EFFECTIVENESS OF ORGANIC CHEMICALS AS CORROSION INHIBITORS IN SATURATED CALCIUM HYDROXIDE SOLUTION WITH REDUCED ALKALINITY

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DECLARATION

I, Rahul Khurana, hereby declare that this thesis entitled **"Effectiveness of organic chemicals as corrosion inhibitors in saturated calcium hydroxide solution with reduced alkalinity"** is an authentic record of my study carried out as requirements for the award of degree of **Master of Engineering** in **Structural Engineering** in the Civil Engineering Department, Thapar University, Patiala under the supervision of **Dr. Shweta Goyal, Assistant Professor,** Department of Civil Engineering, Thapar University, Patiala during July 2013 to July 2014. This matter embodied in this report has not been submitted in part or full to any other university or institute for the award of any degree.

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

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ABSTRACT

Reinforced concrete is the most widely used construction material but its durability issues still exist. Apart from structural design failures, the most significant cause of deterioration and premature failure of RC structures is the corrosion of the steel reinforcement. In last quarter century, many methods have been developed to reduce or prevent corrosion of steel in concrete. From all the methods available for corrosion protection, corrosion inhibitors sound very promising.

In last two decades, corrosion inhibitors have been extensively used to protect steel reinforcement in RC structures. Most of the commercially available corrosion inhibitors are used for chloride (Cl^-) induced corrosion and are not effective for carbonation induced corrosion. Commercially available corrosion inhibitors being very expensive affect the total cost of structure. Due to which, there arises a need to find a cheaper replacement of these corrosion inhibitors.

In this study, effectiveness in corrosion inhibition of some commonly available cheap organic chemicals is evaluated. Corrosion inhibition of Tartaric acid, Maleic acid, Adipic acid, Phthalic acid and Oxalic acid with 0.25%, 0.5% and 1% addition is assessed. Fe 500 HYSD steel bars of 12 mm diameter and 60 mm length are immersed in seven different solutions for 240 hours. Corrosion monitoring of these steel bars is performed at 1 hour, 24 hours, 48 hours, 120 hours and 240 hours of immersion.

It is observed that all the chemicals are adequately effective in corrosion inhibition of steel bar at 0.5 % of addition but do not perform well with 0.25% and 1% addition. Performance of Tartaric acid and Oxalic acid is finest.

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CHAPTER 1
INTRODUCTION

1.1 GENERAL

Concrete is the most abundant man-made material on the earth, with consumption above dozens of billions of tons. Construction and durability of reinforced concrete (RC) structures play an important role in economic development of any country. Reinforced concrete (RC) structures have the potential to be very durable and capable of withstanding a variety of adverse environmental conditions (Song et al. 2007) yet; there are many durability issues related with RC structures. Apart from structural design failures, the most significant cause of deterioration and premature failure of RC structures is the corrosion of the steel reinforcement.

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

1.2 CORROSION OF RC STRUCTURES

Corrosion of RC structures is actually corrosion of steel embedded as reinforcement in concrete. Corrosion of reinforcement in concrete is an electrochemical process (Elsener 2002). In a good quality concrete, the risk of corrosion is minimal as concrete itself provides good chemical and physical protection to the embedded reinforcement. Corrosion of steel reinforcement is generally restricted in an alkaline environment within concrete (pH 13-14) with a chemically stable thin oxide film protecting the steel surface from contact with moisture and oxygen (Parrott 1987). However, corrosion initiation takes place either when sufficient chloride ions have reached the rebar level or when the pH of the concrete pore solution drops to low values (below 10) due to carbonation.

The failure of structures due to corrosion does not necessarily results in total structural collapse but in most of the cases, it is demonstrated by loss of structural serviceability, due to cracking and delamination of concrete (Montermor et al. 2003). The repair work due to cracking and delamination includes high costs, sometimes, much more than initial cost. It is estimated that the cost of corrosion related maintenance and

repairs for concrete infrastructure in the world is around $100 billion per year (Li et al. 2007). The cost of corrosion in India is estimated to be around 3, 60,000 million rupees ($8 billion) as published in Financial Express (financialexpress.com).

1.3 CORROSION PROCESS

Corrosion is degradation of material's properties due to interactions with their environments, and corrosion of most materials is inevitable. Like death and taxes, corrosion is something we hope to avoid; but ultimately it is something we must learn to deal with. Corrosion produces a new and less desirable material from the original metal and can result in a loss of function of the component or system. The three main reasons for the importance of corrosion are: economics, safety and conservation. Corrosion of reinforcement steel, being an electrochemical process, involves few electrochemical reactions. The process of corrosion of steel in accordance with these reactions is discussed below:

Firstly,

(Anode)

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

The iron atom loses some electrons and becomes a positively charged ion allowing it to bond to atoms that are negatively charged.

Other half of the reaction involves water (H_2O) and oxygen (O_2).

(Cathode)

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (1.2)$$

Now,

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

Iron + Water with oxygen → Iron Hydroxide
dissolved in it

Excess of oxygen present in water reacts with the iron hydroxide.

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

Iron hydroxide + oxygen → water + Hydrated iron oxide
(brown rust)

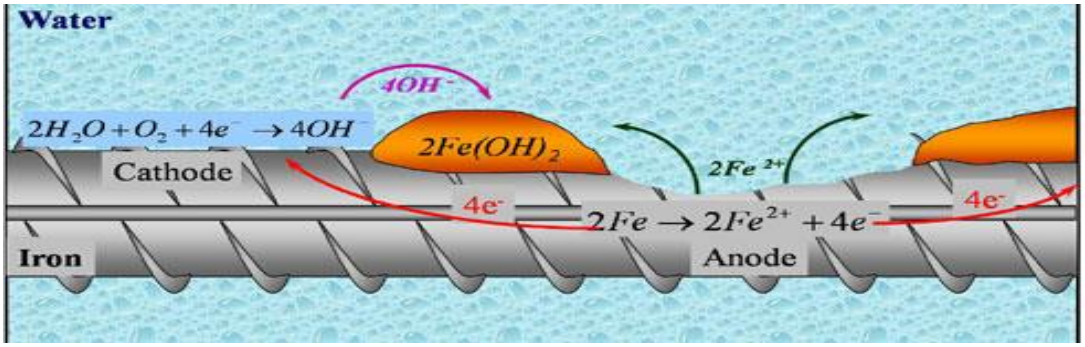


Fig.1.1 Pictorial representation of corrosion process of reinforcement steel

As discussed above, reinforcement steel resists corrosion because of high alkaline (pH 12-13) environment provided by concrete which in fact provides passivation to steel in the form of a thin oxide layer. Therefore, initiation of intense corrosion takes place due to loss of alkalinity of concrete. Loss of alkalinity of concrete occurs mainly due to two causes:

- Carbonation, and
- Chloride contamination.

Fig.1.2 represents the process of corrosion initiation in reinforcement steel due to carbonation or chloride contamination.

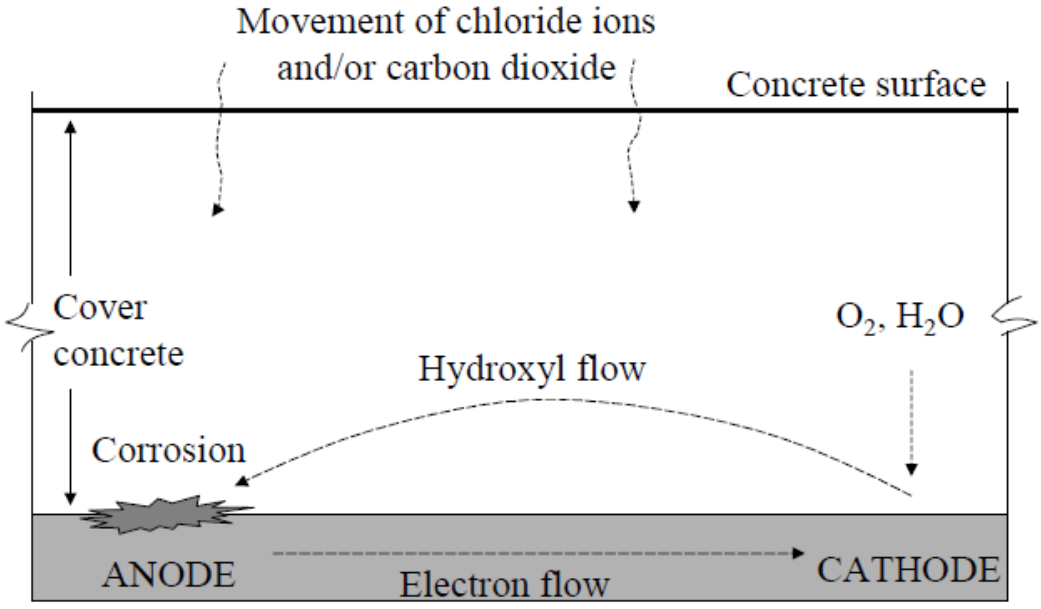


Fig.1.2 Schematic representation of corrosion initiation

Carbonation is a result of the interaction of carbon dioxide gas from atmosphere with the concrete. Carbon dioxide gas diffused from atmosphere can neutralize the

alkalinity of concrete. It can reduce the pH of concrete to approximately 8 or 9 due to which the thin oxide layer is no longer stable. In presence of sufficient moisture and oxygen, corrosion will start.

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

1.4 CORROSION REDUCTION

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

1.4.1 Concrete Removal and Surface Preparation

Spalling of concrete occurs due to change in volume of concrete during corrosion. Rust has 2-3 times the volume of original steel. Spelled and cracked concrete is removed around the bar and a new patch of any cementitious material is applied there. The cementitious material chosen should provide high pH alkaline surrounding to the steel. So that, the reformation of passive layer is encouraged and further corrosion can be stopped.

1.4.2 Impressed Current System

In impressed current system, a small direct current (DC) is passed from a permanent anode fixed to the surface to the reinforcement embedded. To stop the reaction at anode, a sufficient quantity of current is passed from anode to reinforcement:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (1.5)$$

Thus, only the cathodic reaction occurs at steel surface.

Therefore, impressed current system stops current flowing between anodic and cathodic areas. This system works because cathodes are more easily polarised than anodes.

1.4.3 Sacrificial Anode System

This is a cathodic protection system in which a sacrificial anode is directly connected to steel. Materials such as zinc can be used as sacrificial anode as zinc can liberate electrons more readily as compared to steel.

$$Zn \rightarrow Zn^{2+} + 2e^{-} \quad (1.6)$$

1.4.4 Barrier Methods

Barrier methods are generally implied in conjunction with other protection methods. Barrier methods includes use of low permeability concrete, using low water/cement ratio, using mineral admixtures in concrete, use of water proof membranes etc. By using these methods a barrier between steel and corrosion agents can be created.

1.4.5 Corrosion Inhibitors

A corrosion inhibitor can be defined as "a chemical substance that can reduce corrosion rate when present in adequate concentration in any corrosion system". A corrosion inhibitor may not significantly change concentration of any other corrosion agent. A corrosion inhibitor works on principle of developing a thin chemical layer (1-2 molecules thick) on steel surface. This thin layer inhibits the corrosion by immobilising the corrosive ions and preventing them to reach the steel surface (Fadayomi 1977). Inhibitors can interfere with anodic as well as cathodic reactions. Corrosion inhibitors can be mixed in fresh concrete just after addition of mixing water or they can be applied later to the surface of hardened concrete. Corrosion inhibitors are not wonder remedies that completely stop corrosion; rather they buy time by decreasing the rate of corrosion.

1.5 MONITORING OF CORROSION

Usually the condition of the structures is monitored by visual inspection and curative measures are resorted only when the condition becomes very serious. It is desirable to monitor the condition of structures right from the construction stage by carrying out periodic corrosion surveys and maintaining a record of data.

Many non-destructive and electrochemical techniques are available for monitoring of corrosion in RC structures. Corrosion of steel in RC structures can be assessed by following techniques:

1. Open circuit potential (OCP) measurements

2. Surface potential (SP) measurements
3. Linear polarization resistance (LPR) measurement
4. Electrochemical impedance spectroscopy (EIS)
5. Tafel extrapolation
6. Concrete resistivity measurement
7. Harmonic analysis
8. Noise Analysis
9. Galvanostatic pulse transient method
10. Cover thickness measurements
11. Ultrasonic pulse velocity technique
12. X-ray, Gamma radiography measurement
13. Visual inspection

Any possible durability problem can be identified, before they become serious issues, by using these methods.

1.6 FLOW OF THESIS

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

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

CHAPTER 2

CARBONATION AND CORROSION INHIBITORS

2.1 GENERAL

In this chapter, process of carbonation and Carbonation induced corrosion is discussed in detail. This chapter also covers the detailed introduction of corrosion inhibitors. Mechanism of corrosion inhibitors in reducing corrosion rate in any corrosion system is also discussed. Categorisation of corrosion inhibitors is also covered in this chapter.

2.2 CARBONATION

2.2.1 Introduction

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

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

$$CO_2 + Ca(OH)_2 \xrightarrow{H2O,NaOH} CaCO_3 + H_2O \qquad (2.1)$$

Carbonation of concrete does not cause any harm to concrete itself indeed it may reduce its porosity and lead to more strength (Lopez et al. 2003). However, carbonation can greatly affects the steel embedded as reinforcement. It may lead to corrosion of steel if the CO_2 penetrated in concrete reaches the surface of steel.

The pH value of pore water in the hardened concrete is generally 12 to 13. The high alkalinity forms a thin passivating layer around steel and protects it from action of oxygen and water. CO_2 present in atmosphere permeates into concrete and carbonates

it and reduces the alkalinity of concrete. The pH value of pore water will be reduced to around 9.0. When the excess of carbonation occurs, the pH may reduce upto 8.

Due to reduction in alkalinity of concrete, the passive oxide layer is destroyed and the steel is prone to corrosion in presence of moisture and oxygen. Carbonation is one of the main reasons for corrosion of reinforcement steel.

2.2.2 Factors Affecting Rate of Carbonation

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

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

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

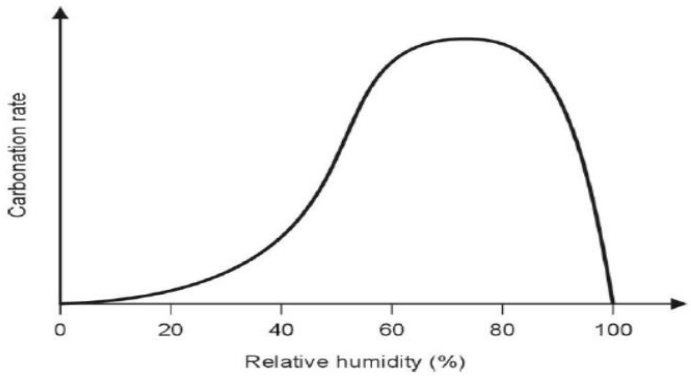


Fig. 2.1 Schematic representation of the rate of carbonation of concrete as a function of the relative humidity of the environment (Bertolini et al. 2004)

Therefore, most critical carbonation occurs at relative humidity of 50-70 %.

Quality of concrete: The carbonation rate also depends on quality of concrete. The less permeable concrete will restrict ingress of CO_2 thus will reduce the rate of carbonation. Depth of carbonation can be related to strength or grade of concrete.

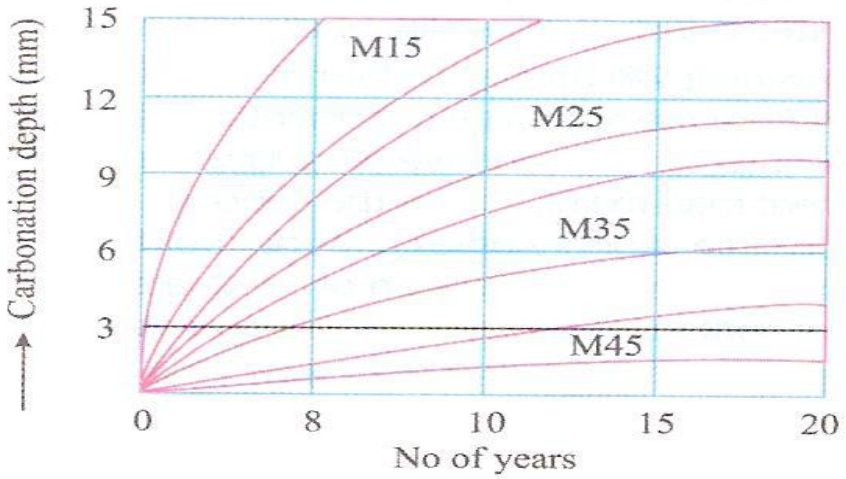


Fig.2.2 Depth of Carbonation with respect to strength (grade) of concrete

CO_2 Concentration: The concentration of carbon dioxide in the atmosphere may vary from 0.03% in rural environments to more than 0.1% in urban environments. Comparatively, high concentrations can be reached under specific exposure conditions, such as inside motor vehicle tunnels. As the CO_2 content in the air increases, the carbonation rate increases.

Temperature: All other conditions being equal, especially that of humidity, which is, in general, the most important single parameter, an increase in temperature will raise the rate of carbonation.

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

2.2.3 Carbonation Depth

Carbonation depth is the depth up to which CO_2 has penetrated. The measurement of the depth of carbonation is generally carried out by spraying an alcoholic solution of phenolphthalein on a freshly broken face. The areas where pH is greater than 9 take on

a pinkish colour, typical of phenolphthalein in a basic environment, while the colour of carbonated areas remains unchanged (Tesfamariam et al. 2008).

The depth of carbonation increases in proportion to the square root of time, which is characteristic of sorption rather than the diffusion, but the carbonation involves an interaction between CO_2 and the pore system. Depth of carbonation 'D' is expressed in millimeters as:

$$D = Kt^{0.5} \qquad (2.2)$$

Where K = carbonation coefficient in mm/year

t = time of exposure in years.

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

2.3 CARBONATION INDUCED CORROSION

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

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (2.3)$$

(Weak acid)

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

$$H_2CO_3 \rightarrow H^+ + HCO^{3-} \qquad (2.4)$$

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

$$HCO^{3-} \rightarrow H^+ + CO^{3-} \qquad (2.5)$$

Solutions containing weak carbonic acid (H_2CO_3) are more corrosive to mild steel as compared to solutions containing strong acids.

Carbonation-induced corrosion causes harms aesthetically and structurally due to expansive corrosion products that cause cracking, delamination, and spalling of the surrounding concrete.

2.4 CORROSION INHIBITORS

2.4.1 General

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

Corrosion inhibitors are chemicals that cause changes at the steel/concrete interface which can result in a reduction of the overall corrosion rate of steel in concrete. An ideal corrosion inhibitor is a chemical which, when added to concrete, can prevent corrosion onset without adverse effects on the mechanical properties of the concrete (Jamil et al. 2003). A past study indicates that inhibitors can extend the service life through delay of depassivation and/or reduction of corrosion rate once propagated.

There are mainly two types of corrosion inhibitors based on the application, some of them are to be added at the time of concrete mixing while other can be applied to surface of concrete. In recent years, surface applicable corrosion inhibitors have been developed for rehabilitation of existing RC structures. Several amine/alkanolamine based corrosion inhibitors have been applied for rehabilitation of reinforced concrete structures suffering from corrosion in past few years. These types of inhibitors have ability to diffuse considerable distance into concrete due to their high vapour pressure (Maeder 1994).

The mechanisms by which the corrosion inhibitors are able to protect reinforcing steel include:

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

Among various methods available to diminish corrosion, inhibitors seem to be attractive because of their easy handling and low cost, compared with other protective methods (Elsener 2001).

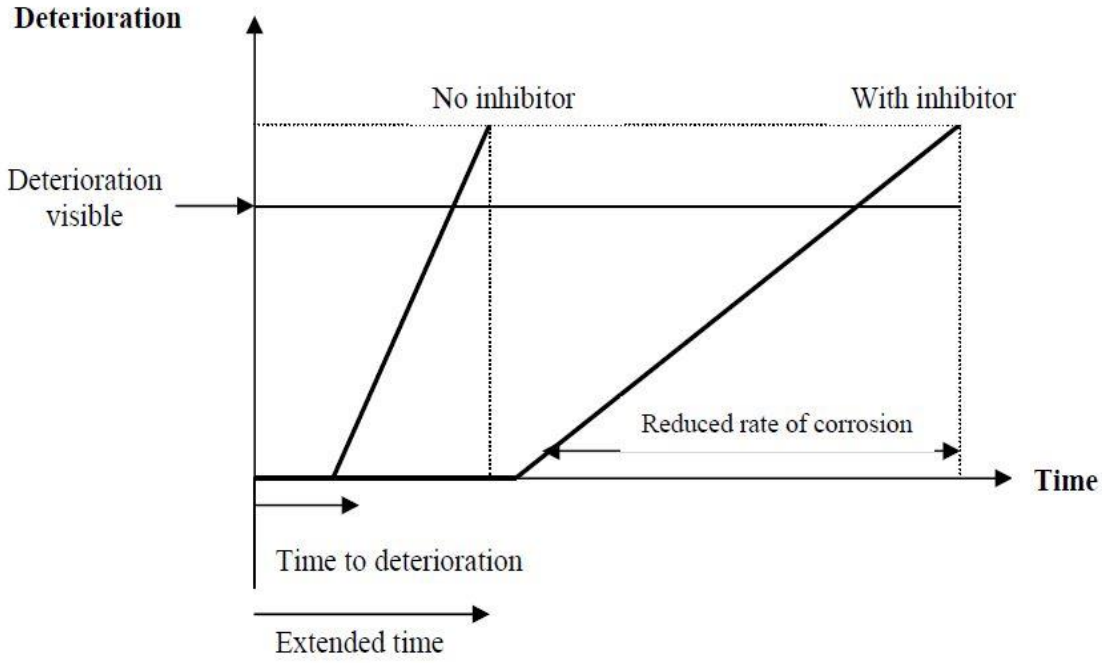


Fig.2.3 Extension of the service life of a concrete structure with corrosion inhibitor treatment

2.4.2 Classification of Corrosion Inhibitors

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

Based upon the physical mode of application:

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

A. Admixed inhibitor

B. Migrating inhibitor

A. Admixed inhibitor

Inhibitors which are added to the fresh concrete at the time of mixing for new structures are known as admixed inhibitors (Jamil et al. 2005)

These inhibitors are added immediately after the addition of water to cement at the time of mixing. Admixed inhibitor influence initial set, later strength gain and other properties like hydration processes of cement. To overcome this, retarders can be added to concrete mix which balances the acceleration of the inhibitors and provide a little more retardation.

The inorganic compounds which are based upon calcium nitrite (Berke et al. 2004), sodium nitrite, sodium benzoate and sodium chromate are used as admixed inhibitors. Organic compounds based upon mixtures of alkanolamines, amines or amino-acids, or based on an emulsion of unsaturated fatty acid ester of an aliphatic carboxylic acid and a saturated fatty acid also proposed as admixed inhibitors.

B. Migrating inhibitors

These are inihibitors which are applied on the hardened concrete surface and are capable of diffusing through concrete to the underlying reinforcement where they act to suppress both the anodic and cathodic corrosion reactions by forming a monolayer film at the steel-concrete interface (Soylev et al. 2008). According to physical mode of application these types of inhibitors are also known as Surface applied corrosion inhibitors or Penetrating corrosion inhibitors. Use of migrating corrosion inhibitors are proposed in the last 15-20 years and are generally proposed for the repair works.

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

They are supposed to be simple alternatives to other available rehabilitation methods such as patch repair or impressed current cathodic protection, but there are still several aspects to be clarified concerned with the effectiveness of surface-applied corrosion inhibitors (Page et al. 2000)

Based upon the mechanisms of protection:

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

A. Anodic inhibitor

B. Cathodic inhibitor

C. Mixed inhibitor

A. Anodic inhibitor:

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

Anodic inhibitors act on the dissolution of the steel and they reduce the corrosion rate by an increase in the corrosion potential of the steel (Soylev et al. 2007). It functions by oxidizing corrosion product - ferrous ions - to ferric ions that precipitate in the alkaline solution of the concrete and form a protective layer on the reinforcement.

Sodium nitrite, sodium benzoate and sodium chromate have also been used (Soylev et al. 2008). But when insufficient quantities of corrosion inhibitors are used, then intensity is localized and causing severe pitting (Vaysburd et al. 2004).

B. Cathodic inhibitor:

Inhibitors which retard the reaction at cathode are called cathodic corrosion inhibitors. These inhibitors prevent oxygen from reaching the reinforcement steel. Cathodic inhibitors act either by slowing the cathodic reaction or by selectively precipitating

cathodic sites. Compounds in this category are strong proton acceptors and their action in contrast to anodic inhibitors is usually indirect. Cathodic inhibitors adsorb on the steel surface and act as a barrier to the reduction of oxygen. The most commonly used cathodic inhibitors are sodium hydroxide and sodium carbonate, which are supposed to increase the pH near the steel, and reduce the oxygen transport by covering the steel surface. Phosphates, silicate and polyphosphates are also used (Soeda et al. 2003).

C. Mixed inhibitors:

Mixed inhibitors influence both the anodic and cathodic regions. They retard the corrosion process both at the anode and the cathode. These combine the benefits of both anodic and cathodic inhibitors at relatively low dosages. A mixed inhibitor is usually more desirable because its effect is all encompassing, covering corrosion resulting from chloride attack as well as that due to microcells on the metal surface. In these category organic migratory mixed corrosion inhibitors are the most widely used.

Migratory mixed corrosion inhibitors are organic inhibitors. They protect the steel at both the anodic and the cathodic sites. The mixed corrosion inhibitor chemistry involves migration of its molecules by electron density distribution to both the anodic and cathodic sites of the steel. They form a monomolecular layer on the reinforcing steel, which strongly adsorbs to the metal surface and interferes with the anodic and cathodic reactions in the area of adsorption **(**Laameen et al. 1996**)** Studies have proved that addition of these types of corrosion inhibitors has no deleterious effect on the properties of concrete.

In mixed type inhibitors, material with the hydrophobic group that has polar groups such as N, S, OH is effective. Organic polymer compounds such as amine and aminoalcohol (AMA) are also used (Soeda et al. 2003).

2.4.3 Mechanism of Some Commonly Used Commercially Available Inhibitors:

Calcium nitrites: Nitrites (calcium or sodium salt) are identified as an anodic inhibitors because they compete with chloride ions for the ferrous ions at the anode to form a film of ferric oxide, Fe_2O_3 as indicated in the equations below (Gaidis 2004):

$$2Fe^{2+} + 2OH^- + 2NO^-_2 \longrightarrow 2NO + Fe_2O_3 + H_2O \qquad (2.6)$$

$$Fe^{2+} + OH^- + NO^-_2 \longrightarrow NO + \gamma\text{-}FeOOH \qquad (2.7)$$

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

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

$$Na_2PO_3F + H_2O \longrightarrow F^- + H_2PO_4^- + HPO_4^{-2} \qquad (2.8)$$

The inhibiting action of Na_2PO_3F may be attributed to the formation of phosphates, and so the anodic formation of a passive layer of Fe_3O_4, γ Fe_2O_3 and $FePO_4.H_2O$. However, as PO_3F^{2-}, PO_4^{3-} and OH^- are all potential corrosion inhibitors, it is difficult to say which, if any, of these ions may be responsible for corrosion inhibition effects induced by Na_2PO_3F. The finding of various research studies confirms this dual effect of the phosphates. Soylev et al. (2008) confirms that at low values of inhibitor to chloride ion ratio, phosphate (sodium phosphate) acts as a cathodic inhibitor, whereas at higher ratios, it becomes a mixed inhibitor

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

Amine ester based: Amine- and ester-based inhibitors have dual actions in concrete as the amine compound acts as an inhibitor whereas the carboxylate ester compound has pore-blocking effect, which blocks the ingress of the chlorides (Gaidis 2004). For Surface applied type amino carboxylates-based inhibitors the pore-blocking effect as a secondary protection mechanism against reinforcement corrosion (Soylev et al. 2007).

The esters become hydrolyzed by the alkaline mix water to form the carboxylic acid and its corresponding alcohol. The reaction proceeds as shown in Eq. below where R and R` represent different hydrocarbon molecules:

$$\underset{\text{(ester)}}{RCOOR`} + \underset{\text{(base)}}{OH^-} \longrightarrow \underset{\text{(acid anion)}}{RO_2^-} + \underset{\text{(alcohol)}}{R`OH} \qquad (2.9)$$

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

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

2.5 CLOSING REMARKS

In this chapter, process of carbonation is thoroughly discussed. Factors affecting carbonation rate and corrosion induced by carbonation are also discussed. This chapter also gives the introduction to corrosion inhibitors, their classification and mechanism.

CHAPTER 3
LITERATURE REVIEW

3.1 GENERAL

In last 2 decades, extensive research have been done for corrosion protection of steel in concrete; but the problems related with corrosion still exists. Many new methods of corrosion protection have been evolved in recent years, from which, corrosion inhibitors are most important. Recent research work has evolved a number of corrosion inhibitors which can be used to protect reinforcement steel in concrete from corrosion. Literature available from recent researches is discussed further in this chapter.

3.2 EFFECT OF CORROSION INHIBITORS ON CORROSION IN REBAR

Literature from previous research shows that use of corrosion inhibitors is useful for preventing the corrosion of steel in concrete. The addition of inhibitors not only increases the compressive strength of concrete but also improve the corrosion resistance properties (Saraswathy et al. 2007). The following studies shows that use of corrosion inhibitors in concrete mix retard the rebar corrosion.

Rosenberg et al. (1977) studied the effect of calcium nitrite as an inhibitor in reinforced concrete. They used polarization techniques for evaluation of the inhibitors and reported that the relative corrosion rates for samples soaked in aggressive saturated sodium chloride solution for 90 days with 2% and 4% admixed calcium nitrite were about a factor of 15 times lower than those without the calcium nitrite admixture.

Maeder (1989) investigated the effectiveness of some mixed types of organic inhibitors in inhibiting reinforcement corrosion. These inhibitors were amines and alkanolamines and their salts were organic and inorganic acids. According to the author, the unique feature of these inhibitors is their ability to diffuse a considerable distance through concrete because of their high vapour pressure. When these inhibitors are added to concrete, they do not delay the time of set. They diffuse to both anodic and cathodic sites and provide protection to reinforcing steel. Furthermore, the author indicates that these inhibitors are preferable over nitrites as they are non-toxic.

Jones (2000) investigated the effect of migrating type corrosion inhibitor on high performance concrete. He found that in high performance concrete with 40 mm cover the application of inhibitor did not show an effect on the corrosion behaviour over the first 20 days but subsequently showed a steady drop in current reaching values of 0.1 mA/m^2 after 40 days. This delayed action is thought to be related to the time the inhibitor takes to migrate through high quality, low permeability and concrete cover. It introduces the concept that in some concretes the inhibitor will not migrate to the reinforcement at a rate that allows sufficient concentration for protection.

Anstice (2000) investigated the behaviour of the various inhibitors in model electrolytes at alkaline or neutral pH values, with or without chloride addition, namely nitrite ions (in the form of sodium nitrite), sodium monofluorophosphate (Na_2PO_3F) and a proprietary alkanolamine-based inhibitor that contains ethanolamine as a major constituent. After immersing mild steel bars in air-saturated aqueous electrolytes for six weeks, he concluded that all of the three inhibitors examined behaved as passivating anodic inhibitors since the corrosion potential was observed to shift in the more positive direction as the corrosion rate was reduced to very low values.

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

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

Jamil et al. (2003) have studied the effectiveness and the inhibition mechanism of an amino alcohol based inhibitor used as admixture to prevent corrosion of steel in concrete. They performed the investigation in the presence of chloride ions, using

solutions simulating the concrete interstitial solution. Electrochemical measurements concluded that, an inhibitor film is formed on the surface hindering the anodic activity. Furthermore, the analytical investigation through the use of X-ray photoelectron spectroscopy (XPS) shows that the inhibitor film is able to complex with the chloride ion.

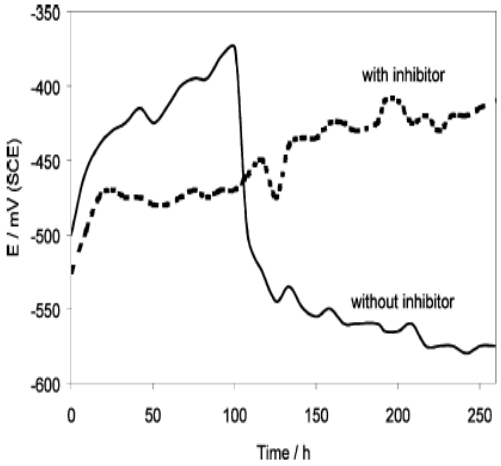


Figure 3.1 Open circuit potential (Jamil et al. 2003)

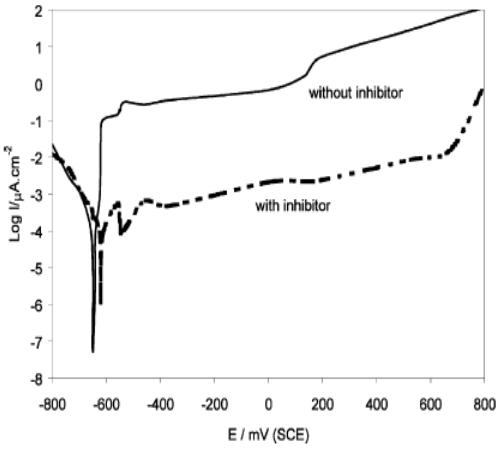


Figure 3.2 Potentiodynamic polarization curves (Jamil et al. 2003)

Open circuit potential values for samples immersed in the working solution contaminated with 2 g/l NaCl with and without inhibitor as shown in Fig. 3.1 indicate that in control sample after 100h, loss of passivation occur and the potential is attaining value nearly -570 mV. But in the presence of inhibitor, the continuous shift of the potential reading towards the anodic direction was observed. They also studied the electrochemical behavior with potentiodynamic polarization curves shown in Fig. 3.2. They observed that in the presence of inhibitor the anodic current is about four orders lower in magnitude than the control sample.

Further, it was observed that the inhibitor layer has the capacity to complex with chlorides, thus increasing the threshold Cl^-/OH^- ratio on the steel surface. The concentration of inhibitor in the solution affects the corrosion behaviour of the steel. The results suggest that a minimum inhibitor concentration is required in the interstitial electrolyte to achieve the desired protection. Threshold inhibitor concentration is suggested to be nearly 1 %, which is below the recommend value by the supplier i.e. 4%.

Malik et al. (2004) investigated the performance of surface applied type dimethyl ethanol amine-based (MCI-A) and triethanol amine-based (MCI-B) inhibitors and vapor based inhibitor (VCI-C). Reinforced concrete specimens coated with migratory inhibitors were exposed to 5% NaCl solution and to the Arabian Gulf seawater for up to 12 months. The condition of the steel bars was evaluated by physical examination and electrochemical measurements.

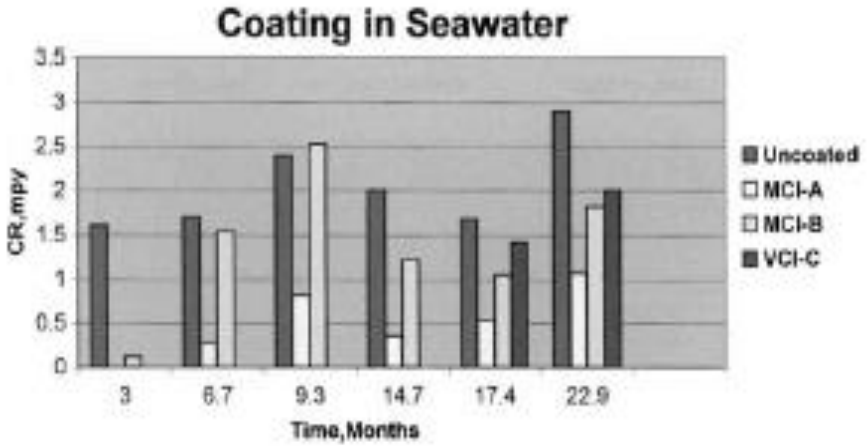


Fig. 3.3 Corrosion rate for different inhibitor immersed in sea water (Malik et al. 2004)

Fig. 3.3 shows that corrosion rate for inhibitor applied specimen are less than the control specimen. MCI- B has higher corrosion rate than MCI- A in sea water as well as in 5% NaCl solution. Presence of VCI-C decrease the corrosion rate but it is not much effective while comparing to MCI-A and MCI-B. The results indicated that the corrosion inhibitors utilized were generally able to decrease the corrosion rate of steel in concrete.

Jamil et al. (2005) studied the effect of use of aminoalcohol based surface applied inhibitor on corrosion protection of rebar. Open circuit potential reading for steel samples in solution with or without inhibitor addition are shown in Fig.3.4

As observed from Figure the potential values for system without inhibitor is around -300 mV (SCE) reveling corrosion onsets. On the other hand, with the presence of inhibitor the potential slowly increases with time reaching value around -160 mV. The continuous shift in the potential reading toward positive value suggests that the inhibitor is able to penetrate through mortar disk, reaching the solution where steel is immersed.

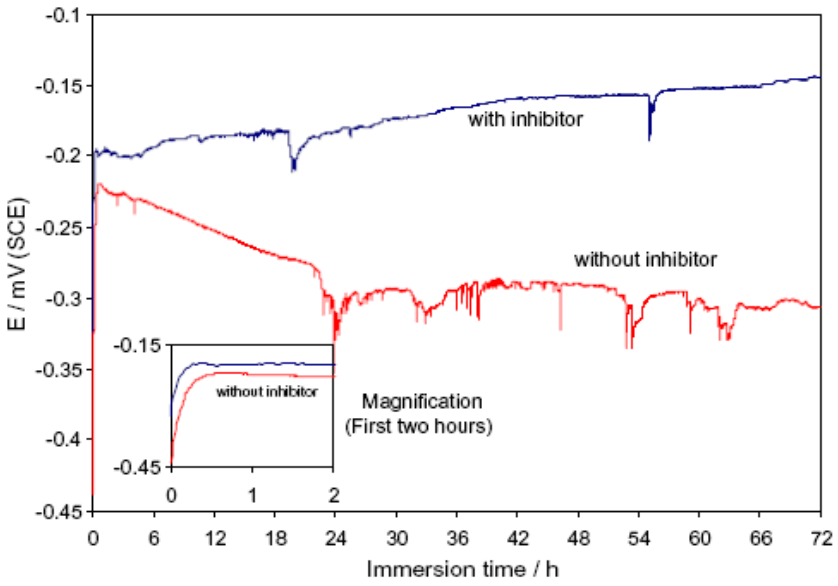


Fig. 3.4 Open circuit potential values with and without inhibitor (Jamil et al. 2005)

Further, they studied the effect of procedure of application of corrosion inhibitor on its performance. They used electrochemical impedance measurements for getting information about the corrosion behaviour of reinforcing steel in the presence of a penetrating and admixed amino alcohol corrosion inhibitor. However, two procedures by which inhibitor were applied consists of (1) Dissolving inhibitor with extract solution (2) Spraying inhibitor on the mortar surface. It was observed that the beneficial effect of inhibitor delayed when the inhibitor is sprayed on the mortar surface. They observed that the procedure used for the application of inhibitor affect the corrosion inhibiting performance.

Scott et al. (2005) conducted a long-term corrosion study to determine the effectiveness of calcium nitrate, silica fume, fly ash, ground granulated blast furnace slag, and disodium tetrapropenyl succinte (DSS) in reducing corrosion of reinforcing steel in concrete. Mixture proportions included: single, double, and triple combinations of these admixtures. Non-cracked and pre-cracked slab specimens were evaluated by visual inspection, macrocell readings, half-cell potentials, and autopsies. Triple combinations of calcium nitrate, silica fume, and either fly ash or ground granulated blast furnace slag, as well as a double combination of calcium nitrate and ground granulated blast furnace slag, performed very well and were recommended in concrete mixtures exposed to severe corrosive environments.

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

Soylev et al. (2007) studied the effectiveness of commercially available surface applied organic based inhibitors namely, ORG1 and ORG2 on concrete slab subjected to 70 g/l NaCl and 5 M NaCl ponding. They used Galva Pulse apparatus for measurement of corrosion potential (Ecorr), corrosion current (Icorr) and resistance of concrete. From the results they observed that new-generation amino alcohol-based inhibitor was effective against corrosion when it is applied before the chloride application or just after the first chloride ponding cycle. It kept the I_{cor} 1 $\mu A/cm^2$, which is accepted as a threshold value for corrosion initiation.

The amino alcohol-based inhibitor (ORG1) and the control specimen have approximately twice I_{corr} as the ORG2 specimens. Once concrete is contaminated with chloride and when the inhibitor was applied after a high corrosion rate (2 $\mu A/cm^2$) both of the inhibitors are ineffective. The effectiveness of the inhibitor may be partly due to blocking effect as the resistivity of the concrete was higher for ORG2-applied specimens. The new-generation amino alcohol-based inhibitor appeared to be a good repair strategy when it is applied before the initiation of corrosion or the corrosion rate is relatively low.

Al-Mehthel et al. (2009) studied the improvement in corrosion-resistance of chloride-contaminated silica fume cement concrete by the use of corrosion inhibitors. They evaluated one generic i.e. Calcium nitrite (Cl-1) and three proprietary i.e. calcium nitrite based admixed inhibitor (Cl-2), calcium nitrite based migrating inhibitor (Cl-3), organic based admixed inhibitor (Cl-4) for their performance in inhibiting reinforcement corrosion in the silica fume cement concrete specimens contaminated with 0.4%, 1%, and 2% chloride concentration, by weight of cement. Some of the specimens were subjected to wetting and drying cycles and reinforcement corrosion was monitored by measuring corrosion potentials and corrosion current density.

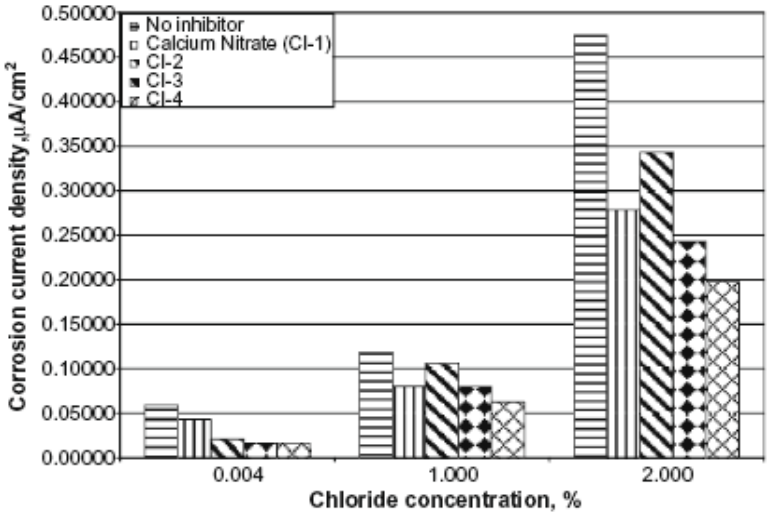


Fig. 3.5 Corrosion current density for concrete specimen (Al-Mehthel et al. 2009)

Fig.3.5 shows the corrosion current density I_{corr} on steel bars in the concrete specimens with or without inhibitors, after 20 months of wet–dry exposure. Figure shows, I_{corr} increases with the increase in chloride concentration in the concrete specimens. Further, the I_{corr} generally decreased with the use of inhibitors. For a particular chloride concentration, I_{corr} was the least in the concrete specimens incorporating CI-4, followed by those on which CI-3 was applied, CI-1 and CI-2. According to the prevailing convention I_{corr} values of more than 0.3 $\mu A/cm^2$ indicate corrosion activation. As per this criterion, corrosion activation was noted in the concrete specimens with no inhibitor and with CI-2 inhibitor at 2% chloride content. They observed, best performance was shown by the inhibitor Cl-4 followed by the inhibitor Cl-3.

3.3 PROTECTION MECHANISM OF CORROSION INHIBITORS

Due to high alkalinity in concrete there is already a protective oxide layer on the steel surface and the inhibition has to be on this layer rather than bare steel. Following studies shows the mechanism of protection by which commercially available organic and inorganic based corrosion inhibitors protect the rebar from corrosion.

Andrade et al. (1992) studied the mechanism by which Organic-based corrosion-inhibiting admixtures provided protection to rebar. They observed that corrosion inhibitors function by providing a physical barrier to the ingress of aggressive agents or by chemically stabilizing the steel surface. These organic materials inhibit corrosion by the same mechanism as that of other organic corrosion inhibitors – by adsorption on the metal surface. The layer enhances the naturally occurring passive layer on the steel surface and offers a significant resistance to the detrimental effect of chloride ions. It is generally accepted that organic corrosion inhibitors bond to metals by adsorption, physically and/or chemically, due to the polar or weakly polar characteristic of the organic compounds typically used in their formulation.

Nmai and Krauss (1994) reported that water-based organic admixtures function by reducing chloride ion ingress into concrete and forming a coating on the surface of the embedded steel. These inhibitors consist primarily of amines and fatty acid esters, made up of organic amides in an aqueous medium, and an aqueous solution of dimethylaminoethanol.

Dhouibi et al. (1998) reported that Organic inhibitors work by forming a monomolecular layer between the metal and the water. In the case of layer forming amines, one end of the molecule is hydrophilic and the other hydrophobic. These molecules will arrange themselves parallel to one another and perpendicular to the reinforcement forming a barrier. Organic corrosion inhibitor - layer inhibitor technology - functions through orientation of the nonpolar tail of the inhibitor molecule approximately normal to the surface of the reinforcement. It is postulated that the hydrocarbon tails mesh with each other, thus forming the layer. The primary effect is the repulsion of aqueous fluids thus inhibiting the deleterious effects of chemical and electrochemical interactions through a barrier effect. A secondary effect is the physical sorption of hydrocarbon molecules by the hydrocarbon tails of the adsorbed inhibitor molecules, thus further increasing the thickness of the hydrophobic

barrier. The organic inhibitors used for the protection of steel in concrete are often amines and aminoalcohols.

Jamil et al. (2003) studied the inhibition mechanism of an amino alcohol based inhibitor used as admixture to prevent corrosion of steel in concrete. The formation of the inhibitor film suggests an initial increase of the anodic activity in some sites on the surface, probably due to displacement of the first hydrated monolayers of the iron oxide film. It is proposed that these anodic points can act as favourable anchorage points for the development of inhibitor monolayers. The evolution of the total impedance, which is an indicator of the quality of the inhibitor, shows that the inhibition layer becomes homogeneous and protective with time. The inhibitor layer has the capacity to complex with chlorides, thus increasing the threshold Cl^-/OH^- ratio on the steel surface. The concentration of inhibitor in the solution affects the corrosion behaviour of the steel. The results suggest that a minimum inhibitor concentration is required in the interstitial electrolyte to achieve the desired protection.

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

When the MFOI is first added to concrete, the esters become hydrolyzed by the alkaline mix water to form the carboxylic acid and its corresponding alcohol. This reaction, under alkaline conditions, is favorable and is not easily reversed. The reaction proceeds as shown in Eq. (3.1), where R and R’ represent different hydrocarbon molecules:

$$RCOOR' + OH^- \longrightarrow RO_2^- + R'OH \qquad (3.1)$$

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

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

Film-forming mechanism the MFOI inhibits corrosion by adsorption on the metal surface. It is generally accepted that organic corrosion inhibitors bond to metals by adsorption, which can be physical and/or chemical in nature, due to the polar or weakly-polar characteristic of the organic compounds typically used in their formulation. The nonpolar tail of the inhibitor molecule is oriented in a direction generally vertical to the metal surface. It is believed that the hydrocarbon tails mesh with each other in a sort of "zipper" effect to form a tight film which repels aqueous fluids, establishing a barrier to the chemical and electrochemical attack of fluids on the base metal. A secondary effect is the physical sorption of hydrocarbon molecules from the process fluids by the hydrocarbon tails of the adsorbed inhibitor molecules. This increases both the thickness and effectiveness of the hydrophobic barrier to corrosion.

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

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

Wombacher et al. (2004) studied the behavior of amino alcohol based (AMA) inhibitors on fresh and hard concrete by electrochemical measurements. The interaction mechanism of the inhibitors with a steel surface has been studied by using sophisticated surface analytical methods. The mode of action was shown by investigating its interaction with the steel surface and the subsequent formation of a

protective layer. Concerning the transport of the surface applied inhibitor it could be shown that the penetration of inhibitors into the concrete dependent the concrete quality, the porosity and the humidity.

3.4 CORROSION INHIBITORS FOR CARBONATION INDUCED CORROSION

After the satisfactory performance of corrosion inhibitors in chloride induced corrosion, studies were performed to control carbonation induced corrosion. Studies performed in recent years in the field of carbonation induced corrosion are discussed in this section.

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

Then he find that after 1 h immersion, specimen omitting the very high frequency arc due to the low solution conductance, EIS spectrum of steel exhibited a single capacitive semicircle in the 10^3– 10^2 frequency range (Fig. 3.6), showing that the corrosion process was mainly charge-transfer controlled at short immersion times.

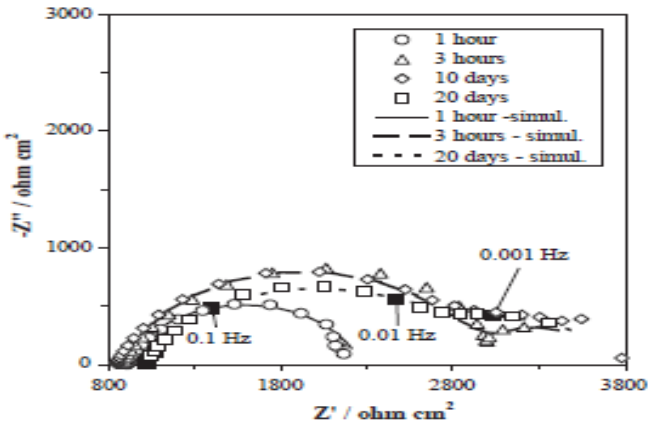


Fig. 3.6 Experimental and simulated EIS spectra recorded in uninhibited SS at different immersion times. (Trabanelli et al. 2005)

Among the additives tested as admixed inhibitors in carbonated concrete, only BEN (benzoic acid) and 2AMB (2-amino benzoic acid) exhibited some inhibitive effect towards the rebar corrosion process. However, in BEN-containing concrete specimens no inhibitive action was maintained till 400 days of exposure, while in the presence of 2AMB inhibiting efficiencies around 60% were still measured at the end of the test. The inhibitor leakage is reputed responsible of the decrease with time in the inhibiting efficiency of both additives.

Heiyantuduwa et al. (2006) study of a penetrating corrosion inhibitor in terms of its effectiveness in controlling corrosion in carbonated concrete. The objective was to improve understanding of the use of such materials, as well as limitations in this approach. The 30 MPa concrete mix was selected for corrosion test specimens. Specimens were demoulded after 24 h and wet cured at 23°C for six days, followed by 21 days curing in air at 23°C and 68% relative humidity .Concrete test specimens were blocks of size 120 mm X120 mm X 380 mm, with each specimen containing a 16 mm high tensile ribbed steel reinforcing bar longitudinally at the centre, at nominal covers of 10 or 20 mm. A single reinforcing bar was used in each block to simplify casting, processing, and measurement. Each group of six had two control specimens, two specimens that were treated with the penetrating inhibitor before the carbonation process, and two specimens that were treated with the penetrating inhibitor after the carbonation process.

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

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

Monticelli et al. (2011) have studied about two corrosion inhibitors, that is sodium 2-amino-benzoate (2AMB) and sodium glycero-phosphate (GPH), in a synthetic solution simulating the composition of the pore solution in a carbonated concrete, containing chlorides. Tests have been performed to verify if the simultaneous use of the two substances is compatible and if their addition can efficiently hinder the corrosion attack in the presence of both chlorides and carbonation. The synthetic solution has been prepared by bubbling carbon dioxide through a saturated (and filtered) solution of $Ca(OH)_2$, containing 0.1M NaCl, in order to reach pH 7. He prepared ribbed AISI 1033 type steel bars of 10mm diameter, commercialized as concrete reinforcement (composition: C=0.31%; Mn=0.94%; Cr=0.26%; Ni=0.19%; Cu=0.50%; Si=0.14%; Co=0.02%; Al=0.04%; S=0.03%; balance iron) with exposed surface area of 4.5 cm^2. These electrodes are exposed to the test solutions after grinding by emery papers up to grade 600, washing with double distilled water and degreasing with acetone.

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

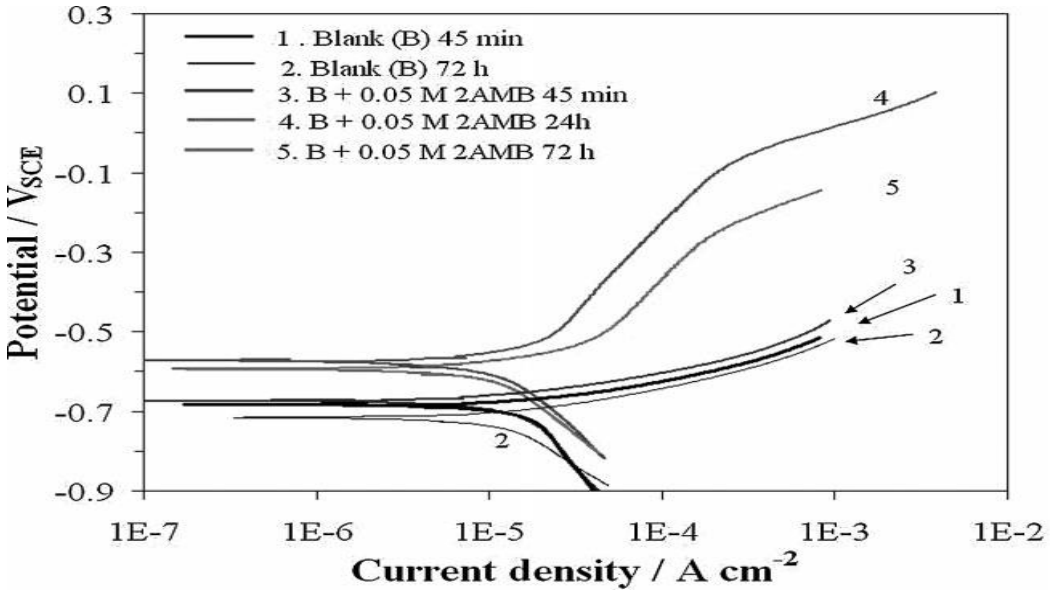


Fig. 3.7 Polarization curves recorded on steel in carbonated chloride solution, both in the absence and in the presence of 0.05M 2AMB (Monticelli et al. 2011)

The addition of 0.05M 2AMB to the blank solution affords no inhibiting effect on the corrosion process after 45 min of immersion (Fig. 3.7). However, after 24 h of immersion E_{COR} is ennobled up to -0.58 VSCE, owing to the increase in the slope of the anodic polarization curve, likely due to the formation of a surface film. The protectiveness of this film is scarce (as suggested by the measured I_{CORR} values which are only slightly lower than those measured in the blank solution) and diminishes with time, as the anodic curve shifts again towards higher current densities, at the end of 72 h immersion (Fig. 3.7).

Polarization curve recording and EIS technique have shown that the mixture inhibiting action develops slowly within 24 h, during which a surface porous film forms with a higher pore resistance and particularly a higher mass transport resistance with respect to those evaluated in the blank solution. The polarization curve analysis suggests that diffusion of Fe^{2+} cations from the metal surface to the aggressive solution may be the mass transport process controlling the steel corrosion rate in inhibited solutions.

3.5 IMPORTANCE OF PRESENT RESEARCH WORK

In last two decades, corrosion inhibitors have been extensively used to protect steel reinforcement in RC structures. There are plenty of corrosion inhibitors available commercially. Most of the commercially available corrosion inhibitors are used for chloride (Cl^-) induced corrosion and are not effective for carbonation induced corrosion.

Commercially available corrosion inhibitors being very expensive affect the total cost of structure. Growing need of corrosion inhibitors is expected in future because of environment becoming aggressive due to increasing pollution. Due to which, there arises a need to find a cheaper replacement of these corrosion inhibitors.

In this research work, attempts have been made to find some cheaper chemicals which can replace the expensive commercial corrosion inhibitors. Effectiveness in corrosion inhibition of some commonly available cheap organic chemicals is evaluated in the present study.

Most of the past research in this field does not involve variation of concentration of corrosion inhibitors. In this study, effectiveness of these organic chemicals is studied at various concentrations. Evaluation of corrosion inhibition effect was performed at 0.25%, 0.50 and 1% addition.

3.6 CLOSING REMARKS

This chapter deals with the study of literature available on the use of corrosion inhibitors. Importance of the present research work is also discussed in this chapter.

CHAPTER 4
EXPERIMENTAL PROGRAMME

4.1 GENERAL

This chapter includes details of the whole experimental setup and testing. The purpose of experimental programme was to evaluate corrosion inhibition efficiency of some common chemical compounds. Experimental setup and the materials used are discussed in following sections.

4.2 MATERIALS

Materials used in the experimental procedure were HYSD steel bar, epoxy, carbon dioxide (CO_2) gas, chemical compounds for preparing pore solution and chemical compounds to be used as corrosion inhibitors. Various properties of the materials used in this study are discussed below:

4.2.1 Steel Rebar

Fe 500 HYSD steel bars of 12 mm diameter and 60 mm length were used to evaluate efficiency of corrosion inhibitors. Properties of steel bar are shown in the Table 4.1.

Table 4.1 Mechanical properties of steel bar

Type of bar	Min yield stress N/mm^2	Min tensile strength N/mm^2	Elongation Percent
Fe 500 HYSD	500	545	12.0

4.2.2 Epoxy

Fevilite® Rapid was used as epoxy adhesive. It is a multipurpose epoxy adhesive which contains two components namely, Resin and Hardener. The mixing procedure and the ratio of each ingredient to be mixed were provided by the manufacturer. These two components were mixed in ratio 1:1 few seconds before use.

4.2.3 Chemical Compounds

a) For pore solution:

   To simulate the environment of concrete, a saturated solution of calcium hydroxide ($Ca(OH)_2$) was used.

b) For pH stabilisation of solutions:

To stabilise the pH of all solutions, 1 M NaOH and 0.1 M HCL were used. Properties of these compounds are shown in Table 4.2.

Table 4.2 Properties of chemical compounds

Sr No.	Compound	Molecular formula	Molar mass	Appearance	Odour	Density	Melting point
1	Calcium hydroxide	$Ca(OH)_2$	74.093 g/mol	White powder	Odourless	2.211 g/cm^3	580 °C
2	Sodium hydroxide	NaOH	39.99 g/mol	White, waxy, opaque crystals	Odourless	2.13 g/cm^3	318 °C
3	Hydrogen chloride	HCl	36.46 g/mol	Colourless gas	Pungent	1.409 g/l	-114.2°C

4.2.4 Carbon Dioxide (CO_2) Gas

Bubbling of carbon dioxide (CO_2) gas was done for simulating carbonation into concrete pore solution. Carbon dioxide from a standard CO_2 cylinder of 99% purity was used for the purpose of bubbling.

4.2.5 Corrosion Inhibitors

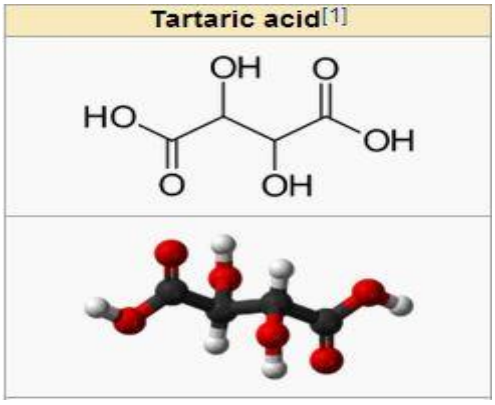
Corrosion inhibitors are the chemical compounds used to reduce corrosion rate of steel. Seven chemical compounds (whose inhibition efficiency was to be evaluated) were selected. These chemical compounds were: Tartaric acid, Maleic acid, Adipic acid, Phthalic acid, Oxalic acid, Gallic acid and Salicylic acid. Properties of these chemical compounds are given in Table 4.3.

Table 4.3 Properties of compounds used as corrosion inhibitors

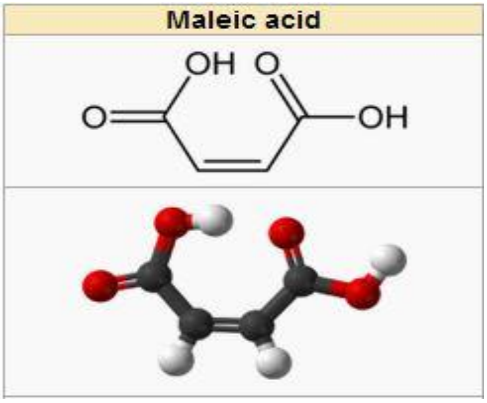
Sr No.	Chemical compound	Molecular formula	Molar mass	Appearance	Density	Melting point	Price INR/500g
1	Tartaric acid	$C_4H_6O_6$	150.08 g/mol	White powder	1.79 g/ml (H_2O)	171-174 °C	1100
2	Maleic acid	$C_4H_4O_4$	116.07 g/mol	White solid	1.59 g/cm^3	135 °C	500
3	Adipic acid	$C_6H_{10}O_4$	146.14 g/mol	White crystals	1.36 g/cm^3	152.1 °C	500
4	Phthalic acid	$C_8H_6O_4$	166.14 g/mol	White solid	1.593 g/cm^3	191-230 °C	280
5	Oxalic acid	$C_2H_2O_4$	90.03 g/mol	White crystals	1.90 g/cm^3	103 °C	400
6	Gallic acid	$C_7H_6O_5$	170.12 g/mol	Yellowish white powder	1.694 g/cm^3	260 °C	500
7	Salicylic acid	$C_7H_6O_3$	138.11 g/mol	Colourless to white crystals	1.443 g/cm^3	158.6 °C	550

Molecular structures and IUPAC names of the chemical compounds are shown in Fig. 4.1.

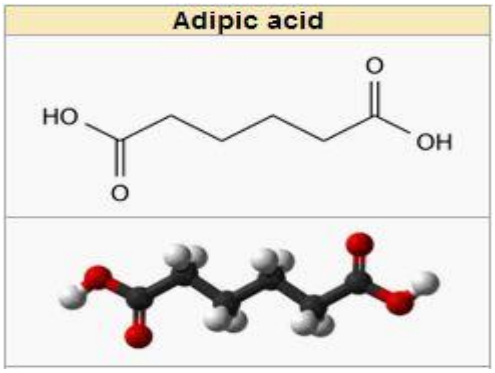
After the initial mixing, Gallic acid and salicylic acid were rejected later due to solubility issues. Salicylic acid was not soluble in carbonated calcium hydroxide solution even with the help of methanol; cloudy precipitates were formed after mixing. Gallic acid gave sticky precipitates after mixing.



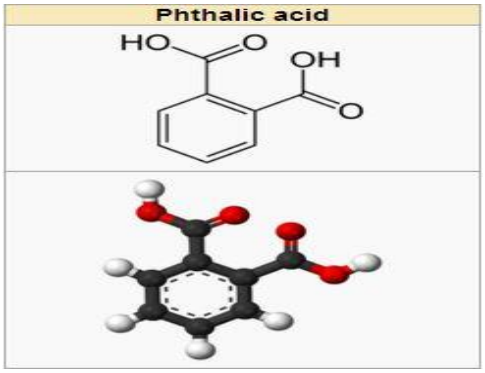
IUPAC Name: 2,3-dihydroxybutanedioic acid



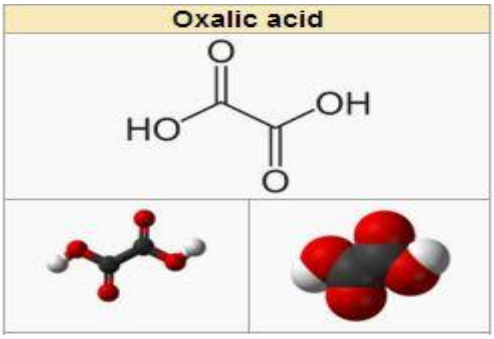
IUPAC Name: (*Z*)-Butenedioic acid



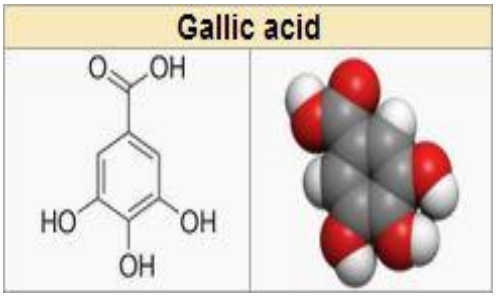
IUPAC Name: hexanedioic acid



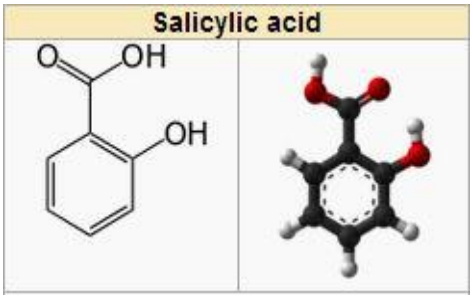
IUPAC Name: Benzene-1,2-dicarboxylic acid



IUPAC Name: Ethanedioic acid



IUPAC Name: 3,4,5-Trihydroxybenzoic acid



IUPAC Name: 2-Hydroxybenzoic acid

Fig. 4.1 Molecular structures of compounds used as corrosion inhibitors

4.3 PREPARATION OF CALCIUM HYDROXIDE ($Ca(OH)_2$) SOLUTION

To simulate the environment of concrete, a saturated solution of calcium hydroxide was prepared. Concrete pore solution was prepared by adding 1 gram of $Ca(OH)_2$ in 1 litre of distilled water with constant stirring. Concrete pore solution had the pH of 12-13. Saturated solution of $Ca(OH)_2$ is also called lime water and has milky appearance. The solution was allowed to stand for 24 hours and the extra powder settled down was removed by using a filter paper. This solution was used as basic control solution.

4.4 PRECONDITIONING AND PREPARATION OF STEEL SPECIMENS

Fe 500 HYSD bars of 12 mm diameter were cut into length of 60 mm. Cross-sectional face of specimens were made smooth using lathe machine. Specimens were drilled at one face with 3.5 mm drill. Then, the specimens were threaded internally with tapping tool of diameter 4 mm and pitch of 0.7 mm.

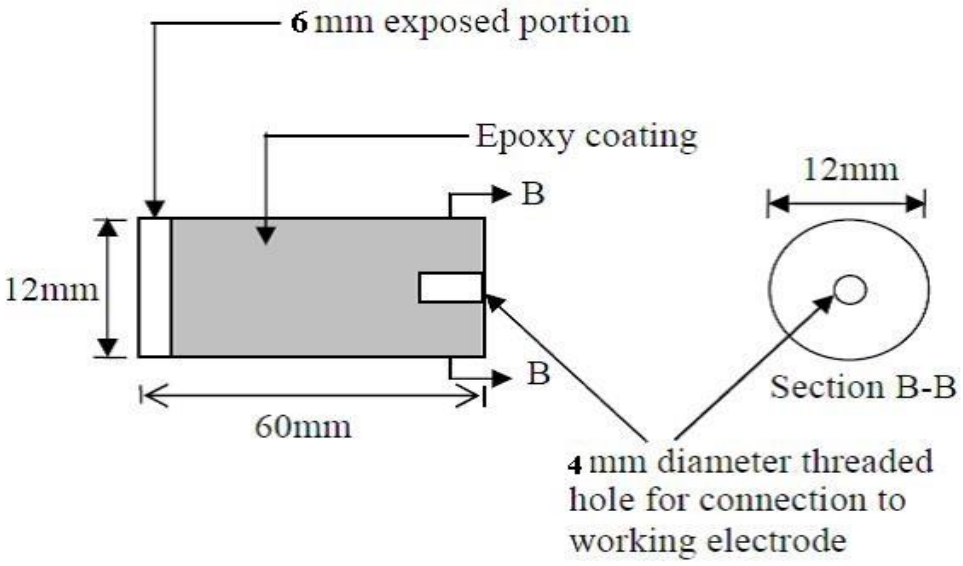


Fig. 4.2 Line diagram of bare steel specimen

Then, the steel specimens were cleaned using wire brush to remove any rust stains present on steel surface. Steel specimens were coated with Fevilite epoxy, leaving 6 mm of length at bottom surface, which was later exposed to corrosion. These specimens were kept for 24 hours. A nut was screwed with two bolts in each specimen to attach them with working electrode by the help of copper wire. Fig.4.2 shows the line diagram of steel specimen. Plate 4.1 shows steel specimens used in this study.

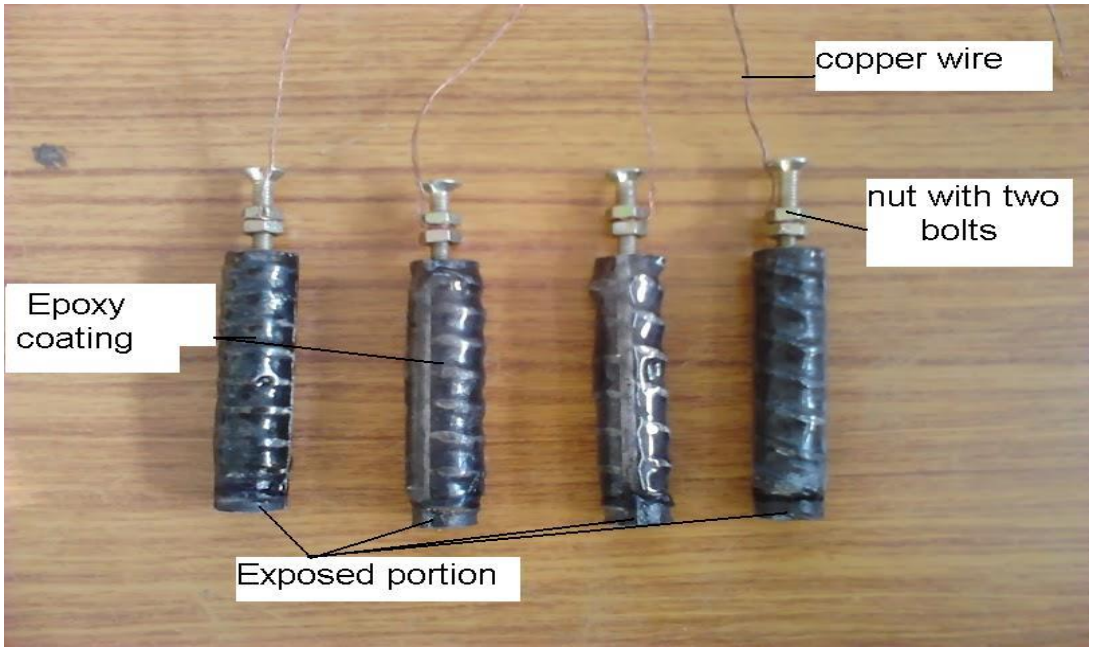


Plate 4.1 Steel specimens with epoxy coating

4.5 PREPARATION OF CARBONATED SOLUTION

Carbonated solution was prepared by bubbling carbon dioxide gas into the saturated calcium hydroxide solution. Standard CO_2 of 99% purity was simply bubbled through the concrete pore solution. Bubbling of CO_2 gas was done to achieve the carbonation condition in concrete pore solution. Purpose of this process was to simulate corrosion prone carbonation state in concrete pore solution. The pH value of solution was reduced from 12 to 8 due to carbonation of calcium hydroxide. By reducing the pH value of solution to 8, a state of extreme carbonation in pore solution was achieved. CO_2 reacts with calcium hydroxide present in lime water to produce calcium carbonate precipitates.

4.6 PREPARATION OF CORROSION INHIBITOR SOLUTION

The experiment was divided into 3 different sets; every different set used different concentration of the corrosion inhibitors. Set I of experiment used 0.25 % (of weight of carbonated calcium hydroxide solution) chemical as corrosion inhibitors. Set II used 0.5% and set III used 1% of chemical as corrosion inhibitors. Corrosion inhibitor solutions were prepared by adding required weight (according to percentage) of chemical in 1kg of carbonated calcium hydroxide solution.

2.5 grams, 5 grams and 10 grams of chemical in 1 kg of carbonated calcium hydroxide solution for 0.25%, 0.5% and 1% solution respectively was mixed.

Some of the chemicals were not completely mixable in carbonated $Ca(OH)_2$ solution. For solubility of these compounds, they were firstly mixed in Methanol (10-20 ml) and then mixed with carbonated solution.

The pH values of solutions were decreased or increased after mixing of chemicals. The pH values were then stabilized using 1 M NaOH and 0.1 M HCl solution.

4.7 DETAILS OF EXPERIMENT

4.7.1 General

Steel specimens coated with epoxy (leaving the bottom 6 mm) were used. The uncovered areas of steel specimens were immersed in 7 different solutions to evaluate inhibition efficiency of these solutions. Later, corrosion monitoring of these specimens was done at different intervals. Intervals used for corrosion monitoring were 1 hour, 24 hours, 48 hours, 120 hours and 240 hours. Current & Voltage per time and Linear Polarization Resistance (LPR) techniques were used for corrosion monitoring.

4.7.2 Details of Experiment Set I

For experiment set I, 0.25% solution of all chemicals in carbonated calcium hydroxide were prepared by adding 2.5 g/litre. Details of the specimen for experiment set I are given in Table 4.4.

Table 4.4 Details of solutions used for experiment set I.

Sr No.	Abbreviation	Detail of solution	pH
1	Soln 0	Saturated calcium hydroxide solution	12.1
2	Soln 1	Carbonated calcium hydroxide solution	8.0
3	Soln 2	Tartaric acid (0.25%)	8.1
4	Soln 3	Maleic acid (0.25%)	8.0
5	Soln 4	Adipic acid (0.25%)	8.1
6	Soln 5	Phthalic acid (0.25%)	8.0
7	Soln 6	Oxalic acid (0.25%)	8.0

4.7.3 Details of Experiment Set II

For experiment set II, 0.5 % solution of all chemicals in carbonated calcium hydroxide were prepared by adding 5g/litre.

Details of specimens used in experiment set II are given in Table 4.5.

Table 4.5 Details of solutions used for experiment set II.

Sr No.	Abbreviation	Detail of solution	pH
1	Soln 2	Tartaric acid (0.5%)	8.0
2	Soln 3	Maleic acid (0.5%)	8.2
3	Soln 4	Adipic acid (0.5%)	8.0
4	Soln 5	Phthalic acid (0.5%)	8.1
5	Soln 6	Oxalic acid (0.5%)	8.2

4.7.4 Details of Experiment Set III

For experiment set III, 1 % solution of all chemicals in carbonated calcium hydroxide were prepared by adding 10g/litre.

Details of specimens used in experiment set III are given in Table 4.6.

Table 4.6 Details of solutions used for experiment set III.

Sr No.	Abbreviation	Detail of solution	pH
1	Soln 2	Tartaric acid (1%)	8.2
2	Soln 3	Maleic acid (1%)	8.1
3	Soln 4	Adipic acid (1%)	8.2
4	Soln 5	Phthalic acid (1%)	8.0
5	Soln 6	Oxalic acid (1%)	8.1

4.8 CORROSION MONITORING

4.8.1 General

After preparing all solutions, specimens were placed in the solutions for required time. Specimens were immersed in the solutions for duration of 240 hours. Corrosion monitoring was done in 5 intervals; 1 hour, 24 hours, 48 hours, 120 hours and 240 hours. Corrosion monitoring was done by using ACM field machine. Details of the equipment and the experiment are discussed in following sections.

4.8.2 Equipment Used

ACM field machine was used for corrosion monitoring. ACM field machine provides many electrochemical techniques like current & voltage / time, long term- LPR sweep, long term- LPR step, Galvanostatic, AC impedance and Potentiostatic for corrosion monitoring.

Current & voltage / time, long term- LPR sweep techniques were used for this experiment. ACM field machine used for the experiment is shown in Plate 4.2.

Plate 4.2 ACM field machine

4.8.3 Current and Voltage per Time

In this experiment, all the specimens were monitored time to time by half-cell potential using a saturated calomel reference electrode (SCE) by placing the electrode in the solutions. The procedure opted was followed by ASTM Standard. The half-cell potential measurement is the most common method used in the bridge deck corrosion surveys. An indication of the relative probability of corrosion activity can be empirically obtained through measurement of the potential difference between a standard portable half-cell placed on the surface of the steel rebar underneath. The ASTM interpretation of half-cell potential (SCE) is summarized in Table 4.7.

Table 4.7 The ASTM Interpretation of Half-Cell Potential Readings

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

This test was performed to stabilize the system. Current & Voltage permits the continuous measurement of potential and galvanic readings. The maximum read rate for Current & Voltage is limited by the mains frequency, 0.02 for 50Hz and .0166667 for 60Hz. The Long Term test was performed with Potential measurement in which the read rate was very frequent i.e. One reading every 1 second. Plate 4.3 shows the input screen for current and voltage per time test.

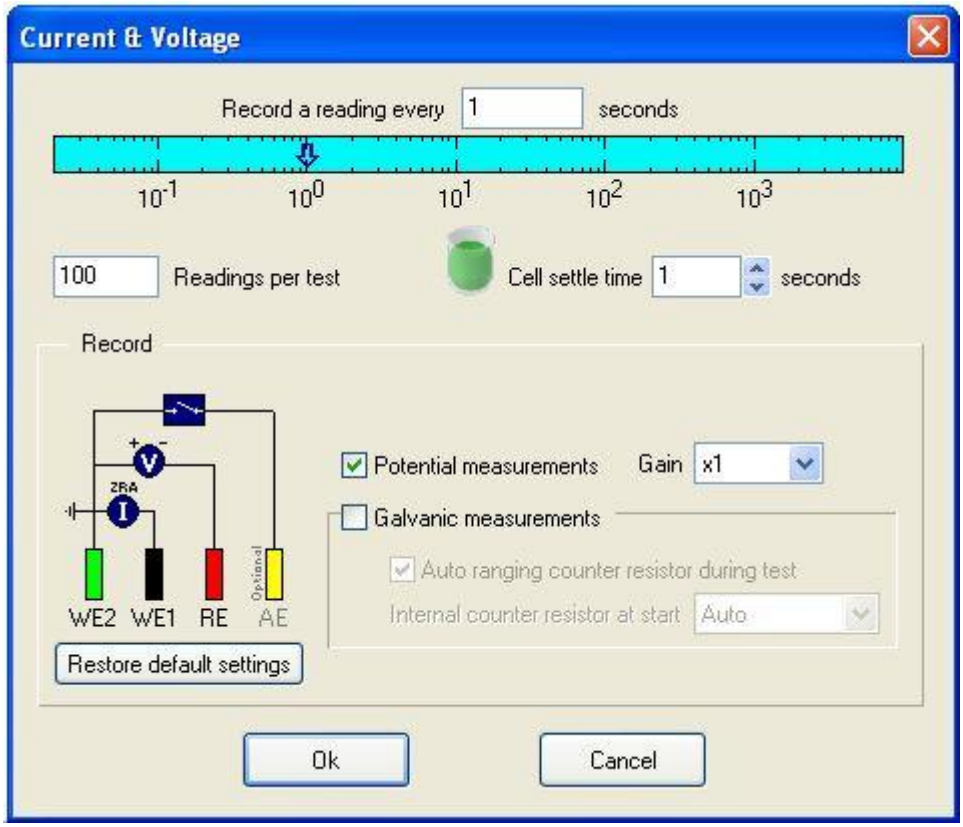


Plate 4.3 Input for current and voltage per time

4.8.4 Long Term- LPR

Long term LPR sweep or potentiodynamic polarization was done to find corrosion current density. Polarisation resistance determinations have been used for more than 50 years for the rapid and relatively accurate determination of corrosion rates or general corrosion trends in single and multiphase fluids.

The LPR technique has become a well-established method of determining the instantaneous corrosion rate measurement of reinforcing steel in concrete (Gowers et al.). The technique is rapid and non-intrusive, requiring only localized damage to the concrete cover to enable an electrical connection to be made to the reinforcing steel. Due to the widespread corrosion of reinforcing steel in concrete structures there has been a concerted demand for the development of non-destructive techniques to enable accurate assessment of the condition of reinforced concrete structures. LPR monitoring has been developed to address this need. The technique is rapid and non-intrusive, requiring only a connection to the reinforcing steel. The data provides a valuable insight into the instantaneous corrosion rate of the steel reinforcement, giving more detailed information than a simple potential survey. The LPR data enables a more detailed assessment of the structural condition and is a major tool in deciding upon the optimum remedial strategy to be adopted. It is thus imperative that the LPR measurements obtained are accurate. In LPR measurements the reinforcing steel is perturbed by a small amount from its equilibrium potential. This can be accomplished potentiostatically by changing the potential of the reinforcing steel by a fixed amount, ΔE, and monitoring the current decay, ΔI, after a fixed time. Alternatively it can be done galvanostatically by applying a small fixed current, ΔI, to the reinforcing steel and monitoring the potential change, ΔE, after a fixed time period. In each case the conditions are selected such that the change in potential, ΔE, falls within the linear Stern–Geary range of 10 – 30 mV. The polarization resistance, R_p, of the steel is then calculated from the equation 4.1 as

$$Rp = \Delta E/\Delta I \qquad (4.1)$$

From which the corrosion rate, I_{corr}, can then be calculated

$$I_{corr} = B/R_p \qquad (4.2)$$

Where, *B* is the Stern–Geary constant. A value of 25 mV has been adopted for active steel and 50 mV for passive steel. In order to determine the corrosion current density (i_{corr}) the surface area (A) of steel that has been polarized needs to be accurately known:

$$i_{corr} = I_{corr}/A \qquad (4.3)$$

The present residual strength and, by extrapolation, the remaining service life of the structure can then be estimated.

In this experiment potentiostatic linear sweep test was carried out on bare steel specimens using the ACM Field Machine. The electrochemical cell consists of a cylindrical jar with a polypropylene lid. It is provided with fittings for connecting the auxiliary electrode, noise reduction probe, reference electrode, thermometer and the specimen. Throughout the test, the reference electrode used was saturated calomel electrode (SCE). The test set-up is shown in Plate 4.5. For testing, the bare steel specimen screwed to the working electrode, the reference electrode, auxiliary electrode, and noise reduction probe were attached to the electrochemical cell. The potentiostatic linear sweep test was carried out from -250 mV to 250 mV with offset from corrosion potential at a sweep rate of 60 mV per minute. The input readings of ACM field machine while performing this test are shown in Plate 4.4.

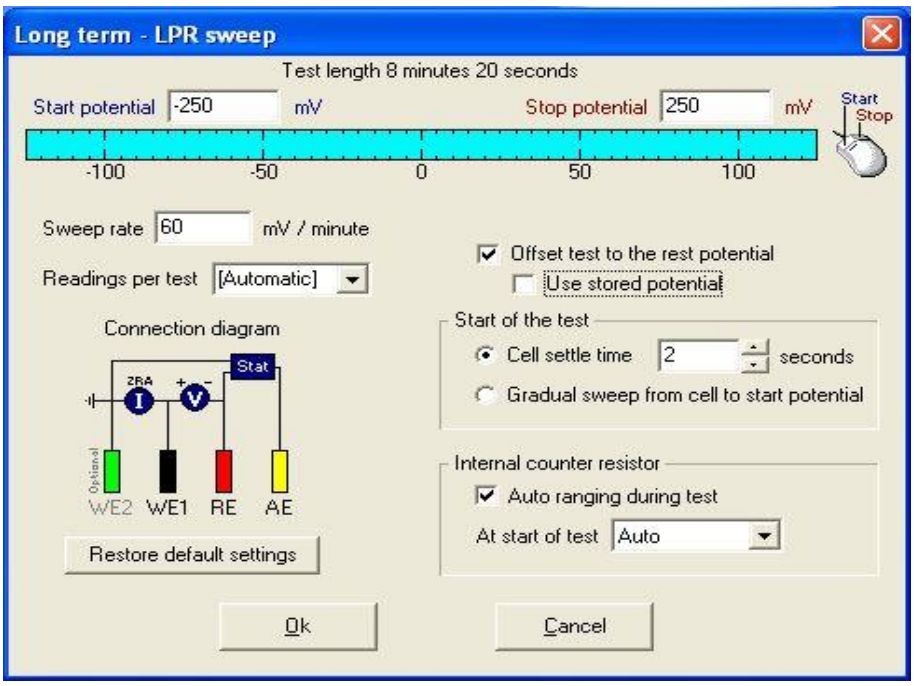


Plate 4.4 Input screen for long term LPR.

The readings of this test were recorded on specific time intervals. Total five readings were recorded at 1, 24, 48, 120, 240 hours from the start of the test. These readings at specific time interval were recorded to understand, when the corrosion inhibitors become effective and form layer around the steel specimen to protect it from corrosion. Plate 4.5 shows the set up for long term LPR test.

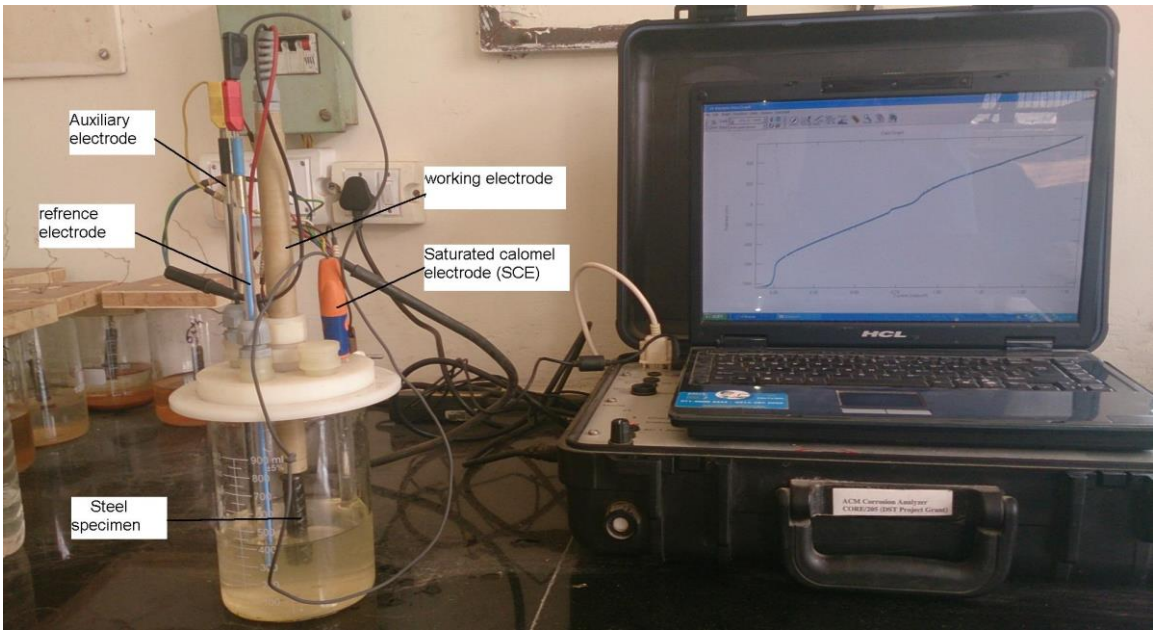


Plate 4.5 Set up for long term LPR.

4.9 CONDITION OF SPECIMENS AFTER TOTAL IMMERSION TIME

Condition of test specimens after the total duration of experiment set I is shown in Plate 4.6.

Plate 4.6 Specimens after experiment set I

Condition of test specimens after the total duration of experiment set II is shown in Plate 4.7.

Plate 4.7 Specimens after experiment set II

Condition of test specimens after the total duration of experiment set III is shown in Plate 4.8.

Plate 4.8 Specimens after experiment set III

Condition of all test specimens after the total duration of experiment is shown in Plate 4.9.

Plate 4.9 All Specimens after experiment

4.10 CLOSING REMARKS

This chapter includes the details of materials, equipment and techniques used in the experimental programme. Complete procedure opted for the experimental study is discussed in detail.

CHAPTER 5
RESULTS AND DISCUSSIONS

5.1 GENERAL

This chapter includes the results obtained from the experimental program. Results were obtained from corrosion monitoring of steel rebar with the help of ACM field machine. The experimental results are discussed briefly in further sections.

5.2 EXPERIMENT SET I

In set I of experiment, 0.25% solutions of all chemical compounds were used. Steel specimens were immersed in these solutions till 240 hours. Monitoring of corrosion was done at 1 hour, 24 hours, 48 hours, 120 hours and 240 hours of immersion. Current and voltage per time and Long term LPR with Tafel extrapolation techniques were used for monitoring of corrosion. Details of the specimens are provided in the Table 5.1.

Table 5.1 Details of solutions used for experiment set I.

Sr No.	Abbreviation	Detail of Solution
1	Soln 0	Saturated calcium hydroxide solution
2	Soln 1	Carbonated calcium hydroxide solution
3	Soln 2	Tartaric acid (0.25%)
4	Soln 3	Maleic acid (0.25%)
5	Soln 4	Adipic acid (0.25%)
6	Soln 5	Phthalic acid (0.25%)
7	Soln 6	Oxalic acid (0.25%)

5.2.1 Results Obtained From Long Term LPR Test and Tafel Extrapolation

Long term LPR technique performed on ACM Field machine was used to record Rest Potential (Rp), I_{corr}, E_{corr} and corrosion rate. Tafel extrapolation technique was used for

further modification of these results. Variation of I_{corr} with respect to immersion time and variation of corrosion rate with respect to immersion time for all the solutions are shown graphically in Fig. 5.1 and 5.2 respectively. Rest Potential (Rp), I_{corr}, E_{corr} and corrosion rate recorded for experiment set I are shown in Table 5.2.

Table 5.2 Experiment set I results by LPR and Tafel extrapolation

Sr No.	Sample	Time	Rp (-mV)	I_{corr} (mA/cm^2)	E_{corr} (-V)	Corrosion Rate (mm/year)
1	Soln 0	1 Hr	408.66	6.93E-04	0.41	7.95E-03
		24 Hr	613.55	3.41E-03	0.62	3.91E-02
		48 Hr	627.98	3.65E-03	0.63	4.16E-02
		120 Hr	497.84	3.93E-03	0.49	4.51E-02
		240 Hr	652.66	8.47E-03	0.65	9.90E-02
2	Soln 1	1 Hr	672.51	1.88E-02	0.67	2.15E-01
		24 Hr	698.22	5.58E-03	0.70	6.41E-02
		48 Hr	747.45	5.85E-03	0.75	6.65E-02
		120 Hr	703.31	5.98E-03	0.70	6.78E-02
		240 Hr	784.11	9.95E-03	0.78	1.15E-01
3	Soln 2	1 Hr	639.04	2.12E-02	0.64	2.43E-01
		24 Hr	426.61	4.30E-03	0.425	4.94E-02
		48 Hr	484.65	4.96E-03	0.48	5.70E-02
		120 Hr	423.87	2.44E-03	0.43	2.81E-02
		240 Hr	426.6	3.21E-03	0.425	3.69E-02
4	Soln 3	1 Hr	569.15	1.97E-02	0.57	2.26E-01
		24 Hr	928.12	2.40E-02	0.93	2.75E-01

		48 Hr	718.07	1.70E-02	0.72	1.94E-01
		120 Hr	784.81	1.20E-02	0.78	1.37E-01
		240 Hr	785.77	3.29E-03	0.785	3.77E-02
5	Soln 4	1 Hr	367.01	2.83E-03	0.365	3.25E-02
		24 Hr	833.87	2.77E-02	0.84	3.19E-01
		48 Hr	745.73	1.66E-02	0.745	1.91E-01
		120 Hr	781.28	6.75E-03	0.78	7.76E-02
		240 Hr	778.56	5.90E-03	0.76	7.13E-02
6	Soln 5	1 Hr	647.26	2.21E-02	0.65	2.53E-01
		24 Hr	734.4	2.88E-02	0.73	3.30E-01
		48 Hr	739.3	2.30E-02	0.74	2.64E-01
		120 Hr	835.61	2.16E-02	0.83	2.48E-01
		240 Hr	847.08	2.81E-02	0.84	2.13E-01
7	Soln 6	1 Hr	449.7	7.88E-03	0.45	9.04E-02
		24 Hr	593.27	1.14E-02	0.59	1.32E-01
		48 Hr	545.56	1.00E-02	0.54	1.15E-01
		120 Hr	601.82	1.23E-02	0.60	1.42E-01
		240 Hr	655.22	1.30E-02	0.65	1.42E-01

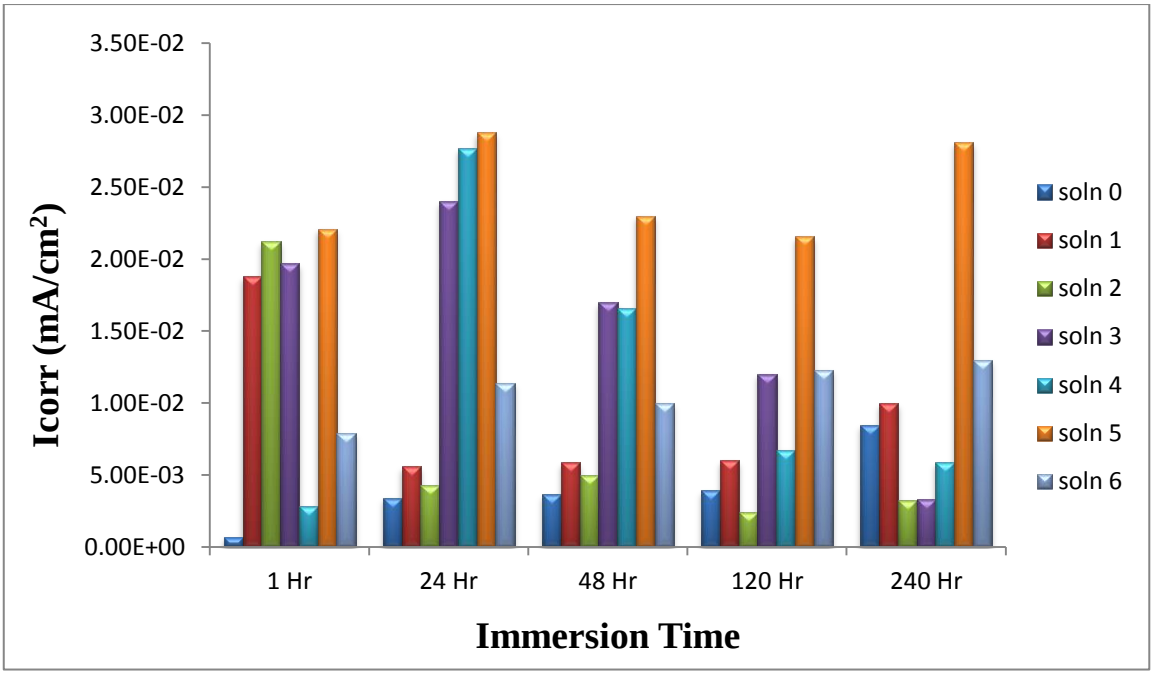


Fig.5.1 Variation of I_{corr} with respect to immersion time for all the solutions in experiment set I.

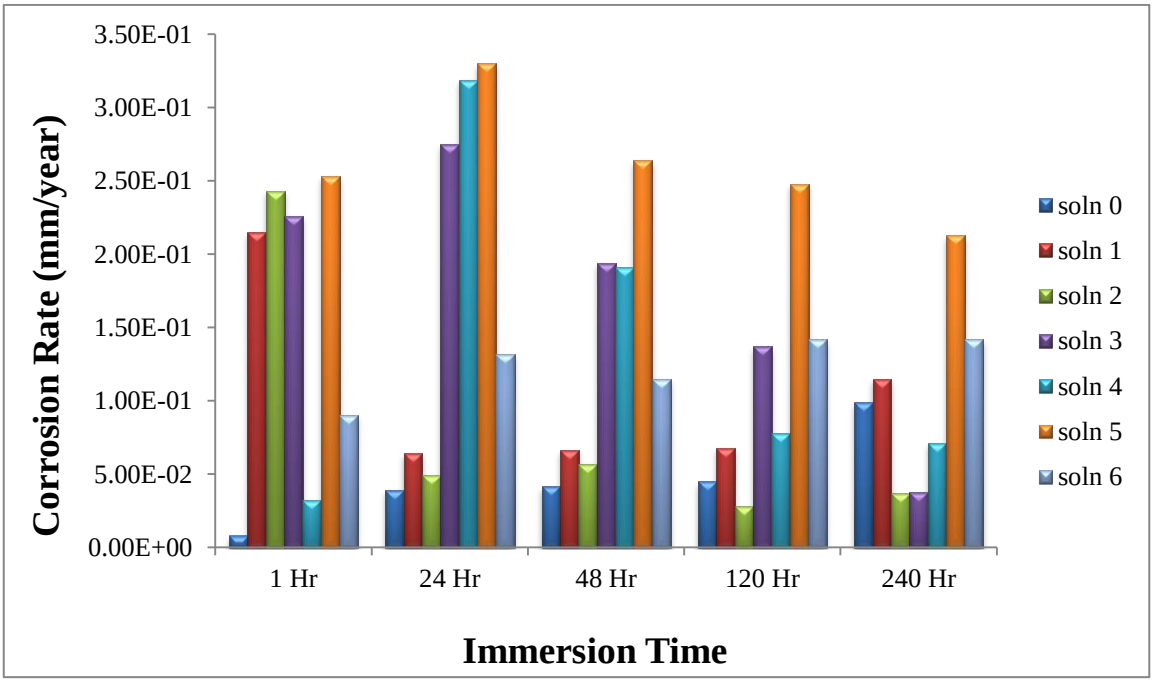


Fig.5.2 Variation of corrosion rate with respect to immersion time for all the solutions used in experiment set I.

The graphs Icorr vs Immersion time and Corrosion rate vs Immersion time for experiment set I depicts that Soln 2 is quite effective in corrosion inhibition of bare steel specimens. Soln 3 and Soln 4 do not perform well in the initial time of

immersion but reduced corrosion rates were observed after 48 hours of immersion. Corrosion rate for the specimen immersed in Soln 6 was high but was not varying much during the total time of immersion. Soln 5 was not at all effective in corrosion inhibition during total immersion time.

5.2.2 Tafel Plots from ACM Field Machine

For better understanding of corrosion inhibition behaviour with respect to immersion time, tafel plots from ACM field machine are discussed for all the specimens.

Tafel plot gives variation of potential (V) at Y-axis with respect to logarithmic current (logI) at X-axis. Tafel plots give more precise values of I_{corr} and Corrosion rate by the use of Tafel extrapolation. Tafel ruler function in sequencer of ACM field machine can be used for Tafel extrapolation. Tafel rulers can only be used on potential vs current graphs where the current axis is logarithmic. Three rulers are placed on the graph, a horizontal ruler which identifies the rest potential. The other rulers indicate Tafel slopes.

The potential curve of the Tafel plot helps us to judge the corrosion potential (E_{corr}) values and the passive behaviour of rebar. Tafel plots of specimens immersed in different solutions at various test durations are presented in Fig 5.3-5.9.

Tafel plot of specimen immersed in Soln 0 shown in Fig. 5.3 depicts; Corrosion Potential (E_{corr}) shifts towards active zone with increasing immersion time. E_{corr} value for this specimen was -0.41 V_{SCE} at 1 hour of immersion which shifted upto -0.66 V_{SCE} at 240 hours without showing an adequate passive behaviour. Small shift of E_{corr} towards passive zone was observed at 120 hours.

As can be observed from Tafel plot of specimen in Soln 1 shown in Fig. 5.4, E_{corr} value shifts toward active zone showing no passive behaviour with increasing immersion time. E_{corr} value for this specimen was -0.68 V_{SCE} at 1 hour of immersion which shifted upto -0.79 V_{SCE} at 240 hours.

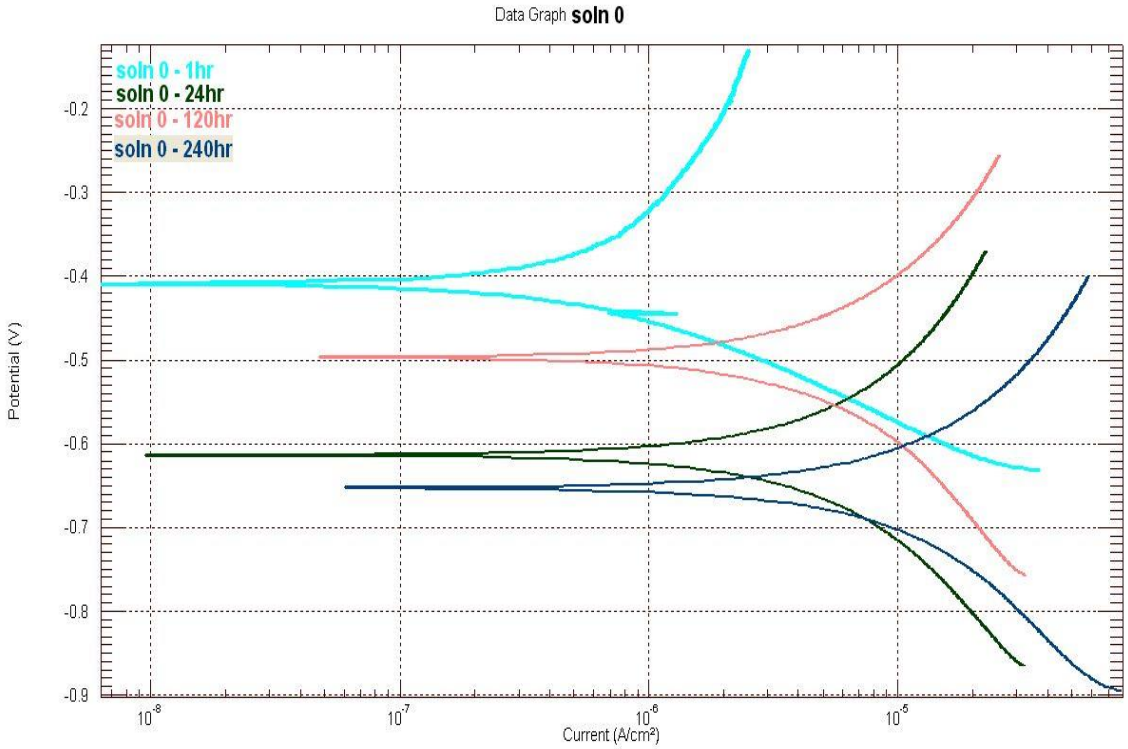


Fig. 5.3 Tafel plot for Soln 0

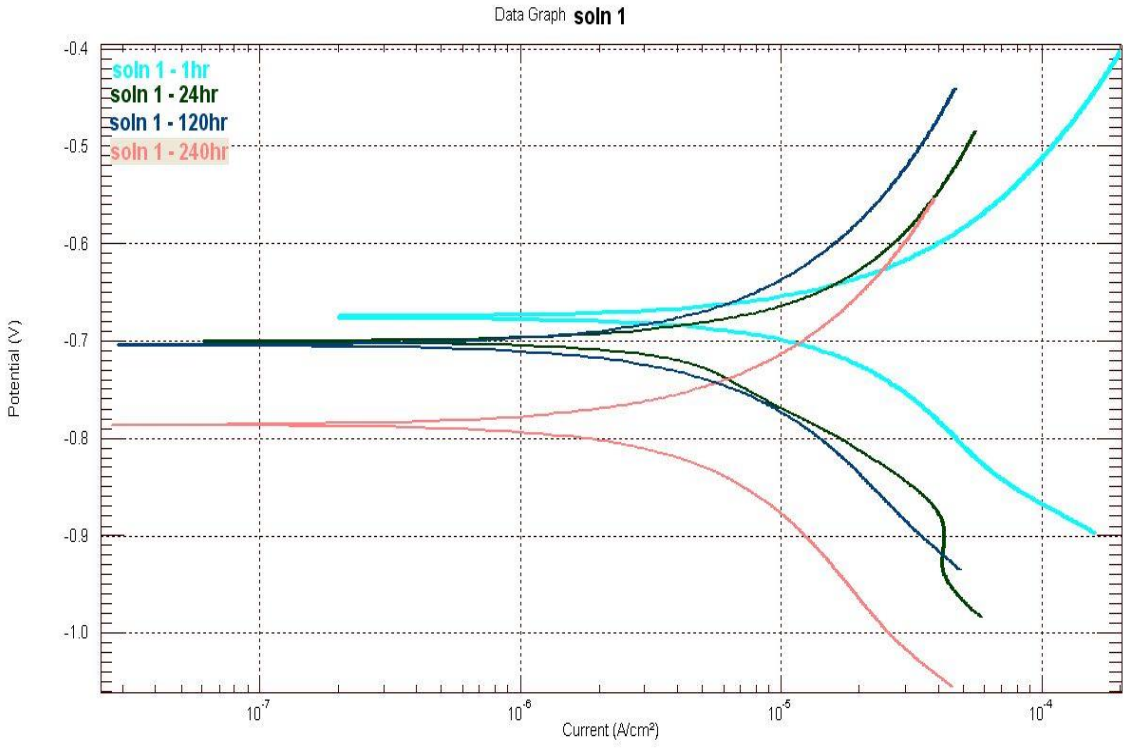


Fig. 5.4 Tafel plot for Soln 1

Tafel plot of specimen immersed in Soln 2 shown in Fig. 5.5 depicts that the E_{corr} for this specimen shift towards passive zone with increasing time of immersion. E_{corr} at 1 hour of immersion -0.64 V_{SCE} shifted to -0.425 V_{SCE} at 240 hours of immersion, showing passive behaviour up to -0.1 $V_{SCE.}$ Therefore, it can be concluded that the Soln 2 shows passive behaviour with increasing time of immersion.

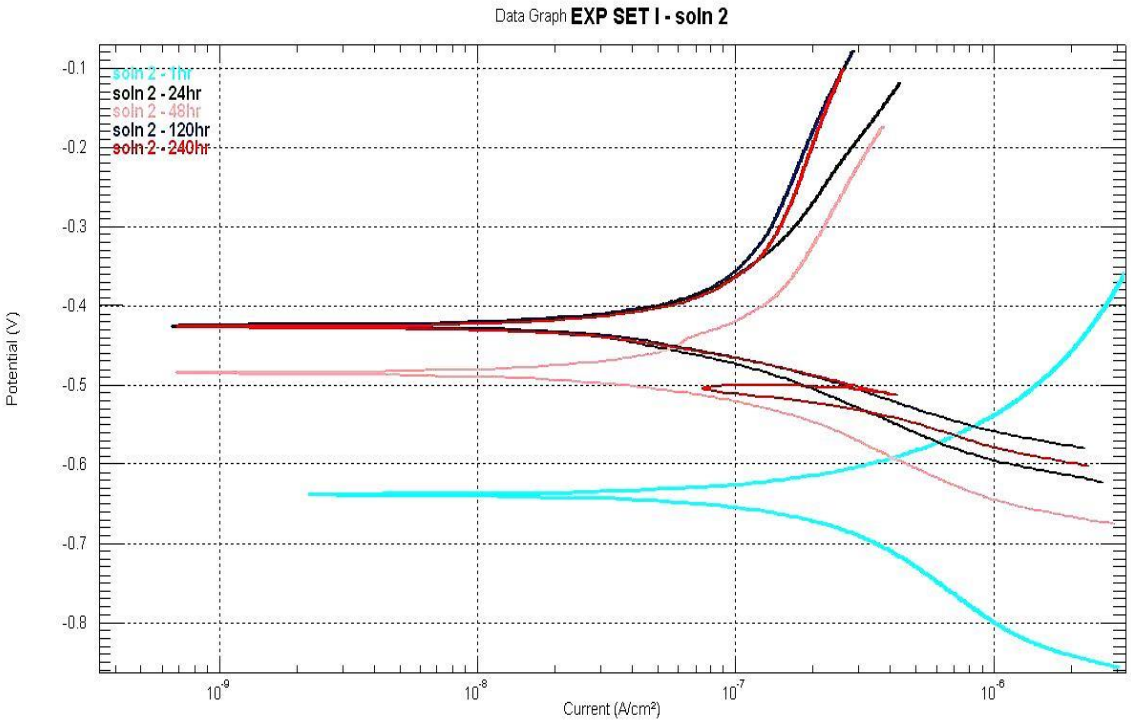


Fig.5.5 Tafel plot for Soln 2 at 0.25%

Tafel plot of specimen immersed in Soln 3 shown in Fig. 5.6 depicts that the E_{corr} for this specimen shifted towards active zone with increasing time of immersion. Specimen immersed in Soln 3 shows a little passive behaviour in later stage of immersion time. It can be concluded that although this specimen shows passive behaviour in later stages yet it will not be effective in corrosion inhibition as the certain amount of corrosion has already been occurred.

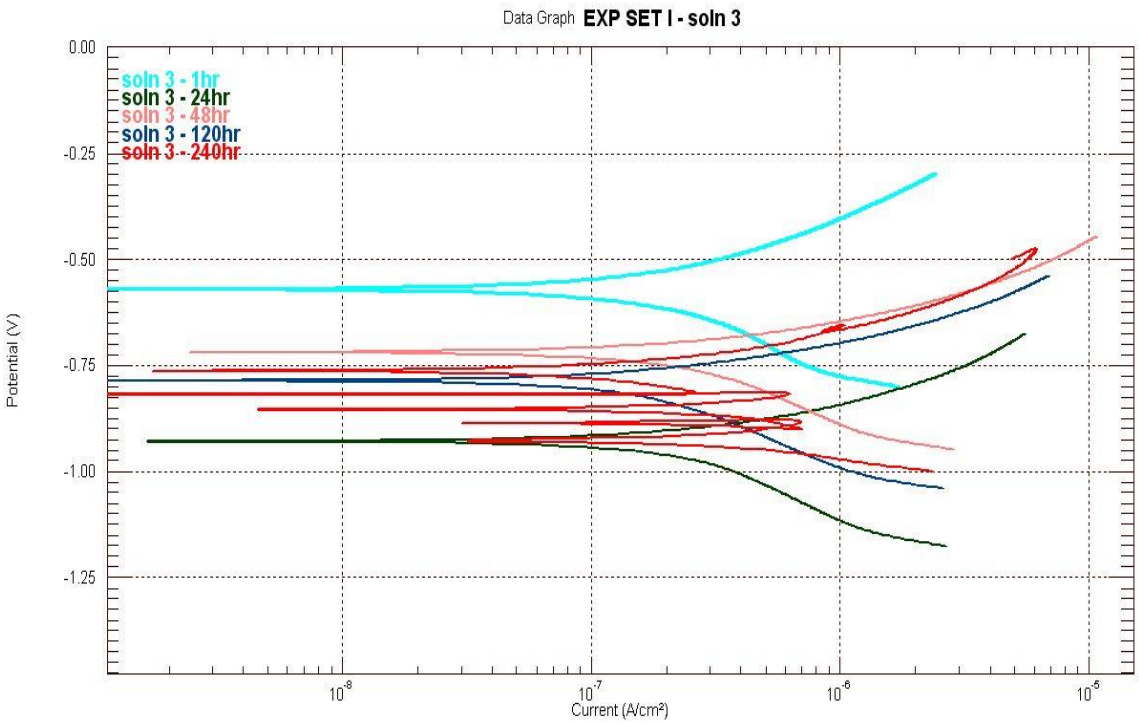


Fig.5.6 Tafel plot for Soln 3 at 0.25%

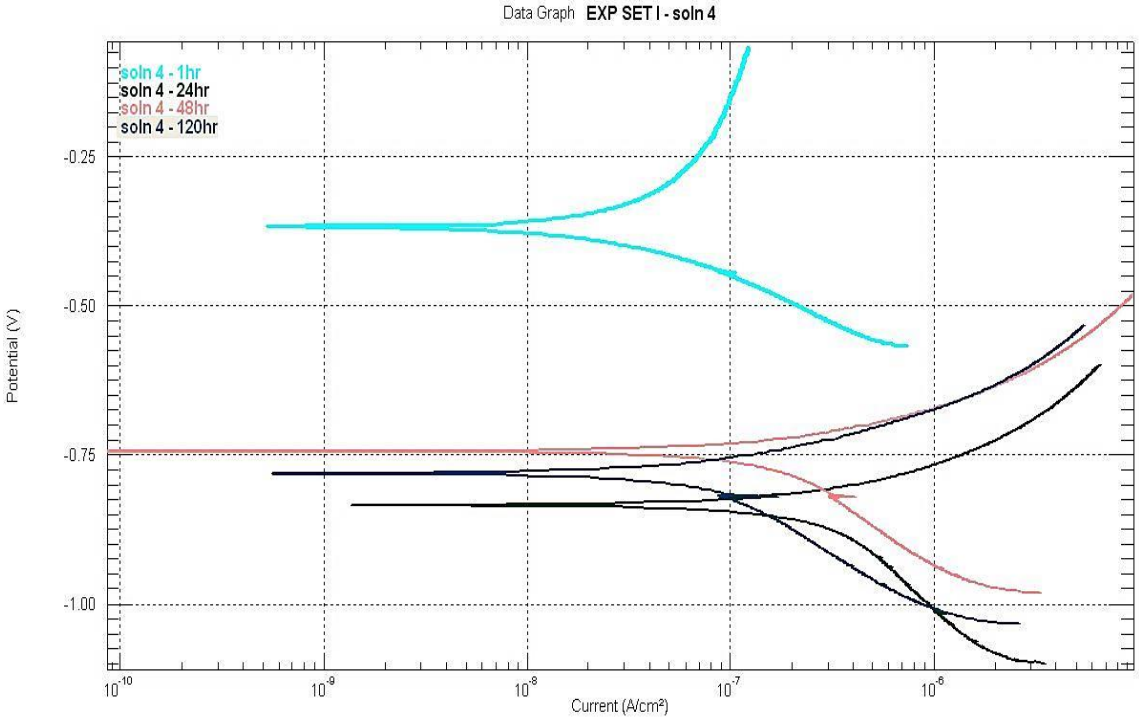


Fig.5.7 Tafel plot for Soln 4 at 0.25%

Tafel plot of specimen immersed in Soln 4 shown in Fig. 5.7 depicts that the E_{corr} for this specimen shifted towards active zone with increasing time of immersion. Specimen immersed in Soln 4 shows a little passive behaviour in later stage of

immersion time. It can be concluded that although this specimen shows passive behaviour in later stages yet it will not be effective in corrosion inhibition as the certain amount of corrosion has already been occurred.

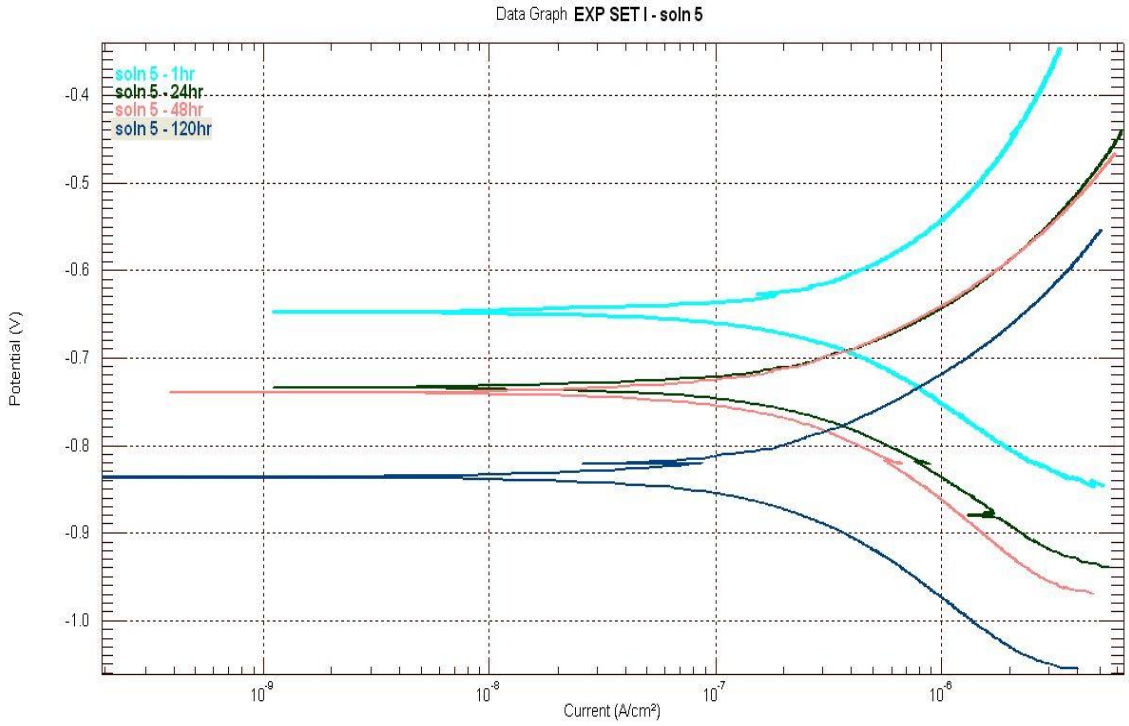


Fig.5.8 Tafel plot for Soln 5 at 0.25%

Tafel plot of specimen immersed in Soln 5 shown in Fig. 5.8 depicts that the E_{corr} for this specimen shifted towards active zone with increasing time of immersion. E_{corr} at 1 hour of immersion -0.65 V_{SCE} shifted to -0.845 V_{SCE} at 120 hours of immersion, showing active corrosion in specimen. Specimen immersed in Soln 5 did not showed any passive behaviour at all.

Tafel plot of specimen immersed in Soln 6 shown in Fig. 5.9 depicts that the E_{corr} for this specimen shifted towards active zone till 24 hours of immersion but a shift in passive zone was observed with further increase in time of immersion. Passive behaviour was observed in this specimen after 24 hours of immersion.

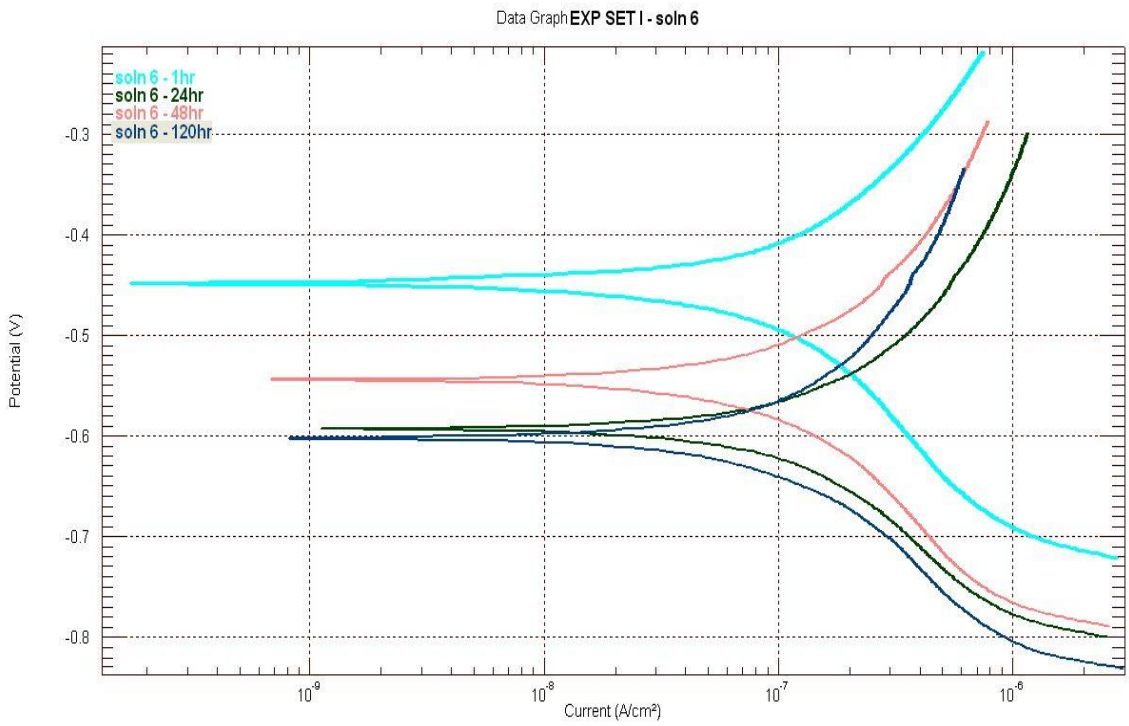


Fig.5.9 Tafel plot for Soln 6 at 0.25%

5.2.3 Comparing Performance of Chemicals as Corrosion Inhibitors

In order to compare the performance of chemicals as corrosion inhibitors, Tafel plots of the specimens immersed in these chemicals are compared with the Tafel plot of the specimen immersed in carbonated calcium hydroxide solution (Soln 1).

For the comparison of saturated calcium hydroxide solution (Soln 0) and carbonated solution (Soln 1), their Tafel plots at 120 hour and 240 hours are compared and presented in Fig. 5.10.

As can be observed from the Fig. 5.10, in sol. 0 (saturated $Ca(OH)_2$ having pH 12.1) steel shows a corrosion potential (E_{corr}) of -0.25 V_{SCE} with passive behaviour up to 0.0 V_{SCE} while in sol. 1 (carbonated solution with pH 8) the corrosion potential shifts towards the active zone with E_{corr} value of -0.70 V_{SCE} and no explicit passive behaviour was observed at 120 hour immersion. By increasing the immersion time to 240h, steel shows stabilized passive behaviour in sol. 0 with E_{corr} shifting to -0.275 V_{SCE} while in carbonated solution the rest potential further shifts towards the active zone with potential value of -0.78 V_{SCE} with no passive behaviour.

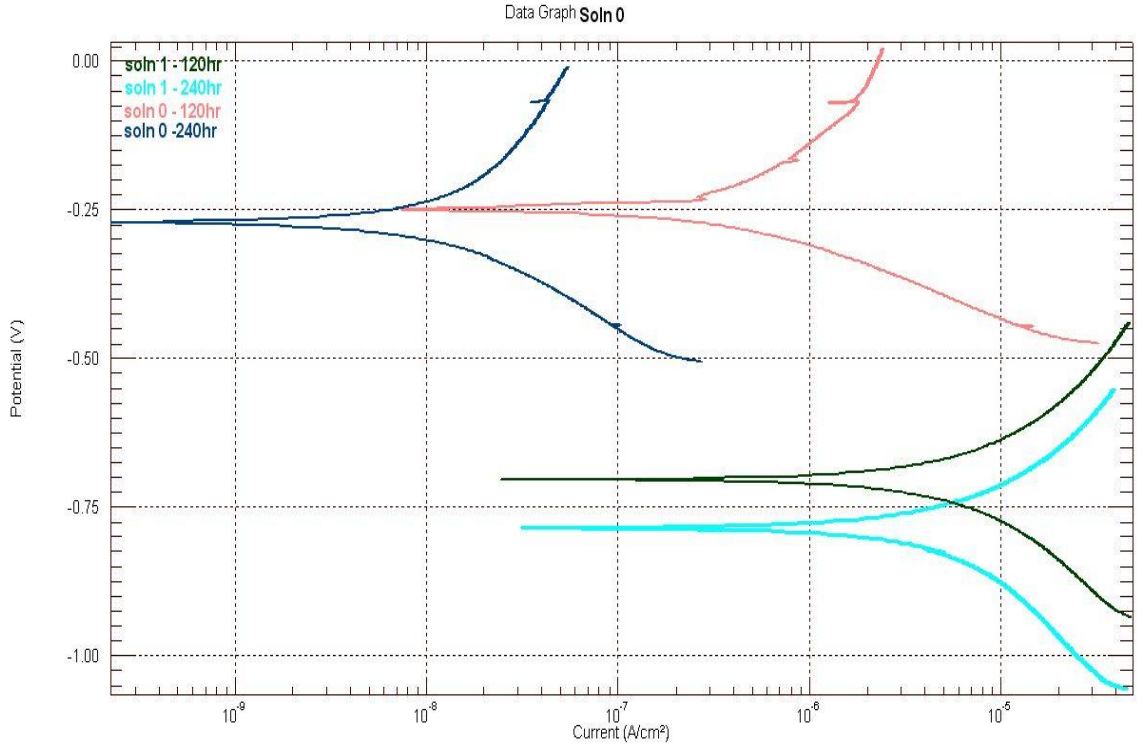


Fig. 5.10 Comparison of saturated and carbonated solution

Now the effect of addition of chemicals to carbonated solution is analysed by comparing the Tafel plots of specimen in different chemicals at various hours with Tafel plot of carbonated solution (Soln 1).

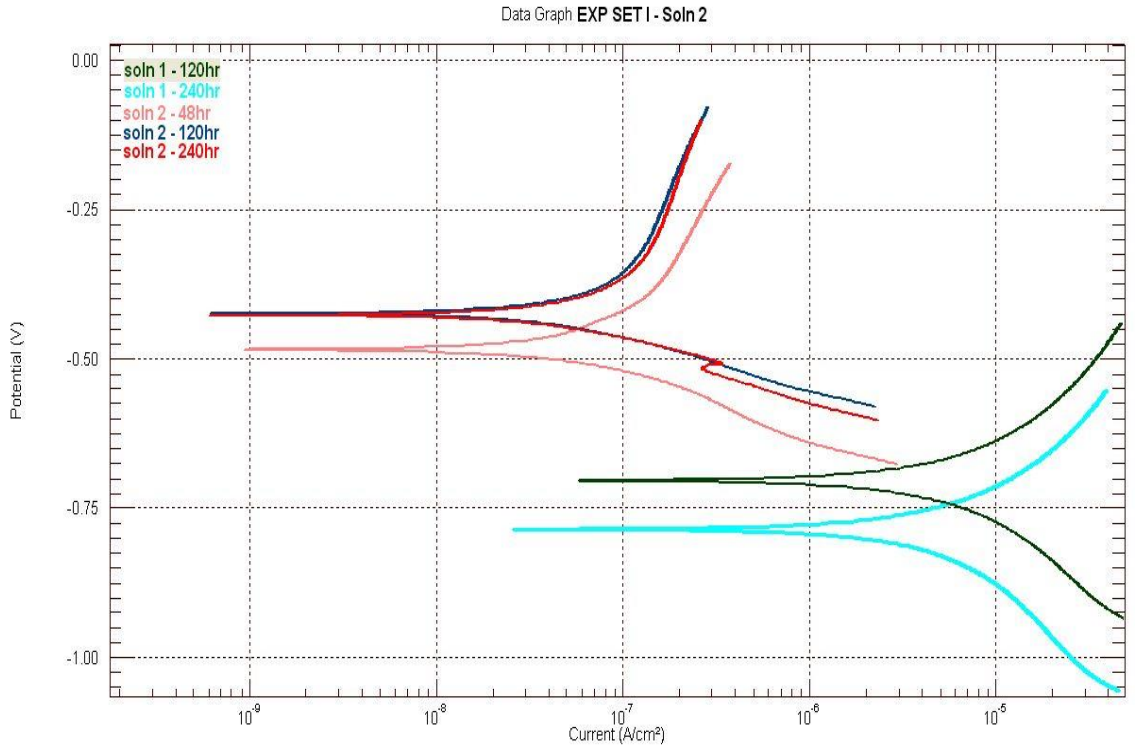


Fig. 5.11 Comparison of Soln 2 at 0.25% and Soln 1

Fig. 5.11, 5.12, 5.13, 5.14 and 5.15 respectively shows the comparison of Soln 2, Soln 3, Soln 4, Soln 5 and Soln 6 with Soln 1.

As can be observed from Fig. 5.11, E_{corr} of specimen in Soln 2 shifts toward passive zone with increasing time of immersion. Soln 2 shows E_{corr} of -0.48 V_{SCE} with passive behaviour upto -0.15 V_{SCE} at 48 hours of immersion, which shifts to -0.41 V_{SCE} with passive behaviour upto -0.10 V_{SCE} for further increase in immersion time. While, Soln 1 shows E_{corr} value of -0.70 V_{SCE} at 120 hours which shifts towards active zone with E_{corr} value of -0.78 V_{SCE} at 240 hours of immersion showing no passive behaviour.

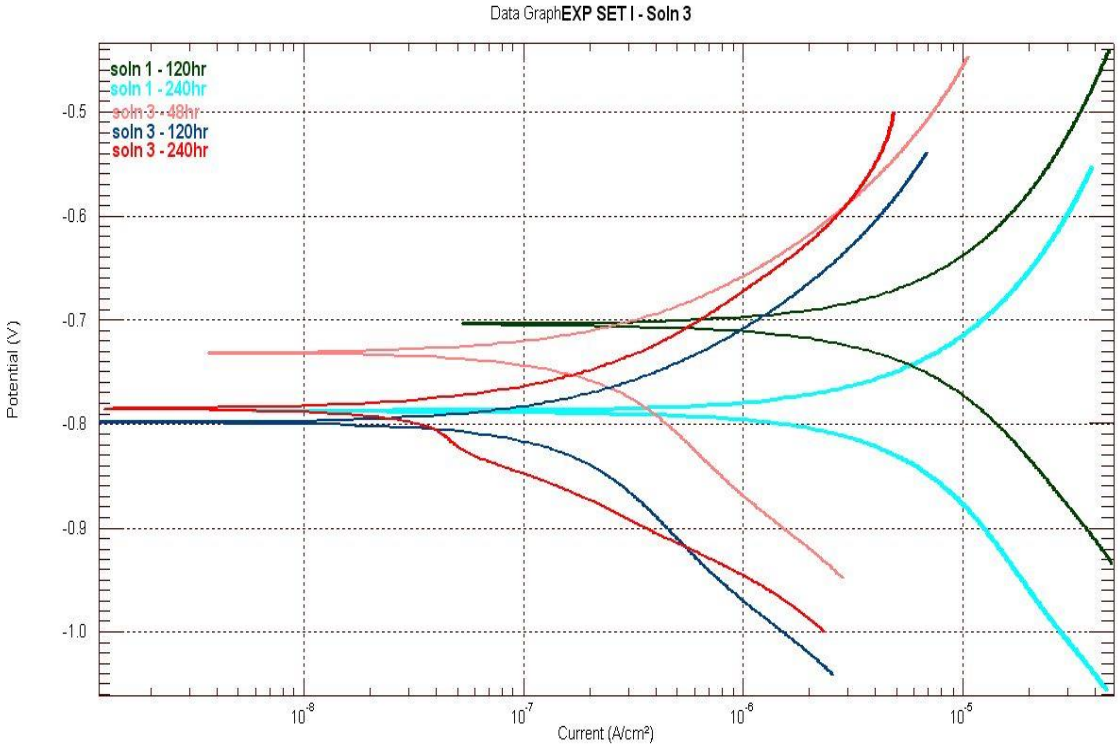


Fig. 5.12 Comparison of Soln 3 at 0.25% and Soln 1

Fig. 5.12 depicts that; Soln 3 shows E_{corr} value of -0.73 V_{SCE} and -0.80 V_{SCE} at 48 and 120 hours of immersion with no passive behaviour. A small shift towards passive zone with E_{corr} value of -0.785 V_{SCE} is observed at 240 hours of immersion. While, Soln 1 shows E_{corr} value of -0.70 V_{SCE} at 120 hours which shifts towards active zone with E_{corr} value of -0.78 V_{SCE} at 240 hours of immersion showing no passive behaviour.

It can be observed from Fig. 5.13; Soln 4 gives E_{corr} value of -0.78 V_{SCE} with no adequate passive behaviour at 120 hours of immersion, which is more negative than E_{corr} value of Soln 1 at 240 hours.

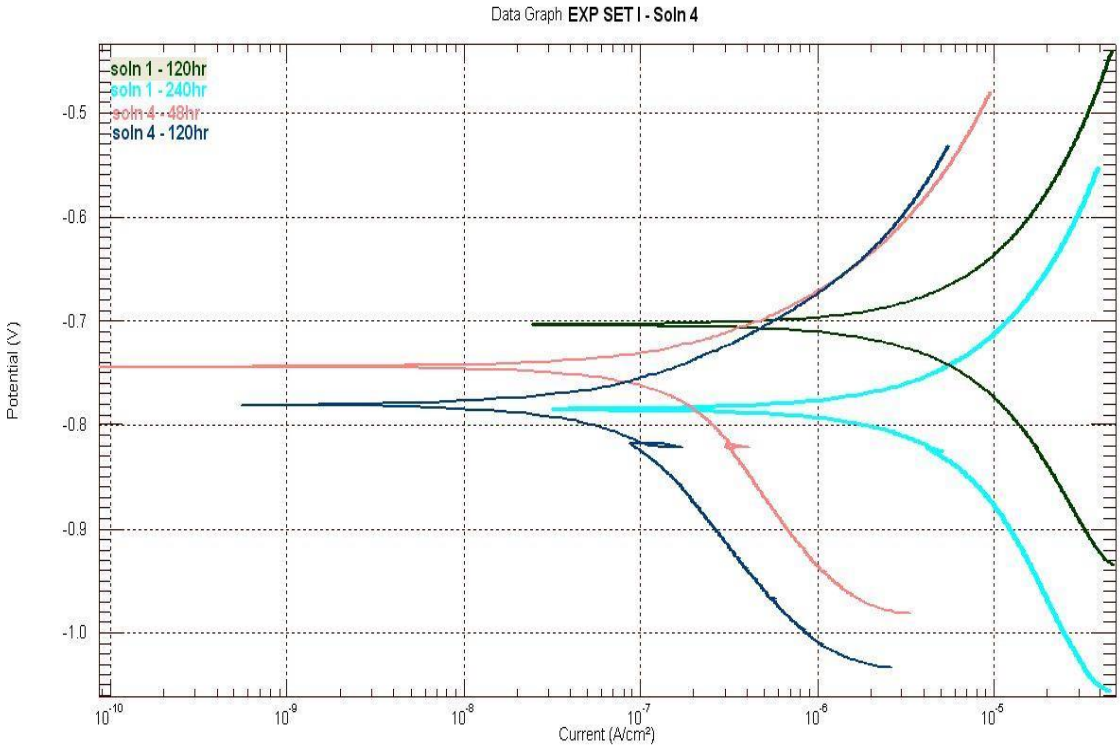


Fig. 5.13 Comparison of Soln 4 and Soln 1

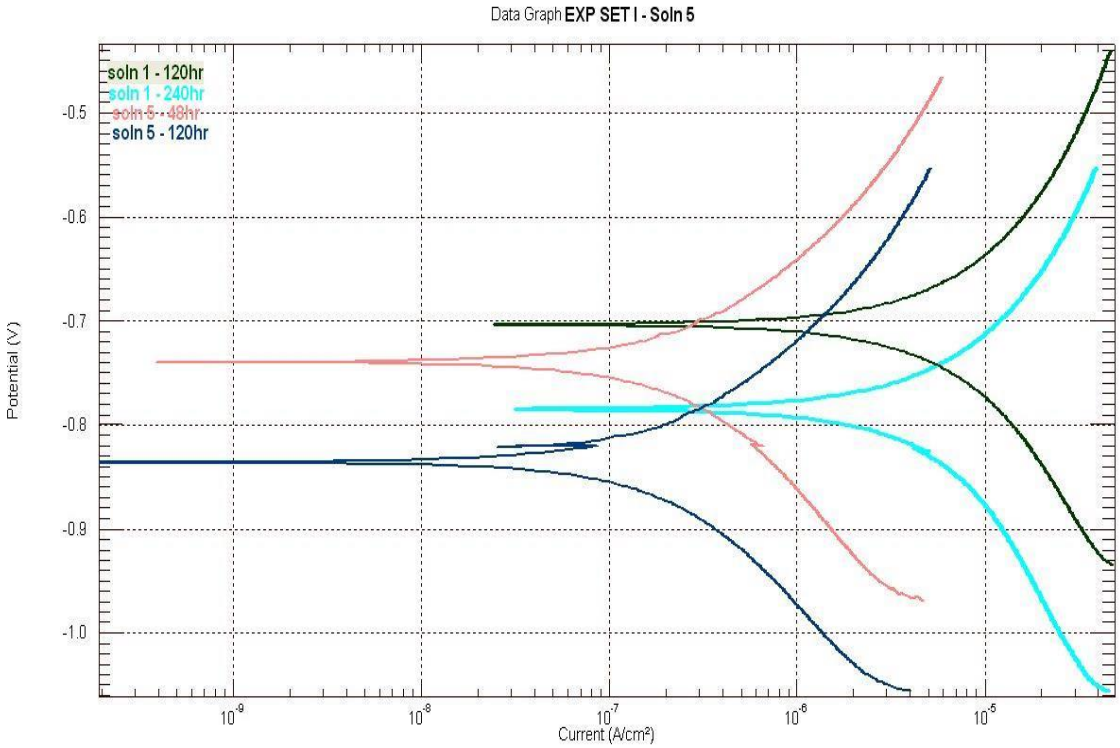


Fig. 5.14 Comparison of Soln 5 at 0.25% and Soln 1

It can be observed from Fig. 5.14; Soln 5 gives E_{corr} value of -0.835 V_{SCE} with no adequate passive behaviour at 120 hours of immersion, which is more negative than E_{corr} value of Soln 1 at 240 hours.

As can be observed from Fig. 5.15, Soln 6 shows E_{corr} value of -0.80 V_{SCE} with passive behaviour upto -0.34 V_{SCE} at 120 hours of immersion. Adequate passive behaviour is observed at all test durations in Soln 6 but the E_{corr} value is very close to E_{corr} value of Soln 1.

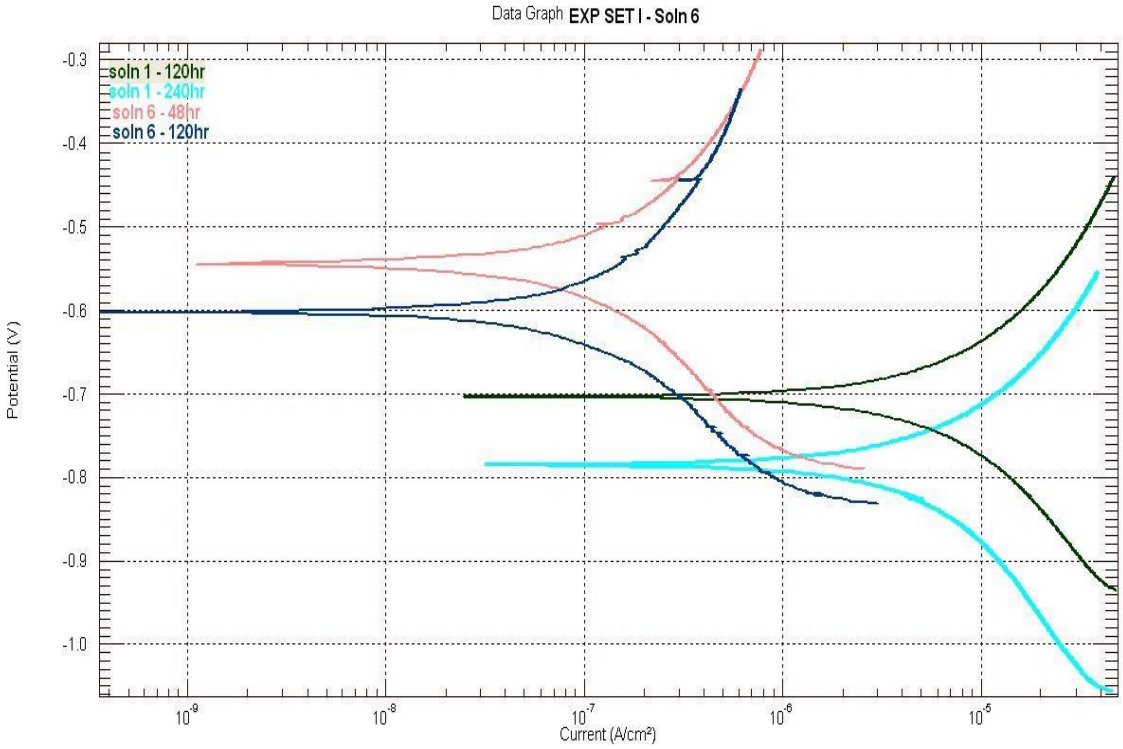


Fig. 5.15 Comparison of Soln 6 at 0.25% and Soln 1

5.2.4 Best Performance Among All Chemicals

From the discussion of results of experiment set I, it can be concluded that; Soln 2 gives the best performance among all the chemicals. Soln 2 was efficient in inhibiting corrosion in steel specimen by providing adequate passive behaviour.

5.3 EXPERIMENT SET II

In set II of experiment, 0.50% solutions of all chemical compounds were used. Steel specimens were immersed in these solutions for 240 hours. Monitoring of corrosion was done at 1 hour, 24 hours, 48 hours, 120 hours and 240 hours of immersion. Current and voltage per time, Long term LPR with Tafel extrapolation techniques were used for monitoring of corrosion. Details of the specimens are provided in the Table 5.3.

Table 5.3 Details of the specimens used in Experiment Set II

Sr No.	Abbreviation	Detail of Solution
1	Soln 0	Saturated calcium hydroxide solution
2	Soln 1	Carbonated calcium hydroxide solution
3	Soln 2	Tartaric acid (0.5%)
4	Soln 3	Maleic acid (0.5%)
5	Soln 4	Adipic acid (0.5%)
6	Soln 5	Phthalic acid (0.5%)
7	Soln 6	Oxalic acid (0.5%)

5.3.1 Results Obtained From Long Term LPR Test and Tafel Extrapolation

Long term LPR technique performed on ACM Field machine was used to record Rest Potential (Rp), I_{corr}, E_{corr} and corrosion rate. Tafel extrapolation technique was used for further modification of these results. Variation of I_{corr} with respect to immersion time and variation of corrosion rate with respect to immersion time for all the solutions are shown graphically in Fig. 5.16 and 5.17 respectively. Rest Potential (Rp), I_{corr}, E_{corr} and corrosion rate recorded for experiment set I are shown in Table 5.4.

Table 5.4 Experiment set II results by LPR and Tafel extrapolation

Sr No.	Sample	Time	Rp (-mV)	I_{corr} (mA/cm^2)	E_{corr} (-V)	Corrosion Rate (mm/year)
1	Soln 0	1 Hr	408.66	6.93E-04	0.41	7.95E-03
		24 Hr	613.55	3.41E-03	0.62	3.91E-02
		48 Hr	627.98	3.65E-03	0.63	4.16E-02
		120 Hr	497.84	3.93E-03	0.49	4.51E-02
		240 Hr	652.66	8.47E-03	0.65	9.90E-02
2	Soln 1	1 Hr	672.51	1.88E-02	0.67	2.15E-01
		24 Hr	698.22	5.58E-03	0.70	6.41E-02
		48 Hr	747.45	5.85E-03	0.75	6.65E-02
		120 Hr	703.31	5.98E-03	0.70	6.78E-02
		240 Hr	784.11	9.95E-03	0.78	1.15E-01
3	Soln 2	1 Hr	577.77	3.64E-03	0.57	4.17E-02
		24 Hr	652.96	4.53E-03	0.65	5.21E-02
		48 Hr	582.56	2.37E-03	0.58	3.47E-02
		120 Hr	540.75	1.09E-03	0.54	1.26E-02
		240 Hr	594.58	2.09E-03	0.59	2.40E-02
4	Soln 3	1 Hr	638.23	2.01E-02	0.63	2.32E-01
		24 Hr	861.6	1.01E-02	0.86	1.26E-01
		48 Hr	845.36	8.70E-03	0.84	8.85E-02
		120 Hr	797.7	6.30E-03	0.80	7.27E-02
		240 Hr	626.7	5.02E-03	0.63	5.77E-02
5	Soln 4	1 Hr	414.14	3.90E-04	0.42	4.49E-03
		24 Hr	676.54	3.21E-03	0.68	3.45E-02
		48 Hr	701.56	3.82E-03	0.72	4.10E-02
		120 Hr	775.65	4.14E-03	0.78	4.76E-02

		240 Hr	864.49	2.33E-03	0.87	2.67E-02
6	Soln 5	1 Hr	365.77	6.11E-04	0.37	7.02E-03
		24 Hr	695.7	6.74E-03	0.69	7.74E-02
		48 Hr	715.23	7.48E-03	0.71	8.45E-02
		120 Hr	770.76	2.95E-03	0.77	3.39E-02
		240 Hr	524.96	1.34E-03	0.53	1.54E-02
7	Soln 6	1 Hr	465.6	7.69E-04	0.47	8.83E-03
		24 Hr	492.31	7.70E-04	0.49	8.87E-03
		48 Hr	501.35	1.02E-03	0.50	9.51E-03
		120 Hr	509.24	1.73E-03	0.51	1.99E-02
		240 Hr	487.62	1.46E-03	0.48	1.67E-02

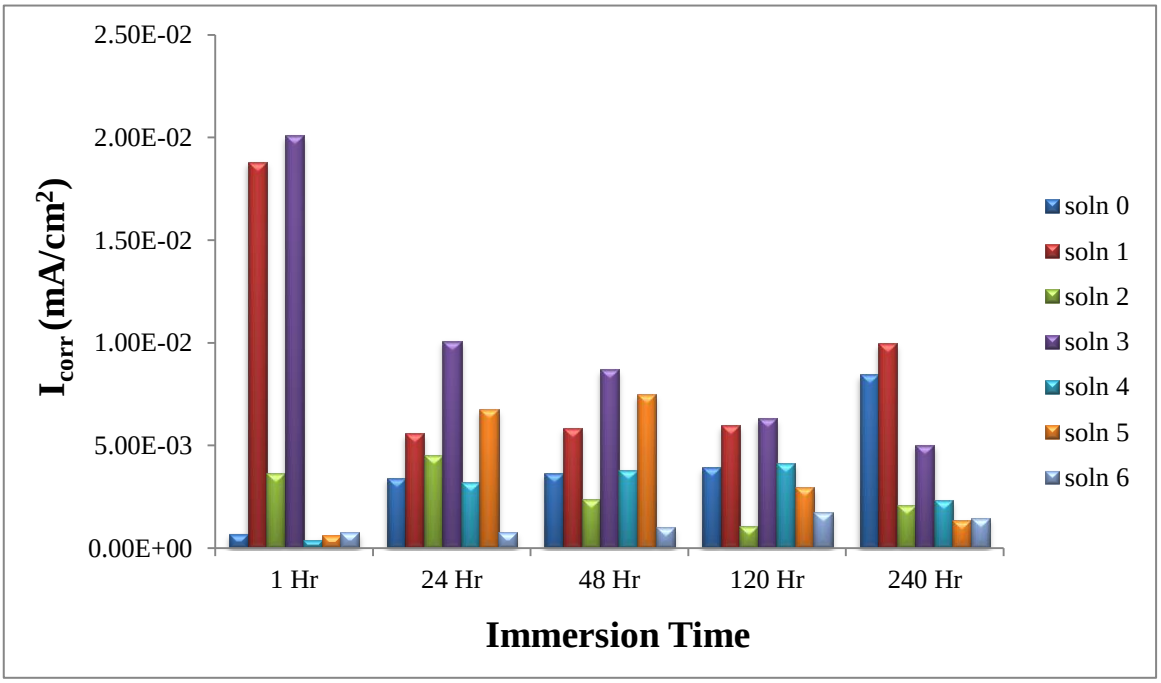


Fig.5.16 Variation of I_{corr} with respect to immersion time for all the solutions in experiment set II.

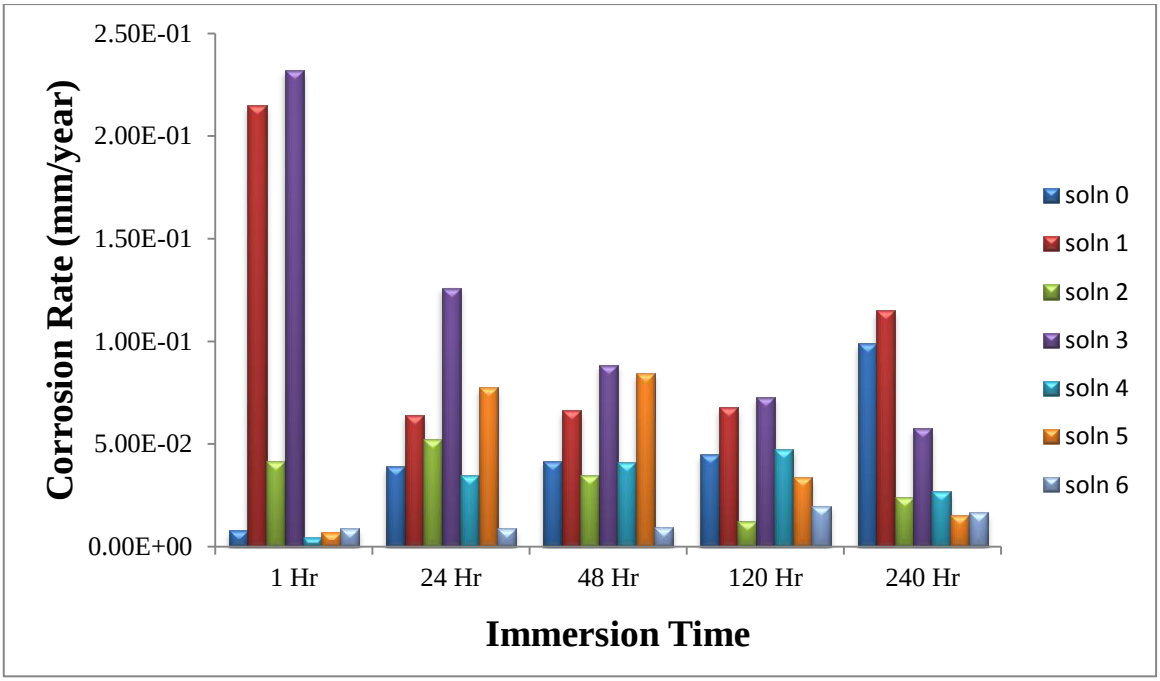


Fig.5.17 Variation of corrosion rate with respect to immersion time for all the solutions used in experiment set II.

The graphs Icorr vs Immersion time and Corrosion rate vs Immersion time for experiment set II shown in Fig. 5.16 and 5.17 depicts that performance of Soln 6 was best, corrosion rate in the specimen immersed in Soln 6 was very low during total time of immersion. Soln 2 also performed very well, corrosion rate was reduced with time of immersion. Soln 4 gave increasing rate of corrosion till 120 hours of immersion but corrosion rate was reduced after that. Soln 5 exhibits high corrosion rate upto 48 hours of immersion but corrosion rate was reduced for further immersion time. Soln 3 gave a very high rate of corrosion as compared to other solutions, corrosion rate was reduced with time of immersion but performance of this solution was not satisfactory.

5.3.2 Tafel Plots from ACM Field Machine

For better understanding of corrosion inhibition behaviour with respect to immersion time, tafel plots from ACM field machine are discussed for all the specimens.

The potential curve of the Tafel plot helps us to judge the corrosion potential (E_{corr}) values and the passive behaviour of rebar. Tafel plots of specimens immersed in different solutions at various test durations are presented in Fig 5.18-5.22.

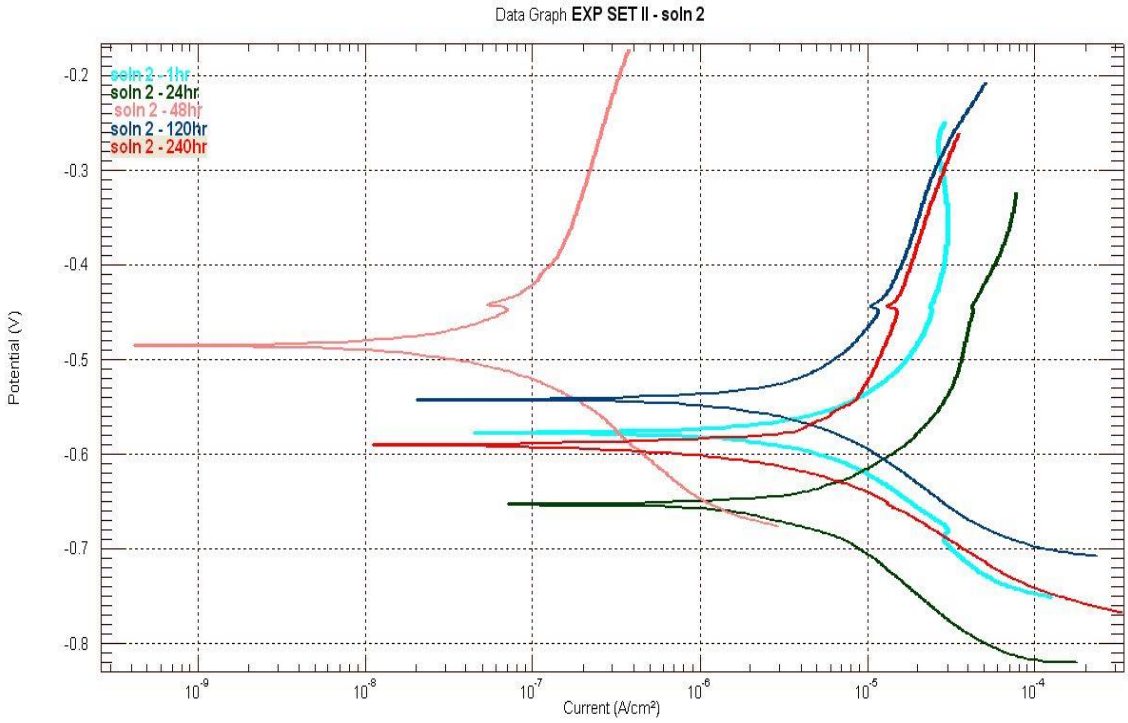


Fig. 5.18 Tafel plot of Soln 2 at 0.5 %

Tafel plot of specimen immersed in Soln 2 shown in Fig. 5.18 depicts that the E_{corr} for this specimen shifts towards active zone after 24 hours of immersion, which further shows adequate shift toward passive zone after 48 hours of immersion. Small shift towards active zone is observed in further increase in immersion time. Soln 2 shows a satisfactory passive behaviour throughout the time of immersion.

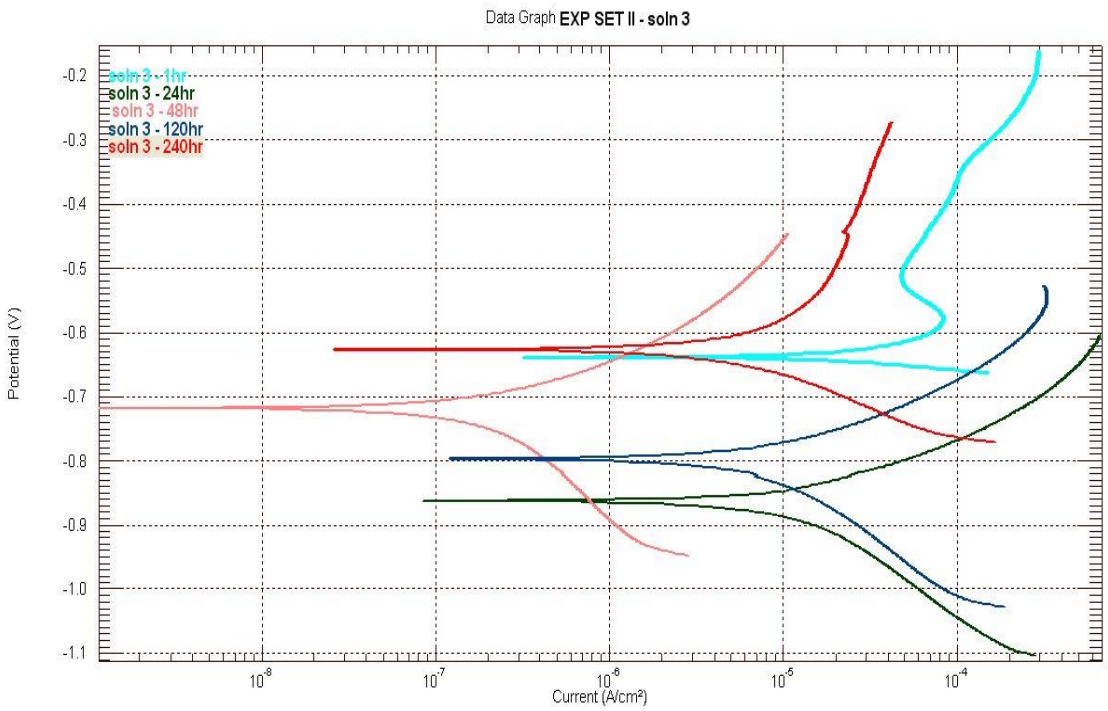


Fig. 5.19 Tafel plot of Soln 3 at 0.5 %

Tafel plot of specimen immersed in Soln 3 shown in Fig. 5.19 depicts that the E_{corr} for this specimen shifts towards active zone after 24 hours of immersion, which further shows adequate shift toward passive zone after 48 hours of immersion. Small shift towards active zone at 120 hours of immersion is observed. At 240 hours of immersion specimen shows an adequate passive behaviour with E_{corr} shifting toward passive zone. No passive behaviour was observed till 120 hours of immersion.

Tafel plot of specimen immersed in Soln 4 shown in Fig. 5.20 depicts that the E_{corr} value for the specimen shifts towards active zone with increasing immersion time. No passive behaviour is observed till 120 hours of immersion while, a little passive behaviour is observed at 240 hours of immersion.

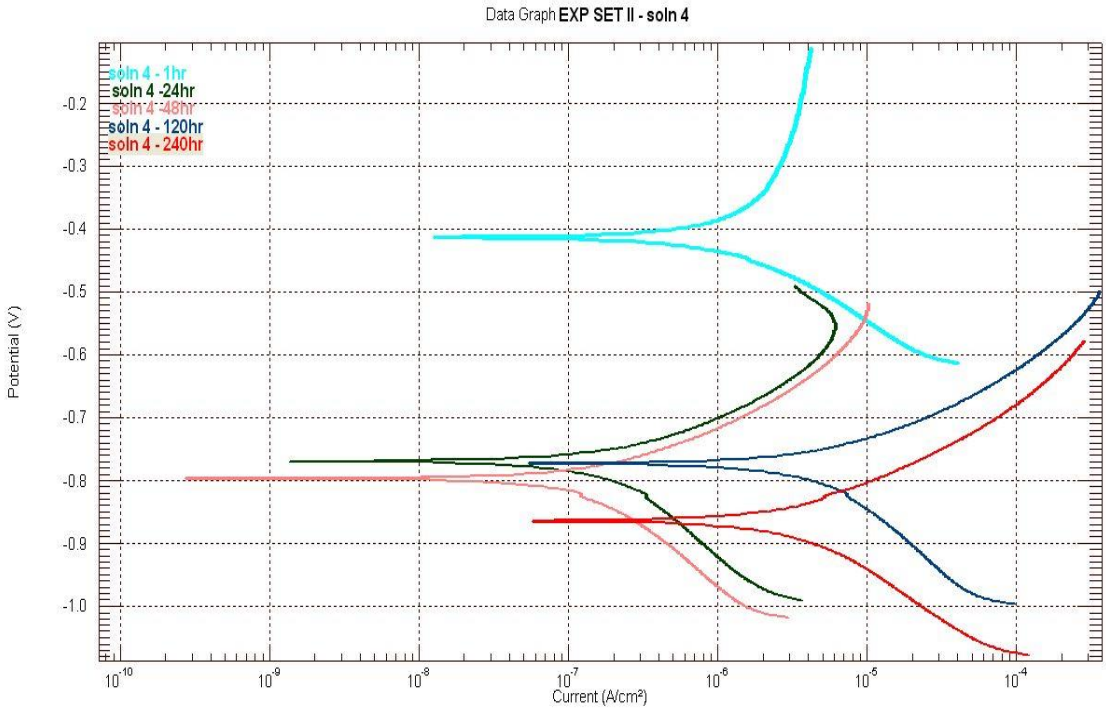


Fig. 5.20 Tafel plot of Soln 4 at 0.5 %

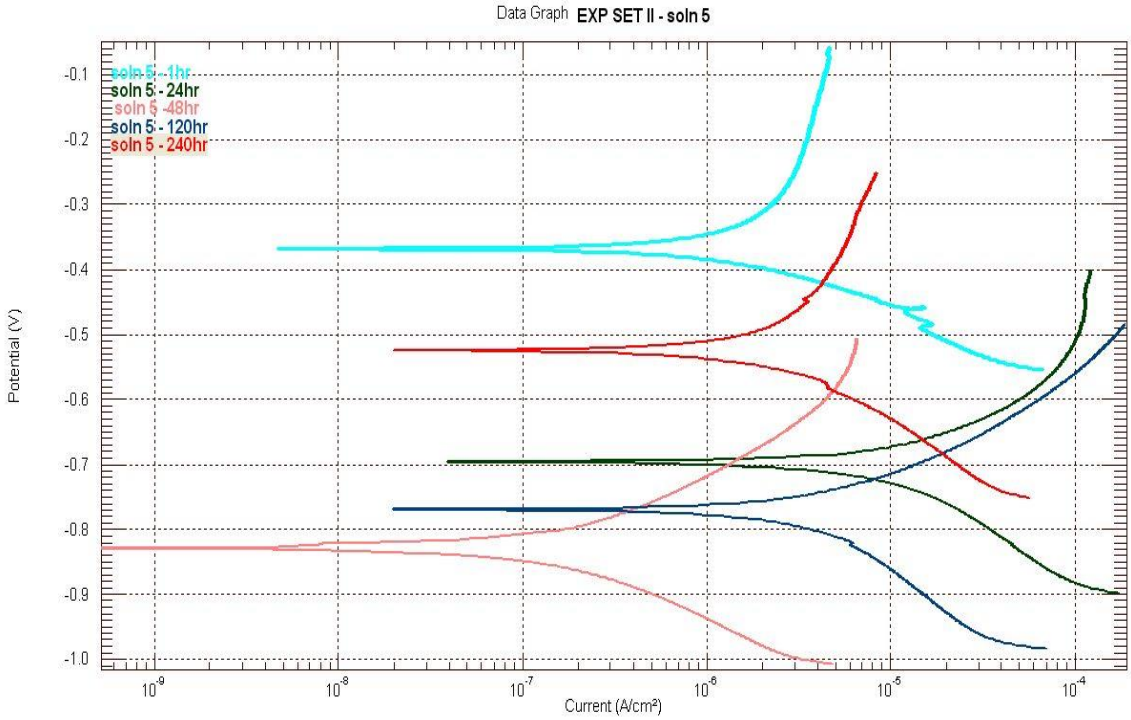


Fig. 5.21 Tafel plot of Soln 5 at 0.5 %

It can be observed from Tafel plot of specimen immersed in Soln 5 shown in Fig. 5.21; Ecorr value this specimen shifts towards the active zone till 120 hours of

immersion but shifts adequately to passive zone at 240 hours of immersion. Passive behaviour was observed at 240 hours of immersion.

Tafel plot of specimen immersed in Soln 6 shown in Fig. 5.22 depicts that the specimen shows noble passive behaviour throughout the total time of immersion. An absurd shift of E_{corr} value towards active zone was observed at 48 hours of immersion except that, the specimen shows very small drop in E_{corr} value till total immersion time. It can be concluded that, this specimen shows an efficient passive behaviour.

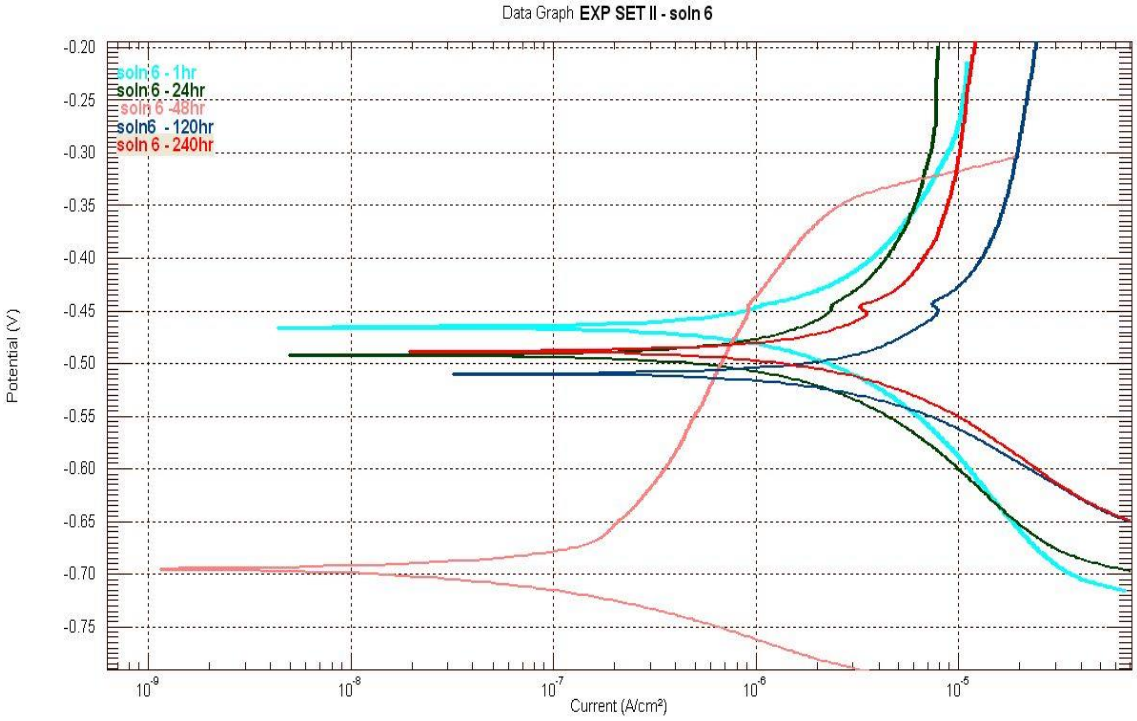


Fig. 5.22 Tafel plot of Soln 6 at 0.5 %

5.3.3 Comparing Performance of Chemicals as Corrosion Inhibitors

In order to compare the performance of chemicals as corrosion inhibitors, Tafel plots of the specimens immersed in these chemicals are compared with the Tafel plot of the specimen immersed in carbonated calcium hydroxide solution (Soln 1).

Fig. 5.23, 5.24, 5.25, 5.26 and 5.27 respectively shows the comparison of Soln 2, Soln 3, Soln 4, Soln 5 and Soln 6 with Soln 1.

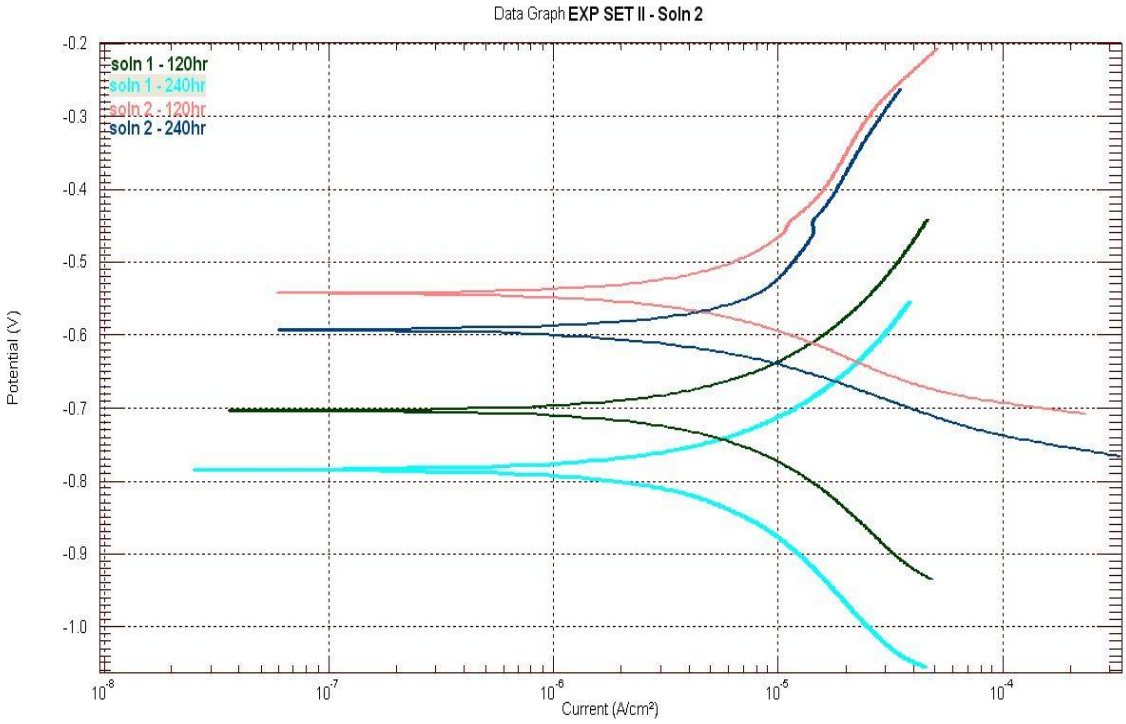


Fig. 5.23 Comparison of Soln 2 at 0.5 % and Soln 1

As can be observed from Fig. 5.23; Soln 2 has E_{corr} values in passive zone as compared to Soln 1. Adequate passive behaviour is observed in Soln 2 with increasing time of immersion. Soln 1 shows no passive behaviour.

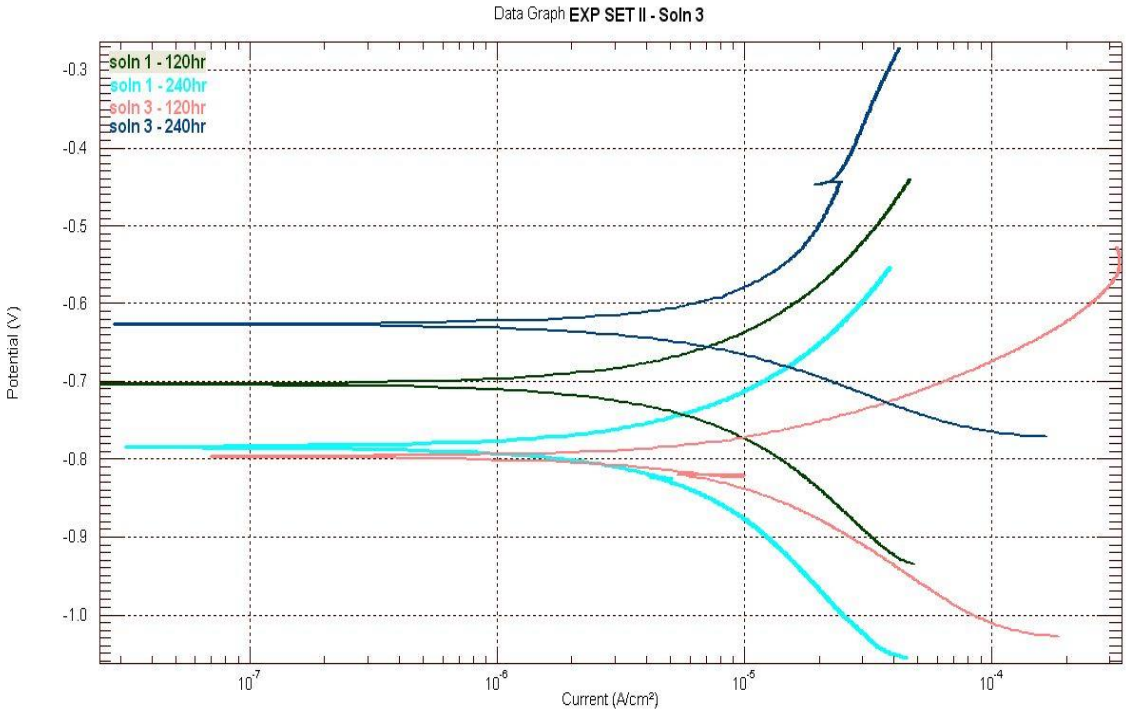


Fig. 5.24 Comparison of Soln 3 at 0.5 % and Soln 1

Fig. 5.24 depicts that; E_{corr} values for Soln 3 fall in active zone till 120 hours of immersion. Adequate shift of E_{corr} value towards passive zone is observed at 240 hours of immersion with satisfactory passive behaviour. E_{corr} values for Soln 3 are not much passive as compared to Soln 1.

Fig. 5.25 depicts that; E_{corr} value of specimen in Soln 4 shifts towards active zone with increasing time of immersion. Soln 4 does not shows satisfactory passive behaviour throughout the time of immersion. E_{corr} values for Soln 4 falls in active zone as compared to Soln 1.

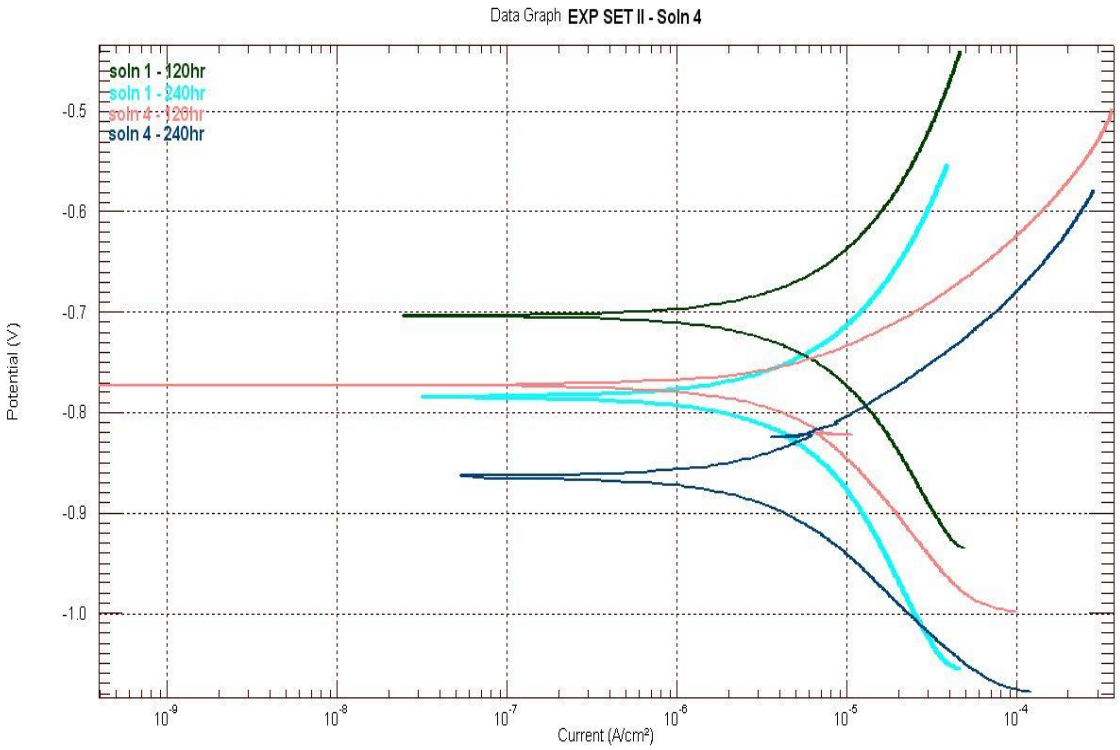


Fig. 5.25 Comparison of Soln 4 at 0.5 % and Soln 1

Fig. 5.26 depicts that; specimen immersed in Soln 5 shows passive behaviour at 240 hours of immersion. Soln 5 shows no passive behaviour till 120 hours of immersion with E_{corr} value falling in active zone as compared to E_{corr} value for Soln 1. E_{corr} value for Soln 5 shows a satisfactory shift towards passive zone at 240 hours of immersion.

Fig 5.27 depicts that; specimen immersed in Soln 6 shows a satisfactory passive behaviour at 120 and 240 hours of immersion. E_{corr} values for Soln 6 at 120 and 240 hours are -0.51 V_{SCE} and -0.49 V_{SCE} respectively, which are very passive as compared to E_{corr} values of Soln 1 at same time of immersion.

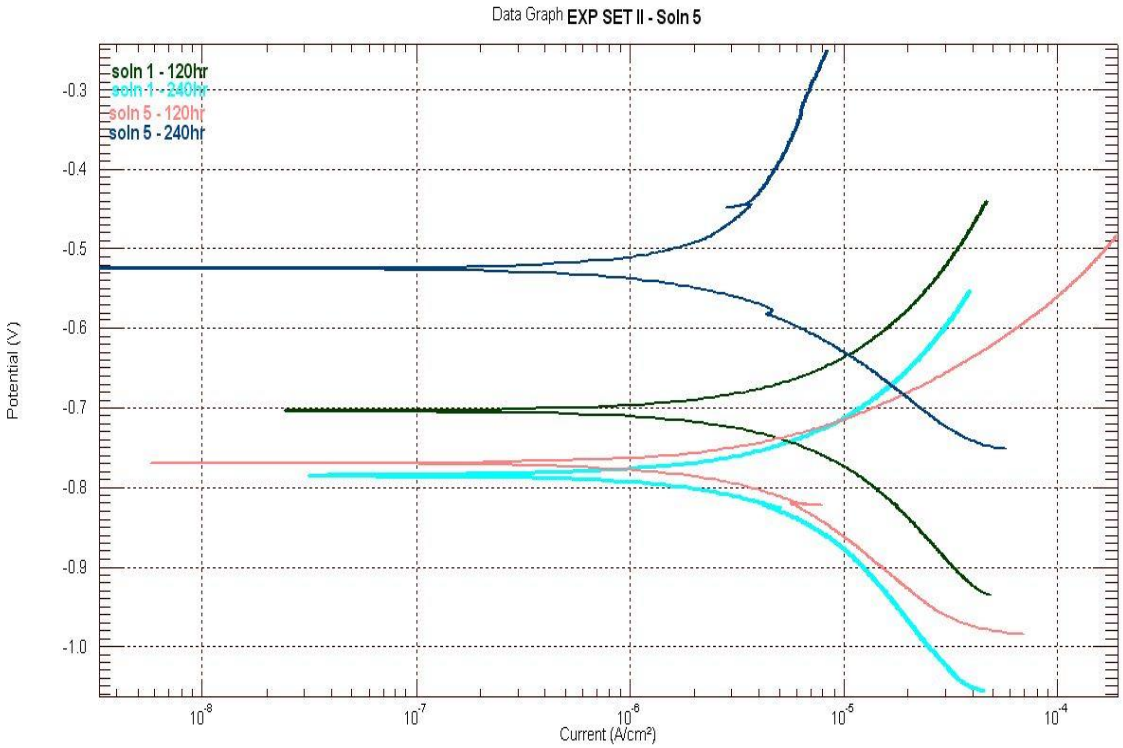


Fig. 5.26 Comparison of Soln 5 at 0.5 % and Soln 1

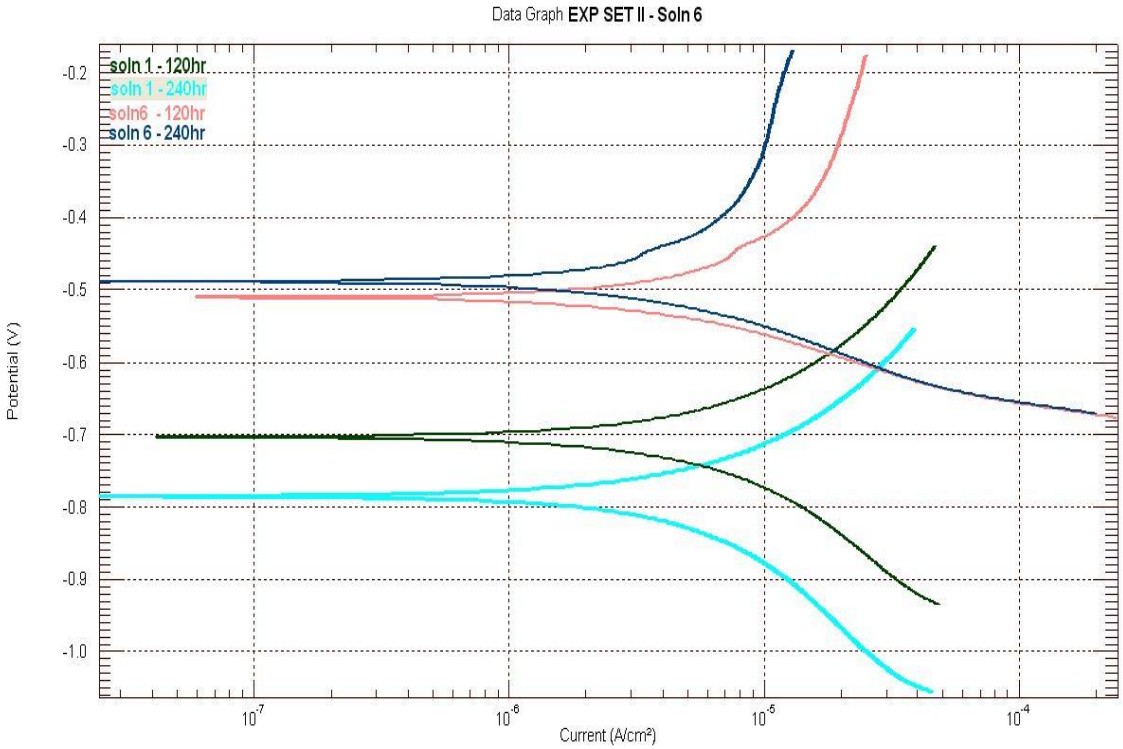


Fig. 5.27 Comparison of Soln 6 at 0.5 % and Soln 1

5.3.4 Best Performance Among All Chemicals

From the discussion of results of experiment set II, it can be concluded that; all chemicals performed adequately with 0.5 %. Soln 2 and Soln 6 give the best performance among all the chemicals. Soln 2 and Soln 6 were efficient in inhibiting corrosion in steel specimen by providing adequate passive behaviour throughout the time of immersion.

5.4 EXPERIMENT SET III

In set III of experiment, 1% solutions of all chemical compounds were used. Steel specimens were immersed in these solutions for 240 hours. Monitoring of corrosion was done at 1 hour, 24 hours, 48 hours, 120 hours and 240 hours of immersion. Current and voltage per time and Long term LPR with Tafel extrapolation techniques were used for monitoring of corrosion. Details of the specimens are provided in the Table 5.5.

Table 5.5 Details of solutions used for experiment set III.

Sr No.	Abbreviation	Details of solution
1	Soln 0	Saturated calcium hydroxide solution
2	Soln 1	Carbonated calcium hydroxide solution
3	Soln 2	Tartaric acid (1%)
4	Soln 3	Maleic acid (1%)
5	Soln 4	Adipic acid (1%)
6	Soln 5	Phthalic acid (1%)
7	Soln 6	Oxalic acid (1%)

5.4.1 Results Obtained From Long Term LPR Test and Tafel Extrapolation

Long term LPR technique performed on ACM Field machine was used to record Rest Potential (Rp), I_{corr}, E_{corr} and corrosion rate. Tafel extrapolation technique was used for further modification of these results. Variation of I_{corr} with respect to immersion time and variation of corrosion rate with respect to immersion time for all the solutions are shown graphically in Fig. 5.28 and 5.29 respectively. Rest Potential (Rp), I_{corr}, E_{corr} and corrosion rate recorded for experiment set III are shown in Table 5.6.

Table 5.6 Experiment set III results by LPR and Tafel extrapolation

Sr No.	Sample	Time	Rp (-mV)	I_{corr} (mA/cm^2)	E_{corr} (-V)	Corrosion Rate (mm/year)
1	Soln 0	1 Hr	408.66	6.93E-04	0.41	7.95E-03
		24 Hr	613.55	3.41E-03	0.62	3.91E-02
		48 Hr	627.98	3.65E-03	0.63	4.16E-02
		120 Hr	497.84	3.93E-03	0.49	4.51E-02
		240 Hr	652.66	8.47E-03	0.65	9.90E-02
2	Soln 1	1 Hr	672.51	1.88E-02	0.67	2.15E-01
		24 Hr	698.22	5.58E-03	0.70	6.41E-02
		48 Hr	747.45	5.85E-03	0.75	6.65E-02
		120 Hr	703.31	5.98E-03	0.70	6.78E-02
		240 Hr	784.11	9.95E-03	0.78	1.15E-01
3	Soln 2	1 Hr	676.6	8.80E-03	0.675	1.00E-01
		24 Hr	718.2	6.00E-03	0.72	6.87E-02
		48 Hr	685.42	1.45E-02	0.68	1.67E-01
		120 Hr	700.87	1.01E-02	0.70	1.16E-01
		240 Hr	720	1.00E-02	0.73	1.15E-01
4	Soln 3	1 Hr	793.4	8.00E-03	0.795	9.20E-02
		24 Hr	795.4	5.20E-02	0.795	6.02E-01
		48 Hr	798.12	7.20E-02	0.80	8.30E-01
		120 Hr	802.28	7.70E-02	0.80	8.75E-01
		240 Hr	811.66	8.70E-02	0.82	9.40E-01
5	Soln 4	1 Hr	415.44	2.46E-03	0.42	2.80E-02
		24 Hr	729.1	1.50E-02	0.72	1.72E-01
		48 Hr	800	3.00E-02	0.80	3.14E-01

		120 Hr	785.7	5.80E-02	0.78	6.72E-01
		240 Hr	839.5	8.70E-03	0.84	1.00E-01
6	Soln 5	1 Hr	403.22	2.70E-03	0.40	3.13E-02
		24 Hr	767.43	1.73E-02	0.77	1.99E-01
		48 Hr	829.5	3.01E-02	0.83	3.16E-01
		120 Hr	782.2	6.70E-02	0.78	7.70E-01
		240 Hr	851	1.30E-02	0.85	1.50E-01
7	Soln 6	1 Hr	400.48	1.40E-03	0.40	1.60E-02
		24 Hr	510.4	4.60E-03	0.52	5.30E-02
		48 Hr	694.8	1.22E-02	0.69	1.41E-01
		120 Hr	644.15	1.72E-02	0.64	2.01E-01
		240 Hr	930.5	3.40E-02	0.93	4.50E-01

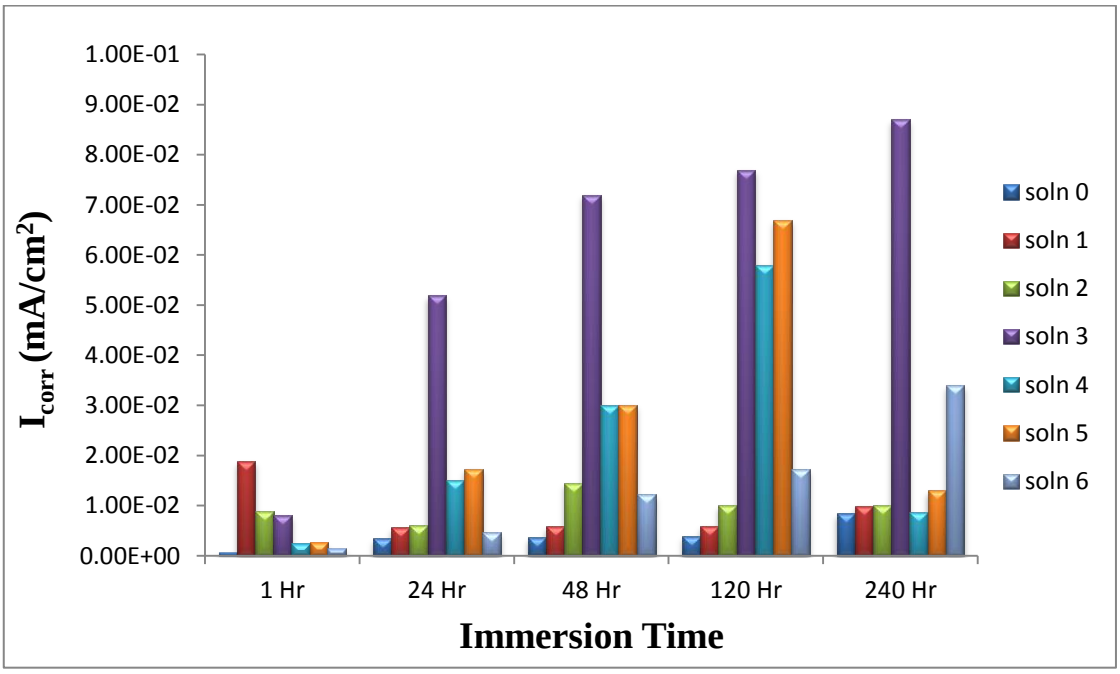


Fig.5.28 Variation of I_{corr} with respect to immersion time for all the solutions in experiment set III.

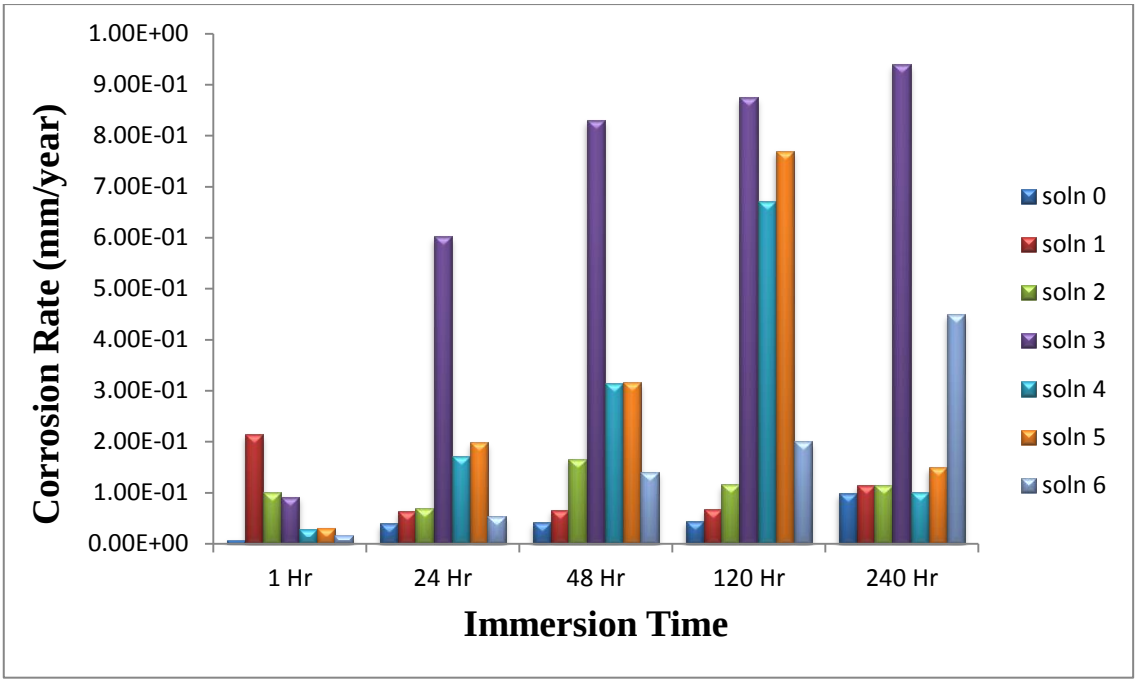


Fig.5.29 Variation of corrosion rate with respect to immersion time for all the solutions used in experiment set III.

The graphs Icorr vs Immersion time and Corrosion rate vs Immersion time for experiment set III shown in Fig. 5.28 and 5.29 respectively depicts that Soln 2 is very effective as corrosion inhibitor, corrosion rate was reduced throughout the immersion time. Soln 6 exhibits low rate of corrosion up to 120 hours but corrosion rate increases after 120 hours of immersion. Corrosion rate in specimens immersed in Soln 4 and Soln 5 was increasing rapidly up to 120 hours but a sudden drop in corrosion rate at 240 hours was noticed. Soln 3 was not at all effective in reducing corrosion rate during total time of immersion in fact corrosion rate was increased very rapidly.

5.4.2 Tafel Plots from ACM Field Machine

For better understanding of corrosion inhibition behaviour with respect to immersion time, tafel plots from ACM field machine are discussed for all the specimens.

The potential curve of the Tafel plot helps us to judge the corrosion potential (E_{corr}) values and the passive behaviour of rebar. Tafel plots of specimens immersed in different solutions at various test durations are presented in Fig 5.30-5.34.

As it can be observed from Fig 5.30; specimen in Soln 2 does not shows satisfactory passive behaviour throughout the immersion time. E_{corr} values for this specimen shift toward active zone with increasing time of immersion.

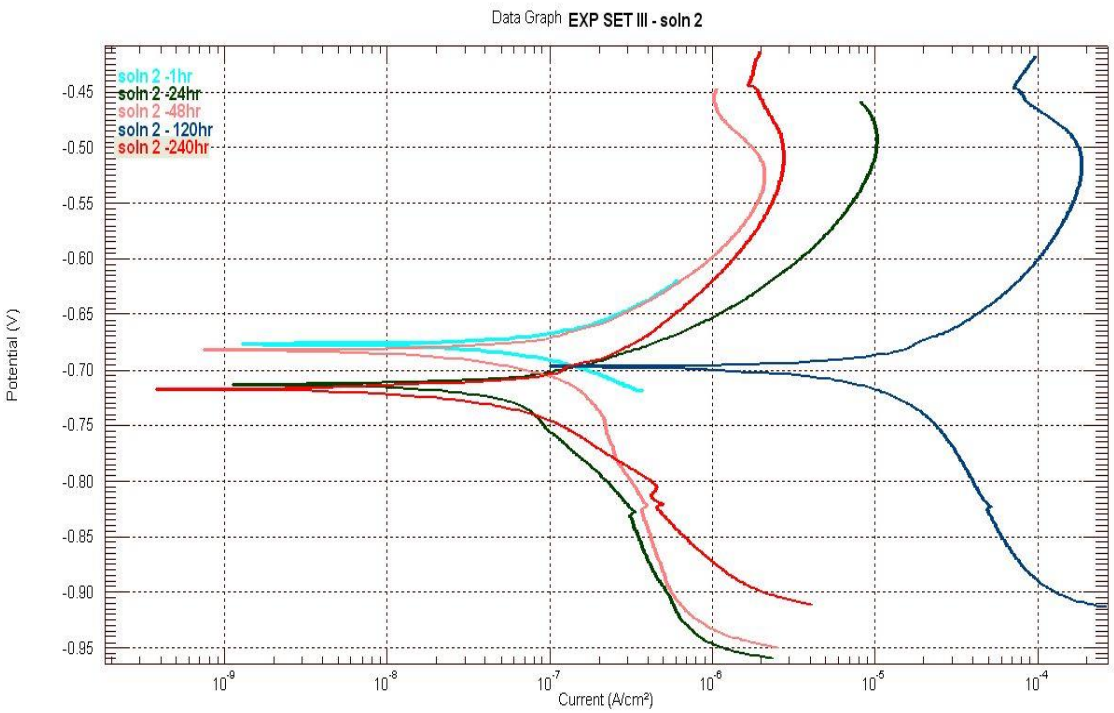


Fig. 5.30 Tafel plot of Soln 2 at 1%

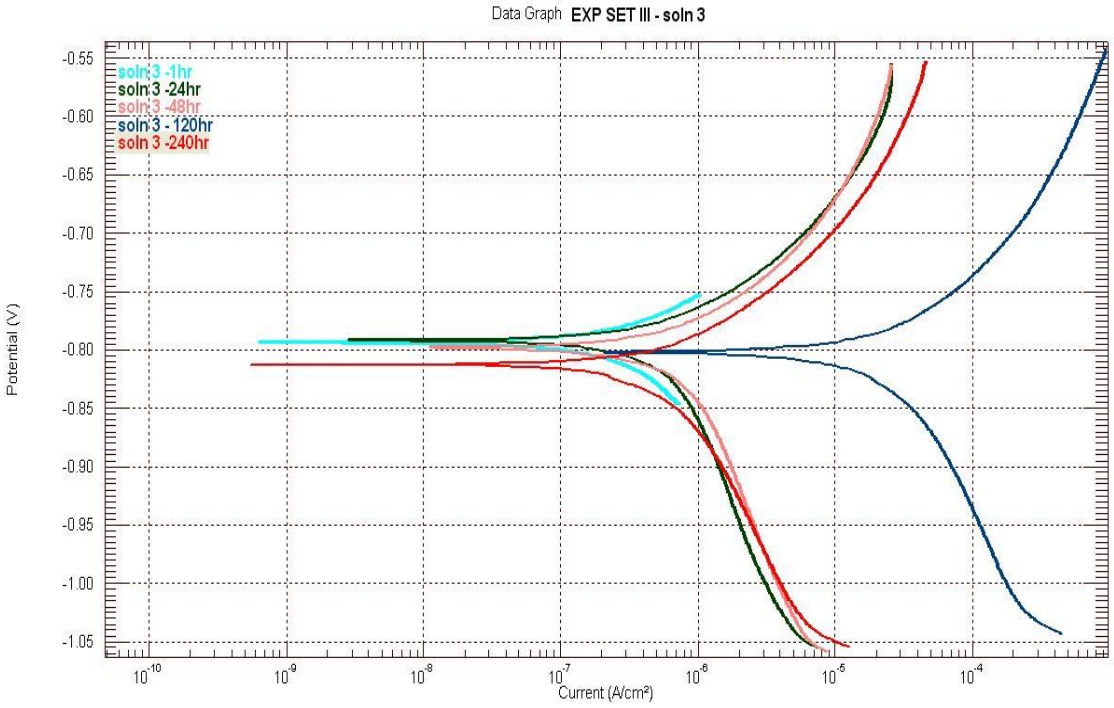


Fig. 5.31 Tafel plot of Soln 3 at 1%

Tafel plot of Soln 3 shown in Fig. 5.31 depicts; E_{corr} values for this specimen shift slightly towards active zone with increasing time of immersion. Specimen immersed in the Soln 3 does not show any passive behaviour throughout the total immersion time. Also, the E_{corr} values of specimen immersed in this solution depict high rate of corrosion.

Tafel plot for specimen in Soln 4 shown in Fig. 5.32 depicts; E_{corr} value for the specimen shifts to active zone with increasing time of immersion. No adequate passive behaviour is observed in the specimen immersed in Soln 4.

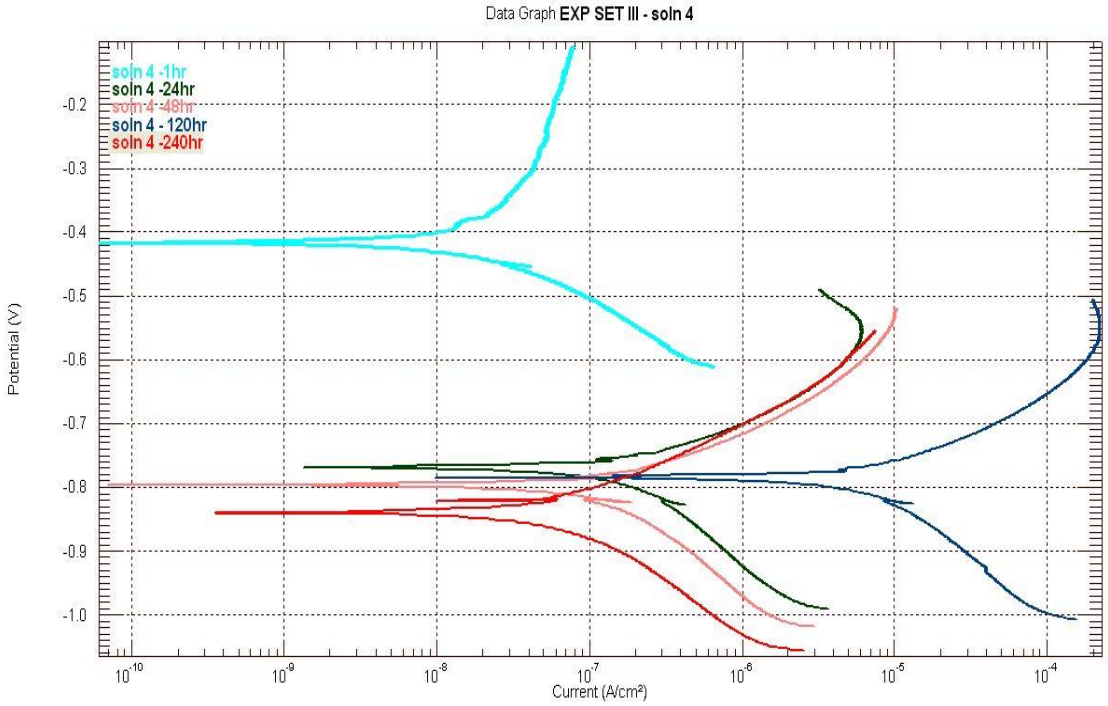


Fig. 5.32 Tafel plot of Soln 4 at 1%

Tafel plot for specimen in Soln 5 shown in Fig. 5.33 depicts; E_{corr} value for the specimen shifts to active zone with increasing time of immersion. Passive behaviour is observed at 240 hours of immersion. No passive behaviour is observed till 120 hours of immersion.

Tafel plot for specimen in Soln 6 shown in Fig. 5.34 depicts; the specimen shows adequate passive behaviour till 120 hours of immersion. Passive behaviour was not satisfactory at 240 hours of immersion. E_{corr} values for the specimen shifts toward active zone with increase in time of immersion. E_{corr} value of specimen shifted from -

0.40 V_{SCE} at 1 hour to -0.92 V_{SCE} at 240 hours. Although this specimen shows an adequate passive behaviour yet, E_{corr} value shifts toward active zone.

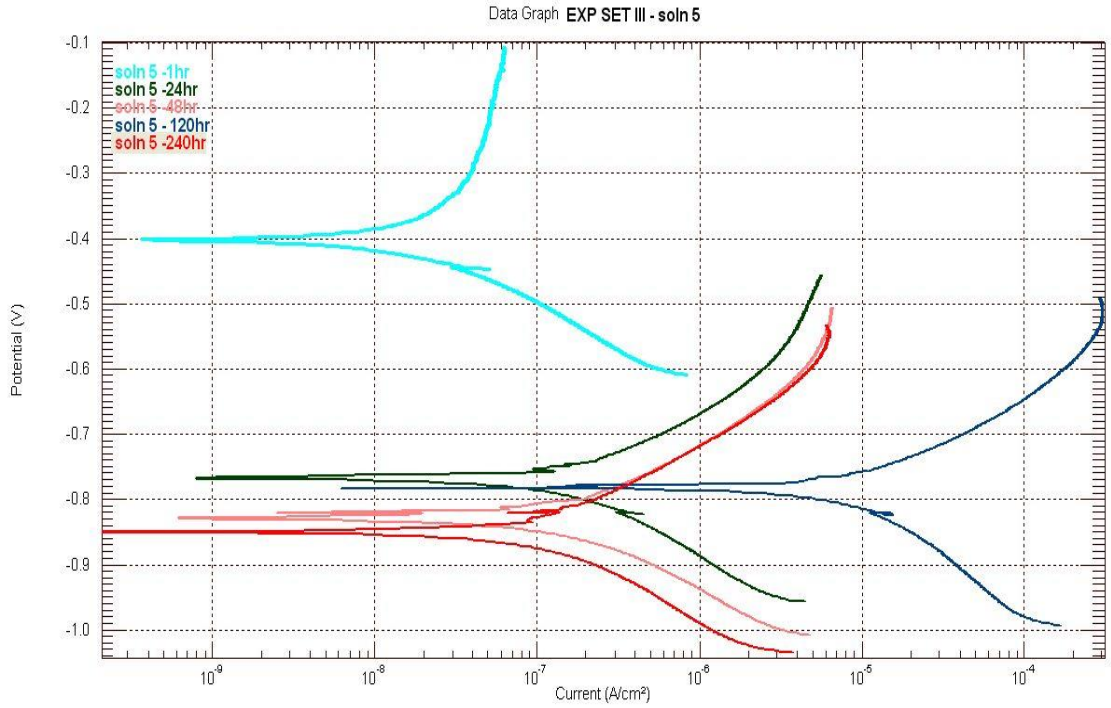


Fig. 5.33 Tafel plot of Soln 5 at 1%

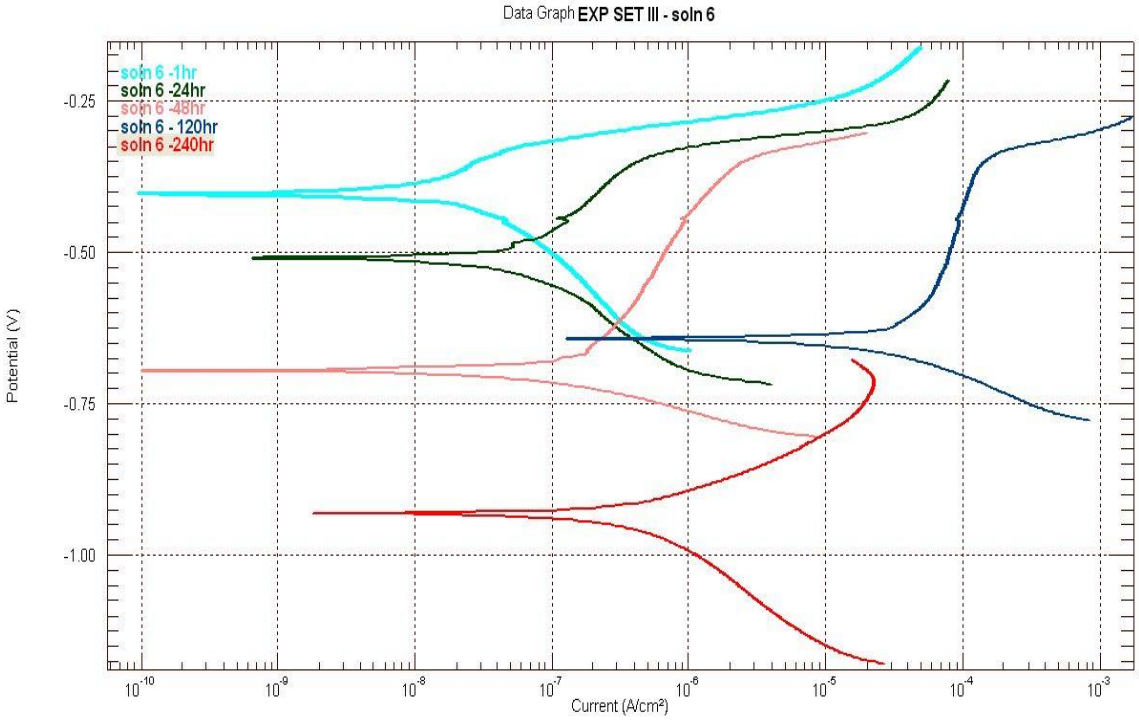


Fig. 5.34 Tafel plot of Soln 6 at 1%

5.4.3 Comparing Performance of Chemicals as Corrosion Inhibitors

In order to compare the performance of chemicals as corrosion inhibitors, Tafel plots of the specimens immersed in these chemicals are compared with the Tafel plot of the specimen immersed in carbonated calcium hydroxide solution (Soln 1).

Fig. 5.35, 5.36, 5.37, 5.38 and 5.39 respectively shows the comparison of Soln 2, Soln 3, Soln 4, Soln 5 and Soln 6 with Soln 1.

As it can be observed from Fig. 5.35; E_{corr} value for the specimen immersed in Soln 2 does not varies much. E_{corr} value for this specimen at 120 and 240 hours of immersion is close to the E_{corr} value of specimen in Soln 1 at 120 hours i.e. -0.70 V_{SCE}. No passive behaviour is observed at any time of immersion.

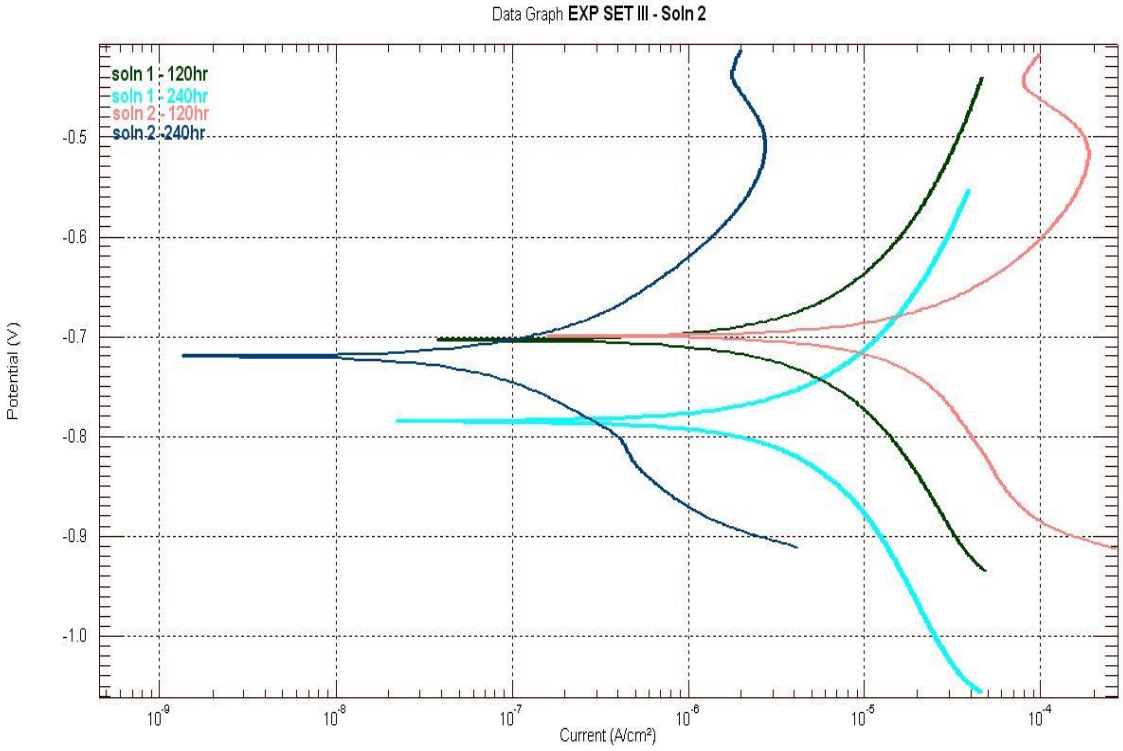


Fig. 5.35 Comparison of Soln 2 at 1% and Soln 1

As it can be observed from Fig. 5.36; specimen immersed in Soln 3 does not show any passive behaviour throughout the total time of immersion. E_{corr} value of this specimen does not vary much with immersion time and is in active zone as compared to specimen in Soln 1.

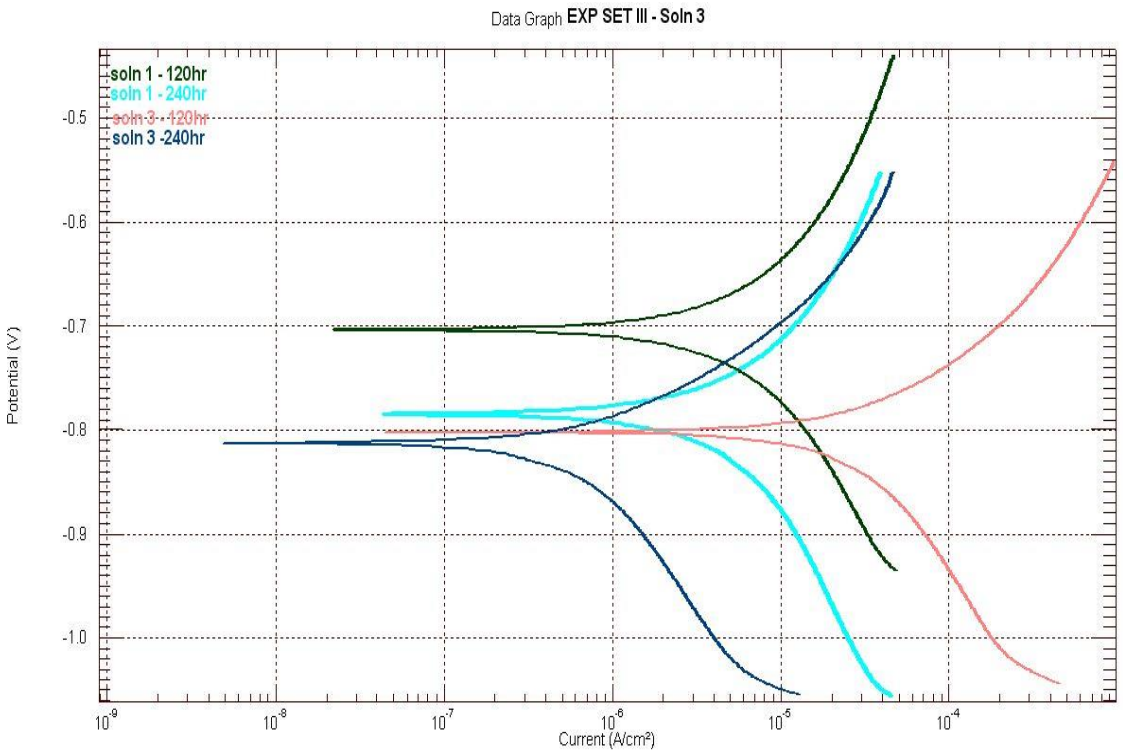


Fig. 5.36 Comparison of Soln 3 at 1% and Soln 1

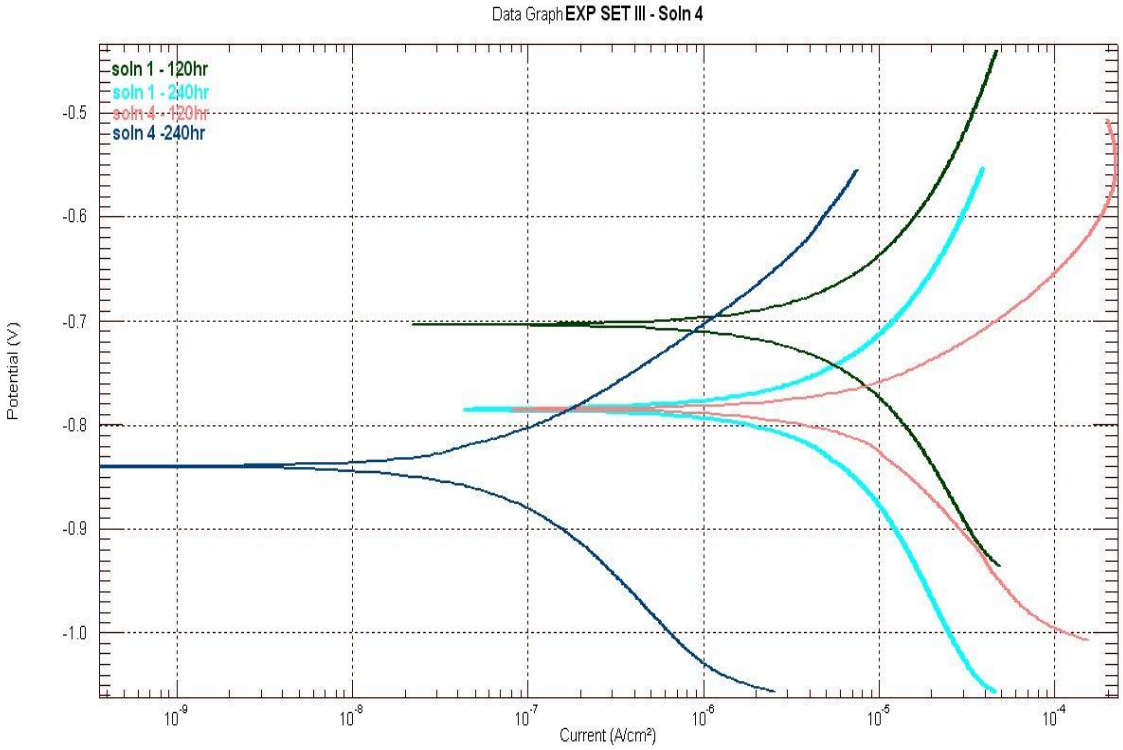


Fig. 5.37 Comparison of Soln 4 at 1% and Soln 1

Fig. 5.37 depicts; specimen immersed in Soln 4 shows no passive behaviour at any time of immersion. E_{corr} value for this specimen shifts toward active zone with increase in immersion time. E_{corr} value of this specimen falls in more active zone as compared to E_{corr} value of the specimen in Soln 1.

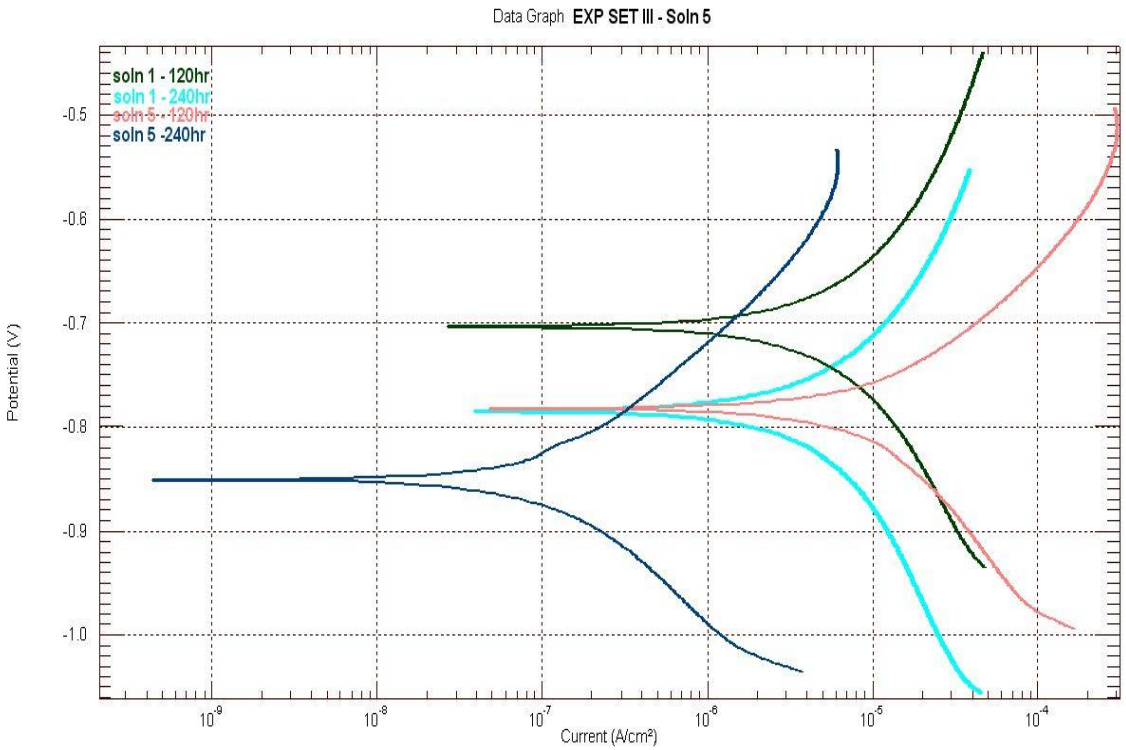


Fig. 5.38 Comparison of Soln 5 at 1% and Soln 1

Fig. 5.38 depicts; specimen immersed in Soln 5 shows a little passive behaviour at 240 hours. No passive behaviour is observed till 120 hours of immersion. E_{corr} value for specimen immersed in Soln 5 shifts to more active zone as compared to E_{corr} value of specimen immersed in Soln 1.

As it can be observed from Fig. 5.39; specimen immersed in Soln 6 shows an adequate passive behaviour till 120 hours of immersion. At 240 hours of immersion, passive behaviour is not satisfactory. E_{corr} value for the specimen immersed in Soln 6 shifts toward more active zone as compared to E_{corr} value of the specimen immersed in Soln 1.

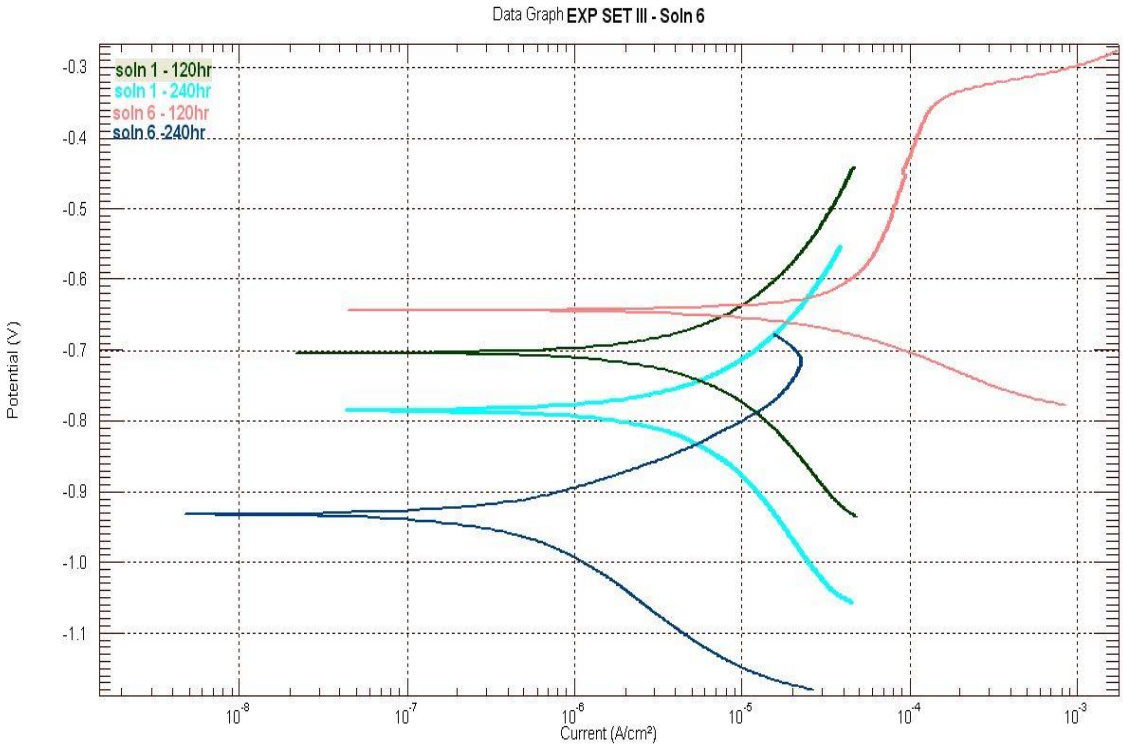


Fig. 5.39 Comparison of Soln 6 at 1% and Soln 1

5.4.4 Best Performance Among All Chemicals

From the discussion of results of experiment set III, it can be concluded that; performance of all the chemicals was not satisfactory.

5.5 INFLUENCE OF PERCENTAGE OF CHEMICALS

5.5.1 General

In this study, different percentages of various organic chemicals were added in carbonated calcium hydroxide solution to check their effectiveness as corrosion inhibitors. The whole experimental programme was divided into 3 different sets based upon the percentage of chemicals used. Experiment set I, experiment set II and experiment set III used 0.25 %, 0.5 % and 1% content of chemicals respectively. In this section, results are compared for different percentages of chemicals used.

5.5.2 Initial Stage of Stabilisation

Corrosion monitoring was executed at time intervals of 1 hour, 24 hour, 48 hours, 120 hours and 240 hours. Results of 1 hour and 24 hours are considered as initial stage of stabilisation. Results of 1 hour are not prominent because system is does not get stabled at this time, therefore, only 24 hours results are considered for comparison.

Fig. 5.40 gives the graphical representation of I_{corr} values for all solutions with different percentages used at 24 hours of immersion.

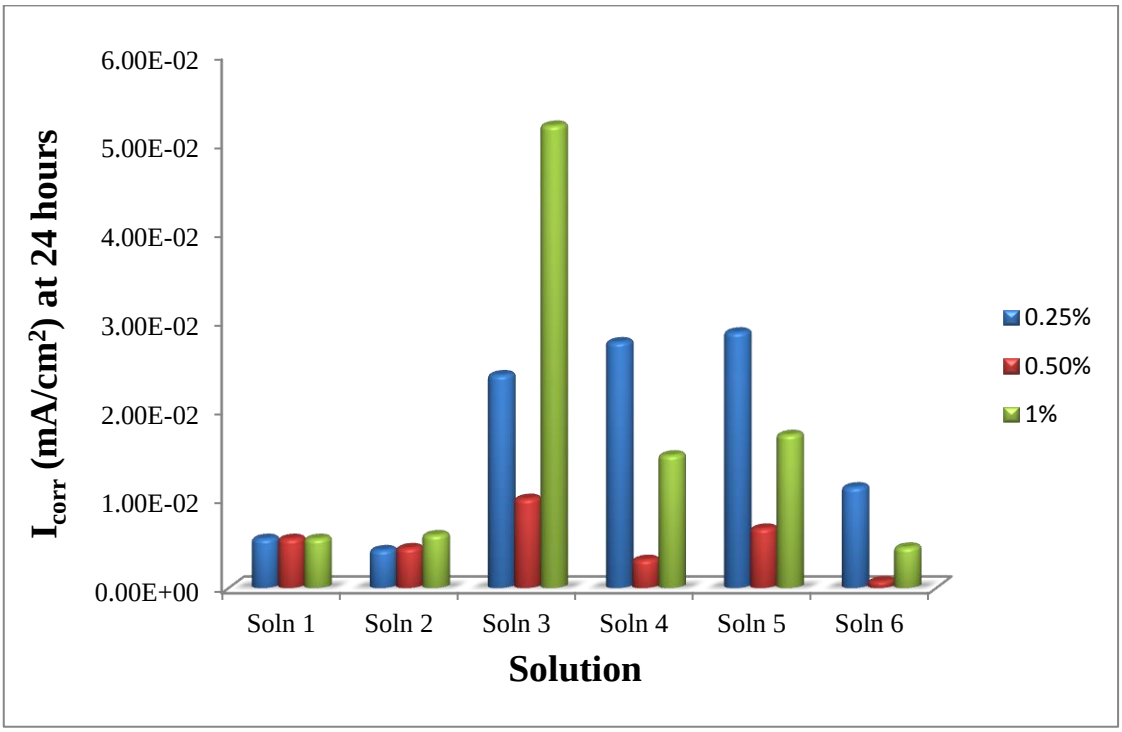


Fig. 5.40 Influence of percentage at 24 hours of immersion

It is observed from Fig. 5.40; at 24 hours of immersion, Soln 2 starts performing well at 0.25% and 0.5 % but do not perform at 1 %. Soln 3 does not perform at any percentage. Soln 4 starts performing well at 24 hours with 0.5 % but do not perform with 0.25% and 1%. Soln 5 does not shows satisfactory performance with any percentage. Soln 6 gives best performance at 0.5 % and do not perform well at 0.25% and 1%.

5.5.3 Towards The End of Stabilisation

Results for 120 hours and 240 hours of immersion are considered as end of stabilisation. Fig. 5.41 and 5.42 gives the graphical representation of I_{corr} values for all solutions with different percentages used at 120 hours and 240 hours of immersion.

It can be observed from Fig. 5.41; at 120 hours of immersion, Soln 2 is very effective at 0.25% and 0.5% but gives poor performance at 1 %. Performance of Soln 3 is not satisfactory at any percentage in fact performance with 1% was very poor. Soln 4 gives satisfactory performance with 0.5 % and poor performance with 0.25% and 1%.

Soln 5 gives good performance only with 0.5 % and poor performance with 0.25% and 1%. Soln 6 gives decent performance with 0.5 % and poor performance with 0.25% and 1%.

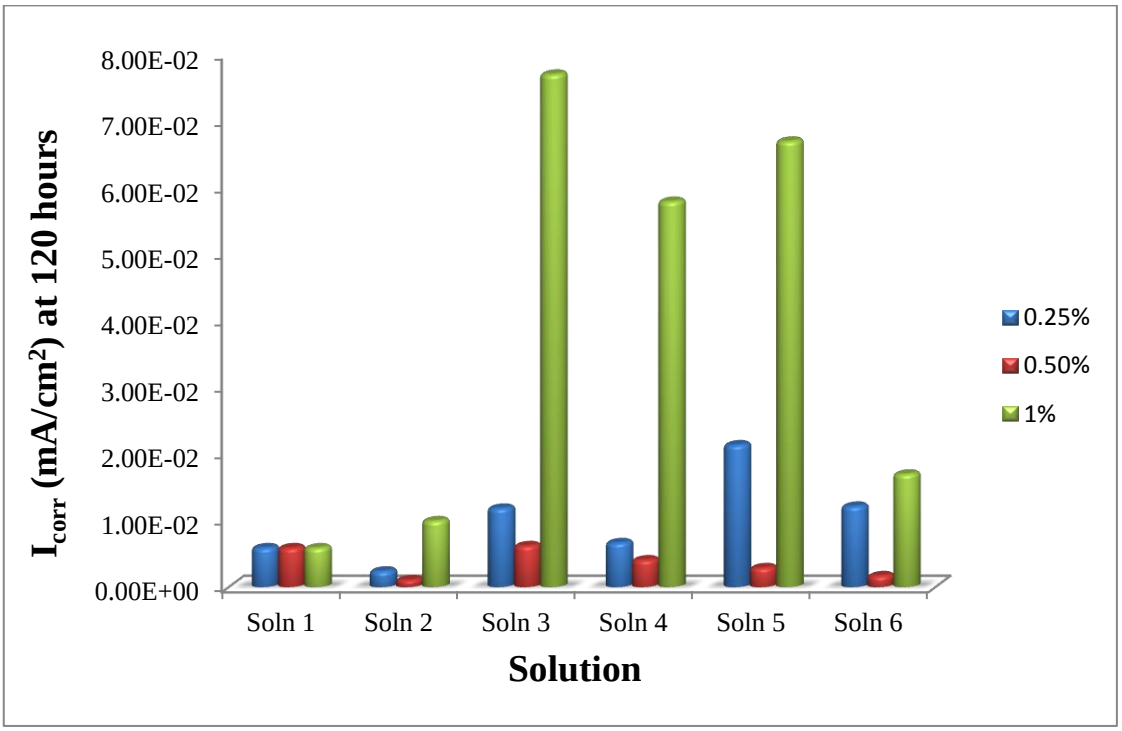


Fig. 5.41 Influence of percentage at 120 hours of immersion

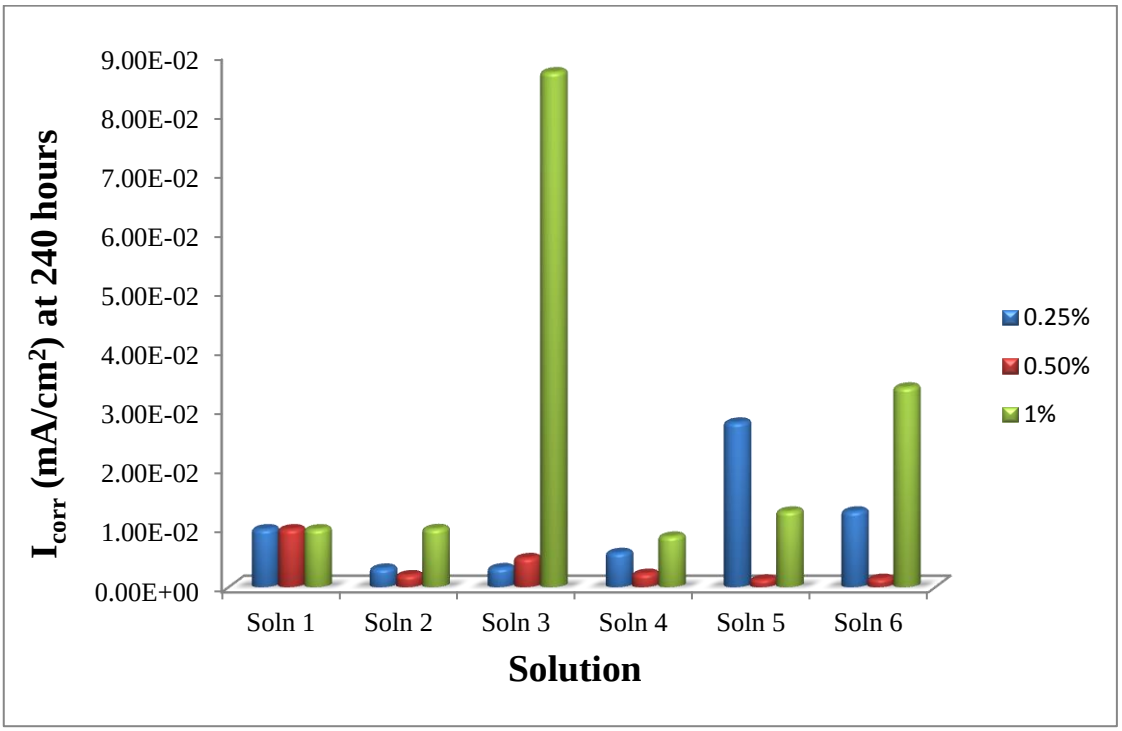


Fig. 5.42 Influence of percentage at 240 hours of immersion

It can be observed from Fig. 5.42; at 240 hour of immersion, Soln 2 gives ample performance with 0.25% and 0.5 % and performance was not satisfactory with 1%. Soln 3 gives satisfactory performance with 0.25% and 0.5 % and poor performance with 1%. Soln 4 performs best with 0.5% and satisfactory performance is observed at other percentages. Soln 5 gives ample performance with 0.5 % and poor performance is observed with 0.25% and 1%. Soln 6 performs best with 0.5 % and gives poor performance with 0.25% and 1%.

5.6 CLOSING REMARKS

All the experimental results are discussed in this chapter. It can be concluded from all the discussions; for 0.25 % solutions Soln 2 gives best performance, for 0.5% solutions all the chemicals give adequate performance but Soln 2 and Soln 6 gives best performance, for 1% performance of all chemicals is not satisfactory.

CHAPTER 6
CONCLUSIONS

From the research done for the study of effectiveness of organic chemicals as corrosion inhibitors in saturated calcium hydroxide solution with reduced alkalinity, following conclusions can be drawn:

- Tartaric acid is very effective in corrosion inhibition of steel bar when added in saturated calcium hydroxide solution with reduced alkalinity. Performance of Tartaric acid with 0.25% and 0.5% addition was ample but not satisfactory with 1% addition.
- Maleic acid is not much effective in corrosion inhibition of steel bar when added in saturated calcium hydroxide solution with reduced alkalinity. Maleic acid with 0.25% and 0.5 % addition shows passive behaviour at later stages of stabilisation but high corrosion rate is observed with 1% addition.
- Adipic acid and Phthalic acid with 0.5% addition provides satisfactory inhibition to corrosion but shows poor performance with 0.25% and 1% addition.
- Oxalic acid with 0.5% addition is very effective in corrosion inhibition of steel bar but is not effective with 0.25% and 1% addition.
- All the chemicals give utmost performance with 0.5% addition.
- None of the chemicals was effective at 1% addition. This behaviour is due to increase in acidity of solutions, which may affect the formation of passive layer on steel bar.

SCOPE OF FUTURE WORK

In this experimental research work, study of effectiveness of organic chemicals as corrosion inhibitors in saturated calcium hydroxide solution with reduced alkalinity was performed. Performance of these chemicals with various percentages of addition was studied.

Following the results of this research work, further investigations in this field can be performed in future. Advanced possible findings in this field are listed below:

- Performance of these chemicals in reinforced concrete can be studied by adding these chemicals in concrete mix.
- Possibility of any adverse effect of these chemicals on other concrete properties like strength, permeability etc. can be studied.
- Corrosion inhibition of these chemicals for various types of steel bars can be studied.
- Probability of any reaction of these chemicals with other admixtures like superplasticisers and air entraining agents can be studied.

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