EFFICIENCY OF ORGANIC BASED ADMIXED INHIBITORS IN COMBINED INGRESS ENVIRONMENT

A Thesis Submitted in Fulfillment of the Requirement for the Award of the Degree of

MASTER OF ENGINEERING

IN

STRUCTURAL ENGINEERING

Submitted By

HIMANSHU GULERIA

Roll No. 801624012

Under Supervision of

Dr. Shweta Goyal

(Associate Professor)

THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

DEPARTMENT OF CIVIL ENGINEERING

THAPAR INSTITUTE OF ENGINEERING AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY), PATIALA, PUNJAB

JULY, 2018

DECLARATION

I, Himanshu Guleria, hereby declare that the work presented in this thesis entitled **"EFFICIENCY OF ORGANIC BASED ADMIXED INHIBITORS IN COMBINED INGRESS ENVIRONMENT"** in fulfilment of requirement for the award of degree **Master of Engineering** in **Structural Engineering,** submitted at Civil Engineering Department, Thapar Institute of Engineering and Technology (Deemed to be University), Patiala, is an authentic record of work carried out under supervision of **Dr. Shweta Goyal, Associate Professor,** Department of Civil Engineering, Thapar Institute of Engineering and Technology (Deemed to be University), Patiala from January 2018 to July 2018. The matter embodied in this has not been submitted either in part or full to any other institute or university for the award of any other degree.

Himanshu

Date: 30-JULY-2018

Himanshu Guleria
Roll No. 801624012

CERTIFICATE

This is to certify that the above declaration made by the student concerned is correct to the best of my knowledge and belief.

Dr. Shweta Goyal
Associate Professor
Department of Civil Engineering
Thapar Institute Of Engineering and Technology
(Deemed To Be University), Patiala, Punjab

ACKNOWLEDGMENT

This thesis work could not have been completed without the help of many people who contributed directly or indirectly through their constructive criticism. It would not be fair on my part, if I don't say a word of thanks to all those whose sincere suggestions made this period a real educative, enlightening, pleasurable and memorable one.

First of all, a special debt of gratitude is owed to my supervisor **Dr. Shweta Goyal, Associate Professor, Department of Civil Engineering, Thapar Institute of Engineering and Technology, Patiala** for her gracious efforts and keen pursuits, which has remained as a valuable asset for the successful completion of the work. Her dynamism and diligent enthusiasm has been highly instrumental in keeping my spirit high. Her flawless and forthright suggestion blended with an innate intelligent application has crowned my task a success.

I would like to express my gratitude to **Dr. Prem Pal Bansal, Head of Department of Civil Engineering**, **Thapar Institute of Engineering and Technology, Patiala** for his kind cooperation and encouragement which helped in the completion of work.

I owe my sincere thanks to Ashish Tiwari, Research Scholar, Civil Engineering Department for his guidance, time and help throughout this work. I do not find enough words with which I can express my feeling of thanks to staff of Department of Civil Engineering and Department of Biotechnology, Thapar Institute of Engineering and Technology for their help in carrying out various experiments.

Finally, I would like to dedicate this thesis work to my family who have always been a great source of support and encouragement especially in all my academic endeavours.

Himanshu

Date: 30-JULY-2018

Himanshu Guleria
(801624012)

ABSTRACT

In today's era, reinforced concrete cement is most used constructional material. But durability of reinforced cement concrete (RCC) is major issue. Corrosion in concrete system has become nemesis to RCC structures. Corrosion in rebars in concrete is like a cancer which slowly and slowly affects the structures and eventually results in the failure of the structure. Factors which influences corrosion process are chloride ions and co_2 gas present in the environment. Corrosion process forms rust on steel surface, which is non-homogeneous and occupies larger volume than normal steel and results into development of tensile and flexural stresses. This eventually leads to cracking, spalling and delamination of concrete structures.

The corrosion inhibitors are the most commonly used preventive measure because of their ease of use. The aim of this thesis study is to examine the performance of two organic: 4-amino benzoic acid (ABA) and tri ethyl phosphate (TEP) compounds as admixed corrosion inhibitor in ingress chloride and carbonation environment. Firstly, both inhibitors were tested in pore solution mimicking concrete environment and then, prismatic concrete specimens of both OPC and PPC were casted and inhibition process of both inhibitor was checked with the help of two electrochemical tests: Linear polarization resistance (LPR) and Half-cell potential (HCP) readings. Concrete cubes were also prepared in order to check free chloride content and carbonation depth.

Results obtained from various experiments showed that ABA successfully able to inhibit inhibitor mechanism into PPC concrete system by acting as chelating agent which creates passive layer and prevent corrosion process and similar result was obtained on pore solution. Whereas TEP performed in pore solution and failed in concrete ingress with chloride and carbonation environment due to single functional group and low dosage of inhibitor in concrete system. Free chloride content and carbonation depth tests on cube specimen also indicates similar results as of prismatic concrete specimens.

KEYWORDS: - Corrosion, durability, organic, concrete, 4-amino benzoic acid, tri ethyl phosphate, mechanism, inhibitors.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATION USED

2AMB	2-amino benzoic acid
ABA	4-amino benzoic acid
ACI	Admixed Corrosion Inhibitors
ACM	Association for Computing Machinery
Al_2O_3	Aluminium oxide
AMA	Amino Alcohol
BEN	Benzoic acid
BIEM	Bidirectional Electro Migration Rehabilitation
CaO	Calcium Oxide
$Ca(OH)_2$	Calcium Hydroxide
CO_2	Carbon Dioxide
DMEA	Dimethylaminoethanol
E_{corr}	Electrochemical Corrosion Potential
EDTA	Ethylene Diamine Tetra Acetic acid
EIS	Electrochemical Impedance Spectroscopy
$Fe(OH)_2$	Ferrous Hydoxide
$Fe(OH)_3$	Ferric Hydroxide
Fe_2O_3	Ferric Oxide
GDP	Gross Domestic Product
H_2CO_3	Carbonic Acid
HCP	Half-Cell Potential
I_{corr}	Corrosion Current Density
LOI	Loss On Ignition
LPR	Linear Polarization Resistance
MCI	Migrating Corrosion Inhibitor
N	Nitrogen
NaCl	Sodium Chloride
Na_2O	Sodium oxide
O	Oxygen
OCIA	Organic Compound Inhibitor Admixture
OH	Hydroxyl ions
OPC	Ordinary Portland Cement
ORG	Organic

PABA	Para Aminobenzoic Acid
pH	Potential of Hydrogen
Ph2AMB	N-phenyl-2-amino benzoic acid
PPC	Portland Pozzolana Cement
RH	Relative Humidity
S	Sulphur
SiO_2	Silicon oxide
SO_3	Sulfur Trioxide
SP	Sodium Phytate
USD	United States Dollar
TEA	Tri Ethanol Amine
TEP	Tri Ethyl Phosphate
TETA	Triethlenetetramine
TMT	Thermo Mechanical Treatment

CHAPTER 1
INTRODUCTION

1.1 GENERAL

Concrete is by far the largest quantity of material which is made up of aggregates, cement and water used in construction sectors like buildings, bridges, tunnels and many other public utility structures. Concrete has strong and weak tendency in compression and tension respectively. Hence, in order to strengthen the concrete structures, a strong material like steel is introduced in the structures which are known as reinforcement in concrete. Concrete structures when reinforced are the most durable and cost-effective structures. It has been seen over a period of time that most of the reinforced concrete structures have given excellent service life with minimum cost maintenance. However, with the methodical increase of pollutants in the environment leads to inflation in chloride ions and global warming caused by gases mainly from the greenhouse, especially carbon dioxide (CO_2) in the environment have led to corrosion process which is a major setback of reinforcement in concrete. The process of corrosion has led to decrease in lifespan and higher cost maintenance of reinforced concrete structures by an increase in deterioration of reinforced concrete structures due to spalling and delamination.

The process of corrosion in reinforced concrete has repercussion on the economy and social wellness including endangering the safety of people who are working in various industries. The annual cost of corrosion worldwide is over 3 % of the worlds GDP *(Source: inspectioneering)*. In a country like India, where economy plays a huge role will drastically change the economy if there were no corrosion. As per the Chairman of CII Corrosion Management Committee India, India losses USD 40 billion which is approximately 4% of total GDP every year on account of corrosion of infrastructure, industrial machinery and other historical heritage.

Hence, the quality of reinforced concrete should be specified in terms of strength and workability with the addition of durability. In order to produce the durable concrete, reinforced steel bars in concrete need to be protected using a different mode of the protection mechanism. The inhibitors come out to be the most effective protective measure against the corrosion. This study was conducted to evaluate the effectiveness of organic corrosion inhibitors in inhibiting reinforcement corrosion particularly when chloride ions ingresses in concrete and carbon dioxide present in the surrounding environment.

1.2 CORROSION PROCESS

The word corrosion is derived from the Latin word “Corrosus” meaning “gnawed away”. The word corrosion means breaking down or destruction of a material especially a metal through chemical reactions. The process corrosion is a naturally occurring chemical and electrochemical attack which is destructive in nature when it comes to the contact of surrounding environment. Even the presence of tiny water droplets which mostly serve the purpose of electrolyte on the susceptible metal surface which can cause electrons to flow from a high state of energy area which is called anode to a lower state of energy area called cathode can initiate and sustain the corrosion.

Concrete has a high concentration of soluble calcium, sodium and potassium oxides. When these oxides react with water they form hydroxides (OH^-) which is very alkaline (pH varies from 11 to 14) in nature *(Soylev et al. (2008)*. This leads to passive protection layer forming on the steel which is dense and impenetrable and leads to very slow corrosion process.

Two conditions which can break down the passivating environment in concrete without attacking the concrete first. One is carbonation and other is chloride attack. Area of rust on steel surface will only show once this passive layer gets broken. Figure 1.1 show anodic and cathodic reaction takes place on steel surface.

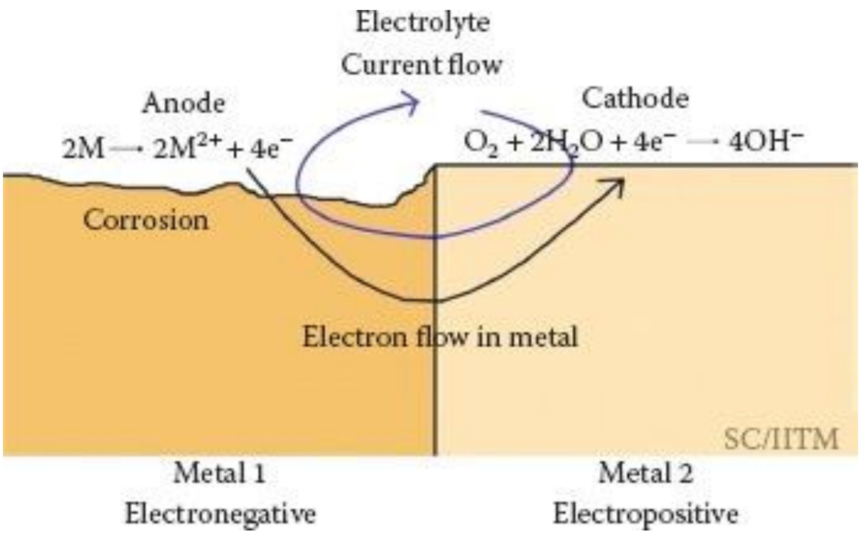


Figure 1.1 Anodic and cathodic reaction (Source: wantarengineering)

1.2.1 Anodic Reaction

$$Fe \rightarrow Fe^{2+} + 2e^{-} \tag{1.1}$$

Anodic reactions are those reactions which consume water and oxygen. In this reaction, the two electrons (2e-) which are created must be consumed elsewhere on the steel surface to preserve electrical neutrality.

1.2.2 Cathodic Reaction

$$2e^{-} + H_2O + {}^{1}/_{2}\,O_2 \rightarrow 2OH^{-} \tag{1.2}$$

Hydroxyl $(OH)^-$ ions are produced in cathodic reactions. Hydroxyl ions increase the alkalinity of concrete and therefore, will strengthen the passive layer which eventually fend off the effects of carbonation and chloride ions at the cathode. The hydroxyl ions combine with the ferrous ions to form ferrous hydroxide.

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

(Ferrous hydroxide)

This Ferrous Hydroxide in the presence of oxygen and water becomes ferric hydroxide and further, it becomes hydrated ferric oxide. Unhydrated ferric oxide Fe_2O_3 has a volume of about twice that of the steel it replaces when fully dense. When it becomes hydrated it swells even more and becomes more porous. This means that the volume increase at the steel or concrete interface is six to ten times. This leads to the cracking and spalling that been observed as the frequent consequence of corrosion of steel in concrete and the red or brown flaky, brittle rust visible on the bar and the rust stains in the concrete.

$$4Fe(OH)_2 + O_2 + H_2O \rightarrow 4Fe(OH)_3 \quad (1.4)$$

(Ferric Hydroxide)

$$Fe(OH)_3 \rightarrow Fe_2O_3.2H_2O \quad (1.5)$$

(Hydrated Ferric Oxide- Rust)

1.3 CAUSE OF CORROSION

The process corrosion happening in reinforced steel bars is the major setback for the concrete in terms of lifespan and economics of the structure. Hence, knowledge of factors which cause corrosion process is an important aspect of construction. Corrosion in steel is happened due to following major two attacks on concrete: -

1.3.1 Carbonation Attack

Carbonation is the process between carbon dioxide (CO_2) gas present in the atmosphere and the alkaline hydroxides present in the concrete. As carbon dioxide gas gets dissolves in water to form an acid. The acid formed due to the reaction of CO_2 and water does not attack the cement paste but neutralizes the alkalis present in the pore water which helps in forming calcium carbonate that lines the pores. Figure 1.2 show carbonation induced corrosion and Equation 1.6 and 1.7 show reaction takes place under carbonation attack.

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (1.6)$$

(Carbonic Acid)

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O \quad (1.7)$$

Figure 1.2 Carbonation induced corrosion on concrete (Source: corrosionengineering)

Calcium hydroxide which is present in the concrete pores that helps in dissolving the pore water and to maintain the pH at its usual level of 12-13. However, as carbon dioxide present in environment reacts with calcium hydroxides present in concrete pores which eventually results in precipitating the calcium carbonate and allowing the pH to fall to a level where steel will corrode. The carbonation induced corrosion mainly results in uniform corrosion on the structures.

1.3.2 Chloride Attack

For commencement of corrosion process, chloride ions present in the environment must penetrate the passive layer in concrete. These chloride ion plays the role of catalyst and initiate the anodic reaction at rapid rate than normal leading to higher corrosion rate. The reaction involved in chloride attack are given by Equation 1.8 and 1.9.

$$Fe^{2+} + + 2Cl^{-} \rightarrow FeCL_2 \quad (1.8)$$

$$FeCL_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl \quad (1.9)$$

Hence, in above reaction Cl^{-} is regenerated so that the rust contains no chloride, although iron chloride is already formed at the intermediate stage. Eventually it makes easier for aggressive agents to ingress towards the steel with a consequent increase in the rate of corrosion and progress of corrosion at the anode reduces the cross-sectional area of the steel which reduce its load carrying capacity. Figure 1.3 shows chloride induced corrosion on concrete surface. Chloride-induced corrosion mainly causes pitting corrosion in the structures.

Figure 1.3 Chloride induced corrosion on concrete (Source: civilengineeringforum)

1.4 CLASSIFICATION OF CORROSION

Corrosion process is destruction of material by means of chemical or electrochemical process. Corrosion can be classified into various different following categories: -

1.4.1 General Attack Corrosion

General attack corrosion is the most common type of corrosion and also known as uniform corrosion. Uniform corrosion is caused by a chemical or electrochemical reaction that results in the deterioration of the entire exposed surface of a metal. Ultimately, results in the deteriorating the metal to the point of failure. General attack corrosion accounts for the greatest amount of metal destruction by corrosion but is considered as a safe form of corrosion, due to the fact that it is predictable, manageable and often preventable. General attack corrosion Occurs in RCC structures when subjected to carbonation induced corrosion due to ions of alkalinity of the whole surface of rebar. Figure 1.4 show uniform corrosion on steel surface.

1.4.2 Localized Corrosion

Localized corrosion is different from the uniform corrosion. This corrosion attack specifically targets one part or area of the metal surface. Hence, this corrosion can be classified into following three types: -

1.4.2.1 Pitting corrosion

Pitting corrosion happens when a small cavity or hole, forms on the metal surface due to depassivation of a small area on the metal surface which results that area to act as anodic whereas the rest part of the remaining metal becomes cathodic which eventually results into galvanic localized reaction. This small area deteriorates with time results into penetration of the metal which lead to failure of metal. Pitting corrosion is rarely detected due to its relatively small size and usually covered or hidden by compounds made up of corrosion. Pitting corrosion found in RCC structures when it is subjected to chloride-induced corrosion as shown in Figure 1.5.

Figure 1.4 Uniform Corrosion (Source: nace)

Figure 1.5 Pitting Corrosion (Source: steelfabservices)

1.4.2.2 Crevice corrosion

Crevice corrosion is related to lifeless microenvironment. Crevice corrosion often found under gaskets, washers and clamps. This corrosion is somewhat similar to pitting corrosion as crevice also occurs at a specific location. Condition such as acidic or oxygen depletion results into crevice corrosion. Crevice corrosion is shown in Figure 1.6.

Figure 1.6 Crevice corrosion (Source: cdcorrosion)

1.4.2.3 Filiform corrosion

Filiform corrosion generally happens underplated or painted surfaces when water passes through the weak coating. At first, filiform corrosion starts at defects in the coating which are small in size and then reaches where it can cause weakness in structure. Figure 1.7 shows filiform corrosion.

Figure 1.7 Filiform Corrosion (Source: airforums)

1.4.3 Galvanic Corrosion

Galvanic corrosion happens when galvanic couple forms between two different sets of metals placed together in a corrosive electrolyte as shown in Figure 1.8. In such case one metal becomes the anodic and other metal acts as cathode which results into deterioration of anodic metal at a much faster rate than it would alone and slowly deterioration of cathodic metal. Galvanic corrosion is also known as dissimilar metal corrosion and it normally happens at large size of structure.

Figure 1.8 Galvanic Corrosion (Source: steelfabservices)

1.4.4 Intergranular Corrosion

Intergranular corrosion happens because of the impurities present in the metal and fact is impurities are high in content near the grain boundaries. Hence, chemical or electrochemical attack near the metal's grain boundaries results into intergranular corrosion as these grain boundaries are prone to corrosion than the rest of the metal surface.

Figure 1.9 Intergranular Corrosion (Source: steelfabservices)

1.4.5 Fretting Corrosion

Fretting corrosion found on uneven rough surface due to repeated vibration and wearing which results into pits and grooves on the rough surface. Fretting corrosion mainly occurs in bolted assemblies, impact machinery, bolted bearings and surface where frequent vibrations happens like during transportation.

Figure 1.10 Fretting Corrosion (Source: performancewire)

1.4.6 Flow-Accelerated Corrosion

Flow-accelerated corrosion occurs when protective oxide layer is removed or vanished by the water or wind on the metal surface leads to exposure of underlying metal results into further deterioration and corrosion of metal surface. Hence, flow accelerated corrosion also known as flow-assisted corrosion.

Figure 1.11 Flow Accelerated corrosion (Source: performancewire)

1.4.7 High Temperature Corrosion

As the name suggest, this corrosion happens in high temperature machinery like diesel engines, gas turbines as shown in Figure 1.12. During the combustion process in these machinery, sulphates compounds are formed with low melting point which are corrosive in nature towards metal alloys which are otherwise resistant to high temperature.

Figure 1.12 High temperature corrosion (Source: amteccorrosion)

1.4.8 Environmental Cracking Corrosion

Environmental cracking corrosion is the conditional corrosion which depends upon the condition of surrounding the metal surface. Conditions such as chemical, temperature and stress-related may affect metal surface. Seasonal cracking of brass and embrittlement of caustic steel are two common types of environmental cracking corrosion. Figure 1.13 show environmental cracking corrosion.

Figure 1.13 Environmental cracking corrsion (Source: performancewire)

1.5 FACTORS INFLUENCING CORROSION

Corrosion process is affected by lot of factors present in the environment which leads to formation of rust on the metal surface which eventually results into failure of concrete structure. These factors are defined as following: -

1. Nature of metal

Nature of metal plays an important and significant role whether the metal will go through corrosion process. Mostly metals with low electrode potential which means more reactive in nature for example sodium, zinc, potassium and others are more influenced by corrosion process and metals like silver, gold are less reactive in nature which signifies their lower corrosion rate.

2. Film protection

Protective film on metal surface acts as physical barrier to rate of corrosion process which results into cutback of corrosion. Metals like Al often forms a protective layer which provides passivation against corrosion.

3. pH

Generally different metals corrode at different pH value. But it has been seen that in lower pH value, corrosion rate is higher as compared to high pH value. Metals like iron, forms protective film on metal surface in alkalinity medium. Similarly, other metals like magnesium, zinc also have high corrosion rate in acidic medium due to rate of hydrogen evaluation. Hence, increasing the pH value may help in forming passive layer and immunity against corrosion.

4. Temperature

Rate of corrosion process is highly dependent on temperature. Generally, corrosion process is influenced by dissolved oxygen and the rate of corrosion becomes twice with every 10 degrees rise in temperature. There is difference in rate of corrosion in open and closed vessel containers, as diffusion of oxygen takes time in closed vessel where rate of corrosion remains high at the end of process whereas in open vessel rate of corrosion remains high at a certain temperature then falls to lower value due to the fact that oxygen is diffused at higher rate as compared to another place.

5. Dissolved oxygen

Dissolved oxygen plays an important role on rate of corrosion. If dissolved oxygen amount is on higher side then corrosion rate will increase as dissolved oxygen gets consumed in cathodic process in every medium. If level of oxygen is zero in neutral and alkaline medium, then corrosion becomes zero.

1.6 PREVENTIVE MEASURES OF CORROSION

To have longer and durable reinforced concrete life, some preventive measures against the corrosion should be taken. These preventive measures have some advantage and disadvantage of their own. Some of these major preventive measures are of as following: -

1. Design as per Indian standard codes

2. Protective coatings

3. Use of sealants

4. Use of non-corrosive metals

5. Corrosion Inhibitors

1.6.1 Design As Per Indian Standard Codes

Corrosion process cannot be prevented thoroughly but limit by designing the structures as per Indian standard codes. First mode of defence against the corrosion in reinforced concrete is assumed to be the cover applied. Hence, cover applied should be strickly based on Indian standard codes.

1.6.2 Protective Coatings

Use of different types of coatings like oxide, phosphate and many others can limit the process of corrosion. Use of iron with zinc can helps in preventing from rust. Coatings can be applied by spraying, electroplating and galvanizing on metal surface. Applying coatings process is quite expensive.

1.6.3 Use of Sealant

Sealant can limit the corrosion process but it cannot stop it from its roots. Sealant is a material of viscous quality which has no flow properties. Sealants can act as barriers to certain substance like dust, fire, air, smoke and other environmental factors. Most common type of sealants used in industries are epoxy, latex, acrylic.

1.6.4 Use of Non-Corrosive Metals

Corrosion can be prevented by using non-corrosive metals instead of corrosive metals. Stainless steel can be use as rebars in concrete to prevent from corrosion. Other than this, glass fiber reinforced plastic (GFRP) can be use as rebars to restraint cracks in structures. The use of non-corrosive metals can be very expensive as compare to use of mild steel.

1.6.5 Corrosion Inhibitors

Among all the available preventive measures from cancer like diseases corrosion, inhibitors seem to be the most significant preventive measure in terms of usage, economics, easy handling and overall effect on durability of concrete structures. Inhibitors are defined as substance made up of chemicals which decrease the rate of corrosion when present at suitable concentration in system without affecting the concentration of any other corrosion agent. Inhibitors can be use as admixed and migratory in concrete system. For fresh concrete, admixed inhibitors have been used since 1970s whereas, in repair work migratory inhibitors have come in existence only in last 10 years.

1.7 THESIS OBJECTIVE

In past, both organic and inorganic compounds have been successfully used as admixed and migratory inhibitors in carbonation and chloride environment separately. But still, there is a lot of work required in the war against corrosion to identify the efficient, economic and environmental friendly corrosion inhibitors. Hence, in this thesis, the efficiency of chemicals like 4-amino benzoic acid and tri ethyl phosphate as inhibitor in combined ingress chloride and carbonation environment is tested. Also, effect of different functional groups (amines, carboxyl and phosphate) in combined environment tested in pore solution and reinforced concrete is checked.

1.8 FORMAT OF REPORT

The format of whole thesis report has been summarized in following six chapters: -

1. In the first chapter of this thesis report, corrosion process and causes of corrosion is discussed.

2. In second chapter of thesis report, inhibitors and classification of inhibitors are presented.

3. Third chapter of the report deals with literature review on corrosion inhibitors.

4. Fourth chapter carries the experimental part which includes various tests includes half-cell potential, linear polarization resistance on pore solution and concrete prism. Also, carbonation depth and chloride content on cubes subjected to both carbonation and chloride environment calculated.

5. Chapter five includes the results and discussion of above mentioned experiments.

6. Chapter six concludes the experiment work taken for thesis report.

CHAPTER 2
CORROSION INHIBITORS

2.1 GENERAL

Rebar corrosion in concrete is major cause behind premature failure which causes deterioration of concrete structures. Hence, various methods have been adopted so far against corrosion mainly use of sealants, various coatings, removal of chloride, corrosion inhibitors and many others. But chemical inhibitors are the most impactful, easy to use and economically sound against the deadly diseases like corrosion.

2.2 HISTORY AND CURRENT SCENARIO

Since the early 19th century, there had been evidence of use of inhibitors to protect metals against aggressive water, acidified oil wells and cooling system. Since the mid of 20^{th} century, with the advancement in field of technology resulted into application of electrochemistry to evaluate corrosion inhibitors.

Now-a-days inhibitors can be applied to commercially used instruments like cooling system, pipelines, chemical products and in various industries for example oil and gases industries, refinery industry and many other manufacturing industries.

According to recent studies, corrosion inhibitors in global market by 2021 is expected to reach USD 8.7 billion rising at 4.6% as compared to 2016. Oil based inhibitors are expected to take USD 1.4 billion which is considered to be fastest growing product whereas water-based corrosion inhibitors will take largest share of USD 6 billion among the total amount because of their easy use and high availability. With emerging economy of Asia-Pacific countries like India, China, Japan corrosion inhibitors industries are growing at rapid pace. Growing need for eco-friendly and nontoxic inhibitors have influenced the market growth (*Source: bccresearch)*.

2.3 DEFINITION OF INHIBITORS

Inhibitors has been considered as the first line of defence against the war of corrosion. Inhibitors are defined as the chemical compounds which decreases the rate of corrosion when added to given material in recommended concentration. The literature on corrosion had suggested many chemical compounds which inherent the inhibitors properties. But out of all these compounds, a few compounds are handful effectively. The reason behind this can be attribute to that desirable properties of inhibitors usually extend beyond to metal protection. Hence, while choosing inhibitors consideration like eco-friendly, cost, availability and easy handling becomes significant.

2.4 MECHANISM OF INHIBITORS

Inhibitors generally follows the following three mechanisms as described below: -

1. Mostly when inhibitors dissolved or mixed in concrete system it generally reacts with corrosive component present in the system.

2. Inhibitors gets adsorbed chemically on the metal surface and leads to formation of protective layer against corrosion.

3. Sometimes, inhibitors also form a protective layer due to the penetration of oxide in metal surface.

2.5 CLASSIFICATION OF INHIBITORS

Inhibitors can be natural and man-made chemicals. They can be classified into following categories: -

1. As per application of inhibitors

2. As per chemical nature of inhibitors

2.5.1 Classification Based on Mode of Application

Corrosion inhibitors can be further divide into following two classifications based on mode of application on concrete: -

1. Admixed Inhibitors

As the name suggest, inhibitors which are added in concrete just after the addition of water to cement. Admixed inhibitors in concrete influence the properties of concrete like initial-final strength, heat of hydration process of cement and others. Mixtures of alkanolamines, amino acids, amines, carboxylic acid and others are identified as organic admixed inhibitors where as nitrate compounds of calcium and sodium, sodium benzoate and sodium chromate identified as inorganic admixed inhibitors.

2. Migratory Inhibitors

Unlike admixed inhibitors, migratory inhibitors are able to diffuse to rebars through concrete when applied on hard concrete surface where they form a monolayer film at interface of steel and corrosion by suppressing anodic and cathodic corrosion reactions. Hence, by physical mode usage migrated inhibitors are also known as surface applied or penetrating corrosion inhibitors. Migratory applied inhibitors are frequently use now a day for the repair work of concrete structures. Organic migratory inhibitors are identified as alkanolamines and amines where as monofluro-phosphate are identified as inorganic surface applied inhibitors.

2.5.2 Classification Based on Chemical Nature

Corrosion can further be divided into two types as per their chemical nature which are as following: -

2.5.2.1 Inorganic Inhibitors

1. Anodic

Inhibitors which reduce the rate of corrosion by increasing the steel corrosion potential value by act on the dissolution of the steel. In simple words, those inhibitors which blocks anodic reaction and influence the natural reaction of passivation are known as Anodic inhibitors. Anodic inhibitors are also known as passivation inhibitors. Sodium nitrate, calcium nitrite ($Ca(NO_2)_2$), sodium benzoate and sodium chromate are most commonly used anodic inhibitors *(Soylev et al. (2008)).* The concentration of anodic inhibitors to have positive effect plays a significant role. If the amount of concentration of inhibitors is not sufficient enough then it will affect the formation of film protection as it will not cover the metal fully, leaves behind metal surface to exposed which leads to localized corrosion.

2. Cathodic

Similar to anodic inhibitors, they reduce corrosion rate by decreasing the corrosion potential by acting on the oxygen reaction on steel surface which means they prevent the occurrence of cathodic reaction. These inhibitors tend to decrease the contact of metal surface with environment by forming a barrier of precipitates over the metal surface. Cathodic inhibitors are considered better than anodic inhibitors as cathodic inhibitors are independent of concentration. Sodium hydroxide and sodium carbonate are two most commonly used cathodic inhibitors which reduce transportation of oxygen by increasing the pH level near the steel surface. Other than this, phosphates, silicates and polyphosphates can be use as cathodic inhibitors *(Soylev et al. (2008).*

3. Mixed

Some organic corrosion inhibitors act both anodic and cathodic which are known as mixed organic inhibitors as they form thin protective layer over the steel surface without changing corrosion potential remarkably. Amine and amino alcohols (AMA) are commonly used as mixed corrosion inhibitors as it forms hydrophobic group which have polar groups such as N, S and OH.

2.5.2.2 Organic Inhibitors

Generally, organic inhibitors act as anodic, cathodic or both together. Organic inhibitors often form film on rebar surface. This process is known as surface adsorption. Organic inhibitors show good inhibition efficiency with minimize environmental risk as compare to inorganic inhibitors. Organic inhibitors form a hydrophobic film of adsorbed molecules over the metal surface which blocks dissolution of the metal when comes in contact with electrolyte. Theoretically, addition of organic inhibitor decreases corrosion current but corrosion potential remains same in polarization curve. Efficiency of organic inhibitors depends upon following points: -

1. Chemical structure of organic compound.

2. Type and number of bonding atoms or molecules (pi or sigma)

3. Capability to form a complex with atom within metal lattice

4. Type of electrolyte solution available in environment

The efficiency of organic inhibitors depends upon polar functional groups like O, N and S which are present in organic compounds. These polar functional group forms hydrophobic part and leads to adsorption process. Concentration of organic inhibitor in medium is critical due to metal surface which is directly proportional to inhibitor concentration. There are some other organic inhibitors also which exist neither as anodic nor as cathodic. Compounds like amines, aldehydes, carboxylic, ascorbic acid, succinic acid, extracts of natural substances are some example of organic inhibitors (*Soylev et al. (2007))*. There are some inhibitors which act in vapor phase known as volatile corrosion inhibitor. Dicicloexilamônio benzoate, diisopropylammonium benzoate, ethanolamine benzoate or carbonate and also the combination of urea and sodium nitrite are some example of volatile corrosion inhibitor *(Dariva et al. (2014))*.

2.6 ORGANIC OVER INORGANIC INHIBITORS

Before choosing certain chemicals as inhibitors, certain aspects need to be considered as choosing wrong corrosion inhibitor will lead to change of anti-corrosive mechanism into a corrosive mechanism. These aspects are pH of metal, composition, temperature, geometry of system, impurities and concentration of inhibitors.

According to global industry analysis market, organic inhibitors has consumed over the 70% of the corrosion inhibitors market in 2012 *(Source: prnewswire.com)*. The reason behind vast consumption of market by organic inhibitors over inorganic inhibitors is absence of metals in organic corrosion inhibitors as compared to inorganic inhibitors which leads to safeguard from any unwanted chemical reactions. Moreover, inorganic based corrosion inhibitors work as anodic passivation which cannot work excellent at high chloride content environment and also requires high concentration of inhibitors in concrete system which is not environmental friendly whereas organic inhibitors work on principle of adsorption over metal surface. Also, organic corrosion inhibitors are hydrophobic in nature have minimum leaching problem as compared to inorganic inhibitors which are more soluble.

2.7 ADVERSITIES OF USING ORGANIC INHIBITORS

Very few things in this world comes with only advantages. Hence, organic inhibitors do come with some adversity. Due to mechanism of inhibit in concrete of inhibitors can neglect their effect on fresh and hardened concrete properties. Organic inhibitors when mixed with concrete system, may react with hydrates and Unhydrated which leads to chemical reaction among them which eventually affect physical and chemical properties of concrete. Chemicals like Triethanolamine (TEA) can act as both an accelerator and retarder depending on type of cement and dosage. At 0.02%, 0.25%, 0.5% and 1% addition of TEA in Portland cement, TEA acts as an accelerator, retarder, severe retarder and strong accelerator respectively *(Aggoun et al. (2008))*. Table 2.1 describes some adversities of organic inhibitors on concrete properties when applied in concrete system: -

Table 2.1 Adversities of organic inhibitors

Sr. No	Parameter	Adversities
1.	Viscosity	Reduction of viscosity in self compacting concrete *(Blankson and Erdem (2015))*
2.	Permeability	Decrease in permeability due to pore blocking effect *(Söylev et al. (2007b))*
3.	Workability	Increase in workability of concrete due to presence of -OH and -COOH *(Söylev et al. (2008))*
4.	Bond	Bond between steel and concrete gets week due to reduction of adhesion *(Söylev et al. (2007b))*
5.	Setting time and Early strength	Depends on dosage and cement type can cause inhibitor to act as accelerator or retarder *(Han et al. (2015)): (Aggoun et al. (2008))*

2.8 CONSIDERATION TO EMPLOY INHIBITORS

Several factors must be considered before employing any chemical as corrosion inhibitor. These factors are mentioned as following: -

1. Inhibitors should be free from toxicity

2. Inhibitors should be easy to handle

3. Mechanism of inhibitors should be known before applying

4.Concentration of inhibitors should be strictly followed as per manufacturer

5. Several factors like pH, geometry, composition and impurities of metals should be known before applying corrosion inhibitors

Hence, by employing above mentioned consideration regarding corrosion inhibitors will helps in achieving following three aspect: -

- ❖ Environmental aspect
- ❖ Technical aspect
- ❖ Economy aspect

2.9 TECHNIQUES FOR ANALYSIS OF INHIBITORS

Techniques which can be deployed for the effectiveness of corrosion inhibitors are as following: -

1. Weight loss measurement
2. Electrochemical Measurement
   - ➢ Linear Polarization Resistance curves
   - ➢ Electrochemical Impedance Spectroscopy
3. Microscopy Techniques
   - ➢ Scanning Electron Microscope
   - ➢ Energy-Dispersive X-ray Spectroscopy

CHAPTER 3
LITERATURE REVIEW

3.1 GENERAL

Beyond a shadow of doubt, corrosion in steel is biggest durability problem in reinforced cement concrete. Even after exhaustive study in past 50 years in the field of research, accurate solution for corrosion haven't found yet. Research process in last decade or so, helps us in understanding the process of corrosion and preventive measures taken against corrosion. World-wide exhaustive study indicates that some chemicals used as inhibitors influenced electrochemical process of corrosion. Hence, literature review presented here focusses on mechanism of organic chemicals used as inhibitors helps in stretching concrete life span by decreasing the rate of corrosion process in reinforced concrete structure.

3.2 ORGANIC GROUPS USED AS INHIBITORS

Different organic groups used as admixed in concrete as inhibitors (ACI) have been present in market since 1970's. Also, migratory corrosion inhibitors (MCI) have been using in repair work from past one or two decades. With the extensive study in this field have paved a way for many organic chemical groups to be used as inhibitors which are eco-friendly in nature too. Mixtures of organic compounds like alkanolamines, amines, saturated and unsaturated fatty acid of carboxylic acid have been used as admixed as well as migratory inhibitors *(Ormellase et al. (2006)).* Numerous number of studies in past, have been done to understand the mechanism of organic admixed inhibitors and their efficiency on concrete structures.

3.3 LITERATURE STUDY OF CORROSION INHIBITORS

I. AMINE GROUP

Morris et al. (2002) studied migratory organic inhibitors based on alkyl-amino alcohol on concrete specimen containing admixed chlorides in two different w/c ratios (0.60 & 0.40) and exposure conditions (Marines and Immersion). A cylindrical concrete specimen containing four rebars having 1 cm diameter were prepared. Inhibitors were applied on the hardened surface of concrete and kept in laboratory environment for 60 days before exposing to given environment. For marine environment, two control and two migratory inhibitor specimen were placed in a cage at the terrace on skyscraper building. These specimens were directly exposed to rainfall and wind. Whereas for immersed environment, specimens were partially immersed in 3.5% NaCl aerated solution. Various electrochemical parameters were obtained through electrochemical measurements. Figure 3.1 and Figure 3.2 show variation of E_{corr} and I_{corr} with time in the marine environment, where a indicate graph for control specimen and b indicate for specimen with inhibitor applied.

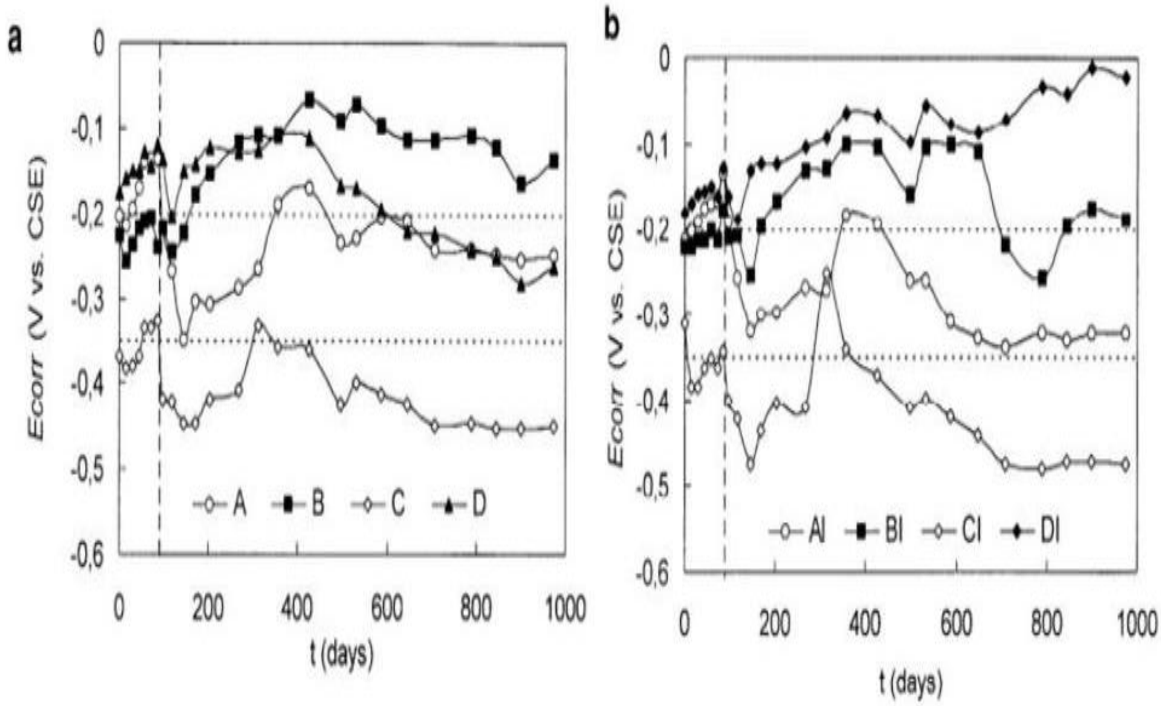


Figure 3.1 E_{corr} vs Time (Morris et al. (2002))

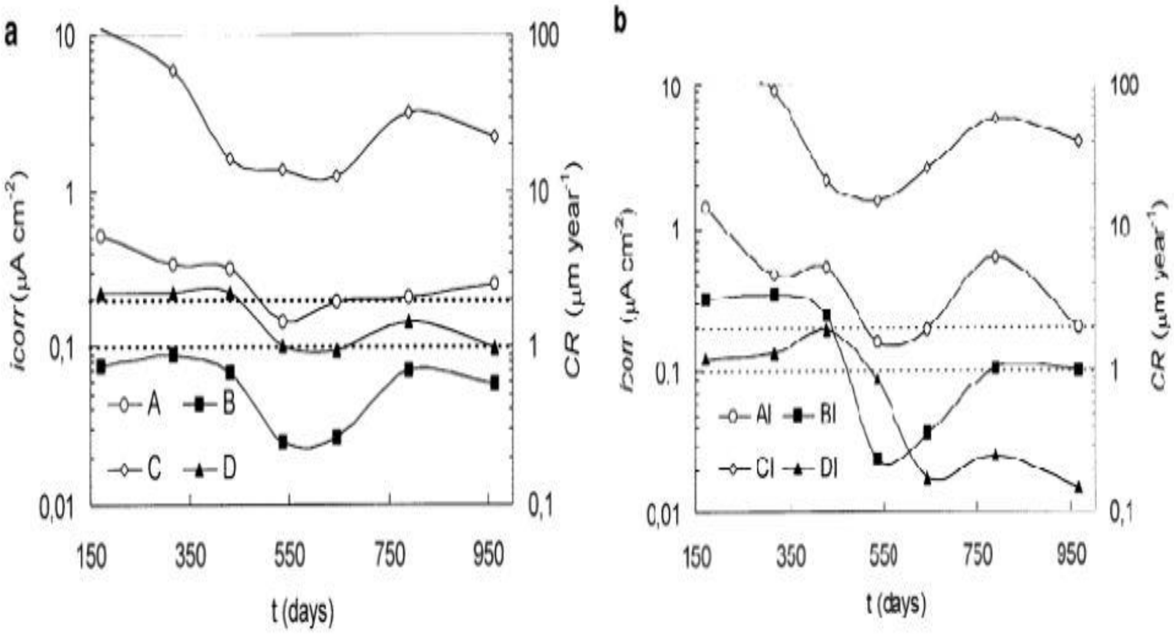


Figure 3.2 I_{corr} vs Time (Morris et al. (2002))

The graph obtained indicate that no significant difference was observed between control and migratory inhibitor specimen in CR values measured of admixed chloride content (A, B, C). Rebar CR of both specimens increased due to increase in chloride content. Whereas in mix D, concrete specimen with CR value which was one lower order of magnitude than control specimen. Inhibitors efficiency strongly depends on the initial chloride ions concentration in concrete. The inhibitor was able to reduce the CR of steel in concrete only when the initial chloride concentration was approximately 0.2 wt. % referred to the content of cement in concrete. In this case, the inhibitor was applied to concrete having no admixed chlorides and even when samples had w/c = 0.6 and were exposed to a marine condition for next 1000 days, the CR decreased almost one order of magnitude to values typical steel in a passive state (CR<1mm year-1). After this period of exposure, the concentration of total chlorides raised up to an approximately 1% at the rebar surface due to the incorporation of chlorides coming from the environment. Whereas specimen with w/c = 0.4 showed no effectiveness when applied with admixed chloride

Saricimen et al. (2002) used admixed organic alkanolamine and inorganic based inhibitor in concrete. Three concrete specimens of each with a dimension of 100 × 65 × 300 mm were prepared with 12 mm diameter reinforced bar. The inhibitor admixed as per manufactures recommendation. Water burlap curing was provided for 7 days followed by air curing under laboratory temperature then prepared specimen was provided with 5% NaCl solution for corrosion process.

electrochemical results indicated that inorganic inhibitor performed better than organic based inhibitor due to the presence of nitrogen group which changes passive film made on steel surface and simultaneously formed a new film on the surface which eventually protects steel against corrosion from chloride ions.

Trabanelli et al. (2005) had taken sodium salts of benzoic acid and its derivative amines i.e. 2-amino benzoic acid (2AMB) and N-phenyl-2amino benzoic acid (Ph2AMB) as corrosion inhibitors in carbonation environment for 400 days. The dimension of concrete specimen was taken as 25 × 25 × 3 cm with two rebars of diameter 1 cm embedded in concrete with a cover of 1 cm. The casted concrete specimen was given 3-day water curing at relative humidity greater than 95% and then kept in the laboratory for 28days for aging purpose. Carbonation for 80days provided and specimen was immersed in water partially up to 400days and then EIS spectra were obtained. Concrete cubes of 100mm were cast for measurement of carbonation depth and Figure 3.3 and Figure 3.4 shows results of carbonation depth and EIS spectra obtained respectively.

Results obtained from polarization curve showed in Figure 3.5 that only 2AMB show some inhibiting efficiency against corrosion whereas BEN polarization curve overlapped of the controlled specimen which means no inhibiting efficiency against corrosion process. Carbonation rate was increasing in 2AMB as compared to BEN and Ph2AMB.

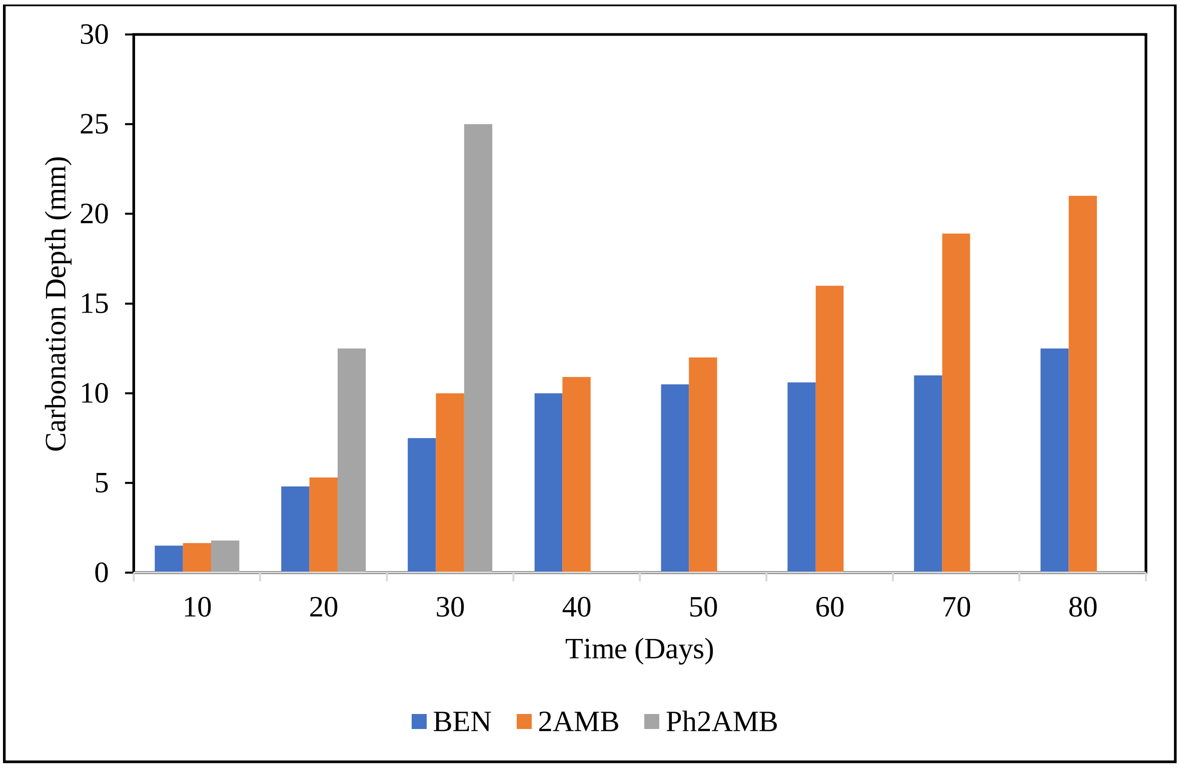


Figure 3.3 Carbonation depth vs time (Trabanelli et al. (2005))

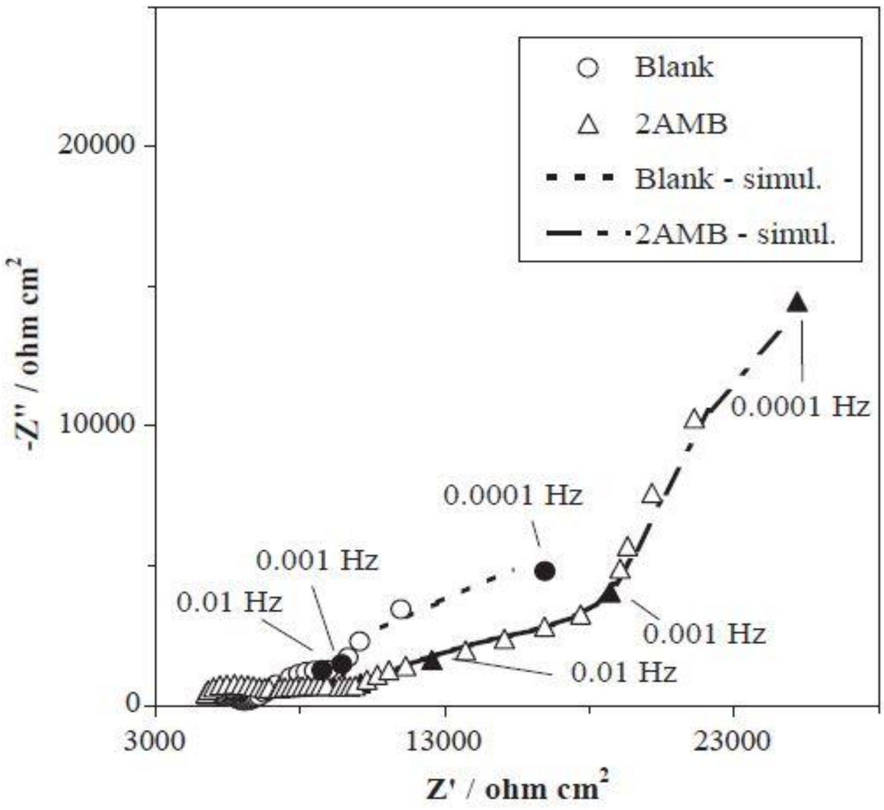


Figure 3.4 EIS Spectra (Trabanelli et al. (2005))

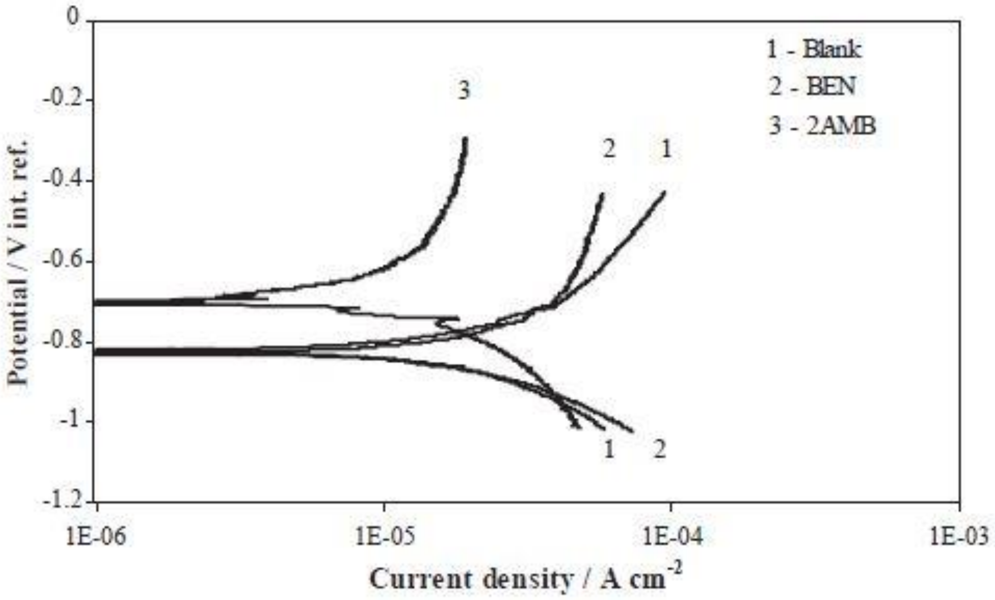


Figure 3.5 Polarization curve (Trabanelli et al. (2005))

Ormellase et al. (2006) used three organic compound inhibitor admixture (OCIA) which were amine-esters (C), amino alcohols (D) and alkanolamines (E) with a nitrite-based inhibitor (N) for comparison. Corrosion was induced through chlorides. This study was done on pore solution and concrete specimen as well.

For solution tests, electrochemical measurements were performed in a saturated solution of $Ca(OH)_2$ with pH equal to 12.6. Rebar of 16 mm diameter was used. Tests were performed on 200 mm2 area which was polished up to 6µm diamond paste to influence the chloride concentration. Only C inhibitor wasn't soluble in the solution prepared. Chlorides were added at 0.2% at every 48 hours up to 3 %. Potentiostatic results showed that in control solution, corrosion Occurred after chloride addition level reached 0.4% whereas in solution with inhibitors 80% of sample corroded by the time chloride concentration reach 1% - 1.4%. Only in C solution, three out of ten sample got corroded once chloride concentration reached 3%. This vast difference can be attributed to presence of volatile amines in D and E inhibitors which evaporates in case test cells were open. Moreover, in C inhibitor adsorption may occur due to its emulsion nature which helped in making distance from chloride ions. Figure 3.11 shows results of the potentiodynamic test in $Ca(OH)_2$ solution. Similar curves were obtained for N, D and E inhibitor as of non-inhibitor. Lower cathodic value was obtained for C inhibitor which confirms results of potentistatic tests.

For concrete tests, two specimens were with European standard cement with w/c equal to 0.5. One specimen contained 300 kg/m^3 cement and other one with 400 kg/m3. Specimen dimension was taken 250 × 160 × 70 mm and reinforced with 10mm diameter bar had exposed length of 170 mm out of total 270 mm. Three series of concrete specimens were prepared. Series 1 include inhibitors added at suggested dosages without and with chlorides mixed at 1.5% and 2.5% by cement weight. Second series include inhibitors added at maximum dosages with chloride content added at 1% and 1.5%. In third series, pounding of chlorides with 0.035 g/cc NaCl were provided rather admixed. electrochemical test measurements show that concrete which were without chlorides were in passive conditions. Polarisation resistance value was lower for series 1 inhibitors with chloride content. Series 2 specimen showed higher resistance value. Similar results were obtained from cathodic potentiostatic polarisation test in chloride free concrete. Only N-based inhibitor showed different behaviour of results in solution and concrete. Results also indicate that all inhibitors showed physical barrier effect due to formation of complex compounds which reduce chloride by blocking pores in concrete. Figure 3.6 show polarization curve results obtained in calcium hydroxide solution.

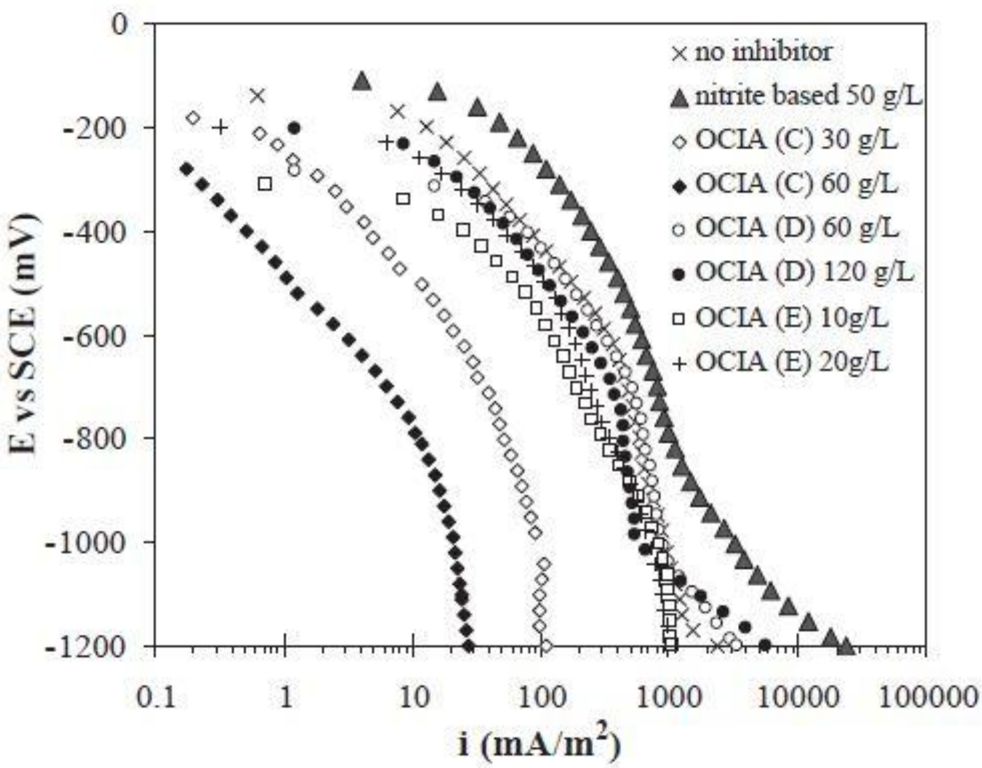


Figure 3.6 Potentiodynamic results in $Ca(OH)_2$ solution (Ormellase et al. (2006))

Hence, results obtained summarized that inhibitors mainly act with cement paste rather than rebars which means this wasn't pure inhibitive effect. All inhibitors which were tested were able to delay penetration of chlorides in concrete but slightly increase in chloride threshold value. But no significant data was obtained which can related to corrosion data. As inhibitors were reducing extent of corroded area and chloride penetration.

Soylev et al. (2007) studied two new generation of organic compounds based on amino alcohols in chloride contaminated environment on surface applied concrete. Concrete specimen with dimension of 280 × 280 × 75 mm were prepared with 18 mm cover for two reinforced bars of 12mm diameter. Chloride environment was provided through chloride pounding over 200mm^2 area. The specimens were prepared in two groups in which chloride concentration was varied. In group 1, for pounding of NaCl for four days was used 70 g/L followed by three-day air drying in laboratory. In group 2, only one pounding was provided with concentration of NaCl equals to 5 M. Inhibitors were applied with the brush on pounding surface before and after NaCl pounding in group 1, whereas in group 2 brush with inhibitors were applied after chloride pounding. Nomenclature used by author for group 1 specimen was ORG1a, ORG1b, ORG2a, ORG2b where number represent type of organic inhibitors and number represent application of chloride pounding. For group 2, ORG1 and ORG2 used. Corrosion potential (E_{corr}) and current density (I_{corr}) were measured. Figure 3.7 and 3.8 shows E_{corr} value for group 1 and group 2 respectively.

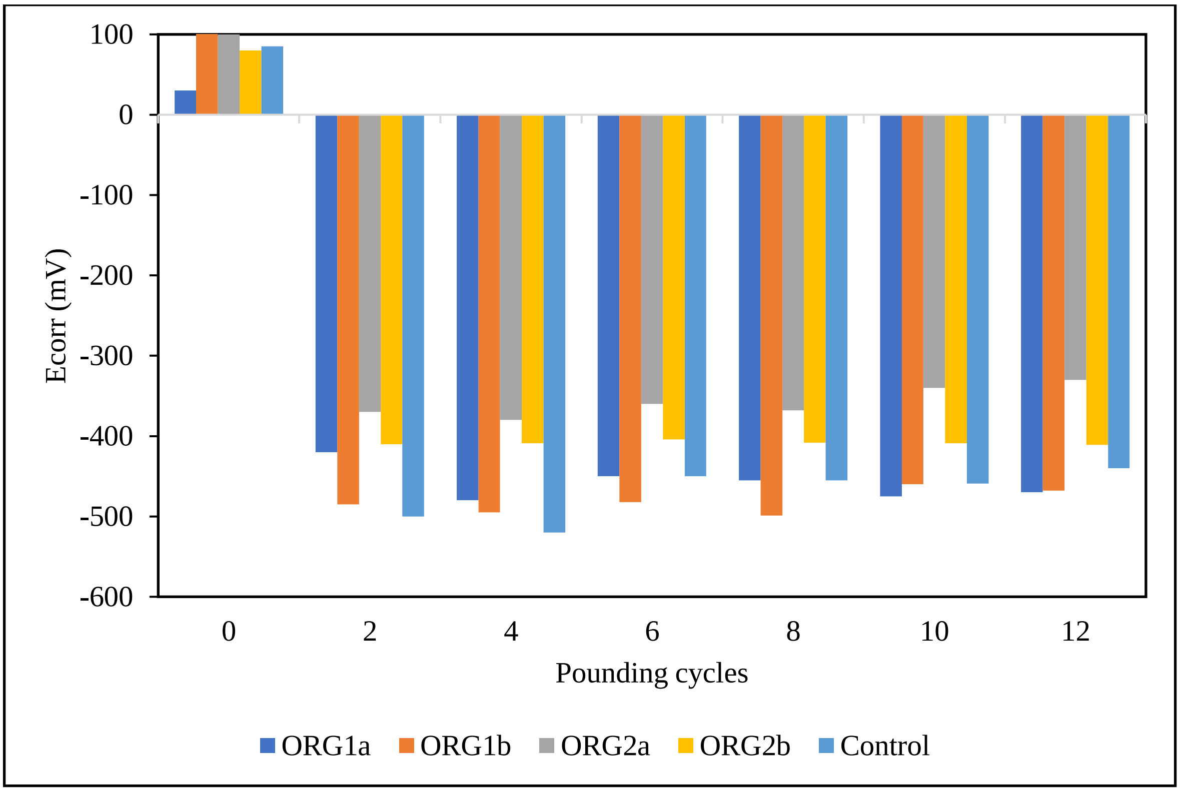


Figure 3.7 Potential vs time (Group 1) (Soylev et al. (2007))

The values obtained after testing indicated that potential value for control specimen decreases with increase in pounding cycle. In group 1, ORG1b displayed lower potential value than ORG1a due application of chloride pounding application. However, there wasn't much difference in ORG1(a, b) and control specimen. Difference was obtained in ORG2a and

ORG2b specimen. ORG2b shows higher value even after increase in chloride pounding. ORG2a specimen showed a decrease in value after an increase in pounding cycles. I_{corr} value followed same trend as of E_{corr} value. In group 2, corrosion rates were on higher side due to presence of high chloride pounding, only one drop was observed in E_{corr} value due to application of chloride.

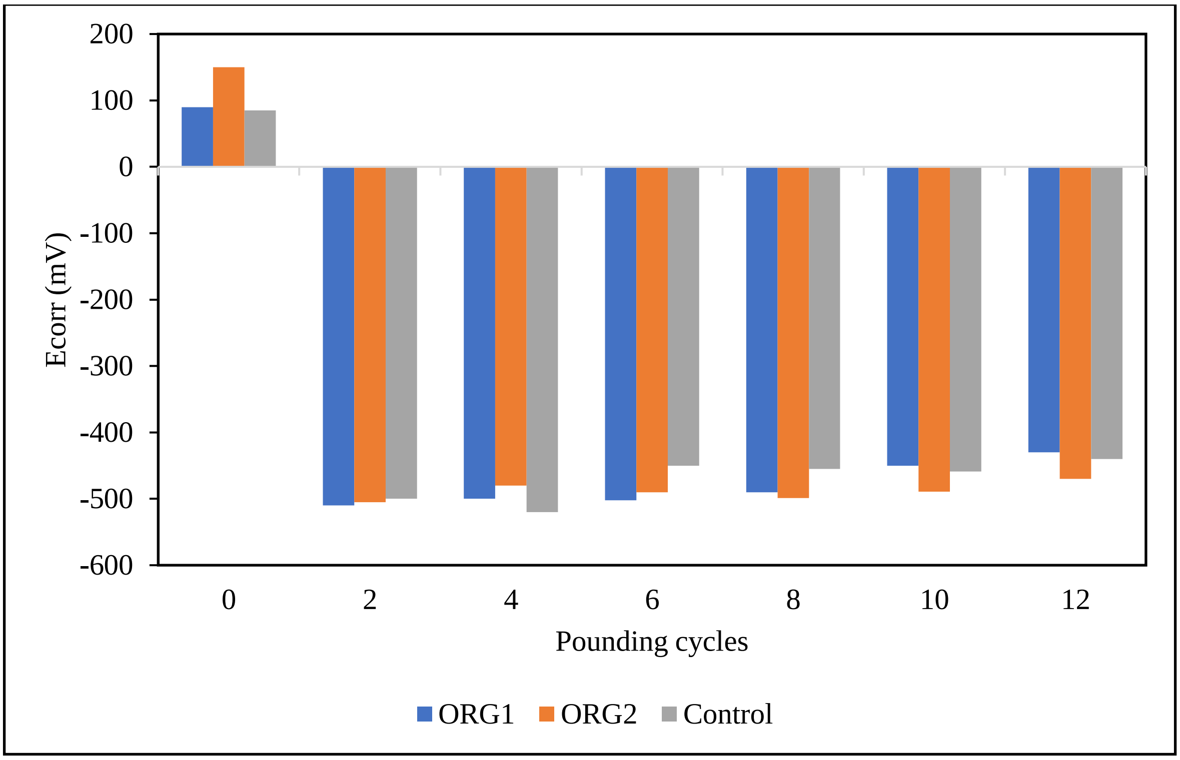


Figure 3.8 Potential vs time (Group 2) (Soylev et al. (2007))

Results conclude that application of chloride content plays role in the effectiveness of corrosion inhibitors. Figure 3.9 show chloride profile of group 1 inhibitors. New generation amino alcohol inhibitors were found to be effective if they used before chloride application. Once chloride was found in high concentration in concrete, both inhibitors found out to be ineffective which was the reason for neither showing efficiency by group 2 specimens. ORG1 specimen showed higher chloride profile than ORG2 in group 1. Lesser chloride in ORG2, due to restriction in moisture movement which indicates higher resistivity which means pore blocking effect results in effectiveness of group 1 inhibitors.

***Zheng* et al. (2012)** had studied amino alcohol (AMA) based organic inhibitors which are commonly used in commercial surface-applied inhibitors. Specimens prepared for this study was of dimension 100×100×50 with three different water/cement ratios.

After treatment with NaCl solutions for 30 days, results of surface applied for inhibitor show that half of the chloride ions were prevented from penetrating into the concrete in low water/cement ratios. Results of the capillary absorption test showed that the inhibitor can prevent chloride penetration in concrete by suppressing capillary absorption. But the proportion of the macro pores and capillaries increased as the water/cement ratio increased. The pore-blocking effect may weaken and the effect of chloride resistance may decrease for the same dosage of inhibitor.

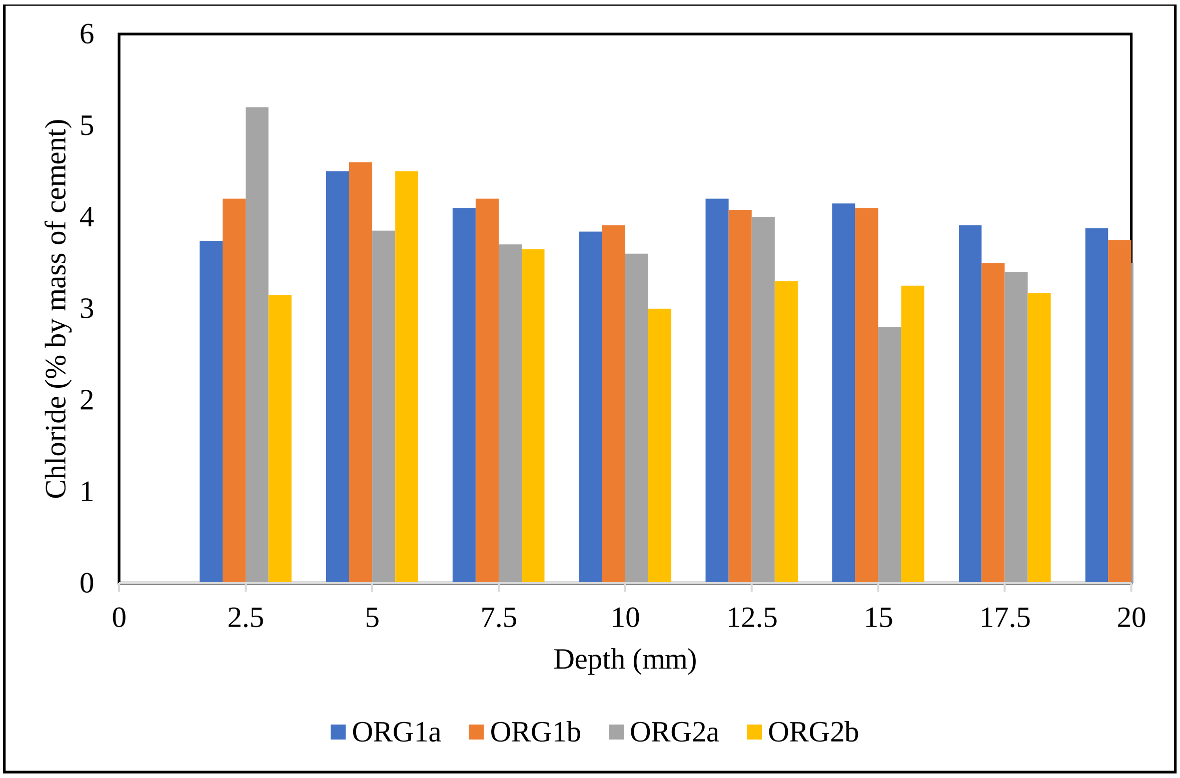


Figure 3.9 Chloride profile of Group 1 specimen (Soylev et al. (2007))

Rakanta et al. (2013) has studied the dimethylaminoethanol (DMEA) organic inhibitor based on amino group. Effect of DMEA for time duration of seven months in presence of chloride ions have been noted. Cylindrical specimen with steel rebar embedded in it were used. They used two types of these specimen with one having only chloride addition with five variations (1% to 5%) and in other specimen inhibitor with 1% and 2% variation added with chloride varied to 1.5%, 2%, 2.5% and 2%, 2.5%, 3% respectively. Techniques like Half-cell potential and LPR had employed to measure potential and rate of corrosion. Results obtained from half-cell potential test are given in Figure 3.10 and Figure 3.11.

Graphs obtained from half-cell potential measurement concludes that value of corrosion potential of ingress chloride ions shift to negative value with increase in chloride concentration whereas with addition of inhibitors, value of corrosion potential shifts towards more positive value.

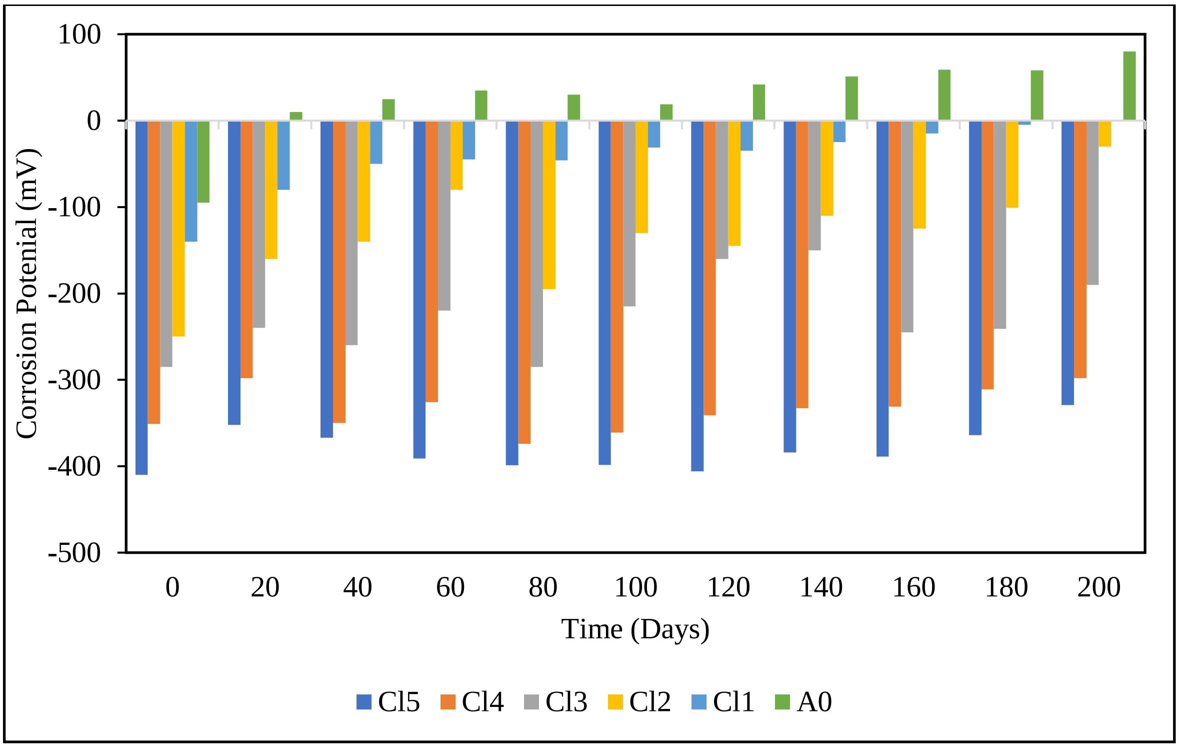


Figure 3.10 Potential vs time without inhibitors (Rakanta et al. (2013))

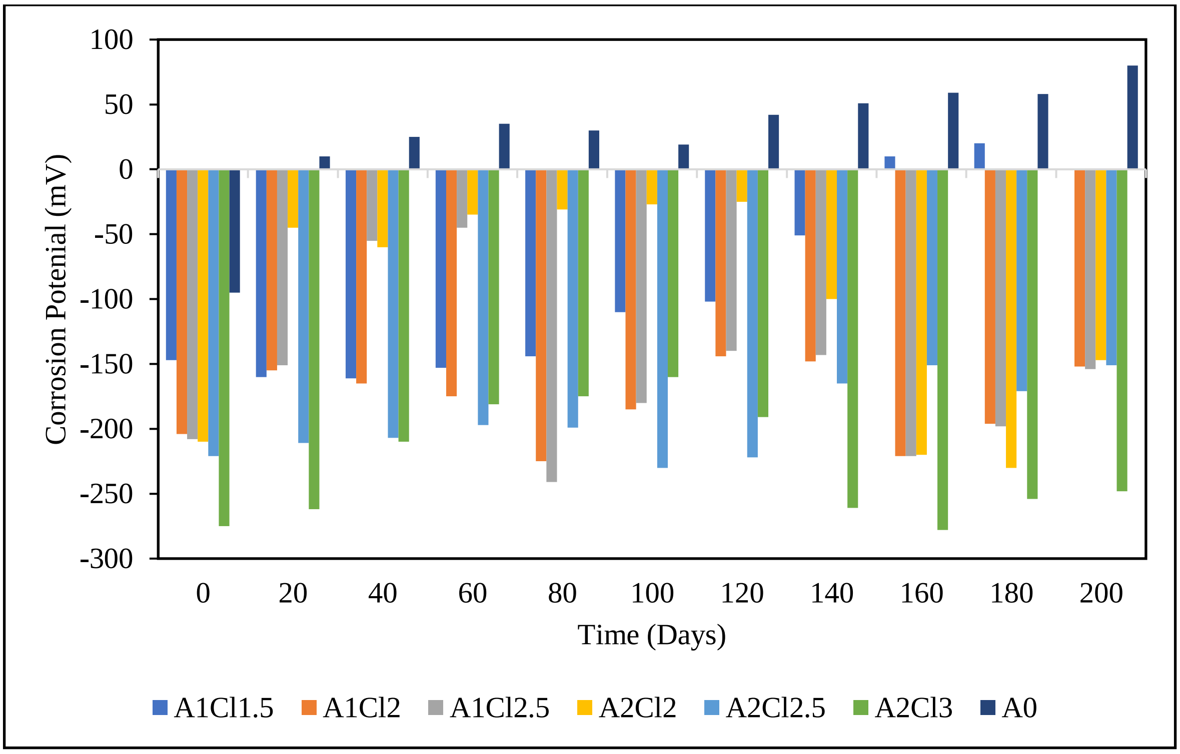


Figure 3.11 Potential vs time with inhibitors (Rakanta et al. (2013))

Kaur et al. (2016) had used ethanolamine (EA), amine-ether (AE), amino alcohol (AA) and anthranilic acid (AnA) organic inhibitor in carbonation environment in both pore solution and concrete. For testing purpose on pore solution, steel specimen of 12mm diameter TMT bar of length 60 mm was used. Saturated calcium hydroxide solution was used to simulate the pore water condition of reinforced concrete having pH equals to 7.

Figure 3.12 indicates that ethanolamine in carbonated solution provide no inhibition effect as steel underwent an active corrosion but an active passive transition occurred. In amine- ether based organic inhibitor shows no explicit passive zone was obtained whereas amino alcohol-based inhibitor shows passive film formation in carbonated solution.

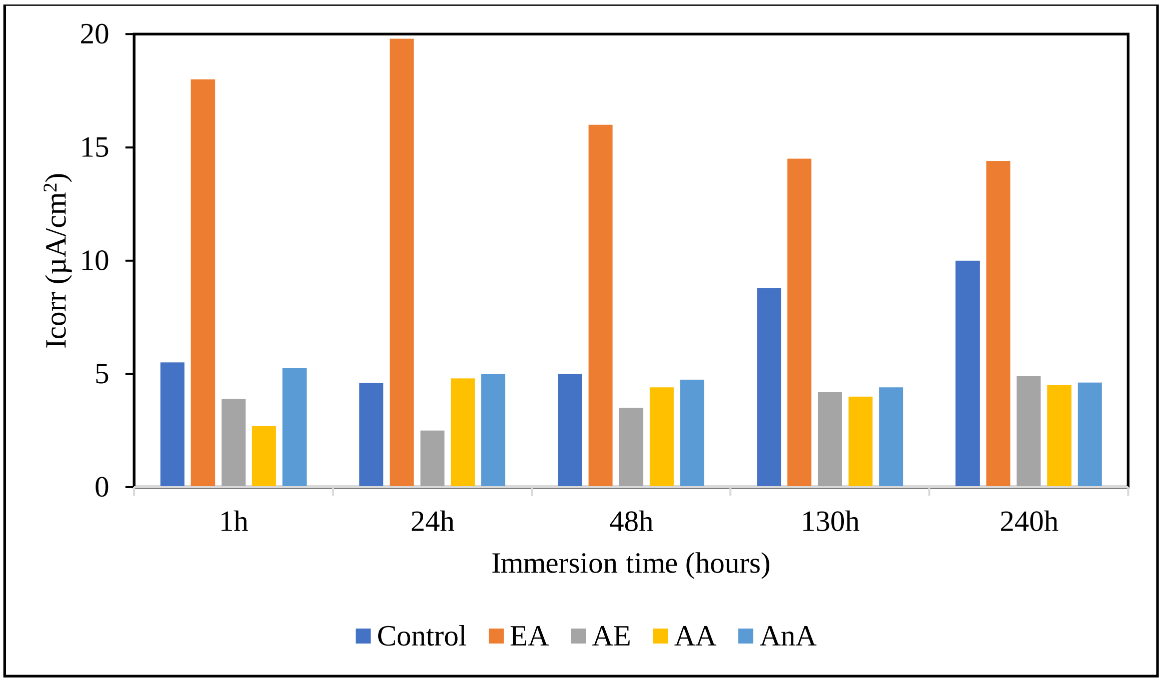


Figure 3.12 Corrosion current density at different immersion time (Kaur et al. (2016))

For testing on concrete specimen, inhibitors that performed better were only taken. Control (1), AA (2) and AnA (3) were only three types of concrete specimens in both OPC (A) and PPC (B) were prepared. Three TMT steel bar of 12mm diameter and length of 360 mm was embedded in concrete specimens of dimension of 300×300×150 mm. One bar was embedded at 5mm cover depth and other two bars at 25mm cover depth from top and bottom of specimen respectively. electrochemical technique like LPR was conducted to evaluate efficiency of inhibitor both in pore solution and concrete. Carbonation depth test using phenolphthalein as indicator was conducted on 100mm concrete cubes to check carbonation front.

Figure 3.13 shows Carbonation depth with time for both OPC and PPC. The results indicate that carbonation coefficient decreased with the use of inhibitors which indicates formation of protective layer by inhibitors on the surface of concrete. This phenomenon was more observed in anthranilic acid. Hence, inhibitors act as pore blocker on concrete surface and resist the carbonation front to ingress into concrete surface. XRD analysis also indicates the same about inhibitors acting as pore blocker.

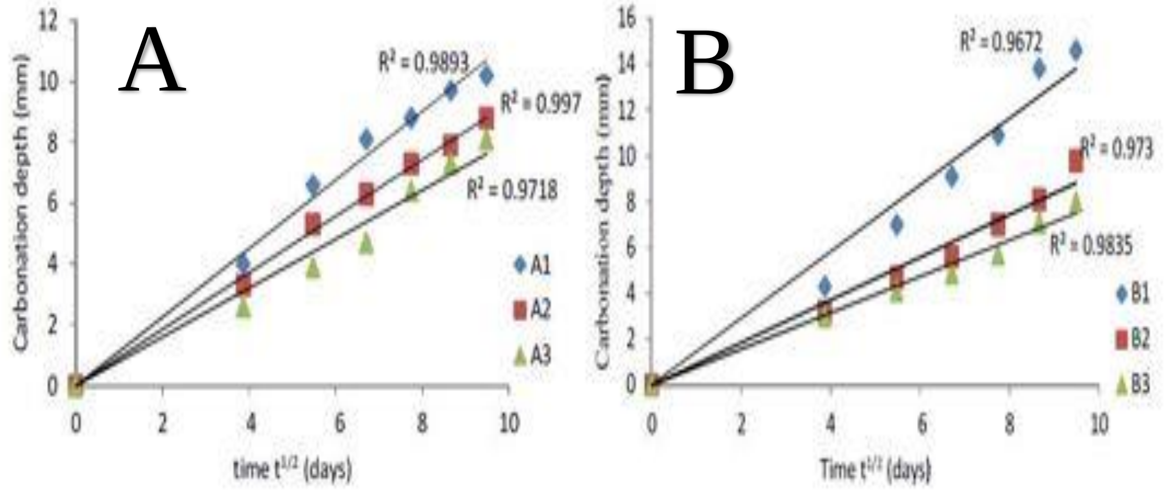


Figure 3.13 Carbonation depth with time for OPC (A) and PPC (B) (Kaur et al. (2016))

Xu et al. (2016) had recently studied triethlenetetramine (TETA) organic corrosion inhibitor in chloride contaminated concrete specimen using technique named bidirectional electro migration rehabilitation (BIEM). Specimen of dimension 150 × 150 × 300 mm were prepared using OPC admixed with NaCl. Two steel bars of 12 mm embedded at interval of 50 mm. After demoulding, specimen were cured for three months. TETA inhibitor was applied, by immersing the specimen into container containing TETA. Chloride penetration profile was obtained through titration with silver nitrate by obtaining concrete powder at every 5mm depth.

Test results indicate that TETA worked as corrosion inhibitor both in carbonated and non-carbonated concrete. In electrochemical test, w/c ratio play significant role. As in lower w/c ratio, some particles were difficult to transfer due to high alkalinity. Treating the samples with BIEM and ECE resulted into reduction of overall porosity in concrete. However, porosity unit was lower for ECE treatment. Whereas concentration of chloride increases after treating with BIEM. Therefore, both techniques can be used simultaneously by applying BIEM first and ECE later due to dichlorination effect of ECE technique. From chloride penetration profile results, it had been cleared that Cl- ions concentration decrease which means ratio of OH^- and Cl^- was increased help in passivation of steel in concrete.

II. CARBOXYLATE

Almobarak et al. (2014) studied effect of various acid like phthalic, salicylic, benzoic, o-aminobenzoic and oxalic acid corrosion inhibitors based on carboxylate group. Solution of 0.01 M NaOH was prepared with addition of NaCl. To evaluate efficiency of these acids in solution electrochemical measurement was done. Table 3.1 show parameters obtained from the electrochemical measurement.

Increase in concentration leads to corrosion potential value E_{corr} toward less negative value as can be check in Table 3.1. Also, shift was observed in anodic value and a negligible shift in current density I_{corr} due to blocking of reaction surface on steel. Hence, it can be said that carboxylic acids helped in decreasing corrosion on rebars in alkaline solution and posses' properties of mixed inhibitor with dominantly as an anodic mechanism. Adsorption mechanism followed by carboxylic acid due to bond formation between iron electrons and unshared electrons pair of nitrogen and oxygen. Adsorption mechanism depends upon electron density and phthalic acid had more electron density. Therefore, the efficiency of phthalic acid, o-aminobenzoic acid, benzoic acid and followed by oxalic acid given in decreasing order of inhibitors based on carboxylic group.

Table 3.1 Parameters of corrosion process

b_c, mV	E_{corr}, mV	I_{corr}, mA/cm^2	Acid Concentration, M
No inhibitor			
109.6	-967.5	0.00539	
Phthalic Acid			
102.8	-921.2	0.00271	2.5×10^{-4}
111.4	-898.2	0.00242	5.0×10^{-4}
Salicylic Acid			
106.8	-949.7	0.00298	2.5×10^{-4}
108.2	-944.2	0.00279	5.0×10^{-4}
Benzoic Acid			
106.2	-725.2	0.00362	2.5×10^{-4}
109.5	-922.7	0.00312	5.0×10^{-4}
o-Aminobenzoic Acid			
109.5	-955.4	0.00414	2.5×10^{-4}
111.2	-915.2	0.00346	5.0×10^{-4}
Oxalic Acid			
112.7	-952.5	00.428	2.5×10^{-4}
106.7	-945.2	0.00365	5.0×10^{-4}

Bolzoni et al. (2014) had studied tartrate, benzoate and EDTA based on carboxylates compound. These inhibitors were tested both on solution and concrete. Dosages of inhibitors taken as 1% by weight except sodium tartrate were added 0.1% due to setting effect. Test was performed both on solution and concrete. Sodium nitrite was used for comparison purpose.

In solution, test was performed on carbon steel rod of diameter 10mm and length 40mm. The solution was prepared from saturated $Ca(OH)_2$ mixed with 0.01 mol/L NaOH. NaCl was added for chlorides. Effectiveness of three inhibitors was evaluated by pitting potential value which should be greater than 50mV. Figure 3.14 showed pitting potential vs chloride concentration graph which indicate that carboxylates showed very good effectiveness. Effectiveness can be due to electron donor effect which influences adsorption process and steric effect which blocks physical barrier by delaying chloride to the metal surface. In polarisation test, only EDTA showed good results in which chloride content was increased.

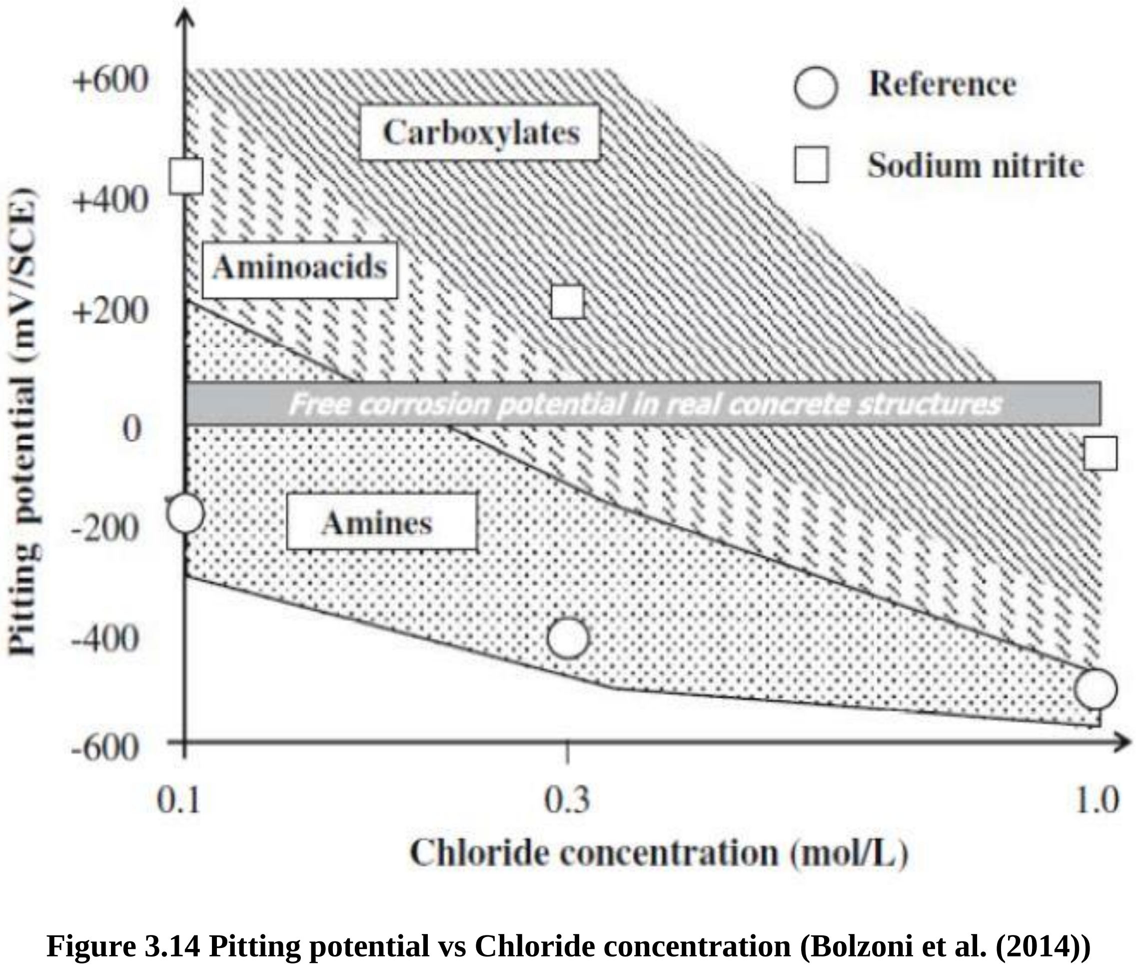


Figure 3.14 Pitting potential vs Chloride concentration (Bolzoni et al. (2014))

For testing of concrete specimens, the sample was prepared of 200×250×50 mm with two rebars of 10 mm in diameter and 290 mm in length. Only 210 mm length was left to exposed for corrosion in concrete. Critical chloride content showed better in carboxylic compounds except for sodium tartrate as shown in Table 3.2.

Table 3.2 Ponding test

Type of specimen	Cycles	Critical Cl^- (% wt. vs cement)
No inhibitor	32-35	1.3-1.6%
Benzoate	42-44	1.8-2.0 %
Tartrate	46-57	1.5-1.6%
EDTA	46-52	1.8-2.1%

Hence, results of solution and concrete specimen tests were different. As sodium tartrate showed best inhibitive efficiency in solution and poor in concrete may be due to the addition of its content which was lesser in concrete (0.1%) than solution (1%). The efficiency of carboxylate compounds in solution and concrete specimen can be attributed to steric effect and electrostatic effect.

III. PHOSPHATE

Etteyeb et al. (2007) had studied sodium phosphate (Na_3PO_4) inhibitor based on phosphate group in alkaline solution contaminated with chloride ions. Inhibitor was used in two ways in the solution. Firstly, inhibitor was added to solution containing chlorides and secondly rebar was pre-treated by immersing into inhibitor solution. Efficiency of both methods than checked by electrochemical techniques. Steel rod of 5 mm diameter was used as working electrode. Two test samples were prepared S1 and S2. S1 included control specimen with 0.5 M NaCl whereas, S2 included S1 solution with addition of corrosion inhibitor. Figure 3.15 show EIS diagram of pre-treated and non-treated samples. In Figure 3.15 (A) two loops, one at high frequency and other in relatively low frequency due to diffusion process with thick finite layer. In S2 solution, diagram indicate that low frequency value was greater magnitude than S1 which means corrosion current density expected to decrease. Whereas in pre-treated bar, similar trend was observed and only loop was obtained.

Gravimetric measurements which includes corrosion potential test also provide similar results. Pre-treatment sample result indicate the passive film formation on rebar surface. Hence, these results indicate that pre-treatment helped the steel bar to formed a protective layer by preventing from anions.

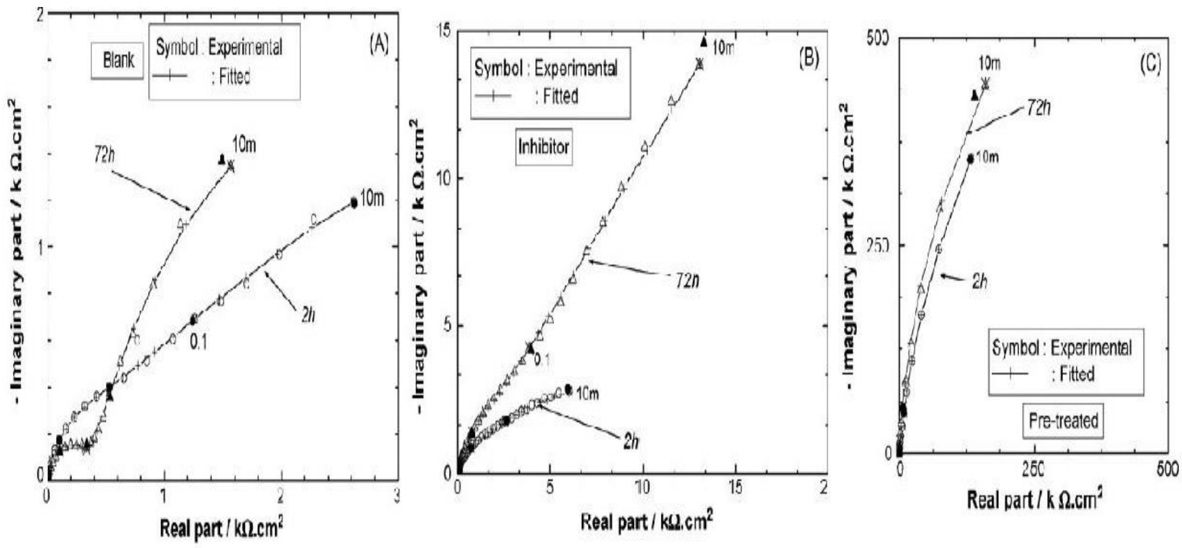


Figure 3.15 EIS diagrams (A) S1 (B) S2 (C) Pre-treated S1

Tang et al. (2012) studied sodium phytate (SP), sodium molybdate and sodium tungstate based on phosphate, molybdenum and tungsten respectively. Other than phytate, both are eco-friendly inorganic inhibitors. Sodium nitrite was taken as reference inhibitor in acidified calcium hydroxide solution. For testing, a specimen of length 10mm and 10mm diameter was taken. $Ca(OH)_2$ solution was prepared with two varied pH values i.e. 12.5 and 8.0. Two concentration range for inhibitors was used wt.% ≤ 0.045% and 0.1% ≤ wt.% ≤ 2% for addition. EIS, polarization and weight loss tests were conducted to check the efficiency of inhibitors in pore solution. Figure 3.16 shows polarization curve of sodium phytate at high concentration in acidified pore solution with pH equal to 8.0.

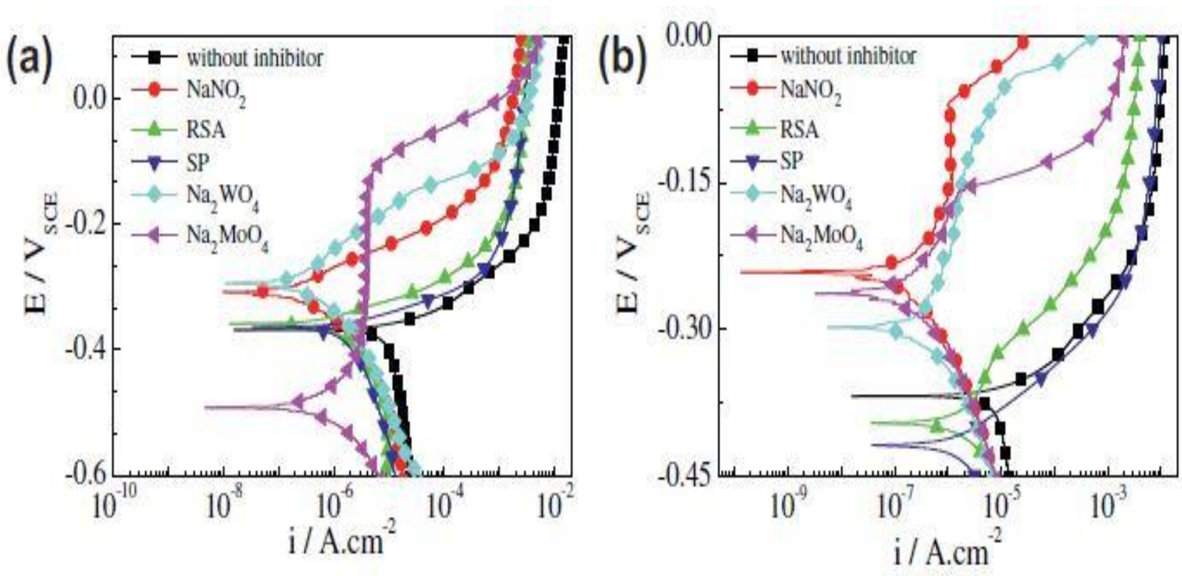


Figure 3.16 Potentiodynamic polarization curve in pore solution (pH 8.0) (A) 0.013% (B) 0.045%

Results showed in Figure 3.16 indicate that even after the addition of sodium phytate as corrosion inhibitor, steel remains in the active state. Similarly, current density too didn't show any changes even after increasing the concentration of SP which means at lower concentration SP as an inhibitor not as effective as another inhibitor. However, increase in the concentration of SP indicates inhibit effectiveness in pore solution. Whereas, sodium molybdate showed good inhibitive effect at low concentration. A similar trend was observed in EIS curves as shown in Figure 3.17.

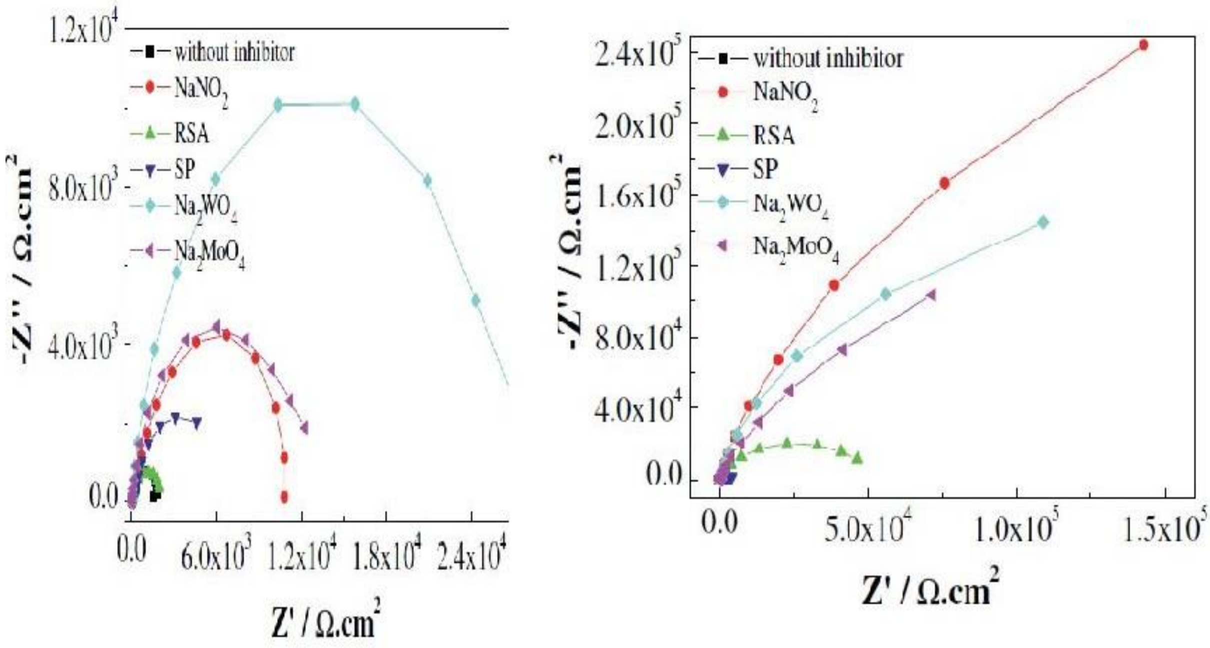


Figure 3.17 EIS diagram (pH 8.0) at concentration of 0.045% (A) & 2% (B)

Hence, sodium phytate showed the only minor effect of inhibition at a concentration level of 0.045% in pore solution where pH equal to 8.0. When concentration reached above 0.5% SP started to show inhibitive effect. The reason behind not showing inhibitive effect can be attributed to a non-adsorption mechanism which was also supported by Raman spectrum.

Nahali et al. (2015) had studied an inorganic compound based on phosphate group. For this, they used trisodium phosphate (Na_3PO_4) in 3% NaCl solution. electrochemical techniques and SEM observation were used to verify the results. Cylinder specimen made with ordinary cement were prepared with a diameter of 30mm and length of 60mm. Rebar of diameter 6mm and 70mm in length was used. Two mortar specimens were prepared, one with or without trisodium phosphate as an inhibitor. The quantity of Trisodium phosphate taken equals to 0.3 mol/L was mixed with water and added to the mortar. Water curing for a week was done.

For acceleration of corrosion process, anodic polarization at $E_{imposed}$ = 1000mV/SCE was done. Electrochemical measurements were carried out three times, one before anodic polarization (cycle 0) second after first anodic polarization (cycle 1) and third after giving two anodic polarization cycles (cycle 2). E_{corr} value at cycle 0 for both specimens was high but after cycle 1, E_{corr} value decrease for specimen without Na_3PO_4 which states that passive layer deteriorates in this sample. Sample with Na_3PO_4 maintained passivity in steel despite strong polarization. Table 3.3 shows value of corrosion potential.

Table 3.3 Value of corrosion potential

Specimen	**E_{corr} (mV) at Cycle 0**	**E_{corr} (mV) at Cycle 1**	**E_{corr} (mV) at Cycle 2**
Without Na_3PO_4	-337	-537	-
With Na_3PO_4	-246	-210	-530

The polarization parameters obtained for both samples at cycle 0 indicates that passivity formed on steel before polarization help in preventing corrosion. Even passive layer was better formed in specimen contained Na_3PO_4. After cycle 1, results indicated no change in sample with Na_3PO_4 due to presence of PO_4^{3-} in environment which precipitates $FePO_4$ and eventually results into blockage of anodic sites and helps in protection against corrosion. Table 3.4 and 3.5 shows electrochemical parameter of two specimens.

Table 3.4 Electrochemical parameters for specimen without Na_3PO_4

Cycle	**I_{corr} (μA/cm^2)**	**I_{200mv} (μA/cm^2)**	**E_{rep} (mV)**	**I_{rep} (μA/cm^2)**	**E_{rev} (mV)**	**I_{rev} (μA/cm^2)**
0	0.5	2.8	-251	0.5	-	-
1	5.9	76.3	-	-	-669	6.2

Table 3.5 Electrochemical parameters for specimen with Na_3PO_4

Cycle	**I_{corr} (μA/cm^2)**	**I_{200mv} (μA/cm^2)**	**E_{rep} (mV)**	**I_{rep} (μA/cm^2)**	**E_{rev} (mV)**	**I_{rev} (μA/cm^2)**
0	0.1	0.9	509	0.4	-	-
1	0.3	1.6	-135	2.6	-	-
2	4.8	75.5	-	-	-354	4.51

3.4 CONCLUDING REMARKS

Chemical compounds as corrosion inhibitors have been in use for some time. Present literature work helps in identifying the mechanism of different organic groups as corrosion inhibitor eventually results in saving of cost and time. Amine based inhibitor able to block pores whereas, carboxylic group showed steric effect. Phosphate based inhibitor works on adsorption mechanism. Also, combination of amine and carboxylic group as inhibitor results in formation of complex compounds due to bond formation between iron electrons and unshared electron pairs of nitrogen and oxygen.

CHAPTER 4

EXPERIMENTAL PROGRAM

4.1 GENERAL

This chapter deals with the experimental procedure to evaluate the efficiency of corrosion inhibitors both as admixed in reinforced cement concrete and in pore solution under the combine influence of chloride and carbonation environment. Various techniques like half-cell test, long term sweep test have been used for monitoring corrosion on both pore solution and concrete. It also describes the test on materials and experimental setup on following section.

4.2 EXPERIMENTAL PROGRAMME

The main aim of experimental programme is to study the efficiency of chemicals like 4-amino benzoic acid (ABA) and triethyl phosphate (TEP) as corrosion inhibitors in combined ingress environment. Concrete specimens like prism and cubes were casted using two different cement types to evaluate effect of above chemicals as corrosion inhibitors. The experimental programme involves: -

1. Pore solution preparation with admixed chloride and carbonation to evaluate effectiveness of both ABA and TEP as corrosion inhibitors.
2. Evaluation of properties of materials used in experiment as per Indian standard specifications. Materials includes cement, fine aggregates, coarse aggregates and steel bars.
3. Prismatic size 300 × 300 × 150 mm with three 12 mm diameter TMT steel bar casted using admixed 4 amino benzoic acid and triethyl phosphate in both PPC and OPC. One steel bar casted with clear cover of 15 mm at top and other two casted at bottom with clear cover of 25 mm from bottom.
4. For determination of carbonation depth and chloride content, 100 mm cubes casted.
5. The prism and cubes specimens were subjected to chloride content (0.035 g/cc in water) and carbonation in a chamber with temperature, relative humidity and CO_2 concentration maintained at 27-33°, 50-70% and 5% respectively.

4.3 PORE SOLUTION

To check effectiveness of ABA and TEP as corrosion inhibitors in concrete specimens, pore solution was prepared. Properties of inhibitors and steel specimens, preparation of steel bars and pore solution, test conducted on pore solution are discussed in this section.

4.3.1 Properties of Inhibitors

Chemicals which are used to prevent corrosion process are known as inhibitors. In this thesis work, two different amine and phosphate organic group inhibitors used. 4-amino benzoic acid and Triethyl phosphate were two inhibitors used based on amine and phosphate organic groups.

4.3.1.1 4-Amino Benzoic Acid

This inhibitor consists of a benzene ring replaced with amino and a carboxyl group as shown in Figure 4.1. Fourth carbon position in benzene ring signifies para position, hence it is also known as para amino benzoic acid (PABA) as shown in Figure 4.2. Table 4.1 provides the properties of 4-amino benzoic acid.

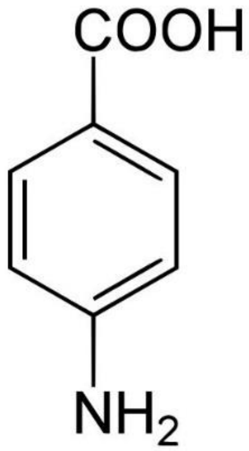


Figure 4.1 Chemical Structure of 4-Amino Benzoic Acid

Table 4.1 Properties of 4-Amino Benzoic Acid

Chemical Formula	$C_7H_7NO_2$
Molar Mass	137.14 g/mol
Physical State	Powder
Appearance	White-Grey
Density	1.374 g/mL
Melting Point	188 °C

4.3.1.2 Triethyl phosphate

Second inhibitor used for thesis work is taken from phosphate group. As the name of inhibitor suggest, it is triester of ethanol and phosphoric acid. Chemical structure of tri ethyl phosphate is shown in Figure 4.3. Figure 4.4 show triethyl phosphate bottle used as corrosion inhibitors and properties of triethyl phosphate is given in Table 4.2.

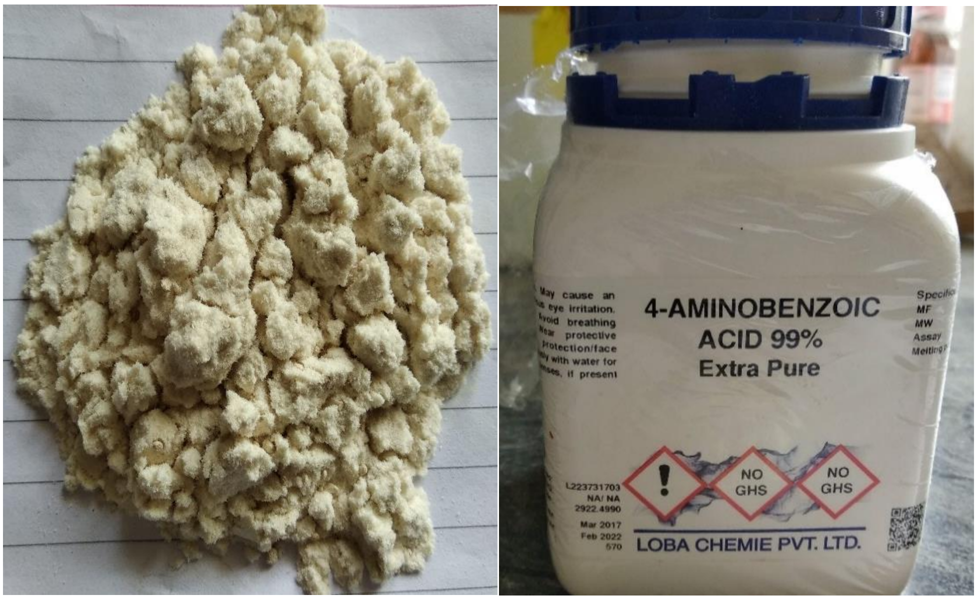


Figure 4.2 4-Amino Benzoic Acid Inhibitor in powder form

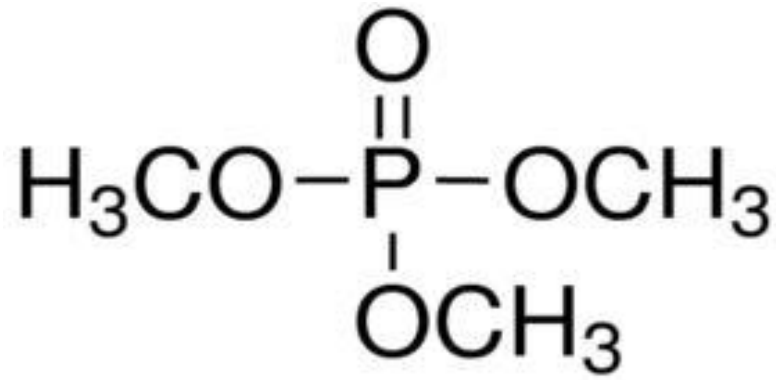


Figure 4.3 Chemical structure of Tri Ethyl Phosphate

Table 4.2 Properties of Tri Ethyl Phosphate

Parameters	**Results**
Chemical Formula	$C_6H_{15}O_4P$
Molar Mass	182.15 g/mol
Physical state	Liquid
Appearance	Colour less
Density	1.072 g/mL
Melting Point	-56.5 °C

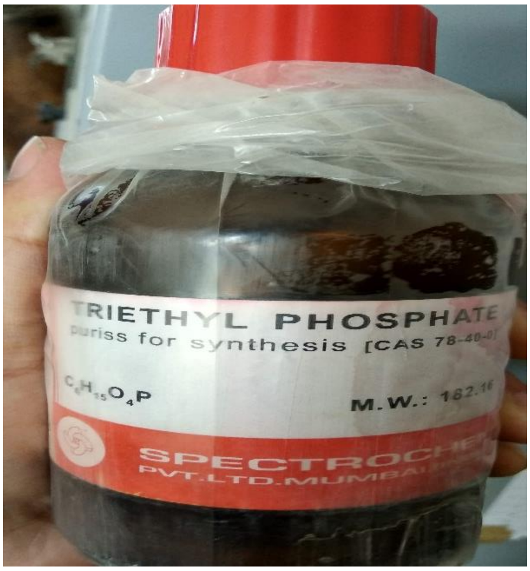


Figure 4.4 Tri Ethyl Phosphate Indicator

4.3.2 Rebar Properties

For reinforcement purpose Fe 500 TMT steel bars of 12 mm diameter were used. Table 4.3 shows the properties of steel bars used in casting.

Table 4.3 Properties of Reinforcement bars

Property	Results obtained	As per IS 1786 Fe 500 (Minimum)
Manufacture	Tata Tiscon	-
Diameter	12 mm	-
Yield Strength (YS)	520	500 MPa
Ultimate Tensile Strength (UTS)	600	545 MPa
Ratio of UTS/YS	1.15	1.08

4.3.3 Preparation of Steel Rebars

For pore solution test, length of 12mm diameter of steel bar was taken as 60mm. Steel bars were threaded from one side as shown in Figure 4.5 so that nut with bolts can be screwed with a copper wire fixed for proper electrical conductivity. These steel bars were cleaned with emery paper before screwing in order to remove rust from steel surface. After that steel bars were dip into analytical chemical regent hexane and air dried for next 24 hours. Two layers of epoxy was coated with minimum 1-hour time difference. After 24 hours, epoxy coated on specimen is ready for pore solution testing.

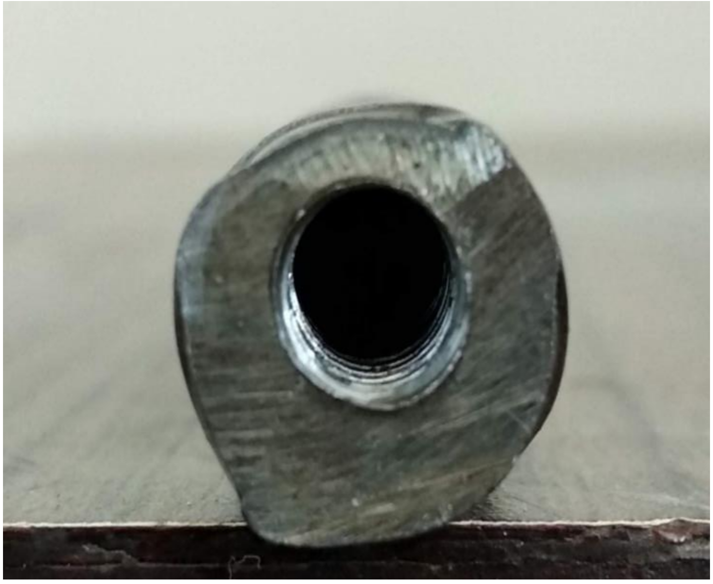


Figure 4.5 Rebar threaded from one side

4.3.4 Preparation of Pore Solution

Basic aim of preparation of pore solution is to provide steel bars similar environment which resembles to concrete environment. Hence, simulated concrete pore (SCP) solution was prepared by dissolving calcium hydroxide ($Ca(OH)_2$), sodium hydroxide (NaOH) and potassium hydroxide (KOH) at concentration of 0.01M, 0.1M and 0.3M respectively in distilled water. After that, wattman filter paper was used for filtration to ascertain that insoluble CaO doesn't come to solution. Value of pH of base pore solution was decreased from 13 to 9 and to provide carbonation environment, CO_2 gas (99% pure) was bubbled through pore solution. Bubbling process needs attention as reaction between CO_2 and $Ca(OH)_2$ gas is very rapid in nature. Hence, attention on pH value is required. NaCl (0.035 g/cc) was added in order to maintain chloride attack in solution. Finally obtained solution was filtered by using filter paper.

4.3.5 Testing Period for Pore Solution

Steel rebars were immersed for total 120 hours in pore solution to evaluate the efficiency of corrosion inhibitor. LPR test was conducted for three times after immersion. First LPR curve was obtained after 24hour immersion. Second and third curves were obtained after 48hour and 120hour respectively.

4.3.6 Test Conducted on Pore Solution

Linear sweep test was conducted with help of ACM field machine. Cylindrical jar was used as electrochemical cell with wooden lid at top as shown in Figure 4.6. Steel specimen, auxiliary electrode and reference electrode as saturated calomel electrode were fitted in wooden lid. Steel specimen was fixed to working electrode whereas, auxiliary and reference electrode were fixed to electrochemical cell. Frequency for potentiostatic linear sweep test was taken from -250mV to +250mV as shown in Figure 4.7.

Figure 4.6 Electrochemical Cell

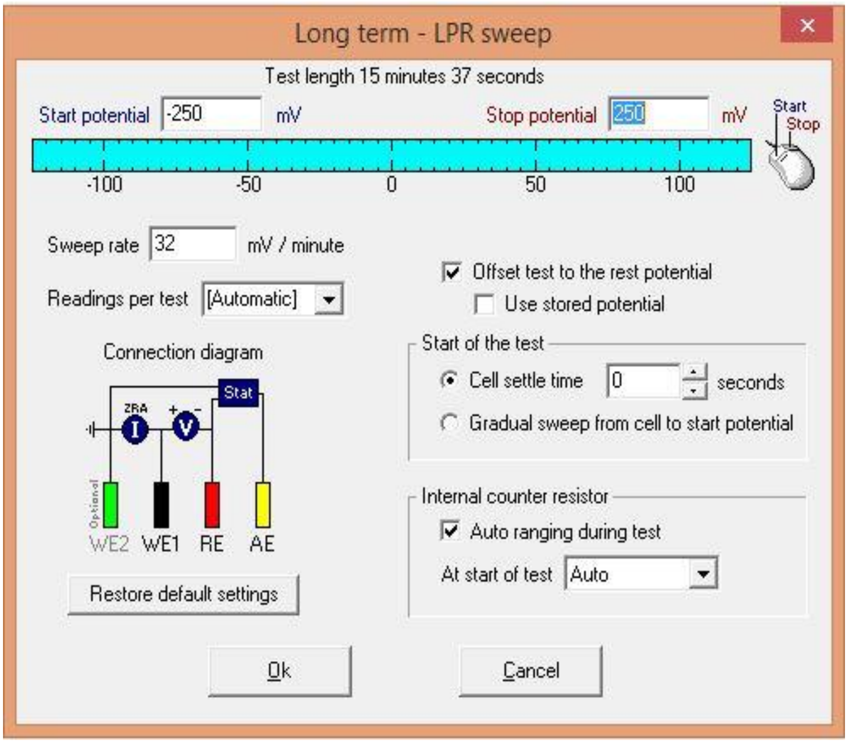


Figure 4.7 Input data for LPR test

4.4 CONCRETE SPECIMENS

To check the efficiency of amine and phosphate based organic group, concrete specimen was prepared using both PPC and OPC cement for comparison purpose. Three type of concrete specimen includes a specimen without inhibitors and specimens with both inhibitors were prepared for each cement. For both cement type, duplicate samples were prepared so that average values can be taken. Testing of various materials, preparation of specimens and test conducted on concrete specimens are discussed in this section.

4.4.1 Material Testing

The main objective of evaluating properties of different materials used is to verify properties of materials as per codes. Properties of following materials like cement, aggregates (coarse and fine), TMT steel bars, water, corrosion inhibitor were evaluated.

4.4.1.1 Cement

A binder material which binds together other constituents like aggregates, water. Cement is a fine grey coloured powder which influence properties of concrete like strength and hardening. In this study both PPC and OPC were used. The physical and chemical properties of both PPC and OPC cement are given in Table 4.4, Table 4.5 and Table 4.6 respectively.

Table 4.4 Physical properties of PPC

Properties	Obtained values	Standard Values (As per IS 1489:1991)
Brand	J.K. Lakshmi	-
Specific gravity	2.89	-
Standard consistency	29 %	-
Initial setting time	90 minutes	30 minutes (Minimum)
Final setting time	300 minutes	600 minutes (Maximum)
Fineness	370 m^2/kg	300 m^2/kg (Minimum)

4.4.1.2 Fine Aggregates

Natural sand with usually size less than 4.75 mm was used as fine aggregate. Fine aggregates also act as a filler material in concrete to fill voids created by coarse aggregate which results into less cracking and shrinkage. Physical properties and sieve analysis of fine aggregates are shown in Table 4.7 and Table 4.8 respectively.

Table 4.5 Physical properties of OPC

Parameter	Obtained values	Standard Values (As per IS 8112:1989)
Manufacture	Ultra tech	-
Grade of cement	43	-
Specific gravity	3.1	-
Standard consistency	23 %	30
Initial setting time	123 minutes	30 minutes (Minimum)
Final setting time	270 minutes	600 minutes (Maximum)
Fineness	255 m^2/kg	225 m^2/kg (Minimum)

Table 4.6 Chemical composition of cement

Constituent	PPC	OPC 43
SiO_2	27.54	21.65
Al_2O_3	8.89	4.69
Fe_2O_3	5.41	3.38
CaO	49.82	63.15
MgO	1.01	1.88
K_2O	1.55	1.48
Na_2O	0.19	0.35
SO_3	2.59	2.87
LOI	1.91	2.25

Table 4.7 Physical properties of fine aggregates

Properties	Results obtained
Grading Zone	Zone II
Specific gravity	2.64
Water absorption (%)	0.87
Fineness modulus	3.02

Table 4.8 Sieve analysis of fine aggregates

Sieve size	Mass Retained (g)	%age mass retained	Cumulative %age mass retained
4.75 (mm)	31	31	3.1
2.36 (mm)	137	168	16.8
1.18 (mm)	238	406	40.6
600 microns	168	574	57.4
300 microns	316	890	89.0
150 microns	65	955	95.5
Pan	45	1000	
			∑ %age retained = 302.4

Fineness modulus= 302.4/100 = 3.02

4.4.1.3 Coarse Aggregates

Coarse aggregates are those aggregates which are "retained over IS sieve size of 4.75 mm". Coarse aggregates play the role of filler in concrete. The aggregate used in this thesis work were obtained from local supplier in Patiala with maximum size of 20 mm (nominal size) and 10 mm. Table 4.9 and Table 4.10 shows results of sieve analysis of 10mm and 20mm respectively done in accordance with IS 383-1970. Table 4.9 shows physical properties of 10mm and 20mm aggregate.

Table 4.9 Sieve analysis of 10mm coarse aggregates

Sieve Size (mm)	Mass Retained (kg)	Cumulative Mass Retained (kg)	Cumulative %age Mass Retained
10	3.65	3.65	36.5
4.75	5.13	8.78	87.8
Pan	1.16	9.94	
Total	9.94		∑%age retained =124.3

Fineness modulus= (195.6+500)/100 = 6.24

Table 4.10 Sieve analysis of 20mm coarse aggregates

Sieve Size (mm)	Mass Retained (kg)	Cumulative Mass Retained (kg)	Cumulative %age Mass Retained
20	0.363	0.363	3.630
10	8.890	9.253	92.53
4.75	0.691	9.944	99.44
Pan	0.040	9.984	
Total	9.984		∑%age retained =195.6

Fineness modulus= (195.6+500)/100 = 6.95

Table 4.11 Physical properties of coarse aggregates

Properties	10 mm	20 mm
Specific gravity	2.84	2.82
Water absorption (%)	0.65	0.53
Fineness modulus	6.24	6.95

4.4.1.4 Water

Water quality can influence many physical and chemical properties of concrete. As per Indian standard clean and fresh tap water was used which was free from silt, chloride content and organic matter for purpose of specimen casting.

4.4.2 Mix Proportion

In this thesis work, concrete is prepared by using both PPC and OPC 43 grade of cement. Concrete mix was designed as per IS 10262:2009. Table 4.12 shows the mix proportions of the mix.

Table 4.12 Mix Design

Material	Quantity
Cement (kg/m^3)	410
Fine Aggregates (kg/m^3)	572.4
Coarse Aggregates 20mm (kg/m^3)	836.34
Coarse Aggregates 10mm (kg/m^3)	360.4
Water (kg/m^3)	180

Hence, water cement ratio (w/c) taken was 0.44. The ratio of cement: fine aggregate: coarse aggregate was taken as 1:1.39:2.91 for casting of concrete.

4.4.3 Preparation of Concrete specimens

Similar to pore solution, concrete specimens were prepared in order to check efficiency of ABA and TEP as chemical corrosion inhibitors in ingress chloride and carbonation environment. Following points discussed the preparation of concrete specimens for testing: -

4.4.3.1 Preparation of rebars

For reinforcement purpose in concrete specimen, 36 steels bars of cutting length 360mm each prepared. These steel bars were threaded from one side as shown in Figure 4.5 in order to insert the nut. Firstly, sanding by hand is done. Secondly, each bar was washed with hexane. After air dry for some time, each bar was concealed with tape followed by epoxy coating at 55mm from both sides and again allowed to air dry and then neoprene rubber pipe was applied to coated portion, so that corrosion process can proceed in middle 250mm portion. Figure 4.8 show prepared rebars ready to use as reinforcement in prismatic concrete specimen.

Figure 4.8 Preconditioned rebars embedded in concrete specimens

4.4.3.2 Prismatic Mould

Two moulds were prepared of size 300 × 300 × 150 mm. On two parallel sides of rectangular mould, one hole of at top with 15mm cover from top and two holes at bottom with 25mm cover from bottom of 12.5 mm diameter were done in order to cast reinforcement in concrete specimen. Figure 4.9 show setup of mould with reinforcement bars before casting of concrete.

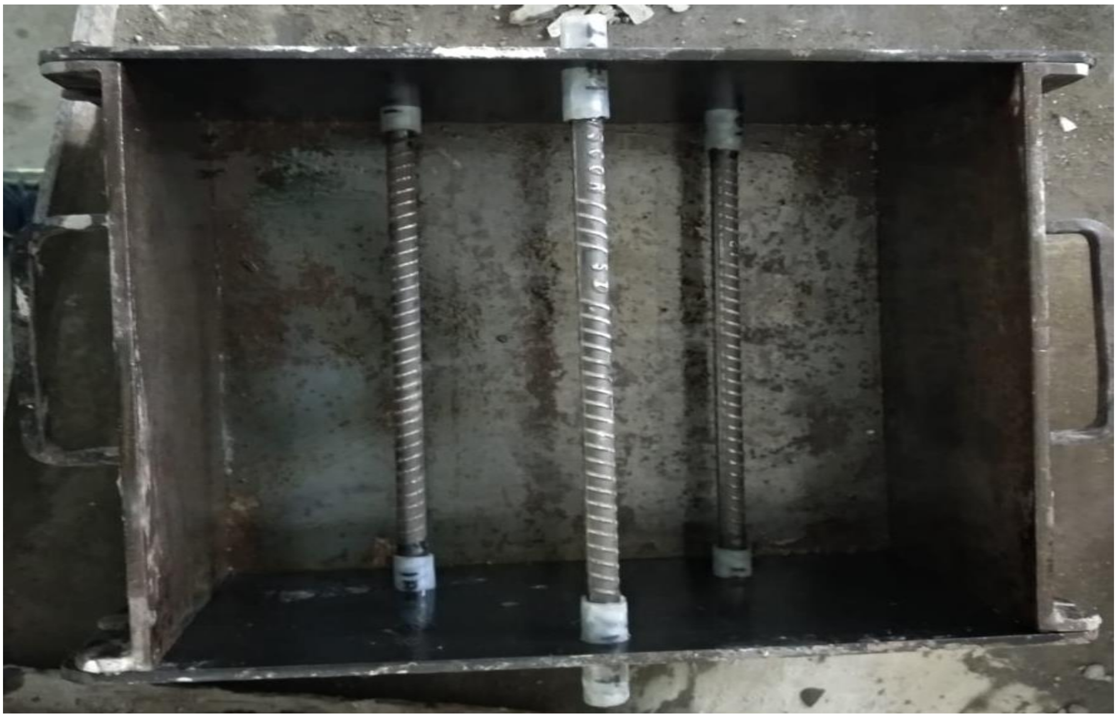


Figure 4.9 Mould setup with reinforcement before casting

4.4.3.3 Casting of prismatic specimen

To evaluate the effect of both inhibitors in two different cement type, a total of 12 prismatic specimen were casted. Before casting, prismatic moulds were cleaned and then oiled from inside so that demoulding process can be done smoothly. Three bars in each specimen were placed perfectly so that size of 30mm covered with rubber pipe from both side stays outside of mould. After this, prepared concrete mix was discharged and using table vibrator vibration process done so that no voids were remained in mould. Demoulding process is done very next day and curing was done using gunny bag for next 15 days. After curing process, epoxy was applied on each side other than top surface. Acrylic plastic sheets were fixed on four sides using m-seal on non-coated surface for chloride penetration. Figure 4.10 show final prepared prismatic specimen.

4.4.3.4 Casting of cubes

Cubes were cast for the purpose of testing carbonation depth and free chloride in combined chloride and carbonation environment. Size of cubes were taken as 100mm and same concrete as casted for prism used in cubes. A total of 36 cubes were casted to test carbonation depth, free chloride and total chloride of each cement. Water curing for 15 days was done. Final prepared cube specimen for testing is shown in Figure 4.11.

Figure 4.10 Prepared prismatic concrete specimen

Figure 4.11 Prepared cube specimens

4.4.4 Testing Period

To evaluate various electrochemical techniques, prismatic specimens after curing were given 6-day cycle which includes 2 days of NaCl (0.035 g/cc in water) pounding as shown in Figure 4.12 (A), one day air dry, two days of storage in carbonation chamber, one day air day followed by testing on 7th day. This cycle repeated for 8 times. For cube testing, same 6-day cycle applied and testing was done after 4th and 8th cycle. Figure 4.12 (B) show set values of RH, temperature and CO_2 in CO_2 incubator.

Figure 4.12 Chloride pounding on prismatic specimen (A) & CO_2 incubator (B)

4.4.5 Tests Conducted on Concrete Specimens

In order to stop a disease like corrosion in concrete, techniques which are non- destructive in nature must be use to predict deterioration, cracks and spalling due to corrosion process. Non-destructive techniques like electrochemical tests and half-cell can helps in predicting the corrosion activity in concrete system. electrochemical tests like half-cell potential and long-term sweep test were performed by versatile portable field machine by ACM instruments serial no. 1463. ACM instrument offers high precision in processing a large data and plotting outputs in graph automatically.

4.4.5.1 Concrete Prisms

After curing process, concrete prisms were tested after every 7th day. Following section gives insight of non-destructive techniques which were performed on concrete prismatic specimen.

1. Half-cell potential

Half-cell potential test helps in evaluating the behaviour of steel. This electrochemical technique provides us potential value. Potential value is directly proportional to the risk of corrosion in concrete. Half-cell potential value taken at four different points along the steel bar in concrete surface. Half-cell potential measurement serves following purpose as well as use: -

a) Helps in a determining the present condition of corrosion on rebar.
b) After repairing, provides efficiency of repairing steel bars
c) During concrete life, test can be done at any time

d) Size of reinforced concrete is independent criteria

Half-cell potential test is conducted with the help of saturated electrode calomel. Electrode calomel is setup on spouge wetted in soup solution for proper electrical conductivity. This electrode calomel is connected to the ACM instrument machine and one end is connected with nut. Final potential values are taken from desktop machine connected to ACM machine using universal serial bus (USB) via rest potential checker software. Table 4.13 provides information regarding corrosion condition as per ASTM C876. Figure 4.13 shows setup of half-cell potential test.

Table 4.13 Relation between Half-cell values & corrosion condition (As per ASTM C876)

Potential values (mV)	Corrosion condition
Less than -426	Severe corrosion, cracking due to corrosion may occur
Less than -276	High risk, 90% probability of corrosion
Between -126 to -275	Intermediate risk, corrosion activity in reduction
Between 0 to -125	Low risk with only 10% probability of corrosion

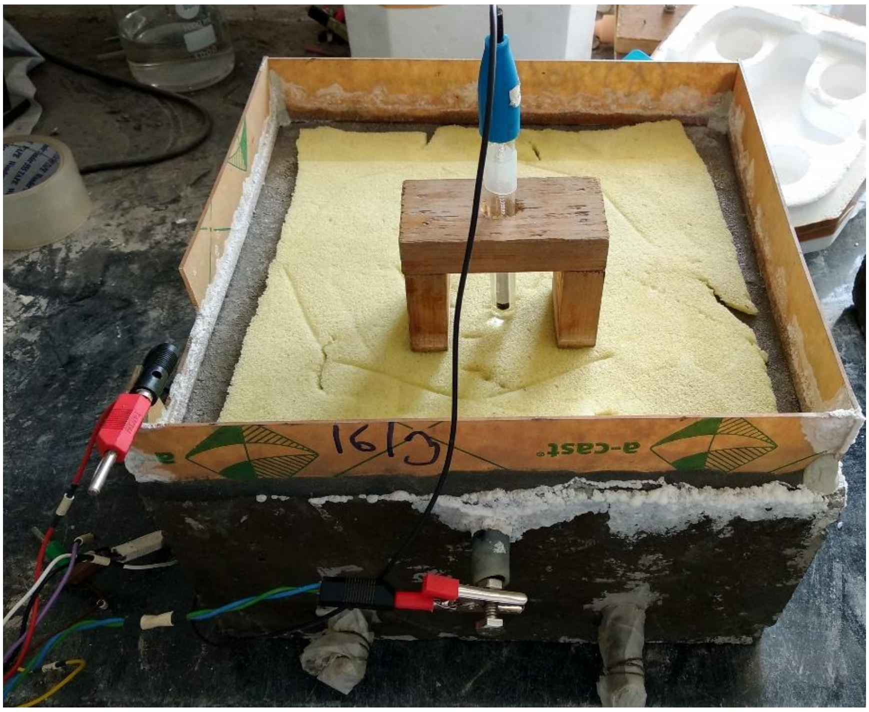


Figure 4.13 Half-cell potential setup

2. Linear Polarization Resistance Technique

Linear polarization resistance technique helps in gaining corrosion process data. This electrochemical technique is good at measuring localized corrosion. LPR technique is basically a relation between current and voltage, which allows measurement of corrosion rates and provides indication on progression of corrosion. Significance and uses of LPR techniques is given in following: -

a) Efficiency of this technique is on higher side
b) LPR technique is a rapid test with instant results
c) Provides indication of metal behaviour due to change in passive to active

LPR technique is measured with help of guard ring placed on sponge wetted on soap solution for smooth electrical conductivity on top of concrete surface. Front panel of guard ring connects with ACM instrument machine via supplied cables as shown in Figure 4.14.

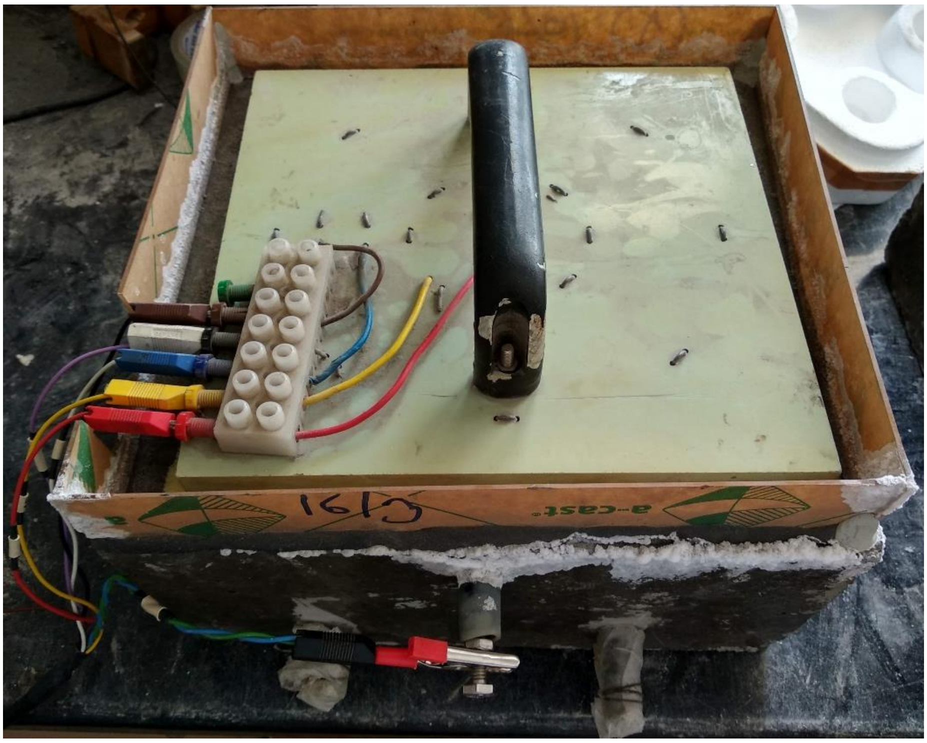


Figure 4.14 LPR test setup with guard ring

The polarization value for steel bar was given ±250mV as shown in Figure 4.7. Surface area for polarization steel is assumed to be only top non-coated surface, taken as 7.86 cm^2 which is lying under guard ring. Stern-Geary equation is used to calculate corrosion current density (I_{corr}).

$$I_{corr} = \frac{B}{Rp}$$

Where,

$$B = \frac{\beta a \; X \; \beta c}{2.3\,(\beta a + \beta c)}$$

B, R_p, βa and βc are known as Stern-Geary constant, polarization resistance, anodic and cathodic Tafel constants respectively. In active condition of steel, B is taken as 26mV.

4.4.5.2 Concrete Cubes

Concrete cubes of size 100mm were used to test the free chloride content and carbonation depth. These cubes are tested after 4th and 8th cycle. Detailed specification of test is elaborated in following section.

1. Chloride Content

To measure free chloride content, cubes were tested after 4th and 8th cycle same as carbonation depth test. For free chloride firstly, powder of cubes obtained by drilling the cubes at 10mm, 20mm, 30mm, 40mm and 50mm depth from exposed surface. The drilling process shown in Figure 4.15.

Figure 4.15 Drilling process

Obtained 3 gram of powder from drilling and mixed it into distilled water. In filtered 10ml sample solution, potassium chromate indicator was added as shown in Figure 4.16 (B) to obtain yellowish colour. This yellowish sample is titrated with 0.1N silver nitrate ($AgNO_3$) as shown in Figure 4.17 (B) till brick red colour obtained and volume of consumed $AgNO_3$ noted.

Using normality equation, free chloride content found out.

Normality Equation,

$$N_1V_1 = N_2V_2$$

Where,

N_1 is normality of $AgNO_3$ and V_1 is volume consumed of $AgNO_3$. V_2 is volume of sample equals to 10mL. Hence free chloride content can be calculated as,

$$\text{Free chloride Content} = N_2 \times 35.5 \text{ g/mL}$$

Where, N_2 was obtained from normality equation.

Figure 4.16 Potassium Chromate Indicator (A) & Silver Nitrate (B)

2. Carbonation Depth

To measure carbonation depth, 100mm cubes were split into two halves using two steel rods at middle of top and bottom side in compressive testing machine as shown in Figure 4.18. Phenolphthalein indicator solution was used to sprayed on the cubes. Uncarbonated part of cubes changes its colour to purple red. Depth of carbonated part was measured using vernier calliper of least count 0.01mm from the exposed side of the cube.

Figure 4.17 Filtration of sample (A) & Indicator used in filtered solution (B)

Figure 4.18 Splitting of cube into two halves

CHAPTER 5

RESULTS AND DISCUSSION

5.1 GENERAL

This chapter is divided into two parts. First part of chapter deals with the results of using admixed corrosion inhibitors in combined ingress chloride and carbonation environment obtained from various techniques like half-cell potential, linear polarization sweep test, carbonation depth and chloride content in concrete. Second part deals with mechanism of 4-amino benzoic acid and tri ethyl phosphate based on multi-functional (amine and carboxylic) and single functional (phosphate) group respectively.

5.2 TESTS ON PORE SOLUTION

Efficiency of both corrosion inhibitors were checked in stimulated pore solution. Pore solution was prepared similar to conditions in which rebar go through in concrete structure. In base solution ($Ca(OH)_2$ +NaOH + KOH), NaCl (0.035 g/cc) and bubbling of CO_2 (99% pure) was added for chloride and carbonation environment respectively. Both corrosion inhibitors were added in base solution separately so that inhibitor to chloride ratio remains equal to 1. Table 5.1 shows nomenclature of sample solution used in pore solution test. Results of LPR tests were discussed in following section: -

Table 5.1 Nomenclature of pore solution

Designation	Description
Solution 1	Saturated $Ca(OH)_2$ (0.01M) + NaOH (0.1M) + KOH (0.3M) + NaCl (0.035 g/cc) + CO_2 (pH = 9)
Solution 2	Solution 1 + 4-amino benzoic acid (0.1 M)
Solution 3	Solution 1 + Tri ethyl phosphate (0.1 M)

5.2.1 Linear Polarization Resistance

Linear polarization resistance tests indicate progression of corrosion process on steel surface by measuring the corrosion current density. LPR test was conducted on all three samples after immersion of steel bars in solution for 24 hours, 48 hours and 120 hours. Figure 5.1 show I_{corr} values for all three solutions after 120 hours. These I_{corr} values have been obtained by Tafel extrapolation method on LPR curves shown in Figure 5.2. Results indicate that I_{corr} value for solution 1 high as compared to inhibitor I_{corr} value which suggest that both inhibitors had shown effect of inhibition in pore solution. I_{corr} value have increased after immersion time for both solution 1 and solution 2 samples. Comparing solution 2 and solution 3, solution 2 shown lower

I_{corr} value which means ABA at 0.1M solution able to inhibit as compared to solution 3. Figure 5.2 show recorded polarization curve for all three solutions. Solution with ABA represented by blue colour curve shifted towards nobler side indicates lower corrosion current density as compared to green curve which represent TEP solution. Base solution represented by red colour curve remains on active side which suggest that both inhibitors compared to solution 1 able to resist corrosion on steel surface. I_{corr} value at nobler site for solution 2 can be due to formation of complex compounds due to chelating process. Chelating process happen due to presence of carboxylic group in ABA inhibitor and able to form up to six-member chelating members. Similarly, I_{corr} value for solution 3 is at nobler site but higher than solution 2 due to PO_4^{3-} which formed new phosphate product on steel surface *(Nahali et al. (2015))*. At first, I_{corr} value for solution 3 at 24 hours was higher as compared to 48 hours. This may be due to presence of higher phosphate content near the rebar surface which forms stable compound and hinder the anodic sites in rebars and leads to decrease of I_{corr} value at 48 hours.

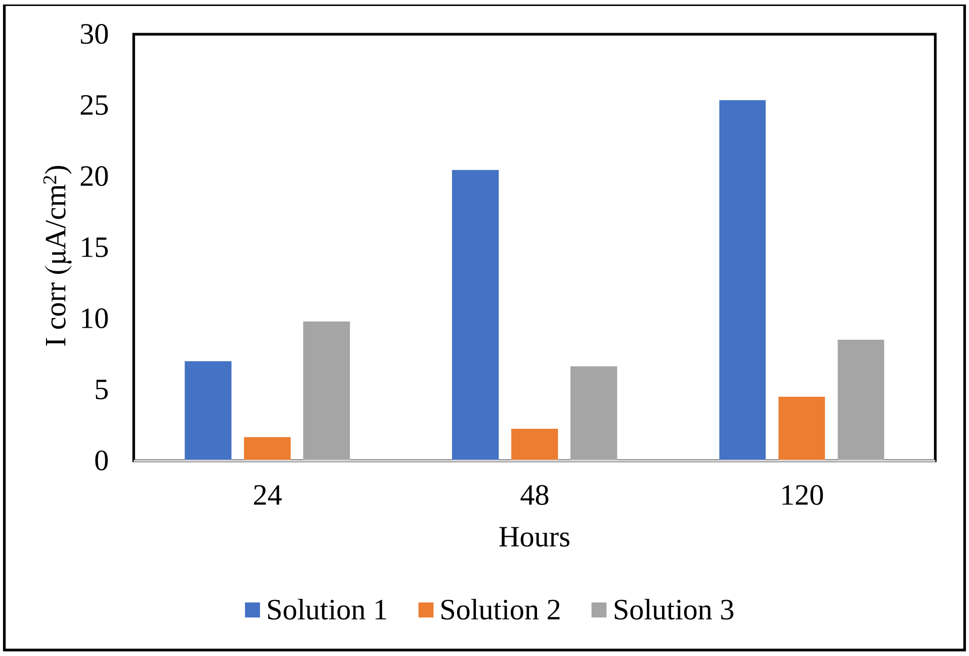


Figure 5.1 I_{corr} values on pore solution

After testing rebars in pore solution, formation of rust was visible on steel surface. Figure 5.3 show rust on rebars immersed in solution 1 at 24h, 48h and 120h. Similarly, rust on rebars immersed in solution 2 and solution 3 are shown in Figure 5.4 and Figure 5.5 respectively. As suggested by I_{corr} values, rust on solution 1 rebars are more as compared to solution 2 and solution 3 rebars. In solution 2 rebars, rust formation is lowest due to chelating compound which is visible by dark colour in Figure 5.4.

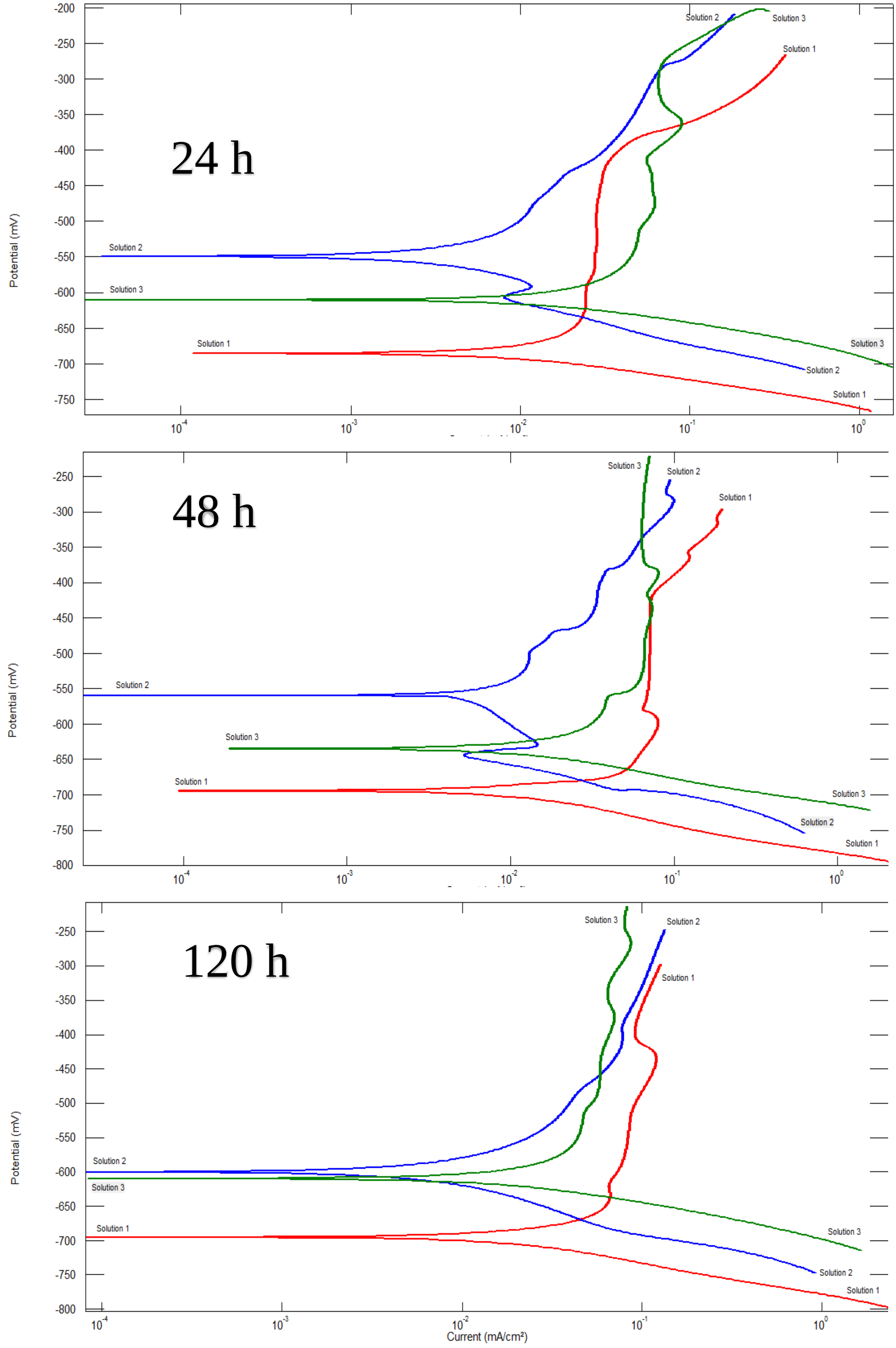


Figure 5.2 Recorded polarization curve of pore solution test

Figure 5.3 Solution 1 specimens

Figure 5.4 Solution 2 specimens

Figure 5.5 Solution 3 specimens

5.3 TESTS ON CONCRETE PRISM

Prismatic concrete specimens were casted to measure electrochemical tests. Based on electrochemical tests, efficiency of ABA and TEP as corrosion inhibitors were checked. Concrete prisms were provided 15-day water curing followed by 7-day cycle including ingress of chlorides and carbonation environment. Table 5.2 shows nomenclature of both OPC and PPC specimens used in electrochemical tests.

Table 5.2 Nomenclature of concrete specimens

Designation	Description
O-C	Control OPC specimen
O-ABA	4-amino benzoic acid (ABA) admixed OPC specimen (1% by cement weight)
O-TEP	Tri ethyl phosphate (TEP) admixed OPC specimen (1% by cement weight)
P-C	Control PPC specimen
P-ABA	4-amino benzoic acid (ABA) admixed PPC specimen (1% by cement weight)
P-TEP	Tri ethyl phosphate (TEP) admixed PPC specimen (1% by cement weight)

5.3.1 Half Cell Potential

Half-cell potential (HCP) test was carried on concrete prismatic specimen. Prismatic specimens were provided with both chloride and carbonation environment consisting of 2-day each including one dry day in between both environment. Readings were taken at the end of every cycle.

Half-cell potential value indicates the corrosion possibility in reinforced concrete. Potential value provides idea of corrosion initiation in concrete system. Depassivation on steel surface can also be indicated by potential values. Half-cell potential reading as per ASTM C876 were discussed in Table 4.12. Table 5.3 shows half-cell potential value obtained by all specimens at different cycles.

1. OPC concrete

Figure 5.4 shows the HCP readings at different cycles of OPC specimens. At cycle 0 and 1, reading of all three specimens were below -275mV which suggest that only 10% probability of corrosion. With increase in cycles, passive potential shifted towards active potential in all specimens in OPC. HCP readings suggested that ABA and TEP failed to perform in OPC concrete.

Table 5.3 Half-cell potential reading at different cycles

Cycles	Half Cell potential (mV)					
	O-C	**O-ABA**	**O-TEP**	**P-C**	**P-ABA**	**P-TEP**
C 0	-205.36	-110.54	-204.98	-178.51	-78.56	-128.68
C 1	-210.92	-125.15	-199.46	-295.42	-102.31	-368.88
C 2	-376.1	-377.07	-374.58	-310.45	-105.77	-410.36
C 3	-385.91	-418.07	-457.19	-335.18	-108.43	-396.65
C 4	-390.01	-423.55	-479.97	-349.21	-112.93	-398.15
C 5	-343.30	-423.33	-479.97	-375.03	-104.58	-421.94
C 6	-392.14	-407.89	-494.96	-350.62	-293.65	-434.04
C 7	-437.07	-430.87	-495.57	-371.66	-314.75	-434.21
C 8	-440.98	-432.25	-497.69	-382.05	-321.23	-441.55

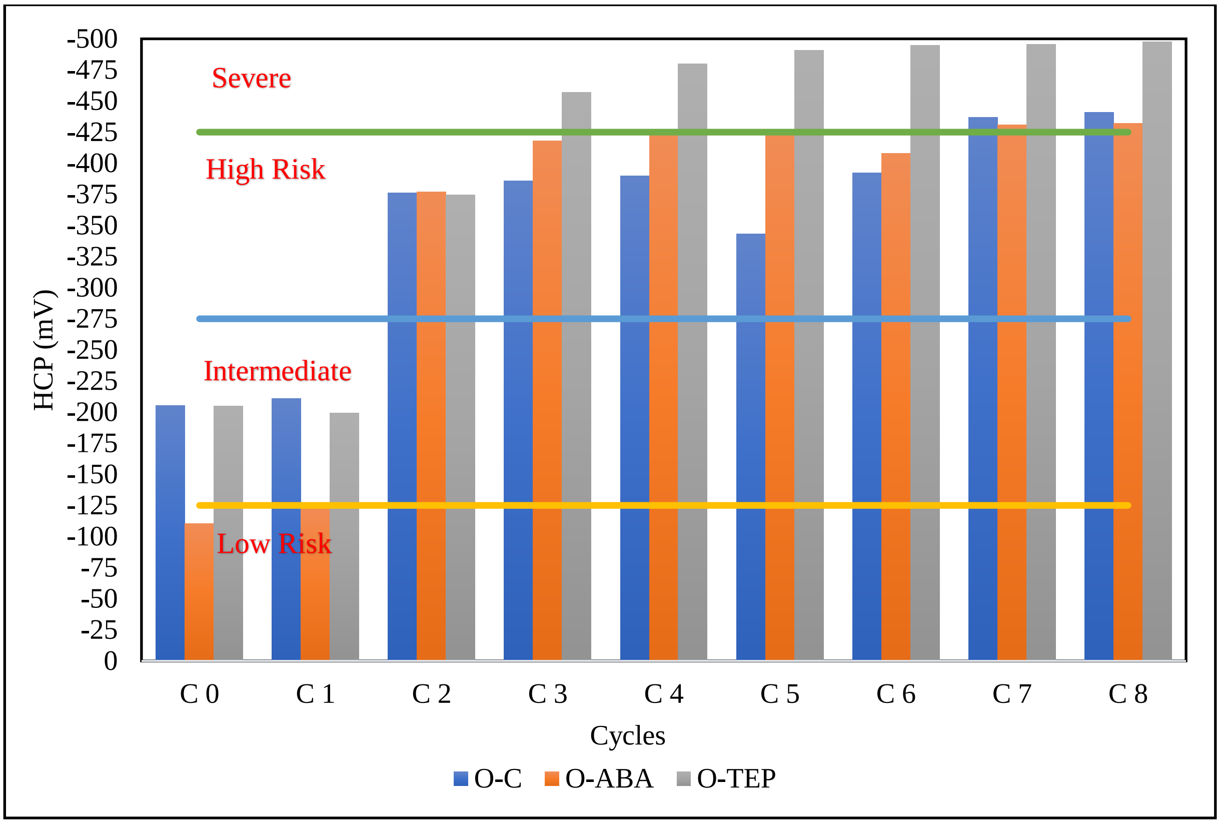


Figure 5.6 Half-cell potential value for OPC specimens

2. PPC concrete

Figure 5.4 shows Half-cell potential readings of PPC concrete at various cycles. P-C and P-TEP specimens performed almost same at all cycles. After C 0, P-C and P-TEP showed high risk of corrosion in steel bars which clearly suggest that TEP failed to inhibit corrosion process. This may be due to lower dosage of inhibitor used at time of casting of specimens. P-ABA gave HCP reading lower than -125mV till 5th cycle which means passive potential in concrete specimens. Even after C 8, HCP values didn't suggest severe corrosion conditions which can induce cracking too in concrete.

Hence, half-cell potential value indicates that ABA helped passive layer to remain in system till 5th cycle in PPC concrete but same cannot be said about ABA in OPC. As the exposure to conditions like chloride and carbonation increased, ABA in PPC maintained nobler potential but other specimens include control specimen couldn't cope up with increase in exposure condition and end up at severe corrosion condition at the end of 8th cycle. No conclusion can be drawn on the basis of half-cell potential test due to the fact that half-cell potential reading only provides probable condition of corrosion. In order to get HCP readings verified, linear polarization resistance test must be conducted.

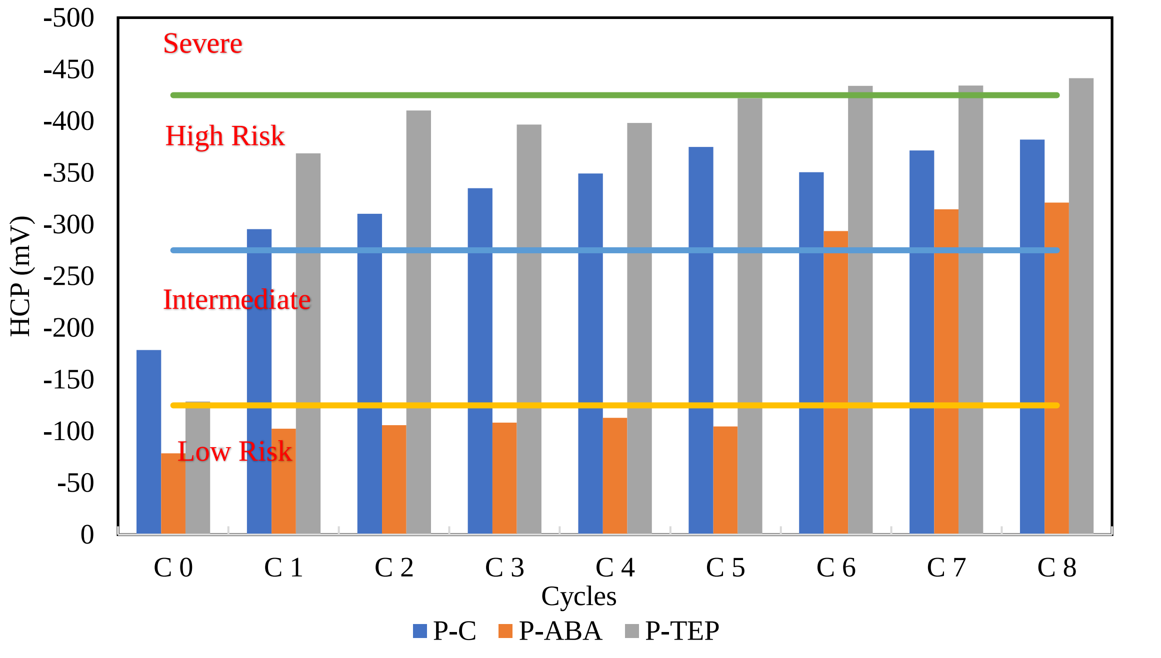


Figure 5.7 Half-cell potential value for PPC specimens

5.3.2 Linear Polarization Resistance

Linear polarization resistance (LPR) is the most non-destructive electrochemical test used. LPR test provides us true information of corrosion in system unlike HCP tests. LPR test was conducted on prismatic concrete specimen after end of each cycle. Table 5.4 defines corrosion current density (I_{corr}) value as per *Stewart et al. 2002*. Polarization curves were obtained after every cycle for all specimens. Tafel extrapolation was done to obtained value of I_{corr} which are given in Table 5.5.

Table 5.4 Corrosion Rate as per current density (*Stewart et al. (2002)*)

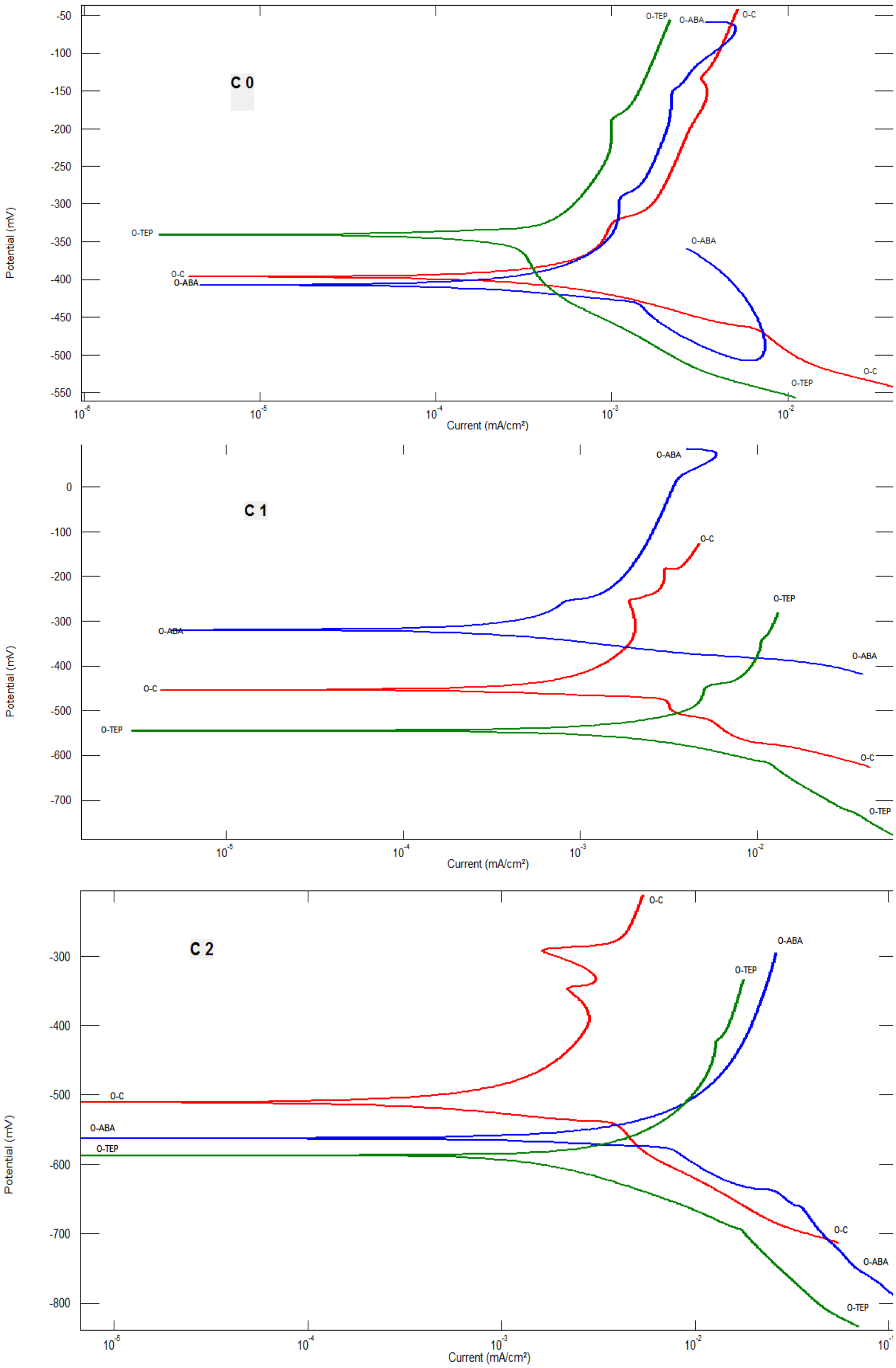
Corrosion Current Density (μA/cm^2)	Corrosion Rate
Less than 0.1	Low
Between 0.1 to 1.0	Moderate
Between 1.0 to 10	High
Between 10 to 100	Very High

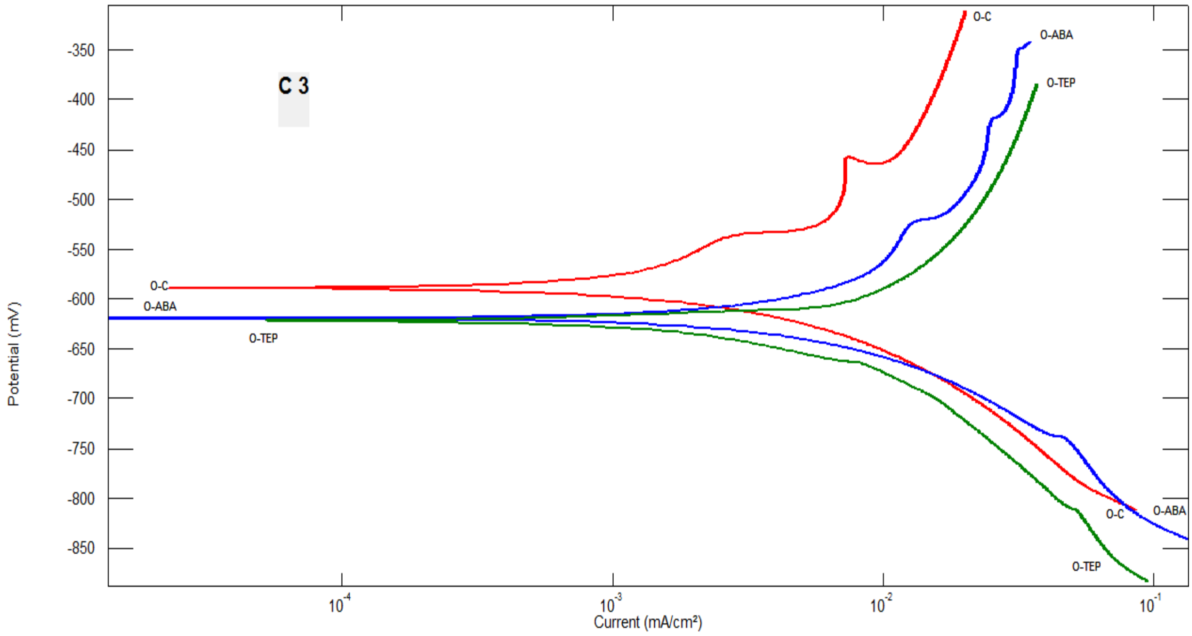
Table 5.5 I_{corr} values

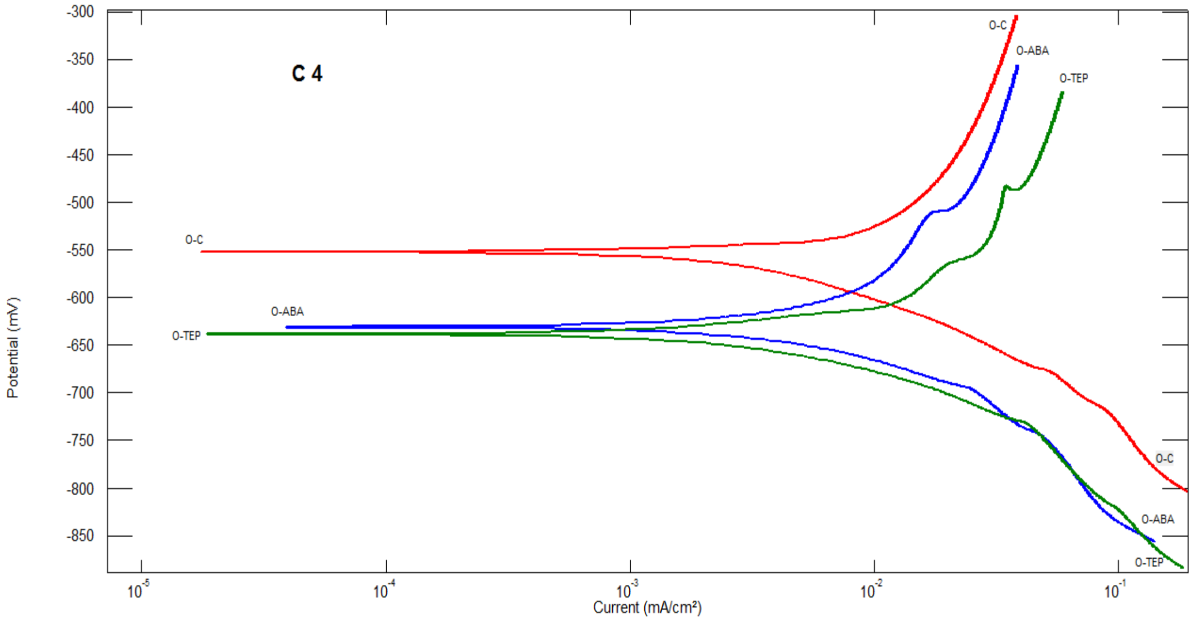
Cycles	I_{corr} (μA/cm^2)					
	O-C	**O-ABA**	**O-TEP**	**P-C**	**P-ABA**	**P-TEP**
C 0	0.315	0.202	0.180	0.313	0.228	0.110
C 1	0.599	0.268	0.835	0.675	0.262	1.370
C 2	0.792	2.498	1.961	1.299	0.326	0.908
C 3	0.811	2.468	2.140	1.836	0.360	1.082
C 4	1.390	2.950	2.190	2.210	0.781	0.921
C 5	1.860	2.540	2.805	1.490	0.826	1.033
C 6	2.230	2.200	2.320	1.400	0.690	1.480
C 7	2.160	1.970	2.710	1.670	0.481	2.060
C 8	2.350	2.010	2.880	1.540	0.449	2.050

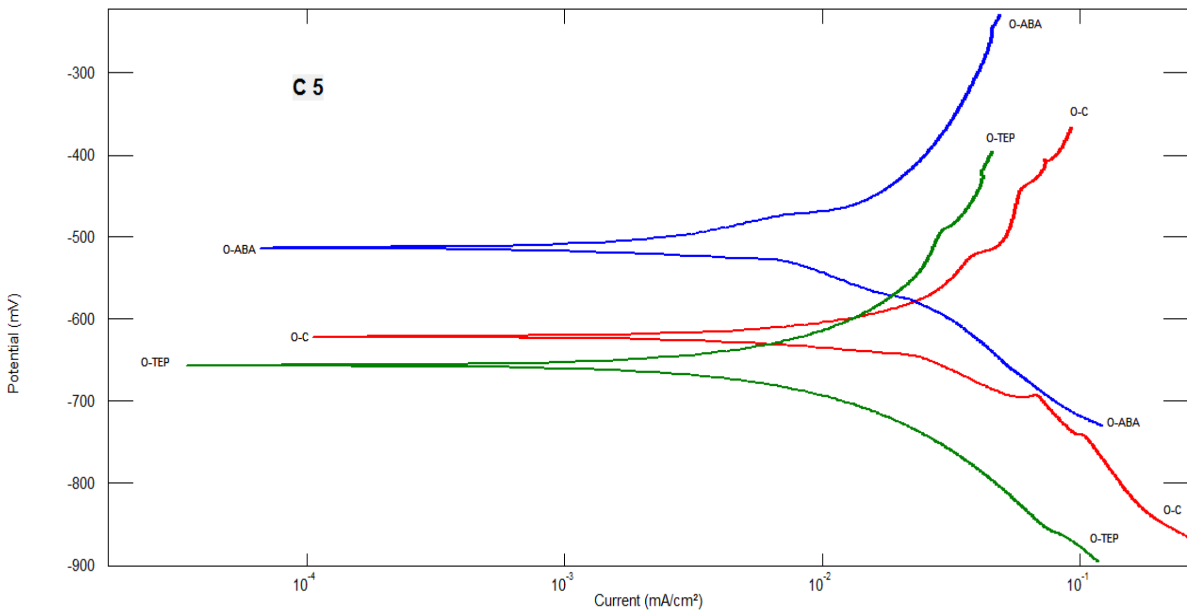
1. OPC Concrete

Figure 5.8 show polarization curve for OPC specimens of all specimens at various cycles. Red, blue and green colour curves indicate O-C, O-ABA and O-TEP specimens respectively. Figure 5.9 shows value of I_{corr} for OPC specimens at different cycles. At C 0, all three specimens showed equal I_{corr} value. In cycle C 1 and C 2, potential was on nobler side for O-C and O-TEP specimens. After that, corrosion current density shifted towards active state. Similar trend was obtained for O-ABA specimen initially. After 4th cycle, I_{corr} value followed decreased trend but with almost negligible difference. These trends signify that both ABA and TEP inhibitor failed as corrosion inhibitor in OPC concrete.


C 0
Potential (mV)
Current (mA/cm²)
O-TEP
O-ABA
O-C
C 1
Potential (mV)
Current (mA/cm²)
O-TEP
O-ABA
O-C
C 2
Potential (mV)
Current (mA/cm²)
O-TEP
O-ABA
O-C


C 3
O-C
O-ABA
O-TEP
Potential (mV)
Current (mA/cm²)
-350
-400
-450
-500
-550
-600
-650
-700
-750
-800
-850
10^{-4}
10^{-3}
10^{-2}
10^{-1}


C 4
O-C
O-ABA
O-TEP
Potential (mV)
Current (mA/cm²)
-300
-350
-400
-450
-500
-550
-600
-650
-700
-750
-800
-850
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}


C 5
O-ABA
O-C
O-TEP
Potential (mV)
Current (mA/cm²)
-300
-400
-500
-600
-700
-800
-900
10^{-4}
10^{-3}
10^{-2}
10^{-1}

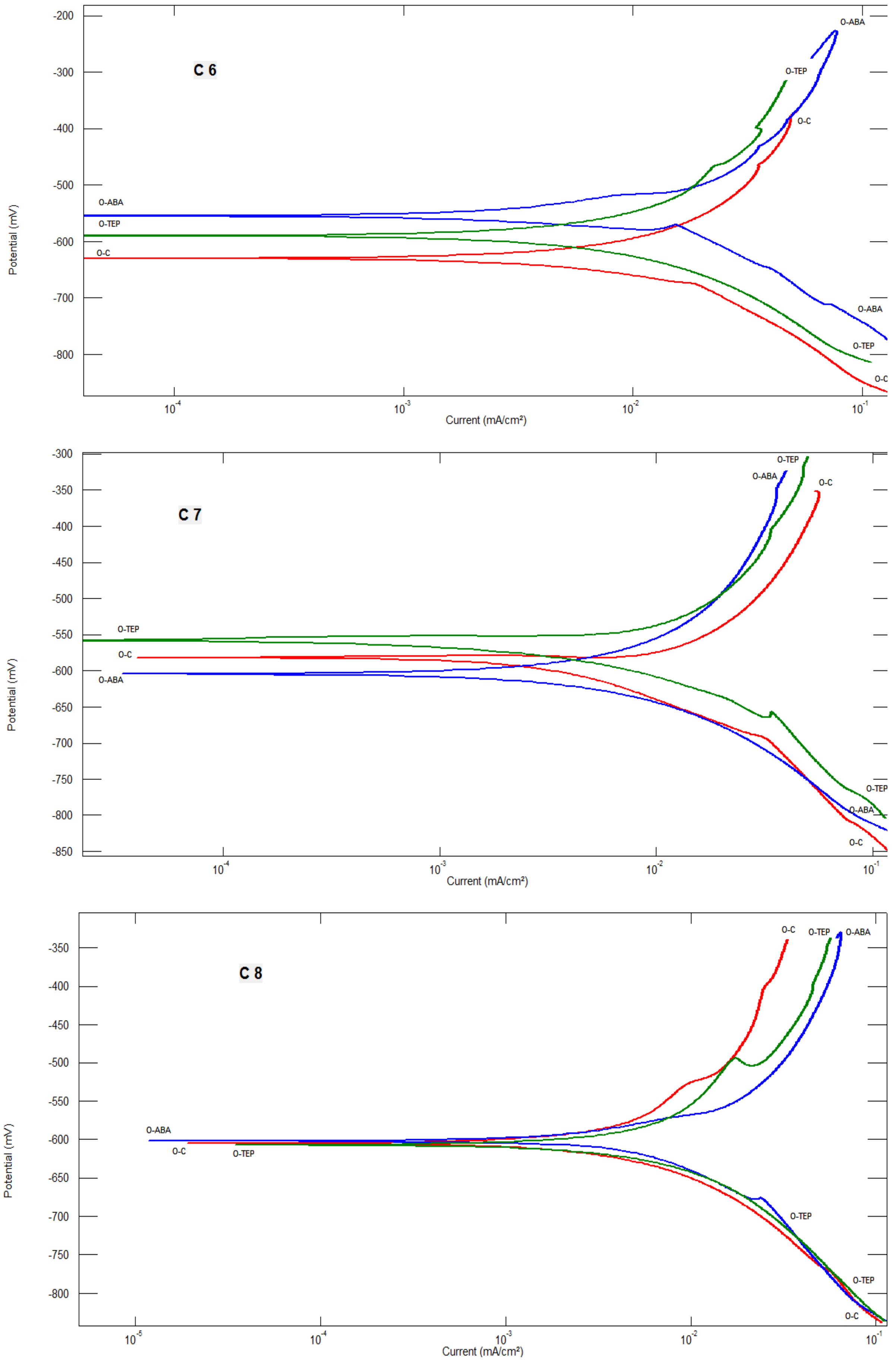


Figure 5.8 Recorded polarization curves of OPC concrete at various cycles

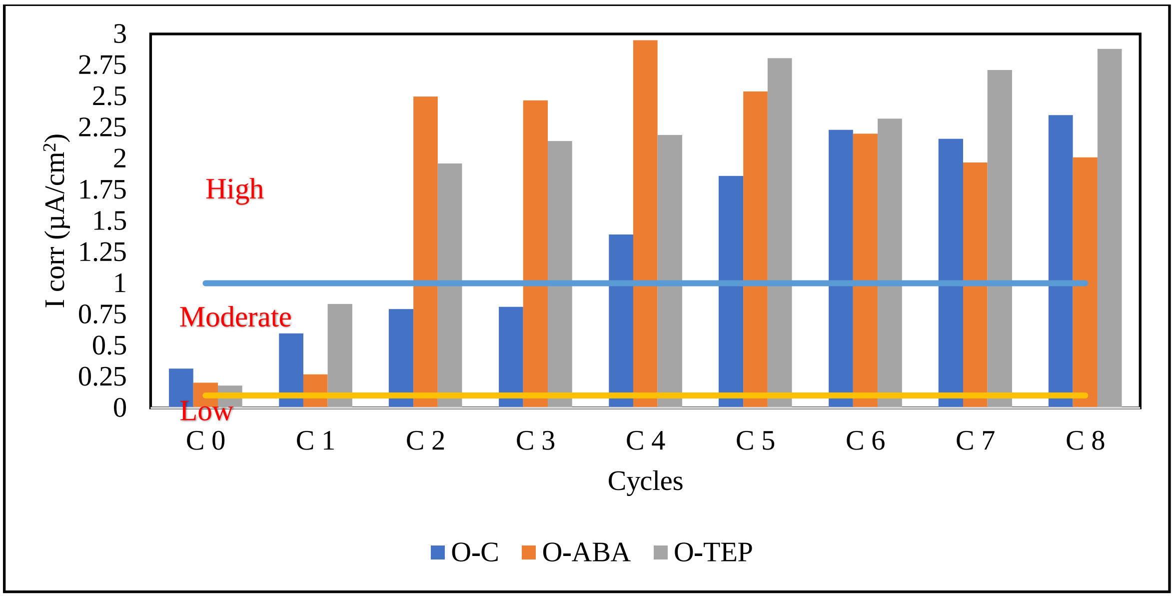


Figure 5.9 I_{corr} values at different cycles for OPC specimens

2. PPC Concrete

Figure 5.10 show variation in I_{corr} values of PPC specimens at various cycles. Similar trend was obtained for TEP inhibitor in PPC concrete as TEP in also. P-ABA specimen showed very low I_{corr} value for first 4 cycles. But with increase in exposure conditions, P-ABA potential shifted a little towards higher state but still less than P-TEP and P-C specimens. Figure 5.11 show recorded polarization curves for all PPC specimens at various cycles. Red, blue and green colour curves indicate P-C, P-ABA and P-TEP specimens respectively. P-ABA curves at all cycles apart from C 1 and C 6 are towards passive state. Whereas, P-TEP curves are lower from P-C curves as shown by green colour and potential is more towards active state in Figure 5.11 which means TEP failed as an inhibitor.

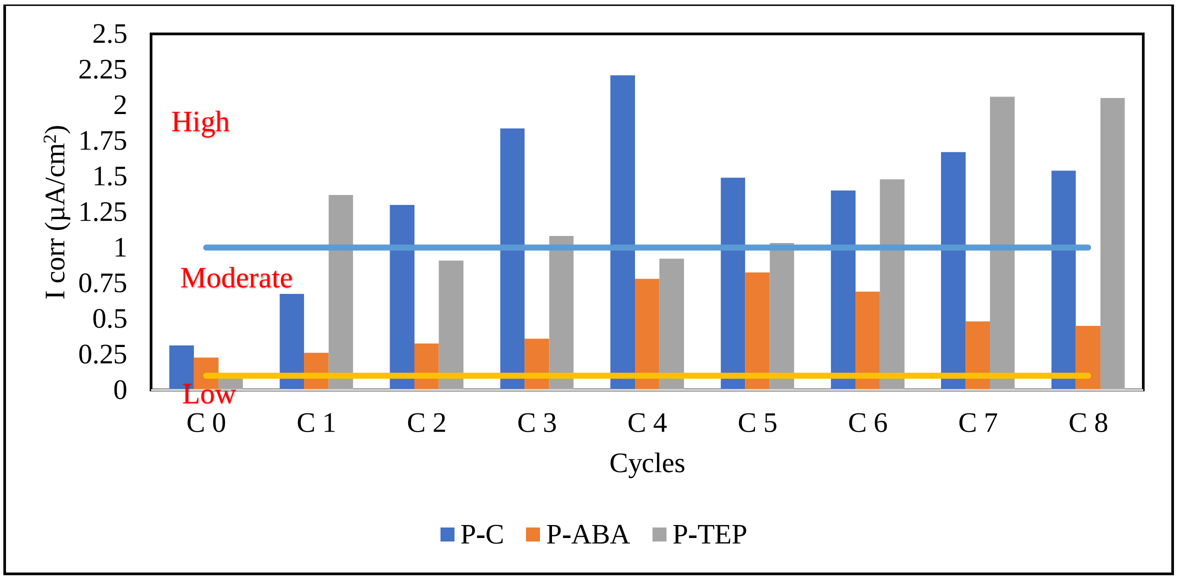
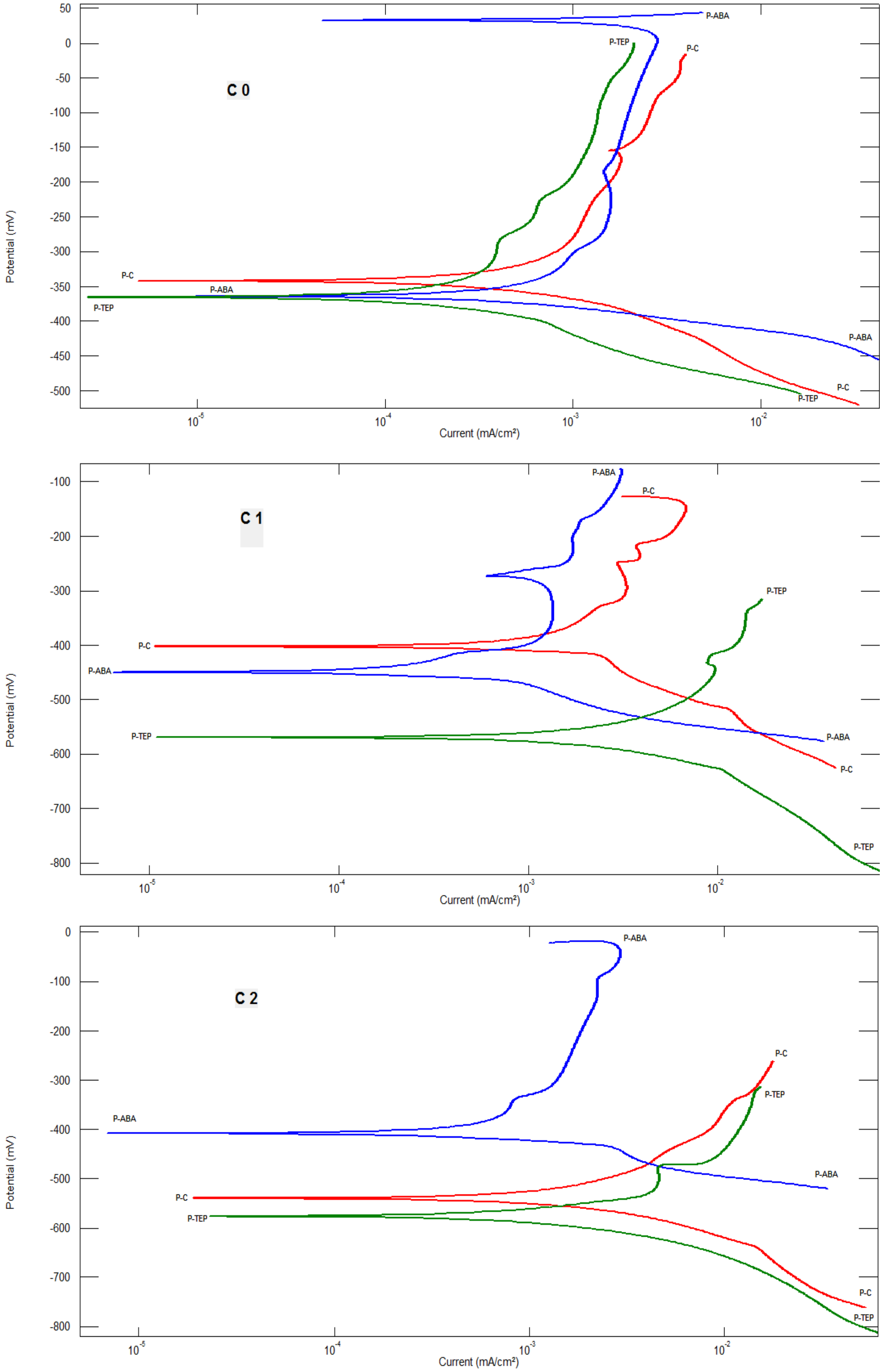
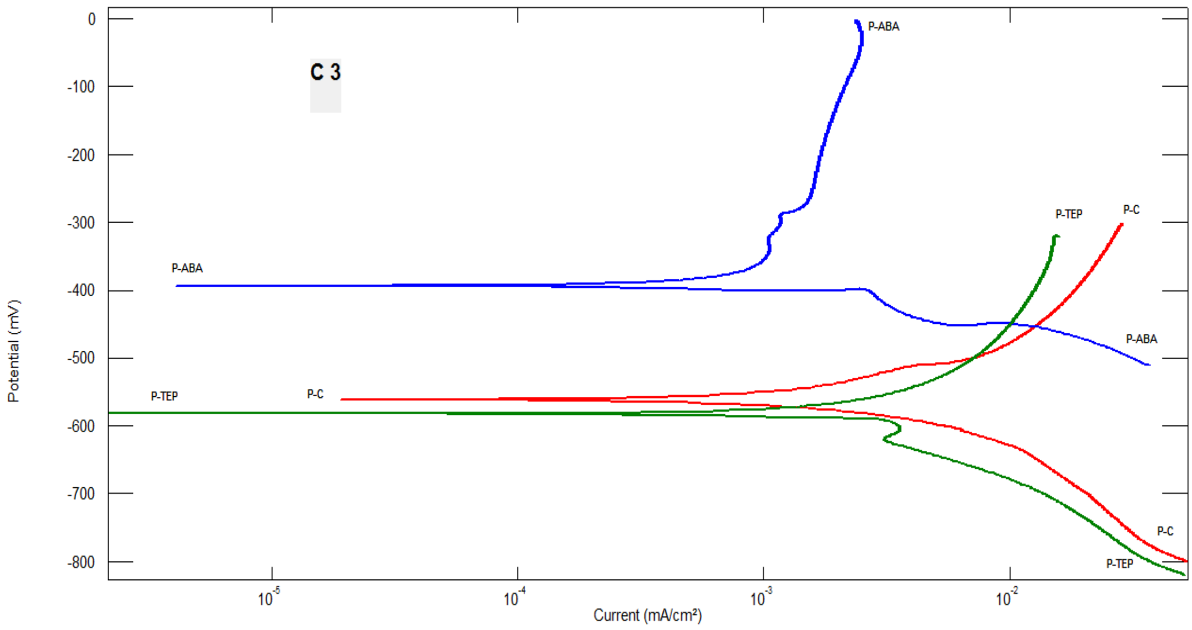
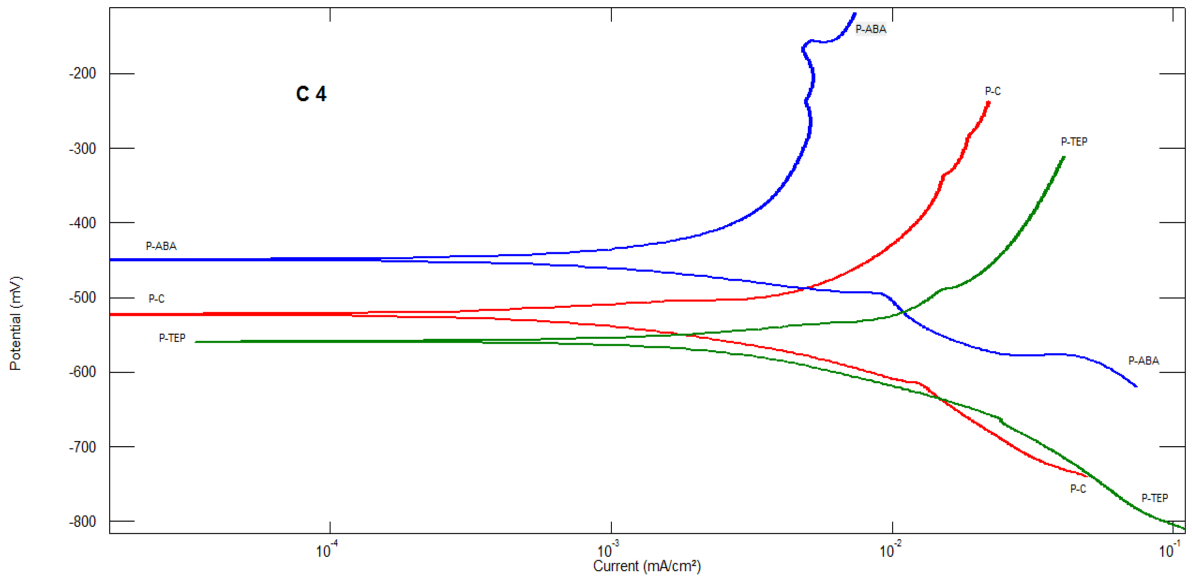
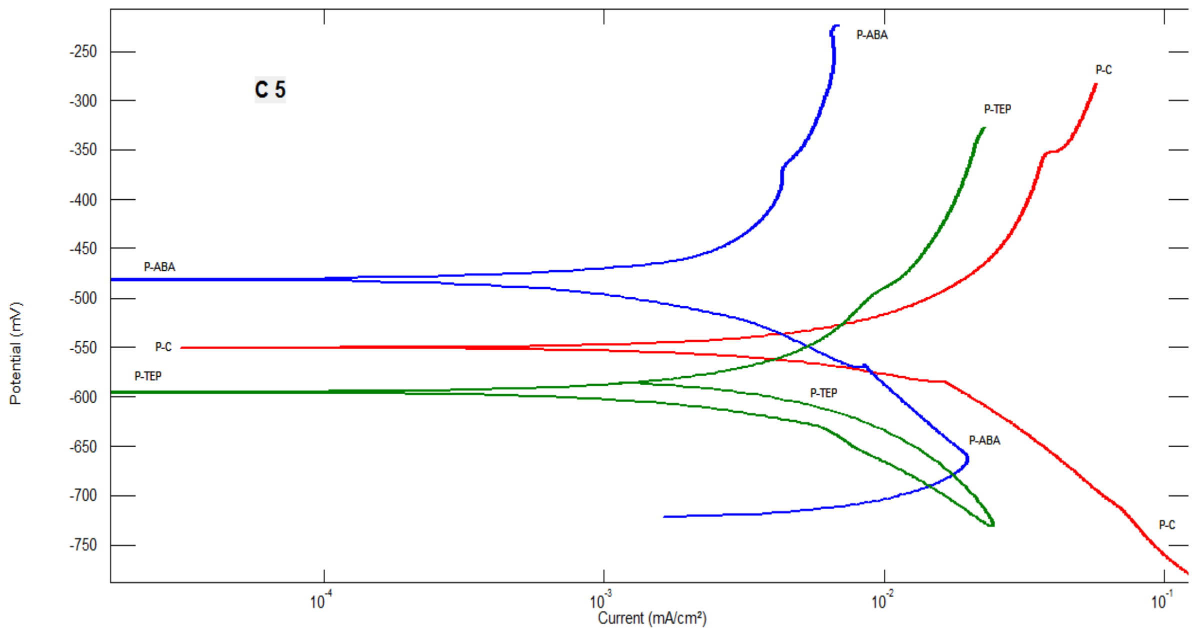


Figure 5.10 I_{corr} values at different cycles for PPC specimens


C 0
P-ABA
P-TEP
P-C
Potential (mV)
Current (mA/cm²)
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
-500
10-5
10-4
10-3
10-2
C 1
-100
-200
-300
-400
-500
-600
-700
-800
C 2


C 3
P-ABA
P-TEP
P-C
0
-100
-200
-300
-400
-500
-600
-700
-800
Potential (mV)
10^{-5}
10^{-4}
10^{-3}
10^{-2}
Current (mA/cm²)


C 4
P-ABA
P-C
P-TEP
-200
-300
-400
-500
-600
-700
-800
Potential (mV)
10^{-4}
10^{-3}
10^{-2}
10^{-1}
Current (mA/cm²)


C 5
P-ABA
P-C
P-TEP
-250
-300
-350
-400
-450
-500
-550
-600
-650
-700
-750
Potential (mV)
10^{-4}
10^{-3}
10^{-2}
10^{-1}
Current (mA/cm²)

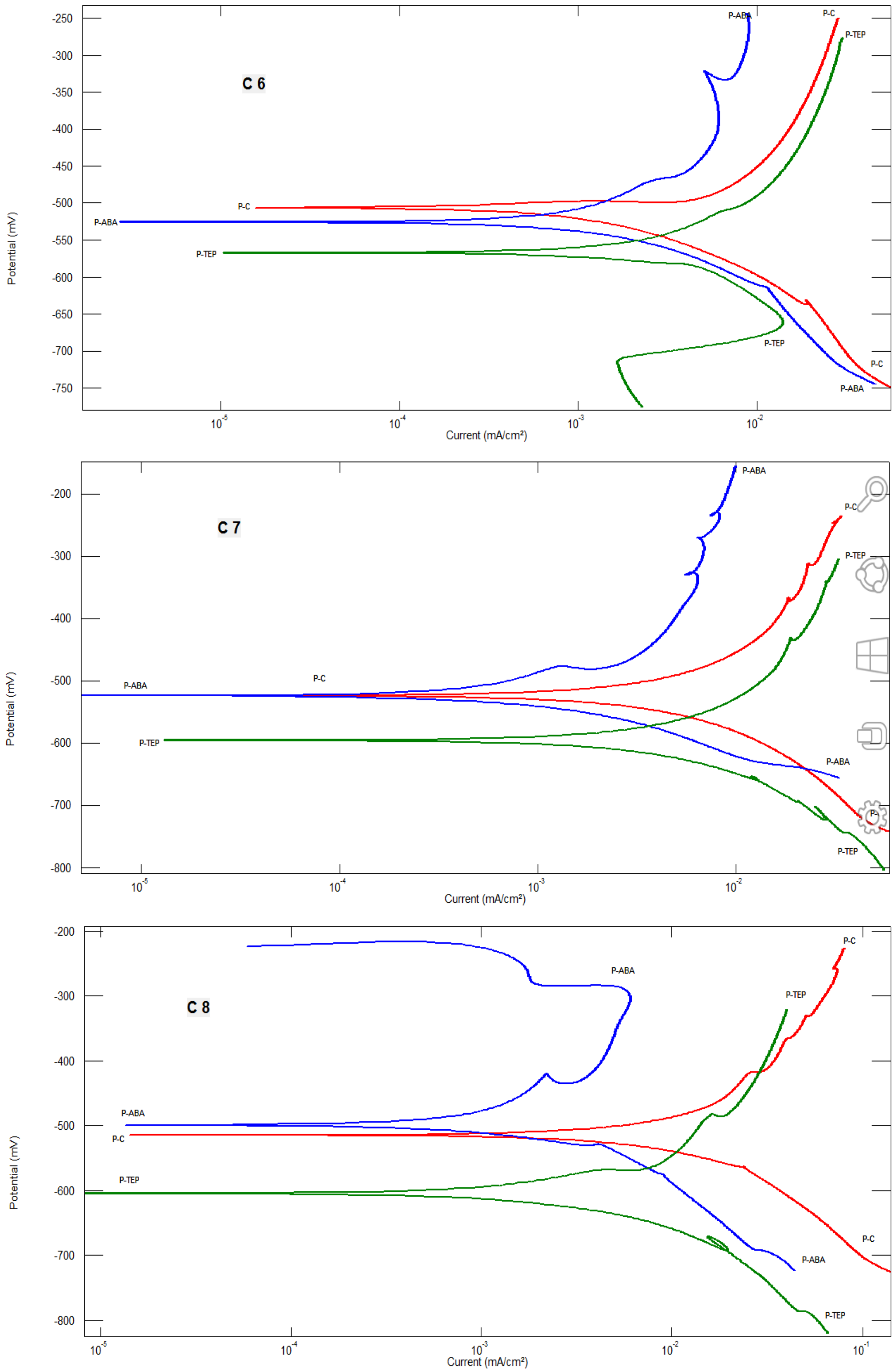


Figure 5.11 Recorded polarization curves of PPC concrete at various cycles

3. Comparison between OPC and PPC concrete

Figure 5.12 show I_{corr} variation at different cycles for ABA as an inhibitor used in both OPC and PPC concrete. Graph clearly indicates that ABA inhibitor when used in PPC concrete show inhibit properties as compared to ABA in OPC concrete. This can be due to presence of two (amine and carboxylic) functional groups in ABA inhibitor. Also, dense pore structure of PPC concrete helps in showing inhibit property of ABA in PPC as compared to OPC concrete. Thin pore structure of OPC concrete leads to high permeability of chloride ions which are missing in PPC concrete. Chloride content is higher in OPC concrete due to absence of fly ash which contains Al_2O_3 and eventually forms chloroaluminates by reacting with available chloride ions *(Saraswathy et al. (2007), Pradhan et al. (2009))*.

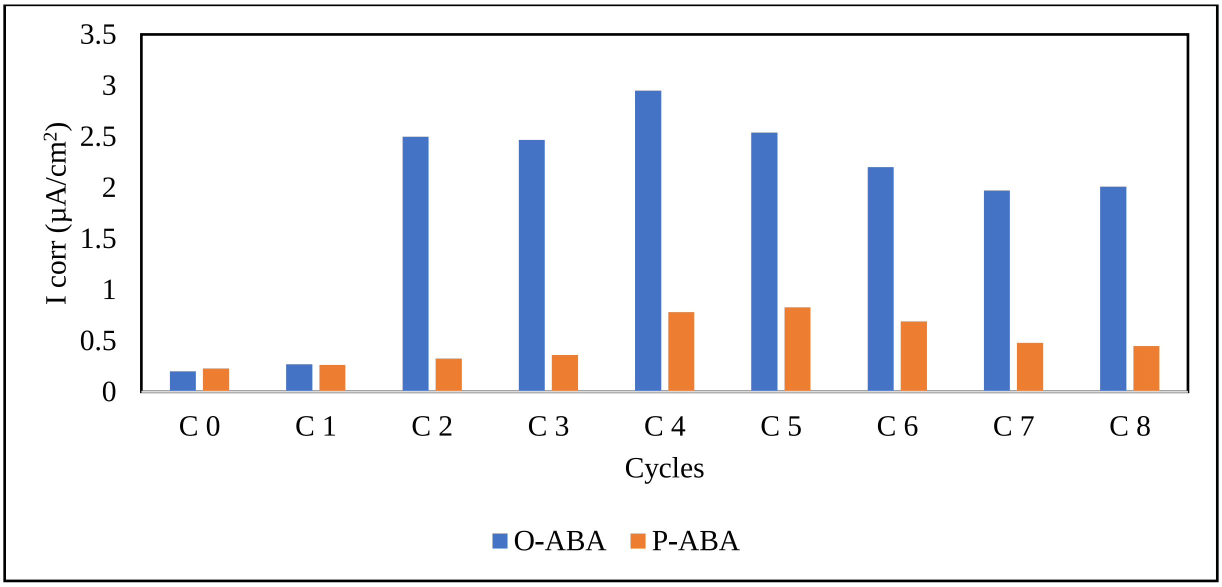


Figure 5.12 I corr value for 4-amino benzoic acid inhibitor in both OPC and PPC

Similarly, Figure 5.13 show comparison of I_{corr} value of TEP as inhibitor in both OPC and PPC concrete. Results indicates that TEP failed to perform both in OPC and PPC concrete as compared to ABA. This could be due to use of low dosage (1% by cement weight) of inhibitor admixed in concrete. Also, presence of single functional group in TEP did not help the cause. On comparing TEP as inhibitor in OPC and PPC, results are better in PPC concrete apart from only in C 1. I_{corr} value was lower in PPC but still considered to be moderate in early exposure cycle. Fineness of PPC may have helped in achieving low I_{corr} value compared to OPC but still considered to be failure as corrosion inhibitor in both OPC and PPC in given used dosage.

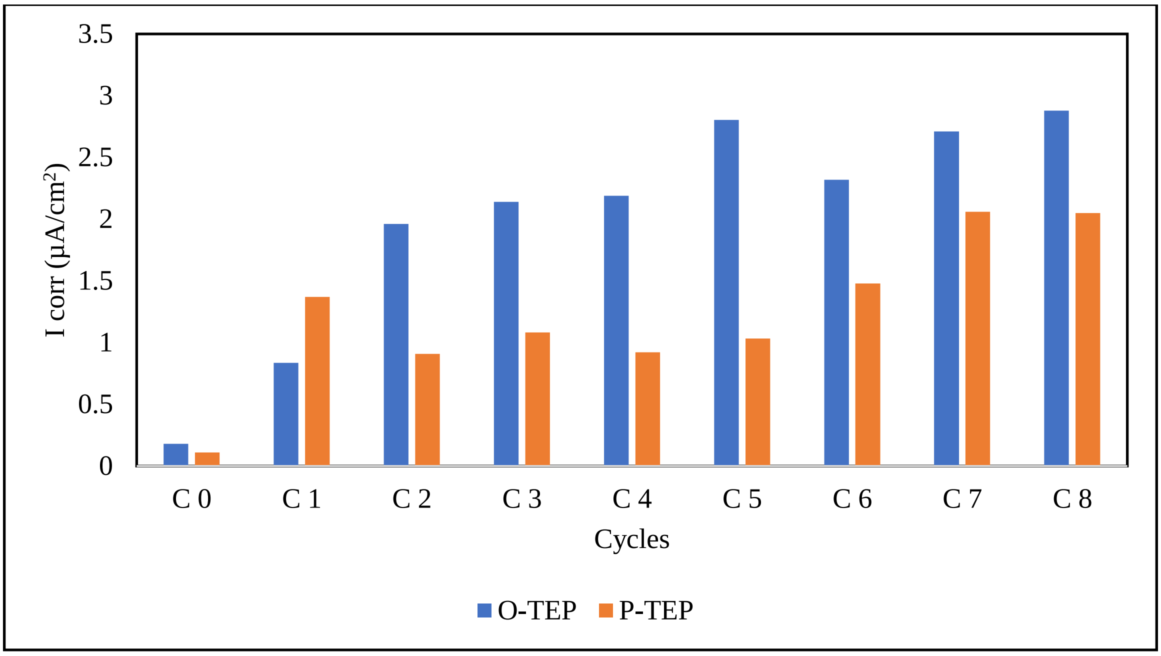


Figure 5.13 Icorr value for Tri Ethyl Phosphate inhibitor in both OPC and PPC

5.3.3 Mass Loss

To evaluate corrosion process in steel rebars in concrete specimens, change in weight (%) of rebar was calculated. Out of top and bottom rebars, only in top rebar (%) weight change was calculated after C 8, due to slow nature of corrosion process progression. Equation 5.1 used to calculate % weight change of rebar. Specimens were broken using hammer on top surface of prismatic specimen.

$$\%\, Weight\ Change = \frac{m\ intial - m\ final}{m\ intial} \times 100 \qquad (5.1)$$

Figure 5.14 (A) show broken specimen after applying hammer to collect rebars for mass loss measurement. Figure 5.14 (B) show all rebars collected from all 12 specimens at the end of nine cycles. Table 5.6 show mass loss measurement which indicate that P-ABA specimen had least (%) weight change out of all other specimens. It can physically verify that, only P-ABA rebars show no sign of corrosion on surface whereas other all specimens show corrosion. O-C and O-TEA specimens show almost equal mass loss which can be verified in Figure 5.6 (B).

Figure 5.15 show ABA rebars used in both OPC and PPC concrete, as ABA performed exceptionally well as corrosion inhibitor in PPC concrete. Hence, physically can be verified that O-ABA rebars show more corrosion whereas P-ABA show almost negligible corrosion on surface. Therefore, mass loss measurement also indicates same results which are obtained from linear polarization resistance test that corrosion current density is on lower side in PPC as compared to OPC concrete when 4-amino benzoic acid used as admixed corrosion inhibitor in combined carbonation and chloride environment.

Figure 5.14 Broken Specimen (A) & All rebars collected after completion of 9 cycles (B)

Figure 5.15 Rebars treated with 4-amino benzoic acid after completion of cycles

Table 5.6 Weight change of all specimens

Parameters	O-C	O-ABA	O-TEP	P-C	P-ABA	P-TEP
ɱ initial (g)	319	319	317	315	310	320
ɱ final (g)	304	306	303	300	306	306
(%) weight change	4.7	4.1	4.4	4.8	1.3	4.4

5.4 TESTS ON CONCRETE CUBES

To validate electrochemical results, concrete cubes were also casted in order to check the effect of ingress environment of chloride and carbonation on admixed corrosion inhibitors. Same nomenclature of Table 5.1 was followed for concrete cubes. Following section explain results of free chloride content in concrete and carbonation depth on all concrete specimens.

5.4.1 Chloride Content

Chloride present in concrete system can be classified into two different states: bound and free *(Zhang et al. (2016))*. The bound chloride present in system is insoluble in pore solution due to chemical bond between pore structure and cementitious material. Hence, bound chloride plays no part in steel corrosion whereas free chloride present in concrete system increase corrosion potential value. Hence, free chloride content was obtained by using titration method with 0.1N $AgNO_3$. For chloride environment, NaCl (0.035 g/cc in water) pounding was provided to specimen for 2 days in week long cycle. Titration was done after 4th and 8th cycle. Powdered 3g sample was filtered in distilled water and yellowish sample was obtained after adding indicator than titrated with $AgNO_3$ till red brick colour was obtained as shown in Figure 5.16. Volume of $AgNO_3$ was noted and using normality equation free chloride concentration was obtained. The chemical reactions involved in chloride free zone is as following: -

$$Ag^+ + OH^- \rightarrow AgOH \rightarrow Ag_2O \quad (5.3)$$

(Brown)

$$Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4 \quad (5.4)$$

(Brick Red)

Generally, chloride content travels in three ways which are penetration, capillary action and diffusion in concrete system. Cause of these three ways are ambient pressure, capillary pressure of fluid surface and concentration difference in concrete pores respectively. Figure 5.17 and Figure 5.18 shows free chloride concentration after C 4 and C 8. Chloride concentration decreases with depth of cube in all specimens. After both C 4 and C 8, 4-amino benzoic acid had lesser chloride penetration as compared to control and tri ethyl phosphate-based specimens in both cements which validates results obtained in carbonation depth. Chloride penetration was almost similar in control and TEP specimens. This may be due to low concentration of TEP solution used in concrete specimens *(Tang et al. (2012))*.

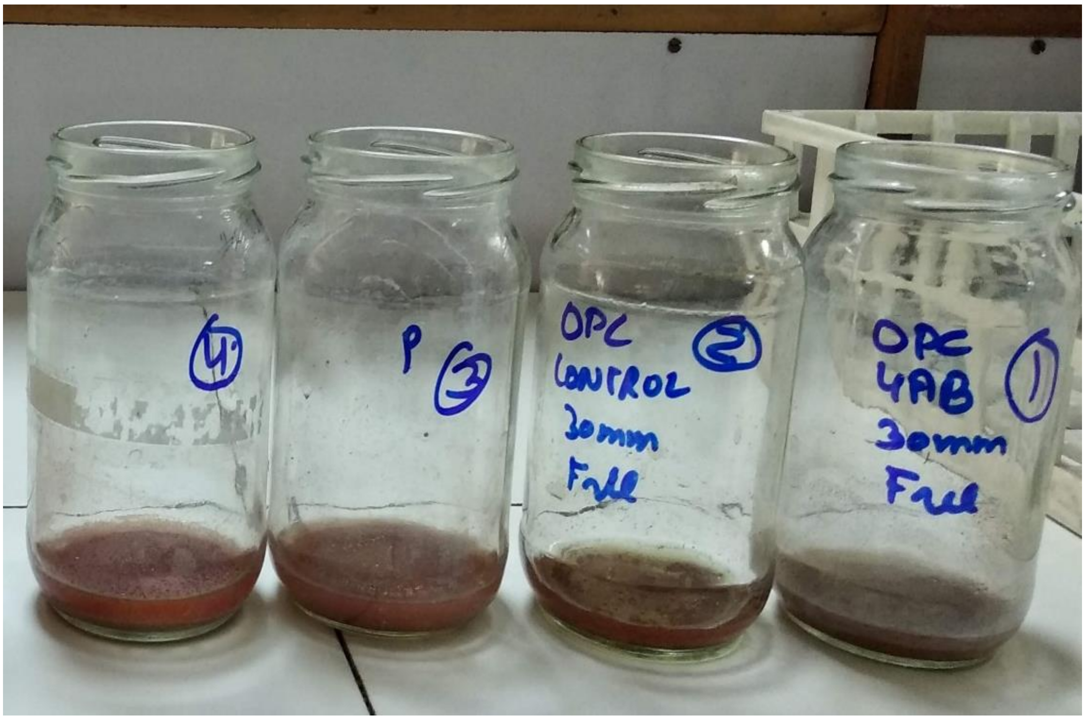


Figure 5.16 Red brick colour obtained after titration process

As ABA inhibit free chlorides ions both in OPC and PPC in comparison to TEP with increase in depth of cube *(Kondratova et al. (2003))*. Figure 5.19 show ABA performed better in PPC as compared to OPC. This may be due to more fineness of PPC as compared to OPC. This leads to dense structure of concrete and make concrete system less permeable.

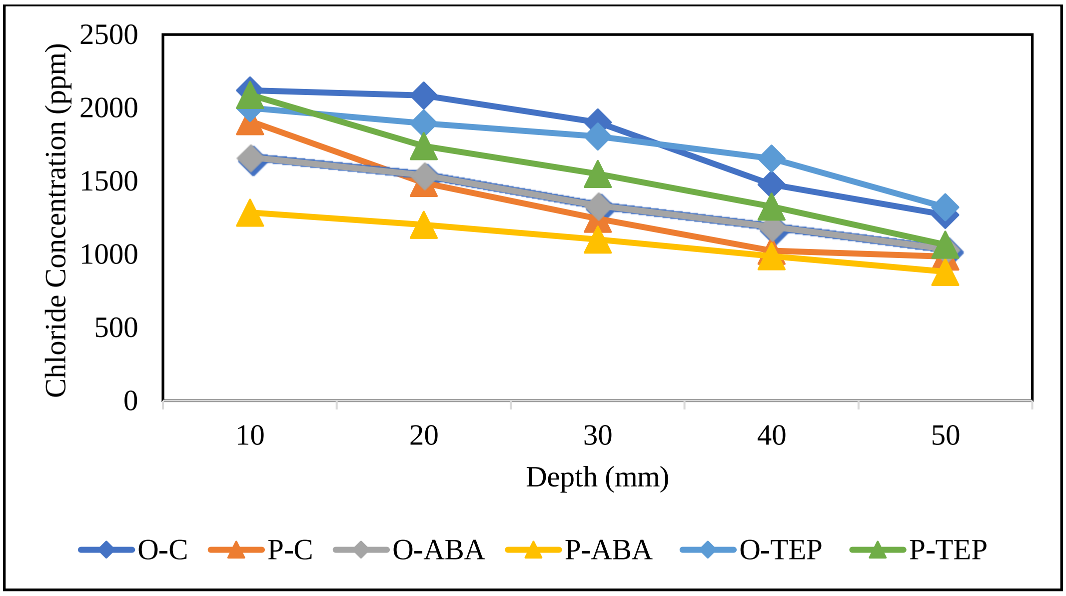


Figure 5.17 Chloride concentration vs depth after C 4

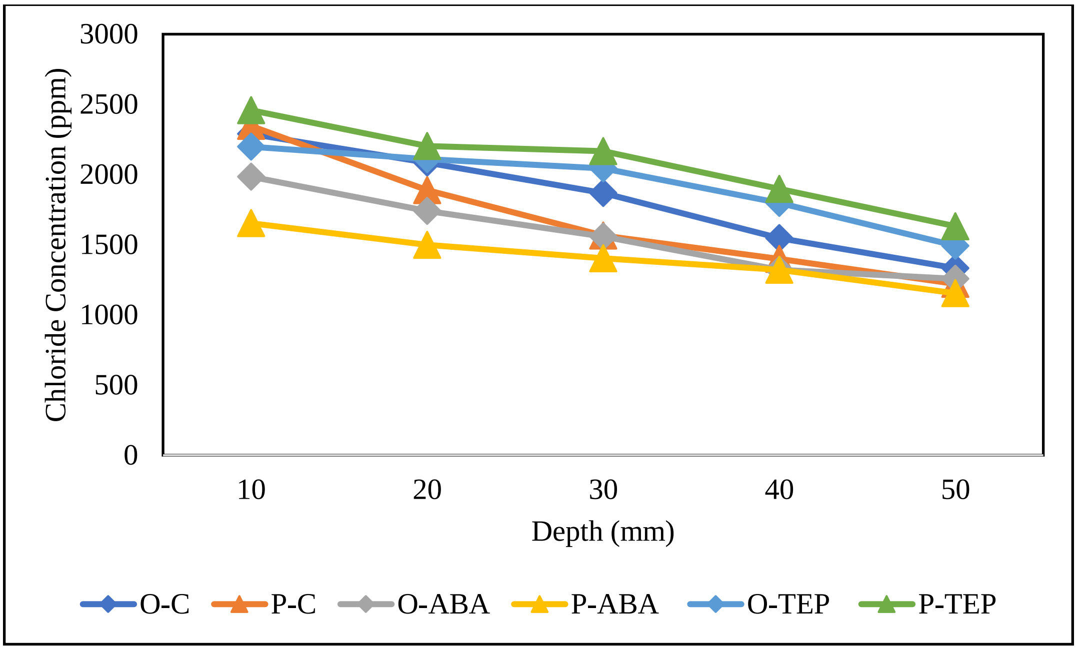


Figure 5.18 Chloride concentration vs depth after C 8

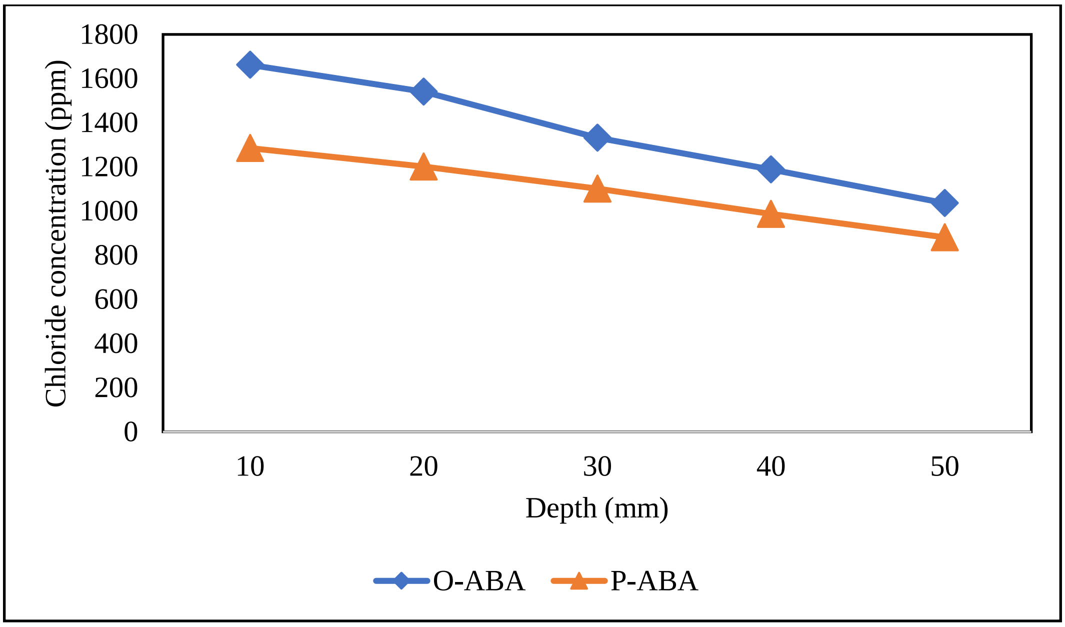


Figure 5.19 Chloride concentration profile of ABA inhibitor

5.4.2 Carbonation Depth

For measuring carbonation depth, 100mm cubes were used for casting. After water curing, cubes were provided one-week cycle of including both chloride and carbonation at 5% in CO_2 incubator with temperature and RH at 28-32° and 50-70 % respectively. Carbonation depth was measured after C 4 and C 8. Phenolphthalein indicator was used to differentiate between carbonated part and uncarbonated part as used by *Kulvinder et al. (2016)* and *Fukushima et al. (1998)*. Readings were taken using Vernier calliper as shown in Figure 5.20 (B). Figure 5.20

(A) shows carbonated and uncarbonated part. Purple colour represents the uncarbonated part whereas colourless portion shows carbonated part.

Figure 5.20 Cube after applying phenolphthalein solution (A) & Depth measurement using Vernier calliper (B)

As per Fick's IInd law,

$$X = k\sqrt{t} \quad (5.2)$$

Whereas, X is carbonation depth, t is exposure to environmental conditions in days and k is known as carbonation coefficient. Table 5.7 show measured carbonation depth of all specimens in both cements. It is clear that depth of carbonation is increased with the increase in cycles in both type of concrete as shown in Figure 5.21. By regress analysis, carbonation coefficient was obtained for all concrete specimens as shown in Figure 5.22 and Figure 5.23 for both OPC and PPC concrete respectively. In both OPC and PPC, value of k is lesser for inhibitor-based specimens than control specimens which indicates efficiency of inhibitors.

In both PPC and OPC, ABA specimens performed better as compared to control and TEP specimens. O-TEP and P-TEP performed almost same as of O-C and P-C respectively which means tri ethyl phosphate failed in inhibiting corrosion process. Slope of carbonation coefficient in both OPC and PPC concrete overlaps with each other as shown in Figure 5.22 and Figure 5.23. Whereas ABA showed inhibiting mechanism as shown by values in Table 5.7 and carbonation coefficient also decreased as indicated by slope in Figure 5.22 and Figure 5.23 in both OPC and PPC concrete which indicates ABA inhibitor act as pore blocker on concrete surface.

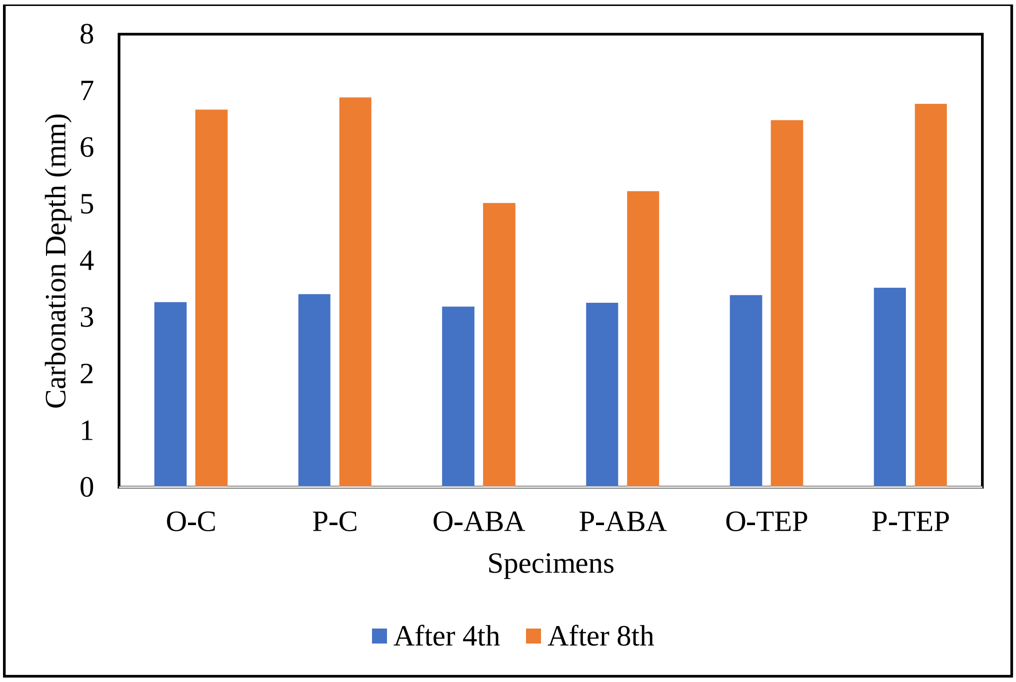


Figure 5.21 Depth of carbonation after 4th and 8th cycle

Table 5.7 Measured carbonation depth of cubes

Cycle	O-C (mm)	O-ABA (mm)	O-TEP (mm)	P-C (mm)	P-ABA (mm)	P-TEP (mm)
After 4th	3.27	3.19	3.39	3.41	3.26	3.52
After 8th	6.67	5.02	6.48	6.88	5.23	6.77

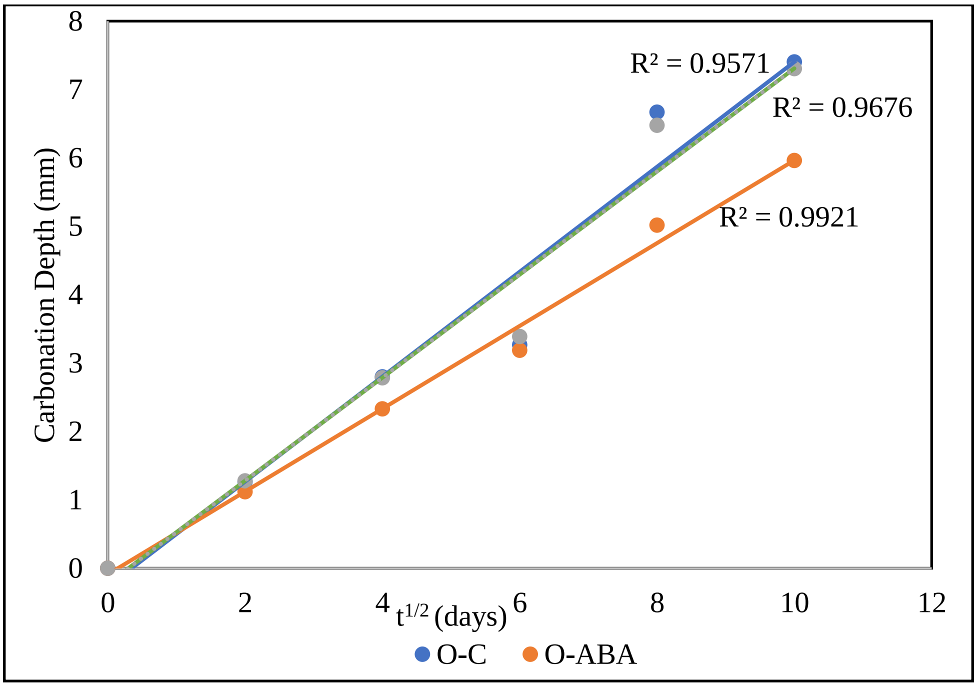


Figure 5.22 Carbonation depth variation with time in OPC specimens

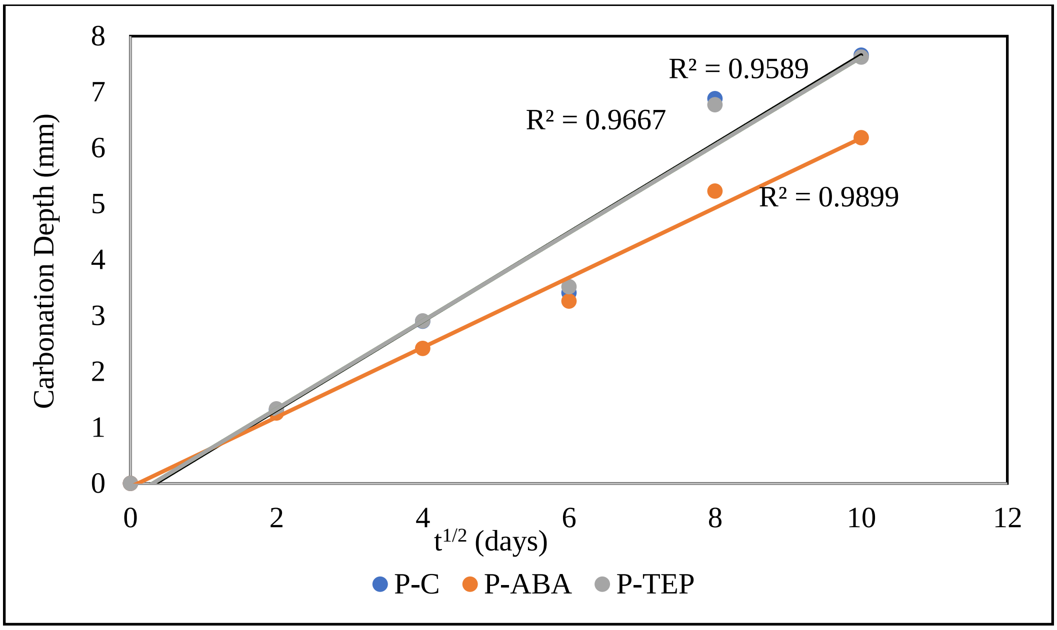


Figure 5.23 Carbonation depth variation with time in PPC specimens

The results obtained suggested that variation in cement type have influence on carbonation depth value. Results indicates that carbonation coefficient was slightly more in PPC specimens as compared to OPC due to presence of fly ash as pozzolana in PPC. Fly ash presence in cement can reduce the amount of $Ca(OH)_2$ obtained at time of hydration of cement eventually leads to carbonation in PPC at faster rate as compared to OPC. Similar trend was obtained by *Montermor et al. (2002)*. In both OPC and PPC, admixed 4-amino benzoic acid showed lesser carbonation coefficient than tri ethyl phosphate due to pore blocking effect of amino alcohols which means better resistance to carbonation *(Soylev et al. (2008); Tritthart (2003))*.

5.5 DISCUESSION ON CORROSION INHIBITOR

Studies have shown that organic compounds have been found as efficient corrosion inhibitors due to structural properties *(Jamil et al. (2003))*. Following section discuss both ABA and TEP as corrosion inhibitor in combined ingress chloride and carbonation environment.

5.5.1 4-Amino Benzoic Acid as Corrosion Inhibitor

Results of various tests on pore solution and concrete specimen had indicated inhibit properties of ABA. Due to chelating effect, ABA able to resist the corrosion compared to base pore solution. Dark colour formation on rebar surface was evident for formation of complex compound due to chelating effect. However, huge difference was found in performance of ABA as corrosion inhibitor, when used in OPC and PPC concrete. This may be due to fineness of PPC which leads to denser pore structure. Also, chloride content which influence corrosion process is absent in PPC due to presence of fly ash in cement. Cube test for chloride penetration also indicate that better performance of ABA in PPC concrete due to low permeability in PPC concrete. Carbonation depth measurement indicates ABA performed good in both OPC and PPC due to mechanism of pore blocking effect.

5.5.2 Triethyl Phosphate as Corrosion Inhibitor

In pore solution, TEP performed exceptionally well as corrosion inhibitor. TEP forms a stable compound near steel surface and blocks anodic sites on steel surface. In contrast to pore solution, TEP failed as inhibitor in both OPC and PPC in combined chloride and carbonation environment. This may be due to use of low dosage of inhibitor admixed in concrete. Even results of chloride content and carbonation depth further verified the fact TEP failed as inhibitor in concrete.

5.5.3 Comparison Between ABA and TEP

As results indicated that, only ABA performed as true corrosion inhibitor in PPC concrete only. Whereas TEP failed to performed in both OPC and PPC concrete. Benzotriazole derivatives when admixed as an inhibitor always performed well compared to other organic inhibitors *(Sheban et al. (2007); Ababneh et al. (2012))*. Performance of ABA as an inhibitor can be due to fact that it contains multi-functional organic group whereas, TEP is single functional group inhibitor. Multi-functional organic inhibitors are considered as most effective inhibitors compared to single functional group inhibitor *(Nmai (2004))*. ABA contains amines and fatty acid esters which results into two-fold mechanism. First, they block chloride ions due to chemical structure. Then they form coating on rebar surface as esters reacts in alkali medium and forms alcohols and carboxylic ions which then reacts with calcium ions. Also, fatty acid lined and chained up the non-polar groups on rebars to form mechanical barrier for destructive elements for corrosion like moisture, chloride ions and oxygen. Another reason of TEP not performing as ABA, due to chelating effect. Multi-functional groups as an inhibitor forms stable compound which is soluble in water by reacting with metal ions and known as chelating agents.

CHAPTER 6

CONCLUSIONS

Efficiency of two organic: 4 amino benzoic acid and tri ethyl phosphate compounds used as admixed corrosion inhibitors in OPC and PPC concrete was checked. These two corrosion inhibitors were provided with chloride (0.035 g/cc in water) and carbonation environment (5%) for two days each. In present thesis work, various experiments were performed on concrete specimens and following conclusions can be drawn regarding the efficiency of ABA and TEP as admixed corrosion inhibitors in OPC and PPC concrete in ingress chloride and carbonation environment: -

1. I_{corr} values on pore solution at 24, 48 and 120 hour suggested inhibiting effect of both ABA and TEP. ABA performed better as corrosion inhibitor as compared to TEP at 0.1M, due to carboxylic group act as chelating agent in ABA. TEP also showed inhibiting effect due to high phosphate content in domain of steel rebar.
2. Half-cell potential reading indicated that ABA in PPC concrete show very low corrosion risk till C 5 of chloride and carbonation environment. Whereas, TEP reading show active corrosion rate from the beginning. Although, HCP readings are probable values but it provides an idea to some extent regarding corrosion process.
3. I_{corr} values indicated that 4-amino benzoic acid inhibits corrosion process in ingress chloride and carbonation environment in PPC concrete only. Whereas, tri ethyl phosphate could not inhibit corrosion process as TEP performed almost similar to control specimen both in OPC and PPC concrete due to single functional group which do not act as chelating agent.
4. Physical verification and mass loss values also indicated the same weight change (%) for all specimen except ABA in PPC concrete which furthered verifies results of HCP and I_{corr} values.
5. Free chloride content was found more in TEP specimen may be due to low dosage mixed in concrete specimens. Whereas free chloride was less in ABA specimen in PPC compared to OPC, due to dense pore structure of PPC concrete.
6. Carbonation depth was reduced in ABA specimens as compared to control specimens. TEP performed almost similar to control specimens which means TEP failed in both OPC and PPC concrete. Performance of ABA showed that type of cement slightly changes carbonation depth. ABA in PPC specimen showed higher carbonation coefficient due to presence of fly ash as pozzolanic material.

REFERENCES

- Ababneh, A.N., Sheban, M.A. and Abu-Dalo, M.A., 2011. Effectiveness of benzotriazole as corrosion protection material for steel reinforcement in concrete. *Journal of Materials in Civil Engineering*, *24*(2), pp.141-151.
- Aggoun, S., Cheikh-Zouaoui, M., Chikh, N. and Duval, R., 2008. Effect of some admixtures on the setting time and strength evolution of cement pastes at early ages. *Construction and Building Materials*, *22*(2), pp.106-110.
- Almobarak, N.A., El-Naggar, M.M., Al-Mufraj, R.S. and Al-Zoghbi, O.A., 2014. Carboxylic Acids: Pitting Corrosion Inhibitors for Carbon Steel in Alkaline Medium and in the Presence of Chlorides. *Chemistry and Technology of Fuels and Oils*, *50*(2), pp.170-178.
- ASTM C 876-09, "Standard test method for corrosion potentials of uncoated reinforcing steel in concrete." ASTM International, West Conshohocken, USA, 2009.
- BIS: 8112-1989, "Indian standard 43 Grade ordinary Portland cement – specification." Bureau of Indian Standards, New Delhi, India.
- BIS: 383-1970, "Indian standard Specification for coarse and fine aggregates from natural sources for concrete." Bureau of Indian Standards, New Delhi, India.
- BIS: 10262-1982, "Recommended guidelines for concrete mix design." Bureau of Indian Standards, New Delhi, India.
- Blankson, M.A. and Erdem, S., 2015. Comparison of the effect of organic and inorganic corrosion inhibitors on the rheology of self-compacting concrete. *Construction and Building Materials*, *77*, pp.59-65.
- Bolzoni, F., Brenna, A., Fumagalli, G., Goidanich, S., Lazzari, L., Ormellese, M. and Pedeferri, M.P., 2014. Experiences on corrosion inhibitors for reinforced concrete. *International Journal of Corrosion and Scale Inhibition*, *3*(4), pp.254-278.
- Dariva, C.G. and Galio, A.F., 2014. Corrosion inhibitors–principles, mechanisms and applications. In *Developments in corrosion protection*. Intech.
- Dhir, R.K., Jones, M.R. and McCarthy, M.J., 1994. PFA concrete: chloride-induced reinforcement corrosion. *Magazine of Concrete Research*, *46*(169), pp.269-277.
- Han, J., Wang, K., Shi, J. and Wang, Y., 2015. Mechanism of triethanolamine on Portland cement hydration process and microstructure characteristics. *Construction and Building Materials*, *93*, pp.457-462.

- Kaur, K., Goyal, S., Bhattacharjee, B. and Kumar, M., 2016. Efficiency of migratory-type organic corrosion inhibitors in carbonated environment. *Journal of advanced concrete technology*, *14*(9), pp.548-558.
- Kondratova, I.L., Montes, P. and Bremner, T.W., 2003. Natural marine exposure results for reinforced concrete slabs with corrosion inhibitors. *Cement and Concrete Composites*, *25*(4-5), pp.483-490.
- Nmai, C.K., 2004. Multi-functional organic corrosion inhibitor. *Cement and Concrete Composites*, *26*(3), pp.199-207.
- Ormellese, M., Berra, M., Bolzoni, F. and Pastore, T., 2006. Corrosion inhibitors for chlorides induced corrosion in reinforced concrete structures. *Cement and concrete research*, *36*(3), pp.536-547.
- Pradhan, B. and Bhattacharjee, B., 2009. Half-cell potential as an indicator of chloride-induced rebar corrosion initiation in RC. *Journal of Materials in Civil Engineering*, *21*(10), pp.543-552.
- Rakanta, E., Zafeiropoulou, T. and Batis, G., 2013. Corrosion protection of steel with DMEA-based organic inhibitor. *Construction and Building Materials*, *44*, pp.507-513.
- Saraswathy, V. and Song, H.W., 2007. Evaluation of corrosion resistance of portland pozzolana cement and fly ash blended cements in pre-cracked reinforced concrete slabs under accelerated testing conditions. *Materials chemistry and physics*, *104*(2-3), pp.356-361.
- Saricimen, H., Mohammad, M., Quddus, A., Shameem, M. and Barry, M.S., 2002. Effectiveness of concrete inhibitors in retarding rebar corrosion. *Cement and Concrete Composites*, *24*(1), pp.89-100.
- Sheban, M., Abu-Dalo, M., Ababneh, A. and Andreescu, S., 2007. Effect of benzotriazole derivatives on the corrosion of steel in simulated concrete pore solutions. *Anti-Corrosion Methods and Materials*, *54*(3), pp.135-147.
- Söylev, T.A., McNally, C. and Richardson, M.G., 2007. The effect of a new generation surface-applied organic inhibitor on concrete properties. *Cement and Concrete Composites*, *29*(5), pp.357-364.
- Söylev, T.A. and Richardson, M.G., 2008. Corrosion inhibitors for steel in concrete: State-of-the-art report. *Construction and Building Materials*, *22*(4), pp.609-622.
- Trabanelli, G., Monticelli, C., Grassi, V. and Frignani, A., 2005. Electrochemical study on inhibitors of rebar corrosion in carbonated concrete. *Cement and Concrete Research*, *35*(9), pp.1804-1813.

- Tritthart, J., 2003. Transport of a surface-applied corrosion inhibitor in cement paste and concrete. *Cement and Concrete Research*, *33*(6), pp.829-834.
- Vu, K.A.T. and Stewart, M.G., 2002. Service life prediction of reinforced concrete structures exposed to aggressive environments. In *Proc. 9th International Conference on Durability of Building Materials and Components, Brisbane, Australia, 17th 21st March*.
- www.airforums.com/ forums/f142/corrosion-problems-with-new-airstreams-31743-161.html
- www.amteccorrosion. co.uk/m_corrosionresistantship.html
- www.bccresearch.com/pressroom/chm/anti-corrosion-coatings-market-to-see-48-annual-growth-through-2022
- www.cdcorrosion.com/mode_corrosion/ corrosion_crevice.html
- www.civilengineeringforum.me/ chloride-ingress-concrete
- www.corrosionengineering.co.uk/knowledge-library/corrosion-of-steel-in-concrete
- www.inspectioneering.com/news/2016-03-08/5202/nace-study-estimates-global-cost-of-corrosion-at-25-trillion-ann
- www.nace.org/corrosion-central/corrosion-101/uniform-corrosion
- www.performancewire.com/understanding-types-of-corrosion
- www.steelfabservices.com.au/a-guide-to-galvanic-corrosion-how-to-treat-it
- www.steelfabservices.com.au/a-guide-to-intergranular-corrosion-how-to-treat-it
- www.steelfabservices.com.au/pitting-corrosion-how-to-treat-it
- www.wantarengineering.com/service-corrosionprotection.html