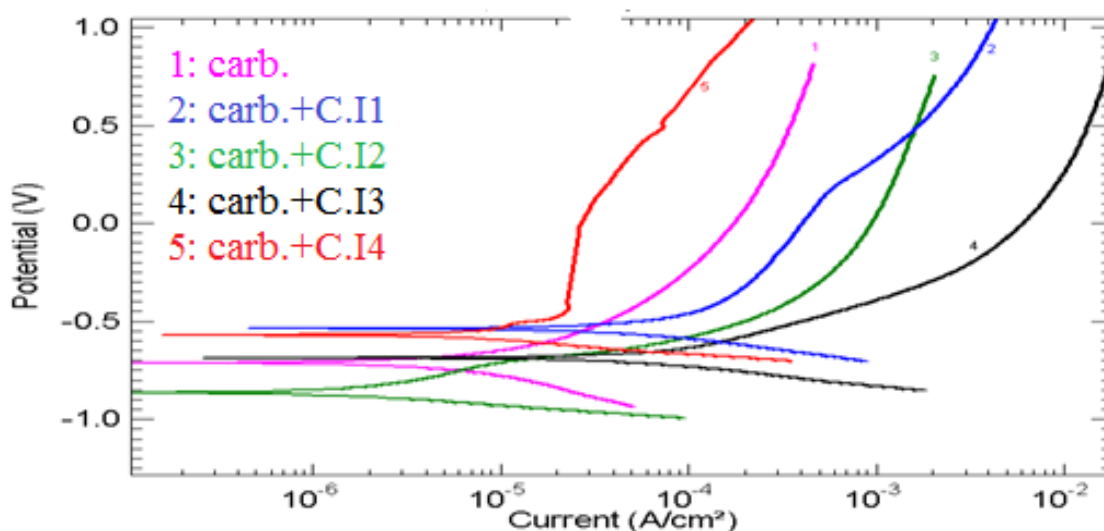


Fig.3.18. Polarization curves recorded in carbonated and commercially available inhibitors at 240h of immersion period

3.5.3 Corrosion current density (i_{corr}) and corrosion potential (E_{corr}) measurements

Corrosion current density (i_{corr}) and corrosion potential (E_{corr}) for each solution was obtained by performing Tafel extrapolation on the polarization curves as discussed in the proceeding sections. The Tafel slope for the anodic and cathodic reactions (as explained in

Chapter 2) were obtained by extrapolation of the linear regions of anodic and cathodic branches of the polarization curve. The point of intersection of the anodic and cathodic Tafel slope lines corresponds to the corrosion current density (i_{corr}) and the potential at which it lies is referred to as the corrosion potential (E_{corr}). The corrosion current densities obtained for generic inhibitors and for commercially available inhibitors at various immersion durations are presented in Figs. 3.19 and 3.20 respectively. The corresponding corrosion potentials for generic and commercially available inhibitors are presented in Fig.3.21 and 3.22 respectively.

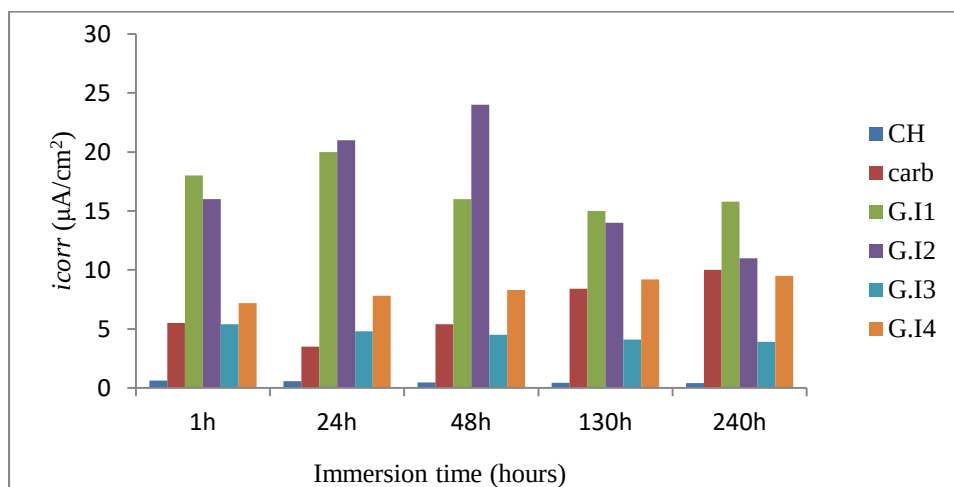


Fig.3.19. Corrosion current density of steel specimens immersed in different solutions containing generic inhibitors

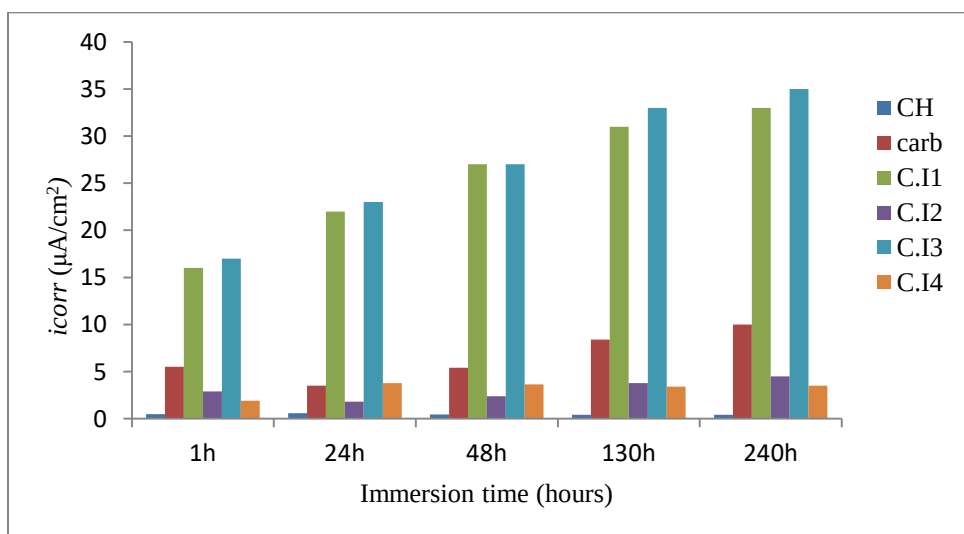


Fig.3.20. Corrosion current density of steel specimens immersed in different solutions containing commercially available inhibitors

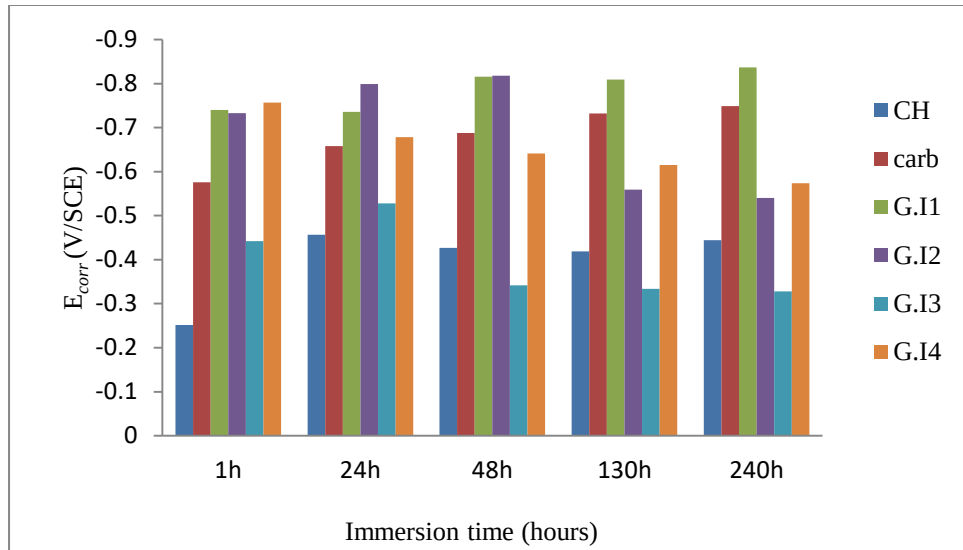


Fig.3.21. Corrosion potential of steel specimens immersed in different solutions containing generic inhibitors

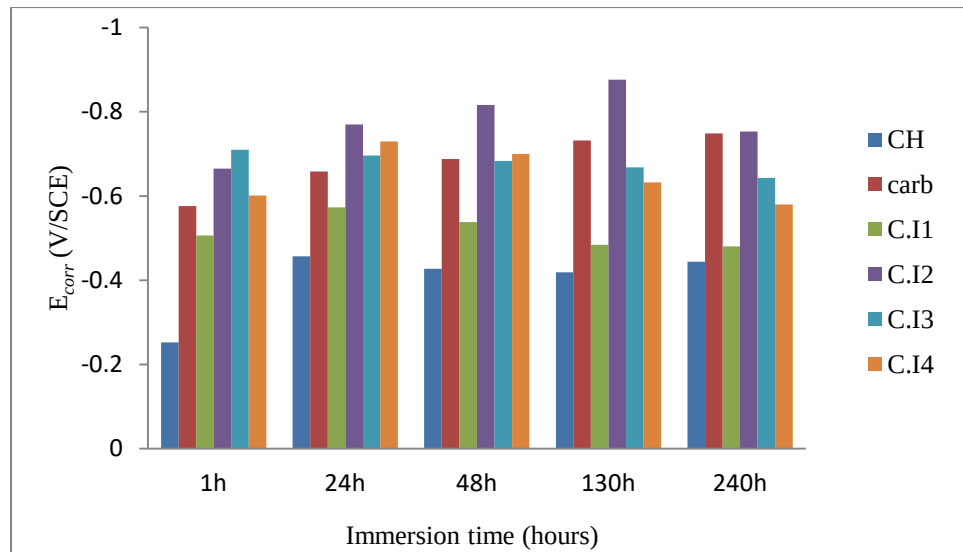


Fig.3.22. Corrosion potential of steel specimens immersed in different solutions containing commercially available inhibitors

It can be observed for Fig. 3.19 that the uncarbonated saturated calcium hydroxide (CH) solution exhibited the smallest corrosion current density ($< 1\mu\text{A}/\text{cm}^2$) as compared to the other solutions. Observed small value of corrosion current density indicates the presence of passive oxide layer on the steel surface in CH solution because of high pH value of the saturated calcium hydroxide solution. However, in carbonated solution, with reduced value of pH at approximately

8.1, continuous increase in i_{corr} was observed after 24h of immersion indicating the de-passivation of steel specimen.

On analyzing the pattern of corrosion current density with increase in immersion duration, for solutions containing generic inhibitors, it was observed that for solutions containing inhibitors G.I1, i_{corr} increased during the initial immersion duration of 24h, thereafter i_{corr} started decreasing and got stabilization. Towards the end of immersion duration of 240h, solutions containing inhibitors G.I2 and G.I4 presented the i_{corr} values similar to the values obtained in the carbonated solution while inhibitor G.I1 still exhibited higher i_{corr} value. The addition of inhibitor G.I3 into the carbonated solution gives lower value of i_{corr} at all immersion durations as compared to the carbonated and other tested inhibitors. Similarly, from Fig. 3.20 it was observed that inhibitors C.I2 and C.I4 presented lower values of i_{corr} at all immersion durations, while inhibitors C.I1 and C.I3 showed continuous increase in i_{corr} at all immersion duration indicating their ineffectiveness to reduce the corrosion rate of steel specimens in carbonated environment. On the basis of i_{corr} values, it can be concluded that the inhibitors G.I3, C.I2 and C.I4 are efficient in reducing the corrosion rate of steel specimens in pore solutions with reduced pH value.

The progressive change in the corrosion potential (E_{corr}) with the increase in immersion duration for generic inhibitors are presented in Fig. 3.21. From the figure, it was observed that the addition of inhibitor G.I1 into the carbonated solution shifted the E_{corr} towards active side at all immersion durations. Solution containing inhibitors G.I2 and G.I4 presented the higher or equivalent E_{corr} as compared to the carbonated solution during the immersion time of 48h, thereafter it demonstrated the lower value of E_{corr} . However, for solution containing inhibitor G.I3, the potential shifted towards nobler side at all immersion durations. Similarly, the trend of E_{corr} for commercially available inhibitors are shown in Fig. 3.22, which clearly show that inhibitor C.I1 gave the lower value of E_{corr} at all immersion durations as compared to all other tested commercially available inhibitors. Inhibitor C.I2 registered the highest value of E_{corr} amongst all the tested solutions. Inhibitor C.I3 and C.I4 exhibited similar behaviour in terms of E_{corr} , in which an initial small increase in potential up to 24 of immersion was observed followed by the shift in potential towards the nobler side.

3.6 INFERENCES DRAWN FROM SYNTHETIC SOLUTION TEST RESULTS

The tests conducted by using synthetic pore solution of calcium hydroxide as a representative concrete pore solution to check the corrosion behaviour of bare steel is established as an alternate test procedure to preliminary check the efficiency of the tested inhibitors in a short period of time. From the preliminary tests, it was established that all types of inhibitors are not effective in carbonated environment.

The inhibiting potential of any tested inhibitor was judged by changes in the value of i_{corr} and E_{corr} with the immersion duration. The efficient inhibitor was desired to shift the E_{corr} to nobler side along with a reduced value of i_{corr} with increase in immersion duration. Among the tested chemicals G.I2, G.I3, C.I2 and C.I4 were able to develop and maintain the inhibiting action throughout the exposure duration. With the inhibitor G.I2, observed distinct passive range indicated the growth of the protective passive layer around the steel specimens. On the other hand, the presence of inhibitor C.I2 reduced the i_{corr} by 46% as compared to carbonated solution although potential shifted towards the active side. The inhibitors C.I4 and G.I3 shifted the potential towards nobler side and also reduced i_{corr} . The maximum inhibiting efficiency achieved in the presence of inhibitor C.I4 and G.I3 was 71% and 61% respectively at 240h of immersion time. Based on the pore solution test results, the inhibitors C.I4 and G.I3 were further investigated for their effectiveness in carbonated reinforced concrete specimens.

CHAPTER 4

CARBONATION BEHAVIOUR OF CONCRETE

4.1 GENERAL

Carbonation is one of the major cause of deterioration of the reinforced concrete structures situated in places enrich in carbon dioxide (CO_2) concentration. In air, the concentration of CO_2 normally varies between 0.03% (rural air) to 1% (urban air). During the 20th century, industrial revolution led to disaster raise in the CO_2 levels in air. Increasing generation of CO_2 emission has further led to increase in the carbonation related distress of concrete structures (*Ulloa et al., 2013*). Many concrete structures suffer advanced degree of carbonation because of high level of CO_2 present in metropolitan cities (*Aperador et al., 2012; Singh and Singh, 2016*).

The microstructure of concrete consists of small interconnected capillary pores which progress towards the inner part of the concrete mass from the surface of concrete structures. During the carbonation process, CO_2 from the environment penetrates into concrete through these capillary pores and reacts with the calcium hydroxide ($\text{Ca}(\text{OH})_2$) to form calcium carbonate (CaCO_3) (*Singh and Singh, 2016*). As has already been established CO_2 itself is not reactive, but in the presence of water, CO_2 gets converted into dilute carbonic acid which reacts with the hydration products of cement (mainly $\text{Ca}(\text{OH})_2$) and reduces the alkalinity of concrete. The alkalinity i.e. pH of the pore solution drops from its normal values of pH 13-14 to values approaching neutrality with the progressive carbonation. Lowering of the pH of pore solution (from 13.5 to nearly 8) breaks down the protective passive layer that protects the rebar from corrosion (*Bertolini et al., 2004; Sisomphon and Franke, 2007; Dong et al., 2014; Aguiar and Junior, 2013*).

The penetration of the carbonation front deeper inside the concrete depends upon the concrete cover, porosity, cement type and moisture content of concrete. Various protective measures like increased concrete cover, use of lower w/c ratio, cement with high $\text{Ca}(\text{OH})_2$ content, applying epoxy resin coating on the surface of concrete etc. are generally adopted to

improve carbonation resistance of concrete (*Atis, 2003; Kulakowski et al., 2009; Aguiar and Junior, 2013; Rabehi et al., 2013*).

Among the various protection measures, use of corrosion-inhibiting admixtures in concrete matrix has gained popularity over the last two decades. An ideal corrosion inhibitor is a chemical which, when added to concrete, can prevent corrosion onset without having any adverse effect on the mechanical properties of concrete (*Jamil et al., 2003; Wombacher et al., 2004; DeSchutter and Luo, 2004*). Corrosion inhibitors function by providing a physical barrier to the ingress of aggressive agents into the concrete by blocking the pores and by developing a protective layer around the rebar surface (*Soylev et al., 2007a*). They are expected to reduce the depth of carbonation front; however, they might have some effect on the resultant compressive strength of the mix. In this chapter, the effect of the corrosion inhibitors finalised after preliminary investigation, on the properties of resultant concrete is discussed. Firstly, the experimental scheme to achieve this objective is described, followed by the details of materials and accelerated exposure condition. The effects of inhibitors on the resultant properties of concrete are studied in terms of change in carbonation depth with progressive CO₂ exposure and the resultant compressive strength of concrete after application of corrosion inhibitors. The results of both these parameters are also discussed in the succeeding sections.

4.2 TEST MATRIX

The test matrix for investigating the effect of inhibitor application on carbonation behavior of concrete is presented in Fig. 4.1. The illustration also provides description about the major test variables, viz: cement type and w/c ratio, as both of these parameters affect the properties of concrete. Type of cement influences the chemistry of concrete and hence influences the basic hydration products formed, while w/c ratio influences the pore structure of resultant concrete.

4.3 MATERIAL SYSTEM

The major materials used for the experimental programme include cement, aggregates, water and chemicals to be used as inhibitors. The details of each material are described in the following sections.

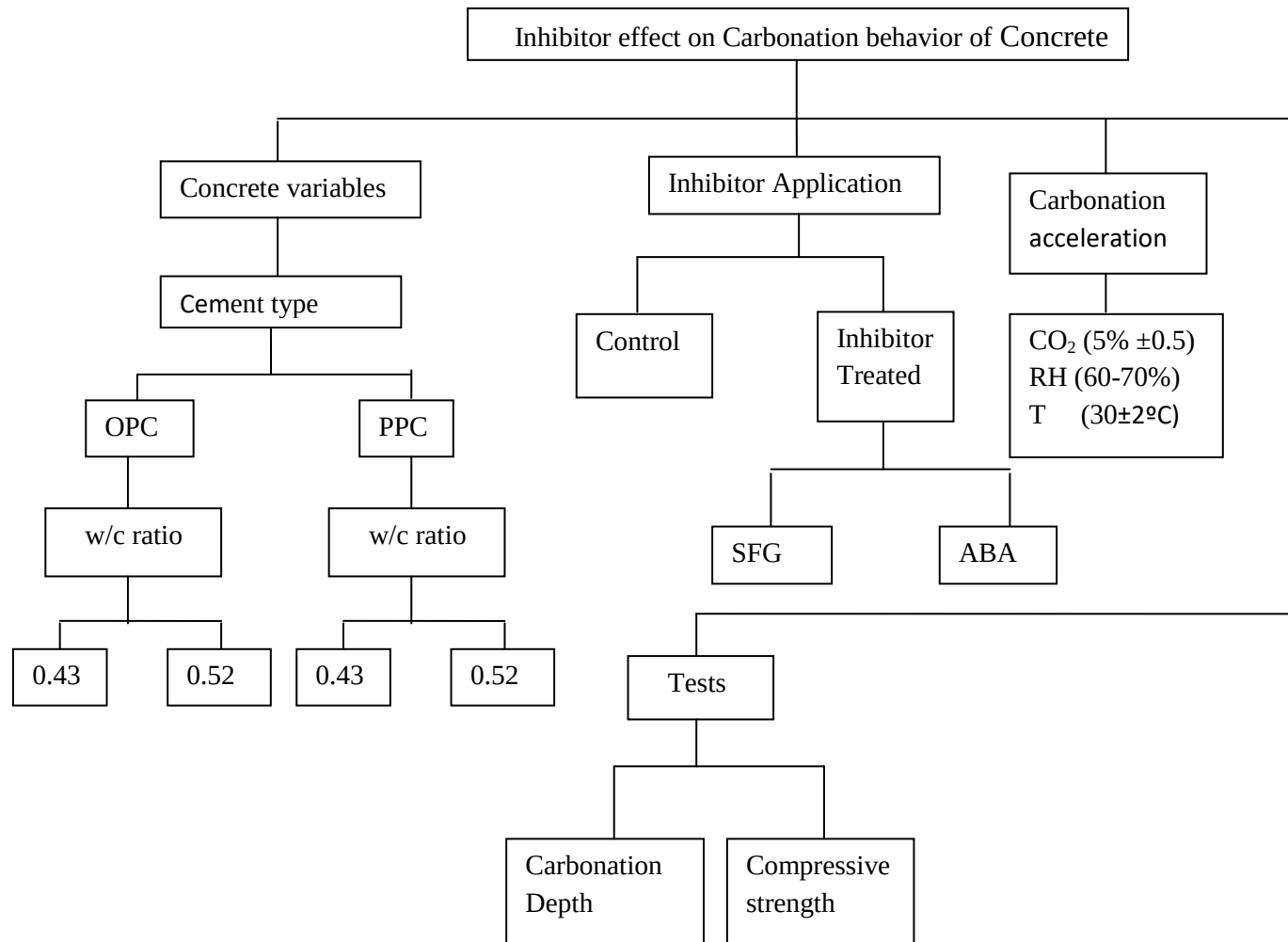


Fig.4.1. Schematic illustration for determination of corrosion inhibitor effect on carbonation behaviour of concrete

4.3.1 Cement

In Indian scenario, generally two types of cement i.e. Ordinary Portland Cement (OPC) and Portland Pozzolana Cement (PPC) are used in the construction industry. Therefore, the present study is carried out for both types of cements. Details of OPC and PPC used in the present investigation are as follows:

(a) Ordinary Portland cement: Portland cement is obtained by burning of naturally occurring argillaceous containing alumina with calcareous materials to a partial fusion at high temperature of around 1450°C (Gambhir, 2004). The burning product known as clinker, is a hydraulic material which consists of at least two-third of C_3S and C_2S by mass with the ratio of CaO to SiO_2 not exceeding 2.0 (Neville, 2012). OPC conforming to Indian standards BIS: 8112-1989 (BIS, 2005) was used in the present study. The chemical composition and physical properties of OPC used in the study are presented in Table 4.1.

Table 4.1 Chemical compositions and physical properties of cement used

Properties			OPC	PPC
Chemical Compounds (%)	Silicon dioxide, SiO_2		20.68	26.73
	Aluminum oxide, Al_2O_3		4.87	9.01
	Ferric oxide, Fe_2O_3		3.35	4.83
	Calcium oxide, CaO		62.13	49.72
	Magnesium Oxide, MgO		1.73	0.97
	Sulfur trioxide, SO_3		2.43	2.34
	Sodium Oxide, Na_2O		0.21	0.17
	Potassium oxide, K_2O		0.69	1.23
	Loss on ignition, LOI		2.04	1.73
Physical properties	Fineness (m^2/kg)		282	352
	Specific gravity		3.12	3.05
	Setting Time(minutes)	Initial	130	190
		Final	170	210

(b) Portland Pozzolana cement: Portland Pozzolana cement is produced by blending pozzolanic materials with Portland cement. Pozzolanic materials like fly ash exhibit cementitious properties when combined with calcium hydroxide. In the present study, PPC having 26-28% Pozzolana content by weight of clinker has been used. The cement used was conforming to the guidelines prescribed by Indian standard BIS: 1489 (Part -1)-1991 (BIS, 2005). The physical properties and chemical compositions of PPC are presented in Table 4.1.

4.3.2 Aggregates

Two types of aggregates i.e. coarse and fine aggregates were used in the present study. The basic properties of both the aggregates are presented in the following sections.

(a) Coarse aggregates: Two types of coarse aggregates in the form of crushed gravel with nominal maximum size of 20 mm and 10mm respectively were used in the present study. The specific gravity and water absorption of 10 mm aggregates were 2.65 and 1.40% and for 20 mm aggregates were 2.63 and 1.38% respectively. The sieve analysis results for 10 mm and 20 mm aggregates are presented in Table 4.2 and 4.3 respectively.

(b) Fine Aggregates: The fine aggregates used in the present study confirmed to Zone-II as per BIS: 383-1970 (BIS, 2002). The values of specific gravity, water absorption and fineness modulus were 2.70, 1.8% and 2.85 respectively. The sieve analysis results for fine aggregates are presented in Table 4.4. From sieve analysis results it can be seen that, since the percentage passing through 600 micron sieve is 44.2%, the fine aggregates falls under the Zone –II recommendations of BIS 383-1970 (BIS, 2002).

Table 4.2 Sieve analysis results for coarse aggregates (10mm)

S. No.	IS-Sieve size (mm)	%age wt. retained	Cum. % wt. retained	%age passing
1.	20	0.0	0.0	100.0
2.	12.5	7.9	7.9	92.1
3.	10	39.6	47.5	52.5
4.	4.75	50.3	97.8	2.2
5.	Pan	2.2	100.0	0.0

Table 4.3 Sieve analysis results for coarse aggregate (20 mm)

S. No.	IS-Sieve (mm)	%age wt. retained	Cum. % wt. retained	Passing (%)
1.	40	0.00	0.00	100.00
2.	20	0.37	0.37	99.63
3.	10	96.01	96.38	3.62
4.	4.75	3.37	99.75	0.25
5.	Pan	0.25	100.00	0.00

Table 4.4 Sieve analysis results for fine aggregate

S. No.	I.S. Sieve size	% wt. retained	Cum. % wt. retained	% Passing	IS limits for Zone II
1	10 mm	0.0	0.0	100.0	100
2	4.75 mm	2.9	2.9	97.1	90-100
3	2.36 mm	7.6	10.5	89.5	75-100
4	1.18 mm	27.0	37.5	62.7	55-90
5	600 micron	18.3	55.8	44.2	35-59
6	300 micron	27.7	83.5	16.5	8-30
7	150 micron	12.1	95.6	4.4	0-10
8	Pan	4.6	100.0	0.0	0

4.3.3 Water

In this present study, tap water was used for casting and curing of the specimens.

4.3.4. Corrosion inhibitors

The focus of the present study is to assess the effectiveness of migrating type corrosion inhibitors against carbonation contaminated environment. For selecting the best performing corrosion inhibitors, preliminary investigation was done on four generic inhibitors and four commercially available inhibitors in the pore solution, the details of which are presented in Chapter 3. As per the preliminary investigation, commercially available inhibitor C.I4 and generic inhibitor G.I3 performed better than the other tested inhibitors. Thus, these two best

performing inhibitors in pore solution tests were further taken for investigating their effectiveness in real concrete specimens. The detail of these two inhibitors is briefly discussed hereunder:

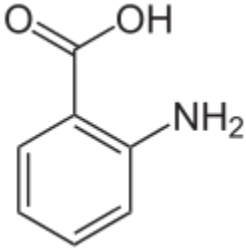
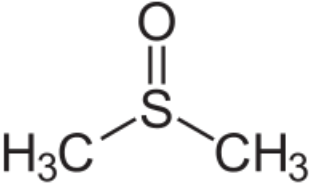
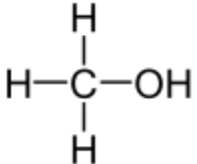
(a) Commercially available inhibitor C.I4 (abbreviated as SFG here): It is a surface applied mixed corrosion inhibitor based on organic compounds such as aqueous solutions of amino alcohols and salts of amino alcohols. As claimed by the manufacturer, this chemical has the ability to penetrate through concrete at a rate of a few millimeters/day to a depth of approximately 25 to 40 mm in one month depending upon the porosity of concrete. The pH value of the inhibitor is 10, density is 1.04 at 20°C and viscosity is 24 mPa.s. The recommended consumption of this inhibitor ranged from 0.300 kg/m² (290 ml/m²) to 0.500 kg/m² (480ml/m²) and the inhibitor was recommended to be applied in two to three coats.

(b) Generic inhibitor G.I3 (abbreviated as ABA here): It is an aromatic acid with the formula C₇H₇NO₂ and molecular structure as given in Table 4.5. As can be seen in the structure, this compound consists of a substituted benzene ring, hence is classed as aromatic with two adjacent functional groups of amine (NH₂⁺) and carboxylic acid (COOH⁻). The density and molar mass of the chemical is 1.4 g/cm³ and 137.14 g/mol respectively. Inhibitor 2-aminobenzoic acid was available in solid form and needs to be converted into aqueous solution form for effective application on concrete surface. In the present study, Dimethyl Sulfoxide (DMSO) and methanol were used as a solvent to convert 2-aminobenzoic acid into aqueous solution. The molecular structure of DMSO and methanol are shown in Table 4.5.

4.3.5 Phenolphthalein indicator

Phenolphthalein (C₂₀H₁₄O₄) is a chemical compound which is often used as an indicator in acid- base titrations. It remain colourless; in acidic conditions (pH < 7), while it turns to a pink colour in basic conditions (pH > 7). Phenolphthalein indicator can be obtained by mixing 1% ethanol solution with 1g phenolphthalein and 90 ml 95.0 V/V% ethanol diluted in water to 100ml (*Fukushima et al., 1998*). The phenolphthalein indicator is also available in market in solution form. In the present study, indicator available in solution form was used and was procured from the local market.

Table 4.5 Molecular structure of ABA, DMSO and methanol

Chemicals	Molecular Structure
2-Aminobenzoic acid	
Dimethyl Sulfoxide	
Methanol	

4.4 CONCRETE MIX PROPORTIONING

The concrete composition has a great influence on the diffusion of CO₂ into concrete matrix and thus on the carbonation rate. A decrease in w/c ratio, decreases the capillary porosity of the hydrated cement paste, and hence can slow down the penetration of carbonation front into concrete (*Bertolini et al., 2004*). Thus, two different concrete mixes viz. Mix 1 (with w/c 0.43) and Mix 2 (with w/c 0.52) were designed to achieve variable porosities. Further, each mix was prepared by using two types of cements namely; OPC and PPC. Both the mixes were designed as per BIS: 456-2000 (*BIS, 2000*) and mix proportions were finalized considering mild exposure conditions. In order to obtain similar workability, the concrete mixes were designed to have a slump lying in range of 60-80 mm. The original concrete mixes, for the two w/c ratios, were designed using Portland Pozzolana Cement as the constituent binder material. In order to understand the effect of change in cement type on carbonation phenomenon, the quantities of the constituent materials designed as a part of the concrete mix, were kept same even while considering mixes using OPC. Further, water content of all mixes was kept constant at 180kg/m³. At this water content, no admixture was required for the mix prepared at w/c ratio of 0.52 to

achieve a slump in the desired range. However, for the mix designed at w/c ratio of 0.43, a naphthalene based admixture at a dosage of 0.3% by weight of cement was needed to obtain the desired slump. The finalized mix proportions for each mix are presented in Table 4.6.

Table 4.6 Mix proportions for concrete specimens

Cement type	w/c ratio	Cement (kg/m ³)	Water (kg/m ³)	Fine aggregate (kg/m ³)	Coarse aggregate(kg/m ³)		Admixture (% weight of cement)
					20mm	10mm	
OPC	0.43	410	180	572.4	836.3	360.4	0.3
	0.52	340	180	621.0	848.7	365.7	-
PPC	0.43	410	180	572.4	836.3	360.4	0.3
	0.52	340	180	621.0	848.7	365.7	-

4.5 PREPARATION OF CONCRETE SPECIMENS AND INHIBITOR APPLICATION

In the present work, effect of inhibitor application was studied on the two properties of the resultant concrete viz. compressive strength and carbonation depth. The cube specimens of size 100 mm were cast for carbonation depth measurement, while cubes of size 150 mm were cast for compressive strength measurements. The concrete mixes were prepared by taking coarse aggregates, fine aggregates and cement in required proportions and mixed thoroughly for about 2 minutes to get a uniform mix in the dry state. After this, water and admixture (for mix prepared at w/c ratio of 0.43) were added to the dry mix and were mixed for another 3 minutes.

All the specimens were demoulded after 24h of casting and were water cured for 7 days at temperature of $27 \pm 2^\circ \text{C}$ and relative humidity of 100%. Subsequently, the cubes were kept in the laboratory environment for 7 days, with relative humidity between 60 – 80%. After 15 days of casting, the inhibitor to be investigated was applied by brush on all the faces of the cubes except in control specimens. As stated earlier in Section 4.3.4, inhibitor SFG was available in aqueous solution form, while inhibitor ABA was available in solid form. Therefore, ABA was converted into liquid form by adding solvents, namely DMSO and Methanol. The objective was to obtain a viscous solution of ABA that could be applied effectively on the concrete surface. A

number of trials were made on various dosages of DMSO and methanol and finally 50ml DMSO with 33ml methanol were mixed per 100 gm of ABA to get the required aqueous solution. The viscous solution of the inhibitors was applied at the rate of 500 gm/m² on all six faces of the cube. This dosage was recommended by the manufacturer for SFG. In order to maintain uniformity in dosage, the same dosage was used for ABA. Therefore, on an average, 30 ml of solution was required for every 100 mm cubes; while 67 ml of inhibitor solution was used for application on every 150 mm cube. The mentioned quantities of inhibitors were applied in three layers, allowing the surface to dry out between the consecutive coats.

With two types of cements and two w/c ratios, a total of 72 cubes of 100 mm size were prepared for carbonation depth measurement. Out of 72 cubes, 24 cubes were kept as control specimens, while the other cubes were treated with specific inhibitors. For compressive strength measurement, a total of 108 cubes of size 150 mm were prepared with the same variables as those for carbonation depth measurement with three replicates. Out of 108 cubes, inhibitors were applied on 72 cubes and 36 cubes were kept as control specimens. The test matrix along with the nomenclature used for each mix is summarized in Table 4.7.

Table 4.7 Nomenclature used for concrete specimens

Cement type	Mix/ (w/c)	Inhibitor treatment	Nomenclature
OPC	Mix 1 w/c 0.43	-	Mix 1 - O/C
		SFG	Mix 1 - O/SFG
		ABA	Mix 1 - O/ABA
	Mix 2 w/c 0.52	-	Mix 2 - O/C
		SFG	Mix 2 - O/SFG
		ABA	Mix 2 - O/ABA
PPC	Mix 1 w/c 0.43	-	Mix 1 - P/C
		SFG	Mix 1 - P/SFG
		ABA	Mix 1 - P/ABA
	Mix 2 w/c 0.52	-	Mix 2 - P/C
		SFG	Mix 2 - P/SFG
		ABA	Mix 2 - P/ABA

4.6 EXPOSURE CONDITIONS FOR ACCELERATED CARBONATION

After the application of respective inhibitors, the 100 mm cubes were kept in the carbonation chamber which is capable of maintaining temperature, relative humidity and CO₂ concentration in the range of 20-50°C, 30-70% and 0-10% by volume respectively. Carbon dioxide was supplied to the chamber by connecting CO₂ gas cylinder externally through the gas supply pipes. The gas pressure was monitored with the help of a pressure gauge mounted on the top of the gas cylinder. An industrial grade gas cylinder with CO₂ gas of 99% purity was used in the present study. The CO₂ cylinder and the carbonation chamber are shown in Fig. 4.2.

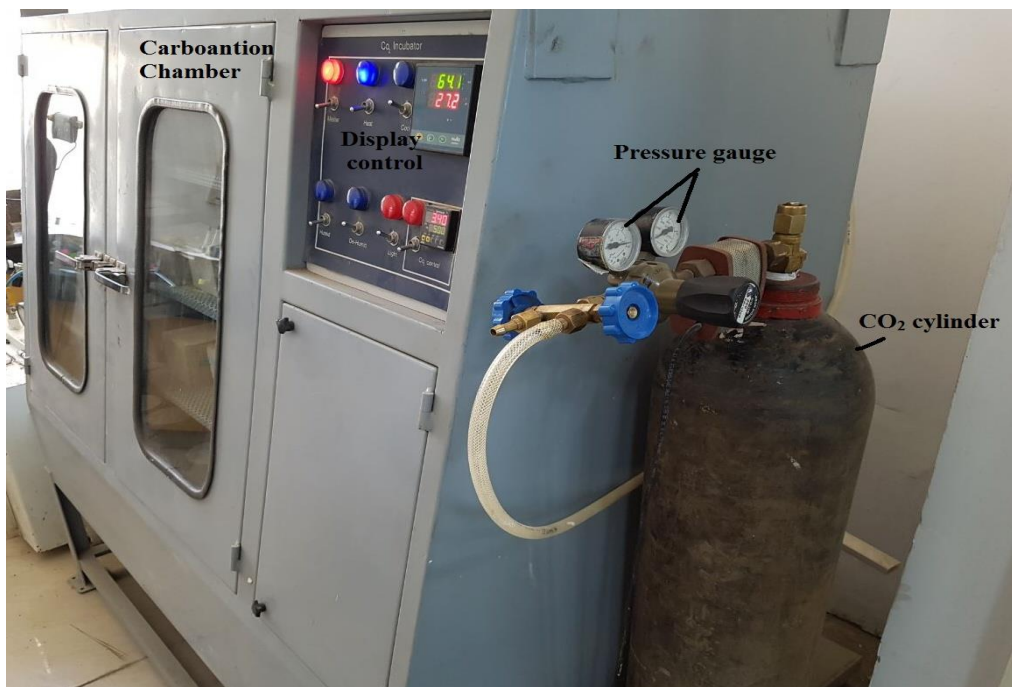


Fig.4.2. Experimental setup for carbonation acceleration

The CO₂ exposure conditions for specimens were decided based on a thorough literature review, which is also discussed in Chapter 2. Most of the researchers accelerated carbonation by maintaining CO₂ concentration between 3 -5%, while keeping temperature of chamber between 25 -30°C and relative humidity between 60-70%. *Dong et al. (2014)* achieved the accelerated carbonation in carbonation chamber maintained at 29-31°C temperature and 65-70% relative humidity. *Montemor et al. (2002)* achieved the carbonation acceleration by 5% CO₂ concentration, 60-70% relative humidity and with room temperature. *Ulloa et al. (2013)*

accelerated the specimens by using carbonation chamber maintained at 25-27°C temperature, 65-70% relative humidity and 3% CO₂ concentration. Therefore, in the present study, carbonation acceleration was done in carbonation chamber maintained at 30± 2°C temperature, 60-70% relative humidity and 5± 0.5 % CO₂ concentration.

Further, many researchers have also suggested the requirement of preconditioning of specimens in order to achieve an even distribution of moisture within the specimens. In the present study also, before subjecting the carbonation depth specimens to accelerated carbonation, they were preconditioned at a temperature of 30± 2° C and a relative humidity of 60-70% for 15 days inside the chamber. The preconditioning was done to facilitate better ingress of carbonation front. After the end of preconditioning, the specimens were subjected to accelerated carbonation by maintaining CO₂ concentration of 5± 0.5 % by volume for a period of 90 days at 30 ± 2° C temperature and 60-70% relative humidity. The inside view of carbonation chamber with placement of cubes specimens are shown in Fig. 4.3. The cubes are placed in chamber by maintaining an approximate gap of 10 mm between the cubes such that each cube is subjected to uniform supply of CO₂.



Fig.4.3. Carbonation chamber with cubes to be tested for carbonation depth

4.7 TESTING OF SPECIMENS

The procedure adopted for carbonation depth and compressive strength measurements are described in the succeeding sections.

4.7.1 Carbonation depth measurement

The carbonation depth was measured after every 15 days of exposure, till the exposure duration of 90 days. At every testing age, the cube specimens were taken out of carbonation chamber and split diagonally into two halves. Immediately after splitting, the exposed surface was cleaned and sprayed with Phenolphthalein indicator. The indicator used was a phenolphthalein 1% ethanol solution with 1g phenolphthalein and 90 ml 95.0 V/V% ethanol diluted in water to 100 ml (*Fukushima et al., 1998*). Phenolphthalein indicator gives purple-red colour for un-carbonated part; while in carbonated part, no coloration occurred (*Talakoula et al., 2016; Hussain and Ishida, 2009*). The average depth of colourless region was measured from twenty four points (twelve readings on each split surface) using a vernier caliper with least count on 0.02 mm. Split specimen after the application of phenolphthalein indicator and the measurement locations are marked on one face as shown in Fig. 4.4.

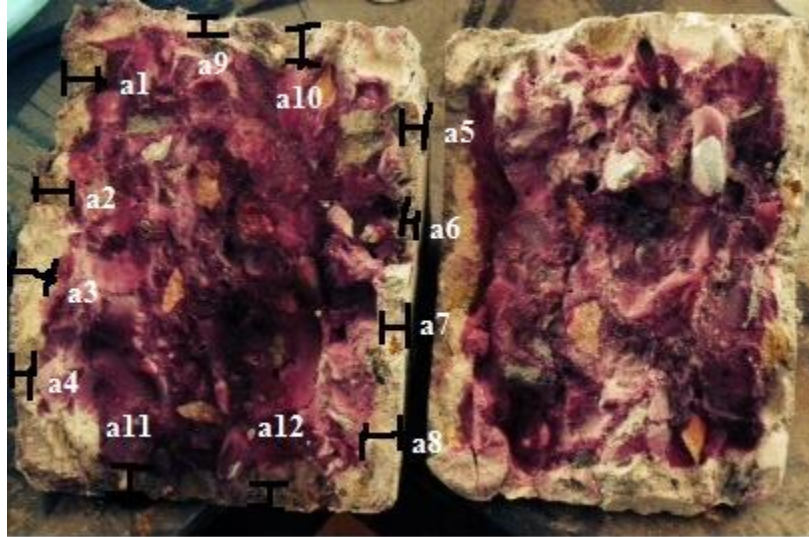


Fig.4.4. Cross section of split cube specimen after application of phenolphthalein indicator

4.7.2 Compressive strength measurement

As has already been stated in Chapter 2 under Section 2.8, when the inhibitors are admixed into concrete at the time of casting, they alter the hydration process of cement. *Ann et*

al. (2006) reported that calcium nitrite based admixed inhibitors increased the early age compressive strength of the concrete with a marginal decrease in the long term strength. Many researchers have reported that variable dosages of inhibitor addition, type of inhibitors and application mode of inhibitor greatly influence the strength properties of concrete (*Wombacher et al., 2004; DeSchutter and Luo, 2004; Saraswathy and Song, 2007; Soylev et al., 2007; Dharmaraj and Malathy, 2016*). Therefore, compressive strength test was done to investigate any undesirable effect of inhibitors on strength of resultant concrete. For this, cube specimens of size 150 mm were cast and water cured for 7 days followed by 7 days of air curing. Then the inhibitor was applied with brush as described earlier in Section 4.5. The specimens were kept in the laboratory environment after application of corrosion inhibitors on the concrete surface. The compressive strength of the specimens was measured at 28 days, 56 days and 90 days of casting. At each testing age, three specimens were tested in accordance with BIS: 516– 1959 (*BIS, 2004*), on compression testing machine of capacity 5000 kN by applying load at a rate of 5 kN/s. The average of the three specimens was taken as the reference compressive strength of the set.

4.8 RESULTS AND DISCUSSION

The effect of inhibitor application on carbonation depth and compressive strength of the concrete mixes is discussed in the following sections:

4.8.1 Carbonation depth results

In the present study, carbonation depth was measured by using the Phenolphthalein indicator which is the simplest method and can be readily used for in-situ testing also. The major influencing parameters includes w/c ratio of the mix, cement type, CO₂ exposure duration and type of inhibitor applied. The effects of all these parameters are discussed in the following sub-sections:

(a) Effect of water-cement ratio

The variation in carbonation depth for concrete mixes designed for two water-cement (w/c) ratios and made by using OPC and PPC is shown in Fig. 4.5 and 4.6 respectively. From both the figures, it was observed that irrespective of cement type, carbonation depth is directly proportional to w/c ratio of the mix. Concrete specimens made by using higher w/c ratio (0.52) have higher carbonation depths as compared to concrete mixes designed for lower w/c ratio

(0.43). In Mix 2-O/C, 59.8% increase in carbonation depth was observed in comparison with Mix 1- O/C.

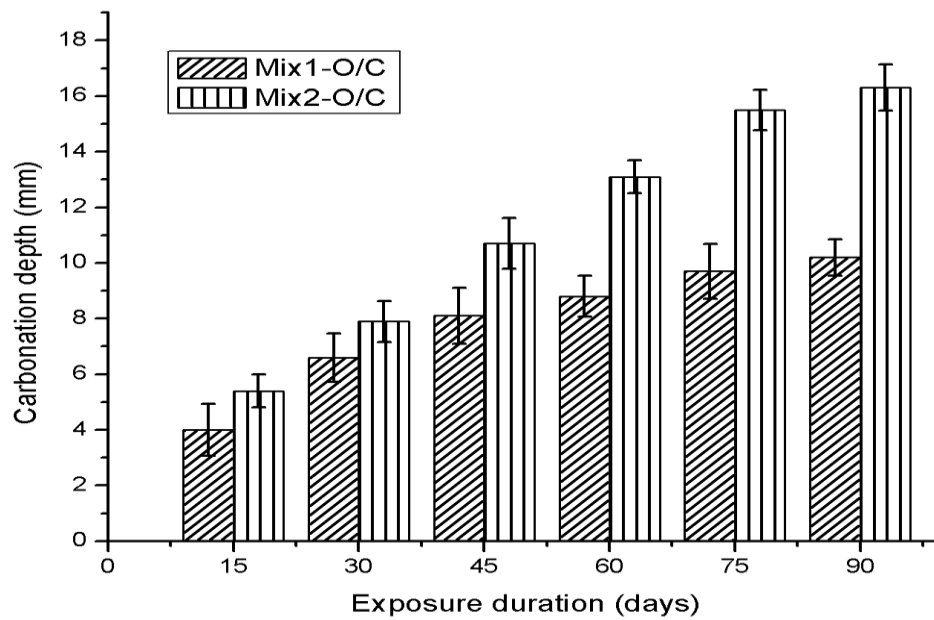


Fig.4.5. Effect of w/c ratio on carbonation depth in OPC concrete specimens

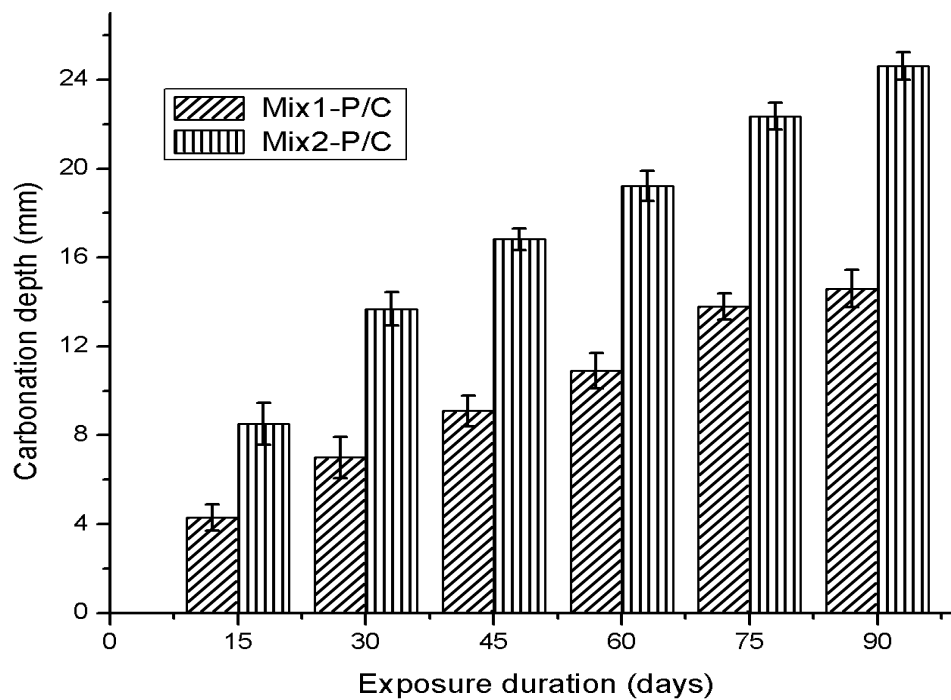


Fig.4.6. Effect of w/c ratio on carbonation depth in PPC concrete specimens

Similarly, Mix 2-P/C concrete demonstrated 68.4% higher carbonation depth as compared to Mix 1-P/C. In other words, with the increase in w/c ratio, the kinetic of carbonation is increased. *Singh and Singh (2016)* also reported increase in carbonation depth with the increase in w/c ratio from 0.48 to 0.65 in normally vibrated concrete. This increase of carbonation is attributed to an increase in the porosity of mix with increase in w/c ratio. This is directly credited to the free water available in the mixes at higher w/c ratios. This free water after evaporation, promotes the formation of more voids. More numbers of voids on one side promote the movement of further free water deeper into the concrete and on another side, leads to penetration and diffusion of CO₂ deeper into the concrete (*Rabehi et al., 2013*).

(b) Effect of cement type

In order to study the effect of cement type, variation in carbonation depth with exposure duration for both cement types i.e. OPC and PPC at w/c ratio of 0.43 was compared and is shown in Fig. 4.7. It can be observed from the figure that during the initial exposure duration of 30 days, PPC concrete shows 6% higher carbonation depth as compared to OPC concrete mixture. However, at the end of exposure duration of 90 days, PPC concrete shows 43.13% higher carbonation depth as compared to OPC concrete.

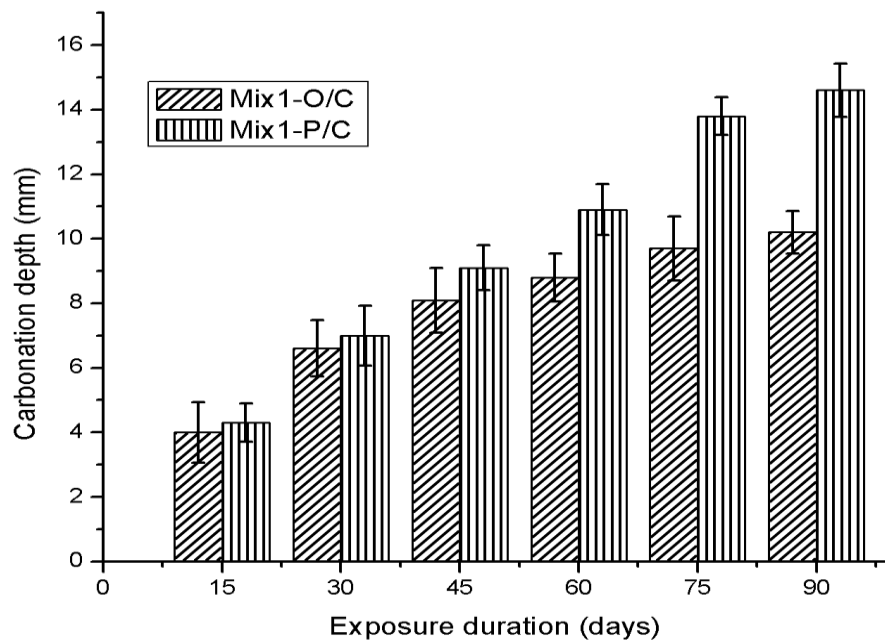


Fig.4.7. Effect of cement type on carbonation depth

Measured higher value of the carbonation depth in PPC concrete can be attributed to the pozzolanic reaction of the fly ash present in PPC. PPC concrete had approximately 25% lower content of CaO and consequently less Ca(OH)_2 was formed. Secondly, some part of the Ca(OH)_2 formed was further consumed by the pozzolanic reaction of Ca(OH)_2 with fly ash. These factors lead to lower percentage of Ca(OH)_2 in the PPC concrete mix. Hence, during the carbonation reaction, lesser amount of CaCO_3 will be formed (Montemor *et al.*, 2002; Rea *et al.*, 2012). CaCO_3 so formed gets precipitated as solid matrix in the pores of concrete, owing to its low solubility and leads to densification of the concrete matrix (Fukushima *et al.*, 1998; Dong *et al.*, 2016). Initially, the carbonation depth of both concretes is similar. However, less CaCO_3 gets precipitated in the pores of PPC concrete with time as compared to OPC concrete, leading to lesser densification of PPC concrete. Therefore, carbonation front can ingress into the PPC concrete more rapidly at later ages and hence, the carbonation depth of PPC concrete was found to be more than OPC concrete.

This trend of lesser resistance of PPC concrete to carbonation than OPC concrete is contrary to the performance of PPC concrete in chloride environment. It has been established that concrete containing fly ash content was more durable and resistant towards the penetration of chloride ions (Thomas and Matthews, 1992). The observed reverse trend shows that the mechanism of carbonation process is different from the chloride mechanism. Thomas and Matthews (1992) suggested that chloride ions initially penetrate into the dry concrete by sorption followed by ionic diffusion with chemical interaction in the saturated concrete at later ages. However, carbonation process involves the conversion of Ca(OH)_2 into CaCO_3 by the action of carbonic acid (H_2CO_3) formed by diffusion of CO_2 into pores water of concrete. This CaCO_3 gets deposited in the concrete pores, thus lowering the rate of ingress of carbonation front with time. The concrete that has higher tendency of CaCO_3 formation will have lesser depth of carbonation front, as is observed in OPC concrete as compared to PPC concrete.

(c) Effect of exposure duration

As generally known, progress in carbonation front is directly related to the increase in exposure duration. From Fig.4.8, it can be observed that carbonation depth increases with

increase in exposure duration for all concrete specimens. Concrete specimens designated at w/c ratio of 0.52 and made with PPC cement gave the highest carbonation depth while, OPC cement concrete designated at w/c ratio of 0.43 shows lowest value of carbonation depth at 90 days of exposure duration.

From Fig. 4.8 it was also observed that, during the initial exposure duration, rate of carbonation ingress is high but it reduced with the enhancement in the exposure duration. *Sisomphone and Franke (2007)* also reported that the rate of carbonation progress reduces with respect to time period and is usually considered as proportional to the square root of the exposure duration. The relationship between carbonation depth with exposure time can be expressed as:

$$X_c = k\sqrt{t} \quad \text{..... (eq.4.1)}$$

where, X_c is the measured carbonation depth (mm), t is the exposure time (days) and k is the carbonation coefficient estimated by the regression analysis.

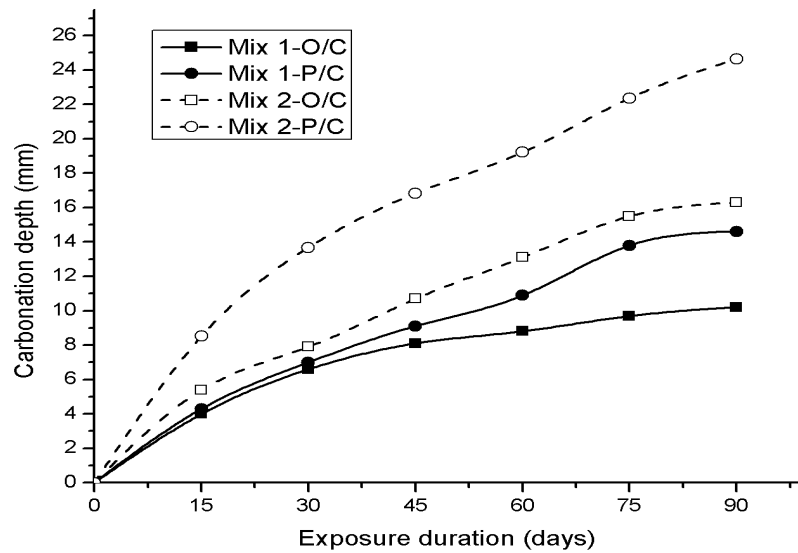


Fig.4.8. Carbonation depth variation with exposure duration

Further, to confirm the established relationship for both types of cement, a graph between the carbonation depth and square root of exposure duration was plotted and is presented in Fig. 4.9. It can be clearly observed that carbonation depth variation against $t^{1/2}$ is linear with high

correlation coefficient for all concrete mixes. The slope of these curves was used to get the carbonation coefficient “k” and statistical analysis results of these curves are shown in Table 4.8.

Table 4.8 Parameters of the fitted curves

Specimens Description	Carbonation coefficient “k”		R ² value
	Value	Standard Error	
Mix 1-O/C	1.12	0.021	0.989
Mix 1-P/C	1.45	0.053	0.967
Mix 2-O/C	1.67	0.047	0.979
Mix 2-P/C	2.53	0.035	0.994

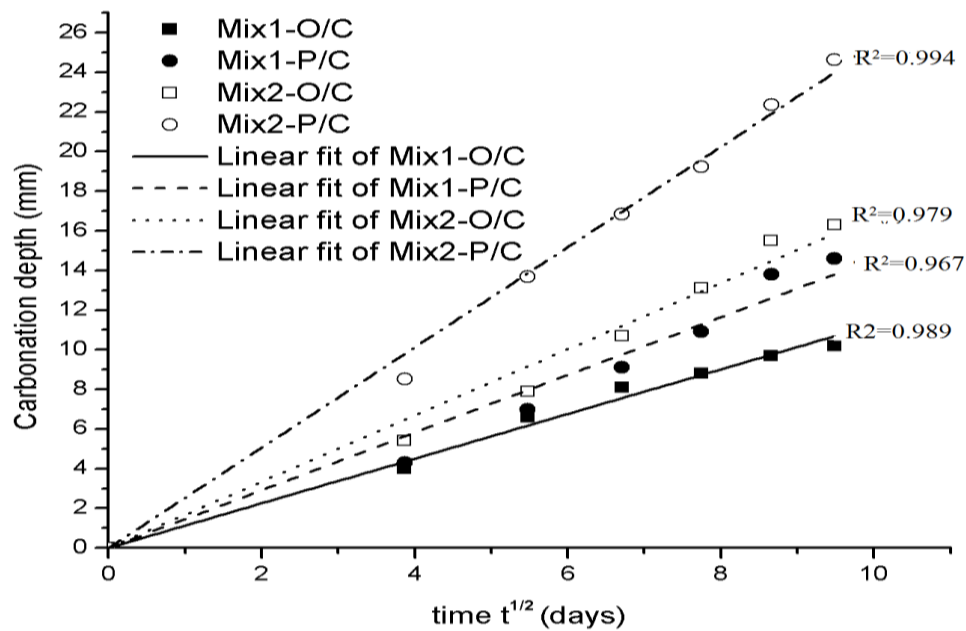


Fig.4.9. Carbonation depth variation with square root of exposure duration

From Table 4.8, it can be observed that cement type as well as w/c ratio have a great impact on the carbonation rate coefficient. Carbonation rate coefficient increased with the increase in w/c ratio irrespective of the cement type. Concrete specimens made with OPC cement at w/c ratio of 0.52 show 49% higher carbonation rate coefficient “k” as compared to the mix

prepared at w/c ratio of 0.43. Similarly for PPC cement, a 74% increase in “k” value was observed at w/c ratio of 0.52 as compared to mix prepared at w/c of 0.43.

(d) Effect of inhibitor application

In order to study the effect of type of inhibitor application on carbonation depth, the variations in carbonation depth with exposure duration for inhibitor applied mixes is compared with the corresponding control mixes and is presented in Figs. 4.10 - 4.13. The corresponding statistics parameters of all the mixes are reported in Table 4.9.

From Figs. 4.10 - 4.13, it was observed that with the application of inhibitors, slope of the curves i.e. carbonation coefficient decreased for all the concrete specimens irrespective of type of cement and variation in w/c ratio. The observed decrease in carbonation coefficient “k” with the application of inhibitors can be due to various effects of applied inhibitors on the properties of concrete, which led to concrete pore refinement and hence decreased the ingress of carbonation front.

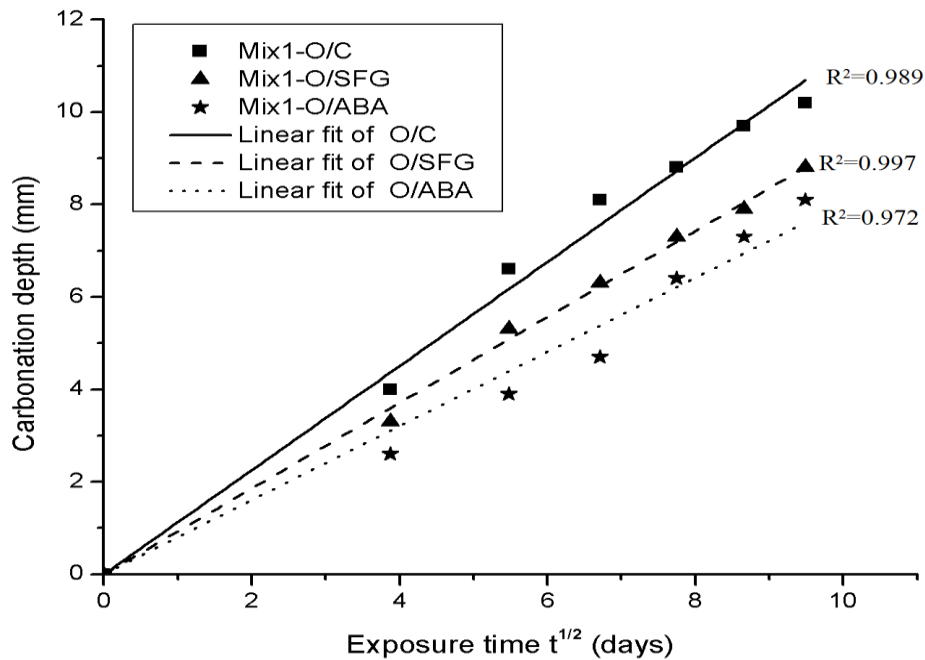


Fig.4.10. Carbonation depth variation with inhibitor application in OPC concrete specimens prepared at w/c ratio of 0.43

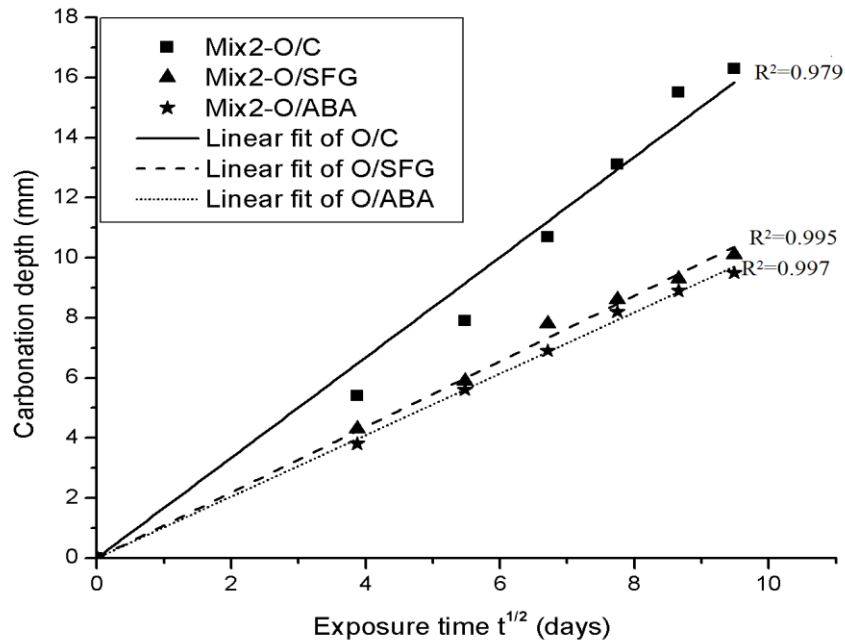


Fig.4.11. Carbonation depth variation with inhibitor application in OPC concrete specimens prepared at w/c ratio of 0.52

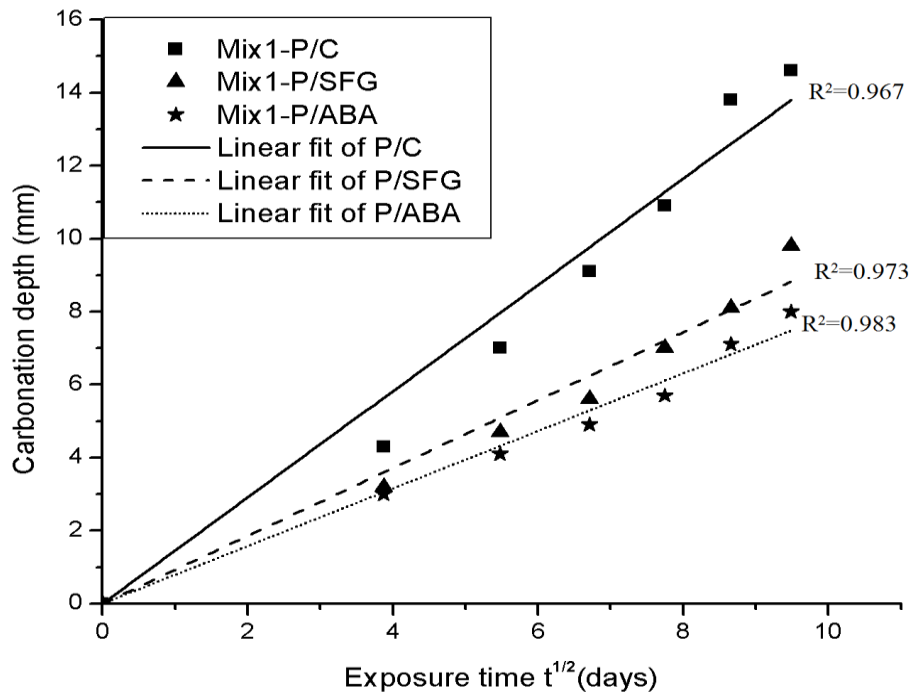


Fig.4.12. Carbonation depth variation with inhibitor application in PPC concrete specimens prepared at w/c ratio of 0.43

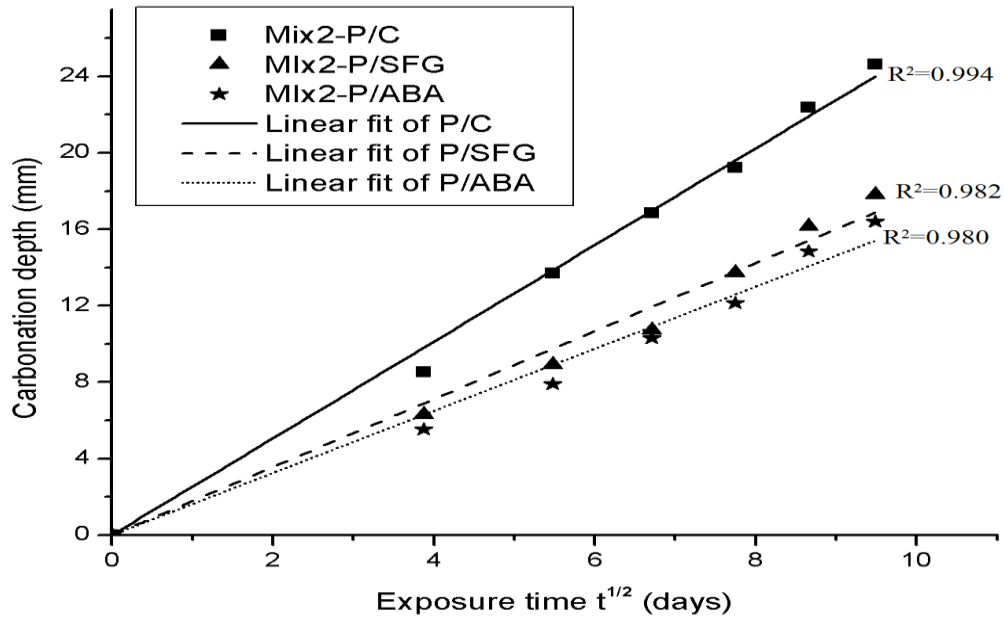


Fig.4.13 Carbonation depth variation with inhibitor application in PPC concrete specimens prepared at w/c ratio of 0.52

Table 4.9 Parameters of the fitted curves with inhibitor application

Series Description	Specimen Description	Carbonation coefficient “k”		Reduction in “k” (%)	R ²
		value	Standard error		
Mix 1-OPC	Mix1-O/C	1.126	0.0213	-	0.989
	Mix1-O/SFG	0.928	0.0094	17.58	0.997
	Mix1-O/ABA	0.802	0.0268	28.77	0.972
Mix 2-OPC	Mix 2-O/C	1.670	0.0474	-	0.979
	Mix 2-O/SFG	1.092	0.0135	34.61	0.995
	Mix 2-O/ABA	1.023	0.0088	38.74	0.997
Mix 1-PPC	Mix1-P/C	1.455	0.0533	-	0.967
	Mix1-P/SFG	0.930	0.0302	36.08	0.973
	Mix1-P/ABA	0.788	0.0194	45.84	0.983
Mix 2-PPC	Mix 2-P/C	2.529	0.0358	-	0.994
	Mix 2-P/SFG	1.779	0.0454	29.65	0.982
	Mix 2-P/ABA	1.625	0.0443	35.74	0.980

Table 4.9 highlights that the reduction in 'k' with inhibitor application lies in the range of 17.58% - 45.84% with respect to the corresponding control specimens. In OPC concrete specimens, the application of inhibitor SFG decreased the carbonation coefficient by 17.58% and 34.61% in Mix 1 and Mix 2 respectively. Similarly, the carbonation coefficient decreased by 28.77% and 38.71% in Mix 1 and Mix 2 respectively with the application of 2-Aminobenzoic acid (ABA). Similar trend was observed in mixes made with PPC, in which carbonation coefficient decreased by 36.08% in Mix 1-P/SFG and 45.84% in Mix 1-P/ABA as compared to Mix 1-P/C. For Mix 2, the carbonation coefficient decreased by 29.65% with the use of SFG, whereas with the use of ABA it decreased by 35.74% as compared to Mix 2-P/C. It indicates that the inhibitors act as pore blockers, when applied on the concrete surface and resist the carbonation front to ingress into concrete. Similar observations were made by *Tritthart (2003)* when amino alcohol based inhibitor was used, wherein it was reported that the inhibitor acts by penetrating into the concrete surface and further reacts with the hydration products which result in gel formation, thereby blocking the pores. Thus reduction in interconnected capillary due to formation of gel results in lowering of "k" leading to lowering of the carbonation depth. The reduction in carbonation coefficient achieved by using corrosion inhibitors further demonstrates the efficiency of all tested corrosion inhibitors in resisting carbonation of concrete.

From the above carbonation depth results, it was also observed that among all the prepared control mixes, Mix 1 made by using OPC at w/c ratio of 0.43 is the most resistant towards ingress of carbonation front into the concrete. The application of corrosion inhibitors to this mix further reduced the carbonation coefficient by blocking the interconnected capillary pores. In order to further investigate the migrating efficiency of the inhibitors, one set of 100 mm cube specimens prepared by using Mix 1-O/C, along with the corresponding inhibitor applied specimens were tested for XRD analysis at the end of exposure duration of 90 days. For this, powdered specimens from a depth of 5 - 10 mm from the top surface were collected and XRD analysis was performed on these specimens. The XRD investigations were performed for diffraction angle 2θ ranging between 10° and 60° in steps of $2\theta = 0.017^\circ$. Target of XRD measurements was to observe any additional peak other than those observed in control specimens that can indicate the presence of corrosion inhibitor at the depth of 5 -10 mm from the surface of concrete.

Fig. 4.14 depicts the XRD patterns for concrete powder obtained from Mix 1-O/C, Mix 1-O/SFG, Mix 1-O/ABA concrete after 90 days of exposure. Obtained XRD pattern shows presence of two additional peaks of $C_4H_4O_4$ (9%) in Mix 1-O/SFG and $C_4H_9NO_2$ (7%) in Mix 1-O/ABA; while no such peak was observed in corresponding control specimen (Mix 1-O/C). The presence of these additional peaks indicates that the inhibitor had reached the depth of 5-10 mm from the surface of concrete and has the tendency to fill surface pores and percolate further. Further, in lower two diffractograms, more number of CH peaks was observed that indicates that both inhibitors hinder the calcium carbonate formation. It is to mention here that the aim of the present research is not to investigate the transport and protection mechanism of the inhibitors. XRD analysis was mainly done to check the penetration ability of the inhibitor into the concrete because the inhibitors used in the present research are migrating type inhibitor rather than admixed inhibitors.

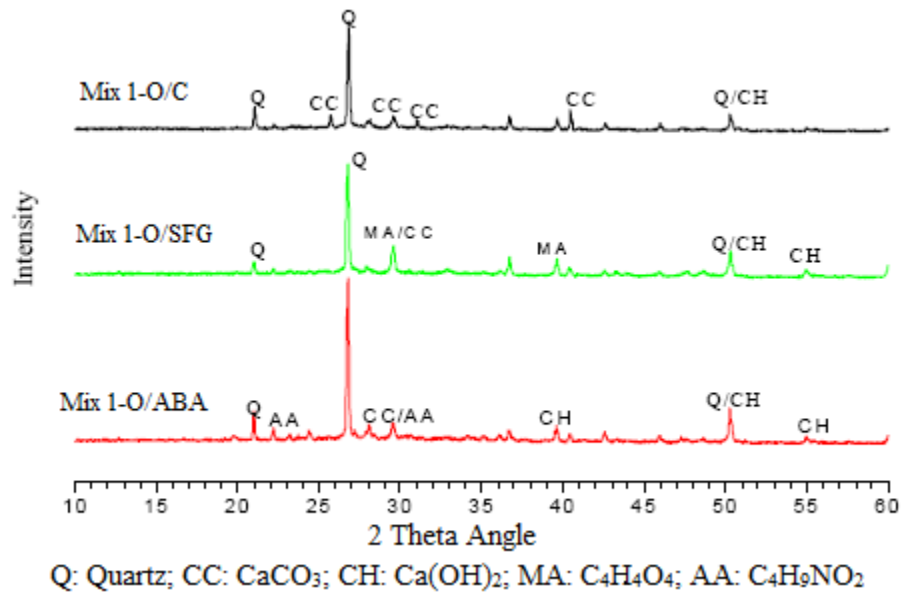


Fig. 4.14 XRD patterns for concrete powder obtained from Mix 1-OPC concrete at 90 days of exposure duration

4.8.2 Compressive strength results

The compressive strength test was done to investigate any undesirable effect of inhibitors on the strength of resultant concrete. Compressive strength of all mixes (with and without

corrosion inhibitors) was measured at 28 days, 56 days and 90 days of casting and the results are presented in Figs. 4.15 - 4.18.

From Figs. 4.15 and 4.16, it was observed that in OPC concrete specimens the application of corrosion inhibitor SFG marginally increased the compressive strength at all testing ages as compared to control mix. While with the corrosion inhibitor ABA, marginal decrease in compressive strength was observed and this decrease became less significant with age of concrete. At 28 days of testing, 3.16% and 4.62% increase in compressive strength was observed with inhibitor SFG in Mix 1 and Mix 2 respectively as compared to the corresponding control specimens. At 90 days of testing, the percentage increase was 6.73% in Mix 1-O/SFG and 10.74% in Mix 2-O/SFG specimens. In Mix 1-O/ABA, an 8.8% decrease in compressive strength was observed at 28 days in comparison with Mix 1-O/C, while this decrease in compressive strength at 90 days was only 3.5%. For concrete mixes prepared at w/c ratio of 0.52 the application of inhibitor ABA decreased the compressive strength by 7.9% at 28 days in comparison with the control mix (Mix 2-O/C). However, at 90 days of testing, 1.6% increase in compressive strength was observed in Mix 2-O/ABA in comparison with the corresponding control mix.

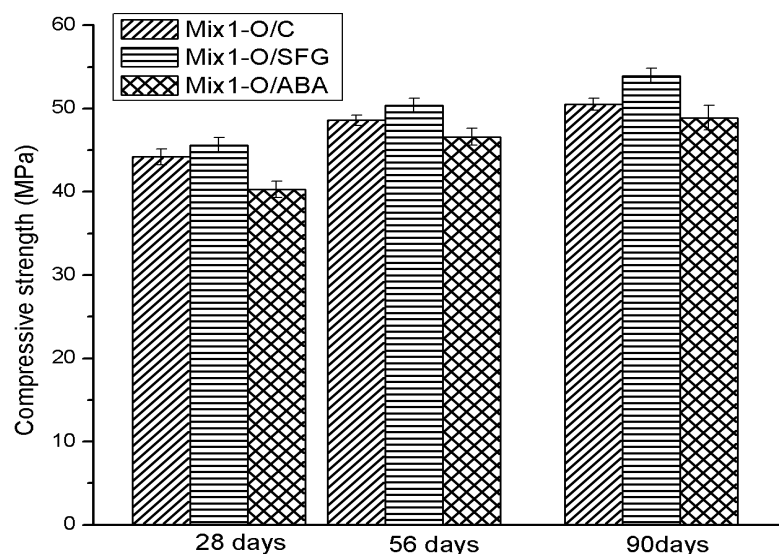


Fig.4.15. Compressive strength of mixes prepared at w/c ratio of 0.43 by using OPC

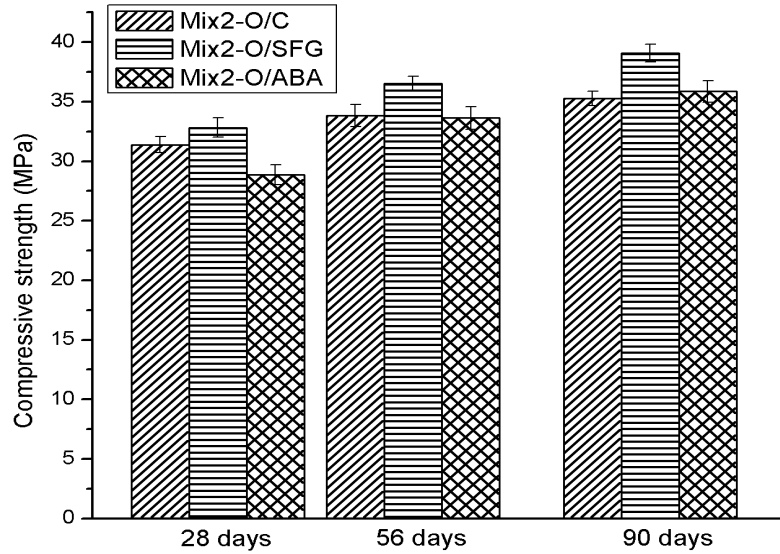


Fig.4.16. Compressive strength of mixes prepared at w/c ratio of 0.52 by using OPC

Similar observations were made in concrete mixes prepared with PPC at w/c ratio of 0.43 (Mix 1). In PPC concrete, application of inhibitor SFG led to an increase in 90 days concrete compressive strength by 7.3%; while for mix with ABA inhibitor, the compressive strength decreased marginally by 1.6% as compared to control mix (Fig. 4.17). However in PPC concrete prepared at w/c ratio of 0.52 (Mix 2) both of inhibitors led to an increase in the compressive strength at all testing ages (Fig. 4.18). At 90 days of testing age, 14.86% and 7.40% increase in compressive strength was observed with inhibitors SFG and ABA, respectively as compared to the control mix.

In general, the compressive strengths for all mixes varied only in narrow range. Previous research indicates a reduction in the compressive strength by the use of organic corrosion inhibitor, when they are admixed into concrete at the time of casting. *De Schutter and Luo (2004)* and *Soylev et al. (2007b)* reported a 10-30% decrease in strength with the use of amine based inhibitors and other organic inhibitors. However, no such reduction in strength was observed in the present study when the inhibitor is applied on the surface of concrete as migrating inhibitor. Results indicate that the application of these chemicals on the concrete surface does not have any detrimental effect on the compressive strength.

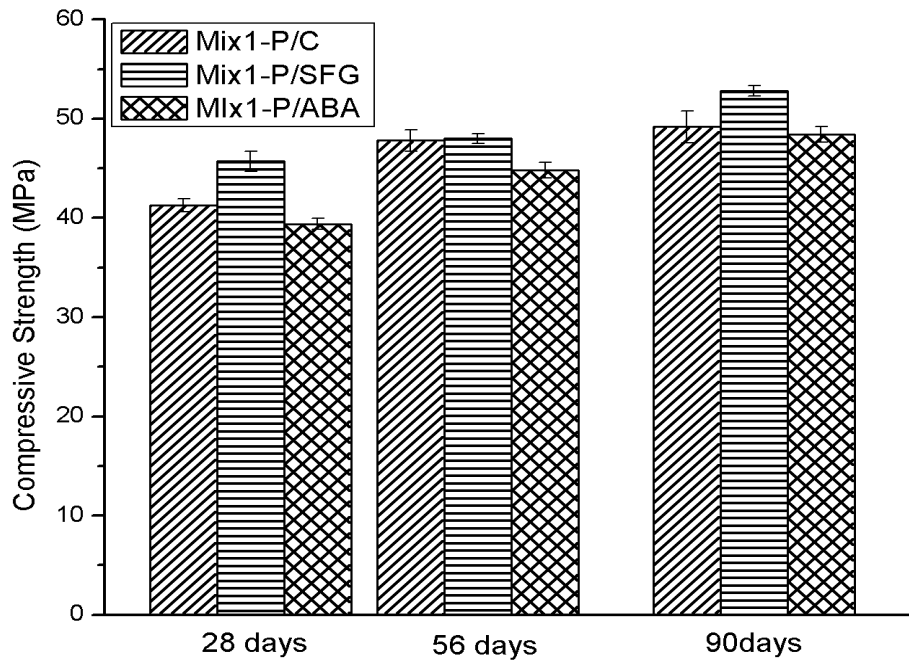


Fig.4.17. Compressive strength of mixes prepared at w/c ratio of 0.43 by using PPC

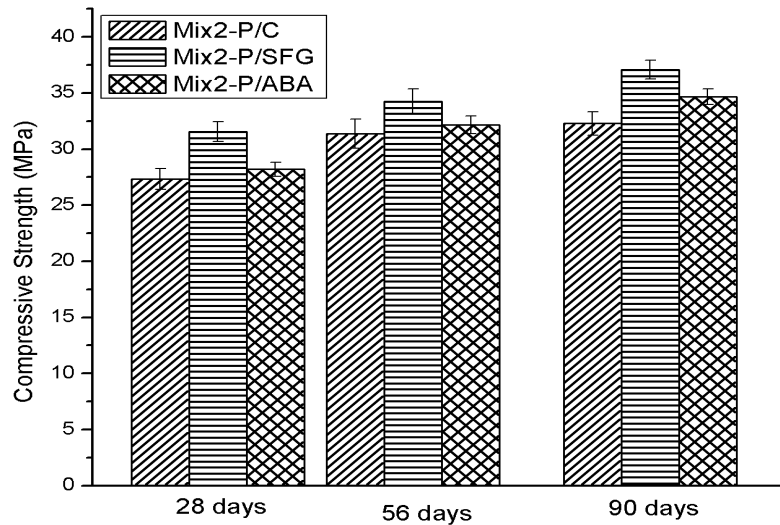


Fig.4.18. Compressive strength of mixes prepared at w/c ratio of 0.52 by using PPC

4.9 CLOSING REMARKS

The present chapter focuses on changes in the primary properties of concrete with the use of migrating type corrosion inhibitors. The effect of inhibitors on carbonation depth and compressive strength of the resultant mixes were investigated. Carbonation depth results confirmed that the cement type and w/c ratio plays an important role in progression of the

carbonation front. Concrete made with Pozzolanic cement (PPC) has higher carbonation coefficient as compared to the concrete made with OPC cement at same w/c ratio. This effect is generally attributed to the lower content of portlandite Ca(OH)_2 in concrete made with PPC cement. By keeping the cement type as constant, concrete made with higher w/c ratio had higher carbonation coefficient as compared to concrete having lower w/c ratio. The carbonation coefficient decreased drastically with the application of inhibitors, indicating the formation of the protective layer by the inhibitors on the concrete surface. Decrease in carbonation coefficient indicates that the inhibitors act as a pore blocker and resist the carbonation front to ingress into concrete. The XRD investigation further support the pore blocker effect in inhibitor treated specimens. The observed two additional peaks in inhibitor treated specimens indicate that the inhibitor has reached the depth of 5 – 10 mm from the surface of concrete and has a tendency to fill the surface pores and percolate further. The compressive strength results demonstrate that surface applied inhibitors did not have any detrimental effect on the resultant strength of concrete.

CHAPTER 5

INHIBITOR EFFECT ON CORROSION BEHAVIOUR OF REBAR EMBEDDED IN CONCRETE

5.1 GENERAL

Reinforced concrete structures are designed to meet the various strength and durability requirements throughout their service life. Concrete is known to provide dual protection to the rebar. Physically, concrete cover act as a barrier for ingress of aggressive chemicals and chemically, the thin passive film of $\gamma\text{-Fe}_2\text{O}_3$ formed around the rebar due to high pH of concrete pore solution protects it from corrosion. However, this protective layer breaks down either due to the carbonic acid formation by reaction of CO_2 with moisture present in environment or by the presence of chloride ions. CO_2 present in air reacts with cement hydration products, such as $\text{Ca}(\text{OH})_2$, C-S-H gel etc., leading to the formation of CaCO_3 which results in lowering the pH of pore solution (Sisomphon and Franke, 2007; Dong et al., 2014; Aguiar and Junior, 2013; Singh and Singh, 2016). Lowering in pH of pore solution from 13.5 to nearly 8 leads to break down of the protective passive layer that protects the rebar from corrosion.

Multiple methods are available for providing protection against rebars corrosion, with varying degrees of efficiency, ease of applicability and economy. Among the various protection mechanisms, corrosion –inhibiting admixtures have gained popularity over the last two decades. As explained in Chapter 2, corrosion inhibitors are the chemicals that should reduce the corrosion rate by developing a layer around the rebar surface. Inhibitors are expected to reduce the corrosion rate by interfering with the corrosion process without having any detrimental effect on concrete quality. The major criteria for the performance of any inhibitor depend upon its potential to reduce the rebar corrosion rate. In the present chapter, the corrosion rate of specimens applied with migrating corrosion inhibitors is investigated. The corrosion behaviour of reinforced concrete specimens is evaluated using different electrochemical techniques.

As explained in Chapter 2, Half-cell potential measurement technique, which indicates the probability of corrosion, is the most widely used technique for corrosion monitoring in reinforced concrete. Along with this, Tafel Extrapolation technique is widely used for

qualitatively measuring the corrosion rate (*Patil et al., 2014; Song, 2000*). In the present study, both these techniques are used to study corrosion behavior of the rebar.

In this chapter the outcomes of the experimental investigation for effectiveness of the migrating type corrosion inhibitors against carbonated polluted concrete specimen is presented. For this purpose, corrosion risk of the rebar was studied by Half-cell potential and Galvanic coupling potential techniques, whereas, the corrosion rate of the rebar embedded in concrete was determined by Tafel Extrapolation technique.

5.2 EXPERIMENTAL PROGRAM

The test matrix for investigating the effect of migrating type corrosion inhibitors on protection against rebar corrosion is presented in Fig. 5.1. The figure provides description about the major test variables, viz. cement type and w/c ratio. Also, the details about the application of corrosion inhibitors, exposure conditions and different tests performed for corrosion rate measurement are presented.

5.3 MATERIAL SYSTEM

Cement type, w/c ratio and corrosion inhibitors are the major test variables considered in the present investigation. The details of cement type, coarse aggregates, fine aggregates, mixing water and corrosion inhibitors has already been discussed in Chapter 4. A brief description of all these materials is provided in the succeeding sections as well.

5.3.1 Cement

Two types of cements were used in present study viz. Ordinary Portland cement (OPC) conforming to BIS: 8112-1989 (*BIS, 2005*) and Pozzolana Portland cement (PPC) conforming to BIS: 1489 (part 1) -1991 (*BIS, 2005*). The physical and chemical compositions of both the cements are presented in Table 4.1.

5.3.2 Aggregates

The coarse aggregate used was crushed gravel with nominal maximum size of 20 mm and 10 mm mixed in a specific ratio, as per design requirements. The specific gravity and water

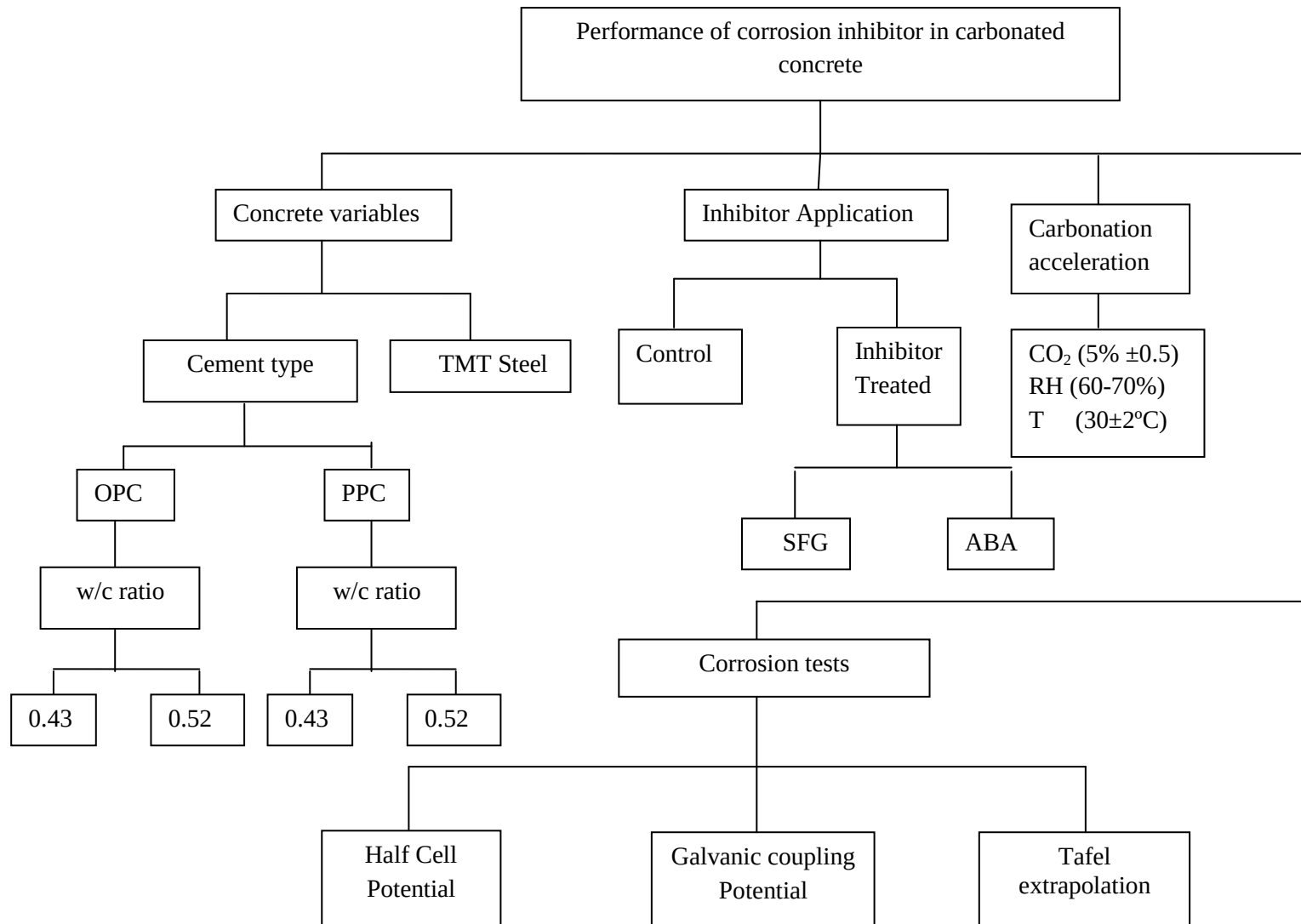


Fig.5.1. Schematic illustration for determination of corrosion inhibitor performance against carbonation induced corrosion

absorption of 10 mm aggregate was 2.65 and 1.4% and for 20 mm aggregate was 2.63 and 1.38% respectively. The fine aggregate used was river sand conforming to Zone-II as per BIS: 383-1970 (BIS, 2002). The specific gravity, water absorption and fineness modulus of fine aggregate was 2.70, 1.8% and 2.85 respectively.

5.3.3 Steel

TMT bars of 12 mm diameter and 360 mm in length conforming to BIS: 1786-1985 (BIS, 2004) were used for the present study. The chemical composition of rebar as obtained from the manufacturer has already been presented in Table 3.1.

5.3.4 Corrosion inhibitors

From the pore solution tests described and discussed in Chapter 3, two inhibitors were chosen for further investigations on concrete specimens.

(a) Commercially available inhibitor SFG: A commercially available inhibitor based on organic compounds such as aqueous solutions of amino alcohols and salts of amino alcohols was used as one of the inhibitor. SFG could penetrate through concrete at a rate of a few millimeters/day to a depth of approximately 25 to 40 mm in one month.

(b) Generic inhibitor ABA: ABA was a generic chemical with the formula $C_7H_7NO_2$ and was available in solid form. Since the inhibitor for the present study was to be applied on the concrete surface, ABA was required to be converted into the liquid form before application on concrete specimens. For the present work, Dimethyl Sulfoxide (DMSO) and methanol were used as solvents for ABA. The required aqueous solution of ABA was prepared by dissolving 100gm of ABA in 50ml of DMSO and 33ml of methanol.

5.4 SPECIMEN PREPARATION AND EXPOSURE CONDITIONS

For monitoring rebar corrosion by electrochemical techniques, prism specimens with rebar at desired location were cast. The description about the concrete mixes used in the present study and detailed procedure for preparation of rebar specimens is presented in the following sections.

5.4.1 Concrete mix proportions

As mentioned in Chapter 4, all the concrete mixes were designed to obtain a slump lying in a range of 60 to 80 mm and the water content in all mixtures was kept constant at 180 kg/m³. To get the desired slump, a chemical admixture was used in the mixes made with w/c ratio of 0.43, while no admixture was required for concrete mix at w/c ratio of 0.52. The final mix proportions for all mixes are presented in Table 5.1.

Table 5.1 Mix proportions for concrete specimens

Cement type	w/c ratio	Cement (kg/m ³)	Water (kg/m ³)	Fine aggregate (kg/m ³)	Coarse aggregate(kg/m ³)		Admixture (% weight of cement)
					20mm	10mm	
OPC	0.43	410	180	572.4	836.3	360.4	0.3
	0.52	340	180	621.0	848.7	365.7	-
PPC	0.43	410	180	572.4	836.3	360.4	0.3
	0.52	340	180	621.0	848.7	365.7	-

5.4.2 Preparation of rebar specimens

The embedded steel used in all specimens was the Thermo Mechanically Treated (TMT) bar conforming to BIS: 1786-1985(BIS, 2004). The steel rebar was 12 mm in diameter and 360 mm in length. Before embedding the steel rebar into concrete, it was prepared as per ASTM G 109 (ASTM, 2005). The steel rebar was cleaned by rubbing with emery paper and laboratory grade hexane to remove the rust particles from the surface of rebar. After air drying the rebar specimens, an insulating tape was applied for a length of 55mm at each end of the rebar in order to leave only a central 250 mm, portion bare. Then, a 3mm thick neoprene tube with 12mm internal diameter was mounted over the insulating tape. Epoxy was then filled along the length of the neoprene tube. To ensure electrical connectivity, a 3 mm threaded hole was made at one end of the rebar. The line diagram of the preconditioned steel specimen is shown in Fig. 5.2. The actual photograph of the preconditioned steel specimens is shown in Fig. 5.3.

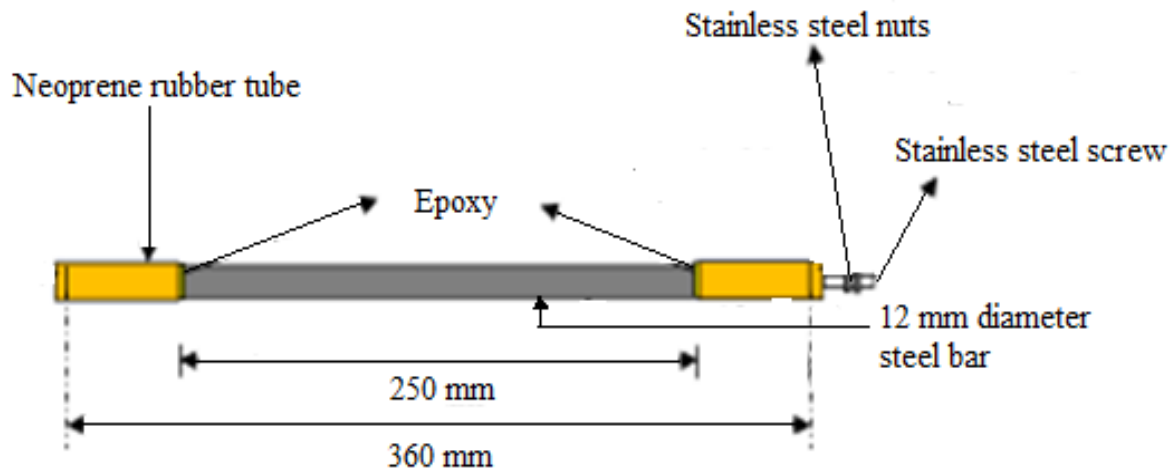


Fig.5.2. Line diagram of preconditioned steel specimen



Fig.5.3. Preconditioned steel specimens

5.4.3 Preparations of prism specimens

The prism specimens of size $300 \times 300 \times 150$ mm were prepared as per guidelines provided in ASTM G 109 (ASTM, 2005) with minor modifications to study the corrosion behaviour of rebar. The prism specimen was prepared with three steel rebars embedded into it; two steel rebars were embedded at the bottom with cover of 25 mm and one rebar was placed at the top with clear cover of 5 mm i.e. an effective cover of 11mm. The casting of prism

specimens was done by using specially prepared steel moulds. The cover depth of 5 mm was maintained accurately by drilling holes of appropriate diameter at exact location in the steel mould. Deliberately, a smaller value of cover was used in the present study so that carbonation front could reach the rebar level within the test duration of 90 days. Also, since 20 mm size of aggregates was used, care was taken that the aggregates do not come in the cover zone during casting. The line diagram of prism specimens is shown in Fig.5.4; while the prepared prism specimens are shown in Fig.5.5.

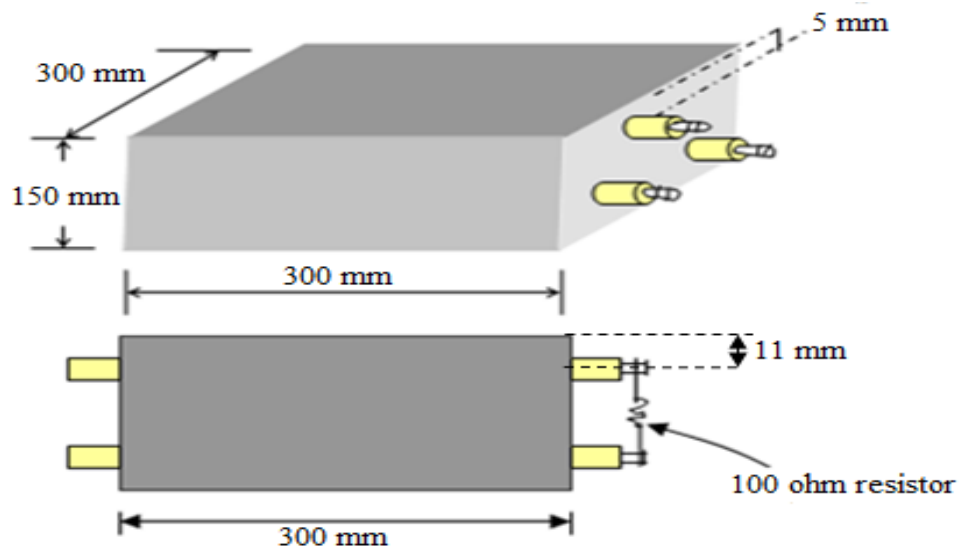


Fig.5.4. Line diagram of prism specimens



Fig.5.5. Prism specimens kept under laboratory conditions

With the two types of cement, two w/c ratios, two inhibitor applications and two replicates, a total of 24 prism specimens were prepared by using the same mixes as used for the preparation of carbonation depth measurement cubes (discussed in Chapter 4). Out of 24 prism specimens, 16 specimens were treated with the migrating type corrosion inhibitor while the remaining prisms were taken as control specimens. Details of the prism specimens along with the nomenclature used are given in Table 5.2.

Table 5.2 Nomenclature for prism specimens

Cement type	w/c ratio	Inhibitor treatment	Nomenclature
OPC	w/c 0.43	-	Mix 1 - O/C
		SFG	Mix 1 - O/SFG
		ABA	Mix 1 - O/ABA
	w/c 0.52	-	Mix 2 - O/C
		SFG	Mix 2 - O/SFG
		ABA	Mix 2 - O/ABA
PPC	w/c 0.43	-	Mix 1 - P/C
		SFG	Mix 1 - P/SFG
		ABA	Mix 1 - P/ABA
	w/c 0.52	-	Mix 2 - P/C
		SFG	Mix 2 - P/SFG
		ABA	Mix 2 - P/ABA

All the prism specimens were demolded after 24hours of casting and wet cured for 7 days with the help of jute bags at a temperature of $27 \pm 2^\circ \text{C}$. Subsequently, the samples were kept in the laboratory environment for 7 days. After 15 days of casting, the side surfaces and the bottom surface of prism specimens were sealed with Duragard sealant in order to ensure unidirectional flow of carbon dioxide and progression of carbonation front into concrete. Thereafter, inhibitors were applied by brush on the top surface of prismatic samples except in the control specimens. The inhibitors were applied at a rate of 500 g/m^2 on the top surface of prism specimens in three consecutive layers. The dosage of the inhibitor to be applied was recommended by the manufacturer for inhibitor SFG. In order to maintain uniformity in dosage, the same dosage was used for inhibitor ABA.

5.4.4 Exposure conditions

After 15 days of casting, all the specimens were kept in the carbonation chamber, capable of maintaining temperature, relative humidity and CO₂ concentration in the range of 20-50°C, 30-70% and 0-10% by volume respectively. In the present study, after the inhibitor application, the specimens were preconditioned at a relative humidity of 60-70% and temperature of $30 \pm 2^\circ\text{C}$ for 15 days inside the carbonation chamber in order to achieve an even distribution of moisture within the specimens.

To study the corrosion rate of the rebar, it is necessary to first ensure the carbonation of concrete. It is reported that the behavior of rebar in carbonated concrete is likely to be the same, independent of whether carbonation was induced in an accelerated condition or occurred in a natural exposure condition (*Kujur, 2012*). The corrosion rate of the rebar embedded in carbonated concrete depends upon CO₂ concentration, temperature and relative humidity maintained inside the carbonation acceleration chamber. Literature suggested that temperature variation between 25-30°C, relative humidity ranging between 60-70% with a CO₂ concentration between 3-5% were the most favorable conditions for carbonation acceleration (*Dong et al., 2014; Montemor et al., 2002; Ulloa et al., 2013*). In the present study, after the end of preconditioning, the specimens were subjected to accelerated carbonation by maintaining CO₂ concentration of 5% by volume for a period of 90 days at $30 \pm 2^\circ\text{C}$ temperature and 60-70% relative humidity. Fig.5.6. shows the prism specimens undergoing accelerated carbonation inside the carbonation chamber.

5.5 CORROSION MONITORING USING ELECTROCHEMICAL TECHNIQUES

Corrosion behaviour of the rebar exposed to carbonation acceleration was determined in terms of corrosion potential and corrosion rate measurement. The corrosion potential of the embedded rebar was determined by Half-cell potential measurement method, which is the most commonly used technique for qualitative measure of corrosion. Corrosion rate of the rebar was determined by performing Tafel Extrapolation (polarization) measurement. The detailed procedure for each of the techniques is described in the succeeding sections.



Fig.5.6. Prism specimens exposed to carbonation acceleration in CO₂ controlled chamber

5.5.1 Potential measurements

The potential measurements were carried out using an Advanced Corrosion Monitoring (ACM) field machine (serial no. 1463) which is capable of processing the input data and plotting the outputs automatically. The machine can perform various electrochemical measurements such as; Rest potential measurement, Cyclic and Galvanic sweep, Custom sweep, Long term Galvanic and Potential measurement, long term LPR sweep, AC impedance measurement etc. The Half Cell Potential (HCP) of the top steel rebar was measured with the help of Saturated Calomel Electrode (SCE) which was used as the reference electrode. In order to provide ionic conduction, a 5mm thick wet sponge was placed between the top surface of prismatic samples and SCE. The measurements were taken parallel to the rebar at five points and the average value was considered as HCP value of the specimens. Since the potential measurements were made over a small concrete cover of 5mm and concrete was uniformly wet, so no correction to the measured potential was required (Montemor *et al.*, 2002). The experimental arrangement used for HCP measurement is shown in Fig.5.7 (a).

Along with the HCP, the Galvanic Coupling Potential (GCP) of the prism specimens was also measured. During the galvanic corrosion, the rebar corrodes preferentially when it is in electrical contact with the other rebar in the presence of electrolyte i.e. the pore solution. Therefore, after measuring HCP of the top rebar, the potential difference between the top rebar and the common terminal of the bottom rebars (GCP) was measured across the 100 ohm resistor connected between the top rebar and the bottom rebars as shown in Fig. 5.7 (b) (ASTM G 109, 2005; Kujur, 2012).

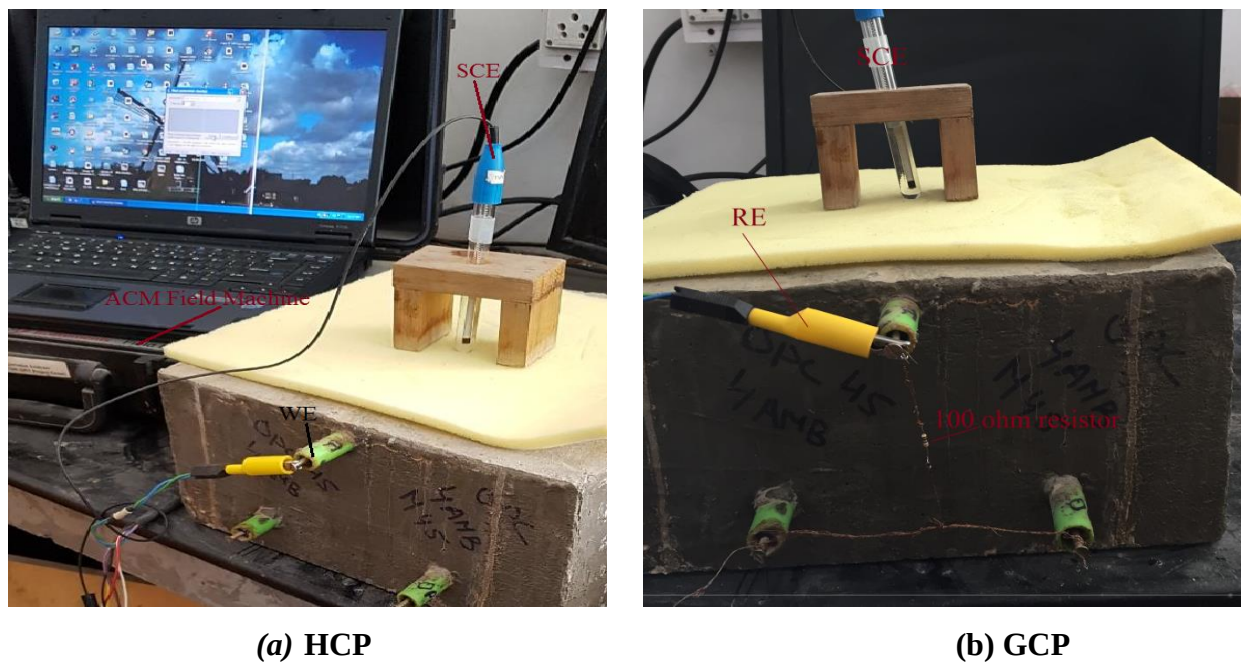


Fig.5.7. Experimental arrangement for potential measurement

The potential measurement was carried out at an interval of 15 days till the end of testing program for all specimens prepared with different types of cement, w/c ratios and treated with migrating type inhibitors. The end of the testing program was decided based upon the carbonation depth results. From Chapter 4, it was observed that during the 90 days of exposure duration in all mixes (with and without inhibitor treatment) the carbonation front exceeded the value of 5mm i.e. the top rebar level in the present study. Therefore, the testing of the prism specimens was discontinued after 90 days of exposure duration.

5.5.2 Corrosion rate measurement by Tafel Extrapolation (Polarization) technique

Tafel extrapolation was conducted on the top rebar of the prism specimens with the help of guard ring arrangement provided along with the ACM field machine. The guard ring probe consisted of two concentrically placed zinc electrodes in which three platinized titanium reference electrodes were inbuilt. Polarization scans were obtained for all prism specimens immediately after measuring HCP and GCP. For polarization measurement, the working electrode was polarized to $\pm 25\text{mV}$ from the equilibrium potential at a sweep rate of 60mV/min . Prior to the test, a 5 mm thick wetted sponge was placed between the top surface of the prism specimens and the guard ring to provide proper ionic conduction. Wetted sponge was kept on the prism specimen at least two hours prior to measurement in order to ascertain uniform moisture content on the cover concrete. The working electrode (top rebar) and guard ring probes were connected with to ACM field machine with the help of connecting electric wires. The line representation of the guard ring arrangement is shown in Fig. 5.8 and actual photograph for experimental set up is shown in Fig. 5.9.

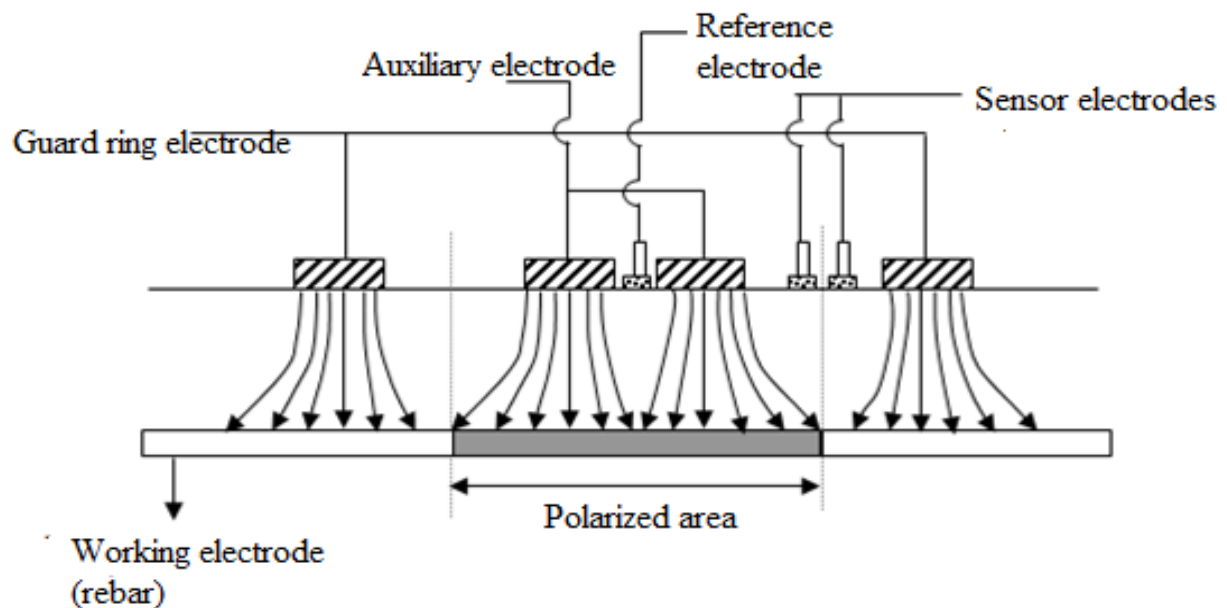


Fig.5.8. Line representation of guard ring arrangement (Andrade and Alonso, 2001; Kujur, 2012)

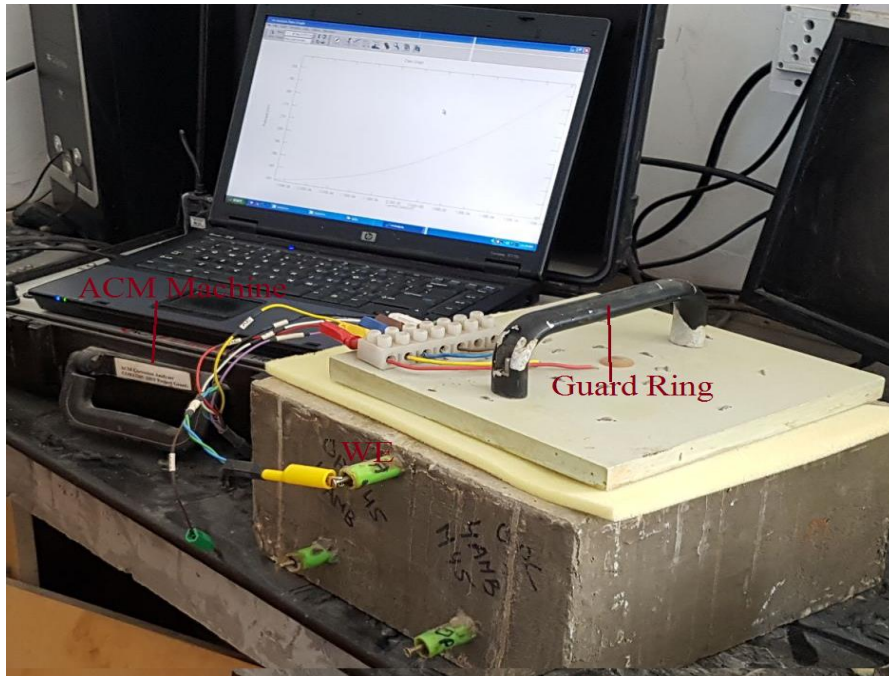


Fig.5.9. Experimental setup for polarization measurements

5.6 RESULTS AND DISCUSSION

The outcomes of the potential (both HCP and GCP) and Tafel extrapolation results for all specimens measured at different exposure durations are presented here under.

5.6.1 Potential measurements

The HCP is the most widely monitored parameter to evaluate the condition of the embedded rebars (*Poursae and Hansson, 2009*). HCP gives information regarding the corrosion state of the rebar embedded in concrete. According to ASTM C 876-91 (*ASTM, 1999*) the corrosion probability is low for HCP values $> -125\text{mV/SCE}$; intermediate for HCP values between -125mV/SCE to -275mV/SCE ; and is high for potential values $< -276\text{mV/SCE}$. Both HCP and GCP were measured at an interval of 15 days on prism specimens made with two types of cements, for two w/c ratio and two types of inhibitors treatment. The test results are discussed in the succeeding sections.

(a) Potential variation with exposure duration in control specimens

(i) *Half cell potential (HCP)*: Fig. 5.10 depicts the HCP variation for control specimens at different exposure durations. It can be observed from the figure that during initial exposure

duration, all the concrete specimens showed lower values of HCP, indicating passive behavior for all prism specimens. However, with increase in exposure duration, the HCP value of the concrete mixes prepared by using PPC increased at faster rate as compared to the mixes prepared using OPC. At 30 days of exposure duration, the lowest potential (-158mV/SCE) was observed in Mix1-O/C, while the highest potential (-270mV/SCE) was observed in Mix1-P/C indicating intermediate probability of corrosion. Beyond this exposure duration, both PPC concrete mixes showed a potential higher than -275mV/SCE , indicating high probability of corrosion. On the other hand, OPC concrete prepared at w/c ratio of 0.43 (Mix 1) showed the potential value lower than -225mV/SCE at the end of exposure duration. From the observed behaviour of HCP, it can be concluded that PPC concrete was more prone to rebar corrosion than the OPC concrete in the similar carbonated environment. The observed trend of HCP is in good agreement with the observations made by previous researchers (*Saraswathy et al., 2001; Montemor et al., 2002; Aperador et al., 2012*).

On making a comparison based upon the w/c ratio, it was observed that irrespective of the cement type, the concrete made at higher w/c ratio of 0.52 had higher value of HCP as compared to the concrete made at w/c ratio of 0.43. With the increase in w/c ratio, the porosity inside the concrete increased which ultimately results in lesser densification of concrete matrix. Due to the porous structure at higher w/c ratio, the equipotential lines could spread over a larger area of the rebar surface, thus increasing HCP value. *Sisomphon and Franke (2007); Morandeau et al. (2014)* was also reported that the increase in w/c ratio alters the carbonation kinetic process.

It could also be observed from the HCP variation that for all the concrete specimens, the HCP values lie in range of -91mV/SCE to -403mV/SCE . This range of potential is contradictory to the potential range generally observed in chloride induced rebar corrosion, where HCP value were found to reach as high as -800 mV/SCE (*Montemor et al., 2000*). It further indicates that the mechanism of corrosion under both aggressive environments is different and hence the results obtained under one environment cannot be directly correlated to the behaviour of the structure in another environment. However, observed HCP values in the present study lies within the range specified by RILEM TC 154-EMC for concrete in carbonated

environment (Elsener *et al.*, 2003). According to RILEM TC 154-EMC, for humid and carbonated concrete, the potential varies between 170mV/SCE to -330mV/SCE . Fig. 5.10 clearly indicate that the observed potential lies within the range specified by RILEM TC 154-EMC, with some minor variations.

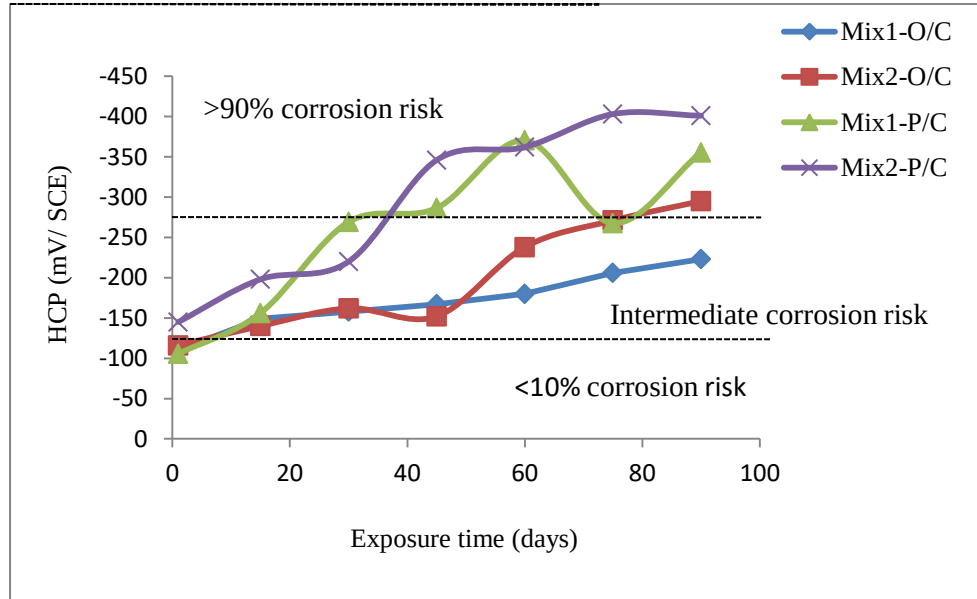


Fig.5.10. HCP variation with exposure duration for control specimens

(ii) *Galvanic coupling potential (GCP):*

The GCP can occur between two visibly separated areas if the embedded rebars are electrically coupled with each other. When these two rebars are in electrical contact through the electrolyte solution (concrete pore solution), the potential of the two rebars shift to a common potential by assuming negligible electrolyte resistance. The active rebar, which has more negative potential is anodically polarized and attains a more positive potential; while the passive rebar having a more positive potential is cathodically polarized and attains a negative potential value because of coupling (Qian *et al.*, 2006). It is well known that the coupling potential reverses its sign from negative to positive with the increase in corrosion risk in case of chloride induced corrosion (Pradhan and Bhattacharjee, 2009).

In the present study, GCP measurements were made by connecting the active (top) rebar with the common terminal of passive (bottom) rebars. The values obtained for four sets of control specimens are presented in Fig. 5.11. No reversal of sign from negative to positive was

observed in GCP values obtained for all specimens. This is contrary to the general observation of sign reversal made in concrete subjected to chloride induced corrosion (*Pradhan and Bhattacharjee, 2009*). In case of chloride induced corrosion, the potential difference between the active and passive rebar is large and also pits are formed on the active rebar surface. This large difference in the potential and pitting corrosion is responsible for sign reversal in chloride exposure. However, carbonation induced corrosion leads to general or uniform corrosion on the rebar surface due to progress of carbonation front and uniform decrease in alkalinity of the pore solution. The observed coupling potential varied between -37mV/SCE to -177mV/SCE for all concrete specimens with no reversal in sign till the end of exposure duration. The corresponding HCP for all specimens varied between -100mV/SCE to -400mV/SCE during the testing duration. Because of less variation in HCP of the top rebar, the GCP also lies between the narrow ranges with no reversal in sign. *Qian et al. (2006)* also observed the fluctuation in GCP between -150mV/SCE to -250mV/SCE when they coupled active carbon steel with the passive carbon steel in concrete specimens.

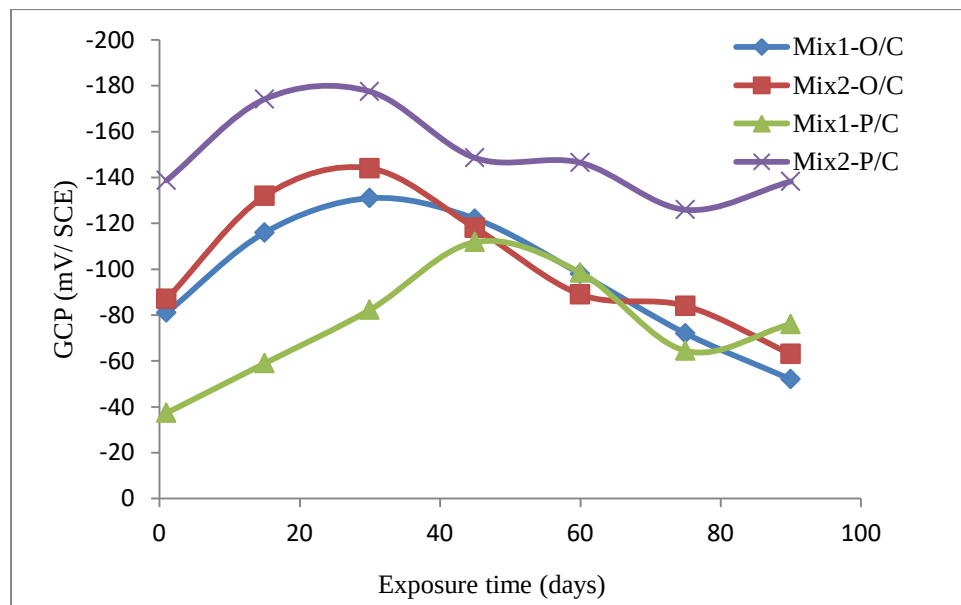


Fig.5.11. GCP variation with exposure duration for control specimens

(b) Potential variation with exposure duration for inhibitor treated specimens

(i) Half Cell Potential (HCP):

The variation in HCP of concrete specimens treated with surface applied migrating type corrosion inhibitors are presented in Figs. 5.12 to 5.15. Fig 5.12 corresponds to the HCP variation with exposure duration of OPC concrete specimens prepared at with w/c ratio of 0.43 viz. Mix 1-O/C, Mix 1-O/SFG and Mix 1-O/ABA. From the figure, it can be observed that HCP of all the specimens remained in the range corresponding to intermediate corrosion risk till the end of exposure duration. For the control specimens, a potential shift towards the more negative side was observed with progressive exposure durations. However, in inhibitor treated specimens a different behaviour was noted. The application of inhibitor SFG initially raised the potential towards active side, with the potential reaching a highest value of -207mV/SCE at 30days of exposure. However, with the increase in exposure duration, the potential shifted towards the nobler side and the potential at the end of exposure duration was lower than the corresponding value obtained for control specimens. In concrete specimens treated with inhibitor ABA, a small variation in potential, ranging between -160mV/SCE to -91mV/SCE , was observed. The potential observed in ABA treated specimen at 90 days of exposure duration was -91 mV/SCE , which falls in the category of low corrosion risk. The potential observed in control, inhibitor SFG and inhibitor ABA treated specimens at 90 days of exposure duration were -223mV/SCE , -163mV/SCE and -91mV/SCE respectively.

In the Fig. 5.13, a similar effect of inhibitor treatment was observed, corresponding to OPC concrete mix designed at higher w/c ratio of 0.52 viz. Mix 2-O/C, Mix 2-O/SFG and Mix 2-O/ABA. From the figure, it was observed that for both inhibitor treated specimens, potential varied in the range corresponding to the intermediate corrosion risk; while for control specimen, HCP values approached the range corresponding to higher than 90% risk of corrosion towards end of exposure duration.

Figs. 5.14 and 5.15 represents the effect of inhibitor treatment on PPC concrete specimens made with w/c ratios of 0.43 (Mix 1) and 0.52 (Mix 2) respectively. From Fig. 5.14, it was observed that, during the initial exposure duration, the potential for all the specimens lied in

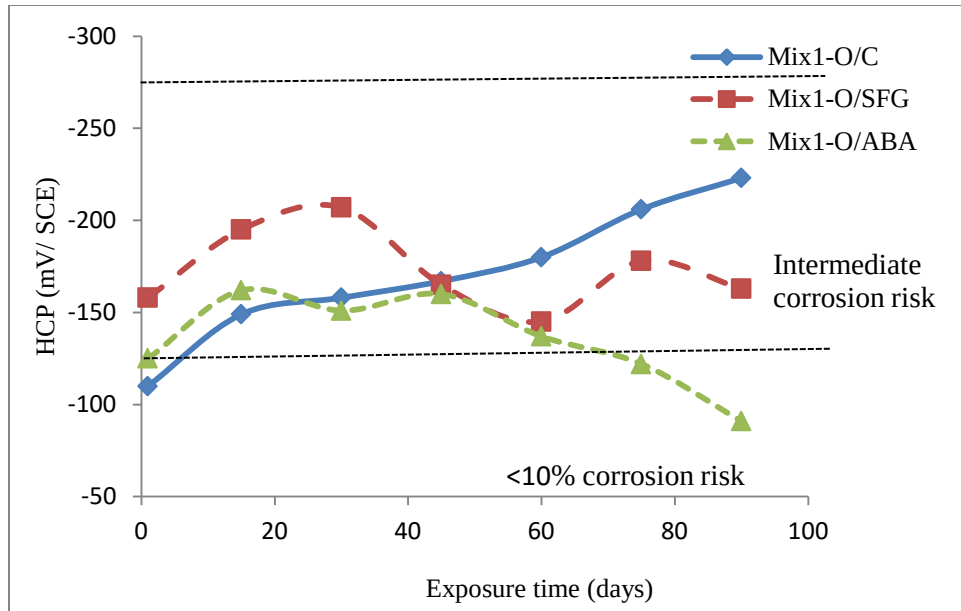


Fig.5.12. HCP variation with exposure duration in inhibitor treated OPC concrete prepared at w/c ratio of 0.43

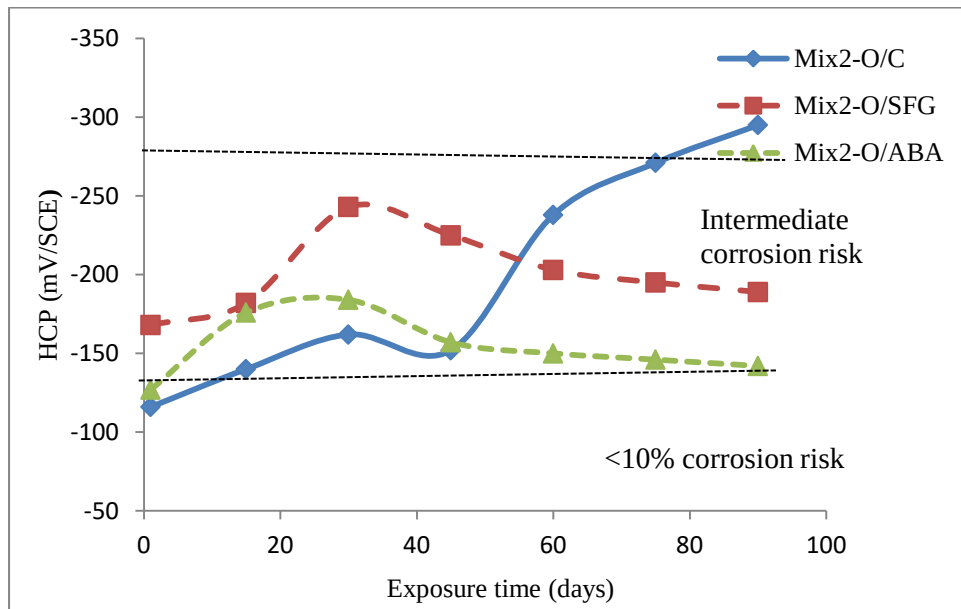


Fig.5.13. HCP variation with exposure duration in inhibitor treated OPC concrete prepared at w/c ratio of 0.52

the range of -105mV/SCE to -130mV/SCE , indicating passive potential. As the exposure durations were prolonged, the potential shift towards the active side was observed in control specimens; while inhibitor applied specimens still demonstrated the nobler potential. Towards

the end of exposure, a nobler potential of -89mV/SCE and -164mV/SCE was observed in inhibitor SFG and ABA treated specimens, respectively; while control specimen registered a potential of -355mV/SCE , which lies in the range of high probability of corrosion. Similarly, for PPC concrete prepared at w/c of 0.52, the potential observed at the end of exposure duration of 90 days was -401mV/SCE , -160mV/SCE and -213mV/SCE for control, inhibitor SFG, inhibitor ABA treated specimens, respectively (Fig. 5.15).

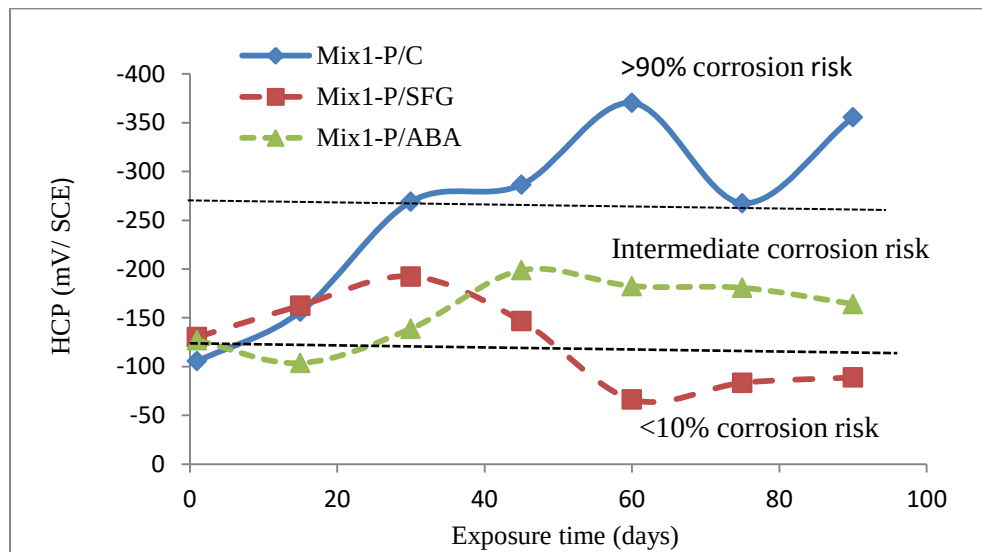


Fig.5.14. HCP variation with exposure duration in inhibitor treated PPC concrete prepared at w/c ratio of 0.43

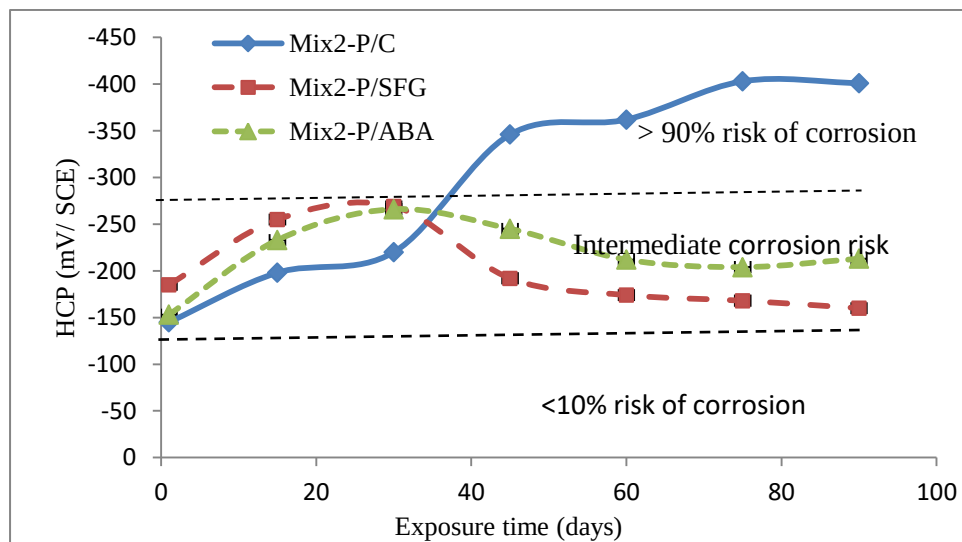


Fig.5.15. HCP variation with exposure duration in inhibitor treated PPC concrete prepared at w/c ratio of 0.52

From the above discussion, it is evident that all inhibitor treated concrete specimens show a corrosion potential in the range of -89mV/SCE to -213mV/SCE at 90 days of exposure duration, while for control specimens the values lie in the range of -223mV/SCE to -401mV/SCE . These values suggest passive state of rebar for inhibitor treated specimens, while rebar reached active state for control specimens towards the end of the exposure duration, irrespective of the type of cement and w/c ratio.

In OPC concrete, inhibitor ABA was found to be more effective than inhibitor SFG for both concrete mixes. However, in PPC concrete, inhibitor SFG was observed to be more effective than the inhibitor ABA. This behaviour shows that cement type plays an important role for the inhibitors to develop their inhibiting action in the concrete specimens. Further, it was observed that both these inhibitors develop their inhibiting action after 30 days of exposure duration in all concrete specimens as indicated by the initial shift in potential towards the more negative side. From this observation, it can be concluded that transport of the inhibitors from the surface of the concrete takes time to reach the rebar level. Once the inhibitor reaches the rebar surface and forms a protective layer around the rebar, the potential starts shifting towards the nobler side. The protective layer inhibits both ferrous decomposition (anodic reaction) and restricts oxygen access (cathodic reaction) to the rebar and improves the HCP of the rebar (*Batis et al., 2003*). *Heiyantuduwa et al.* (2006) also observed an improvement in the HCP with the use of migrating type inhibitors as compared to the control specimens.

(ii) Galvanic Coupling Potential (GCP):

After measuring HCP of the top rebar, potential difference between the top rebar and the common terminal of the bottom rebars i.e. GCP was measured across the 100 Ohm resistor connected between the top rebar and the bottom rebars. Figs. 5.16 to 5.19 shows the GCP variation with exposure durations for all concrete specimens treated with corrosion inhibitors. In case of chloride induced corrosion, the reversal in the sign of potential between the top rebar and bottom rebars indicates that the top rebar has become anodic (*Pardhan and Bhattacharjee, 2009*). However, no such reversal in sign of the measured GCP was observed in any of the specimens, till the end of exposure duration of 90 days. As already explained, it can be due to generalized corrosion occurring due to the progression of carbonation front and decrease in

alkalinity of the concrete pore solution. Thus in case of carbonation induced corrosion; GCP does not give any significant conclusion

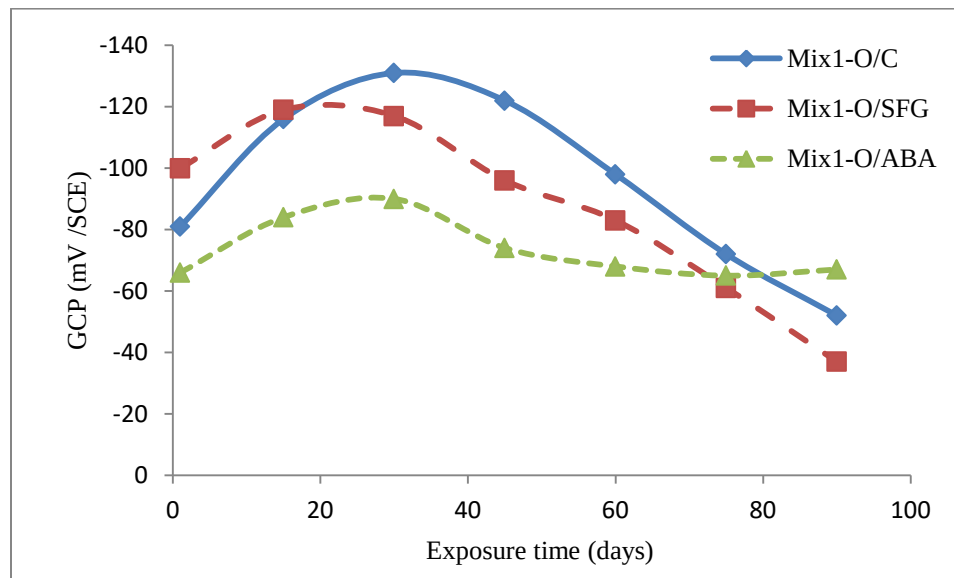


Fig.5.16. GCP variation with exposure duration in inhibitor treated OPC concrete prepared at w/c ratio of 0.43

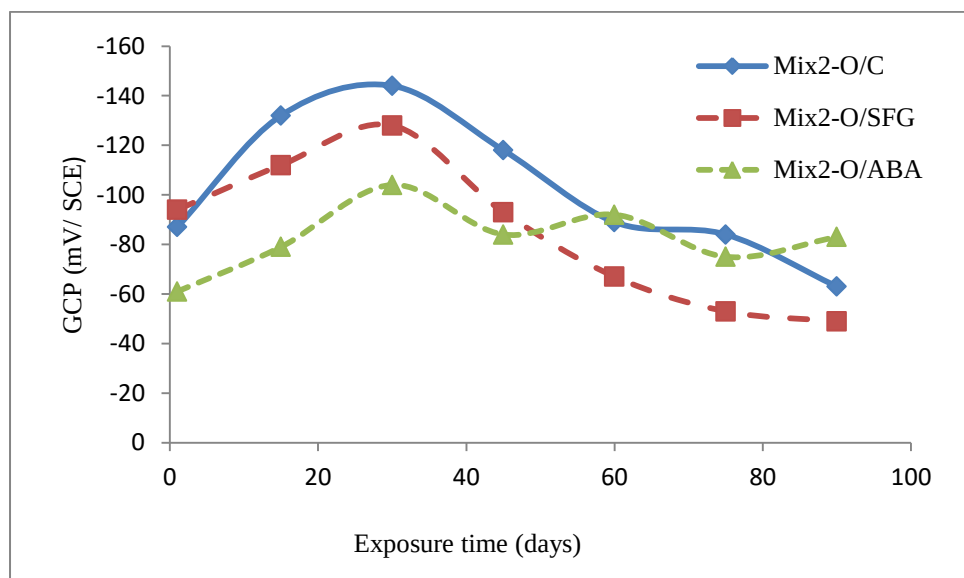


Fig.5.17. GCP variation with exposure duration in inhibitor treated OPC concrete prepared at w/c ratio of 0.52

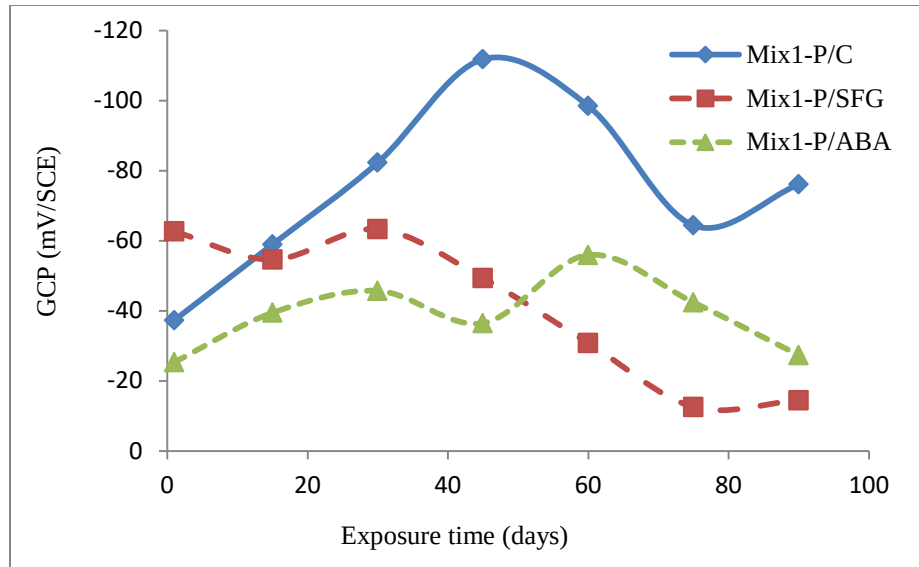


Fig.5.18. GCP variation with exposure duration in inhibitor treated PPC concrete prepared at w/c ratio of 0.43

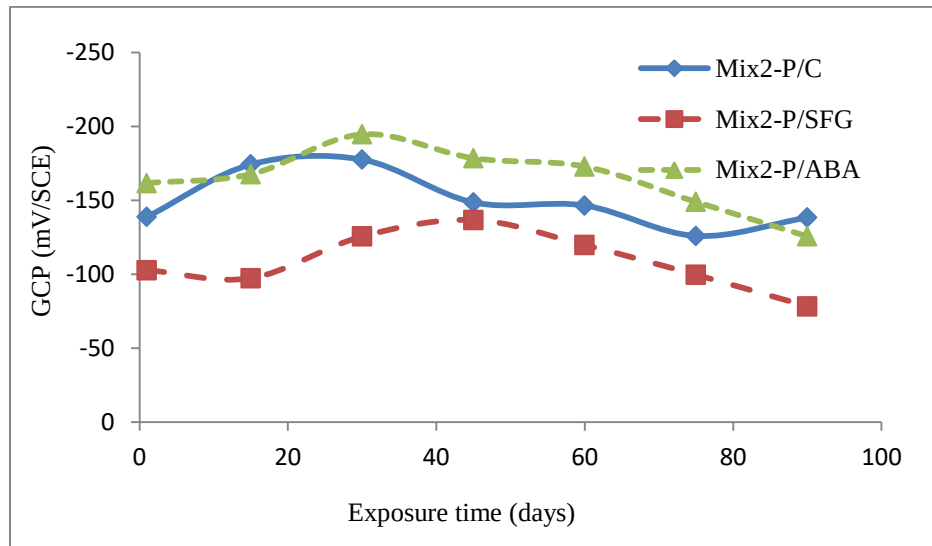


Fig.5.19. GCP variation with exposure duration in inhibitor treated PPC concrete prepared at w/c ratio of 0.52

5.6.2. Corrosion rate measurement by Tafel Extrapolation technique

Similar to the measurements of HCP and GCP, Tafel Extrapolation (polarization) measurements were made on prism specimens after every 15 days of exposure till the end of exposure duration of 90 days. The procedure adopted for the polarization scans has been described under Section 5.5.2. The typical polarization curve with pure Tafel behaviour has two

branches, namely anodic branch and the cathodic branch. In order to obtain the corrosion current density (i_{corr}), Tafel extrapolation is performed on the recorded polarization curves. The Tafel slope for the anodic and cathodic reactions is then obtained by extrapolating linear regions of the polarization curve. The point observed by extrapolating back both of the anodic and cathodic regions corresponds to the corrosion current density (i_{corr}) and the potential at which it lies refer to the corrosion potential (E_{corr}). The typical polarization curve and the intersection of extrapolated linear regions are shown in Fig.5.20.

In the present study, polarization scan was performed on prism specimens made with two types of cements, two w/c ratio and two types of inhibitor treatments. For polarization scans, the working electrode was polarized from the equilibrium potential at a sweep rate of 60mV/min. The variation in polarization curves obtained for all specimens at different exposure duration are presented in the following sections.

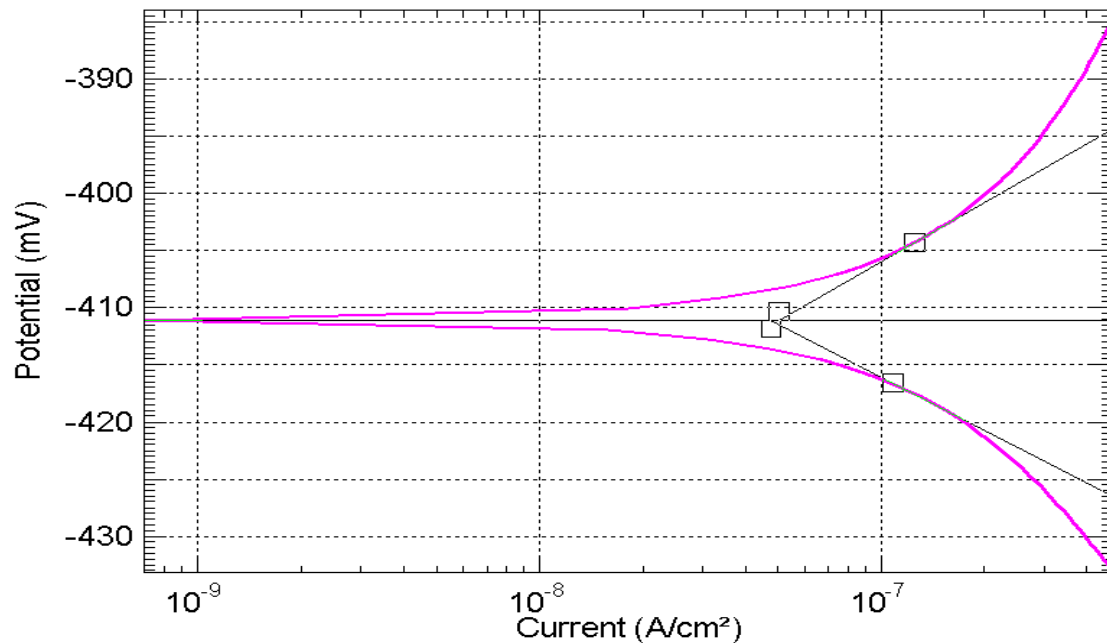


Fig.5.20. Typical polarization curve with pure Tafel behaviour

(a) Variation in polarization curves for control specimens

The typical polarization curves obtained for OPC and PPC concrete mixes at 90 days of exposure duration are shown in Figs. 5.21 and 5.22 respectively. From Fig. 5.21 it was observed that in Mix 2-O/C (made at w/c ratio of 0.52) more negative potential with higher i_{corr} value was

observed on comparison with Mix 1-O/C (made at w/c ratio of 0.43). However, in case of PPC concrete, potential and i_{corr} did not follow the similar trend. In this case, potential of Mix 2-P/C was nobler than the Mix 1-P/C potential; and the i_{corr} value observed in Mix 2-P/C was much higher than Mix 1-P/C (Fig. 5.22).

The variation in polarization curves with the exposure duration ranging from 1 day to 90 days (1 day, 15 days, 30 days, 45 days, 60 days, 75 days and 90 days) are presented in Appendix IA. The value of i_{corr} was obtained from the curves by extrapolation of linear regions of both anodic and cathodic branches of each curve. The values so obtained for OPC and PPC concretes at different exposure durations are presented in Figs. 5.23 and 5.24 respectively. From the figures, it is clear that i_{corr} value increases with the increase in exposure duration, irrespective of the w/c ratio of the mix and the type of cement used. However, with the same cement type, concrete containing higher w/c ratio was more prone to corrosion as compared to the mix prepared with lower w/c ratio. The observed trend in i_{corr} value was in good agreement with the HCP value measurement for the same prism specimens.

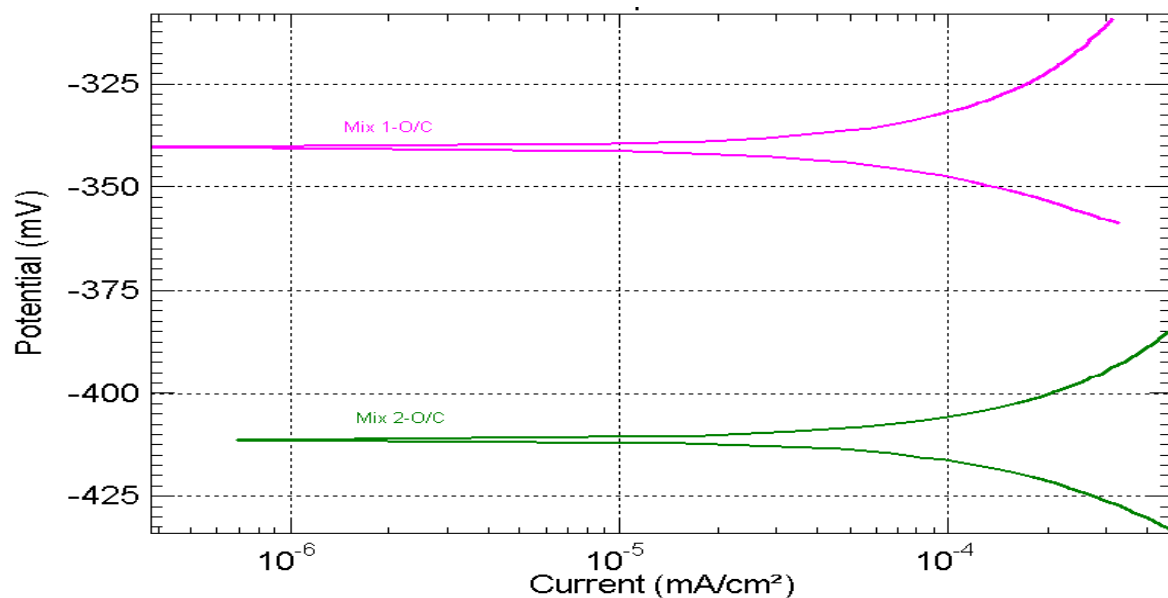


Fig.5.21. Polarization curves recorded in OPC concrete at the end of exposure duration of 90 days

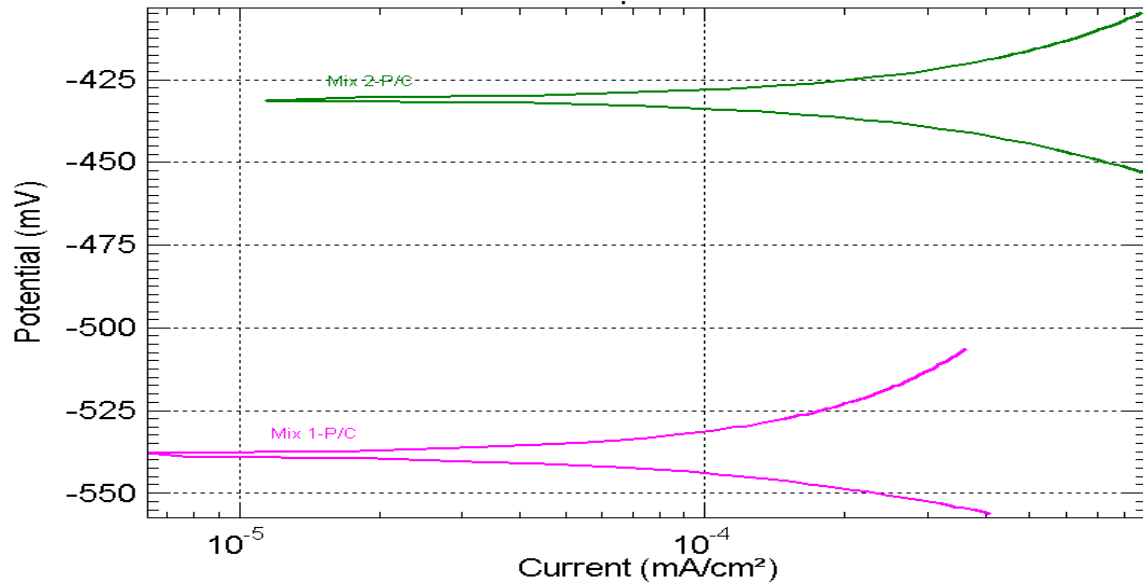


Fig.5.22. Polarization curves recorded in PPC concrete at the end of exposure duration of 90 days

From the Fig. 5.23 it was observed that in Mix 1-O/C, i_{corr} values lie below the passive limit ($0.1 \mu\text{A}/\text{cm}^2$) (Ngala et al., 2002; Pech-Canul and Castro, 2002) for the rebar during the entire exposure duration, indicating the presence of passivation film on the rebar surface. Measured HCP values also indicated an intermediate corrosion risk in Mix 1-O/C during 90 days of exposure duration. However, in Mix 2-O/C, the i_{corr} value reached the levels associated with depassivation ($0.1 \mu\text{A}/\text{cm}^2$) at 60 days of exposure duration, which indicates the breakdown of passivation layer present on the rebar surface. The corresponding HCP values for both mixes also supported the trend observed for i_{corr} values.

A similar effect of w/c ratio on the i_{corr} values was also observed for the PPC concrete specimens (Fig. 5.24). Mix 2 -P/C registered higher i_{corr} values as compared to Mix 1-P/C at all exposure durations. From the Fig. 5.24 it was clearly seen that in concrete made with PPC, both mixes (Mix 1-P/C and Mix 2-P/C) exceeded the passive limit during the exposure duration of 90 days. Comparing the performance of mixes made with different cement types, it can be observed that corrosion current of PPC concrete was higher than the corresponding value obtained for OPC concrete.

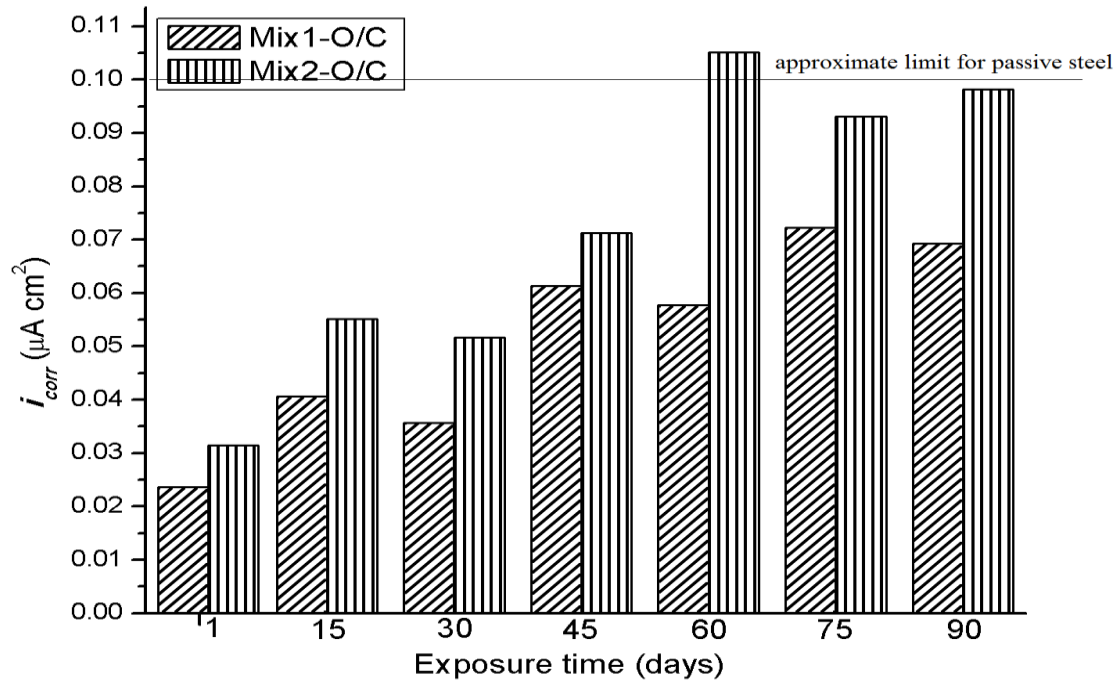


Fig.5.23. Variation in corrosion current density with exposure duration in OPC concrete

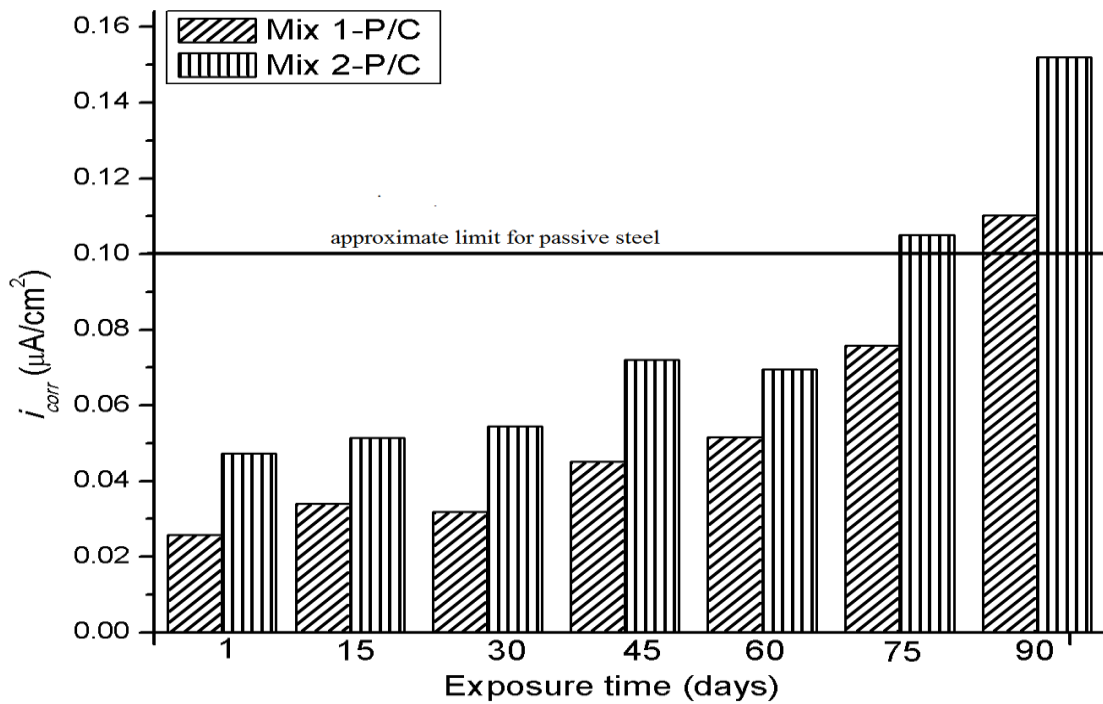


Fig.5.24. Variation in corrosion current density with exposure duration in PPC concrete

(b) Variation in polarization curves for inhibitor treated specimens

The typical polarization curves obtained at 90 days of exposure duration with and without corrosion inhibitor treatment for OPC and PPC concrete for both w/c ratios are presented in Figs. 5.25 to 5.28. Fig. 5.25 depicts that in Mix 1-O/C specimens, the anodic branch of the polarization curve starts at -340mV ; while for the inhibitor treated specimens, the anodic branch of the specimens starts at nobler potential. For inhibitor treated specimens, the anodic branch of the polarization curve start at -198mV potential for Mix 1-O/SFG, while the corresponding potential observed for Mix 1-O/ABA was -175mV . Along with this shift in the potential towards nobler side, a minimal passive behaviour in the anodic branch of the polarization curve was also observed in both the inhibitor treated specimens. Whereas, in control specimens observed activation control behaviour indicating loss of passive layer from the rebar surface was observed. From the obtained polarization curves (Figs. 5.26 -5.28) it was clearly seen that the treatment of concrete specimens with migrating type corrosion inhibitors led to shift in potential towards the less negative (nobler) side along with the reduction in i_{corr} value.

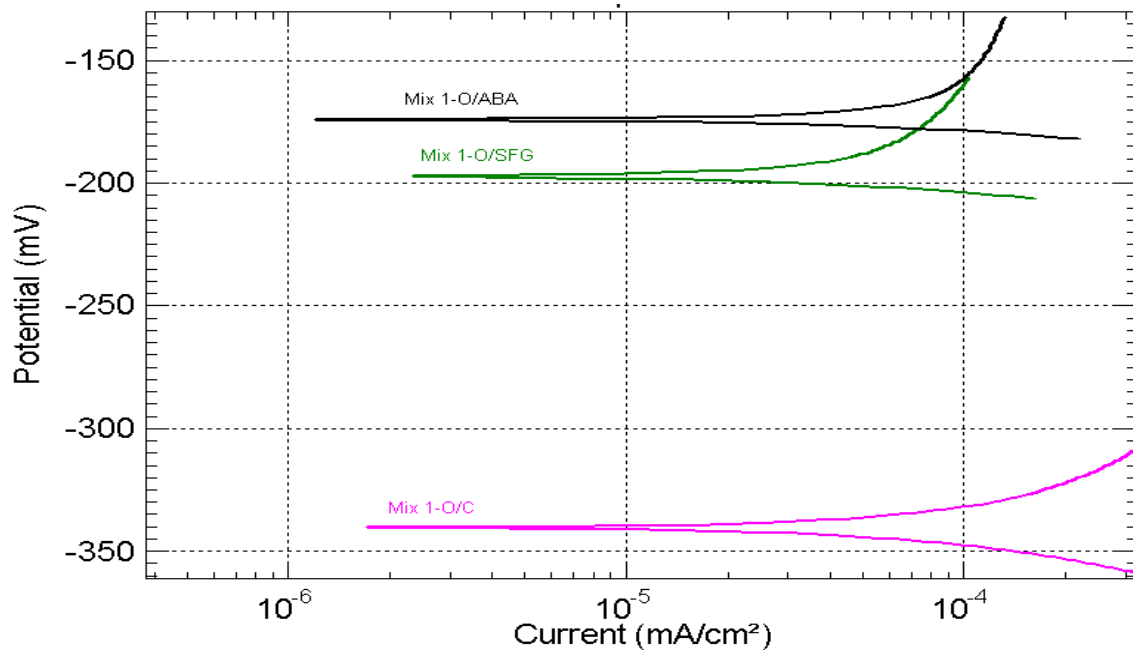


Fig.5.25. Corrosion inhibitors effect on polarization curves recorded in OPC concrete prepared at w/c ratio of 0.43 at 90 days of exposure duration

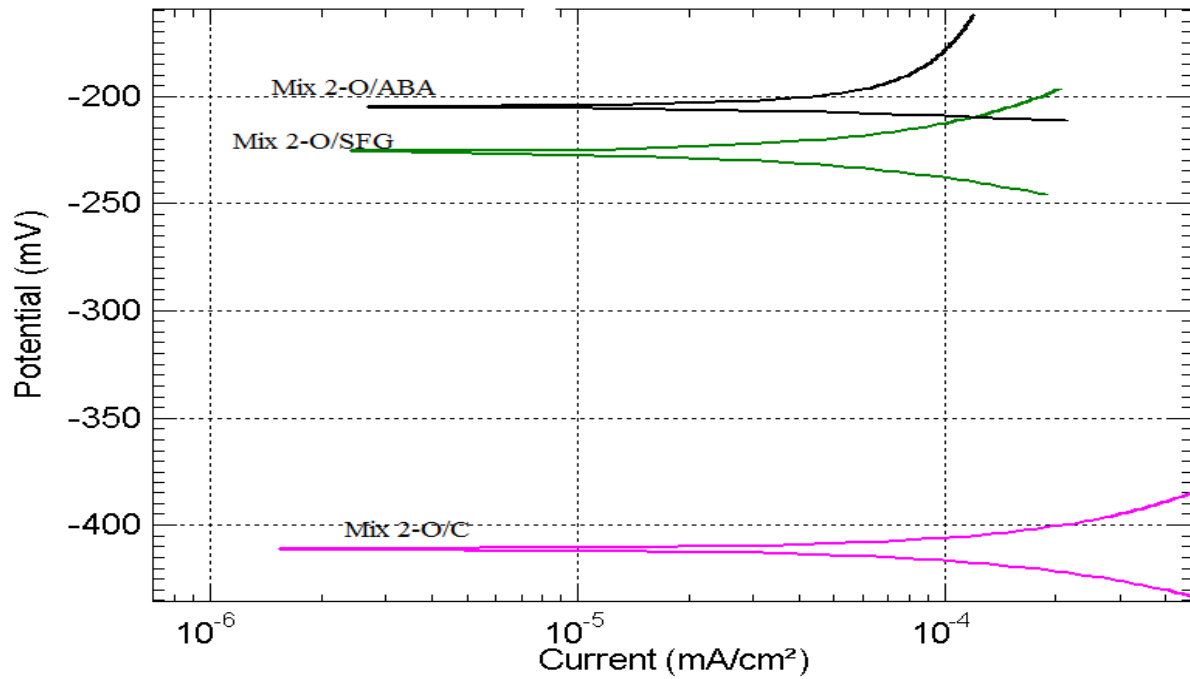


Fig.5.26. Corrosion inhibitors effect on polarization curves recorded in OPC concrete prepared at w/c ratio of 0.52 at 90 days of exposure duration

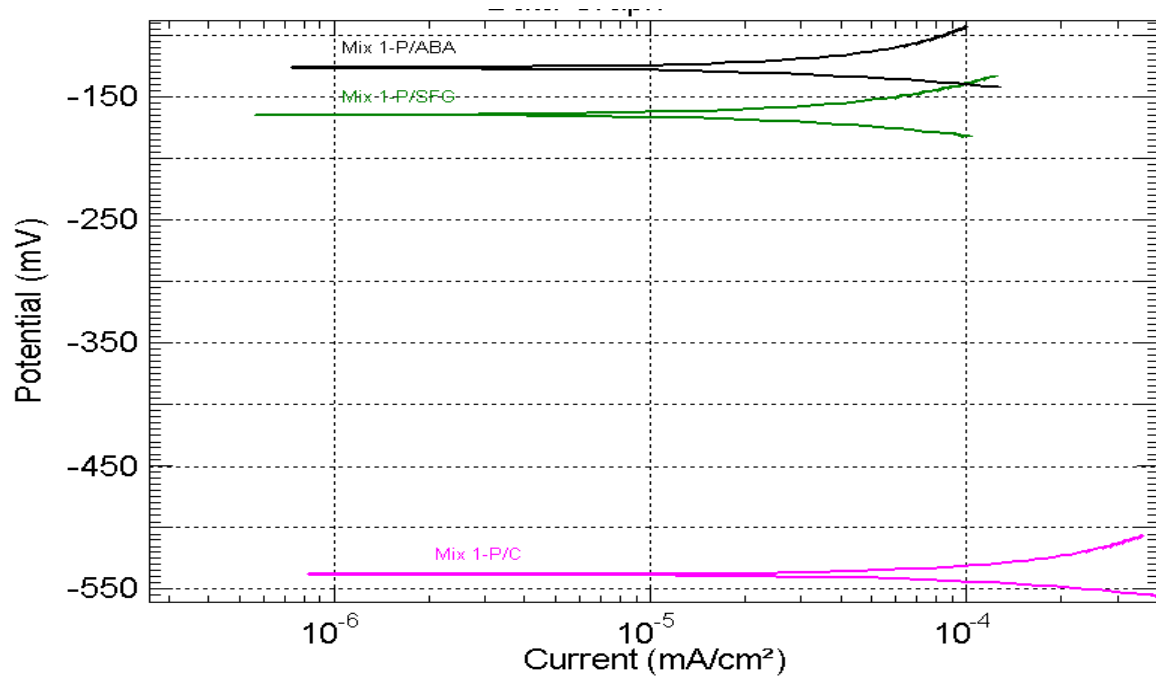


Fig.5.27. Corrosion inhibitors effect on polarization curves recorded in PPC concrete prepared at w/c ratio of 0.43 at 90 days of exposure duration

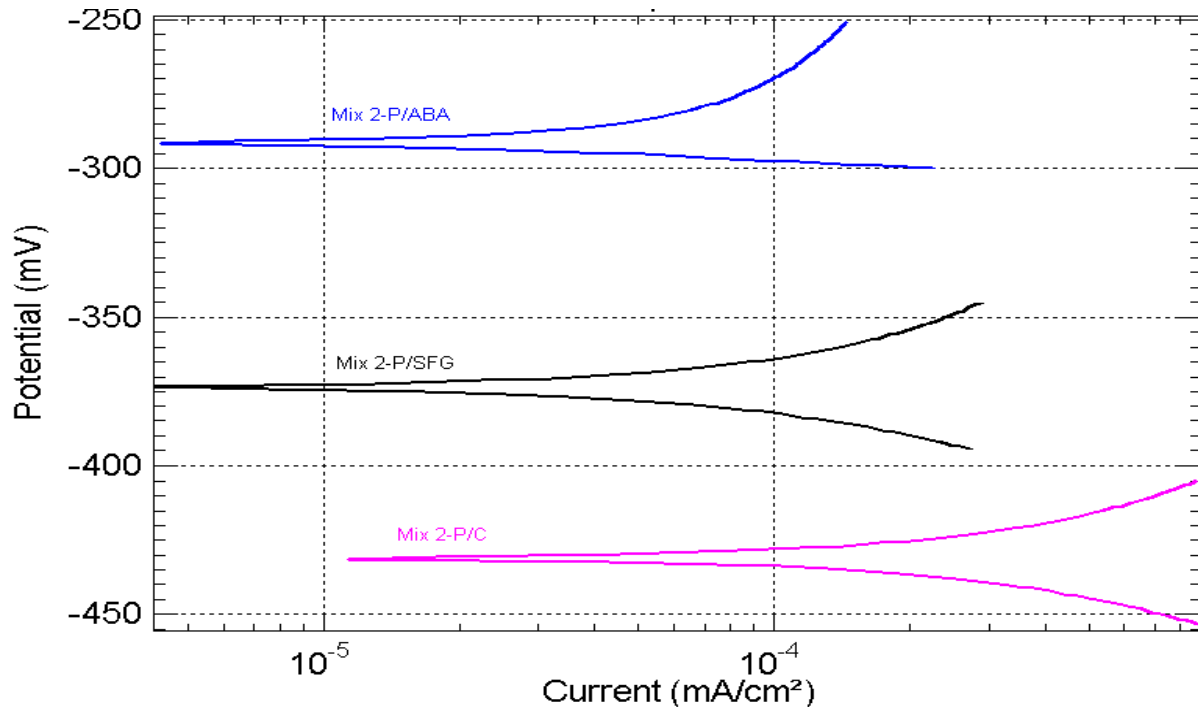


Fig.5.28. Corrosion inhibitors effect on polarization curves recorded in PPC concrete prepared at w/c ratio of 0.52 at 90 days of exposure duration

The polarization curves with the exposure duration from 1 day to 90 days (1 day, 15 days, 30 days, 45 days, 60 days, 75 days and 90 days) for all inhibitor treatment concrete specimens are presented in Appendix IIA. The i_{corr} value was then obtained by performing Tafel extrapolation on the recorded polarization curves. The variations in i_{corr} value, with inhibitor treatment at all exposure durations are presented in Figs. 5.29 -5.32 for both cement types and at both w/c ratio. As can be observed from the figures, the corrosion current density increases with increase in the exposure duration for control specimens; while for inhibitor applied specimens; i_{corr} became stable and remained within the passive limit till the end of exposure. It confirms that both inhibitors decreased the corrosion rate of the rebar when applied on the surface as migrating type inhibitors.

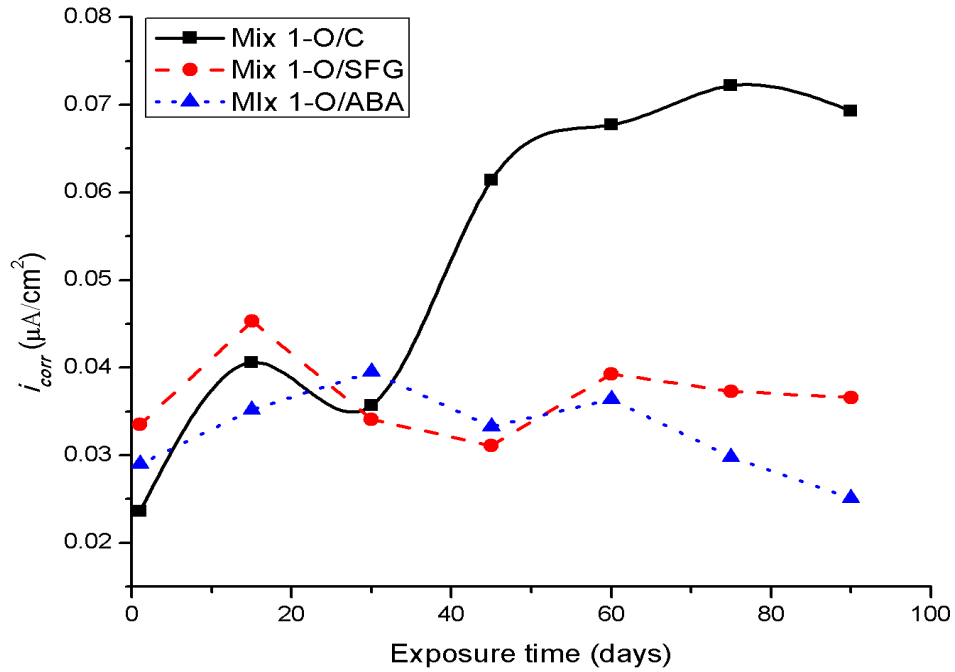


Fig.5.29. Variation in i_{corr} with exposure duration in inhibitor treated specimens of OPC concrete (w/c ratio of 0.43)

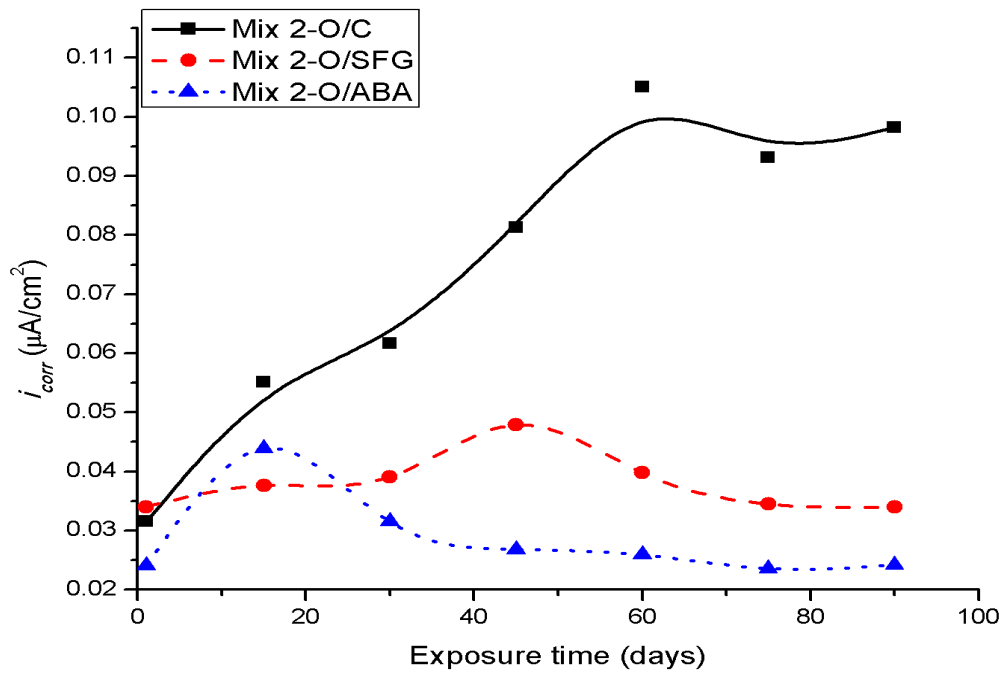


Fig.5.30. Variation in i_{corr} with exposure duration in inhibitor treated specimens of OPC concrete (w/c ratio of 0.52)

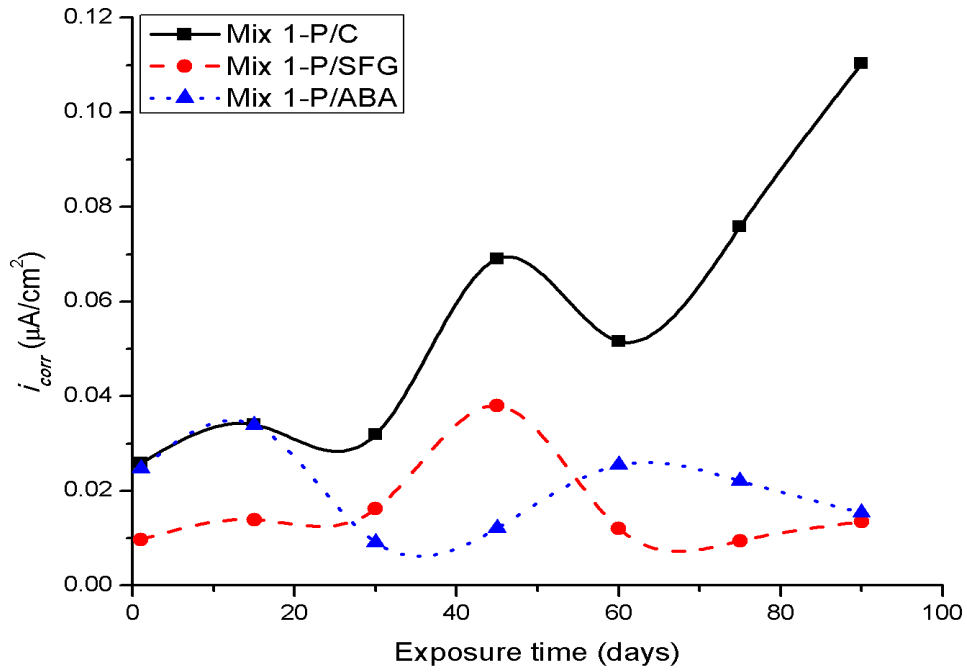


Fig.5.31. Variation in i_{corr} with exposure duration in inhibitor treated specimens of PPC concrete (w/c ratio 0.43)

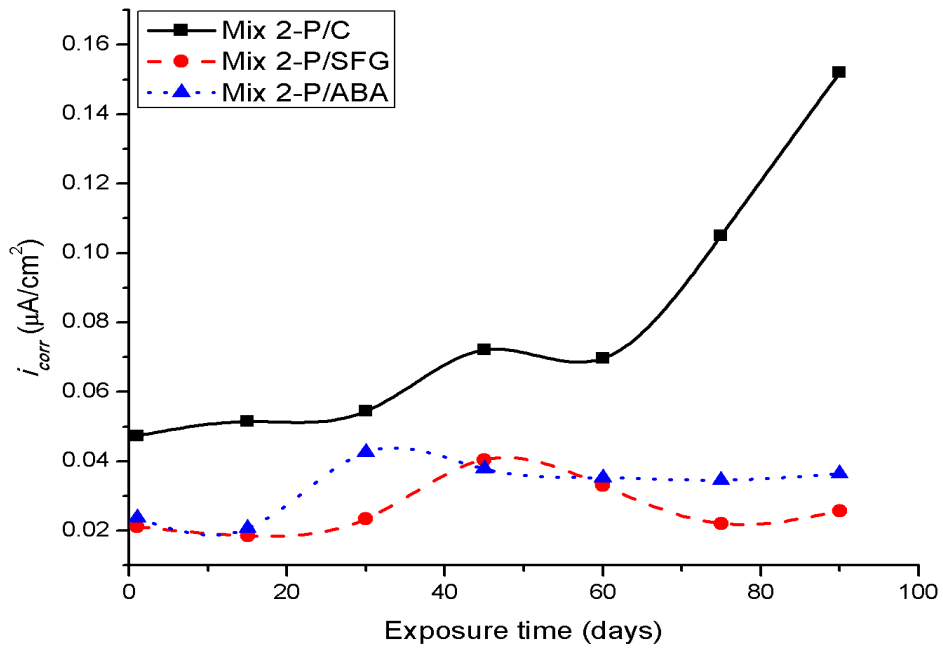


Fig.5.32. Variation in i_{corr} with exposure duration in inhibitor treated specimens of PPC concrete (w/c ratio of 0.52)

Fig.5.29 shows that during 30 days of exposure duration, the i_{corr} value varied approximately in the similar range for both the control as well as the inhibitor treated specimens. A small i_{corr} value during this duration of exposure indicates the presence of protective passive layer on the rebar surface. However, after this exposure duration, a large increase in an i_{corr} value was observed only in control specimens; while both inhibitors treated specimen showed stabilized i_{corr} behaviour till the end of exposure duration of 90 days. A reduction in i_{corr} value with the application of inhibitors indicates that the inhibitor has reached the rebar surface and formed a protective layer around the rebar surface. In the present study, transport and inhibition mechanisms of the inhibitors were not investigated. But literature suggested that, organic based inhibitors diffuse into concrete both in vapour and solution phase through capillary suction. On reaching the surface of the rebar, they get adsorbed at the metal surface forming a protecting barrier. The efficiency of these organic corrosion inhibitors is related to the presence of polar and weakly polar functional groups typically used in their formation (Tritthart, 2003; Nmai, 2004). The penetration of the inhibitors up to rebar and subsequent adsorption at the metal surface thus results in formation of protective layer on the surface of rebar, thereby, inhibiting corrosion. The protective layer inhibits both ferrous decomposition (anodic reaction) and restricts oxygen access (cathodic reaction) to the rebar. The formation of protective layer varies with the type of inhibitor used. The chemistry involved during the formation of protective layer on the rebar surface by the organic compound present in the inhibitor is discussed in the following sections.

5.6.3 Chemistry involved between inhibitors and rebar surface

The type of functional organic group present in the inhibitor influences the protective layer formation on the rebar surface. The chemistry so involved for both the inhibitors used in the present study is discussed hereunder.

(a) Inhibitor SFG: Inhibitor SFG is commercially available inhibitor and the manufacturer disclosed only the active ingredients of this inhibitor, while exact composition was kept secret. According to the manufacturer, inhibitor SFG consisted of aqueous solution of amino alcohols and a compound which forms salt with aminoalcohol. In amino alcohol based inhibitors, the main component is amino alcohol, which is a volatile component and migrates inside the concrete through gas diffusion. The second component of the inhibitor is generally an acid component. Thus, this inhibitor inhibits the corrosion through a two-fold mechanism; the film

forming amine component forms a bond with the rebar surface and the non polar tails of acid component forms a tight mesh that restricts the oxygen and moisture availability to the rebar surface. Therefore, this inhibitor acts as a mixed inhibitor because of the amine component and its associated radicals cover all the anodic and cathodic sites (Nmai, 2004; Wombacher *et al.*, 2004). The manufacture of this inhibitor also claimed through secondary ion mass spectroscopy that the amino acids get absorbed on the rebar surface by forming a bond between amino functional group and the hydroxide group on the rebar surface. This causes the formation of insoluble iron oxide complexes that retard the corrosion by stabilizing the oxide layer (Kepler *et al.*, 2000).

(b) Inhibitor ABA: Inhibitor ABA was a generic type inhibitor with a chemical formula $C_7H_7NO_2$. The structural representation of this compound is shown in Fig. 5.33 (a) while the interaction of this compound with the metal surface is shown in Fig. 5.33 (b). Literature suggested that presence of amine ($-NH_2$) and hydroxile ($-OH$) functional groups form a stable five or six membered chelate ring through bonding between these groups. Formation of chelates enhance and strengthen the chemisorptions of the inhibitors on the cation metal surface such as Fe^{+2} (as shown in Fig. 5.33 (b)) (Nmai, 2004). These chelates after being adsorbed on the rebar surface, provide a barrier to the ingress of aggressive agents to reach the rebar surface.

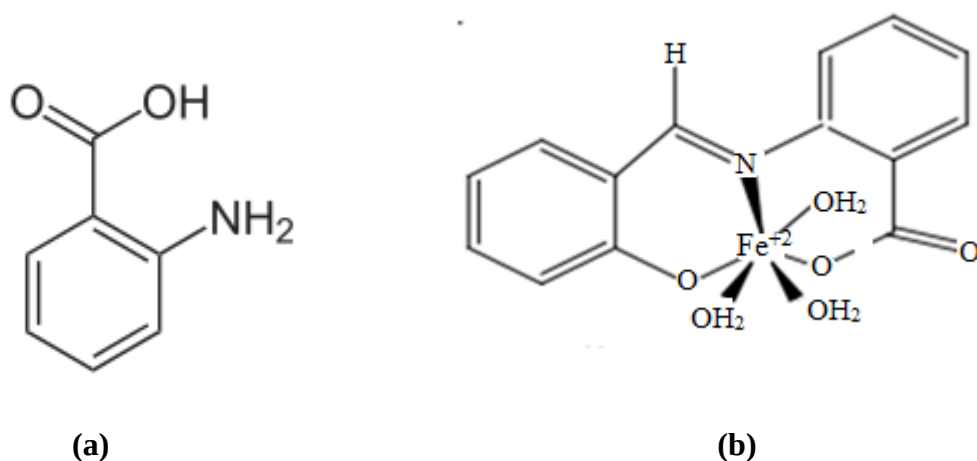


Fig. 5.33 (a) Structural representation of inhibitor ABA (b) Chelate ring formed between inhibitor ABA and rebar

From the above discussions, it can be concluded that both the inhibitors used in the present study are mixed type inhibitors. Both inhibitors influence the anodic and cathodic reaction sites, either by forming a chelate ring or adsorptive film on the rebar surface. Polarization curves and observed i_{corr} values also support this behaviour. It was reported that the anodic inhibitors reduce the corrosion rate of the rebar with the rise in corrosion potential; while cathodic inhibitors reduce the cathodic reaction rate with the shift in corrosion potential towards the active side. In other words, anodic inhibitors inhibit the rebar corrosion by reacting with the corrosion products and cathodic inhibitors inhibit the rebar corrosion by acting as an oxygen barrier to the rebar. On the other hand, the mixed inhibitors influence both the anodic and cathodic reaction sites (*Wombacher et al., 2004*). Observed decrease in i_{corr} value along with the shift in potential towards the nobler side indicates the nature of the inhibitors as mixed type inhibitors.

5.7 CLOSING REMARKS

In the present chapter, inhibitor effect on corrosion behaviour of the embedded rebar has been studied in terms of change in Half cell potential (HCP), Galvanic coupling potential (GCP) and Tafel extrapolation measurement. HCP results indicate that higher w/c ratio concrete mixes had higher value of HCP as compared to the concrete designed for lower w/c ratio, with the same cement type. Cement type also has a great influence on the corrosion behaviour of the embedded rebar under carbonation induced corrosion. PPC concrete shows greater than 90% risk of corrosion after 45 days of exposure duration; while in OPC concrete HCP values represented intermediate corrosion risk. Towards the end of exposure duration, more active potential (-400mV/SCE) was shown by PPC concrete while in OPC concrete the potential was limited to -295mV/SCE . Similar to the behaviour observed for HCP values, corrosion current density (i_{corr}) values also indicated lesser resistance of PPC concrete as compared to the OPC concrete towards the carbonation induced corrosion. At the end of exposure duration of 90 days, increases in i_{corr} value with the PPC concrete was to be reported as 59.16% (0.43 w/c ratio) and 54.78% (0.52 w/c ratio) as compared to corresponding OPC concrete.

The application of the inhibitors to the concrete surface reduced the corrosion risk of the rebar as compared to the respective control specimens. In OPC concrete, application of inhibitors

(SFG and ABA) initially raised the potential towards the more negative potential side till 30 days of exposure duration, thereafter a shift in potential towards nobler potential side was observed. In PPC concrete, less negative potential reported with inhibitor SFG (-160mV/SCE) and ABA (-213mV/SCE) as compared to corresponding control specimens (-401mV/SCE), indicate the effectiveness of these inhibitors in carbonated environment. In all inhibitor treated specimens, lower i_{corr} was observed as compared to corresponding control specimens after 30 days of exposure duration. The treatment of OPC concrete specimens with inhibitor SFG registered 47-65% decrease in i_{corr} value, while 63-75% decrease was registered with inhibitor ABA at the end of exposure duration of 90 days. Similarly, in PPC concrete a 83-88% decrease in i_{corr} value was observed with the inhibitor SFG and a 75-86% decrease was reported with inhibitor ABA.

Reduction in i_{corr} value with the application of inhibitors confirmed that the inhibitors had reached the rebar surface and formed a protective layer around the rebar surface. The chemical interaction between the inhibitors and the rebar surface showed that both the used inhibitors are mixed type inhibitors. Both inhibitors influence the anodic and cathodic reaction sites, either by forming a chelate ring or adsorptive film on the rebar surface. Thus, both the inhibitors are capable of decreasing the corrosion rate of the rebar when applied to the surface as migrating type inhibitors.

CHAPTER 6

INVESTIGATION ON EFFECTIVENESS OF INHIBITORS THROUGH ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

6.1 GENERAL

Electrochemical Impedance Spectroscopy (EIS) involves analysis of the material by applying an alternating current (AC) signal to a sweep of frequencies (*Braganca et al., 2014*). Impedance is a measure of the ability of a circuit to resist the flow of electrical current. Since rebar corrosion is also an electrochemical process, this technique can be effectively used to monitor the behavior of steel embedded in concrete. Electrochemical impedance gives information regarding the corrosion kinetics, corrosion mechanism, morphology of corrosion and conditions of the rebar due to corrosion (*Ribeiro and Abrantes, 2016*). It also has the capability of studying the charge dynamics in the bulk and the interfacial regions of solid and liquids (*Dong et al., 2014*).

Recently, EIS has become increasingly popular as a non-destructive technique (NDT) for investigating the electrochemical behaviour of complex heterogeneous systems, like reinforced concrete. EIS has been used by various researchers as an effective method to provide information regarding microstructure of concrete, corrosion rate and reaction at the steel-concrete interface (*Dong et al., 2014; Dhouibi et al., 2002; Ismail and Ohtsu, 2006; Duarte et al., 2014; Montemor et al., 2002; Ribeiro and Abrantes, 2016; Braganca et al., 2014; Criado et al., 2012; Trabanelli et al., 2005*).

Although EIS has been widely used for analyzing corrosion rate and the resulting mechanism at the steel-concrete interface (*Dhouibi et al., 2002; Ismail and Ohtsu, 2006; Duarte et al., 2014*), little research has been performed with regards to prediction of carbonation behavior of concrete by using EIS (*Dong et al., 2014*). As EIS can be performed in-situ also, thus there is a need to look into the potential of EIS in carbonation depth prediction. Besides, EIS may predict the onset of de-passivation of rebar as well.

In the present study, the effectiveness of migrating type corrosion inhibitors in carbonated environment is assessed by EIS technique, along with the previously discussed

electrochemical techniques viz. half-cell potential and tafel extrapolation technique. In this chapter, the data obtained by EIS is analyzed and correlated with the properties of concrete and the behaviour of the embedded rebar.

6.2 MATERIALS AND EXPERIMENTAL PROGRAM

The major materials used for the experimental programme include two types of cement (OPC and PPC), two types of corrosion inhibitors (SFG and ABA), coarse aggregates, fine aggregates and TMT steel rebar. The details properties of these materials have already been presented in the Chapter 5 under Section 5.3. The purpose of the present study was to correlate the EIS parameters with the progressive properties of concrete and rebar. Since, monitoring by EIS technique takes longer time than other electrochemical techniques; it was decided to reduce the test variables of test matrix for this study. Considering this, the EIS studies were conducted for concrete mix designed for w/c ratio of 0.43 only. The resultant test matrix is schematically represented in Fig.6.1.

6.3 SPECIMEN PREPARATION AND EXPOSURE CONDITIONS

EIS measurements were made on the same prism specimens which were used for the measurement of Half cell potential (HCP) as reported in Chapter 5. Briefly, EIS measurements were made on prism specimens of size $300 \times 300 \times 150$ mm with three rebars embedded into it; two rebars were placed at the bottom with a clear cover of 25 mm and one rebar was placed at the top with clear cover of 5 mm i.e. effective cover of 11mm. The detailed information regarding preparation of the rebar and prism specimens has already been explained in Chapter 5 under the Section 5.4.2 and 5.4.3 respectively. The prepared prism specimens are shown in Fig.5.5. After 15 days of casting, the two inhibitors namely, SFG and ABA were applied at the rate of 500 g/m^2 on the top surface of the prism specimens in three consecutive layers. With two types of cement, two inhibitors applications and two replicates, a total of 12 prism specimens were used for the EIS measurements. The exposure conditions were kept similar to the HCP and Tafel extrapolation measurement and details has already been presented in Chapter 5 under Section 5.4.4. The detail and nomenclature of prism specimens used for EIS measurements are presented in Table 6.1.

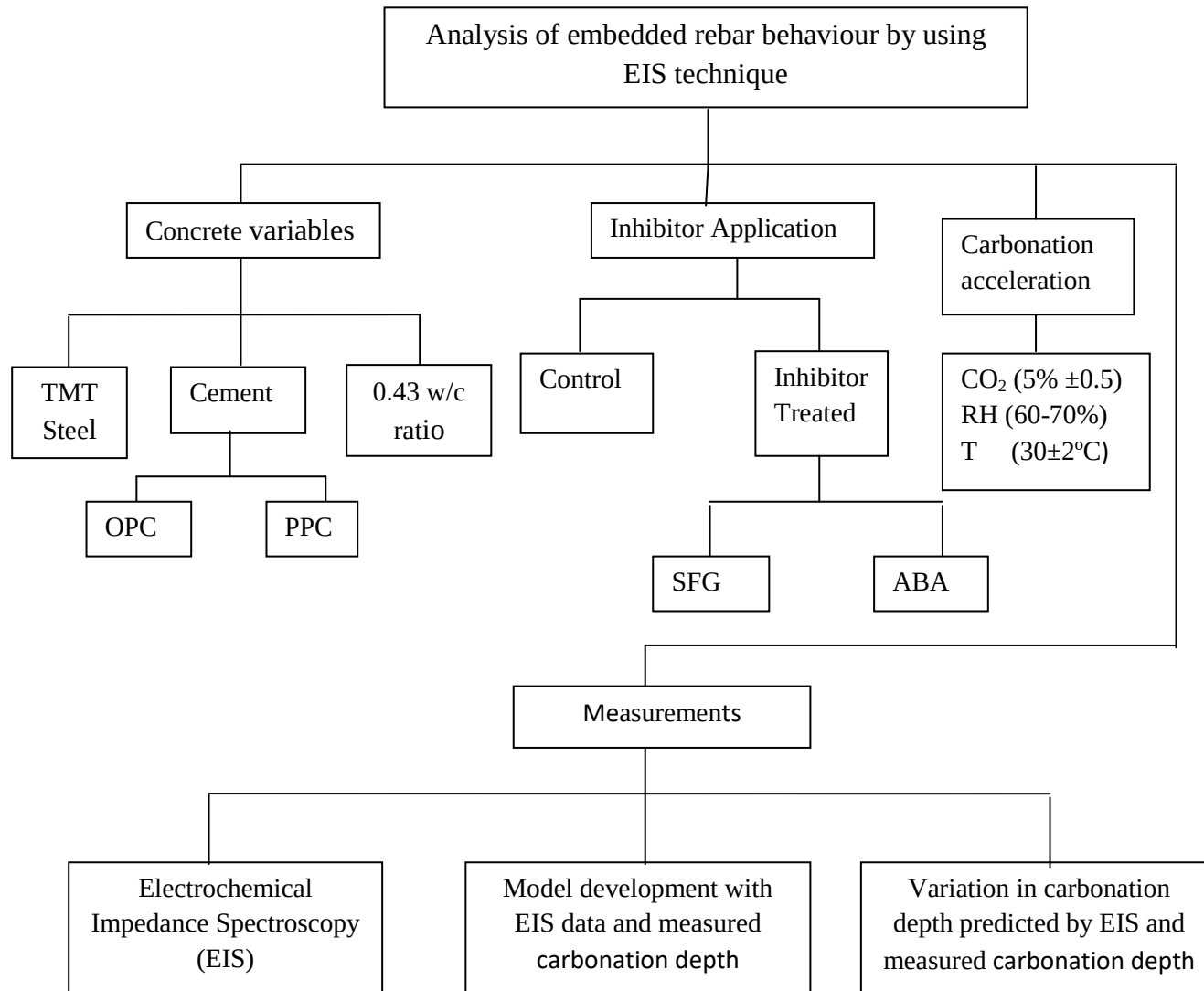


Fig.6.1. Schematic illustration for EIS measurement against carbonation induced corrosion with corrosion inhibitors

Table 6.1 Nomenclature of prism specimens used for EIS measurements

Mix (w/c ratio)	Cement type	Inhibitor treatment	Nomenclature
Mix 1 w/c 0.43	OPC	-	Mix 1 - O/C
		SFG	Mix 1 - O/SFG
		ABA	Mix 1 - O/ABA
	PPC	-	Mix 1 - P/C
		SFG	Mix 1 - P/SFG
		ABA	Mix 1 - P/ABA

6.4 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) MEASUREMENTS

EIS studies were performed on prism specimens, at every 15 days of exposure till the end of test duration of 90 days. The EIS measurements were carried out with the help of Advanced Corrosion Monitoring (ACM) field machine (serial no. 1463). Wherein, a Guard ring probe assembly was used for the measurements. The guard ring probe consisted of inbuilt two concentrically placed zinc electrodes and three platinized titanium reference electrodes. In order to provide ionic conduction, a 5mm thick wet sponge was placed between top surface of prism specimen and the guard ring as shown in Fig. 6.2. The wetted sponge was kept on the prism specimen at least two hours prior to the measurement in order to ascertain uniform moisture content on the cover concrete. Also, all the measurements were performed using the same arrangement in order to minimize the error induced by geometry. The experimental set up used for EIS measurement is shown in Fig. 6.2.

During the EIS measurements, an AC signal was supplied with a 25mV RMS for a frequency range of 100kHz to 10mHz with five points obtained per decade. The frequency range for the experiments was decided based on through literature survey after it was observed that the similar frequency range was used by previous researchers for studying corrosion mechanism in reinforced concrete (*Dhouibi et al., 2002; Ribeiro and Abrantes, 2016; Dong et al., 2016; Liu et al., 2017*).



Fig.6.2. Experimental setup for EIS measurement

6.5 ANALYSIS OF EIS DATA

The EIS data was obtained in the form of Nyquist and Bode plots, which was further analysed by using equivalent circuits. The EIS results in the form of both plots and equivalent circuits can be interpreted in terms of the assumed mechanisms occurring in RC. Both these representations and the correlations with the assumed mechanisms are discussed in detail in Chapter 2 under Section 2.11.4 and are briefly, discussed in the following sections:

6.5.1 Nyquist and Bode plots

According to ASTM G3 (ASTM, 2004) EIS data can be represented in two formats, viz. Nyquist plot and Bode plot. Nyquist plot corresponds to the graph of real and imaginary part of impedance, $Z = Z' + jZ''$ (where Z' is the real part and Z'' is the imaginary part), plotted at different frequencies. The Bode plot format further has two representations i.e. the Bode magnitude plot and the Bode phase angle plot. In the Bode magnitude plot, the base-ten logarithm of frequency is plotted on abscissa and modulus $|Z|$ or base-ten logarithm of impedance magnitude is plotted on ordinate (Ismail and Ohtsu, 2006). In the Bode phase angle plot, negative of the phase angle is plotted against base-ten logarithm of frequency. Typical Nyquist and Bode plots in both formats with single time constant have been presented in Chapter 2 in the Fig. 2.9.

In the RC structures, a single time constant could not be applied to interpret the EIS spectra, due to complexity at the steel-concrete interface. It is due to simultaneous occurrence of several overlapping phenomena and presence of noise in the measurement (*Ribeiro and Abrantes, 2016*). The most commonly observed Nyquist plot in RC structures has three distinct features (A, B, C), as shown in Fig. 6.3 (*Ford et al., 1998*). The high frequency feature 'A', generally observed in kHz range, is related to the bulk properties of the concrete. Feature B, observed in Hz frequency range, corresponds to the corrosion products formed in the pores of the cement paste. The lowest frequency feature C, observed in the mHz frequency range, is associated with the formation of extremely resistive product layer on the rebar surface (*Ribeiro and Abrantes, 2016; Ford et al., 1998*). Generally, feature B gets besieged by feature C in the plot. The existence of feature B can be emphasized by the deviation of the plot from the fitting line for arc C (as shown in Fig.6.3). The deviation of the actual curve from the straight line indicates the presence of feature B.

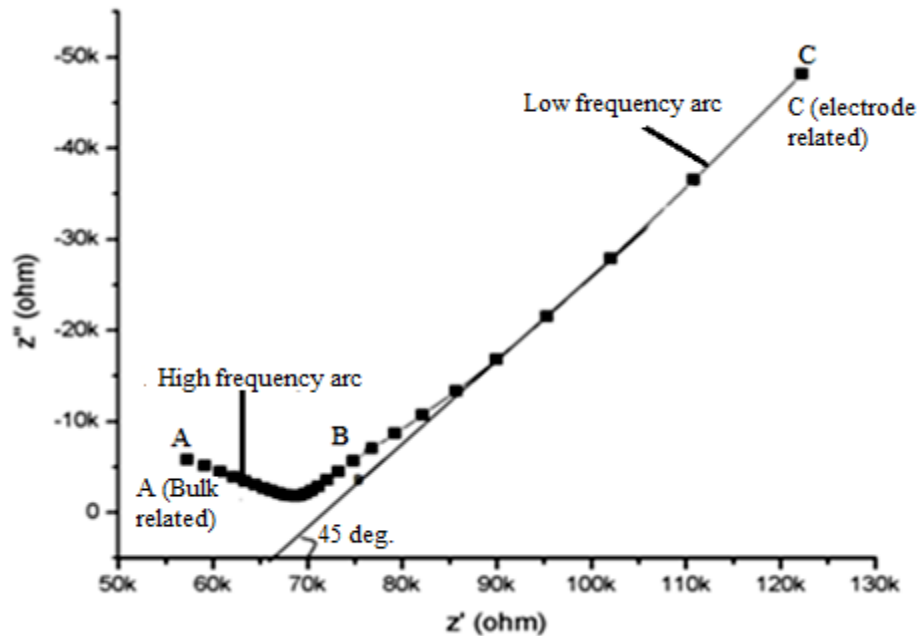


Fig.6.3. Nyquist plot with three distinguish features (A,B,C)

6.5.2 Equivalent electrical circuits

In order to interpret obtained impedance plots, an equivalent circuit is generally applied and in the present study, ZMAN software was used for mathematical analysis of the EIS spectra. The most basic equivalent circuit for the EIS plot is Randles circuit; which consists of resistance

R_e in series with the parallel combination of capacitance C and resistance R_1 as shown in Fig.6.4. In this circuit, R_e refers to the electrolytic resistance of pore solution, whereas, R_1 and C corresponds to the resistance and double layer capacitance respectively at the concrete-rebar interface (*Ribeiro and Abrantes, 2016*). However, due to complexity of the reinforced concrete interface, basic Randles circuit could not be applied to interpret the impedance spectra. The physical model that describes a typical steel-concrete interface is presented in Fig. 6.5. It clearly shows that steel-concrete interface consists of various interface layers such as layer of compact iron oxide film and interfacial film adjoined by the concrete matrix. The interfacial layer consists of Ca(OH)_2 , CaCO_3 , and other cement hydration products deposited on the surface of steel (*Ramachandran and Beaudoin, 2000*).

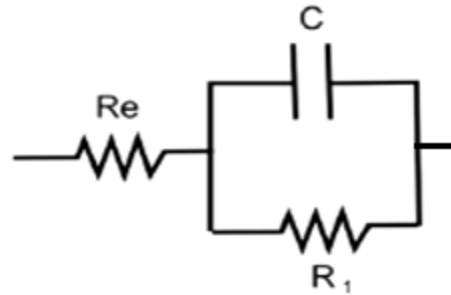


Fig.6.4. Simple equivalent Randles circuit (*Ribeiro and Abrantes, 2016*)

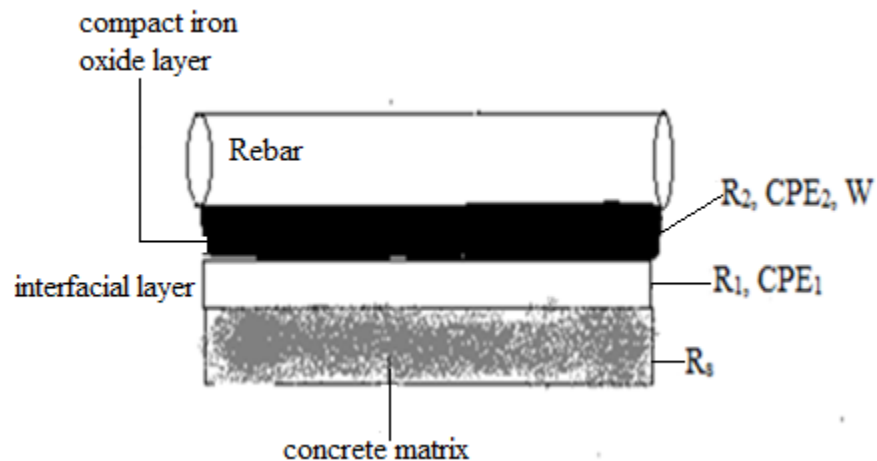


Fig.6.5. Physical model to describe steel concrete interface

From Fig. 6.5, it can be pronounced that since the corrosion process itself involves several physical processes, therefore, the equivalent circuits used to interpret EIS data has to be composed of several circuit elements. Previous researchers (*Dong et al., 2014; Ismail and Ohtsu, 2006; Duarte et al., 2014; Montemor et al., 2002; Ribeiro and Abrantes, 2016; Braganca et al., 2014; Criado et al., 2012*) have proposed several equivalent circuits to model the different stages of reinforced concrete corrosion process which are already discussed in Chapter 2 under Section 2.11.4. In the present work also, several models were tried to obtain the best fit equivalent circuit. Two such equivalent electrical circuits (EEC) that fitted best for the experimental data are presented in Fig. 6.6. Out of the two chosen equivalent circuits, EEC-A represents single time constant while EEC-B accounts for two time constants. In both these equivalent circuits, R_s stands for electrolytic resistance of pore solution in concrete, which is followed by a series of impedances that can be related to the steel-concrete interface. Impedance is further composed of a constant phase element (CPE) and a resistive element. The constant phase elements are widely used in impedance data fittings to allow dispersed semi-circle. The dispersion in the semi-circle is caused due to surface reactivity, surface in-homogeneity, roughness, porosity of concrete, irregularities on the rebar etc (*Dong et al., 2014; Monticelli et al., 2011; Braganca et al., 2014; Criado et al., 2012; Ramachandran and Beaudoin, 2000*). The impedance (Z) of a constant phase element depends on the angular frequency as:

$$Z_{CPE} = \frac{1}{Y(j\omega)^\alpha} \quad \dots (6.1)$$

Where Y is an admittance, ω is the angular frequency, $j^2 = (-1)$, α represents the degree of perfection of the capacitor and a measure of the arc depressed below the real impedance axis and lies in the range of $0 < \alpha < 1$. When $\alpha = 0$, CPE is a pure resistor and when $\alpha = 1$, CPE is pure capacitor (*Fajardo et al., 2014; Criado et al., 2012*). Sometimes, Warburg element is also introduced in the impedance to account for diffusion of ionic species.

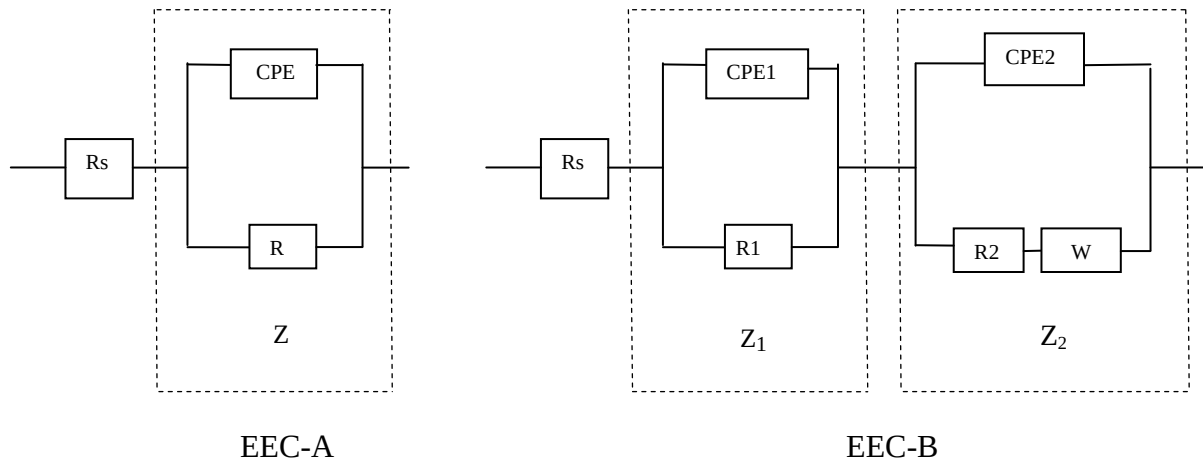


Fig.6.6. Equivalent circuits used to fit the impedance data

EEC-A consists of R_s which corresponds to the electrolytic resistance of pore solution in concrete and an impedance Z which corresponds to the Faraday's procedure between the interfacial films and the rebar. In this circuit, impedance Z is composed of a constant phase element (CPE) between the interfacial film and steel and resistance (R) caused by charge transfer procedure within rust product on the surface of the rebar. Thus, the impedance Z observed in lower frequency region corresponds to the corrosion reaction ($\text{Fe}^{+2}/\text{Fe}^{+3}$) that occurs at the rebar surface.

EEC-B accounts for two time constants. In this circuit, first impedance (Z_1) corresponds to Faraday's procedure inside the concrete; while the second impedance (Z_2) corresponds to Faraday's procedure between the interfacial films and the rebar. Impedance Z_1 consists of a constant phase element (CPE_1) between the solid/ liquid phase in the bulk concrete and the resistance (R_1). While, impedance Z_2 is composed of a constant phase element (CPE_2) between the interfacial film and steel, resistance (R_2) caused by the charge transfer procedure within rust product on the surface of the rebar and Warburg element (W). Warburg element has been introduced in low frequency region to account for diffusion of ionic species at the electrode/electrolyte interface. Generally, a Warburg element is connected in series with the charge transfer resistance, due to the reason that the response from Faradic process occurs at the interface (*Ribeiro and Abrantes, 2016*). The impedance elements (CPE_1 , R_1) in higher frequency region correspond to the bulk properties of the concrete, while impedance elements (CPE_2 , R_2 ,

W) in lower frequency region correspond to the corrosion reaction ($\text{Fe}^{+2}/\text{Fe}^{+3}$) that occurs at the rebar surface.

6.6. RESULTS AND DISCUSSION

The EIS plots for all specimens were recorded at 1, 15, 30, 45, 60, 75 and 90 days of exposure. The changes in the plot and the corresponding changes in the properties of various elements in the equivalent circuit are discussed in the following sections:

6.6.1 Impedance behaviour of rebar in OPC concrete

Nyquist and Bode plots recorded in OPC control and inhibitors treated specimens with experimental (raw) and fitted data are presented in Figs. 6.7 - 6.15. In all these figures, Nyquist and Bode plots corresponding to 1, 30, 60 and 90 days of exposure are presented while other plots obtained at 15, 45, 75 days of exposure are omitted as they were following similar trends. In all impedance plots presented in the succeeding sections, the discrepancy between the raw and fitted data is less than 5%, indicating that the adopted equivalent circuits describe the steel-concrete interface effectively. However, the analytical results from the equivalent circuit are provided for all exposure durations in Appendix B.

(a) Impedance spectra for Control specimens

Fig. 6.7 depicts the impedance spectra recorded in Mix 1-O/C at different carbonation exposure durations. From Fig. 6.7, it was observed that the Nyquist plots have two capacitive arcs except for the plot obtained at 1 day of exposure duration. As has already been explained, the first capacitive arc (observed between frequency range of 10kHz to 10Hz) corresponds to bulk properties of the concrete, while the second capacitive arc (observed between frequency range of 10Hz to 10mHz) corresponds to electrode related features (*Ford et al., 1998*). During the initial exposure duration of 1 day, first capacitive arc in high frequency range was not observed. It indicates the presence of natural pores and highly conductive OH^- ions at the steel-concrete interface. A large second capacitive arc observed at low frequency range at 1 day of exposure indicates the presence of an extremely resistive passive layer on the rebar surface because of high pH of the pore solution (*Jamil et al., 2004, Ford et al., 1998*). The corresponding Bode magnitude plot is shown in Fig. 6.8. In Bode magnitude plot the behavior of the specimen also took a shift from resistive (high frequency) to capacitive side (low frequency) at 1 day of

exposure duration. The observed capacitive behavior suggests the presence of homogeneous protective layer on the rebar. The corresponding phase angle has also attained a value of -54° at 1 day of exposure suggesting passive behaviour of the rebar (Fig. 6.9).

Fig. 6.7 shows that the increase in exposure duration leads to increase in high frequency arc with the corresponding decrease in low frequency arc. The increase in high frequency arc is attributed to the alteration in chemical composition at the interfacial layer adjoining the concrete matrix. Progressive carbonation leads to the conversion of Ca(OH)_2 into the CaCO_3 , which has very low solubility and gets precipitated as a solid matrix in the pores present in concrete, hence densifying the microstructure of concrete and decreasing the porosity of concrete (*Montemor et al., 2002*). *Dong et al. (2014)* and *Riberio and Abrantes (2016)* also observed the increase in radius of high frequency arc with progressive carbonation. Decrease in low frequency arc with the increase in exposure duration accounts for continuous de-passivation of the resistive oxide layer initially present on the rebar surface. Observed increase in radius of high frequency arc with enhancement in exposure indicates densification caused by the progressive carbonation of concrete, while decrease in low frequency arc indicates loss of passive layer at the rebar surface.

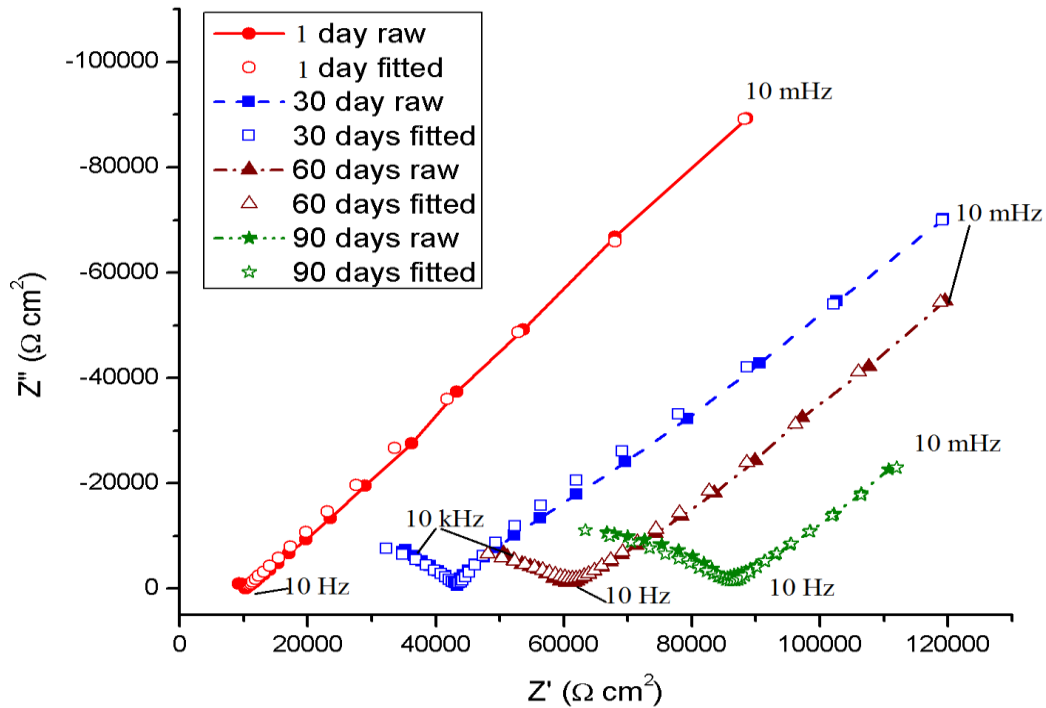


Fig.6.7. Nyquist plot variation with carbonation exposure duration (Mix 1-O/C)

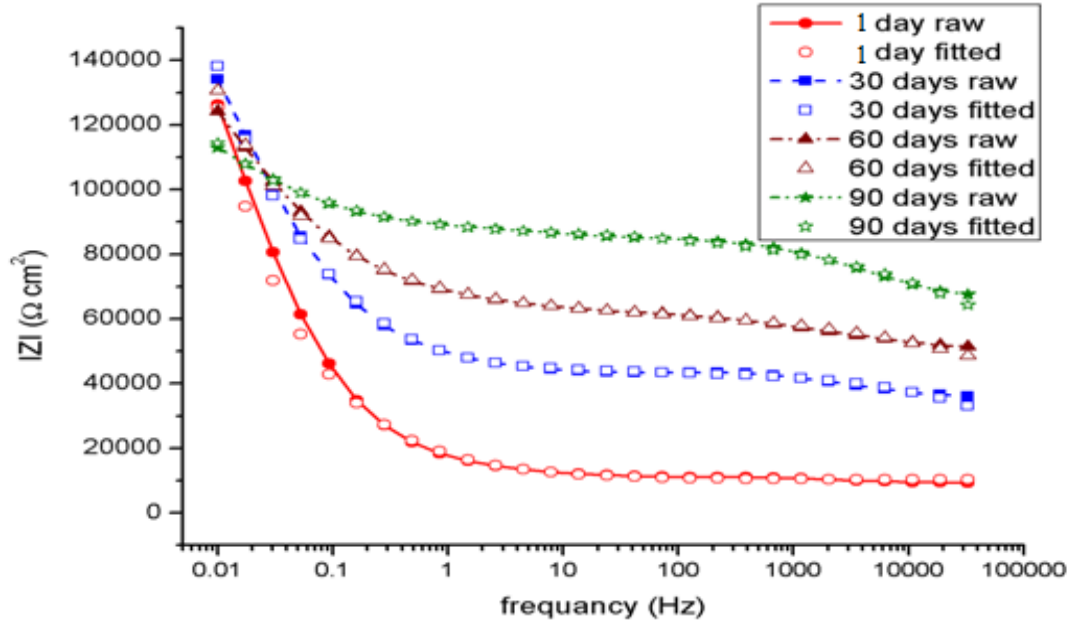


Fig.6.8. Bode magnitude plot variation with carbonation exposure duration (Mix 1-O/C)

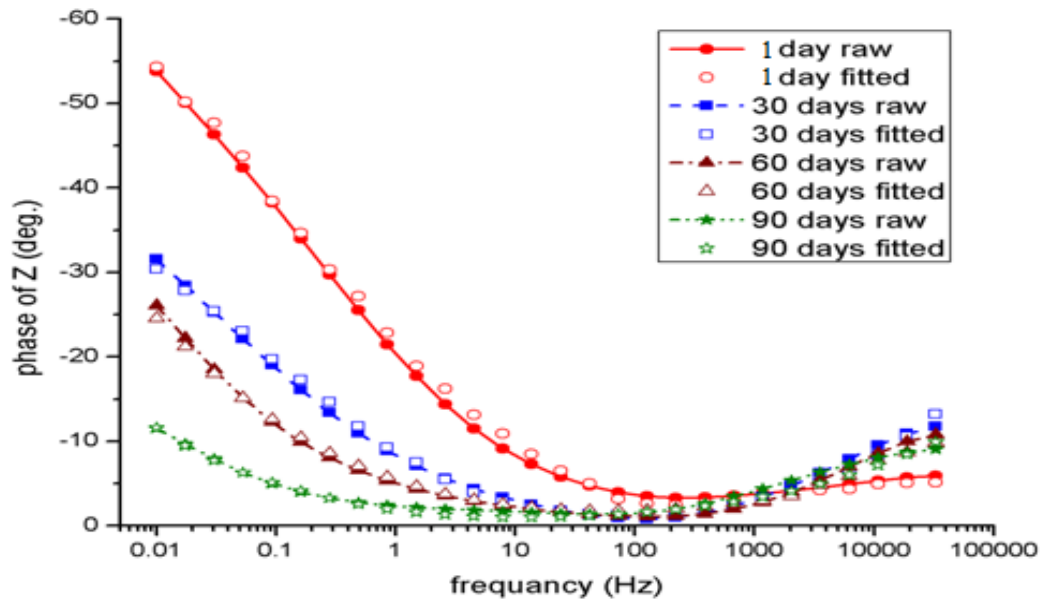


Fig.6.9. Bode phase angle plot variation with carbonation exposure duration (Mix 1-O/C)

Bode magnitude plot representing variation of modulus of impedance $|Z|$ with frequency, is shown in Fig. 6.8. The figure shows a continuous shift in the impedance towards higher side with enhancement in exposure duration. At 10 kHz frequency, the $|Z|$ observed at 1 day of exposure duration was $9.52 \text{ k}\Omega \text{ cm}^2$, which reached upto $47.04 \text{ k}\Omega \text{ cm}^2$ towards the end of

exposure duration. Sharp increase in $|Z|$ was observed during initial 30 days of exposure duration followed by a gradual increase.

The increase in $|Z|$ observed from 30 days to 60 days of exposure was 16 % and from 60 days to 90 days was 8.7%. This behaviour is attributed to changes in the bulk properties of concrete due to continuing hydration process of concrete. At the early exposure duration, the cement particles are not sufficiently hydrated which leads to lesser expansion of the particles and at this stage; paste is linked with the continuous conducting path (CCP). Enhancement in exposure duration leads to expansion in gel particles, which are more likely to block CCP that ultimately results in increase in impedance (*Guangling, 2000*). The percentile decrease in $|Z|$ towards the end of exposure shows blocking of CCP and slowing down of the hydration process. The slopes of the arcs observed in low frequencies domain of Fig. 6.8 indicate either capacitive or resistive behaviour. Modulus slope of approximately 0.8 at 1 day of exposure duration; indicates capacitive like behaviour with the corresponding phase angle having the highest value of -54° (Fig. 6.9). The modulus slope and the corresponding phase angle register a continuous decrease with the enhancement in exposure duration. This decrease in slope modulus and phase angle suggests a shift in the capacitive behaviour towards the resistive side (*Fajardo et al., 2014*).

(b) Impedance spectra for SFG inhibitor treated specimens

Figs. 6.10 - 6.12 show the progressive variations in the Nyquist plots and two types of Bode plots with increase in exposure duration for concrete specimens treated with inhibitor SFG (Mix 1-O/SFG). These figures illustrate that concrete specimens treated with inhibitor SFG behave differently from the control specimens except at 1 day of exposure duration. It is due to the fact that during initial exposure duration of 1 day, the carbonation front is limited to the surface of concrete, irrespective of the type of inhibitor treatment.

During 30 days of exposure duration, a sudden shift in spectra towards higher impedance side was observed (Fig.6.10). Along with this shift, it was observed that the high frequency arc had an increase in radius as compared to the arc obtained at 1 day of exposure duration. Similar nature of high frequency arc was observed at 60 days and 90 days of exposure duration. From the

Bode magnitude plot (Fig 6.11), it was observed that corresponding to 10 kHz frequency, shift in $|Z|$ from $8.5 \text{ k}\Omega \text{ cm}^2$ (1 day) to $35.38 \text{ k}\Omega \text{ cm}^2$ (30 days) was observed, which got stabilized after 60 days of exposure duration. While in the corresponding control specimens a continuous shift in impedance was observed till the end of exposure duration corresponding to 10 kHz frequency level. The stabilized behaviour observed in SFG inhibitor treated specimens indicates that the inhibitor treated specimens behave differently as compared to the corresponding control specimens. The observed behaviour indicates that the inhibitor functions, firstly, by blocking the surface pores. Once the surface pores are blocked, uniform dispersion of the inhibitor in bulk concrete takes place. Secondly, the radius of high frequency in inhibitor treated specimens arc was smaller than the radius of the high frequency arc observed in control specimens. This smaller high frequency arc radius indicates the presence of the OH^- ions in the bulk concrete.

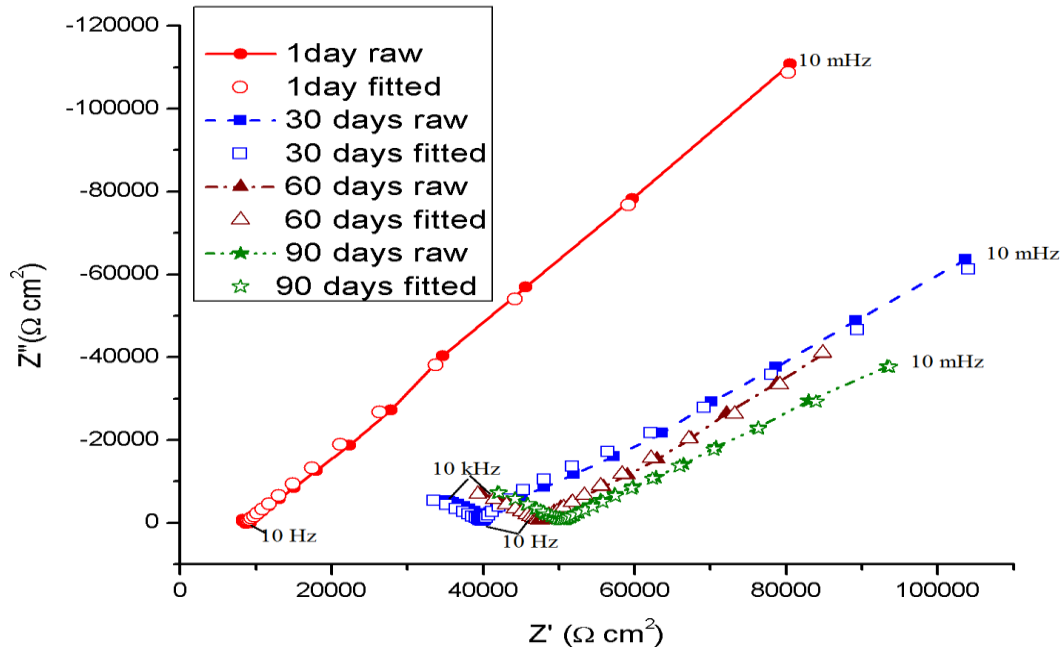


Fig.6.10. Nyquist plot variation with carbonation exposure duration (Mix 1-O/SFG)

The Nyquist plot observed in low frequency domain shows a large capacitive arc at 1 day of exposure duration. At 30 days of exposure duration, some deviation in low frequency arc was observed. This deviation represents occurrence of diffusion control phenomenon at the rebar surface. *Ford et al. (1998)* and *Trabanelli et al. (2005)* also reported that the application of inhibitors introduce diffusion control mechanism in the low frequency domain. At 90 days of exposure, observed large capacitive arc at low frequency in SFG treated specimens as compared

to the corresponding arc for control specimen indicates the presence of protective oxide layer on the rebar surface. The amine component present in the inhibitor forms a bond with the rebar surface and the non polar tails of acid component form a tight mesh that restricts oxygen and moisture availability to the rebar surface (Nmai, 2004; Wombacher et al., 2004).

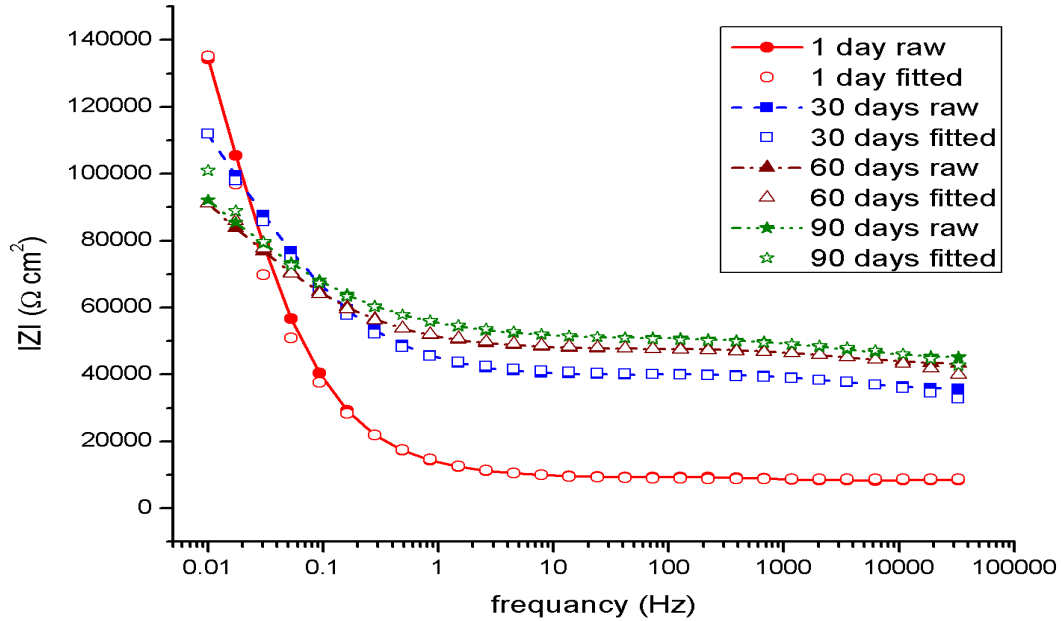


Fig.6.11. Bode magnitude plot variation with carbonation exposure duration (Mix 1-O/SFG)

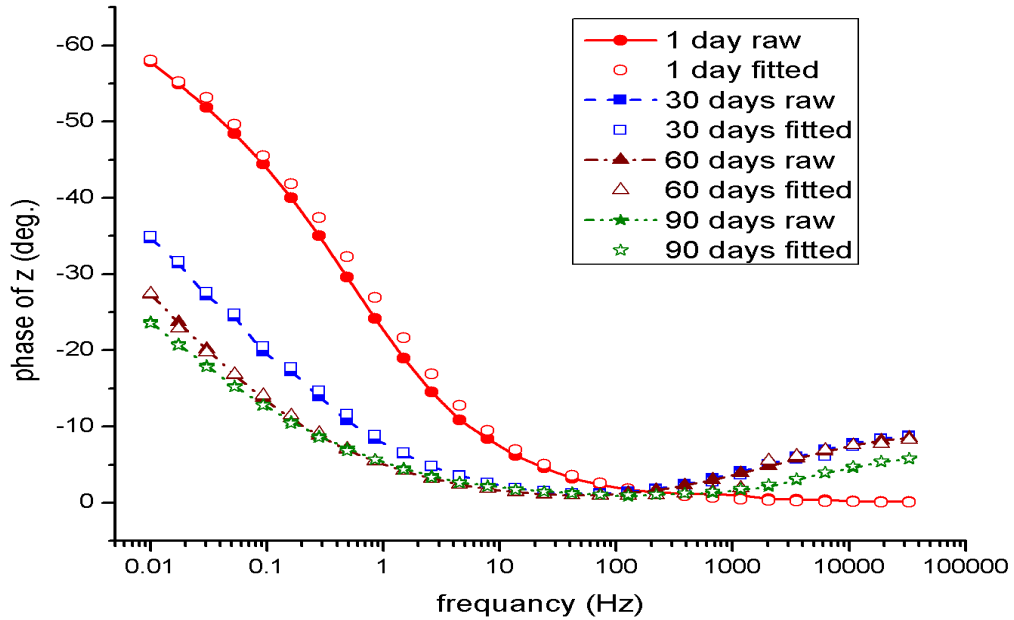


Fig.6.12. Bode phase angle plot variation with carbonation exposure duration (Mix 1-O/SFG)

The frequency versus phase angle plot variation with exposure duration for SFG inhibitor treated specimens is presented in Fig. 6.12. The figure clearly shows that at 1 day of exposure duration, the phase angle at high frequency remained at nearly zero degree and approaches a maximum value of approximately -60° at low frequency. The zero degree phase angle shows the resistive like behaviour associated with the electrolyte resistance while -60° shows the capacitive like behaviour at rebar surface. *Fajardo et al. (2014)* reported that the maximum phase angle smaller than -90° and value of impedance modulus slope lower than unity suggests deviation of the system from an ideal capacitor. This deviation from an ideal capacitor in RC is mainly due to irregularities on the electrode surface, surface roughness and the process associated with an irregular distribution of the applied potential. With the increase in the exposure duration, the phase angle decreased and became constant after 60 days of exposure duration. However, the final phase angle observed towards end of exposure duration remained higher in SFG treated specimens (approximately -25°) as compared to the phase angle observed in control specimens (approximately -12°).

(c) Impedance spectra for ABA inhibitor treated specimens

Figs. 6.13 - 6.15 show the Nyquist and Bode plots variation with exposure duration for concrete specimens treated with inhibitor ABA (Mix 1-O/ABA). At 1 day of exposure, the impedance spectra were similar to the corresponding spectra obtained in control and SFG inhibitor treated specimens. After this exposure duration, ABA inhibitor treated specimens registered impedance spectra different than the control as well as the SFG inhibitor treated specimens. Comparing the changes in the high frequency arc with the exposure duration (Fig. 6.13), it was observed that the behaviour of high frequency arc in ABA treated specimens is similar to the high frequency arcs of SFG inhibitor treated specimens. From the changes in the Bode magnitude plot with exposure duration, as shown in Fig. 6.14, it can be observed that the impedance $|Z|$ shifted towards higher side during 30 days of exposure, thereafter, it got stabilized and remained within the same range after 60 days of exposure duration. This high frequency arc behavior of ABA treated specimens is similar to the SFG inhibitor treated specimens. The similar behaviour shows that the inhibitor ABA also functions by blocking the pores present in the bulk concrete.

Comparing the changes in low frequency arc with the exposure duration, it was observed that at low frequency, the large capacitive arcs were present in ABA inhibitor treated specimens at all exposure durations. This large capacitive arc indicates the presence of strong passive oxide layer on the rebar surface. On the other hand, a highly diminished low frequency arc was observed in the control specimens. Also, in SFG treated specimens, the low frequency arc diminished at lower rate with the exposure duration. The observed behaviour of low frequency arc indicates that the increment in exposure duration does not have any impact on the passive layer around the rebar surface in the presence of ABA inhibitor. It was reported that the presence of functional groups such as $-NH_2$ and $-OH$ in ABA inhibitor form a stable five or six membered chelate ring through bonding between these groups. A formation of chelates enhances and strengthens the chemisorptions of the inhibitors on the cation metal surface such as Fe^{+2} (Nmai, 2004). These chelates after adsorbing on the rebar surface provide a barrier to the ingress of aggressive agents to reach the rebar surface.

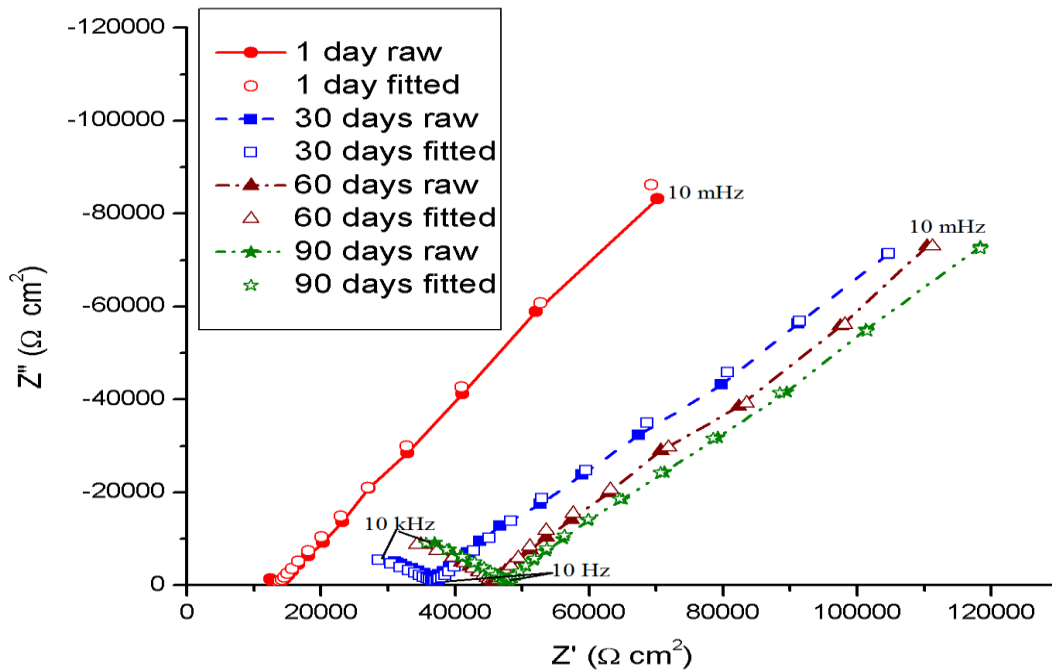


Fig.6.13. Nyquist plot variation with carbonation exposure duration (Mix 1-O/ABA)

Bode magnitude plot (Fig. 6.14) shows the capacitive behaviour, which is characterized by the slope of impedance modulus at lower frequency. The observed capacitive behaviour

represents a situation of passivity at rebar surface (*Montemor et al., 2002*). The same capacitive behavior was observed till the end of exposure duration in ABA treated specimens. At low frequency, phase angle observed was also higher than the corresponding other two (control and SFG treated) specimens towards the end of exposure duration of 90 days (Fig. 6.15).

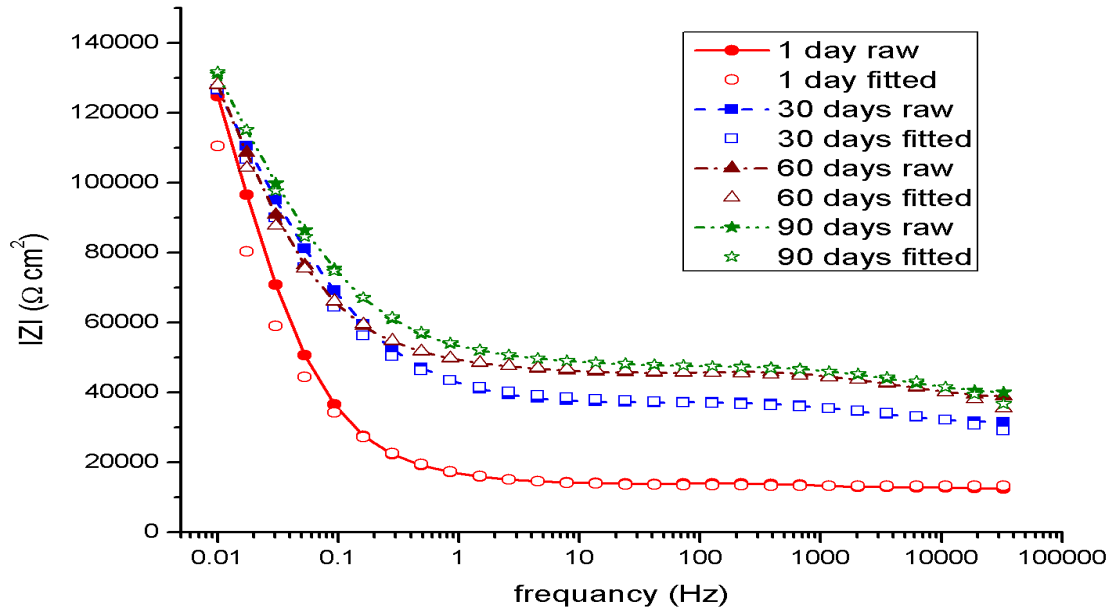


Fig.6.14. Bode magnitude plot variation with carbonation exposure duration (Mix 1-O/ABA)

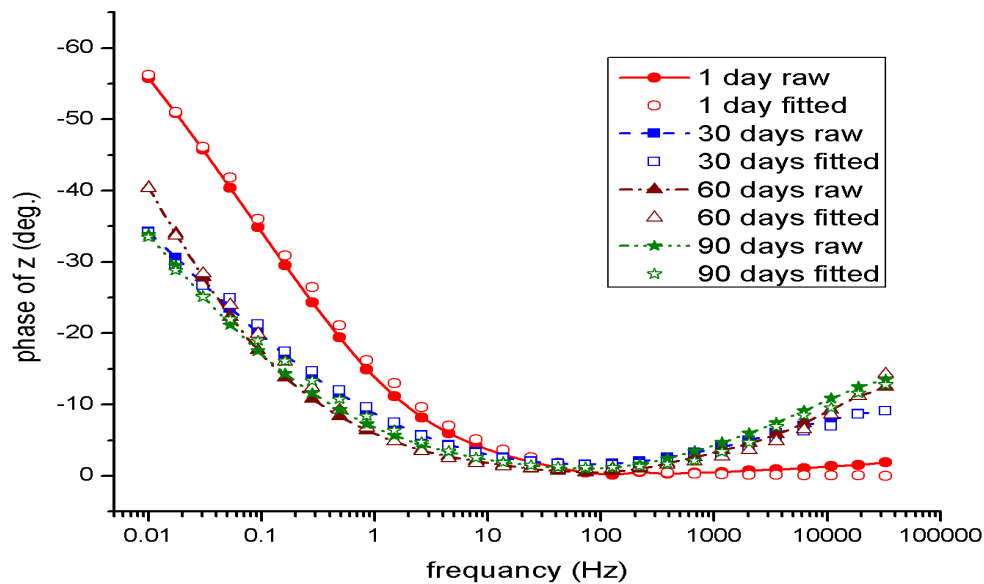


Fig.6.15. Bode phase angle plot variation with carbonation exposure duration (Mix -1O/ABA)

6.6.2 Impedance behaviour of rebar in PPC concrete

Nyquist and Bode plots recorded in PPC control and inhibitors treated specimens with experimental (raw) and fitted data are presented in Figs. 6.16 - 6.24. Similar to the OPC concrete, in all these figures, Nyquist and Bode plots corresponding to 1, 30, 60 and 90 days of exposure are presented while other plots obtained at 15, 45, 75 days of exposure are omitted as they were following similar trends. However, the analytical results from the equivalent circuit are provided for all exposure durations in Appendix B.

(a) Impedance spectra for Control specimens

Impedance spectra recorded for the control PPC concrete specimens at different carbonation exposure durations are presented in Figs. 6.16 - 6.18. From Fig. 6.16 it was observed that in all Nyquist plots two distinct capacitive arcs were observed except in case of 1 day of exposure duration similar with the Mix 1-O/C. First capacitive arc was observed between frequency range of 10 kHz to 10 Hz which can be correlated to bulk properties of concrete, while the second capacitive arc (observed between frequency 10Hz to 10mHz) correspond to electrode related features (*Ford et al., 1998*). The absence of high frequency arc at 1 day of exposure duration indicates the presence of natural pores and highly conductive OH^- ions in the bulk concrete. A larger second capacitive arc observed at low frequency during 1 day of exposure indicates the presence of an extremely resistive passive layer on the rebar surface because of high pH of the pore solution.

With increase in exposure duration to 30 days, the capacitive arc in high frequency range starts increasing, with a corresponding decrease in low frequency arc was observed. The presence of small capacitive arc at high frequency range indicates the presence of porous structure at interface; while the decrease in low frequency arc indicates the initiation of breakdown of protective layer on the rebar surface.

The behavior of the impedance spectra changed drastically at 60 days of exposure duration. A larger increase in radius of first capacitive arc (high frequency) was observed during this exposure duration. This increase in arc occurs due to the alteration of chemical composition at the concrete rebar interface. Progressive carbonation led to the formation of CaCO_3 , which has

very low solubility and gets precipitated as solid matrix in the pores present in concrete, hence densifying the microstructure of the concrete and decrease the porosity of concrete (Montemor *et al.*, 2002). At low frequency, a further decrease in the second capacitive arc shows continuous de-passivation at rebar surface. The behavior of the high frequency arc recorded at 90 days of exposure duration was similar to 60 days of exposure duration with a marginal increase in radius of arc. This small variation in radius of arc indicates the slowdown of the hydration process and slower carbonation front due to densification of concrete matrix (Montemor *et al.*, 2002). However, the second arc at low frequency becomes highly diminishing. It indicates a complete breakdown of the resistive oxide layer on rebar surface. This layer was formed when a passive oxide film grew on the rebar due to high pH of the concrete. On looking at the plots and specifically observing the variation in the frequency arcs, at 90 days of exposure, it can be concluded that the large increase in radius of high frequency arc is indicative of carbonation of concrete, whereas, a smaller low frequency arc indicates loss of passive layer at the rebar surface.

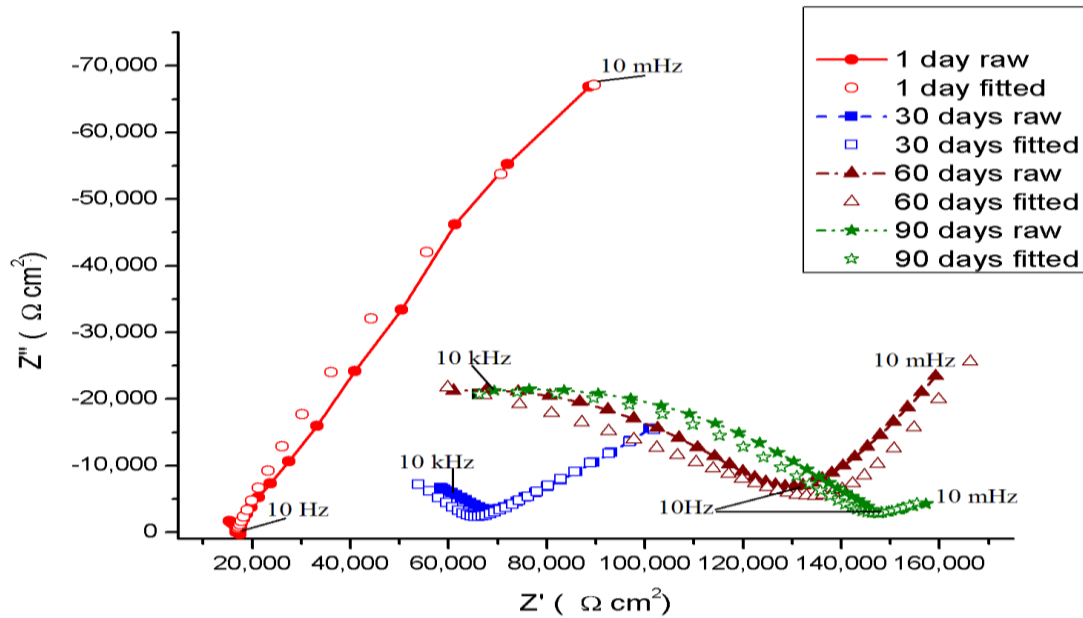


Fig.6.16. Nyquist plot variation with carbonation exposure duration (Mix 1-P/C)

In the Bode magnitude plot (Fig. 6.17), sharp increase in high frequency $|Z|$ was observed with the increase in exposure duration from 1 day to 30 days. Thereafter, $|Z|$ increased gradually and got stabilization at 60 days of exposure duration. At 1 day of exposure

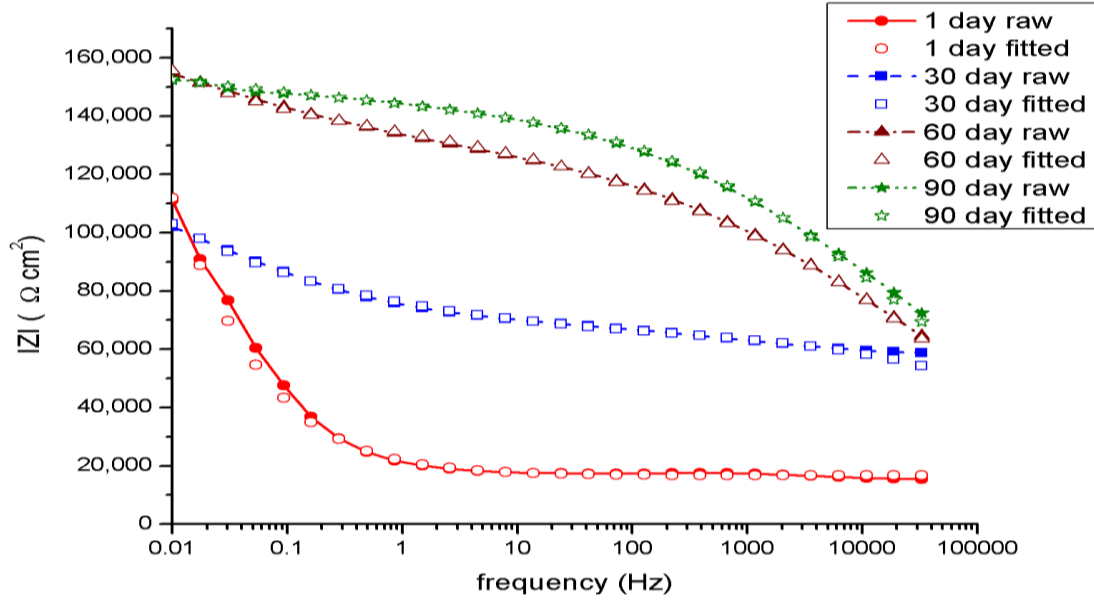


Fig.6.17. Bode magnitude plot variation with carbonation exposure duration (Mix 1-P/C)

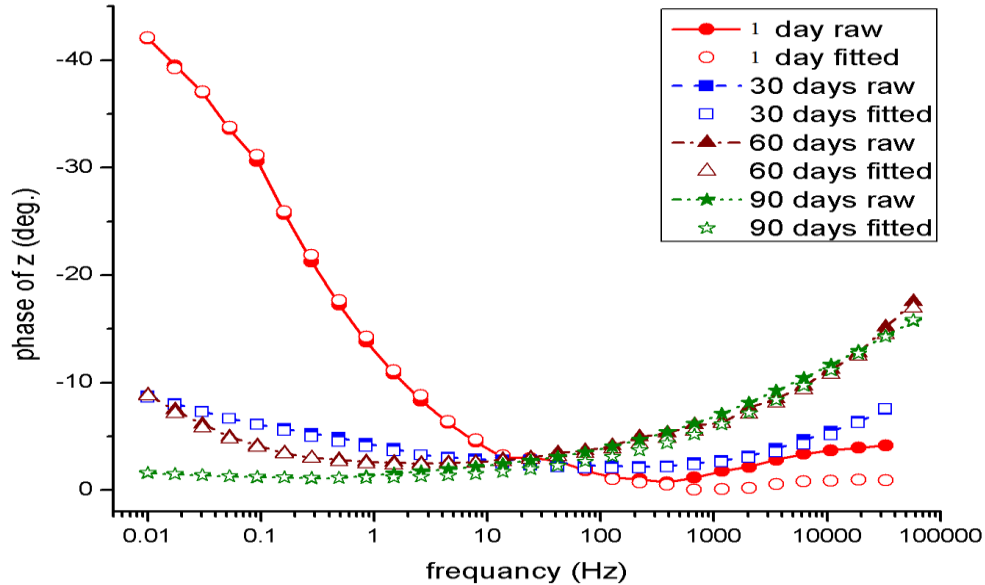


Fig.6.18. Bode phase angle plot variation with carbonation exposure duration (Mix 1-P/C)

duration, the behavior of the specimen took a visible shift from resistive (high frequency) to capacitive side (low frequency). The observed capacitive behavior in low frequency range suggests the presence of homogeneous protective layer on the rebar surface (*Jamil et al., 2004; Ford et al., 1998*). While at 60 days and 90 days of exposure, the Bode magnitude plot shows a significantly different behaviour. At these durations, a slanted impedance modulus was observed

in high frequency range; while the impedance modulus approached a straight line at low frequency which indicates resistive like behaviour. The corresponding phase angle at low frequency also decreased from 43° to a nearly zero degree with increase in exposure duration to 90 days. These changes further support the occurrence of depassivation phenomena at the rebar surface (Fig. 6.18).

(b) Impedance spectra for SFG inhibitor treated specimens

Impedance and Bode plot variation with exposure duration for SFG (Mix 1-P/SFG) treated specimens are presented in Figs. 6.19 - 6.21. Fig. 6.19 indicates that behavior of SFG treated specimens was different from the corresponding control specimen after 1 day of exposure duration. From the Nyquist plots obtained at various exposure durations, it was observed that the high frequency arc had an initial large increase in radius as compared to the arc obtained at 1 day of exposure duration; thereafter it increased at slower rate till the end of exposure duration of 90 days. Similar behaviour of high frequency arc was also observed in OPC concrete specimens treated with SFG inhibitor (Mix 1-O/SFG). However, in Mix 1-P/SFG the observed radius of the high frequency arc was comparatively larger than the radius of high frequency arc observed in Mix 1-O/SFG. Observed higher radius in Mix 1-P/SFG indicates the possibility of lesser amount of $(OH)^-$ in the bulk concrete as compared to the Mix 1-O/SFG. Further, an abrupt increase in high frequency arc at 30 days of exposure clearly indicates that the presence of inhibitor altered the bulk properties of concrete. The inhibitor could have blocked the surface pores, thus increasing the resistance of bulk concrete. Once the surface pores are blocked, uniform dispersion of the inhibitor in bulk concrete takes place.

The behaviour of low frequency arc observed in Mix 1-P/SFG is also identical with the arc observed in Mix 1-O/SFG. At low frequency, a large capacitive arc was observed at 1 day of exposure in Mix 1-P/SFG. Whereas, with the increase in exposure duration, a small decrease in the low frequency arc was observed. Also, a distinct straight line at 45° angle could be observed, which represents occurrence of diffusion control phenomenon at rebar surface (*Ribeiro and Abrantes, 2016; Ford et al., 1998*). The presence of higher arc in the low frequency region represents the presence of passive layer on the surface till the end of exposure duration of 90 days.

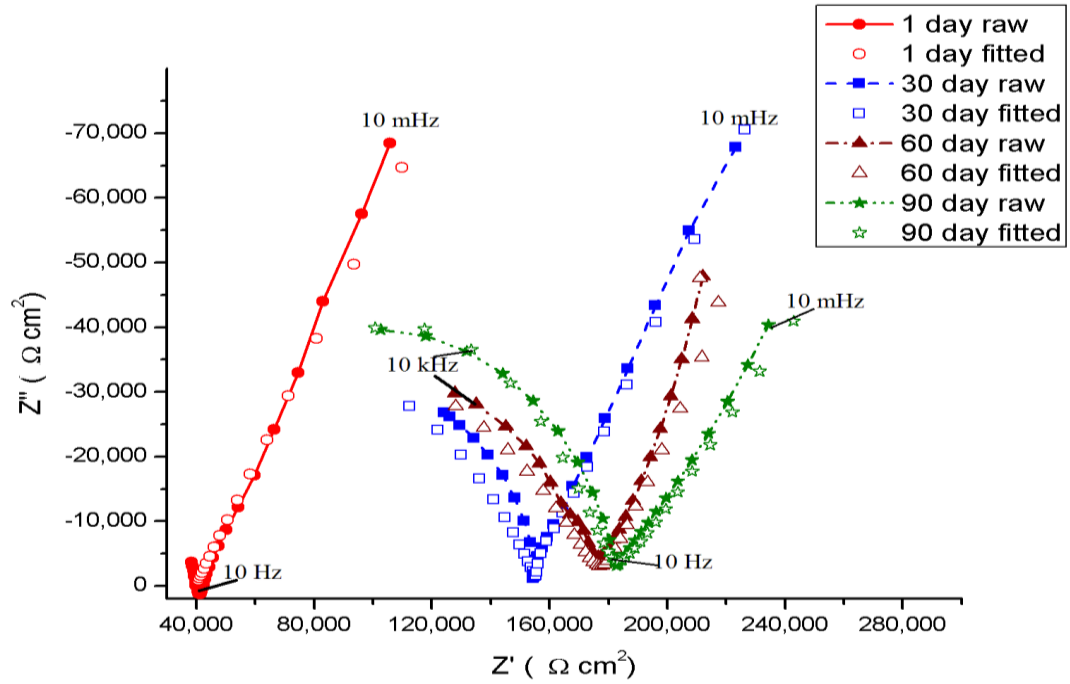


Fig.6.19. Nyquist plot variation with carbonation exposure duration (Mix 1-P/SFG)

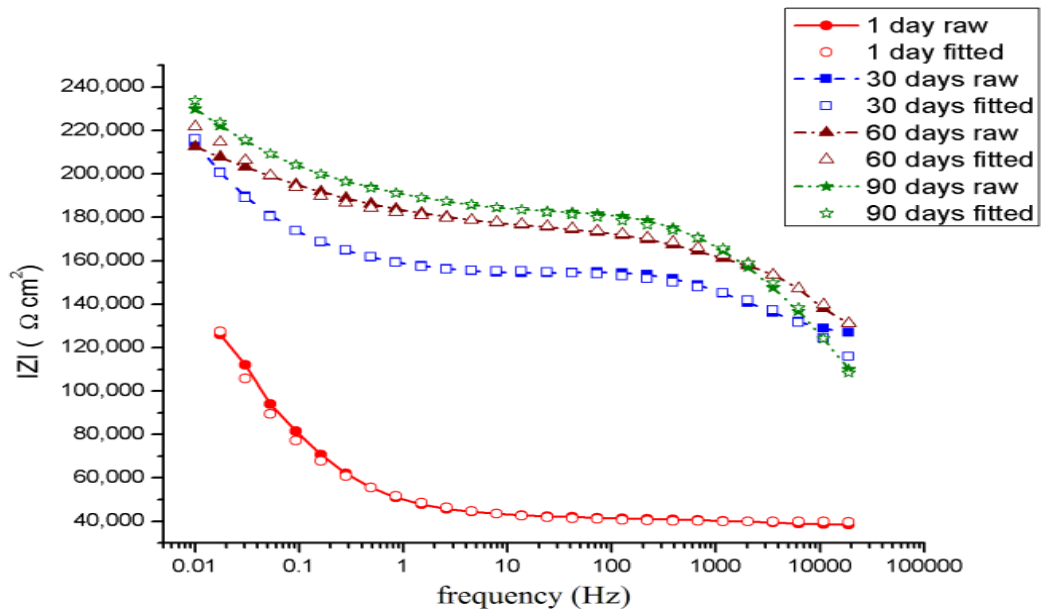


Fig.6.20. Bode magnitude plot variation with carbonation exposure duration (Mix 1-P/SFG)

The Bode magnitude plot at all exposure durations is presented in Fig. 6.20. As indicated in the figure, there is an abrupt increase in $|Z|$ at 10 kHz frequency from $39 \text{ k}\Omega \text{ cm}^2$ (1 day) to

132 k Ω cm² (30 days), which got stabilized after that till 90 days of exposure duration. An increase in impedance at 30 days of exposure represented the alteration made by inhibitors in the concrete pore matrix. Once the inhibitor blocked the pores, no further alteration in the matrix was observed till the end of exposure duration. In the Bode phase angle plot (Fig. 6.21), a significant decrease in angle from -34° (1 day) to -18° (30 days) was observed. This was followed by a relatively smaller decrease in the phase angle. However, at end of exposure duration of 90 days, the phase angle observed in Mix 1-P/SFG remained higher than the phase angle observed in Mix 1-P/C.

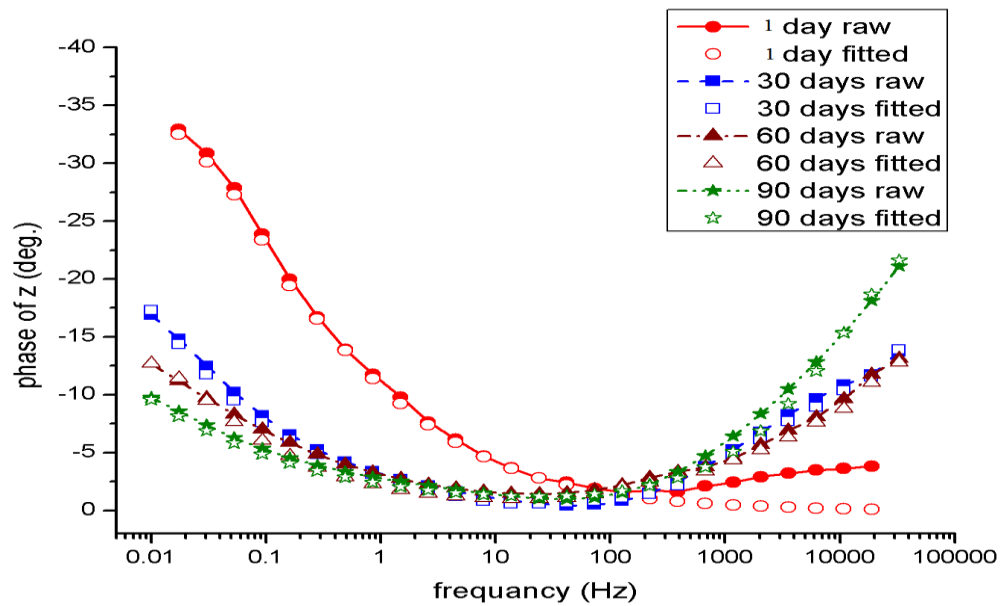


Fig.6.21. Bode phase angle plot variation with carbonation exposure duration (Mix 1-P/SFG)

(c) Impedance spectra for ABA inhibitor treated specimens

Figs 6.22 - 6.24 depict the Nyquist and Bode plots variation with exposure duration in ABA inhibitor treated specimens. Fig. 6.22 indicates that inhibitor ABA treated specimens behaves differently from SFG inhibitor treated as well as the control specimens. A gradual increase in radius of the first capacitive arc (at high frequency) was observed till 90 days of exposure duration. It indicates that the pore blocking effect developed gradually with increase in exposure duration. A continuously increase in the impedance along with smaller radius of the high frequency arc represented the presence of conductive ions (OH^-) in the pore solution.

The behaviour of the low frequency arc observed in Mix 1-P/ABA was similar to the behaviour observed in Mix 1-O/ABA. Fig. 6.22 clearly depicts that the second arc observed in low frequency range was not so much affected by increase in exposure duration. It indicates that the passive oxide layer on the rebar surface remained effective in ABA treated specimens till the end of exposure duration of 90 days.

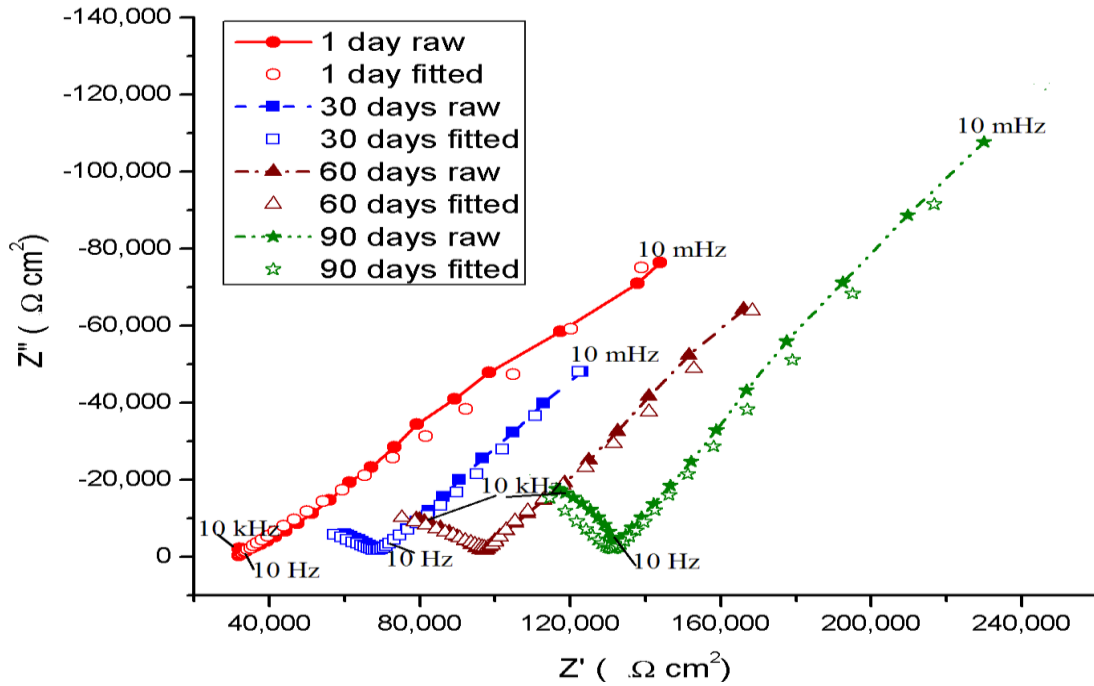


Fig.6.22. Nyquist plot variation with carbonation exposure duration (Mix 1-P/ABA)

The Bode magnitude plot (Fig. 6.23) represents a continuous shift in $|Z|$ towards higher side with the increase in exposure duration at high frequency. The impedance measured at 1 day, 30 days, 60 days and 90 days of exposure duration, corresponding to 10 kHz frequency, was $39 \text{ k}\Omega \text{ cm}^2$, $65 \text{ k}\Omega \text{ cm}^2$, $82 \text{ k}\Omega \text{ cm}^2$ and $120 \text{ k}\Omega \text{ cm}^2$ respectively. Further, the behaviour of the plot remained similar at all exposure durations. The behaviour so observed was resistive like at high frequency and capacitive like at low frequency. At 90 days of exposure, the observed higher impedance modulus slope (approximately 0.8) indicates the presence of a strong passive layer on the rebar surface. The Bode phase angle plot (Fig. 6.24) also shows a higher angle than the control specimens at 90 days of exposure duration.

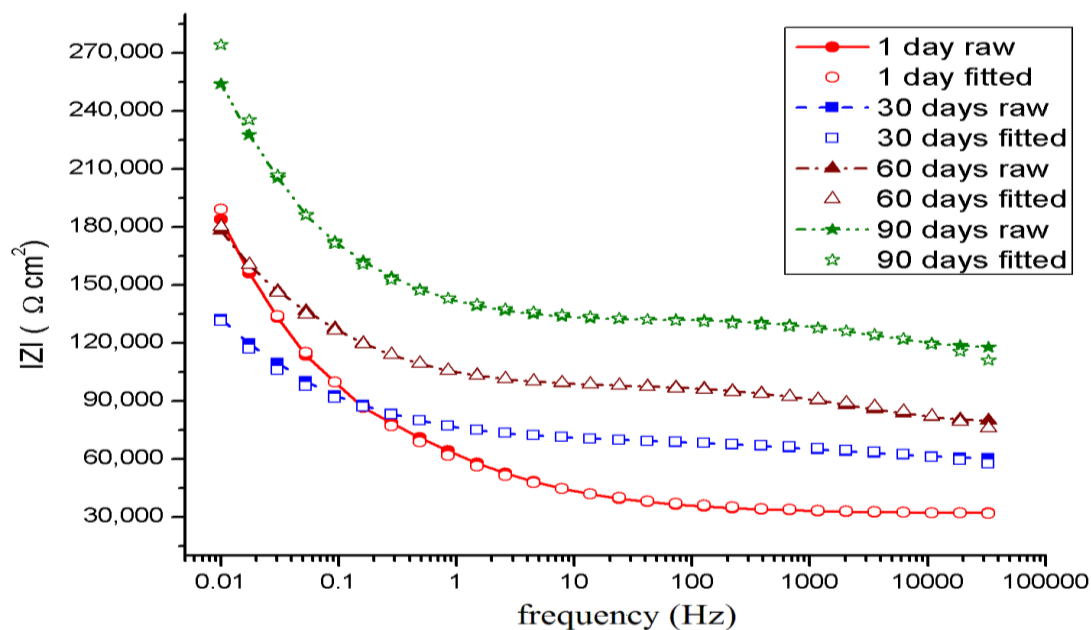


Fig.6.23. Bode magnitude plot variation with carbonation exposure duration (Mix 1-P/ABA)

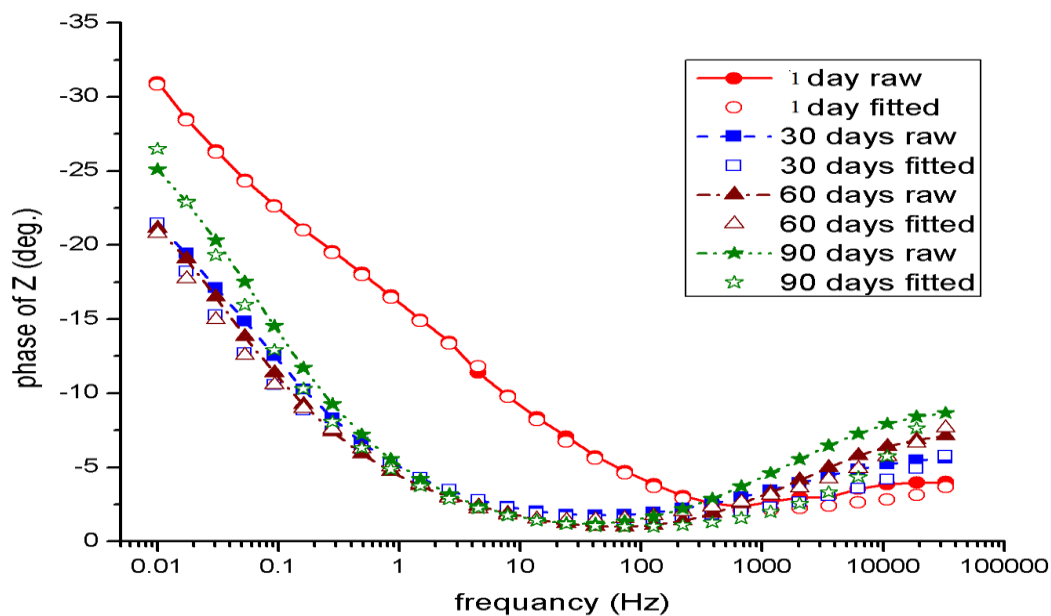


Fig.6.24. Bode phase angle plot variation with carbonation exposure duration (Mix 1-P/ABA)

6.7 ANALYSIS OF EIS RESULTS

The impedance plots so obtained were further analyzed based upon the raw data and fitted data. Raw data refers to the experimental data while fitted data refers to the data obtained

by using appropriate equivalent electrical circuit. The detailed analysis is presented in the following sub-sections.

6.7.1 Analysis of raw data at three distinct frequencies

In order to find the correlation of impedance with progressive change in the properties of bulk concrete and rebar under carbonation exposure, impedance values at three reference points in the impedance spectra were noted. The reference points were decided as three frequency levels, viz. 10kHz, 10Hz and 10mHz, corresponding to high frequency, intermediate frequency and low frequency respectively. The points are marked in the Nyquist plots for each specimen described in the previous sections. In each Nyquist plot, 10kHz corresponds to start of the arc, 10Hz corresponds to the sudden change in the arc and 10mHz is near the end of the plot. The differences in the impedance values obtained at these frequency levels was calculated and presented in Tables 6.2 and 6.3 for specimens made with OPC and PPC concrete, respectively. In the tables, “ Z_{DH} ” refers to impedance difference between 10Hz-10kHz frequency, whereas, “ Z_{DL} ” refers to impedance difference between 10mHz-10Hz frequency. From the tables, it was observed that the trend of impedance difference with increase in exposure duration is similar in all specimens, irrespective of the type of cement.

It can be seen from the Tables 6.2 and 6.3 that for all specimens, impedance difference at high frequency (10Hz – 10kHz) “ Z_{DH} ” continuously increased with exposure duration, while the impedance difference at low frequency (10mHz -10Hz) “ Z_{DL} ” mark continuously decreased with exposure duration. The impedance difference, Z_{DH} is related to the properties of bulk concrete, while Z_{DL} is correlated to the passive oxide layer on the rebar surface.

Table 6.2 presents the values of impedance difference “ Z_{DH} ” and “ Z_{DL} ” obtained from raw EIS data for OPC concrete specimens with and without inhibitor treatment at different exposure durations. From the Table, it was observed that Z_{DH} increased with increase in the exposure duration for all concrete specimens. However, the control specimens had higher value of Z_{DH} as compared to both inhibitor treated specimens at all exposure durations. Towards the end of exposure duration of 90 days, a 26.38% and 20.15% decrease in Z_{DH} was observed in

Mix 1-O/SFG and Mix 1-O/ABA respectively, as compared to the control specimen. Measured lower value of Z_{DH} in inhibitor treated specimens indicates lesser carbonation depth.

Table 6.2 Variation in impedance difference with exposure duration obtained from the raw EIS data in specimens made with OPC concrete

Exposure duration (days)	Impedance difference between the respective frequencies					
	10Hz-10kHz “ Z_{DH} ” ($k\Omega\text{ cm}^2$)			10mHz-10Hz “ Z_{DL} ” ($k\Omega\text{ cm}^2$)		
	Mix 1-O/C	Mix 1-O/SFG	Mix 1-O/ABA	Mix 1-O/C	Mix 1-O/SFG	Mix 1-O/ABA
1	2.55	1.26	1.35	114.16	124.78	110.73
15	4.59	2.94	2.95	96.25	118.15	104.25
30	6.64	4.72	4.21	79.51	94.76	97.19
45	7.36	5.72	5.01	65.32	85.81	94.76
60	8.29	6.83	6.73	48.93	79.04	90.93
75	9.61	7.21	7.17	36.14	78.47	92.42
90	10.12	7.54	8.08	24.91	78.61	91.92

Table 6.3 Variation in impedance difference with exposure duration obtained from the raw EIS data in specimens made with PPC concrete

Exposure duration (days)	Impedance difference between the respective frequencies					
	10 Hz-10 kHz “ Z_{DH} ” ($k\Omega\text{ cm}^2$)			10 mHz-10 Hz “ Z_{DL} ” ($k\Omega\text{ cm}^2$)		
	Mix 1-P/C	Mix 1-P/SFG	Mix 1-P/ABA	Mix 1-P/C	Mix 1-P/SFG	Mix 1-P/ABA
1	2.06	4.08	2.84	98.89	104.38	121.02
15	4.36	9.44	5.18	64.68	102.79	118.01
30	8.03	16.68	8.09	32.55	97.04	122.05
45	14.65	20.05	9.39	26.48	73.21	107.58
60	28.79	21.96	11.68	21.79	66.02	90.83
75	35.45	22.75	12.04	13.75	66.17	86.17
90	41.78	24.47	12.93	8.36	67.58	82.83

The impedance difference corresponding to the low frequency (Z_{DL}) continuously decreased with increase in exposure duration in control specimens; while in inhibitor treated specimens Z_{DL} value got stabilized after 60 days of exposure duration. In control mixes, a continuous decrease in Z_{DL} can be attributed to the continuous depassivation of the passive oxide layer present on the rebar surface. However, both inhibitors applied specimens had higher value of Z_{DL} at all exposure durations as compared to the control mix. In Mix 1-O/ABA and Mix 1-O/SFG the observed higher value of Z_{DL} , 91.92 $k\Omega\text{ cm}^2$ and 78.61 $k\Omega\text{ cm}^2$ respectively as compared to the corresponding value for control specimen (24.91 $k\Omega\text{ cm}^2$) clearly indicates the presence of a strong passive layer around the rebar surface even till the end of exposure duration of 90 days.

Table 6.3 presents the impedance differences, viz. Z_{DH} and Z_{DL} obtained from the raw EIS data for PPC concrete specimens with and without inhibitor treatment at different exposure durations. From the table it was that PPC concrete also exhibited behaviour similar to the OPC concrete. The control specimens showed a higher value of Z_{DH} as compared to the all other mixes. The large increase in Z_{DH} indicated a progressive increase in the carbonation front, thus densifying the pore matrix due to deposition of carbonation products with exposure duration. On the other hand, SFG and ABA inhibitors treated samples show 41.43% and 69.1% lower value of Z_{DH} , respectively, as compared to the control sample at the end of exposure duration. At low frequency, for control specimens, a large decrease in Z_{DL} value was associated with the breakdown of the passive oxide layer with exposure duration. While both the inhibitor treated specimens registered higher value of Z_{DL} as compared to the control specimens at the end of exposure duration. This large increase in impedance values 67.58 $k\Omega\text{ cm}^2$ for Mix 1-P/SFG and 82.8 $k\Omega\text{ cm}^2$ for Mix 1-P/ABA as compared to Mix 1-P/C (8.4 $k\Omega\text{ cm}^2$) indicated the formation of protective inhibitor layer at the rebar surface.

6.7.2 Analysis of fitted data obtained from equivalent circuits

The impedance plots obtained for all the tested specimens were further analysed using the equivalent circuits shown in Fig. 6.6. In the present study, two equivalent electrical circuits namely EEC-A and EEC-B were used and are presented in the Fig. 6.6. While EEC-A was used for the fitting of impedance plots obtained at initial exposure duration of 1 day; EEC-B was used

for the fitting of impedance plot obtained at all other exposure durations. The typical feature observed in the impedance plots obtained at 1 day of exposure duration was the absence of high frequency arc in all specimens, irrespective of the type of cement used and the inhibitor application. At 1 day of exposure, only second capacitive arc corresponding to low frequency region was observed. Therefore, equivalent circuit composed of electrolyte resistive element and impedance element (composed of resistance and CPE) corresponding to the ionic resistance of the film of corrosion product formed on the metal surface was required. With the enhancement in the exposure duration, one more capacitive arc in the high frequency region was introduced in the impedance spectra, which was followed by the low frequency arc. Therefore, to simulate the presence of two arcs in the impedance spectra, another impedance element was added in the equivalent circuit for the fitting of the arc observed in high frequency region.

There are a number of parameters which are obtained from the equivalent circuit corresponds to both the low frequency arc and the high frequency arc. All these parameters so obtained are presented in Tables B1–B6 in Appendix –B. Out of all the obtained parameters, the resistive parameters are more useful in estimating the carbonation related behavior of the specimens. In the present study, high frequency resistive parameter (R_1) obtained after fitting equivalent circuit into the raw data was used further for prediction of carbonation depth by means of the EIS data. Also, since the resistive parameters obtained by fitting of low frequency arc are said to be closely related to the charge transfer resistance (*Liu et al., 2014*), therefore, in the present study, the resistive parameter (R_2) obtained after fitting of the low frequency arc was analyzed for changes in the charge transfer resistance with inhibitor application and with exposure duration. This charge transfer resistance is also referred to as polarization resistance R_p (*Ismail and Ohtsu, 2006; Criado et al., 2012*) and can be used for finding out the inhibitor efficiency. These two resistive parameters, namely R_1 and R_2 obtained after fitting the raw data with equivalent circuit are presented in Tables 6.4 and 6.5 corresponding to OPC and PPC concrete respectively. Other parameters of the equivalent circuit include the capacitive parameters and a Warburg element as well.

The capacitive parameter tells about the separation of ions present in pore solution from the electrode surface. The capacitance values (Y_1) of the high frequency arc obtained for all

mixes varied in the range of 1- 65 nF cm⁻². This order of magnitude is indicative of the bulk effect (*Ford et al., 1998*). However, the capacitance values (Y_2) corresponding to the fitting of low frequency arc varied in the range of 1-100 μFcm^{-2} for all the tested specimens. The observed high capacitance values can be associated with the formation of product layer on the rebar surface. *Ford et al. (1998)* also reported that the capacitance value corresponding to 20 μFcm^{-2} is consistent with typical values of ionic double layer at electrode in electrochemical reactions.

As explained above in Section 6.5.2, the measured resistive parameter, R_1 corresponds to the resistance caused by charge transfer inside the bulk concrete; while R_2 corresponds to the resistance caused by charge transfer procedure on the surface of the rebar (*Dong et al., 2014; Montemor et al., 2000*). From Table 6.4, it can be observed that for control specimens, the resistance R_1 increased while resistance R_2 decreased with increase in exposure duration. In Mix 1-O/C, a continuous increase in resistance (R_1) from 26 $\text{k}\Omega\text{cm}^2$ (at 15 days of exposure) to 62 $\text{k}\Omega\text{cm}^2$ (at 90 days of exposure) was observed, while resistance R_2 decreased from 108 $\text{k}\Omega\text{cm}^2$ (at 1 day of exposure) to 24 $\text{k}\Omega\text{cm}^2$ (at 90 days of exposure). It has been reported that the R_2 value higher than 100 $\text{k}\Omega\text{cm}^2$ typical corresponds to the passive state of rebar, while the value below 10 $\text{k}\Omega\text{cm}^2$ characterizes an actively corroding rebar.

Table 6.4 Fitted resistive parameters for OPC concrete samples exposed to 5% CO₂ in the presence and absence of corrosion inhibitors

Exposure duration (days)	Mix 1-O/C		Mix 1-O/SFG		Mix 1-O/ABA	
	R_1 ($\text{k}\Omega\text{cm}^2$)	R_2 ($\text{k}\Omega\text{cm}^2$)	R_1 ($\text{k}\Omega\text{cm}^2$)	R_2 ($\text{k}\Omega\text{cm}^2$)	R_1 ($\text{k}\Omega\text{cm}^2$)	R_2 ($\text{k}\Omega\text{cm}^2$)
1	-	108	-	200	-	158
15	26	97	18	164	21	127
30	43	83	40	125	35	98
45	49	68	37	91	38	102
60	54	53	47	83	45	108
75	59	36	48	85	47	110
90	62	24	51	86	48	112

The application of inhibitor SFG sharply increased the resistance R_1 during the initial 60 days of exposure duration. Thereafter, a gradual increase in resistance R_1 from $47 \text{ k}\Omega\text{cm}^2$ (at 60 days of exposure) to $51 \text{ k}\Omega\text{cm}^2$ (at 90 days of exposure) was observed. However, the value of R_2 decreased with the application of SFG inhibitor but remained higher than the control specimens at all exposure durations. At the end of exposure duration of 90 days, the observed higher value of R_2 ($86 \text{ k}\Omega\text{cm}^2$) in SFG inhibitor treated specimens as compared to R_2 value observed in control specimen ($24 \text{ k}\Omega\text{cm}^2$) indicate the presence of passive film on the rebar. Also, a Warburg resistance with values in the range of $22\text{-}45 \text{ k}\Omega\text{cm}^2$ was observed after 1 day of exposure duration. Both the values of R_2 and presence of Warburg resistance suggest that SFG corrosion inhibitor decreased the corrosion rate by retarding the diffusion phenomena.

A gradual increase in resistance R_1 from $21 \text{ k}\Omega\text{cm}^2$ (at 15 days of exposure) to $48 \text{ k}\Omega\text{cm}^2$ (at 90 days of exposure) was observed in ABA inhibitor treated specimens. The concrete samples treated with inhibitor ABA exhibited 29% lower value of R_1 as compared to the control sample at the end of exposure duration of 90 days. This may be due to the formation of different reaction products and presence of highly conductive ions inside the concrete. For ABA inhibitor treated specimens, observed R_2 values increased after 30 days of exposure duration and remained higher than the control specimens. Observed higher value of R_2 ($112 \text{ k}\Omega\text{cm}^2$) suggested that the ABA inhibitor reinforced the passive film on the rebar, probably by surface adsorption (*Criado et al., 2012*). *Jamil et al. (2004)* also suggested that amino alcohol based inhibitors are able to displace hydrated layer of the iron oxides/ hydroxides surface film in order to create more favourable anchorage sites for formation of protective inhibitor layer.

The resistive parameters of specimens made by using PPC concrete at all exposure duration are presented in Table 6.5. The data indicates that the tested PPC concrete specimens exhibited resistive behaviour similar to the OPC concrete specimens. Table 6.5 clearly shows that in control specimens, resistance R_1 continuously increased with increases in exposure duration; while the resistance R_2 registered a continuous decrease with increase in exposure duration, indicating the persistent depassivation of the rebar. The application of inhibitor SFG sharply increased the resistance R_1 during the initial 30 days of exposure duration. On comparison with control specimens, SFG inhibitor treated specimen registered a 70% higher

resistance at 30 days of exposure duration. This increase in resistance may be caused by the pore blocking effect of inhibitor. Also, it could be validated from the observation that the carbonation depth for SFG inhibitor treated specimen was lower as compared to the control specimen. Thereafter, a gradual increase in resistance R_1 from $78 \text{ k}\Omega\text{cm}^2$ (at 45 days of exposure) to $108 \text{ k}\Omega\text{cm}^2$ (at 90 days of exposure) was observed. However, the value of R_2 decreased with the application of SFG inhibitor but remained higher than the corresponding control mix at all exposure durations. Similar to the case of Mix 1-O/SFG, a Warburg resistance with values in the range of 8-19 $\text{k}\Omega\text{cm}^2$ was observed after 1 day of exposure duration in Mix 1-P/SFG. Concrete sample treated with inhibitor ABA exhibited 67% lower value of R_1 as compared to the control sample at the end of exposure duration of 90 days. This may be due to the formation of different reaction products and presence of highly conductive ions inside the concrete. For ABA inhibitor treated sample, R_2 value observed was also higher than the control sample at all exposure durations.

Table 6.5 Fitted resistive parameters for PPC concrete samples exposed to 5% CO_2 in the presence and absence of corrosion inhibitors

Exposure duration (days)	Mix 1-P/C		Mix 1-P/SFG		Mix 1-P/ABA	
	R_1 ($\text{k}\Omega\text{cm}^2$)	R_2 ($\text{k}\Omega\text{cm}^2$)	R_1 ($\text{k}\Omega\text{cm}^2$)	R_2 ($\text{k}\Omega\text{cm}^2$)	R_1 ($\text{k}\Omega\text{cm}^2$)	R_2 ($\text{k}\Omega\text{cm}^2$)
1	-	91	11	230	-	95
15	19	73	45	130	12	87
30	38	49	65	98	21	63
45	87	32	78	75	29	76
60	107	29	84	45	37	89
75	129	11	97	32	42	84
90	141	7	108	35	46	81

6.8 EFFICIENCY OF CORROSION INHIBITORS

The resistive parameter R_2 (also referred to as polarization resistance, R_p) obtained from the equivalent circuit in lower frequency region of the Nyquist plots was used to estimate the

efficiency of inhibitors. The inhibition efficiency (IE) was calculated by using the following equation.

$$IE = \frac{R_{p,inh} - R_{p,control}}{R_{p,inh}} \times 100 \quad \dots (6.2)$$

where, $R_{p,inh}$ and $R_{p,control}$ are the polarization resistance values estimated from the Nyquist plots in the presence and absence of the inhibitors, respectively.

Similar procedure for calculating the inhibitor efficiency was followed by some previous researchers as well (*Ismail and Ohtsu, 2006; Criado et al., 2012*). The Table 6.6 presents the IE of the corrosion inhibitor in percentage (%). It can be seen from the table that during 30 of exposure duration, SFG inhibitor exhibited higher IE as compared to inhibitor ABA in both OPC and PPC concrete mixes. After 45 days of exposure duration, higher IE was observed for ABA inhibitor treated specimens. The inhibitor efficiency achieved at the end of 90 days of exposure duration for SFG inhibitor treated specimens was 72% and 80% respectively in Mix 1-O/SFG and Mix1-P/SFG. The similar values of inhibitor efficiency obtained for ABA inhibitors at the end of exposure duration was 78% and 91% for Mix 1-O/ABA and Mix 1-P/ABA respectively. These values of IE indicate that both the inhibitors are effective in resisting carbonation induced corrosion.

Table 6.6 Inhibition efficiency (IE) values for concrete specimens treated with inhibitors

Exposure duration (days)	Inhibition efficiency, IE (%)			
	Mix 1-O/SFG	Mix 1-O/ABA	Mix 1-P/SFG	Mix 1-P/ABA
15	41	24	44	16
30	34	15	50	22
45	25	33	57	58
60	36	51	35	67
75	57	67	65	86
90	72	78	80	91

6.9 PREDICTION OF CARBONATION DEPTH FROM EIS DATA

It has already been discussed that the first capacitive arc of Nyquist plot can be related to the properties of bulk concrete, which gets affected by progressive carbonation process. It indicates that the carbonation depth can be correlated to the data corresponding to this arc of impedance spectra. Therefore, the relationship between the impedance difference measured between 10Hz to 10kHz frequency range (Z_{DH}), fitted resistive value of high frequency arc (R_1) and carbonation depth was attempted. For this, carbonation depth measured on 100 mm cubes, as explained in Chapter 4 under Section 4.8.1 for control and inhibitor treated specimens was taken at the same exposure durations at which EIS readings were recorded. For ready reference, the values of Z_{DH} , R_1 and measured carbonation depth are presented in Tables 6.7 and 6.8 for all OPC and PPC concrete specimens respectively. The measured carbonation depth was correlated with Z_{DH} parameter of raw data and with R_1 parameter of fitted data. The models generated by the developed correlation are presented in the subsequent sections.

Table 6.7 High frequency arc parameters and measured carbonation depth values in OPC concrete specimens

Exposure duration (days)	Mix 1-O/C			Mix 1-O/SFG			Mix 1-O/ABA		
	Z_{DH} ($k\Omega cm^2$)	R_1 ($k\Omega cm^2$)	C.D* (mm)	Z_{DH} ($k\Omega cm^2$)	R_1 ($k\Omega cm^2$)	C.D* (mm)	Z_{DH} ($k\Omega cm^2$)	R_1 ($k\Omega cm^2$)	C.D* (mm)
15	4.6	26	4.0	2.9	18	3.3	2.9	21	2.6
30	6.6	43	6.6	4.7	40	5.5	4.2	35	3.9
45	7.4	49	8.1	5.7	37	6.3	5.0	38	4.7
60	8.3	54	8.8	6.8	47	7.1	6.7	45	6.4
75	9.6	59	9.7	7.2	48	7.9	7.2	47	7.3
90	10.1	62	10.2	7.5	51	8.8	8.1	48	8.1

C.D*: Measured carbonation depth by phenolphthalein indicator

Table 6.8 High frequency arc parameters and measured carbonation depth in PPC concrete specimens

Exposure duration (days)	Mix 1-P/C			Mix 1-P/SFG			Mix 1-P/ABA		
	Z_{DH} (kΩcm ²)	R_1 (kΩcm ²)	C.D* (mm)	Z_{DH} (kΩcm ²)	R_1 (kΩcm ²)	C.D* (mm)	Z_{DH} (kΩcm ²)	R_1 (kΩcm ²)	C.D* (mm)
15	4.4	19	4.3	9.5	45	3.2	5.2	12	3.0
30	8.0	38	7.0	16.7	65	4.7	8.1	21	4.1
45	14.7	87	9.1	20.1	78	5.6	9.4	29	4.9
60	28.8	107	10.9	21.9	84	7.0	11.7	37	5.7
75	35.5	129	13.8	22.7	97	8.1	12.0	42	7.1
90	41.8	141	14.6	24.5	108	9.8	12.9	46	8.0

C.D*: Measured carbonation depth by phenolphthalein indicator

6.9.1 Carbonation depth predication using Z_{DH} parameter of raw data

On the basis of impedance data and measured carbonation depth, presented in Tables 6.7 and 6.8, it was observed that carbonation depth can be correlated to impedance difference at high frequency (Z_{DH}). A logarithmic relationship, which was thus obtained between the carbonation depth and impedance difference Z_{DH} is of the following form:

$$D(t) \approx A [\log\{Z_{DH}(t) - Z_{DH}(1)\}] \pm B \quad \text{..... (6.3)}$$

where, D(t) refers to carbonation depth at exposure duration 't', $Z_{DH}(t)$ refers to impedance difference measured between 10Hz -10kHz frequency range at exposure duration 't' and $Z_{DH}(1)$ refers to impedance difference measured between 10Hz -10kHz frequency range at 1 day of exposure, A & B are constants, which vary depending upon the type of cement. From regression analysis the corresponding relationships so obtained for OPC and PPC concrete mixes, respectively, are represented in equations (6.4) and (6.5).

For OPC control and inhibitor treated concrete specimens:

$$D(t) \approx 10.02[\log\{Z_{DH}(t) - Z_{DH}(1)\}] + 0.295; \quad R^2=0.88 \quad \text{..... (6.4)}$$

For PPC control and inhibitor treated concrete specimens:

$$D(t) \approx 10.99[\log\{Z_{DH}(t) - Z_{DH}(1)\}] - 0.368; \quad R^2=0.92 \quad \text{..... (6.5)}$$

The best fitted regression curves highlighting relationship between carbonation depth and logarithm of impedance difference for OPC and PPC concrete mixes are shown in Figs. 6.25 and 6.26 respectively. It was observed that good relation was established between carbonation depth and impedance difference at high frequency with correlation coefficient R^2 nearly 0.9 in both mixes.

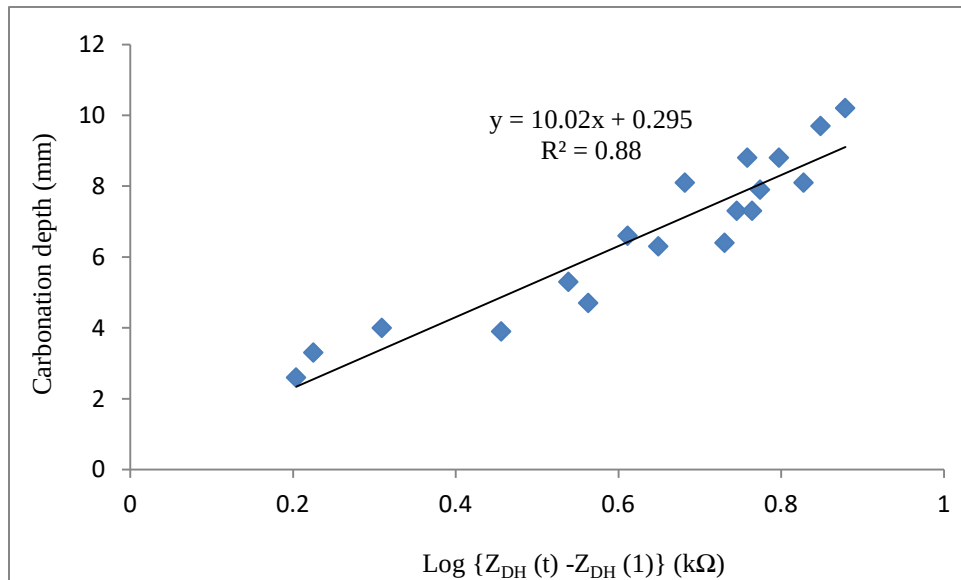


Fig.6.25. Relationship between measured carbonation depth with difference in impedance values for OPC concrete specimens

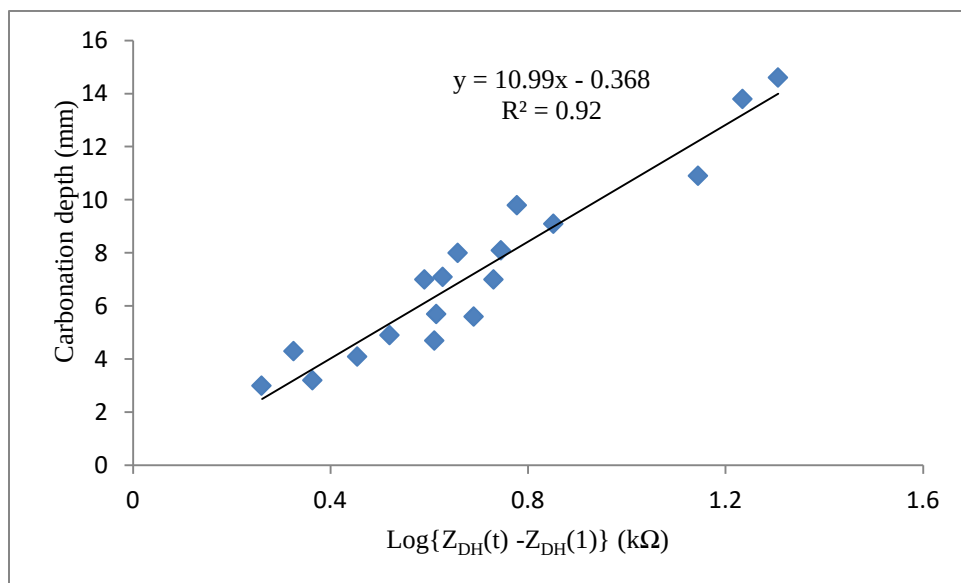


Fig.6.26. Relationship between measured carbonation depths with difference in impedance values for PPC concrete specimens

6.9.2 Carbonation depth predication using R_1 parameter of fitted data

Similar to the relationship developed between the impedance difference parameter (Z_{DH}) of high frequency arc with the carbonation depth, the relationship between resistive parameter (R_1) of the equivalent circuit in the high frequency range and the measured carbonation depth was also developed. As already discussed, the resistive parameter of high frequency arc (R_1) corresponds to the resistance caused by ions transfer inside the bulk concrete and hence can be related to the carbonation depth of concrete. The basic relationship between carbonation depth and resistance R_1 was derived and is presented as below in equation (6.6)

$$D(t) \approx A\{R_1(t) - R_1(1)\} \pm B \quad \dots (6.6)$$

where, $D(t)$ refers to carbonation depth at exposure duration 't', $R_1(t)$ refers to resistance R_1 value at 't' days of exposure duration and $R_1(1)$ refers to resistance R_1 value at 1 day of exposure duration, A & B are constants, which vary depending upon the type of cement.

From regression analysis the corresponding relationship so obtained for OPC and PPC concrete mixes is elaborated, respectively, in equations (6.7) and (6.8).

For OPC control and inhibitor treated concrete specimens:

$$D(t) \approx 0.179\{R_1(t) - R_1(1)\} - 1.091; R^2 = 0.92 \quad \dots (6.7)$$

For PPC control and inhibitor treated concrete specimens:

$$D(t) \approx 0.081\{R_1(t) - R_1(1)\} + 2.207; R^2 = 0.86 \quad \dots (6.8)$$

The best fitted regression curves highlighting relationship between carbonation depth and resistance $\{R_1(t) - R_1(1)\}$ for OPC and PPC concrete mixes are shown in Figs. 6.27 and 6.28 respectively. The high value of R^2 for both mixes clearly indicates that there is a significant correlation between fitted resistance R_1 and the carbonation depth of concrete.

6.9.3 Variation in predicted and measured carbonation depths

Based upon the above established relationships between carbonation depth and the corresponding high frequency parameter of either raw data or fitted data, the predicted carbonation depth values were evaluated for all mixes at different exposure durations and are presented in Tables 6.9 and 6.10. Table 6.9 shows that in Mix 1- O/C, carbonation depth

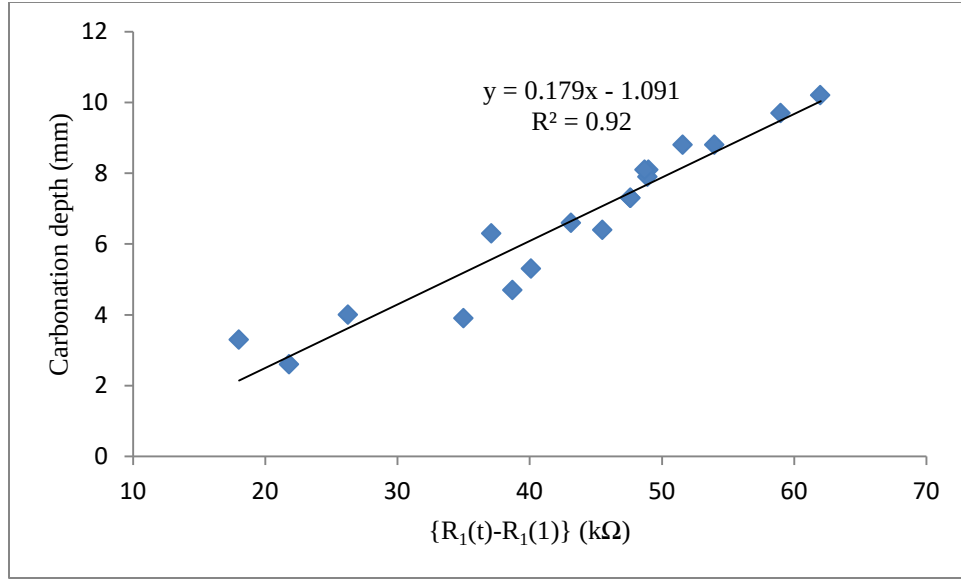


Fig.6.27. Relationship between measured carbonation depth with fitted R_1 values for OPC concrete specimens

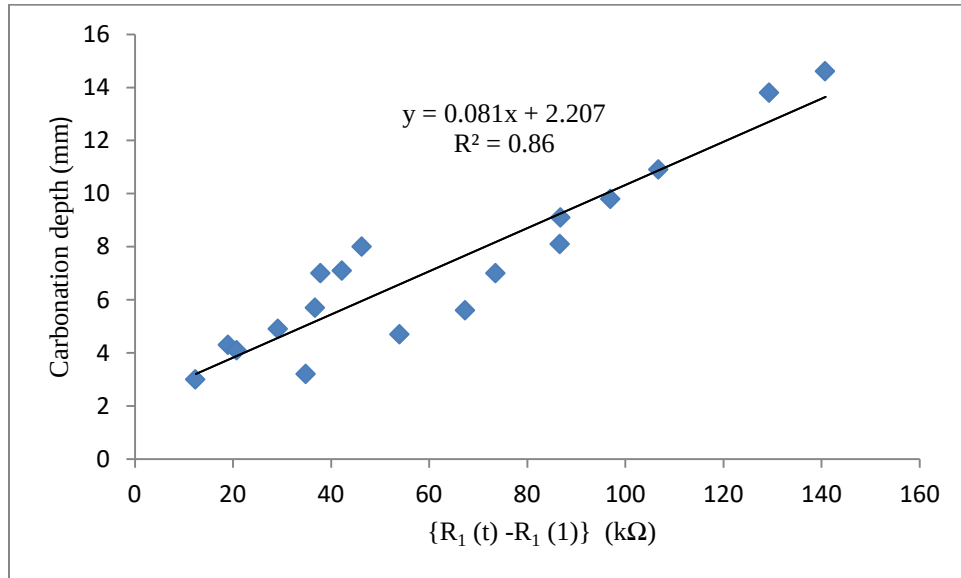


Fig.6.28. Relationship between measured carbonation depth with fitted R_1 values for PPC concrete specimens

measured from phenolphthalein indicator reached to 10.2 mm while the predicted depth using impedance difference parameter was 9.1 mm and whereas, the predicted depth by using resistive parameter (R_1) was 10.0 mm at 90 days of exposure duration. Similarly, with inhibitor SFG from Z_{DH} and R_1 value 5.6% and 6.8% lower value of carbonation depth was predicted at 90 days of exposure. In case of inhibitor ABA treated specimens, carbonation depth predicted with Z_{DH} are

3.7% higher than the measured value of carbonation depth at 90 days of exposure. Table 6.10 illustrate that in PPC mix the variation in measured carbonation depth and the depth predicted by using the established relationship varied in the range of 2-20% during 90 days of exposure duration.

Table 6.9 Comparison between measured carbonation depths with predicted carbonation depth based upon Z_{DH} and resistance R_1 in OPC concrete

Exposure duration (days)	Specimens	Carbonation depth (mm)				
		Measured (mm)	Predicted by eq. (6.4)		Predicted by eq. (6.7)	
			Predicted (mm)	Variation (%)	Predicted (mm)	Variation (%)
15 days	Mix 1-O/C	4.0	3.4	15.0	3.6	10.0
	Mix 1-O/SFG	3.3	2.6	21.0	2.2	33.3
	Mix 1-O/ABA	2.6	2.3	11.5	2.8	5.6
30 days	Mix 1-O/C	6.6	6.4	3.0	6.6	0
	Mix 1-O/SFG	5.3	5.6	5.6	6.1	15.0
	Mix 1-O/ABA	3.9	4.7	20.5	5.2	33.3
45 days	Mix 1-O/C	8.1	7.2	11.1	7.7	4.9
	Mix 1-O/SFG	6.3	6.8	7.9	5.6	11.1
	Mix 1-O/ABA	4.7	5.9	25.5	5.8	23.4
60 days	Mix 1-O/C	8.8	7.9	10.2	8.6	2.3
	Mix 1-O/SFG	7.3	7.7	5.4	7.4	1.3
	Mix 1-O/ABA	6.4	7.6	18.7	7.1	9.8
75 days	Mix 1-O/C	9.7	8.8	9.2	9.5	2.0
	Mix 1-O/SFG	7.9	8.0	1.2	7.7	2.5
	Mix 1-O/ABA	7.3	7.9	8.2	7.4	1.3
90 days	Mix 1-O/C	10.2	9.1	10.7	10.0	2.0
	Mix 1-O/SFG	8.8	8.3	5.6	8.1	6.8
	Mix 1-O/ABA	8.1	8.5	3.7	7.6	6.5

As can be seen from the Tables 6.9 and 6.10, the variation in the predicted and measured carbonation depth is below 15% for all the mixes at most of the exposure durations. On the basis of above discussion, it can be concluded that both the raw as well as the fitted data of impedance

spectra can be used effectively to evaluate the carbonation behavior of concrete using the developed prediction model. Since EIS being a non-destructive technique, its use in predicting carbonation depth can proven to be highly beneficial for monitoring the extent of carbonation front in the actual structures located in carbonated environment.

Table 6.10 Comparison between measured carbonation depths with predicted carbonation depth based upon Z_{DH} and resistance R_1 in PPC concrete

Exposure duration (days)	Specimens	Carbonation depth (mm)				
		Measured (mm)	Predicted by eq. (6.5)		Predicted by eq. (6.8)	
			Predicted (mm)	Variation (%)	Predicted (mm)	Variation (%)
15 days	Mix 1-P/C	4.3	3.2	25.6	3.7	13.9
	Mix 1-P/SFG	3.2	3.6	12.5	5.0	36.2
	Mix 1-P/ABA	3.0	2.5	16.6	3.2	6.6
30 days	Mix 1-P/C	7.0	6.1	12.8	5.3	24.3
	Mix 1-P/SFG	4.7	6.3	34.0	6.5	27.6
	Mix 1-P/ABA	4.1	4.6	12.2	3.9	4.8
45 days	Mix 1-P/C	9.1	8.9	2.1	9.2	1.0
	Mix 1-P/SFG	5.6	7.2	28.5	7.6	26.3
	Mix 1-P/ABA	4.9	5.3	9.3	4.5	8.1
60 days	Mix 1-P/C	10.9	12.2	11.9	10.9	0
	Mix 1-P/SFG	7.0	7.6	8.5	8.2	17.1
	Mix 1-P/ABA	5.7	6.3	10.5	5.2	8.7
75 days	Mix 1-P/C	13.8	13.2	4.3	12.7	7.9
	Mix 1-P/SFG	8.1	7.8	3.7	9.2	11.9
	Mix 1-P/ABA	7.1	6.5	8.4	5.6	21.1
90 days	Mix 1-P/C	14.6	13.9	4.7	13.6	6.8
	Mix 1-P/SFG	9.8	8.2	16.3	10.0	2.0
	Mix 1-P/ABA	8.0	6.9	13.7	6.3	21.2

6.10 CLOSING REMARKS

In this chapter, the effectiveness of migrating type inhibitors in resisting carbonation induced corrosion in concrete specimens was studied using non-destructive EIS technique. The

EIS data so obtained were presented through Nyquist and Bode plot formats. The Nyquist plots recorded in OPC and PPC concrete, with and without inhibitor application had two capacitive arcs. The first capacitive arc was generally observed between a frequency range of 10kHz to 10Hz and correspond to bulk properties of the concrete, while the second capacitive arc (observed between frequency range of 10Hz to 10mHz) correspond to the rebar (electrode) related features. The interpretation of the obtained impedance plots was done through equivalent electrical circuits using the ZMAN software. In all the obtained impedance plots, the discrepancy between the raw and the fitted data was less than 5%, indicating that the adopted equivalent circuits describe the steel-concrete interface effectively.

The progressive change in the Nyquist plots with increase in exposure duration for control specimens shows an increase in radius of the high frequency arc with a corresponding decrease in the low frequency arc. The increase in radius of the high frequency arc represents conversion of Ca(OH)_2 into CaCO_3 during progressive carbonation, while the decrease in low frequency arc represents continuous de-passivation of the resistive oxide layer from the rebar surface. The concrete specimens treated with migrating type corrosion inhibitors SFG and ABA exhibit behaviour different from that observed in the control samples. The concrete specimens treated with inhibitor SFG showed efficient behaviour right from the beginning, which later stabilized towards the end of exposure of 90 days. On the other hand, efficiency of specimens treated with inhibitor ABA improved with time i.e. it was less efficient at smaller exposure duration, but gained efficiency as it reached towards the end of exposure duration of 90 days. It indicated that the mechanism of protection provided by both the tested inhibitors varied. The inhibitor SFG decreases the corrosion rate by retarding the diffusion process, while ABA provides double protection, in terms of controlling diffusion of carbonation front and retarding the charge transfer reaction on the rebar surface.

The impedance difference parameter (Z_{DH}) measured between 10Hz to 10kHz frequency range, fitted value of R_1 and measured carbonation depth show a strong correlation between them, as can be observed from the high values of regression coefficient (0.86 - 0.92). On comparing the measured carbonation depth with difference in impedance obtained at “t” time and impedance obtained at one day, it was observed that the carbonation depth had a logarithmic relationship with the impedance difference. On the other hand, carbonation depth also had a

strong linear relationship with the fitted resistive parameter R_1 of high frequency arc. The variation in the predicted carbonation depths by using the developed relationship and measured carbonation depths was below 15% for most of the exposure durations. Thus, it can be concluded that all these relationships can be used effectively to predict the carbonation depth from EIS data, which is a non-destructive technique and can be performed in-situ also.

CHAPTER 7

CONCLUSIONS AND SCOPE FOR FUTURE WORK

7.1 GENERAL

The aim of the present research work is to investigate the effectiveness of migrating type corrosion inhibitors in inhibiting the carbonation induced rebar corrosion. In reinforced concrete, the occurrence of corrosion phenomena would take long time. Therefore, the initial selection of corrosion inhibitors for further detailed investigations was based upon the preliminary investigation done on synthetic solution of saturated calcium hydroxide with reduced pH, which simulates the pore water chemistry of reinforced concrete under carbonation attack. Performances of the bare steel specimens in different solutions have been studied through potentiodynamic polarization technique. During this preliminary stage, the performance of four generic inhibitors namely; Ethanolamine (G.I1), Sodium gluconate (G.I2), 2-Aminobenzoic acid (G.I3) and Dicyclo-hexalamine (G.I4) and four commercially available inhibitors; Aminoalcohol and Aminocarboxylates based (C.I1), organic based (C.I2), organic based (C.I3) and Aminoalcohol based (C.I4) were explored.

Based on the preliminary investigations, two best performing inhibitors were selected and their performance as surface applied migrating type corrosion inhibitor was investigated by applying them on the surface of reinforced concrete specimens. The test variables for the present investigation were two different cement type (OPC and PPC), two w/c ratio (0.43 and 0.52) and two types of inhibitors (SFG and ABA). The carbonation acceleration in the specimens was achieved in the carbonation chamber maintained at relative humidity of 60 -70%, temperature of $30 \pm 2^{\circ}\text{C}$ and $5 \pm 0.5\%$ CO_2 concentration by volume. The investigations were carried out to study variations in carbonation depth, compressive strength and rebar corrosion. Concrete cubes of 100mm and 150mm were respectively prepared for carbonation depth and compressive strength measurements; while prism specimens of size 300 x 300 x 150mm were cast for rebar corrosion measurements. Inhibitor effect on corrosion behaviour of the embedded rebar was studied in terms of Half-cell potential, Tafel Extrapolation measurement and Electrochemical Impedance Spectroscopy (EIS). The effectiveness of the inhibitors application has been compared with the

behaviour of corresponding control specimens. To quantify the carbonation depth using EIS technique, mathematical models have been developed using regression analysis.

The present chapter deals with major conclusions drawn on various parameters for evaluating the effectiveness of the migrating type inhibitors against carbonation induced corrosion.

7.2 PERFORMANCE OF BARE STEEL IN SYNTHETIC SOLUTION

1. The tests conducted using synthetic pore solution of calcium hydroxide as a representative concrete pore solution to check the corrosion of bare steel is established as an alternate preliminary test procedure to check the efficiency of the tested inhibitors in a short period of time.
2. There is a remarkable difference in the potentiodynamic polarization curves obtained for uncarbonated solution and carbonated solution. In the uncarbonated solution (pH 12.5), three distinct zones of corrosion namely; active, passive and transpassive zone are clearly identified. However, no such explicit passive behaviour could be seen in the carbonated solution (pH 8.1). As the corrosion current density (i_{corr}) in carbonated solution was higher than the uncarbonated solution, it can be concluded that the rebar in the carbonated solution is at higher corrosion risk.
3. All the four tested generic type inhibitors influenced the polarization behaviour of the specimens, which varied based on the type of inhibitor added to the carbonated solution. Higher corrosion current density shown by inhibitor G.I1 ($15.8 \mu\text{A}/\text{cm}^2$) and G.I4 ($7.2 \mu\text{A}/\text{cm}^2$) proves the ineffectiveness of these inhibitors towards carbonated induced corrosion. Inhibitor G.I2 could not improve the corrosion current density of the steel, but the formation of active/ passive transition zone supported the growth of passive layer on the steel surface. The lower i_{corr} value ($3.9 \mu\text{A}/\text{cm}^2$) along with the stabilized active/passive transition zone in inhibitor G.I3 signified the effectiveness of this chemical in CO_2 polluted environment. Therefore, it can be concluded that among the tested chemicals, 2-Aminobenzoic acid is the most efficient generic inhibitor against carbonation induced corrosion.

4. On comparative analysis of the four commercially available inhibitors used in the preliminary investigation, it was found that inhibitors C.I1 and C.I3 had higher i_{corr} value of $33\mu\text{A}/\text{cm}^2$ and $35\mu\text{A}/\text{cm}^2$ respectively; clearly indicating the ineffectiveness of these inhibitors in CO_2 contaminated solution. The presence of inhibitor C.I2 demonstrated contradictory behaviour. Wherein, it was able to reduce the i_{corr} by 46% as compared to the carbonated solution without inhibitor, however, the corresponding potential shifted towards the active side. Decrease in i_{corr} value with the potential shift towards the nobler side observed with use of inhibitor C.I4, confirmed its effectiveness in resisting corrosion in the carbonated solution. Therefore, in the category of commercially available inhibitors C.I4 was found to be most efficient inhibitor.
5. At 240h of immersion time, maximum inhibiting efficiency of 71% and 61% was achieved in the presence of inhibitor C.I4 and G.I3 respectively. Thus, based upon the pore solution results, inhibitor C.I4 and G.I3 were selected for further investigation to check their effectiveness as surface applied migrating inhibitors in carbonated environment.

7.3 INHIBITOR PERFORMANCE ON CARBONATION BEHAVIOUR OF CONCRETE

1. Carbonation depth results indicate that the variation in w/c ratio had a great influence on carbonation behaviour of concrete. In OPC concrete, increase in w/c ratio from 0.43 to 0.52 lead to a 59.8% increase in carbonation depth; where as in PPC concrete, this increase was reported to be higher as 68.4%. This increase in carbonation depth for higher w/c ratio is attributed to an increase in the porosity of mix.
2. At the end of exposure duration of 90 days, PPC concrete showed 43.13% higher carbonation depth as compared to OPC concrete. This behaviour is attributed to the lower content of portlandite $\text{Ca}(\text{OH})_2$ in concrete made with PPC cement. Thus, considering the variation in cement type, it can be concluded that PPC concrete is more prone to carbonation induced corrosion.
3. Carbonation depth increases with an increase in the exposure duration, wherein, the variation in carbonation depth could be correlated to the square root of exposure duration in days.
4. On comparative analysis, it could be found that the inhibitor SFG decreased the carbonation coefficient with respect to the control specimens by 17.58% and 34.61% in OPC concrete at

w/c ratio of 0.43 and 0.52 respectively, whereas in the PPC concrete the corresponding decrease in carbonation coefficient reported was 36.08% and 29.65% respectively for the two w/c ratios. In ABA treated specimens, the decrease in carbonation coefficient registered at w/c of 0.43 and 0.52 was 28.77% and 38.71%, respectively in OPC concrete, as compared to the corresponding control specimens. Similarly, in PPC concrete, this decrease was registered as 45.84% and 35.74% respectively. Thus, it can be concluded that the treatment of concrete surface with inhibitors decreases the carbonation depth of concrete, irrespective of the cement type and w/c ratio of the mix.

5. A decrease in carbonation coefficient with the application of inhibitors indicate that the inhibitors act as pore blockers on the concrete surface and resist the ingress of carbonation front into concrete. This conclusion was further verified through additional peaks in inhibitor treated specimens during XRD measurement. The observed additional peak of $C_4H_4O_4$ (9%) with SFG inhibitor and $C_4H_9NO_2$ (7%) with inhibitor ABA supports the percolation of inhibitors deeper inside the concrete.
6. The strength results demonstrate that surface applied inhibitors did not have any detrimental effect on the compressive strength of concrete.

7.4 INHIBITOR EFFECT ON CORROSION BEHAVIOUR OF REBAR EMBEDDED IN CONCRETE

1. The Half Cell Potential (HCP) results indicate that concrete mix designed for a higher w/c ratio had higher value of HCP as compared to the concrete mix for a lower w/c ratio, wherein the cement type was kept constant. This behaviour is attributed to the development of porous structure in the concrete designed for higher w/c ratio. This leads to the spreading of equipotential lines over a larger area of the rebar surface, thus resulting in increase in HCP value.
2. The concrete mix made with PPC cement shows a high risk of corrosion after 45 days of exposure duration; while in OPC concrete, the majority of HCP values indicate an intermediate corrosion risk. Towards the end of designated exposure duration (90 days), higher active potential (-400mV/SCE) was shown by PPC concrete while in OPC concrete the potential was limited to -295mV/SCE . This further confirmed the conclusion that PPC

concrete is more prone to rebar corrosion as compared to OPC concrete in carbonated environment.

3. The surface applied inhibitors took some time to migrate through the concrete pores to reach the rebar level. Once the inhibitors reached the rebar surface, they were able to form a protective layer around the rebar. It was demonstrated by HCP values which shifted towards more negative potential side till 30 days of exposure, followed by shift towards nobler potential side. Towards the end of designated exposure duration, with the inhibitor ABA, less than 10% risk of corrosion was observed in OPC concrete. In PPC concrete, less negative potential is reported with inhibitor SFG (-160mV/SCE) and ABA (-213mV/SCE) as compared to corresponding control specimens (-401mV/SCE) indicating the effectiveness of these inhibitors in carbonated environment.
4. From the HCP values, it is further concluded that cement type plays an important role for the inhibitor to develop inhibiting action in the concrete specimens. In this study, in OPC concrete, the inhibitor ABA was found to be more effective; while in PPC concrete, the inhibitor SFG was more effective.
5. The Galvanic Coupling Potential (GCP) measurements conducted did not present any reversal in potential till the end of full exposure duration consider in the study, for all the control as well as in the inhibitor applied specimens. This observation is contradictory to the chloride induced corrosion and can be attributed to the difference in the type of corrosion in both environments. While uniform corrosion with progression of carbonation front is the typical feature of carbonation induced corrosion, pitting corrosion is the prominent feature of chloride induced corrosion.
6. Similar to the HCP values, corrosion current density (i_{corr}) results also interpret lesser resistance of PPC concrete as compared to OPC concrete towards the carbonation induced corrosion. At end of complete exposure duration, PPC concrete showed 59.16% and 54.78% higher i_{corr} value as compared to OPC concrete at w/c ratio of 0.43 and 0.52, respectively.
7. All the inhibitor treated specimens, with lower i_{corr} as compared to corresponding control specimens, performed better after 30 days of exposure duration. The treatment of OPC concrete specimens with inhibitor SFG registered a 47- 65% decrease in i_{corr} value while a 63-75% decrease was registered with the inhibitor ABA at the end of full exposure duration of 90 days. Similarly, in PPC concrete, 83-88% decrease in i_{corr} value was observed with the

inhibitor SFG and 75-86% decrease was reported with inhibitor ABA. This reduction in i_{corr} value with the application of inhibitors show that inhibitors had reached the rebar surface and formed a protective layer around the rebar surface. Thus, it can be concluded that both the inhibitors are capable of decreasing the corrosion rate of the rebar when applied on the surface as migrating type inhibitors.

7.5 EFFECTIVENESS OF INHIBITORS THROUGH EIS

1. Nyquist plots recorded for OPC and PPC concrete mixes with and without inhibitor application show two capacitive arcs. First capacitive arc is generally observed between the frequency range of 10kHz to 10Hz and corresponds to bulk properties of the concrete, whereas, the second capacitive arc is observed between the frequency range of 10Hz to 10mHz, which corresponds to electrode related features.
2. The interpretation of the obtained impedance plots was done by using equivalent electrical circuit in ZMAN software. In all the obtained impedance plots, the discrepancy between the raw and fitted data is less than 5%, leading to the conclusion that the adopted equivalent circuits describe the steel-concrete interface effectively.
3. Nyquist plots show that in control specimens, an enhancement in the exposure duration leads to increase in high frequency arc with a corresponding decrease in the low frequency arc. The increase in high frequency arc represents conversion of Ca(OH)_2 into CaCO_3 during progressive carbonation, while the decrease in low frequency arc is marked with continuous de-passivation of the resistive oxide layer from the rebar surface. On comparing the high frequency arcs obtained for OPC and PPC concrete, it was found that OPC concrete had smaller high frequency arcs as compared to the corresponding high frequency arcs observed in PPC concrete, which can be correlated to lesser progress of the carbonation front into the OPC concrete.
4. The impedance plots obtained during EIS test indicate that concrete surface treated with corrosion inhibitors SFG and ABA show behaviour different from the control sample as the exposure duration is enhanced. The efficiency of specimens treated with inhibitor SFG was maximum at the starting of exposure, which stabilized at the lower level towards the end of exposure. However, the efficiency of specimens treated with inhibitor ABA improved with increased exposure duration. At the end of full exposure duration, with the inhibitor SFG,

inhibition efficiency of 72% and 80% was achieved for OPC and PPC mixes respectively. On the other hand, with inhibitor ABA, the achieved inhibitor efficiency was 78% and 91% for OPC and PPC mixes respectively, at 90 days of exposure duration. Such high inhibitor efficiencies in all cases clearly establish the effectiveness of tested inhibitors for surface applied applications in carbonation induced corrosion.

5. There is a strong correlation between the measured carbonation depth and the high frequency arc of Nyquist plot. A logarithmic relationship is also established between the impedance difference (measured between frequency range 10Hz to 10kHz) and carbonation depth (measured by phenolphthalein indicator):

For OPC concrete specimens: $D(t) \approx 10.02 [\log \{Z_{DH}(t) - Z_{DH}(1)\}] + 0.295$; $R^2 = 0.88$

For PPC concrete specimens: $D(t) \approx 10.99 [\log \{Z_{DH}(t) - Z_{DH}(1)\}] - 0.368$; $R^2 = 0.92$

Similarly, a relationship was also established between the R_1 value of equivalent circuit (corresponding to the resistance caused by ions transfer inside the bulk concrete) and the measured carbonation depth, for both concrete types:

For OPC concrete specimens: $D(t) \approx 0.179\{R_1(t) - R_1(1)\} - 1.091$; $R^2 = 0.92$

For PPC concrete specimens: $D(t) \approx 0.081\{R_1(t) - R_1(1)\} + 2.207$; $R^2 = 0.86$

All the established relationships had a high regression coefficient R^2 near to 0.9, for all concrete mixes, indicating that these expressions can effectively be used in evaluating the carbonation depth.

6. There is a below 15% variation in the predicted carbonation depths, by using developed models and measured carbonation depths for most of the exposure durations. Thus, it can be concluded that all these relationships can be used effectively to predict the carbonation depth using Non destructive technique (NDT), which is generally used for in-situ health monitoring of structures. The impedance results obtained for reinforced concrete exposed to accelerated CO₂ environment for 90 days indicate that EIS technique can also be used as NDT to monitor the carbonation behaviour in reinforced concrete.

7.6 SCOPE FOR FUTURE WORK

Some issues that require further investigation are summarized as under:

1. The transport and protection mechanism of the migrating type corrosion inhibitors can be investigated in detail against carbonation induced corrosion.

2. The effect of the tested inhibitors in more aggressive environment corresponding to simultaneous presence of chlorides and carbon dioxide can be investigated.
3. In the present work, the inhibitor is applied prior to carbonation, i.e. it is studied as a pre-carbonation treatment. It will be interesting to investigate the use of migrating corrosion inhibitors as a post carbonation treatment procedure.
4. The EIS technique has proved to be highly efficient in carbonation induced corrosion. The technique can serve the dual purpose of predicting the progressive changes in the properties of both concrete as well as rebar with exposure duration. This technique can be studied more extensively to predict the behaviour of carbonated RC systems.

APPENDIX

APPENDIX -IA

VARIATION IN POLARIZATION CURVES WITH EXPOSURE DURATION IN CONTROL SPECIMENS

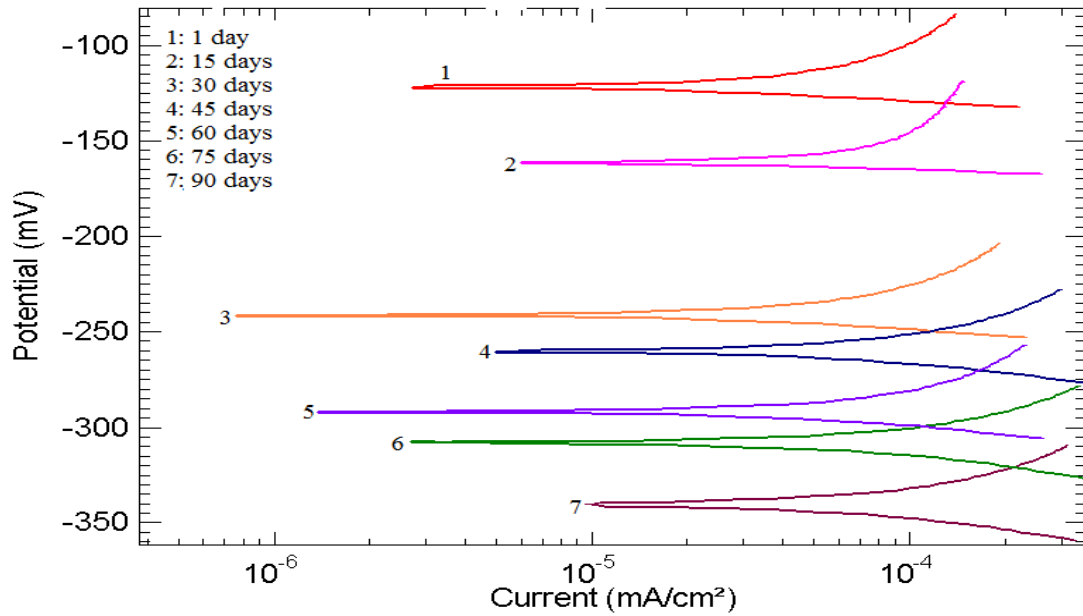


Fig.IA-1. Variation in polarization curves with exposure duration in Mix 1-O/C

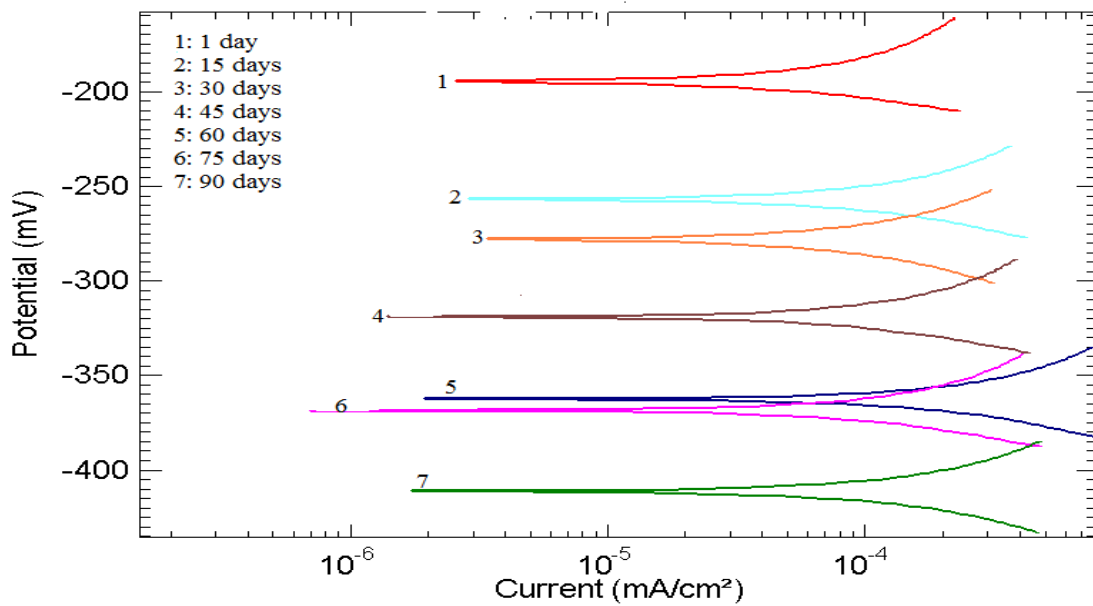


Fig.IA-2. Variation in polarization curves with exposure duration in Mix 2-O/C

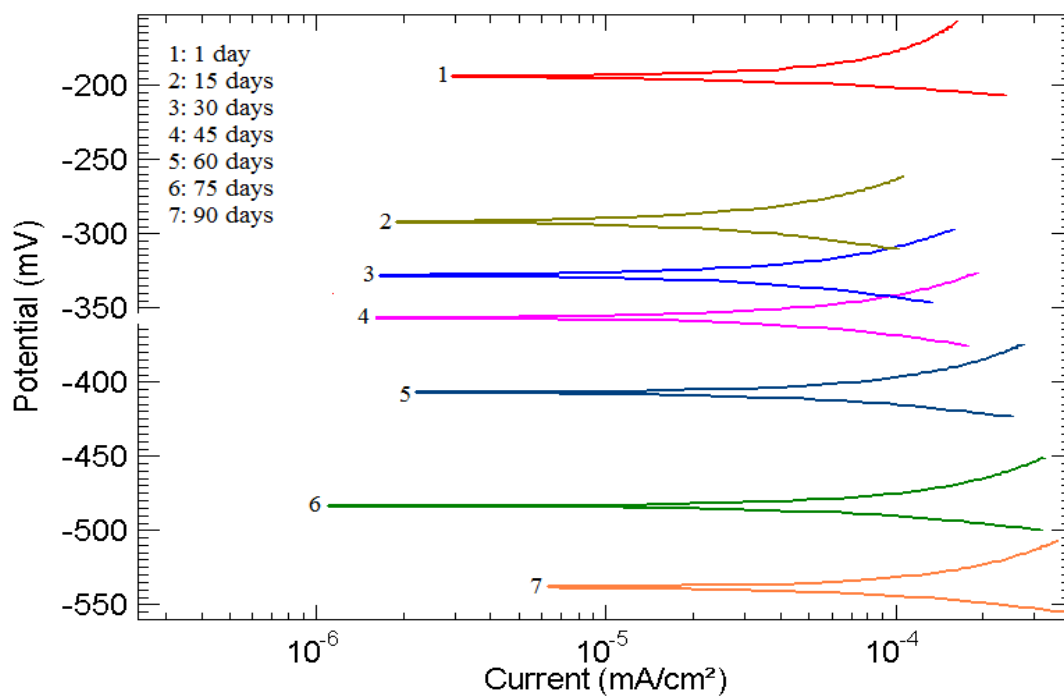


Fig.IA-3. Variation in polarization curves with exposure duration in Mix 1-P/C

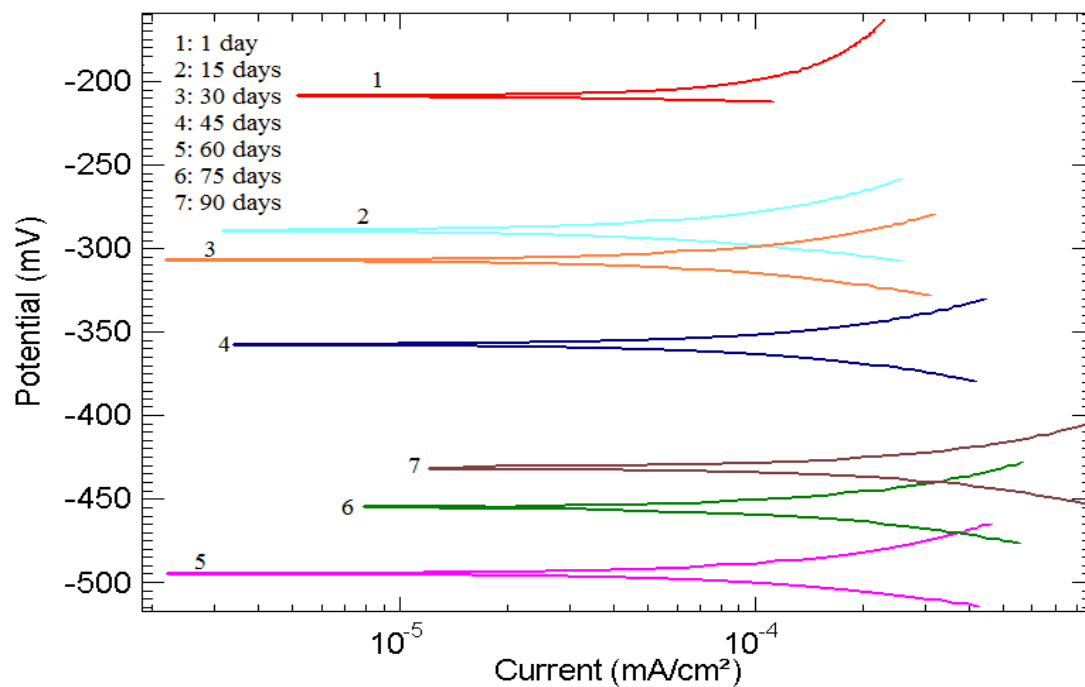


Fig.IA-4. Variation in polarization curves with exposure duration in Mix 2-P/C

APPENDIX –IIA

VARIATION IN POLARIZATION CURVES WITH EXPOSURE DURATION IN INHIBITOR TREATED SPECIMENS

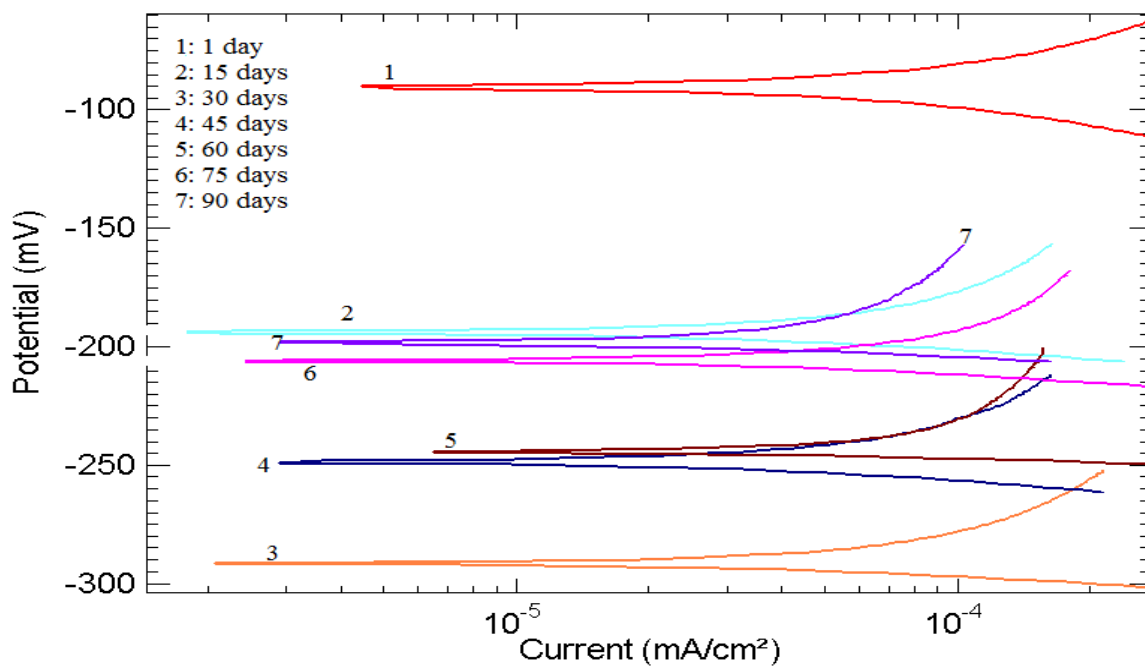


Fig.IIA-1. Variation in polarization curves with exposure duration in Mix 1-O/SFG

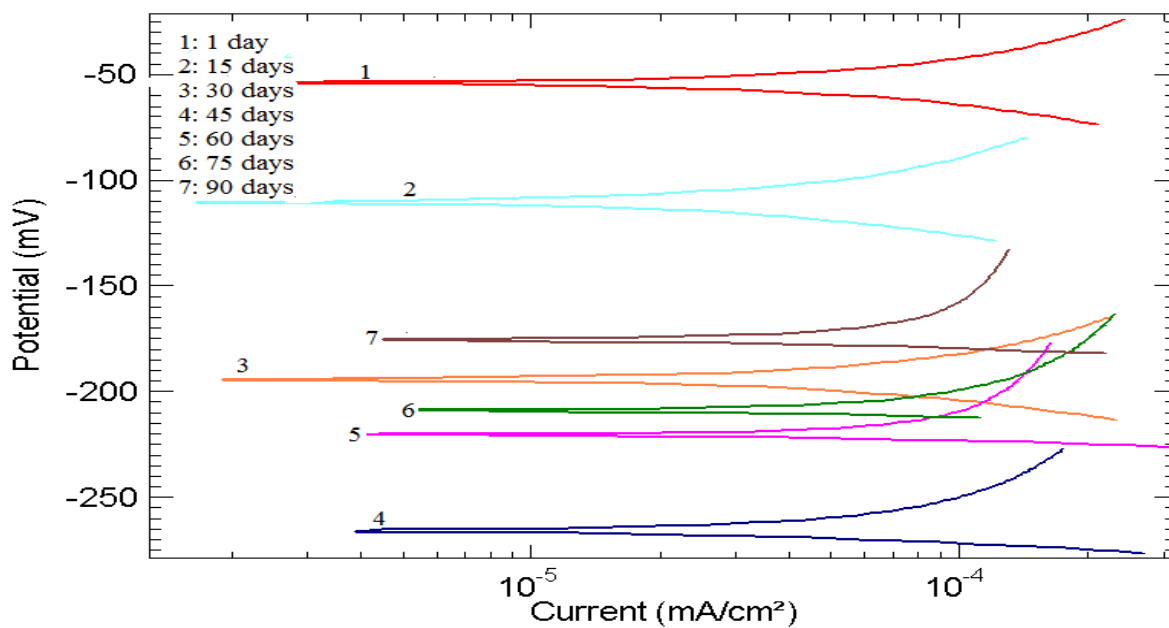


Fig.IIA-2. Variation in polarization curves with exposure duration in Mix 1-O/ABA

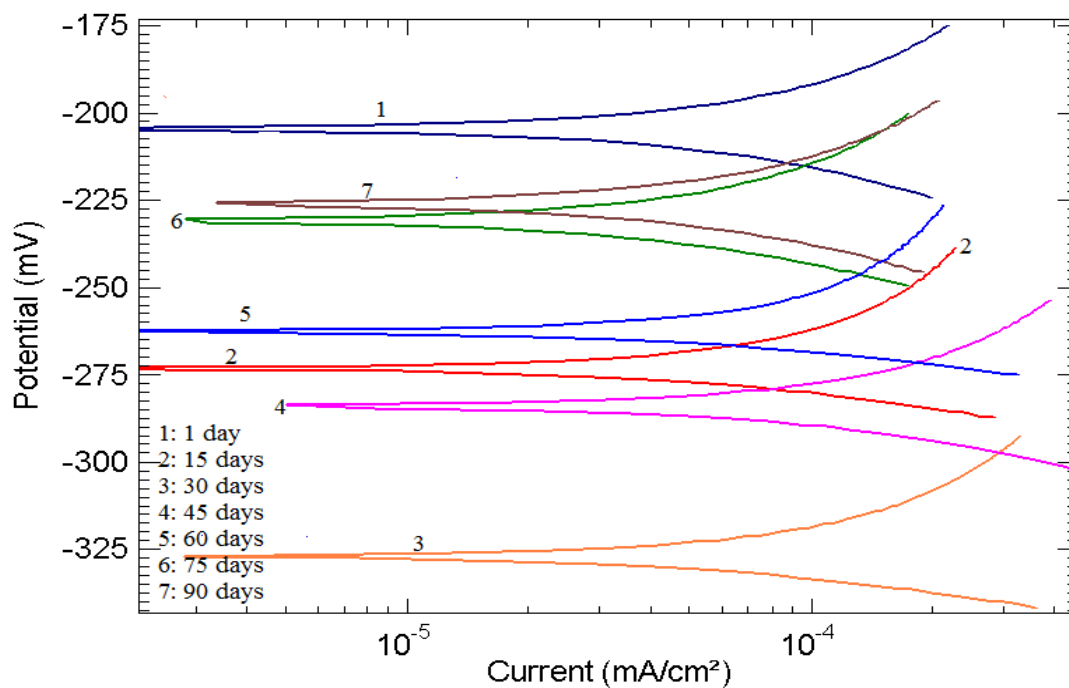


Fig.IIA-3. Variation in polarization curves with exposure duration in Mix 2-O/SFG

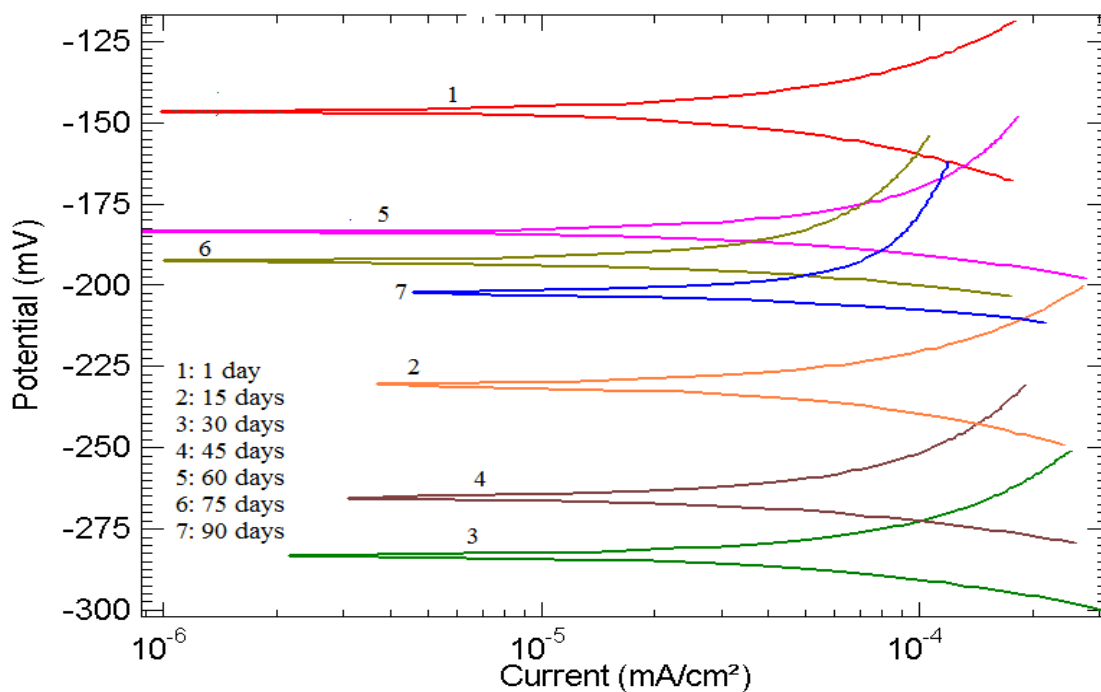


Fig.IIA-4. Variation in polarization curves with exposure duration in Mix 2-O/ABA

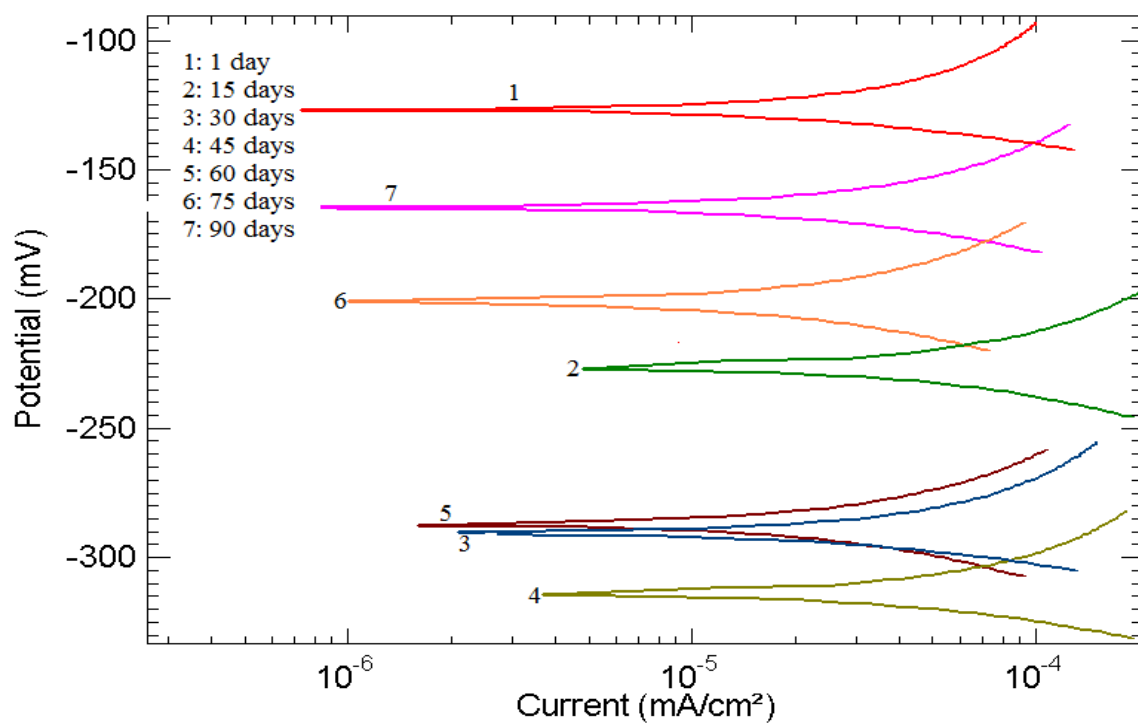


Fig.IIA-5. Variation in polarization curves with exposure duration in Mix 1-P/SFG

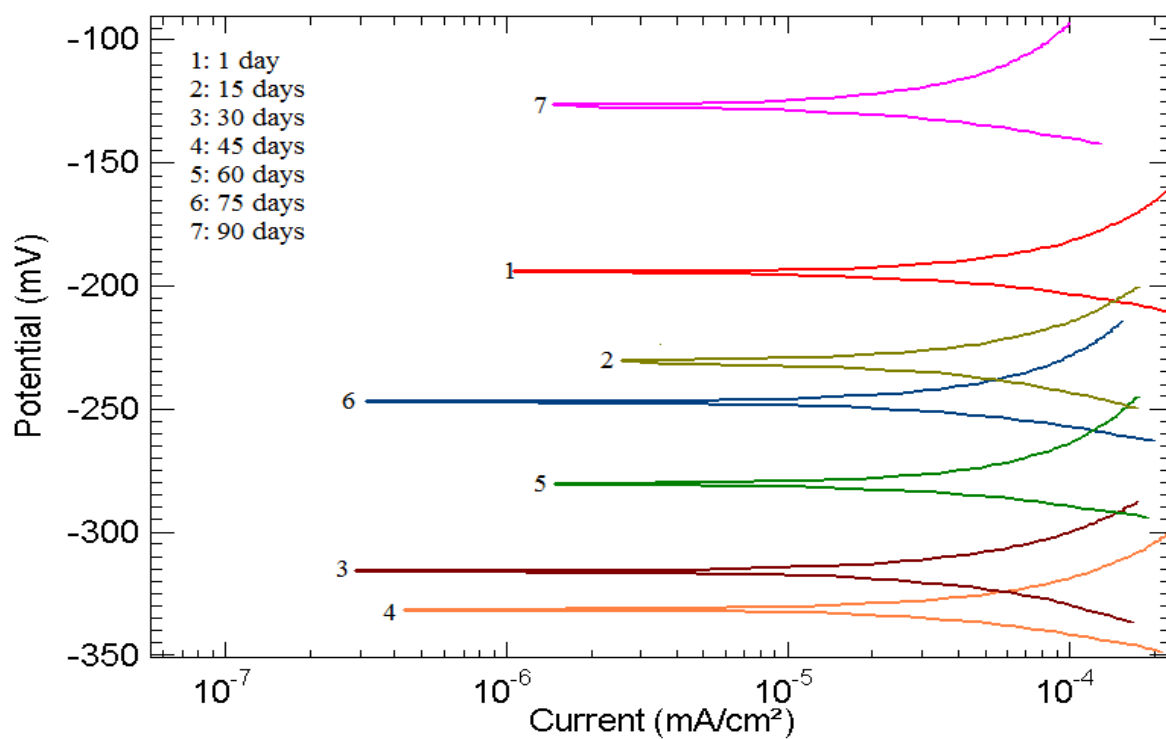


Fig.IIA-6. Variation in polarization curves with exposure duration in Mix 1-P/ABA

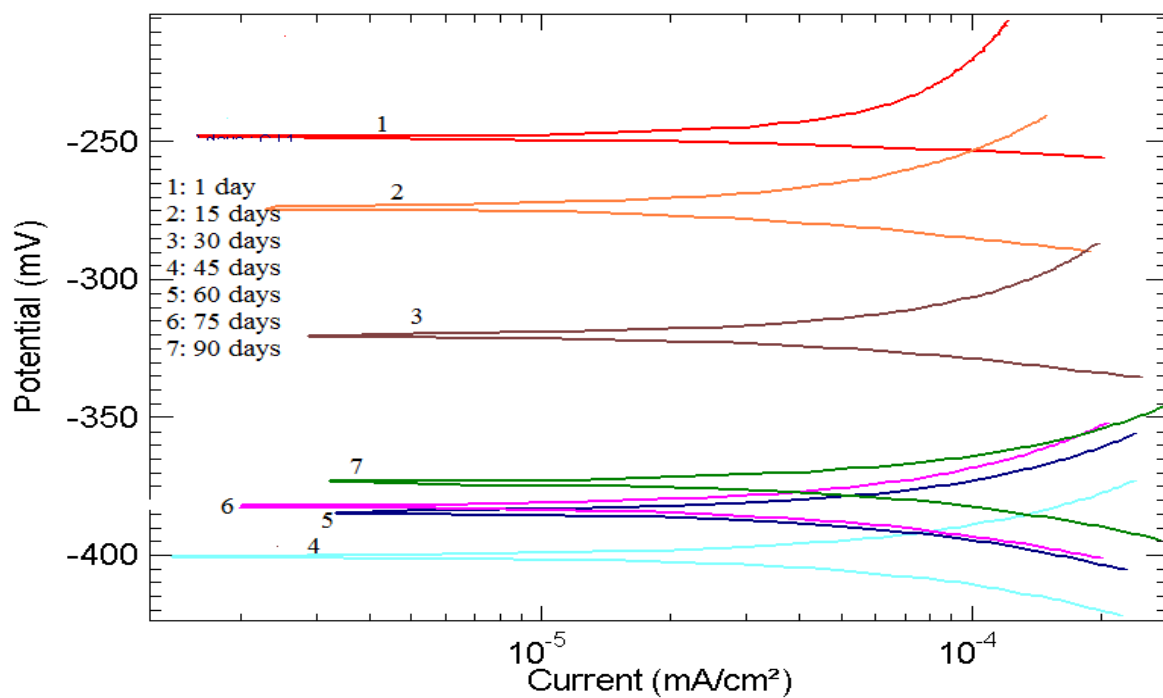


Fig.IIA-7. Variation in polarization curves with exposure duration in Mix2-P/SFG

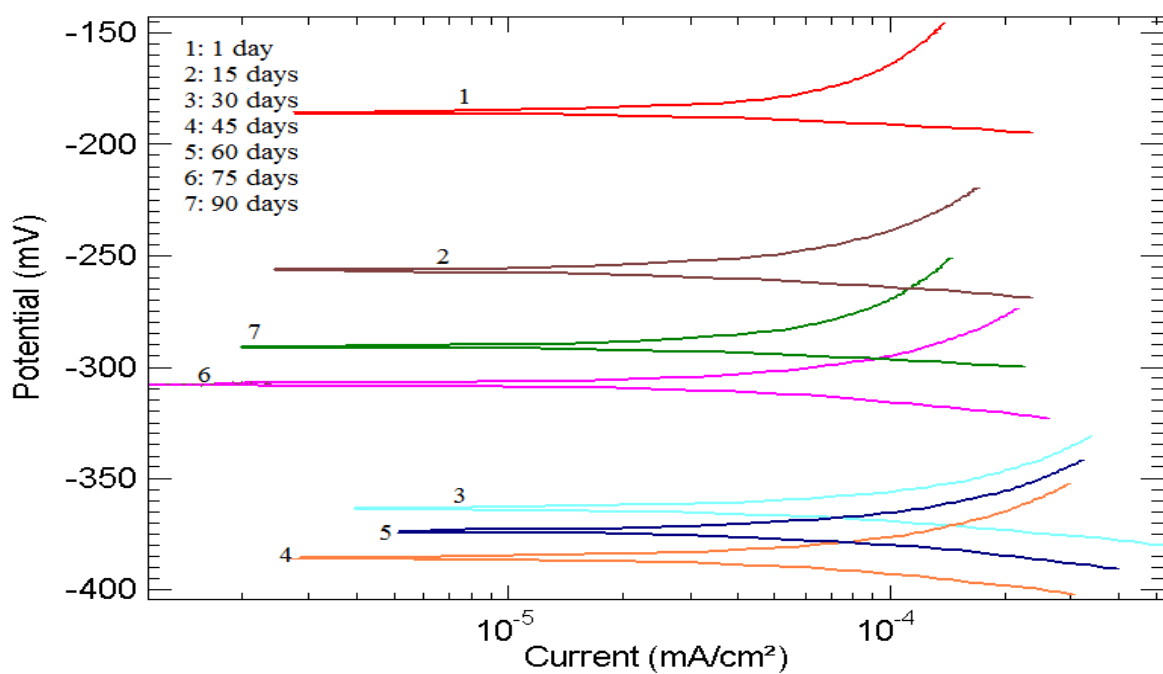


Fig.IIA-8. Variation in polarization curves with exposure duration in Mix2-P/ABA

APPENDIX- B

IMPEDANCE PARAMETERS OBTAINED FROM EQUIVALENT CIRCUIT FOR CONTROL AND INHIBITOR TREATED SPECIMENS

Table B1. Fitted impedance parameters obtained from equivalent circuit for Mix 1-O/C

EIS parameters	Exposure duration (days)						
	1	15	30	45	60	75	90
R_s ($k\Omega\text{ cm}^2$)	11	26	32	49	49	56	61
R_1 ($k\Omega\text{ cm}^2$)	-	26	43	49	54	59	62
Y_1 ($nF\text{cm}^{-2}$)	-	15	12	25	32	38	41
α_1	-	0.69	0.64	0.57	0.59	0.62	0.58
R_2 ($k\Omega\text{ cm}^2$)	108	97	83	68	53	36	24
Y_2 ($\mu F\text{cm}^{-2}$)	47	42	36	34	27	21	16
α_2	0.6	0.62	0.56	0.62	0.58	0.54	0.58
R_w ($k\Omega\text{ cm}^2$)	-	-	-	2.6	2.9	2.5	3.2
χ^2 (10^{-5})	8.2	7.8	12.2	7.3	2.9	5.2	2.59

Table B2. Fitted impedance parameters obtained from equivalent circuit for Mix 1-O/SFG

EIS parameters	Exposure duration (days)						
	1	15	30	45	60	75	90
R_s ($k\Omega\text{ cm}^2$)	9	11	35	41	39	42	43
R_1 ($k\Omega\text{ cm}^2$)	-	18	40	37	47	48	51
Y_1 ($nF\text{cm}^{-2}$)	-	20	13	10	8	4	4
α_1	-	0.63	0.58	0.52	0.57	0.57	0.59
R_2 ($k\Omega\text{ cm}^2$)	200	164	125	91	83	85	86
Y_2 ($\mu F\text{cm}^{-2}$)	44	48	50	56	59	60	74
α_2	0.73	0.87	0.79	0.60	0.67	0.64	0.60
R_w ($k\Omega\text{ cm}^2$)	-	22	43	41	45	39	38
χ^2 (10^{-5})	9.7	8.4	6.9	6.4	7.0	9.7	4.2

Table B3. Fitted impedance parameters obtained from equivalent circuit for Mix 1-O/ABA

EIS parameters	Exposure duration (days)						
	1	15	30	45	60	75	90
R_s (k Ω cm ²)	12	28	32	34	40	41	42
R_1 (k Ω cm ²)	-	21	35	38	45	47	48
Y_1 (nFcm ⁻²)	-	37	24	16	14	9	7
α_1	-	0.63	0.58	0.63	0.59	0.63	0.67
R_2 (k Ω cm ²)	158	127	98	102	108	110	112
Y_2 (μ Fcm ⁻²)	36	42	64	70	76	84	86
α_2	0.73	0.75	0.79	0.58	0.72	0.68	0.70
R_w (k Ω cm ²)	-	-	68	57	22	29	20
$\chi^2(10^{-5})$	5.4	6.7	3.6	9.1	4.3	5.8	6.0

Table B4. Fitted impedance parameters obtained from equivalent circuit for Mix 1-P/C

EIS parameters	Exposure duration (days)						
	1	15	30	45	60	75	90
R_s (k Ω cm ²)	16	23	30	29	28	24	21
R_1 (k Ω cm ²)	-	19	38	87	107	129	141
Y_1 (nFcm ⁻²)	-	33	29	19	12	8	6
α_1	-	0.73	0.57	0.53	0.58	0.53	0.57
R_2 (k Ω cm ²)	91	73	49	32	29	11	7
Y_2 (μ Fcm ⁻²)	42	73	58	43	38	18	12
α_2	0.85	0.82	0.60	0.58	0.63	0.59	0.56
R_w (k Ω cm ²)	-	22	10	5	-	-	-
$\chi^2(10^{-5})$	3.2	1.6	6.8	5.5	4.7	8.8	2.3

Table B5. Fitted impedance parameters obtained from equivalent circuit for Mix 1-P/SFG

EIS parameters	Exposure duration (days)						
	1	15	30	45	60	75	90
R_s (k Ω cm ²)	38	56	93	96	101	80	72
R_1 (k Ω cm ²)	11	45	65	78	84	97	108
Y_1 (nFcm ⁻²)	66	59	51	46	39	32	23
α_1	0.73	0.67	0.58	0.62	0.57	0.56	0.58
R_2 (k Ω cm ²)	230	130	98	75	45	32	35
Y_2 (μ Fcm ⁻²)	62	49	45	36	29	24	19
α_2	0.63	0.58	0.62	0.54	0.67	0.62	0.60
R_w (k Ω cm ²)	-	-	8.5	12.9	16.3	18.5	17.9
χ^2 (10 ⁻⁵)	4.2	5.6	3.1	7.3	2.9	3.7	3.1

Table B6. Fitted impedance parameters obtained from equivalent circuit for Mix 1-P/ABA

EIS parameters	Exposure duration (days)						
	1	15	30	45	60	75	90
R_s (k Ω cm ²)	31	43	48	57	63	70	86
R_1 (k Ω cm ²)	-	12	21	29	37	42	46
Y_1 (nFcm ⁻²)	-	11	18	12	16	32	30
α_1	-	0.59	0.53	0.60	0.62	0.66	0.62
R_2 (k Ω cm ²)	95	87	63	76	89	84	81
Y_2 (μ Fcm ⁻²)	98	71	64	58	55	53	42
α_2	0.62	0.69	0.83	0.73	0.74	0.68	0.71
R_w (k Ω cm ²)	-	10.6	15.2	18.3	20.3	30.1	31.6
χ^2 (10 ⁻⁵)	3.6	7.0	6.2	2.6	7.1	5.3	5.9

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