Efficiency of resonating compounds of Aminophenols as corrosion inhibitors for reinforced concrete under carbonated environment

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DECLARATION

I, **Uday Sharma**, hereby declare that this thesis entitled "**EFFICIENCY OF RESONATING COMPOUNDS OF AMINOPHENOLS AS CORROSION INHIBITORS FOR REINFORCED CONCRETE UNDER CARBONATED ENVIRONMENT**" in fulfilment of the requirements for the award of the Degree of Master of Engineering in Structure Engineering and submitted in the Civil Engineering Department, Thapar Institute of Engineering & Technology, Patiala is an authentic record of my work carried out during a period from July 2018 to July 2019 under the supervision of **Dr. Shweta Goyal**, Associate Professor, Department of Civil Engineering, TIET, Patiala.

The research reports and the results presented in this thesis have not been submitted in parts or in full to any other University or Institute for the award of any degree or diploma.

Date: 31/7/19

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CERTIFICATE

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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(Uday Sharma)

ABSTRACT

The steel reinforcement in concrete has an inherent property of forming an oxide layer which inhibits corrosion causing reactions of steel with air and moisture. This passive oxide layer is facilitated by the alkaline nature of the concrete. However, with permeation of carbon-dioxide, the calcium hydroxide in concrete reacts with carbon-dioxide to form neutral calcium carbonate compounds which results in gradual breakdown of protective oxide layer.

Many single-chained organic compounds containing $-NH_2$ as a functional group are used as commercial corrosion inhibitors in concrete. In this research, the corrosion inhibiting properties of generic compounds 2-Aminophenol, 3-Aminophenol and 4-Aminphenol which are resonating structures containing cyclic double bond and $-NH_2$ as a functional group, were tested. Electrochemical tests (Half-cell potential and linear polarization resistance) were conducted on steel samples immersed in synthetic carbonated pore-solution for 24 hours, 72 hours, 120 hours and 240 hours with the chemicals individually at three different concentrations: 0.01 M, 0.05M and 0.1M. Further, to test their effectiveness as migratory corrosion inhibitors, carbonation depth test and sorptivity test were conducted on concrete samples and electrochemical tests (Half-cell potential and linear polarization resistance) were conducted on reinforced concrete samples treated with chemical at concentration of 1M.

All the three chemicals were very successful in reducing probability of corrosion in steel samples immersed in carbonated synthetic pore-solution at all concentration level. 2-Aminophenol was slightly more effective than 3-Aminophenol, while 4-Aminophenol was least effective in inhibiting corrosion of steel samples in pore solution. 0.05M was the optimum concentration of chemicals in pore solution. As surface applied inhibitor, 4-Aminophenol was most efficient. Results indicated that position of functional group plays an important role in altering properties of reinforced concrete. The ortho position of amine group had better chelate formation leading to reduction in corrosion current density. On the other hand, para position of amine group had better penetration ability, making chemical most efficient as migratory corrosion inhibitor.

Keywords:

Passive layer, Corrosion inhibitors, Resonating compounds, Positioning, Aminophenols, Pore solution, Pore-blockers, Migratory corrosion inhibitors.

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CHAPTER 1
INTRODUCTION

1.1 GENERAL

Concrete is most widely used material in construction work all over the world. Due to its compressive strength and high durability, it is extensively used in construction of buildings, bridges, roads, tunnels etc. Although concrete has very high compressive strength, it is weak in bearing tensile stresses. With the objective of increasing its tensile strength, it is common practise to reinforce concrete with steel. The reinforced concrete has found widespread application because of its high overall strength and economic viability. However, increase in proportion of pollutants and green houses in the environment occurring inadvertently is enhancing chloride ions and causing global warming which increase chances of corrosion of steel embedded in the concrete. Corrosion of steel embedded in concrete causes major damage to strength of structure. It is responsible in reducing service life of RC structures which results in economic loss besides posing major threats to the life and property. Reinforcement corrosion in concrete initiates due to the following two most common causes: presence of Chloride ions, which are the root cause for occurrence of localized destruction of the passive film formed on the steel and carbonation which leads to uniform break down of passive film on surface of steel reinforcement.

The cost of rectification of corroded RC structures all over the world is huge. Every year the cost of corrosion is over 3 % of the world's GDP. In a country like India, the construction of RC structures is rapidly growing, corrosion has great impact on its economy. As per the Chairman of CII Corrosion Management Committee India, India losses USD 40 billion which is approximately 4% of total GDP every year on account of corrosion of infrastructure, industrial machinery and other historical heritage.

Different methods are being studied all over the world to prevent corrosion of steel in concrete.one of the method is use of some substances such as chemicals for this purpose as inhibitors. Corrosion inhibitors have been reported to be very effective in checking corrosion of steel rebars. The present study was therefore planned and undertaken to determine corrosion inhibiting ability of Aminophenols in carbon dioxide contaminated environment.

1.2 MECHANISM OF CORROSION OF EMBEDDED STEEL IN CONCRETE

Steel has the tendency to react with air and moisture to shift to a more stable state. It is more stable in its oxide form. The high pH of concrete provides suitable condition for steel to form a layer of

oxide on its surface (a passive film) which reduces the metal loss from the steel surface due to corrosion.

However, presence of chloride ions in the solutions or a pH levels of less than 9 makes the passive film unstable. With passage of time, chlorides and carbon-dioxide from environment penetrate the concrete and makes it neutral (Hansson *et. al* 2012). This leads to destruction of the passive film by chlorides or carbonation of the concrete and steel reinforcement becomes open to occurrence of active corrosion at very high rates. This process is responsible for major damage to the concrete structures in reinforced concrete.

Corrosion is an electrochemical process which involves establishment of anodic and cathodic half-cell reactions on steel surface. In an alkaline solution without chloride ions, dissolution of anodic takes place as:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (1.1)$$

$$1/2\ O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-} \qquad (1.2)$$

And passive layer is formed when $Fe2^{+}$ ions reacts with the OH^{-} ions as follows:

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^{+} \qquad (1.4)$$

The ferrous hydroxide is then rapidly oxidized to ferric hydroxide.

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \qquad (1.5)$$

De-hydrolysis of this product leads to the formation of the rust which is usually found on the surface of steel.

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O \qquad (1.6)$$

Unhydrated ferric oxide is about twice the amount of the steel. It swells even more when it becomes hydrated and becomes more porous. This leads to swelling of concrete, which results in spalling and cracking and hence, reinforced steel gets directly exposed to aggressive environment without any protection from concrete.

Spalling of concrete due to corrosion of rebars is shown in Fig 1.1.

Fig.1.1: Spalling of concrete cover due corrosion of rebars

1.3 CAUSES OF CORROSION IN RC STRUCTURES

The alkalinity of concrete provides suitable environment to steel in concrete to develop an oxide layer which acts as protective layer against corrosion. But due to ingress of aggressive acidic ions, alkalinity of concrete gets neutralized and hence passive layer is deteriorated with passage of time. The causes of deterioration of passive layer and hence causes of corrosion in steel samples are presented in this section.

1.3.1 Chloride induced corrosion

Incorporation of chloride ion into the passive film reduces its resistance. But this incorporation is uneven and wherever occurs, allows a more rapid reaction leading to establishment of an anodic area for occurrence of corrosion while rest of the steel remains passive.

Chloride ions compete with hydroxyl ions to react with ferrous ions. As the chloride ions reacts with ferrous ions to form soluble compounds, there is no passive film on steel which leads to dissolution of metal. Expansive corrosion products are formed due to diffusion of soluble compounds away from steel which ultimately breaks down.

The free chloride ions migrate back to anode and reacts with steel. But OH^- ions are continuously consumed, making solution acidic and, hence enhancing corrosion. As chloride ions are not consumed, the reaction becomes “autocatalytic”. Ultimately the strength of rebars is substantially reduced.

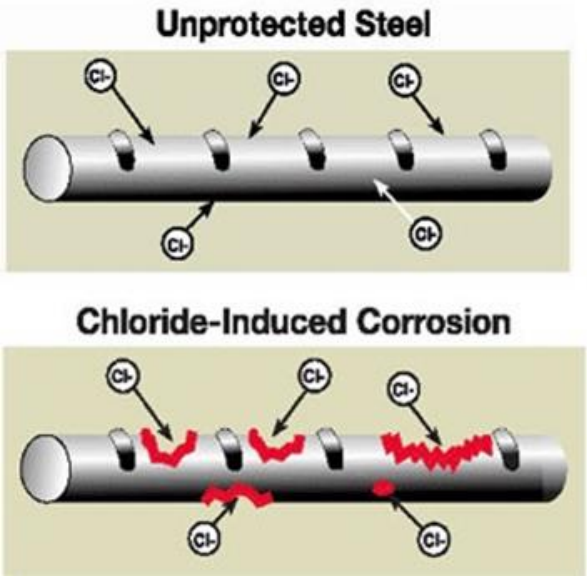


Fig. 1.2: Pitting corrosion due to chloride ion contamination

Both the above reasons can explain local nature of the attack often found in chloride induced corrosion. The local activity becomes anode while remaining areas of steel act as cathode for reduction of oxygen. The localized corrosion which is also known as pitting corrosion is shown in Fig. 1.2.

1.3.2 Carbonation induced corrosion

The reaction between hydroxides present in concrete reacts with Carbon-dioxide to form acidic compounds as follows:

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

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (1.8)$$

The compounds so formed neutralizes the pH of pore solution of concrete. In this pH, passive layer of steel is destroyed which leads to initiation of corrosion process. Carbonation causes damage to the passive layer by decreasing the concentration of the OH- ions in the concrete pore water. Poor concrete quality and thin concrete cover favours carbonation. Thus, pore solution is neutralized effectively. Carbonation is responsible for neutralization of alkalinity of concrete's pore solution. The pH gets down to 8 in regions where hydroxides have reacted with carbon-dioxide, whereas pH of rest of the regions is more than 12.5. The carbonation depth, which also depends on relative humidity (RH) increases with passage of time.

Touching of steel by the carbonation front leads to instability of passive layer and active corrosion starts. This corrosion process is generalized and relatively homogeneous unlike chloride induced corrosion. The signs of carbonation corrosion are visible as rust stains on concrete as shown in Fig. 1.3. The compounds after corrosion are more soluble in neutral carbonated concrete leading to diffusion instead of precipitation in concrete. Therefore, cracking and spalling are not visible initially in carbonation induced corrosion.

The corrosion rate due to carbonation is lower than due to chloride environment, but with passage of time, significant deterioration of cross section of rebars without causing any visible damage to concrete may occur.

Although an intermediate RH range is the most favorable for carbonation penetration, active corrosion does not occur in this range. Alternate semi-dry and wet cycles are the most congenial environment for carbonation induced corrosion. Deterioration of reinforced concrete structures can be commonly seen in coastal area where, concrete is subjected to cycles of hot climates resulting in drying of concrete followed by wetting due to rainstorms.

Fig. 1.3: Rust stains on concrete surface due to carbonation induced corrosion

1.4 PREVENTIVE METHODS OF CORROSION IN RC STRUCTURES

In order to check corrosion of steel in reinforced concrete structures, different preventive measures can be taken. The various preventive measures taken to control corrosion of steel in concrete are:

- **Adequate concrete cover in RC structures**

By providing adequate concrete cover to reinforcement in RC structures, considerable protection against corrosion can be ensured. Proper concrete cover in RC structures in aggressive environments like underwater structures, can increase the service life of structure manifold. However, the increase in concrete cover can make structure economically less viable. Supervision is required to check proper concrete cover in structure.

- **Use of coatings on steel**

Reinforced steel can be applied with coating that helps in preventing corrosion. Several commercially used anti-corrosive coating are commercially used nowadays. But these coatings can be very expensive which may increase the overall cost of RC structures.

- **Use of Sealants**

Sealants can be used to seal the surface to aggressive environment. With the use of sealants, the exposure to moisture and air can be prevented but the application of sealant requires expert supervision.

- **Galvanization**

Galvanization of steel bars galvanization is the process of applying zinc coating to steel to check its corrosion. But this technique required skilled labour and expert supervision. This is a comparatively new method.

- **Corrosion inhibitors**

Corrosion inhibitors are compounds which can decrease corrosion probability of RC structures when present in concrete at suitable concentration. Corrosion inhibitors reduces the corrosion rate of steel embedded in concrete without affecting properties of concrete. They are being used as admixtures as well as migratory surface applied corrosion inhibitors. The usage Corrosion Inhibitors as admixture has been in practice since 1980’s while application of corrosion inhibitors as migratory inhibitors for repair have come in significance in last decade only.

1.5 CORROSION INHIBITORS

1.5.1 General

Any chemical substance, which reduces the corrosion rate in corrosion system, when present in suitable concentration without causing appreciable change in the concentration of any other agent of corrosion is known as corrosion inhibitor (*ISO 8044-1989*). Coatings, pore blockers and other materials which change the concentrations of water, oxygen or chloride content are not considered as corrosion inhibitors. Although some corrosion inhibitors have additional property of blocking the pores of concrete, but this is not their principal property. The success of a corrosion inhibitor depends on a number of factors such as composition of corrosion system, quantity of water and flow regime. One of the most common mechanism in controlling corrosion consists of formation of a coating also known as passivation layer which keeps metal out of reach to corrosive environment.

Objective of use of corrosion inhibitors in concrete is to increase the service life of reinforced concrete structure at minimum cost. The use of corrosion inhibitor in concrete has to be economically viable. Before using the corrosion inhibitor in concrete, following factors must be considered:

- Corrosion inhibitor's performance and long-term stability
- Corrosion propagation after initiation
- Effect on concrete's fresh, mechanical and durability properties of concrete and overall effect on service life of structure.

The dosage of corrosion inhibitor to be added should also be considered and an insufficient might not be effective while an over-dosage might lead hindrance in hydration reaction which can lead to adverse effects on mechanical properties of concrete. Over dosage of inhibitors might not be economically viable. The inhibitor must be used at optimum concentration after scrutinizing all the factors mentioned above.

1.5.2 Corrosion inhibitors over other preventive methods

The use of corrosion inhibitors has been increasing rapidly as preferred corrosion preventive method. Many factors are responsible for this reason. Some of these factors are:

- Concrete properties are not affected
- Easy of availability and application

- Nontoxic
- Environment friendly
- Economical than preventive methods

1.5.3 Classification of corrosion inhibitors

Corrosion inhibitors in RCC can be classified in following ways:

1.5.3.1 On the basis of method of application inhibitors

Admixture corrosion inhibitors: The inhibitors which are added in water at the time of casting of concrete are called admixed inhibitors. They are added to the fresh concrete. Addition of admixed inhibitors can influence setting times of concrete and can affect mechanical properties of concrete. They are the most popular type of corrosion inhibitors. These types of inhibitors are in use since 1960's. Some commonly used admixed inhibitors are calcium nitrite sodium nitrite, sodium benzoate and sodium chromate. Some organic compounds based upon mixtures of alkanol-amines, amines or amino-acids, or based on an emulsion of unsaturated fatty acid ester of an aliphatic carboxylic acid and a saturated fatty acid are also used as admixed inhibitors.

Migratory corrosion inhibitors**:** These are the type of corrosion inhibitors which are applied on the surface of hardened concrete. The research on use of surface applied corrosion inhibitors have increased significantly in last 10-15 years. Surface applied inhibitor are known to diffuse into the concrete and form a protective layer at concrete-steel interface. These inhibitors are typically based either on mixtures of alkanol-amines and amines or on inorganic compounds based upon Monofluro-phosphate. Amino alcohols, such as ethanolamine and dimethyl ethanolamine, can act at the cathode and prevent oxygen reduction to hydroxyl ion by a blocking mechanism, following adsorption on the steel surface.

1.5.3.2 Classification based on mechanism of protection

Based on protection mechanism of corrosion inhibitors, they can be classified as

- **Anodic Inhibitors**: Anodic inhibitors are those which act as the anodic part on the metal. They hinder the corrosion reaction on anodic part of metal by forming a layer of oxide on the surface of metal which inhibits the corrosion reaction. They are also called passivators as they cause significant anodic shift of corrosion potential which forces the metallic surface into passive region. Chromates, nitrates, tungstate, molybdates are some examples of anodic inhibitors.

- **Cathodic inhibitors**: Cathodic inhibitors are those which slow down or hinders the reaction as cathodic part on the metal. They do not allow metals to form a cathodic region. This can be achieved using cathodic poisons. One of the major limitations of using cathodic poisons is that these inhibitors induce cathodic charging which can lead to adsorption of hydrogen on metal surface which can cause hydrogen induced cracking. Thus, metals is prone to hydrogen cracking if cathodic poisons are used. Oxygen scavengers that react with dissolved oxygen are capable of reducing the corrosion rates. Sulfite and bisulfite ions can combine with oxygen to form sulfate. So they are examples of oxygen scavengers.
- **Mixed corrosion inhibitors:** Mixed corrosion inhibitors are the chemicals which inhibit the corrosion phenomenon by acting on both cathode and anode regions of the metal. They are essentially a film forming compounds which protect metal surface from aggressive environment such as oxygen, chloride ions etc. Metals subjected to hard water are less prone to corrosion than metals subjected to soft water because the minerals in hard water reach with surface of metals to form of layer of salt precipitates on the surface of metals which protects metal from exposure to contamination. However, the efficiency of these corrosion inhibitors also depends on pH of solution. Silicates and the phosphates usually inhibit corrosion by this mechanism. Sodium silicate is a commonly used corrosion inhibitor. Steel, brass and copper, in aerated hot water systems are protected by sodium silicate. The examples of organic mixed corrosion inhibitors include Amino-alcohol and Amine-esters.

1.5.4 Importance of amine group as corrosion inhibitors

Amine are the compound that contain a fundamental nitrogen element with a lone pair of electrons. Amines wherein at least one hydrogen atom have been replaced by a substituent, for example alkyl or aryl groups. Amines can be classified on the basis of number of hydrogen atoms attached to the nitrogen. When alkyl or aryl group replaces one hydrogen atom and gets bonded with nitrogen, then the structure compound is called primary amine.

When two hydrogen atoms are replaced then it is called secondary and when all the hydrogen atoms are replaced then the structure is said to be tertiary amine. The structures of primary, secondary and tertiary amines are shown in Fig. 1.4

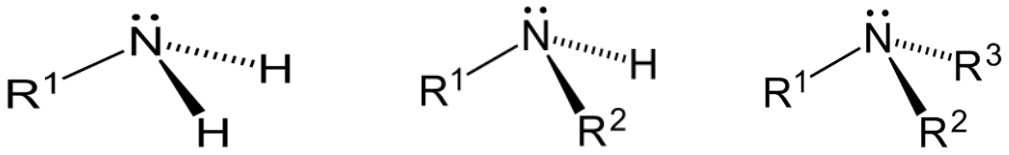


Fig.1.4: Structures of Primary, Secondary and Tertiary amines

Amine based inhibitors can be broadly classified in two categories: Alkanol-amines (AMA) and Amine-ester based. Besides, having difference in their structure the method of action against corrosion is also different.

Alkanol-amines corrosion inhibitors consists two components: Amino-alcohols as main component which are volatile in nature and an acidic component which reacts with amino-alcohol to form a salt. When used as surface applied corrosion inhibitors, the amino-alcohol component which is a very volatile component migrates into concrete pore and forms a protective film around reinforced steel. To ensure that amino-alcohol is not evaporated in environment, a small quantity of acidic component is required (*Soylev 2007).*

Amine-esters, consists of ester group attached with amine functional group. The amine group which has an unshared pair of electrons, inhibits corrosion by adsorbing on surface of reinforced steel. Thus, a protective film is formed which inhibits corrosion. On the other hand, ester groups reacts with alkaline pore solution of concrete to form carboxylic ions. These carboxylic ions further reacts to form precipitates of calcium salts which are hydrophobic in nature. These water-repellent precipitates provide a coating in pores of concrete *(Nmai, 2004).*

1.6 THESIS OBJECTIVES

- To confirm the effectiveness of Aminophenols in inhibiting the corrosion of steel in concrete when added in simulated concrete pore solution and to find out the optimum concentration of chemical required.
- To find out if the amino-phenols can act as migratory corrosion inhibitors for concrete in carbon dioxide contaminated environment.
- To find out if change in position has any effect on its corrosion inhibiting property.
- To confirm that Aminophenols can act as pore-blockers in concrete and to find out the effect of change in position of functional group on this property.

1.7 THESIS OUTLINE

- In the first chapter, the corrosion process and causes of rebar corrosion are discussed firstly. In the second part, the importance of corrosion inhibitors, its mechanism and classification are discussed.
- In the second chapter, literature review of corrosion inhibitors is discussed.
- In third chapter, detailed experimental program to analyze the effectiveness of chemicals is discussed.
- The fourth includes chapter results and discussions of above-mentioned tests.

Conclusion on the basis of results and discussions are included in fifth chapter, followed by list of references used in the study.

CHAPTER 2
LITERATURE REVIEW

2.1 GENERAL

The effectiveness of organic based corrosion inhibitors in concrete and in chemical solution that represents the concrete environment has been extensively studied by researchers around the world. Summaries of studies on the topic of present investigation conducted over last two decades under different environments are presented in this chapter.

2.2 EFFECT OF CORROSION INHIBITORS IN RESISTING CORROSION OF REBARS

Ryu et al. (2016)

Studied the commercially used N, N' Dimethyl ethanol amine (DMEA) inhibitor using potential time, EIS and potentio-dynamic Sweep tests. The inhibitor solution was prepared by mixing inhibitor and saturated $Ca(OH)_2$ in double distilled water by maintain pH at 12.6 at room temperature. The solution was contaminated by chloride by mixing Nacl solution of different concentration. Mild steel rebars of diameter 16 mm were polished with sandpaper and coated with acid/alkali resistant resin.

Three electrode system was used to carry out electrochemical analysis comprising of steel rebar as working electrode (WE), platinum electrode as counter electrode and silver chloride as reference electrode. An area of 0.78 cm^2 was kept exposed portion of working electrode for every test in every solution. The results of corrosion potential time plots on steel rebars in saturated $Ca(OH)_2$ solution with different concentration of Nacl and DMEA inhibitor are presented in Fig. 2.1.

The corrosion potential of samples immersed in pore solution was significantly more negative than samples immersed in inhibitor mixed pore solution.

Further, with increase in concentration of DMEA, the corrosion probability reduced further. Authors reported that this was due film forming property of amines around steel in pore solution. With increase in concentration, corrosion inhibition action improved.

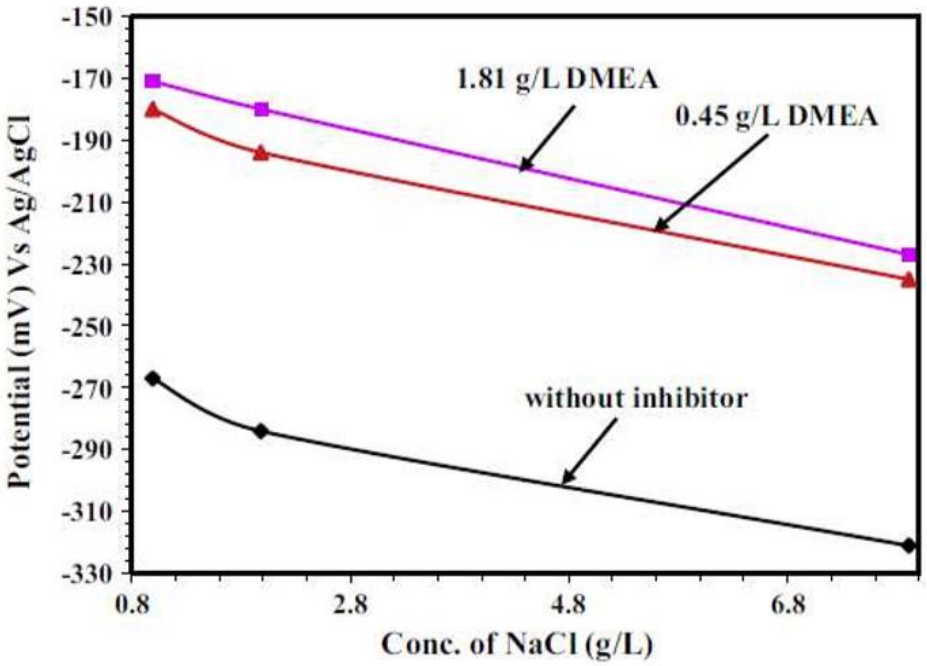


Fig. 2.1 Corrosion potential time plots on steel rebars in saturated $Ca(OH)_2$ solution with different concentration of Nacl and DMEA (*Ryu et al. 2016)*

Cabrini et al. (2015)

They tested the carbon steel samples in concrete pore solution. The solution was maintained at pH range of 12.6 to 13.8. The inhibitors tested were aspartic and lactic acid salts in order to find the critical chloride concentration. The chemical structures of chemicals are shown in Fig. 2.2 and 2.3. The tests were monitored through multiple specimen in non-carbonated concrete by using potentio-static tests on passive rebar.

Potentio-static polarization sweep tests were used in which chloride concentration was increased step by step. Infra-red spectra were used to detect presence of organic inhibitor on passivity film. Figures below structures of the inhibitors that were tested.

They reported that Aspartic ions were found to be adsorbed on ferrous oxide layer due to their chelating properties and the inhibiting effect was due to negative charge repulsion by their non-adsorbed carboxylate groups which leads to increase in critical chloride content. The optimum concentration of inhibitor used as admixture was found to be 0.1M.

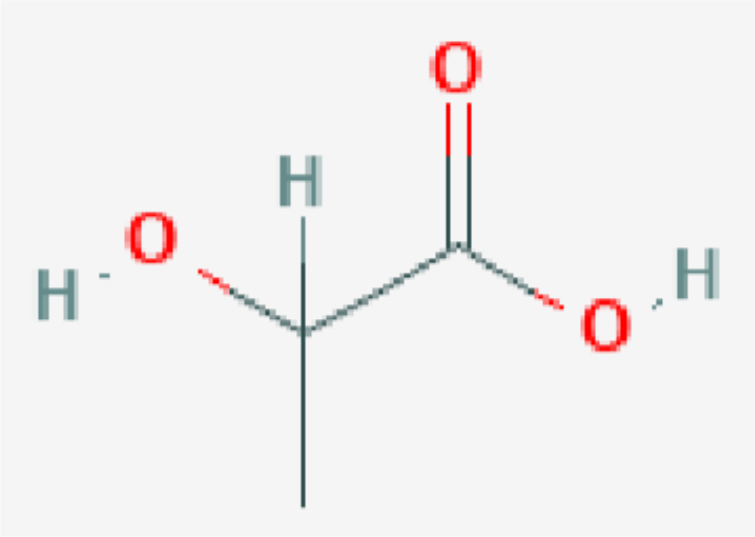


Fig. 2.2 Molecular structure of lactic acid (*orgchem.com*)

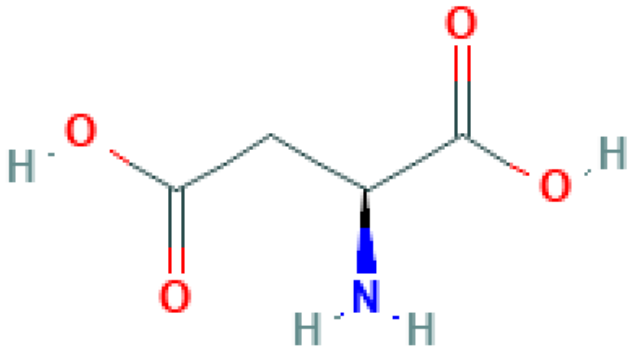


Fig. 2.3 Molecular -structure of aspartic acid (*orgchem.com*)

Rakanta et al. (2013)

Conducted potentio-dynamic test on steel samples which were in the form of a disk of diameter 12mm and thickness 10mm to find out corrosion rate and pitting potential under chloride environment. Samples were treated with chemical N-N' dimetheylaminoethanol which was tested as corrosion inhibitor by exposing to saturated $Ca(OH)_2$ solution mixed with the chemicals for 24 hours. The results are shown in Table 2.1.

Table 2.1 Potentio-dynamic test results at different percentages of DMEA (***Rakanta et al. 2013***)

Corrosion inhibitor (wt %)	**Nacl concentration (wt. %)**	**I_{corr} ($\mu A/cm^2$)**	**R_p (k ohms)**	**Corrosion rate (mm/y)**	**Pitting potential (mV)**
0	0	0.487	44.57	0.4461	535
	1	1.732	12.54	1.586	419
	2	5.73	3.79	5.246	185
	3	6.042	3.594	5.532	119
	4	10.74	2.021	9.836	117
	5	13.24	1.641	12.12	85
1	0	0.2494	87.08	0.2283	660
	1	0.763	28.44	0.6992	570
	2	4.056	5.353	3.714	496
	3	5.235	4.148	4.793	233
	4	5.64	3.982	4.993	131
	5	0.172	3.85	5.164	114
2	0	0.172	126.244	0.1574	757
	1	0.717	30.284	0.6564	658
	2	2.896	7.497	2.6515	458
	3	3.202	6.781	2.9317	263
	4	4.298	5.0521	3.9352	220
	5	5.195	4.1797	4.7565	134

Corrosion rate was presented as loss of cross-section in millimeters per year (mm/y).

On the basis of tests performed to measure corrosion potential, corrosion rate and weight loss of cement mortar specimen reinforced with inhibitor dipped rebars, it was reported that the corrosion potentials in cement mortar specimens adulterated with chloride ions moved to more negative values as the chloride concentration increases. Addition of corrosion inhibitor made the corrosion potentials to shift towards more positive values. Addition of 2 wt. % of DMEA inhibitor decreased mass loss of the steel rebar by about 43%. This shows that N,N'dimethylaminoethanol checks reinforcement corrosion. Increase in concentration chloride ions increased the rate of corrosion of steel reinforcement. However, increase in the concentration of the corrosion inhibitor decreased the rate of corrosion. To monitor pitting corrosion in steel samples, a fiber optical microscope was used after being exposed to chloride environment for 7 months. It was reported that pitting corrosion was resumed to great extent with use of N, N'dimethylaminoethanol. The effectiveness

of DMEA in inhibiting corrosion in pore solution was due to its film forming property around steel surface which act as protective layer against aggressive environment like chloride ions.

Monticelli et al. (2011);

The effectiveness of sodium 2-amino benzoate (2AMB) and sodium glycerol-Phosphate (GPH) as corrosion inhibitors in steel rebars in simulated concrete pore solution was determined in this study. Simulated concrete pore solution which consisted to saturated and filtered calcium hydroxide solution was bubbled with carbon dioxide till the pH of solution reached 7. The solution was also added with 0.1 M Nacl. 10 mm diameter ribbed rebars were immersed in this solution. The exposed surface area of rebar specimen was 4.5 cm^2.

Potentio-dynamic linear polarization test was used to obtain polarization curves which were extrapolated to find corrosion current density. From the results, it was reported that there was no substantial deflection of rebar corrosion behavior even after increasing the immersion duration from 45 minutes to 72 hour which indicated that there was no protecting film growing on metal surface. There was no significant reduction on corrosion by adding 0.05M of 2 AMB even after 45 minutes. However, there was a change in corrosion potential value after 24 hours which might be due to formation of surface film. But the film formed is very unstable as anodic curves shifted towards higher corrosion current densities at the end of 72 hours.

EIS test was also used which confirmed that there was a slow protecting action of mixture during the first 24 hours. The protection is provided by the film which resists higher mass transport as compared to that in control solution. From the analysis of polarization curves, it was suggested that Fe^{2+} cations diffused surface of metal to aggressive solution could be due to the controlled transport of mass which affects the corrosion rate in inhibited solutions.

Tommaseli et al. (2009):

They studied the well-known commercially used corrosion inhibitors; sodium nitrite and sodium molybdate in simulated concrete pore solution which was prepared by using saturated calcium hydroxide. The solution was contaminated with sulphuric acid and nitric acid.

The corrosion monitoring was done using anodic polarization curve and electrochemical impedance spectroscopy tests. Sodium molybdate reduced corrosion current density by 67% while sodium nitrite reduced it by 52% at concentration of 0.013%. It was reported that there is no significant change in efficiency even when concentration of inhibitor was increased to 0.04%.

Soylev et al. (2007)

They tested the effects of surface applied aminoalcohol based organic corrosion inhibitor on the hardened and durability properties of concrete. Properties tested were compressive strength, tensile strength, bond strength, permeability, drying shrinkage and freeze and thaw action. Two sets of concrete samples were casted. These sets of samples were classified based on their mix design. Samples belonging to set A were casted with denser cement and lower water-cement ratio than samples belonging to set B. inhibitors were applied on the surface 42 days after the casting. Since in this experiment permeability was the most important because other properties were also dependent on this property. Permeability was tested using three methods. Auto-clam permeability test was used to determine air permeability into concrete samples. Three samples each for control and treated samples were prepared in both the sets. In this test, concrete samples were put inside an apparatus and pressure inside the apparatus was raised to 0.5 bar and decay of pressure was observed at specified time interval. The decay of pressure was monitored for 15 minutes or until the pressure became zero which ever was faster. A graph between natural log of pressure vs time was obtained and slope of graph between 5 minutes to 15 minutes was used as air permeability index. Other tests used were ISAT (BS- 1881-5) which determines initial surface absorption by concrete samples and third test was determining density using open water porosity test (EN-12397). In this test the difference in difference between water absorption values water cured samples were noted and cores were drilled for finding density of samples. In ISAT test, two different types of curing methods were used: air curing and water curing. The curing period for water cured samples was 28 days. Other properties which were determines were compressive strength according to guidelines in EN 12390-4, tensile strength using EN-12396, drying shrinkage and freeze- thaw action by following guidelines in EN-12390-9.

From the test results of ISAT, the difference in control samples and treated samples was clearly visible. Samples of set B, where w/c ratio was higher, and cement was less dense showed less absorption values than control samples from same set. The values were reduced to almost one-third in set B whereas values of absorption of samples of set A treated with inhibitor reduced to half the values of control samples in set A. The difference in absorption values in both the sets kept on decreasing with time. On the other hand, there was no significant difference between control samples and treated samples in air permeability values in set ‘A’ as shown in Figures. In

sample set ‘B’ the average of slope of treated sample is almost half than that of control sample of same set. Fig.2.4 and Fig.2.5 shows results of Auto-clam air permeability test of sample set A and B respectively. There was no significant difference found in densities of control and treated samples

They concluded that there decrease in permeability was result of pore blocking effect of amino alcohol based organic corrosion inhibitor. Amino alcohol based organic corrosion inhibitor has a volatile component which is the main element and due to which amino alcohol gets transported due to diffusion of gas.

The second component of inhibitors was acid component which reacted with hydrated products to form compound on surface of concrete which led to blocking of pores.

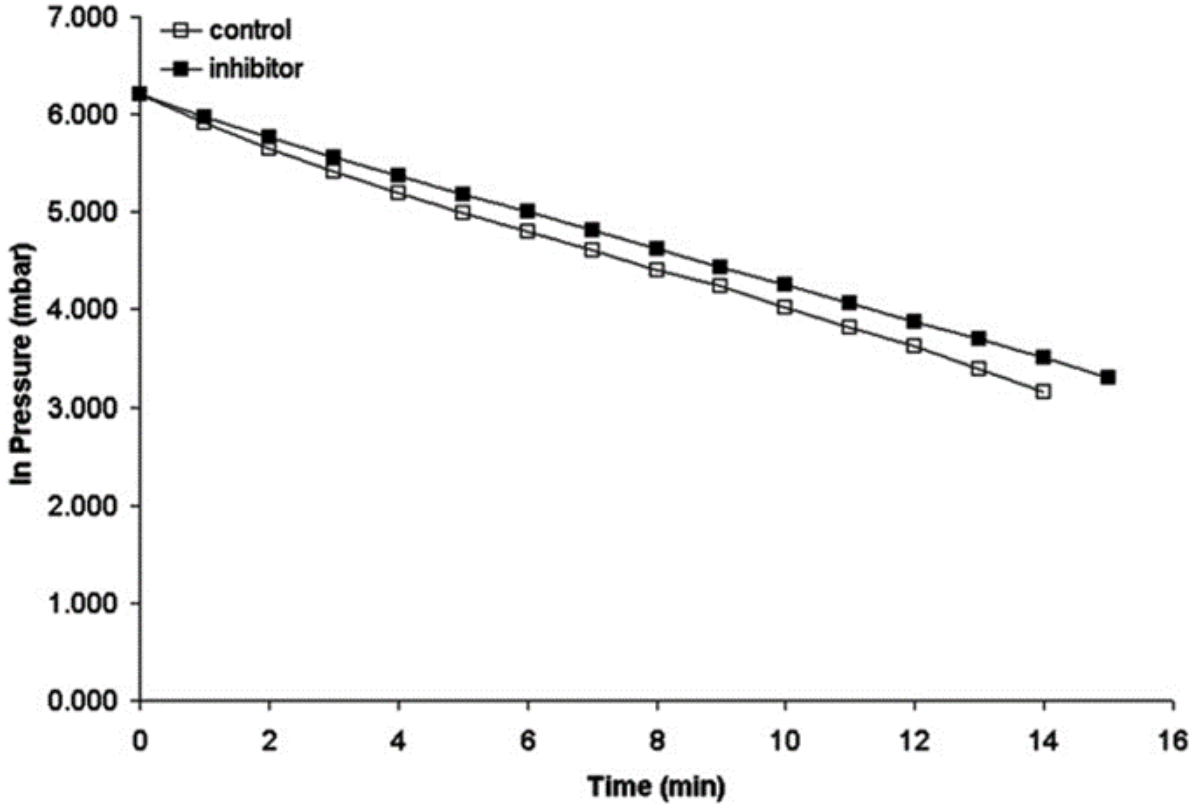


Fig. 2.4 Auto-clam air permeability test in sample set ‘A’ (lower w/c ratio)

(Soylev et al. 2007)

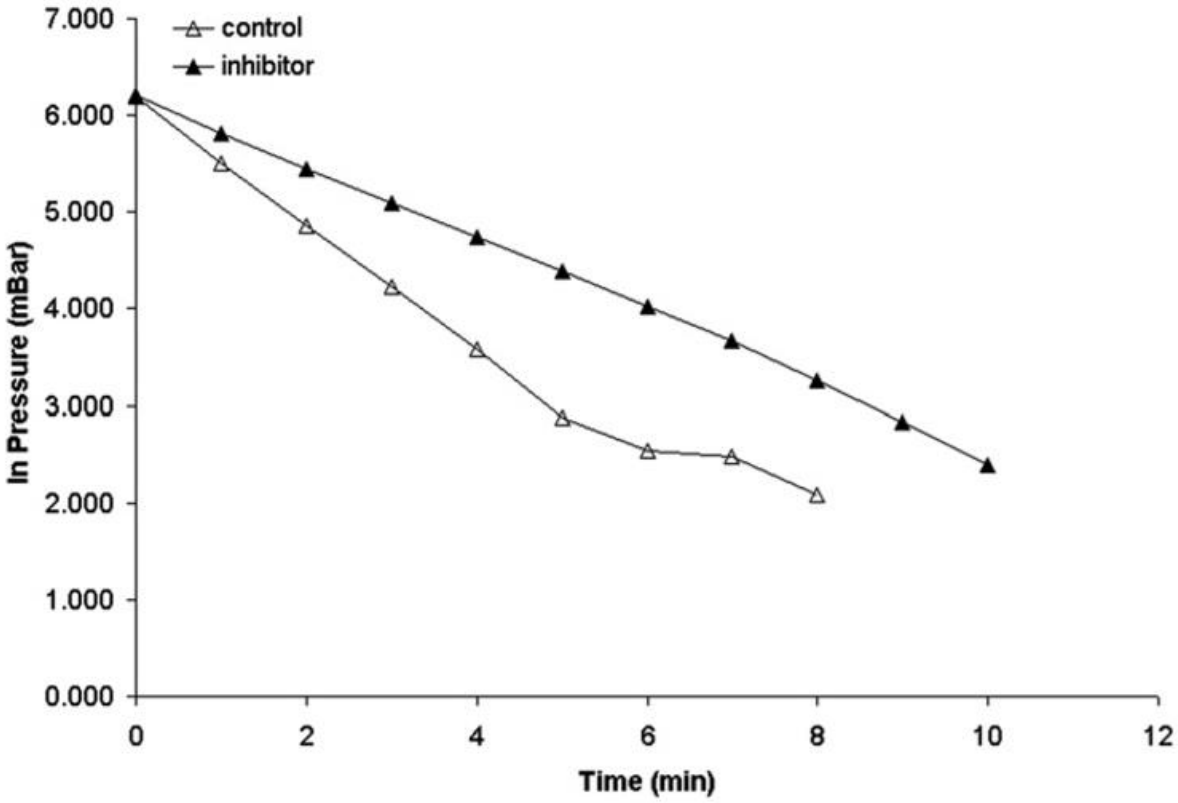


Fig. 2.5 Auto-clam air permeability test in sample set 'B' (higher w/c ratio)

(*Soylev et al. 2007)*

Saraswathy and Song (2007)

Carried out gravimetric weight loss method to find corrosion rate and hence compared the effectiveness of different type of inhibitors (sodium nitrite, zinc oxide, mixed which includes a mixture of ZnO and $NaNO_3$, mono-ethanolamine, and tri-ethanolamine) at different concentrations. Concrete specimen of size 55mm in diameter and 60 mm in height were used with water-cement ratio 0.53 and with a mix 1:2.29:3.90. Rebars, 12 mm in diameter and 50mm long, were embedded in the center of each specimen. After curing for 28 days, triplicate specimen were subjected to six complete cycles of 7 day immersion in 3% Nacl solution 7 day dry at room temperature. The results are shown in bar graph in Figure 2.6.

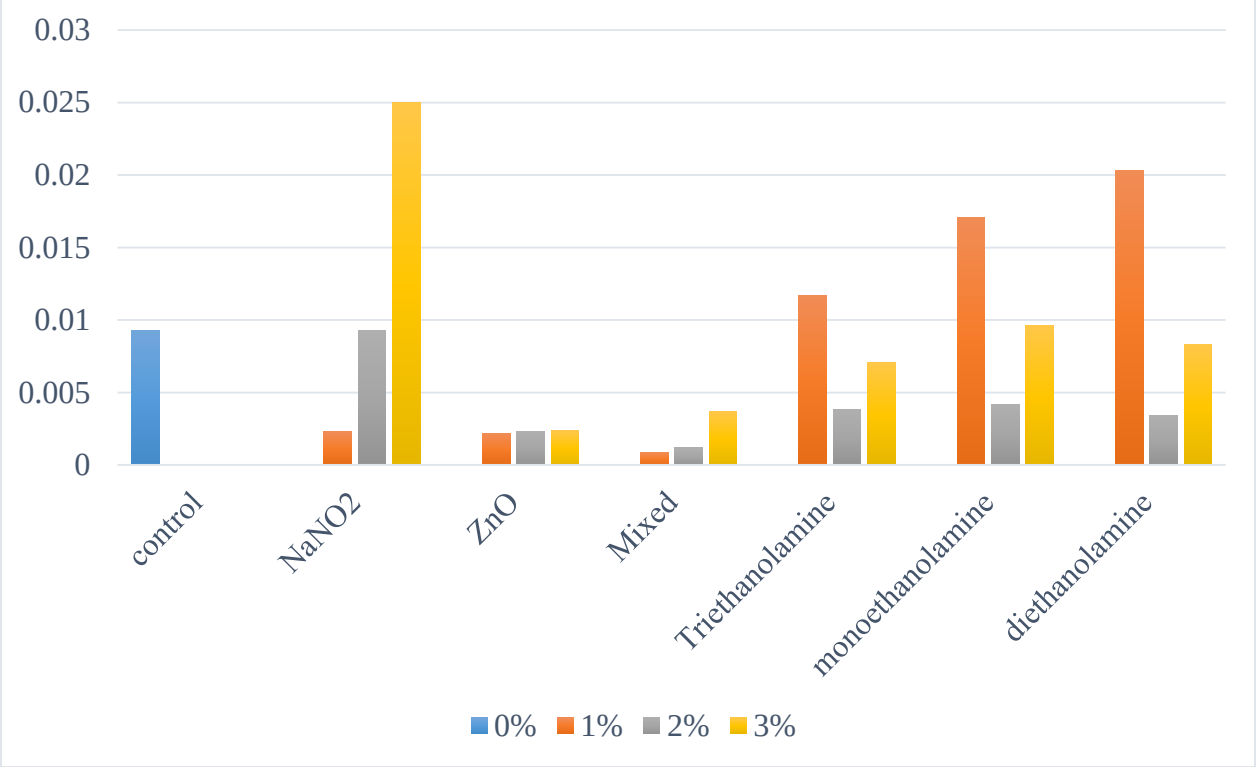


Fig. 2.6: Corrosion rate at different percentage of inhibitors (*Saraswathy and Song, 2007)*

It was reported that, at 1% inhibitor addition, chemicals NaNO, mixed, and ZnO were equally most effective in reducing corrosion rate. Chemicals monoethanolamine, diethanolamine and triethanolamine were not effective at 1% concentration. When concentration of chemicals was increased to 2%, all the chemicals were effective in reducing corrosion rate in samples. ZnO and mixed were again most effective chemicals. These two chemicals were also very effective when added at 3% concentration all other chemicals were ineffective at this concentration.

Ormellese *et al*. (2006)

Tested the effectiveness of organic corrosion inhibitors which were commercially used in inhibiting corrosion induced by chloride contaminated environment. Different corrosion inhibitors tests were: Nitrite based, Amine-esters, Aminoalcohols and Alkanolamines. The effect of inhibitors on corrosion initiation and on chloride threshold were found out and reported by the Authors. Three different sets of concrete samples were prepared with different dosage of inhibitors. The recommended dosage of inhibitors used is presented in Table 2.2. Samples were subjected to chloride contamination by adding chlorides as admixtures at different concentrations. Electrochemical tests were also performed in saturated Ca $(OH)_2$ pore solution.

Table 2.2 Recomendded dosage of corrosion resistance

(Ormellese et al. 2006)

Inhibitor	Dosage suggested by the producer in concrete (g/l)	Maximum allowed dosage (g/l)
Nitrite based (29%)	7.5	20
OCIA-C (AMINE ESTER)	5	7.5
OCIA-D (AMINEOALCOHOLS)	10	16
OCIA – E (ALKANOAMINES)	1.6	4

It was reported that there was no sign of corrosion in rebars immersed in chloride free concrete. When inhibitors were added at dosage suggested by producer in samples with chlorides concentration 1.5% or 2.5% by weight of cement, there was significant reduction in corrosion potential and polarization resistance values. Corrosion potential values were reduced to -300 and -400 mV/SCE and polarization resistance values were reduced to less than 10 Ω m^2 when inhibitors were added at recommended dosage. Polarization resistance of steel bars in concrete specimens in which chlorides concentration was 1% and 1.5% by weight of cement and inhibitors concentration as the maximum allowed concentration suggested by producer was more than 10 Ω m^2, but lower than in concrete samples without chlorides. It was reported that amine-based inhibitors performed better in inhibiting chloride induced corrosion than nitrite-based inhibitors. The tests results in pore solution are presented in Figures 2.7 and 2.8. The authors reported that with addition of amine-based inhibitors that corrosion initiation in steel bars was delayed. However, it was suggested that the delay in corrosion initiation was due to inability of chloride ions to penetrate concrete to reach steel surface which was due to pore-blocking effects of amine-based inhibitors. Authors reported that the protection of steel due to chemistry between inhibitors and steel surface was not significant.

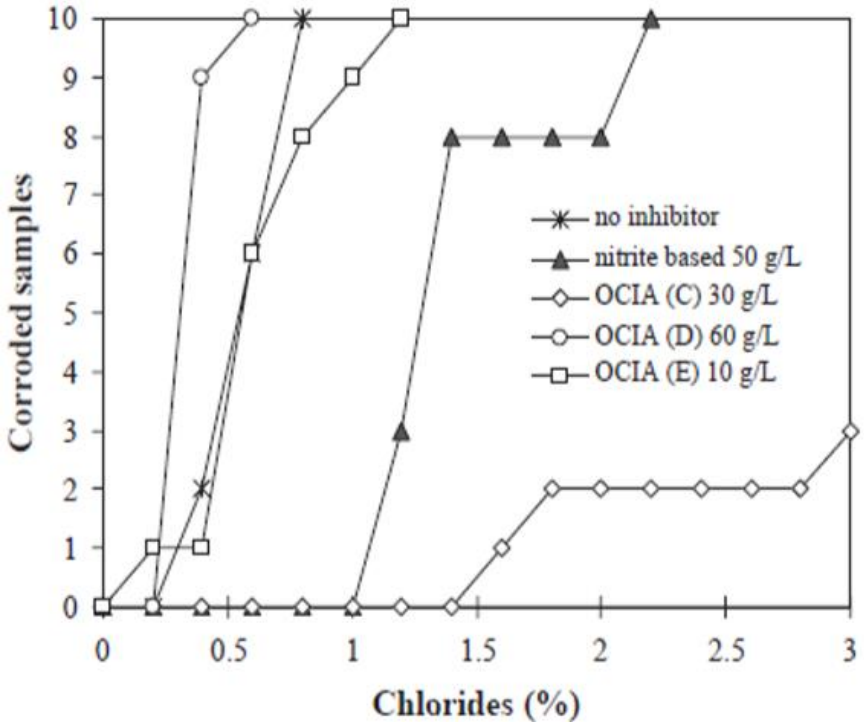


Fig 2.7: Potentio-dynamic curve with and without admixed type inhibitor.

(Ormellese et al. 2006)

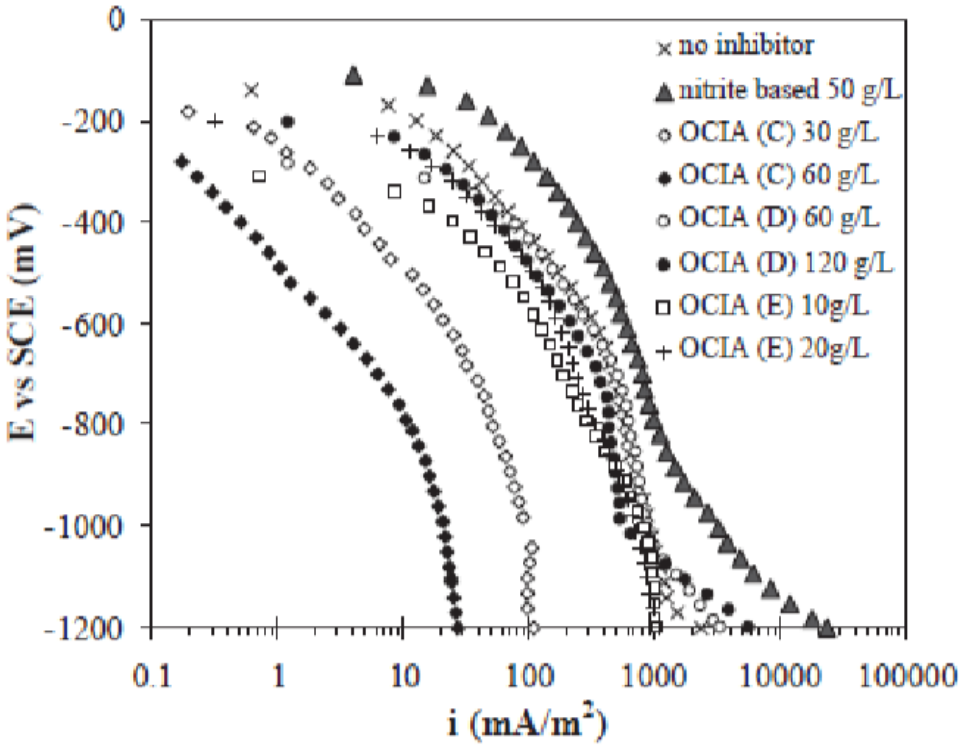


Fig. 2.8: Cathodic potentio-dynamic polarization curves in saturated $Ca(OH)_2$ solution
(Ormellese et al. 2006)

Reilly et al. (2006)

They evaluated the effectiveness of three commercially available corrosion inhibitors which consisted of calcium nitrite, solution of amine-esters and an alkenyl-substituted succinic acid salt by comparing corrosion rate, mass loss and finding critical chloride corrosion threshold values (CCCT) both in steel embedded concrete samples and in pore solution. It was confirmed at that amine-ester inhibits the corrosion by forming a film around metal surface. It was also reported that these chemicals formed insoluble salts and thus blocks the pores in concrete. The inhibiting property of succinic acid salts was explained on the basis the compound has a polar end tail which can bind on to the steel reinforcement. Thus, protects it from corrosion. This compound is also known for its hydrophobic properties which helps in resisting moisture to enter into concrete. Succinic acid salts were most successful in delaying the initiation of corrosion. This chemical delayed the corrosion 28 week followed by calcium nitrite which delayed the corrosion by 26 weeks and AE by 19 weeks. The results of corrosion loss (metal loss) are displayed in Fig. 2.9. All the commercially available inhibitors were found to be successful in inhibiting corrosion. ASSA was found to be most effective of them all.

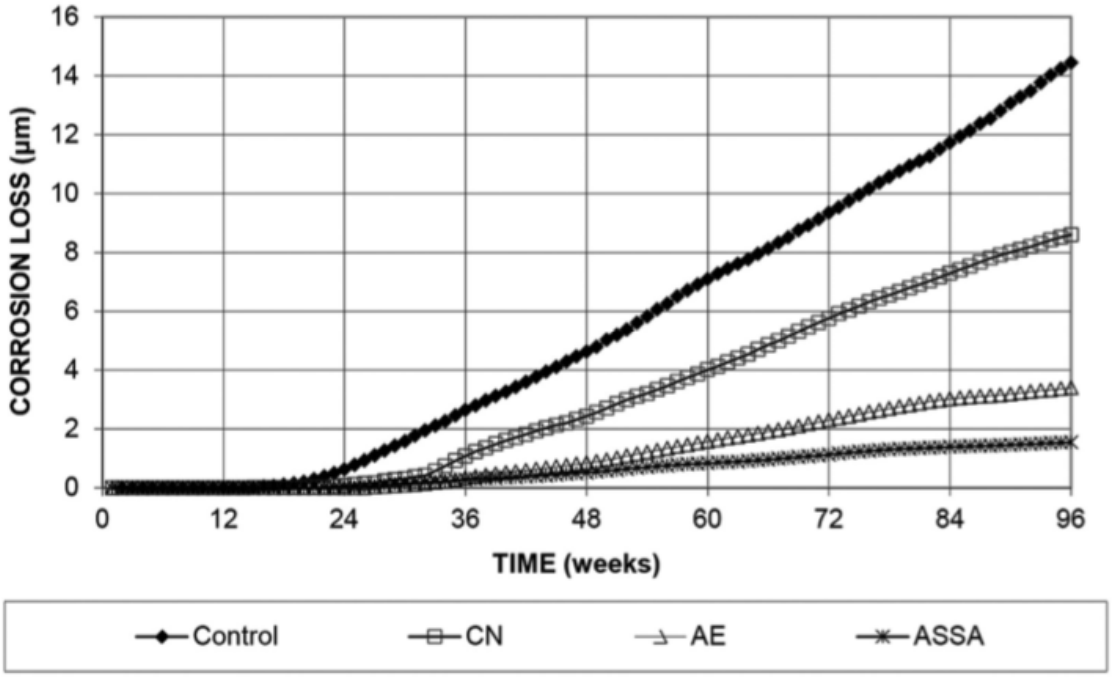


Fig.2.9: Corrosion loss (metal loss) of samples treated with inhibitors

(Riley et al. 2006)

Trabanelli et.al (2005)

They performed electrochemical impedance spectroscopy test to monitor corrosion inhibiting properties of derivatives and salts of benzoate salts. EIS test was performed on rebar steel samples immersed in saturated $Ca(OH)_2$ solution. Solution was contaminated with CO_2, by bubbling the solution with CO_2 gas till pH of solution came down to 7. This test was also performed on steel embedded concrete samples where inhibitors were added as admixture while casting. Concrete samples were kept in carbonation chamber in carbon dioxide environment at 68% RH at room temperature for 80 days. It was reported that in simulated concrete pore solution, there was formation of a long-lasting passive layer on rebar by amino-derivatives and di-carboxylates salts of benzoate.

EIS results showed that there was only one capacitive semicircle in 102-103 range of frequency which indicates that corrosion process was due to transfer of charge during short immersion times. It was also reported that there was very low solution conductance after 1 hour of immersion only which led to low frequency results. It was seen that corrosion inhibiting property of chemicals improved with time. On the other hand, only two compounds of benzoate; benzoic acid and 2-Amino-benzoic acid were able to control corrosion when tested as admixtures in concrete samples. The effect of benzoic acid was visible only after 40 days of exposure while corrosion inhibiting efficiency of 2-Amino-benzoic acid was found to be about 60%.

Wombacher et al. (2004)

They presented and summed up the behavior of corrosion inhibitors based on amino alcohol. Case studies and new techniques were used to find and present the properties of these water-based corrosion inhibitors concrete or to prolong corrosion initiation and to minimize corrosion rate. The corrosion inhibitor tested was an aqueous mixture of partially neutralized amino alcohol.

Penetration of AMA's into carbonated concrete was tested by ion chromatography. In this, they prepared two sets of concrete specimen viz high strength and low strength with low and high water-cement ratios respectively. In these samples, concrete was casted in two parts in which the outer part was exposed to accelerated carbonation (4% CO_2) and the other part of same quality was then casted. AMA based corrosion inhibitors were used to treat concrete samples.

The concentration of inhibitor applied was 400 g/m^2 in 1 year. The concrete samples were then layered and crushed. The crushed concrete was then extracted and resulting solution was filtered

through 0.45µ membrane and inhibitor was detected by ion chromatography. Electrochemical tests in solution were also performed. The solution was made using inhibitors concentration of 0-7.5%. Solution was subjected to chloride contamination. To reach the chloride concentration of 2.5%, 25ml of 1M $KMnO_3$ solution and deionized water at pH of 11.5. Cathodic Potential-dynamic polarization test were performed at scan rate of 10mV/s in for 30 minutes. Results are shown in Table 2.3. Potential, current density and EIS tests were performed on concrete mortar specimen of w/c ratio=0.7 with steel embedded in them. Reading were taken after 90days of storage in 80% RH and curing of probes in 0,1%, 2%, 3% and 4% chloride ions by weight. Measurements were made using three electrode system. Results are shown in Fig. 2.10. From the results, they concluded that inhibitors penetrated into the concrete. It was also seen that inhibitor penetration was better in concrete of lower grade. Maximum inhibitor-chloride ion concentration was 1%. These results confirmed the effectiveness of surface applied inhibitors which can be applied on surface of concrete by brushing, spraying or ponding. The inhibitor was reported to migrate to steel surface successfully

Table 2.3: Corrosion Potential values obtained from potentio-dynamic tests

Wombacher et al. (2004)

Chloride ion Percentage concentration	Inhibitor concentration (on solution)			
	0%	3.50%	5%	7.50%
0%	--------	719	681	756
0.50%	-201	800	744	678
1%	-203	314	335	490
1.50%	-211	305	330	352
2%	-244	17	141	204
2.50%	-249	-50	-47	163

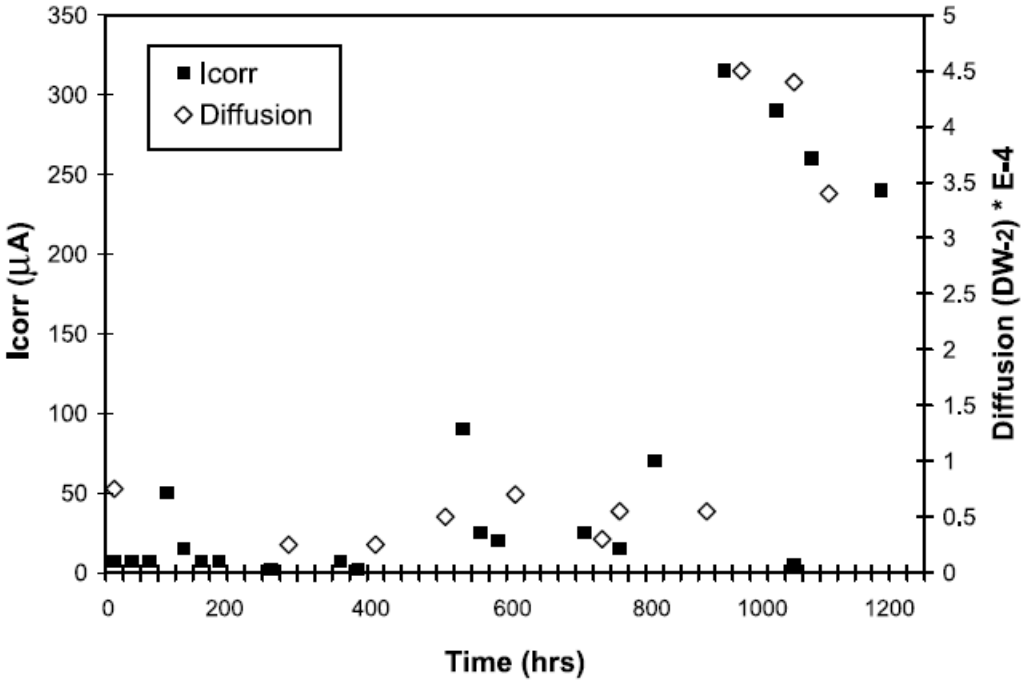


Fig. 2.10: Potentio-dynamic polarization test was performed at scan rate of 10mV/s in cathodic direction (*Wombacher et al. 2004)*

Jamil et al. (2004)

Electrochemical methods were used to test and compare the corrosion inhibiting properties of commercially available amino alcohol based corrosion inhibitors. Two types of corrosion inhibitors were used and tested; admixture type which are also known as preventive corrosion inhibitors which are added into water while casting. Seconds are migratory corrosion inhibitors which are applied on concrete and they are known to migrate inside the pores of concrete. The chemicals were tested in simulated concrete pore solution with contamination of 4g/l of chloride ions. The pH of solution was maintained at 12.5 before contamination. Electrochemical tests which include potentio-dynamic linear polarization test, electrochemical impedance spectroscopy test and scanning vibrational electrode techniques were used to monitor corrosion. From the results it was reported that corrosion current density values were reduced by 4 times when corrosion inhibitor was added. It was seen that only anodic curve values were affected. Therefore, it was reported that admixture type corrosion inhibitor acted as anodic inhibitor. Infact both the inhibitors were able to reduce corrosion current density values in concrete pore solution mixed with 2g/l of sodium chloride. It was reported that admixture type inhibitors were adsorbed on surface of steel which led to complete of hindrance of anodic activity at later stage of testing. Whereas on the other

hand migratory inhibitors are effective even when corrosion already was already existing on the surface. A stable and active film was formed by the inhibitors which was adsorbed on the active sites of the rebar. The results of electrochemical tests are presented in the Figures 2.11 and 2.12.

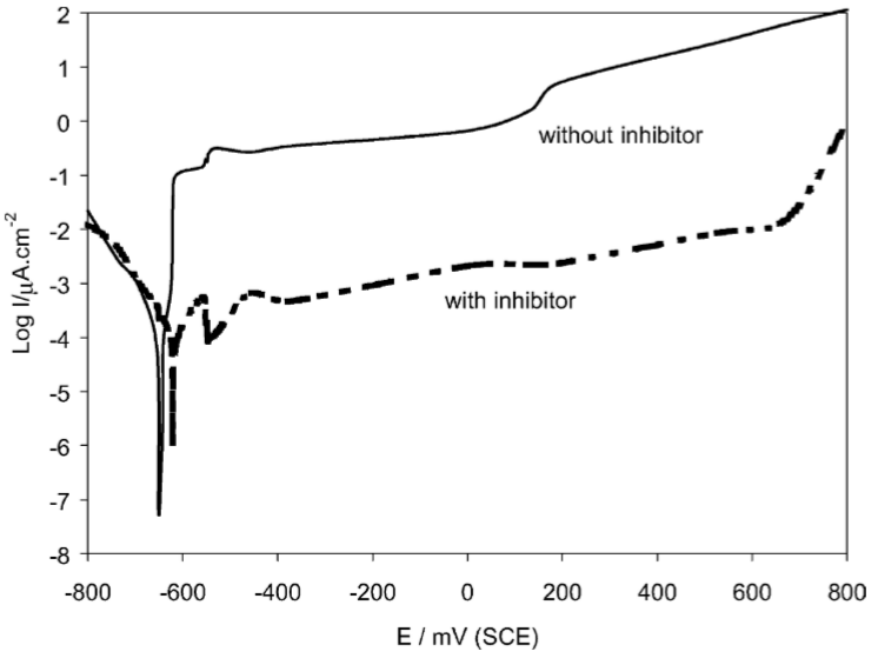


Fig. 2.11: Potentio-dynamic curve with and without admixed type inhibitor (*Jamil et al. 2004*)

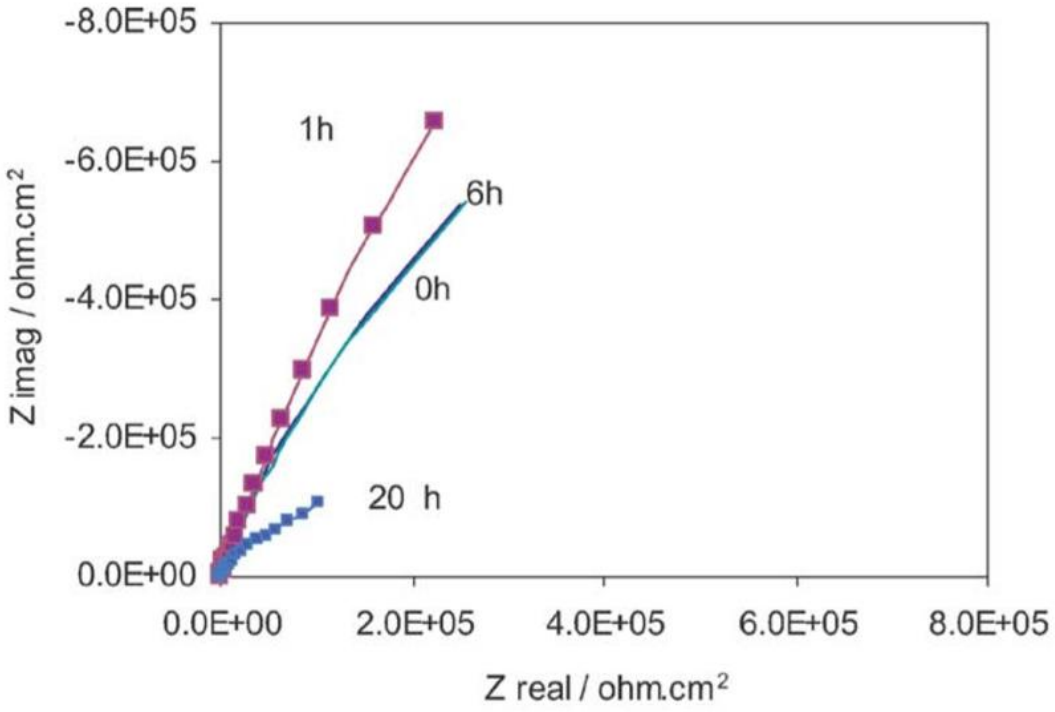


Fig. 2.12 Impedance spectra of control samples (*Jamil et al. 2004)*

Elsener et al. (1999)

Determined the effectiveness of hydroxyalkylamines as migrating corrosion inhibitor in inhibiting corrosion of mild steel in saturated calcium hydroxide solutions and in steel embedded concrete samples. Their effectiveness against localized corrosion caused by chlrode ions and uniform corrosion caused by carbonated environment was determined. In pore solution, saturated calomel electrode (SCE) and a multimeter were used to determine corrosion potential). In mortar, Corrosion monitoring was done by galvanostatic pulse measurement. Carbonation depth test was also conducted on cylindrical concrete samples.

From the results it was reported that the tested chemical was effective as migratory inhibitor at high concentration only in pore solution when solution was subjected to 1M/L chloride contamination. Non-volatile component of migratory corrosion inhibitor plays an important role in determining its efficiency. Tested chemical was ineffective in inhibiting corrosion under carbonated contaminated environment both in pore solution and in reinforced concrete samples. No significant reduction in carbonation depth was reported even after 200 days of testing. Steel bars were found to be damaged about 30-70% after 380 days. The chemical was reported to be lost as due to evaporation loss of volatile component of chemical when it applied on the surface of concrete samples. Therefore, the prediction of effectiveness of corrosion inhibitor on real structure was difficult as the inhibitor was found to evaporate from the concrete surface. This corrosion inhibiting properties were lost due to evaporation. Hence, the long-term effectiveness of hydroxyalkylamine was not confirmed.

2.3 SUMMARY

In this literature review, researches on different type of organic corrosion inhibitors which amine as functional group was discussed. Most of the commercial used corrosion inhibitors are amine based. Several single-chained simple hydrocarbons containing alcohol and amine as functional groups have been extensively studied and found to be effective as corrosion inhibitors when added as an admixture into the concrete as well as when applied on the surface of concrete. However, the research on double chained cyclic hydrocarbons containing amine and alcohol as functional groups to be used as corrosion inhibitors in concrete and the effect of positioning of the main functional group on corrosion inhibiting property of that compound, is very limited. Therefore, the chemicals which are studied in this research are 2-Aminophenol, 3-Aminophenol and 4-Aminophenol.

CHATPTER 3

EXPERIMENTAL PROGRAM

3.1 GENERAL

In this chapter, the experimental setup which was used in order to achieve the objectives of this research are presented and discussed. The principle of tests, working and equipment used in experiments are also discussed in detail. Properties of material used, quality and guidelines which were followed during testing are also presented in this chapter. In this chapter, chemical and physical properties of the material used in electrochemical tests in pore solution is discussed. The quality of material, grade and brand of material is also mentioned. The materials are discussed one by one.

3.2 EXPERIMENTAL SET UP

The main aim of this research was to study the effectiveness of resonating structures of Aminophenols- 2-Aminophenol (2AP), 3-Aminophenol (3AP) and 4-Aminophenol (4AP) as corrosion inhibitors in carbon dioxide contaminated environment. Fig. 3.1 presents the experimental set used for determining efficiency of these chemicals as corrosion inhibitors in the form of a flow chart.

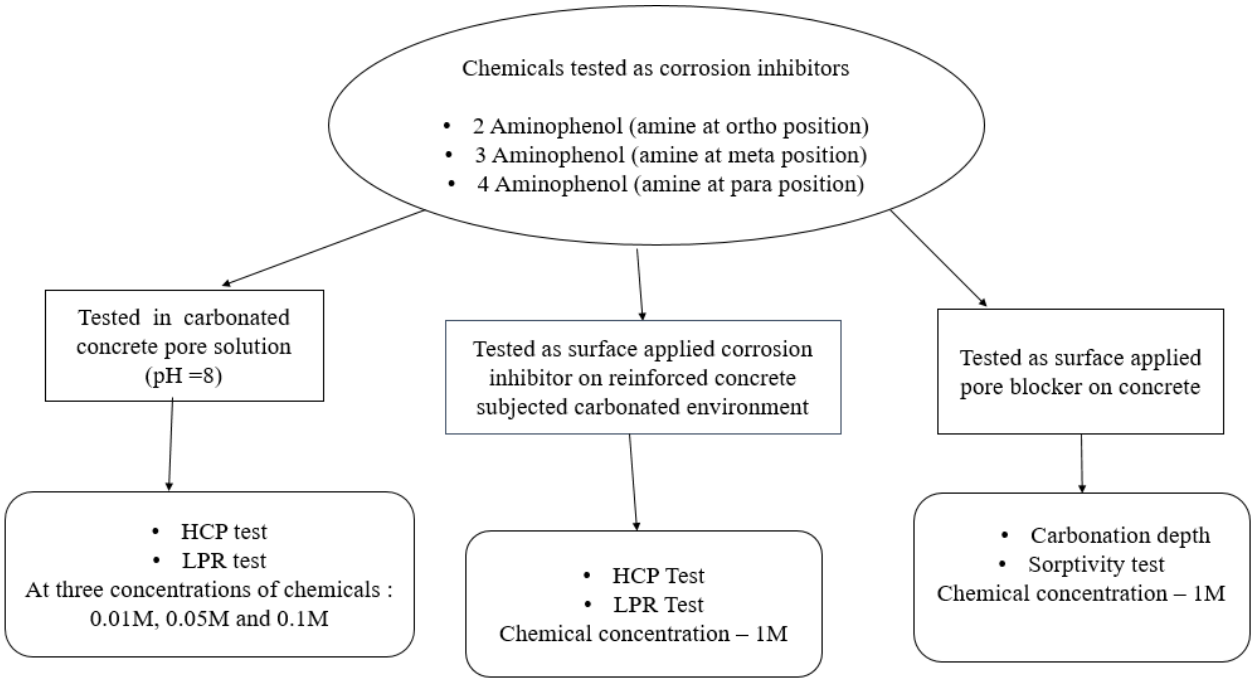


Fig. 3.1: Experimental set up to test efficiency of chemicals as corrosion inhibitors

3.3 STUDY ON SIMULATED CONCRETE PORE SOLUTION

To test the efficiency of the resonating structures of 2AP, 3AP and 4AP as corrosion inhibitors, electrochemical tests were conducted in pore-solution. Chemical and physical properties of inhibitors, preparation of pore solution, preparation of samples and testing procedures in pore solution are discussed in this section.

3.3.1 Materials

The materials and chemicals used for preparation of samples for conducting tests in pore solution are discussed in this section.

3.3.1.1 Chemicals used as corrosion inhibitors

The effectiveness of organic compounds having amine as functional group has been confirmed by many researchers but the study on effect of positioning of amine functional group in a compound on corrosion inhibiting properties is very limited. The amine functional group is present at ortho, meta and para positions in 2-Aminophenol, 3-Aminophenol and 4-Aminophenol respectively. The chemical and physical properties of these three chemicals are presented in Table 3.1. The actual appearance of the chemicals can be seen from Fig. 3.2.

Table 3.1: Properties of inhibitors (www.chemspider.com)

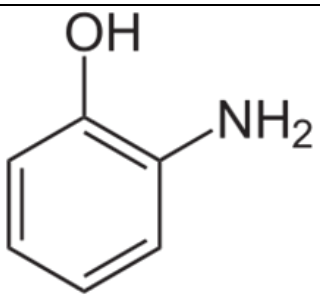
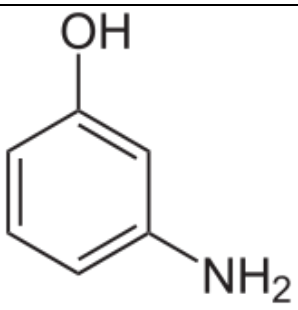
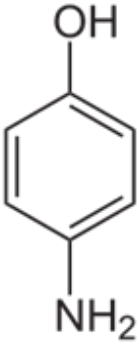
Chemical name	**2-Aminophenol**	**3-Aminophenol**	**4-Aminophenol**
Structure			
Appearance	**Reddish brown pyramidal needles**	**White orthorhombic crystals**	**Colorless to reddish-yellow crystals**
Molar mass	**109.13 g/mol**	**109.13 g/mol**	**109.13 g/mol**
Density	**1.328 g/cm^3**	**1.195 g/cm^3**	**1.13 g/cm^3**

Fig. 3.2: Physical appearance of inhibitors used

3.3.1.2 Chemicals other than inhibitors

Calcium hydroxide ($Ca(OH)_2$), potassium hydroxide (KOH) and sodium hydroxide (NaOH) were also used in preparation of pore solution. Calcium hydroxide was available in powdered form while potassium hydroxide and sodium hydroxide were available in white crystals pellets.

3.3.1.3 Steel Bars

Thermo-mechanically treated (TMT) steel bars of diameter 12 mm, grade Fe-500 d belonging to TATA TISCON were used in the experiment.

Table 3.2 Chemical Composition of Steel rebar samples (www.tatatiscon.in)

Properties	Constituent	Fe500 (% Max.)
Chemical properties	Carbon	0.30
	Sulphur	0.055
	Phosphorus	0.055
	Nitrogen	120
Physical properties	Minimum Yield Strength (N/mm^2)	500 N/mm^2
	Minimum Ultimate tensile strength (N/mm^2)	601 N/mm^2
	Minimum Elongation %	12.0

3.3.1.4 Epoxy

Fig. 3.3: Resin and Hardener used as epoxy

All-purpose epoxy adhesive of "fevitite" brand (shown in Fig 3.3) was used to make the samples waterproof wherever applied. Equal quantities by volume of resin and hardener were taken and mixed thoroughly. The mixture was applied with the help of plastic spatula on steel and concrete samples.

Once applied, the adhesive action of mixture of resin and hardener starts immediately. However, it takes about 180 minutes for epoxy to complete set on the surface. Proper gloves and gears must be used while applying epoxy as it is very adhesive to skin.

3.3.3 Preparation of simulated concrete pore solution

A concrete pore solution was simulated by mixing 1g $Ca(OH)_2$, 8g KOH and 4g NaOH in 1 litre of distilled water. The mixture was then left undisturbed for 24 hours. Thereafter, mixture was filtered to separate the precipitates with the help of a filter paper. The solution thus obtained was simulated concrete pore solution with pH more than 13. Carbon dioxide gas was bubbled into the mixture till the pH of the mixture came down 8 in order to simulate carbon-dioxide contaminated environment to concrete samples.

The chemicals 2AP, 3AP and 4AP were mixed in the prepared pore solution at three different concentrations. Details of inhibitors mixed solutions are presented in Table 3.3.

Undisturbed triplicate solution for each test were prepared. The pH of every pore solution prepared was brought down to 8 from 13 by bubbling carbon-dioxide into the solution. Undisturbed Triplicate solutions were prepared for every testing period: 24 hours, 72 hours, 120 hours and 240 hours. Steel samples immersed in prepared pore solutions can be seen in Fig. 3.4.

Table 3.3: Details of carbonated pore solutions prepared for testing

Sr No.	Details of solution
1	Carbonated Control Pore solution
2	Pore solution + 0.01 M 2AP
3	Pore solution + 0.05 M 2AP
4	Pore solution + 0.1 M 2AP
5	Pore solution + 0.01 M 3AP
6	Pore solution + 0.05 M 3AP
7	Pore solution + 0.1 M 3AP
8	Pore solution + 0.01 M 4AP
9	Pore solution + 0.05 M 4AP
10	Pore solution + 0.1 M 4AP

Fig. 3.4: Steel samples immersed in prepared solution after 24 hours

3.3.4 Preparation of Steel Rebars

HYSD bars of grade 500-d of TATA TISCON were cut into 60mm pieces. Fig. 3.5 shows the schematic representation and specifications of steel samples. The actual prepared steel sample is presented in Fig. 3.6. A hole with threads was drilled on one end of the steel rebars to fit the screws on which connections were made. The plain end of the sample and bar up to 4 mm from that end was exposed to pore solution. Rest of the specimen was covered with two layers of epoxy coating. Undisturbed triplicate samples, 120 in number were prepared for tests in pore solution.

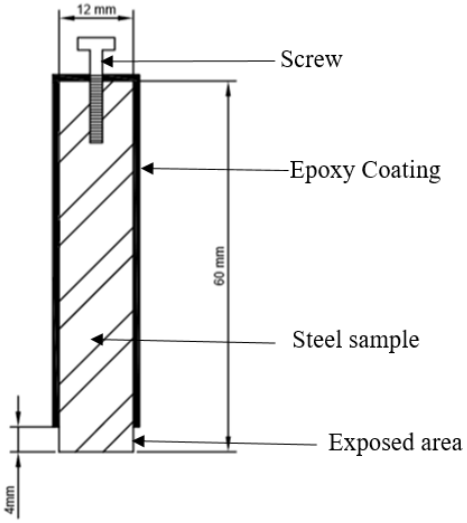


Fig. 3.5: Specifications of steel sample used in pore solution for electrochemical tests

Fig. 3.6: Prepared steel sample attached with wooden lid

3.3.4 Tests on pore solution

3.3.4.1 Half-Cell Potential Test

Half-cell potential measurement test helps in monitoring corrosion buy determining the potential difference between working electrode and standard calomel electrode which was used as reference electrode. The half-cell potential gives an idea about the ease of flow of electrons in solution. The more negative values of half-cell potential mean more probability of corrosion. To carry out this test, three electrode system was used. The working electrode was the steel sample itself. Calomel standard electrode was used as reference electrode. This electrode was dipped directly into the solution. The third electrode used was auxiliary electrode whose main function was to reduce the

noise and deviations in the experiment results. ACM field machine Serial no 1463 was used for all the electrochemical tests. The image of machine is presented in Fig. 3.7. The set up for conducting the test is shown in Fig. 3.8.

Fig. 3.7: ACM field Machine serial no. 1463 used for electrochemical tests

Fig. 3.8: Electro-chemical testing in carbonated pore solution using three electrode system

3.3.5 Linear Polarization Resistance Test

In this test potentio-dynamic linear sweep test was carried out on bare steel specimens using the ACM Field Machine. The electrochemical cell consists of a beaker with a wooden lid. It is provided with fittings for connecting the auxiliary electrode, reference electrode, and the specimen. Throughout the test, the reference electrode used was saturated calomel electrode (SCE). For testing, the bare steel specimen screwed to the working electrode, the reference electrode and auxiliary electrode were attached to the electrochemical cell.

The potentio-dynamic linear sweep test was carried out from -900 mV to +900 mV with offset from corrosion potential at a sweep rate of 60 mV per minute. Fig. 3.10 shows the input values for LPR test in pore solution. In this experiment, area exposed was 263.76 mm^2. Tafel curves were obtained from this test and corrosion current density values and corrosion potential values can be obtained as shown in Fig. 3.9. Typical Tafel plot obtained from LPR test is shown in Fig. 3.10. The condition of steel samples after electrochemical tests can be seen in Fig. 3.11.

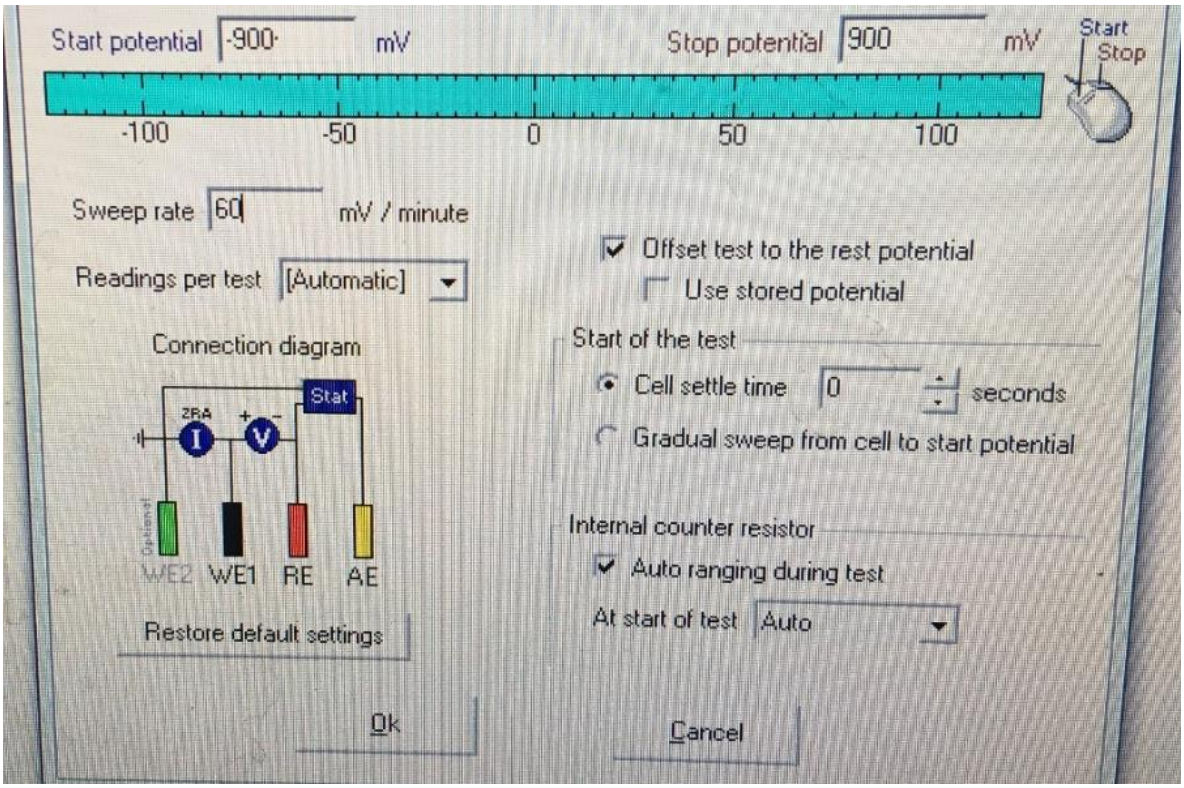


Fig. 3.9: Input values for LPR test in carbonated pore solution

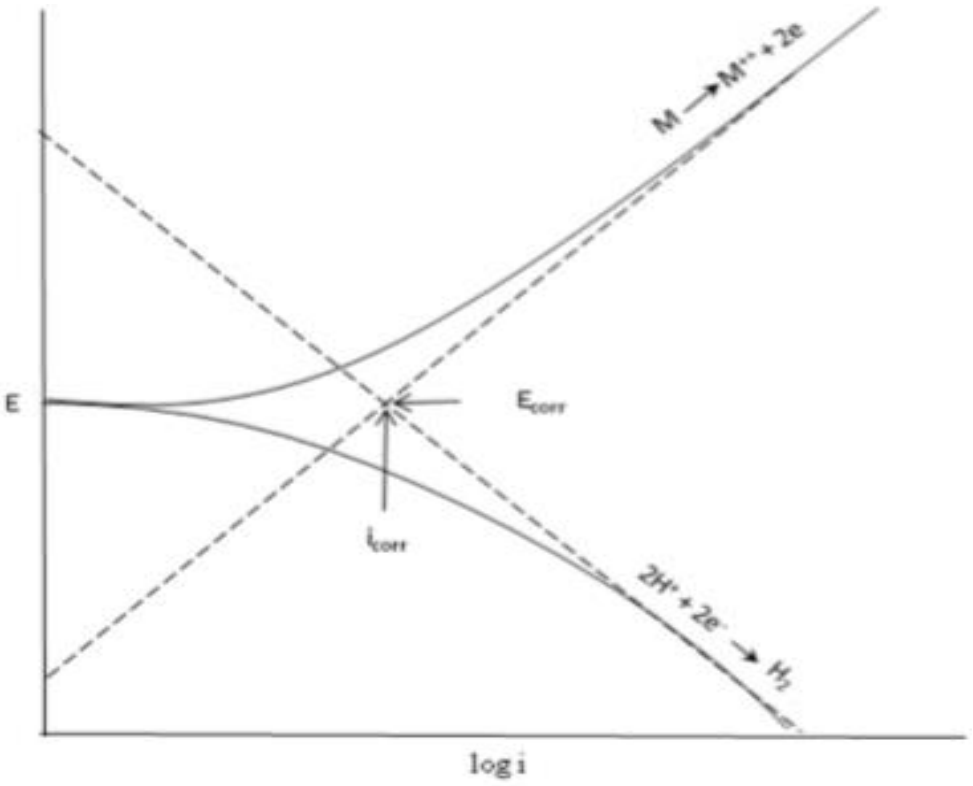


Fig. 3.10: Typical Tafel curve obtained from LPR test

Fig. 3.11: Steel samples after LPR test in carbonated pore solution

3.4 STUDY ON CONCRETE AND REINFORCED CONCRETE SAMPLES

To check the efficiency of 2AP, 3AP and 4AP as surface applied corrosion inhibitors, concrete samples were cast. The specifications of material used, preparation of concrete samples and testing procedures are discussed in this section.

3.4.1 Material

The specifications of materials used in preparation if concrete samples are presented in this section. Materials properties like composition of cement, specific gravity of aggregates, and grade of concrete samples were found out which are discussed in this section.

3.4.1.1 Cement

Ordinary Portland cement of 43 grade, conforming to IS: 8112-1989 (BIS, 2005) was used in casting of concrete samples. “Shree-ultra” brand OPC cement was available from local dealer. The chemical composition and physical properties of cement are presented in the Table 3.4 and Table 3.5 respectively.

Table 3.4: Chemical composition of OPC cement used

Compound	Percentage in OPC
SiO_2	20.68
Al_2O_3	4.87
Fe_2O_3	3.35
CaO	62.13
MgO	1.73
SO_3	2.43
Na_2O	0.21
K_2O	0.69
LOI	2.04

Table 3.5: Physical properties of OPC cement used

Specification	Value
Grade of cement	43-OPC
Specific gravity	3.1
Consistency	25%
Initial setting time	117 minutes
Final setting time	480 minutes

3.4.1.2 Fine aggregates

River sand was used as fine aggregate in concrete samples. Physical properties of sand such as water absorption, fineness modulus and specific gravity were determined which are presented in Table 3.6. Table 3.7 presents the results of sieve analysis on fine aggregates.

Table 3.6: Sieve Analysis of fine aggregates

Sieve size	Mass retained (g)	Cumulative mass retained (g)	Cumulative % mass retained
4.75 mm	34	34	3.4
2.36 mm	129	163	16.3
1.18 mm	175	338	33.8
600 microns	215	553	55.3
300 microns	340	893	89.3
150 microns	68	961	96.1
Pan	39	1000	
Fineness modulus – 294.2/100 = 2.942			**Σ %age retained = 294.2**

Table 3.7: Physical properties of fine aggregates

Properties	Results
Fineness modulus	2.942
Zone	II
Water absorption %	1.38
Specific gravity	2.66

3.4.1.3 Coarse aggregates

Crushed gravel with nominal maximum size of 10 mm and 20 mm were used as coarse aggregates in casting of concrete samples. Specific gravity and water absorption values of both types of coarse aggregates were determined which are presented in Table 3.8.

Table 3.8: Physical Properties of Coarse aggregates

Properties	10 mm	20 mm
Water absorption	0.63	0.55
Specific gravity	2.71	2.73

3.4.1.4 Epoxy

All-purpose epoxy adhesive of "fevitite" brand was used to make the seal the concrete samples surface. The mixing of resin and hardener was same as discussed earlier in section 3.3.1.4.

3.4.2 Preparation of steel bars

Steel rebars of length 230 mm and diameter 12 mm were used in reinforced concrete samples. A hole with threads was drilled on one end of the bar to fit the screw. Upto 50 mm length from that end, two coats of epoxy were applied on rebar. The second coat of epoxy was applied 2 hours after the first coat. The rebars were then allowed to air dry. Epoxy coated rebar can be seen in Fig. 3.12.

Fig. 3.12: Steel rebars used in concrete tests marked for application of epoxy

3.4.3 Concrete Mix Proportion

The concrete and reinforced concrete samples were cast of the grade M20. Many studies have confirmed that effectiveness of surface applied corrosion inhibitors decreases with increase in grade of concrete. This is because difficulty in penetration of migratory corrosion inhibitors in dense matrix of higher grade concrete. The mix design used for preparation of concrete samples is presented in Table 3.9.

Table 3.9: Mix design used to prepare concrete samples

Content	Quantity
Cement content (kg/m^3)	470
Weight of water (kg/m^3)	235
Weight of Fine aggregates (kg/m^3)	585
Weight of 20 mm aggrgates (kg/m^3)	920
Weight of 10 mm aggregates (kg/m^3)	590
w/c ratio	0.5

3.4.4 Casting and Curing Of Specimen

The casting and curing procedure of concrete samples and reinforced concrete samples for different tests is discussed in this section.

For Carbonation depth test, 60 Cubical concrete samples of size 100 mm of grade M20 were cast. Specimen were taken out of the mould, 24 hours after casting. Then they were immersed in water to cure for 14 days. The specimen were then allowed to air dry for 48 hours before application of epoxy and chemicals.

For sorptivity test, 12 cylindrical specimen of diameter 100 mm and height 50 mm were used in accordance with ASTM C 1585 – 04e1. The samples were cast in the moulds of 100 mm diameter and 200 mm height. The samples were taken out of the moulds after 24 hours and kept in water tank for curing for 14 days. Thereafter, cylinders were cut into height of 50 mm using concrete cutter.

Cylindrical concrete samples of height 200 mm and radius 100 mm were cast LPR and Half-cell potential tests. Prepared Steel bar of diameter 12 mm and length 230 mm were embedded in concrete at the time of casting. A clear cover of 20 mm was provided from the bottom of the cylindrical mould and 50 mm bar with end having hole was projected outside the cylinder as shown in Fig. 3.13. The samples were put inside water tanks for curing for 14 days, 24 hours after casting. Fig. 3.14 presents the actual picture of moulds at the time of casting.

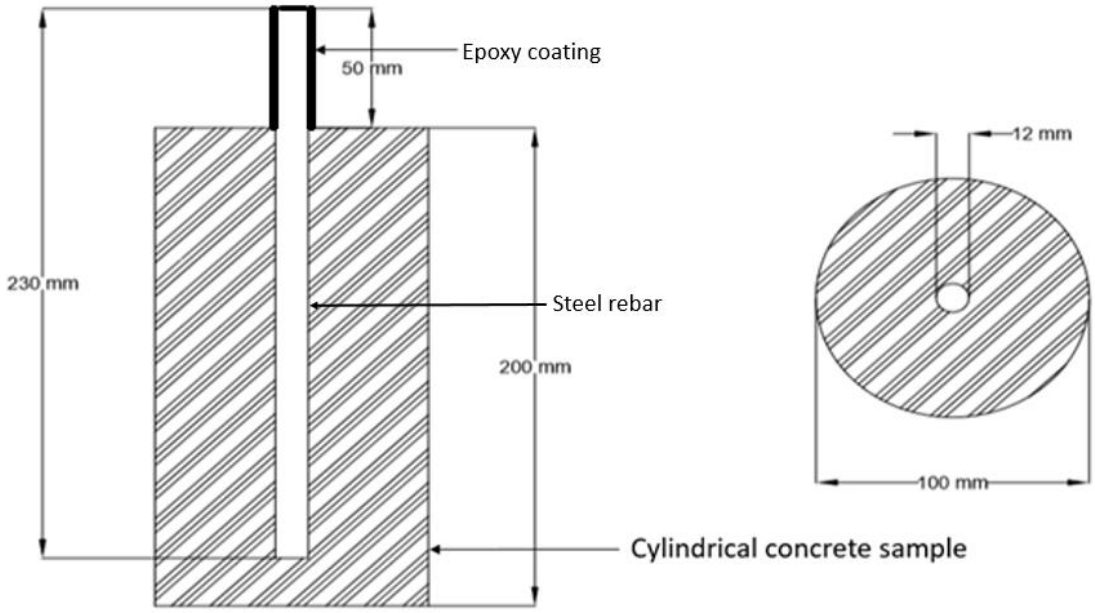


Fig. 3.13: Specifications of steel embedded cylindrical concrete samples

Fig. 3.14: Steel bars embedded in concrete samples at the time of casting

3.4.5 Preparation of samples after casting

Two coats of Epoxy was applied on five faces of cubes samples prepared for carbonation depth test after air drying. The face on which epoxy was not applied is called exposed face. The carbonation depth measurement was done perpendicular this face as carbon-dioxide will penetrate through exposed face only.

The cylindrical samples prepared for sorptivity test were preconditioned in the oven at temperature of 50^0C and RH 80% for 3 days. Thereafter, samples were placed in different sealed plastic boxes for 15 days. After the preconditioning, epoxy (water proofing) was applied on the sides of the cylindrical samples and one face of the sample was sealed with loose plastic sheet as shown in Fig. 3.15. The other end of the sample was called exposed face.

Fig. 3.15: Sample prepared for Sorptivity test covered with loose plastic sheet and epoxy

3.4.6 Application of Inhibitors

To test the efficiency of chemicals as surface applied migratory corrosion inhibitors, 1 M of each chemical was applied on concrete and reinforced concrete samples. In order to prepare 1M solution, chemicals were mixed in distilled water. 2AP and 4AP were soluble in hot distilled water (at temperature about 60^0 C) and required constant stirring to dissolve whereas 3AP was soluble in water at room temperature but required constant vigorous stirring. 1 M solution of each chemical was prepared. For 2AP solution, 21.8 grams of chemicals was added in 200 ml of hot water followed by constant stirring by a glass rod till the chemical powder in completely dissolved. Same procedure was followed to prepare 1 M solution of 4AP. For 3AP solution, 21.8 grams of chemical was added in 200 ml of water at room temperature followed by rigorous stirring till the chemical powder was fully dissolved. The three solutions prepared were then applied on their respective concrete samples.

Three layers of each inhibitor was applied on the exposed face of cubical specimen with the help of a brush. After application of one layer of inhibitor, the samples were left undisturbed and next coat was applied after 2 hours. After application of three layers of inhibitors, samples were left overnight to dry and ready to be put in carbonation chamber as shown in Fig. 3.16. All three inhibitors were applied in the same way. Same procedure was followed for application of chemicals on exposed face of cylindrical samples of sorptivity test. The prepared samples are presented in Fig. 3.17 and Fig. 3.18. The inhibitors were applied on all the sides of steel reinforced cylindrical samples in the same way.

Fig. 3.16: Prepared cubical samples for carbonation depth test

Fig. 3.17: Prepared steel embedded cylindrical concrete samples for electrochemical tests

Fig. 3.18: Prepared samples for sorptivity test

3.4.7 Exposure to Carbonated Environment

Reinforced concrete samples and cubical samples, after application of inhibitors were transferred into a sealed chamber where they were subjected to carbonation at temperature 27^{o}C, RH 70% and a CO_2 concentration of 5% by volume as shown in Fig. 3.19 and Fig. 3.20.

Fig. 3.19: Concrete samples subjected to accelerated carbonation inside carbonation chamber

Fig. 3.20: Concentration of CO_2 inside the incubator

3.4.8 Testing Of Concrete Samples

3.4.8.1 Carbonation Depth Test

The pH of concrete is around 12 -13, thus alkaline in nature. Indicator Phenolphthalein changes its colour from colourless to Pink in alkaline media so its colour upon it application on concrete that has pH value of more than 12 will change to pink. However, due to penetration of carbon di oxide, the pH of concrete lowers from 12 to 7 or 8, which is a neutral range. Spray of phenolphthalein solution on such concrete does not show any change in colour up-to the depth of carbon dioxide penetration.

Triplicate samples from each set were taken out of the carbonation chamber every 15 days and split from the exposed edge as shown in Fig. 3.1. After splitting the concrete samples, the freshly split surface was cleaned and sprayed with a phenolphthalein pH indicator as shown in Fig. 3.22 and Fig 3.23. In the noncarbonated part of the specimen, where the concrete was still highly alkaline, a purple-red color was obtained. In the carbonated part of the specimen where the alkalinity of concrete is reduced, no coloration occurred. The average depth 'X_p' of the colorless phenolphthalein region was measured at three points, perpendicular to the edge of exposed face after splitting of cube, immediately after spraying the indicator. The depth of carbon dioxide penetration into the concrete specimen was measured at 15 days interval starting from 15 days upto 75 days.

Fig. 3.21: Splitting of cubes for carbonation depth test

Fig. 3.22: Cube split from middle for carbonation depth

Fig. 3.23: Change in colour of concrete after application of phenolphthalein solution on split cube sample

3.4.8.2 Sorptivity Test

Sorptivity test was carried out by the procedure narrated in standard ASTM C 1585 – 04e1 "*Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic- Cement Concrete*". This test was conducted to compare the rate of absorption (sorptivity) of water by hydraulic cement concrete to that with cement concrete of same grade applied with chemicals which are to be tested as migratory corrosion inhibitors which is done by measuring the increase in the mass of a specimen resulting from absorption of water as a function of time when only one

surface of the specimen is exposed to water and compare. Mathematically, sorptivity can be calculated by

$$I = St^{1/2} \qquad \text{……. (3.1)}$$

Where 'I' is the cumulative water absorption per unit area of inflow surface, 'S' is the sorptivity and t is the elapsed time.

The cumulative change in weight was noted, the average cumulative absorption was calculated according to the equation 3.2:

$$I = M_t / A \times d \qquad \text{…. (3.2)}$$

M_t is difference in mass 'A' is area exposed to water and

'd' is water density in g/mm^3

Exposed area was 7850 mm^2 and Density of water 0.001 g/mm^3. From these calculations initial rate of absorption and secondary rate of absorption were calculated. The initial rate of water absorption (mm/s$^{1/2}$) is defined as the slope of the line that is the best fit to I plotted against the square root of time (s$^{1/2}$). The Schematic representation of the procedure of sorptivity test is shown in Fig 3.24.

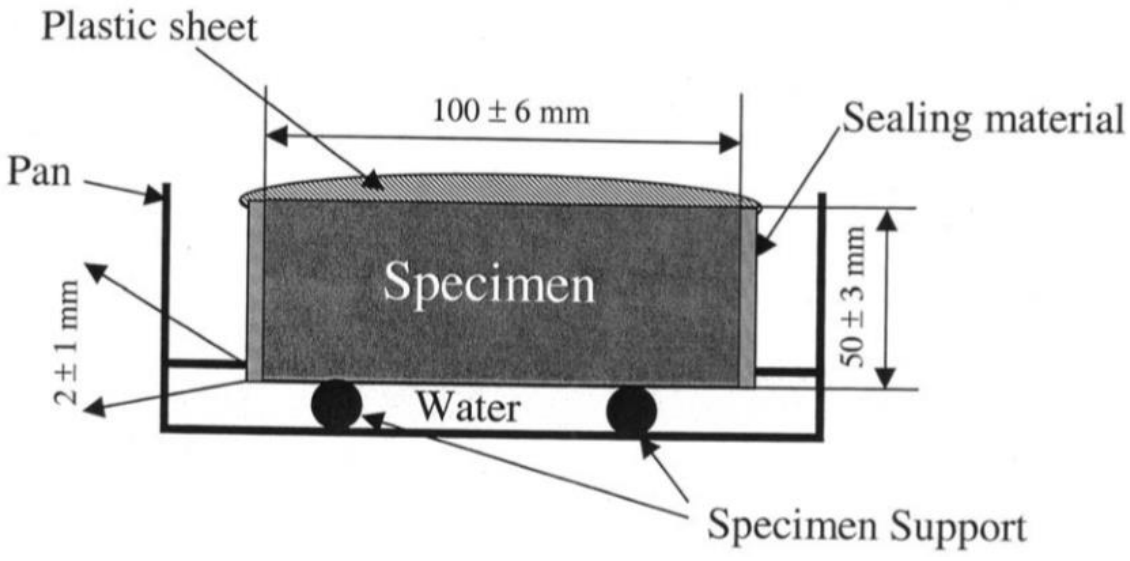


Fig. 3.24: Schematic representation of the procedure of sorptivity test

3.4.9 Testing Of Reinforced Concrete Samples

3.4.9.1 Half-Cell Potential Test on Steel Embedded Concrete Samples

Half-cell potential is the potential when there is no flow of current. Half-cell potential values give an indication of de-passivation of steel and hence the probability of corrosion.

Half-cell potential test was conducted on reinforced cylinder concrete samples. ACM machine Serial no. 1463 was used to carry out this test. A metallic guard-ring was wrapped around concrete sample. Half-cell potential values were obtained with respect to Saturated Calomel Electrode (SCE) as reference electrode. The embedded steel acted as working electrode and Saturated Calomel Electrode acted as reference electrode. Auxiliary electrode was attached with the guard ring. Rest potential checker was used to obtain rest potential values. The experiment set up is shown in Fig. 3.25. Half-cell potential which is also known as rest potential or equilibrium potential in pore solution and in concrete samples was recorded before initiating LPR test.

ASTM C876- 91 suggests that the probability of rebar corrosion, embedded in concrete when the Half-cell potential value is lower than -276 mV (SCE) is higher than 90%. In addition, when the Half-cell potential is more than -126 mV (SCE) the corrosion risk is lesser than 10%. However, between these values of -126 mV and -275 mV, the probability of corrosion is intermediate. Half-cell potential which is also known as rest potential can be measured in the beginning of the test before any application of current.

Fig. 3.25: Connections on steel embedded concrete samples for electrochemical tests

3.4.9.2 LPR Test on Steel Embedded Concrete Samples

Linear Polarization resistance test (LPR) was conducted son reinforced concrete samples to obtain Tafel curves and corrosion current density values. Corrosion current density values gibes an idea about the corrosion condition of the samples. Test was conducted on reinforced concrete sample which were treated with 2AP, 3AP and 4AP separately. Triplicate samples for each chemical were prepared. The LPR test results were compared with results of control samples.

For testing, the concrete samples were placed in a bucket containing 3.5% Nacl solution. A metallic net which acted as guard ring was tightly wrapped around the cylindrical concrete sample. A reference electrode, which connected to the ACM field machine was also immersed inside the solution. As LPR on concrete is a nondestructive test, tests were performed on same samples after every 15 days of exposure to carbonation. In this experiment, start potential was chosen at -25mV and end potential at 25mV with sweep rate of 10mV/minute as shown in Fig. 3.26. The test lasted for 5 minutes. Polarization curve was obtained after test and Tafel scale was used to measure I_{corr} and corrosion rate. The exposed area was 68.98 cm^2.

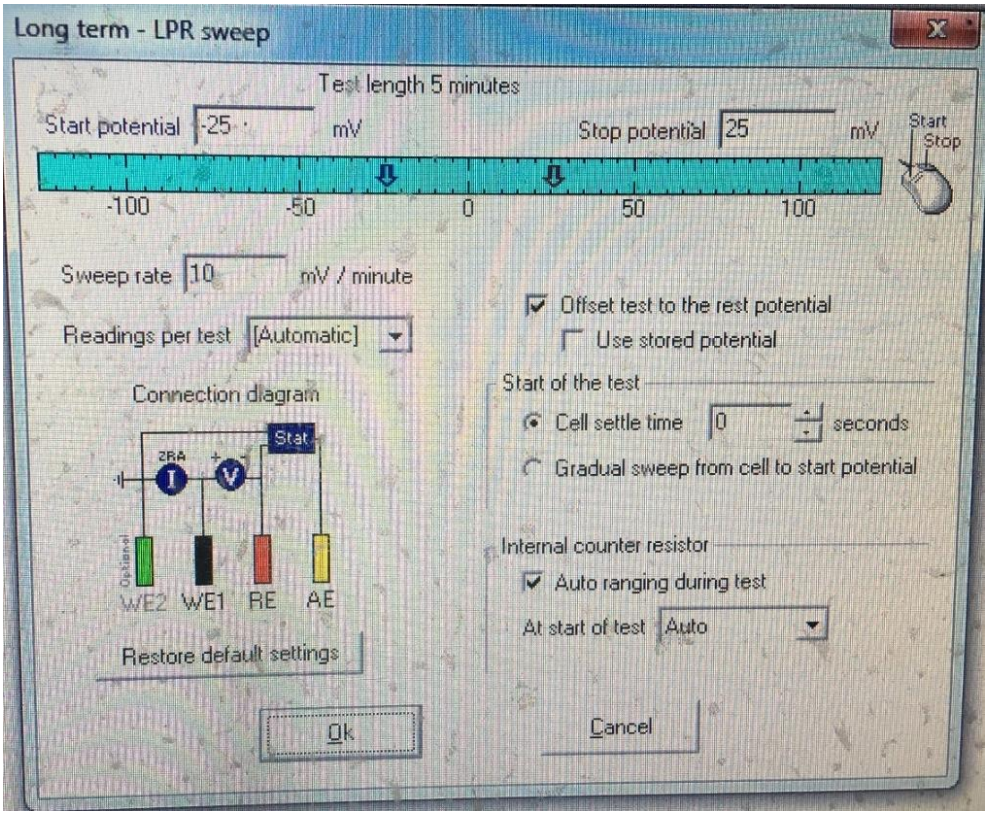


Fig. 3.26: Input values for LPR test on steel embedded concrete samples

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 GENERAL

This chapter presents the experimental results with a discussion on their significance. As discussed earlier, the main objective of this research was to examine and evaluate the corrosion inhibiting properties of the chemicals, their optimum concentration in solution and to find out the effect of change in positioning of main functional group on corrosion inhibiting properties in carbon di-oxide contaminated environment.

In this research, three levels of tests were conducted. Results of tests in pore solution are discussed in sections 4.2 to section 4.4. Results of tests on concrete samples are discussed in Sections 4.5 and section 4.6. Test results on reinforced concrete samples are discussed in section 4.7.

4.2 HALF-CELL POTENTIAL TEST IN PORE SOLUTION

Half-cell potential test was conducted on steel samples immersed in carbonated concrete pore solution mixed with different concentrations of 2-Aminophenol, 3-Aminophenol and 4-Aminophenol. Half-cell potential values, also called rest potential values were directly recorded from rest potential checker with the help of ACM machine. Rest potential values provide a clear indication of an active or passive state of sample.

The half-cell potential values obtained for different specimen immersed in solution containing different chemicals viz. 2AP, 3AP and 4AP as corrosion inhibitors and tested at 24 hours, 72 hours 120 hours and 240 hours are presented in Table 4.1. ASTM C 876-91 provides corrosion conditions of steel embedded in concrete samples on the basis of Half-cell potential values. As per this standard, half-cell potential values less than -276 mV/SCE represents more than 90% percent corrosion probability. However, as half-cell potential test was conducted in pore solution, the half-cell potential values obtained from this test cannot be compared with ASTM standard values. The corrosion condition of different samples was determined based on the principle that sample with more negative half-cell potential value was more likely to corrode than sample with less negative half-cell potential value.

It can be seen from Table 4.1 that average half-cell potential values of control samples was in the range -800 to -1000mV/SCE, whereas average half-cell potential values of samples immersed in chemical mixed pore solution ranged between -400mV/SCE and -600mV/SCE which is a

significant difference. This shows that probability of corrosion of samples immersed in chemical mixed pore solution was much less than samples immersed in control solution.

Table 4.1: Half-cell values at different concentration of inhibitors (mV/SCE)

Average Half-cell potential values (mV/SCE)					
			0.01M concentration		
Sr no.	**Time of immersion (Hours)**	**Control**	**2AP**	**3AP**	**4AP**
1	24	-912.52	-681.0	-473.40	-248.10
2	72	-925.41	-753.61	-492.17	-749.90
3	120	-782.40	-679.37	-342.95	-513.40
4	240	-940.16	-375.40	-374.5	-275.10
Average Half-cell potential (mV/SCE)					
			0.05M concentration		
Sr no.	**Time of immersion (Hours)**	**Control**	**2AP**	**3AP**	**4AP**
1	24	-912.57	-252.29	-772.17	-525.40
2	72	-925.43	-237.44	-534.0	-754.60
3	120	-782.42	-515.67	-413.70	-466.21
4	240	-940.18	-520.12	-676.30	-403.45
Average Half-cell potential (mV/SCE)					
			0.1 M concentration		
Sr no.	**Time of immersion (Hours)**	**Control**	**2AP**	**3AP**	**4AP**
1	24	-912.5	-480.2	-347.1	-478.15
2	72	-925.4	-237.1	-524.5	-517.45
3	120	-782.4	-262	-261.7	-355.0
4	240	-940.1	-620.4	-520.6	-502.55

4.2.1 Effect of type of chemical on Half-Cell potential values

The effect of investigated chemicals on Half-cell potential values at concentration 0.01M, 0.05M and 0.1M is provided in the form of bar graphs in Figures 4.1, 4.2 and 4.3 respectively.

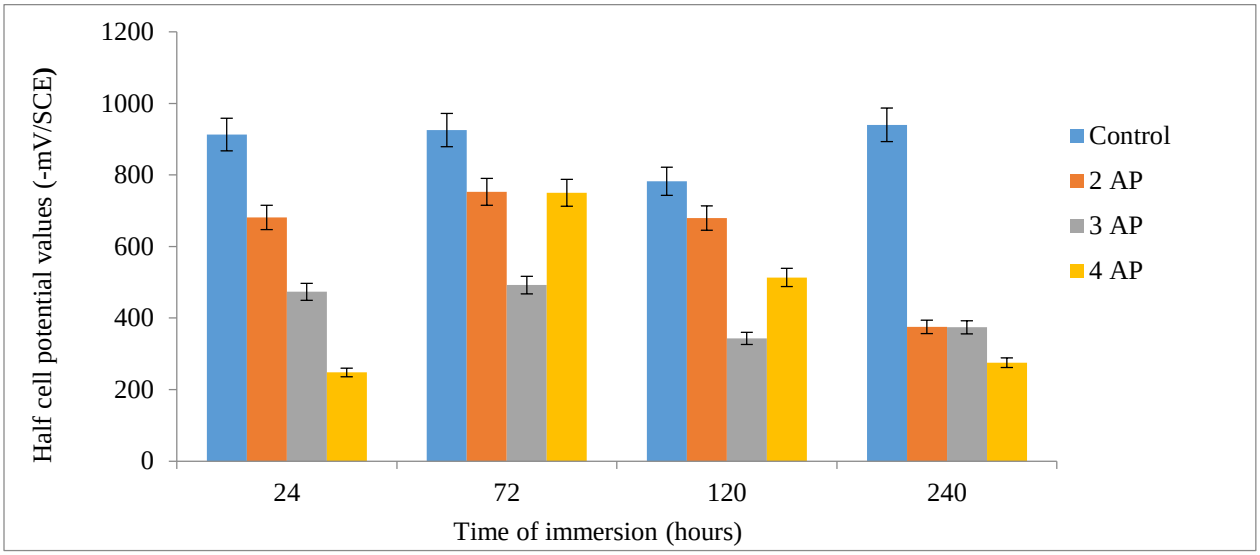


Fig. 4.1 Half-cell potential values (-mV/SCE) at values of steel specimen immersed in chemical mixed pore solution at 0.01M concentration

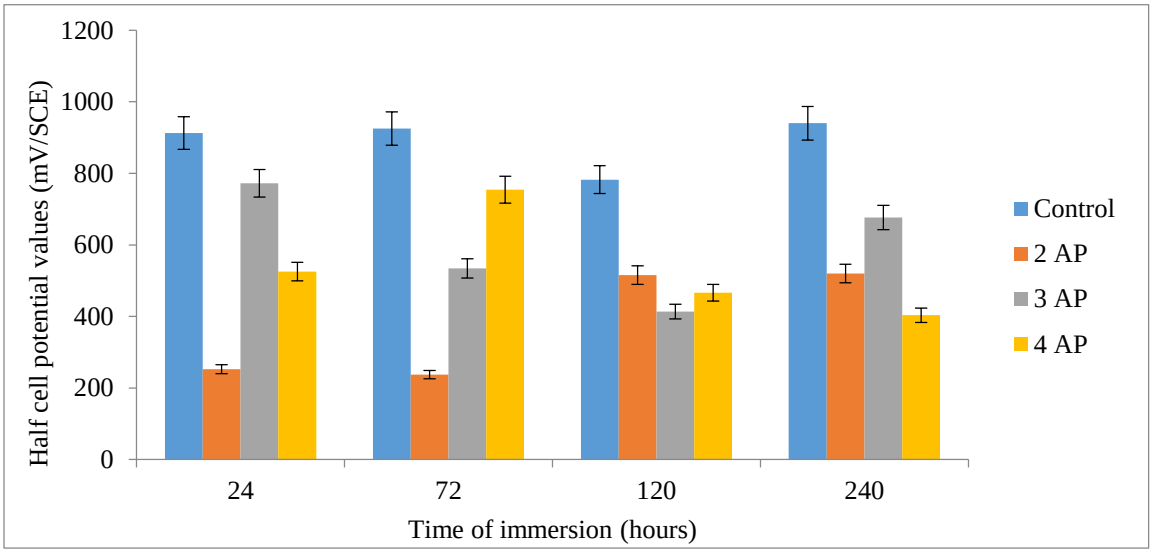


Fig. 4.2: Half-cell potential values at values (-mV/SCE) of steel specimen immersed in chemical mixed pore solution at 0.05M concentration

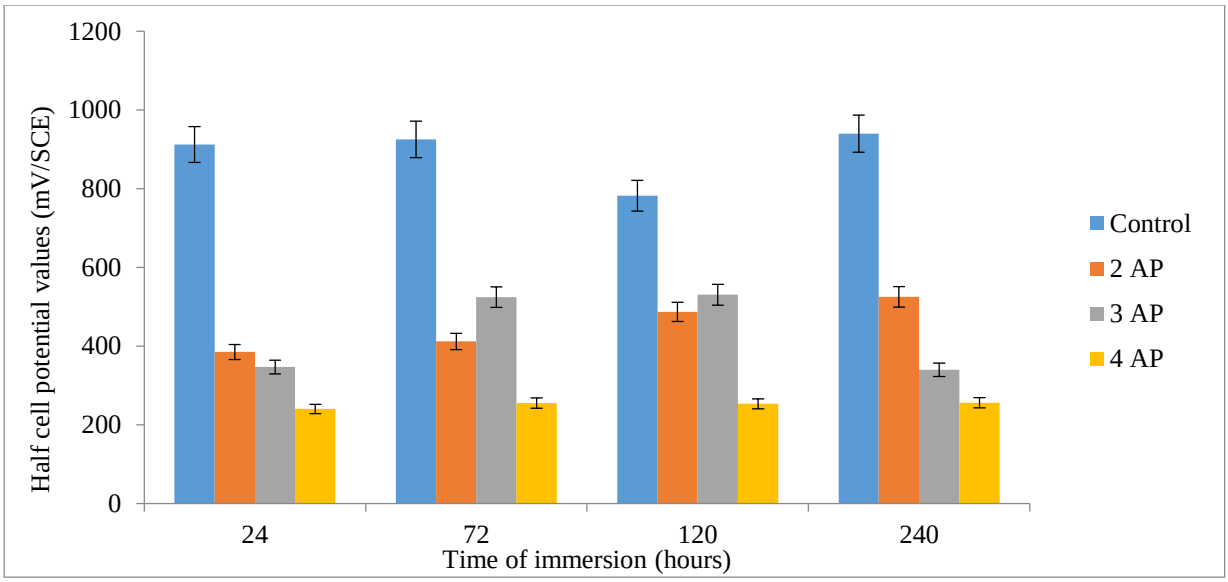


Fig. 4.3: Half-cell potential values at values (-mV/SCE) of steel specimen immersed in chemical mixed pore solution at 0.1 M concentration

From the bar graphs, it can be seen that half-cell potential of samples immersed in control solution attained more negative value with passage of time. High risk of corrosion of sample in pore solution at pH of 8 is evident in results. With passage of time, the extent of electrochemical reaction keeps on increasing, thus more electrons leave the anodic part of metal which results in making rest potential values more negative. This is exactly the phenomenon in actual concrete when carbonation happens to such an extent that pH of concrete surrounding the steel comes down from 13 to 8 which breaks the inherent protective oxide layer on steel and thus, leads to rapid corrosion in samples immersed in control solution.

From these results, it can be inferred that all three chemicals regardless of position of functional group were able to reduce probability of corrosion in steel samples. Rest potential values of samples immersed in 2AP either decreased with passage of time or remained stable with passage of time at all three concentrations. Similar trend was observed in samples immersed in 4AP mixed pore solution. The half-cell potential values of samples immersed in 3AP assumed stable values with passage of time.

The chemicals were effective in controlling corrosion in all three concentrations however, the efficiency of all three investigated chemicals in inhibiting corrosion in steel samples was higher at 0.1M concentration. The difference in half-cell potential values between control and chemical mixed solution was most significant at 0.1M concentration. At 0.1M concentration 4AP was the

most effective chemical in inhibiting corrosion in steel samples and 2AP was the second most effective chemical.

4.3 LINEAR POLARIZATION RESISTANCE TEST IN PORE SOLUTION

Linear polarization resistance test was conducted on steel samples immersed in pore solutions containing 2Aminophenol, 3Aminophenol and 4Aminophenol at three concentrations of 0.01M, 0.05M and 0.1M as discussed earlier in section 3.3.5. In this test start potential and end potential were taken as -900mV and +900mV respectively with sweep rate of 60mV/sec. From this test, Tafel curves and corrosion current densities were obtained. LPR test results of control samples are discussed firstly followed by results of samples immersed in 2AP, 3AP and 4AP at three different concentrations of 0.01M, 0.05M and 0.1M.

4.3.1 LPR test results of steel samples in control pore solution

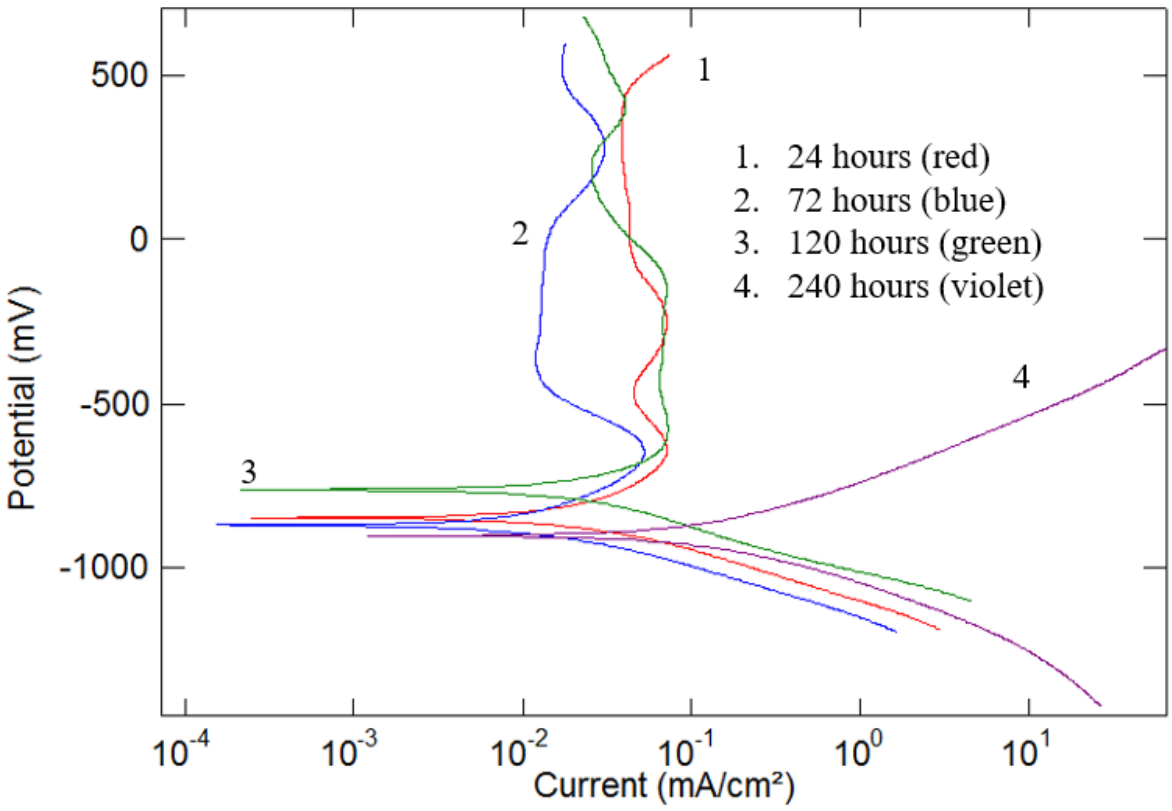


Fig. 4.4: Tafel curves of steel specimen immersed in Pore Solution (Control)

Table 4.2: Corrosion current density values of steel specimen immersed in carbonated control pore solution (Control)

Sr no.	Time of immersion (Hours)	I_{corr} (µA/cm^2)
1	24	8.87
2	72	11.57
3	120	12.45
4	240	20.77

Tafel curves of steel samples immersed control solution at different times of testing are presented in Fig. 4.4 and corrosion current densities are presented in Table 4.2. From Tafel curves, it can be seen that there was formation of passive layer on steel samples initially as curves shifted towards passive region however, after 240 hours, there was breakdown of passive layer as the curve shifted sharply towards active region.

From Table 4.2, it can be seen that initially the change in corrosion current densities was not very significant with passage of time. This could be due to formation of oxide layer on steel sample which act as passive layer and provides protection from further corrosion. But this passive layer seems to have been completely vanished after 240 hours. At this stage, anodic current densities invariable increased with the increase in potential. With the passage of time, the extent of electrochemical reaction keeps on increasing, thus more electrons leave the anodic part of metal which results in high I_{corr} values. In this experiment, the I_{corr} value increased from 8.876 µA/cm^2 after 24 hours to 20.772 µA/cm^2 after 240 hours. The increase in I_{corr} value was about 134% in 10 days.

4.3.2 LPR Test Results of Steel Samples Immersed In 2AP Mixed Pore Solution

LPR Test was conducted in 2-Aminophenol mixed carbonated pore solution at three concentrations 0.01M, 0.05M and 0.1M. Tafel curves of steel samples immersed in 2AP mixed pore-solution at three concentrations 0.01, 0.05M and 0.1M concentrations are presented in Figures 4.5, 4.6 and 4.7 respectively. The corrosion current densities for all the samples immersed in 2AP, obtained from LPR tests are presented in Table 4.3.

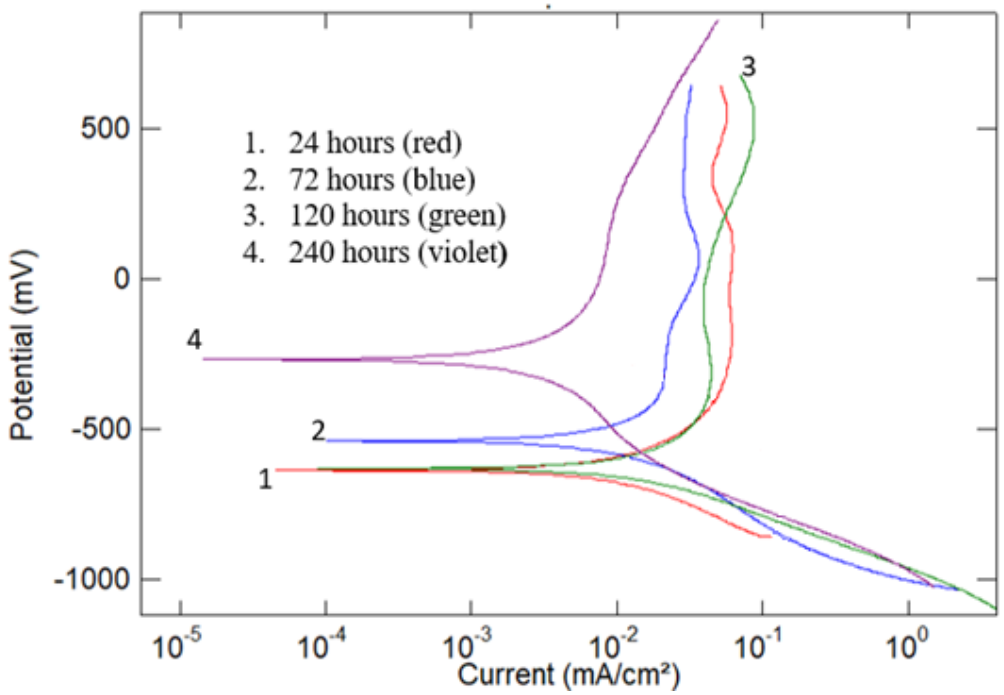


Fig. 4.5: Tafel curves of steel specimen immersed in 0.01M 2AP Mixed pore solution

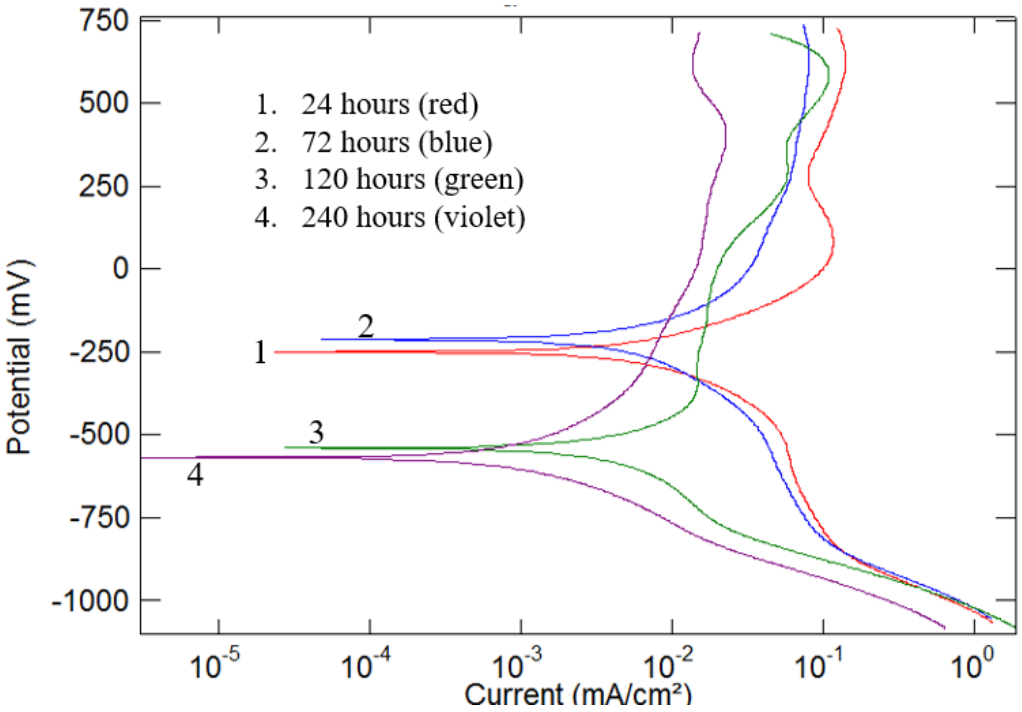


Fig. 4.6: Tafel curves of steel specimen immersed in 0.05M 2AP Mixed pore solution at different times of immersion

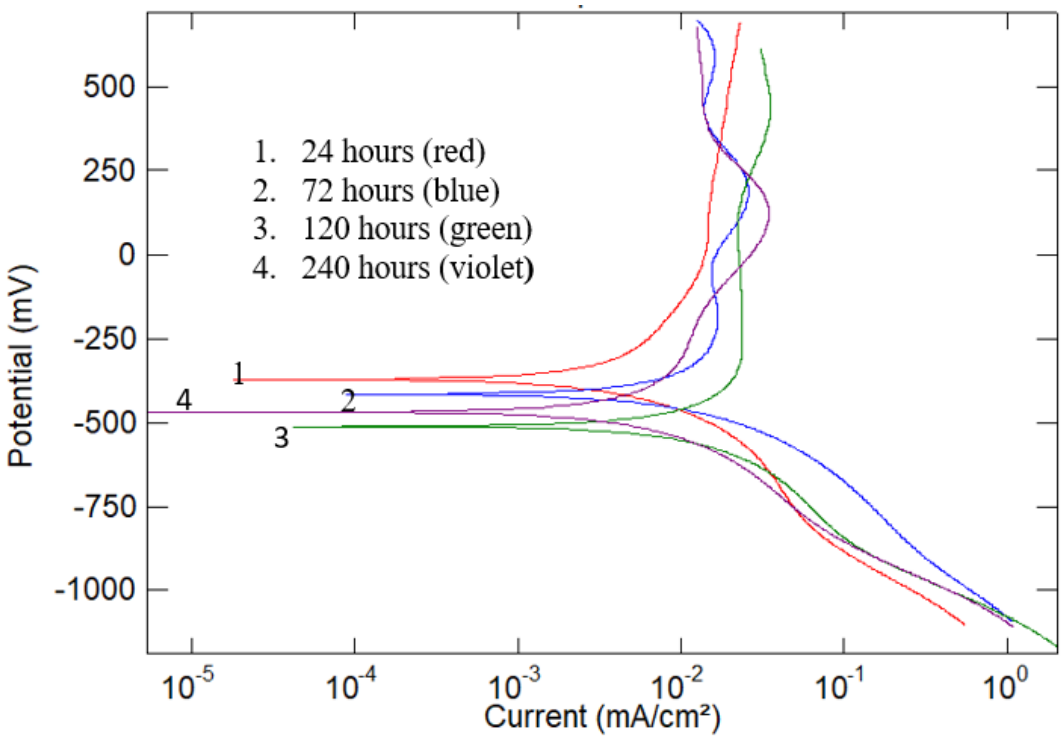


Fig. 4.7: Tafel curves of steel specimen immersed in 0.1M 2AP Mixed pore solution at different times of immersion

Table 4.3: Corrosion of steel specimen immersed in three different concentrations of 2AP mixed pore solution

Corrosion current density I_{corr} (µA/cm^2)				
Sr no.	**Time of immersion (Hours)**	**0.01 M concentration**	**0.05M concentration**	**0.1M concentration**
1	24	3.83	3.76	3.56
2	72	3.51	3.02	3.44
3	120	3.03	2.93	3.72
4	240	0.56	2.22	3.37

It can be seen from the Tafel curves in Fig. 4.5, that at concentration of 0.01M of 2AP a shift in anodic curves towards passive region with increase in time of immersion occurred, which could be due to formation of film around steel specimen. As concentration of 2AP was increased to 0.05M**,** a clear indication of formation of passive layer as anodic curves enter passive region with

increase in potential was observed. This passive region seems to grow stronger with time as anodic curves after 240 hours was in more passive state than after 120 hours followed by 72 hours and 24 hours. When concentration of 2AP was further increased to 0.1M, Tafel curves for all times of immersions were almost similar. A significant shift after 240 hours towards more passive region in Tafel curves was observed, which also explains the decrease in corrosion current density value after 240 hours. The shift towards passive region could be due to formation of film around steel samples which inhibited reaction responsible for corrosion.

From corrosion current values presented in Table 4.3, corrosion current density of samples immersed in 2AP mixed solution was considerably lower than control samples at all the concentrations. The I_{corr} values at all the concentration decreased with increase in time of immersion. The lower corrosion current density represents lower probability of corrosion. The corrosion current density values at all three concentrations were similar. Efficiency of 2AP in inhibiting corrosion increased with time.

4.3.3 LPR test results of steel samples immersed in 3AP mixed pore solution

Tafel curves of steel samples immersed in 3AP mixed pore-solution at variable concentrations of 0.01M, 0.05M and 0.1M concentrations are presented in Figures 4.8, 4.9 and 4.10 respectively. Data on corrosion current densities is presented in Table 4.4.

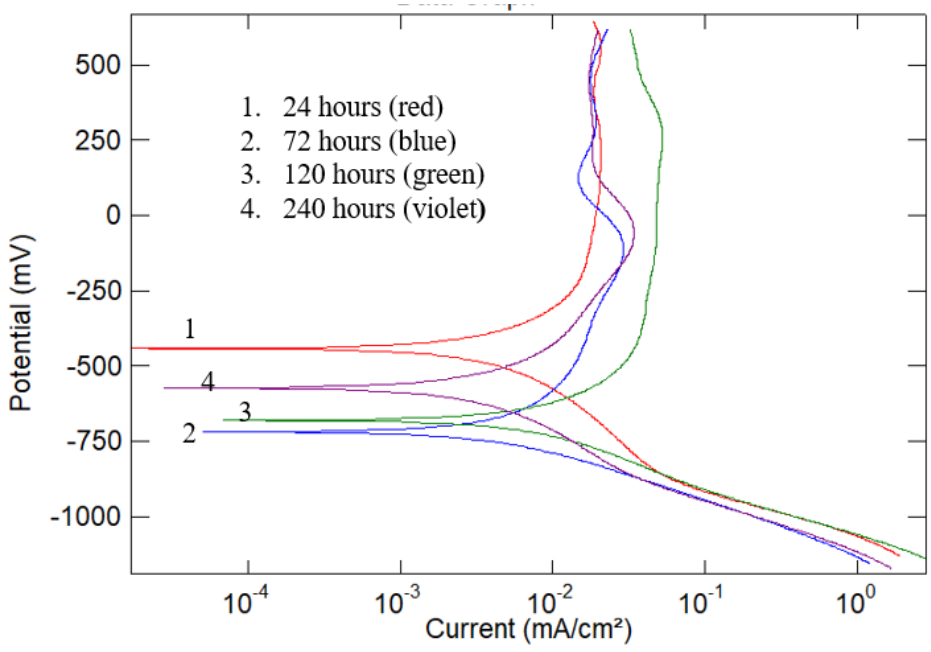


Fig. 4.8: Tafel curves of steel specimen immersed in 0.01 M 3AP Mixed pore solution at different times of immersion

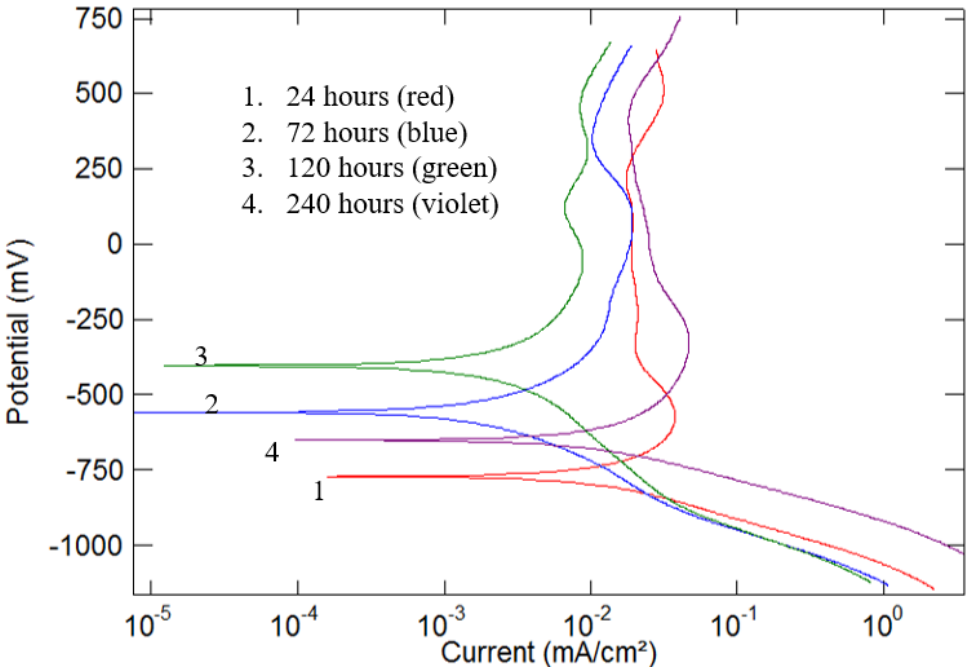


Fig. 4.9: Tafel curves of steel specimen immersed in 0.05 M 3AP Mixed pore solution at different times of immersion

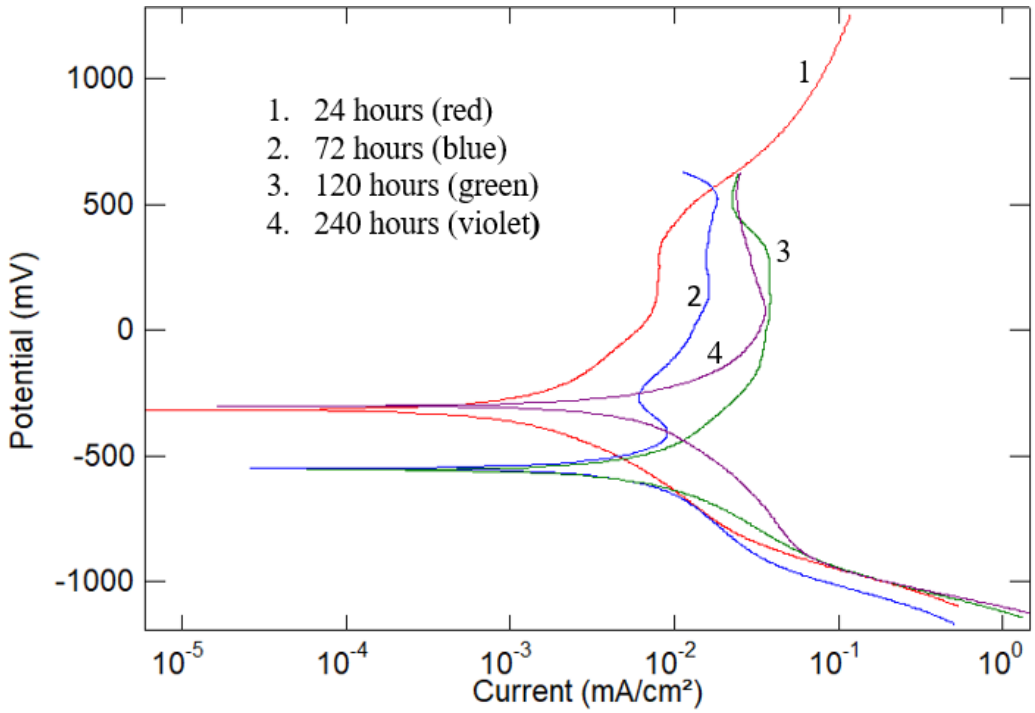


Fig. 4.10: Tafel curves of steel specimen immersed in 0.1 M 3AP Mixed pore solution at different times of immersion

Table 4.4: Corrosion current density values of steel specimen immersed in three different concentrations of 3AP mixed pore solution

Corrosion current density I_{corr} ($\mu A/cm^2$)				
Sr no.	**Time of immersion (Hours)**	**0.01 M concentration**	**0.05 M concentration**	**0.1 M concentration**
1	24	3.05	3.01	2.10
2	72	3.88	2.91	3.18
3	120	3.35	2.55	2.90
4	240	2.23	2.43	2.58

From Tafel curves in Fig. 4.8, it can be seen that at concentration of 0.01M of 3AP, a clear transition of anodic curves of Tafel plots towards passive region occurred. Difference in trajectory of anodic curves at 24 hours, 72 hours and 120 hours was not significant. At concentration of 0.05M of 3AP, anodic curve transited to passive region after 24 hours only. However, difference in anodic curves at different times of immersion was apparent at concentration 0.1M of 3AP. These results indicate an increase in effectiveness of 3AP in inhibiting corrosion rate with time. This could be due to late chelate formation around metal ion or passive layer formation around metal at later stage.

From corrosion current density values in Table 4.4, it can be seen that corrosion current densities of samples dipped in 2AP at all the concentrations mixed pore solution were considerably low as compared to control samples. Corrosion current density values were slightly lower at 0.05M concentration. On the basis of corrosion current density values it can be inferred that 3AP was also able to inhibit corrosion in steel samples.

4.3.4 LPR test results of steel samples immersed in 4AP mixed pore solution

Tafel curves of steel samples immersed in 4AP mixed pore-solution of variables concentration 0.01M, 0.05M and 0.1M are presented are presented in Figures 4.11, 4.12 and 4.13 respectively. The corrosion current densities are presented in Table 4.5.

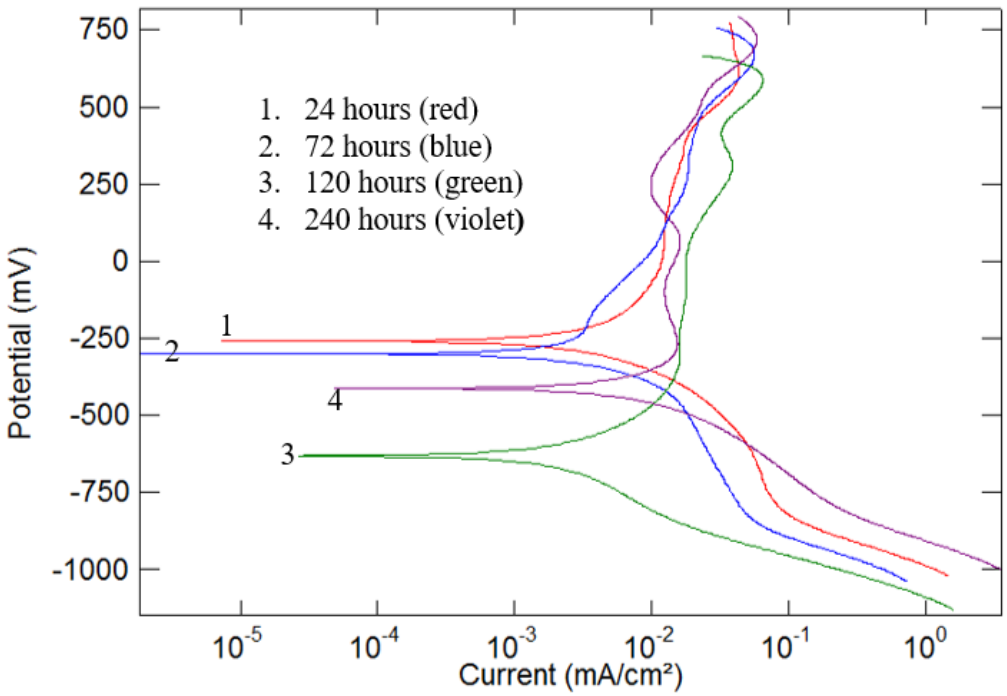


Fig. 4.11: Tafel curves of steel specimen immersed in 0.01 M 4AP Mixed pore solution

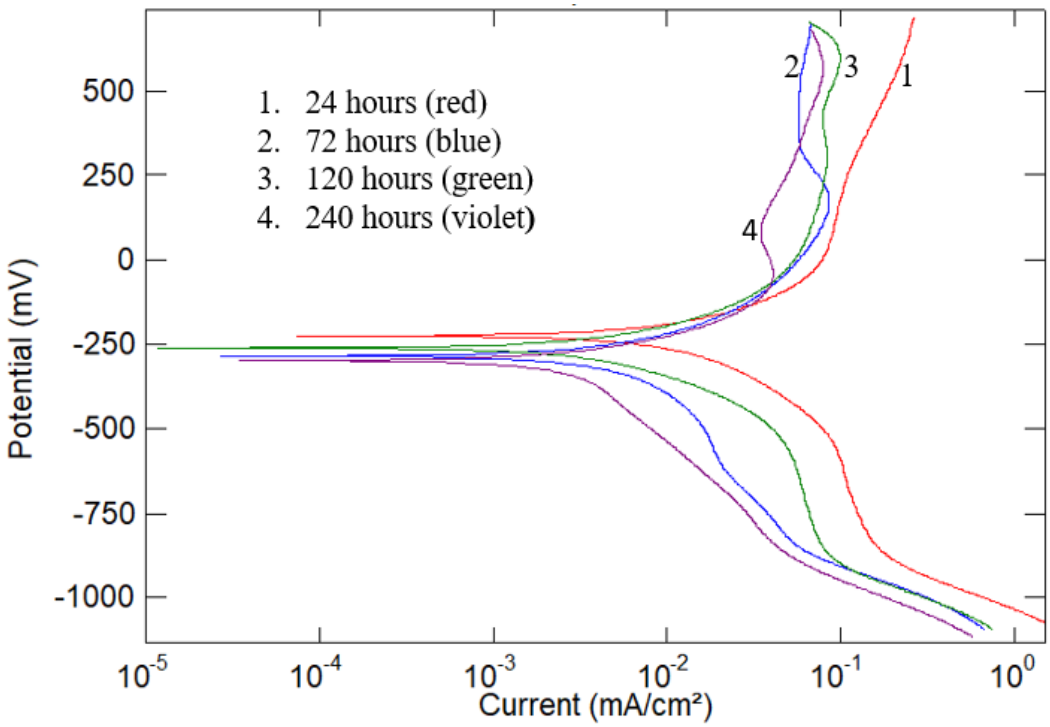


Fig. 4.12: Tafel curves of steel specimen immersed in 0.05 M 4AP Mixed pore solution

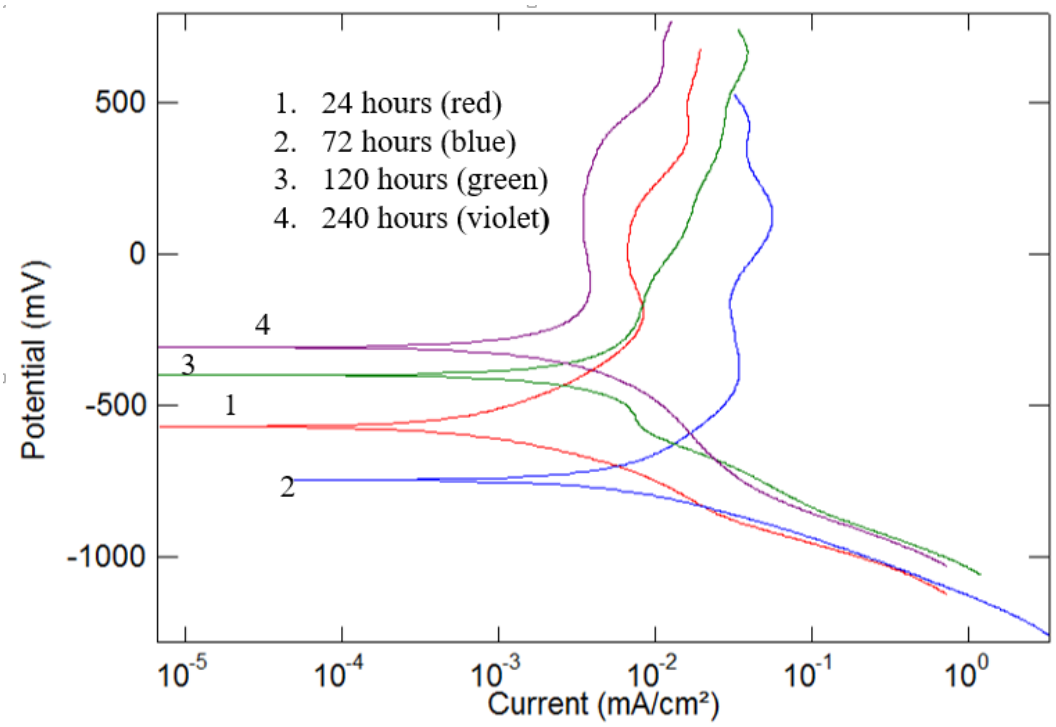


Fig. 4.13: Tafel curves of steel specimen immersed in 0.1M 4AP Mixed pore solution

Table 4.5: Corrosion current density values of steel specimen immersed in three different concentrations of 4AP Mixed pore solution

Corrosion current density I_{corr} (µA/cm²)				
Sr no.	**Time of immersion (Hours)**	**0.01 M concentration**	**0.05 M concentration**	**0.1 M concentration**
1	24	9.53	5.12	6.60
2	72	8.70	6.02	3.21
3	120	7.04	4.61	3.74
4	240	7.84	4.14	3.38

When the concentration of 4AP was 0.01M, it can be seen from Tafel plot that curves at 24 hours at 72 hours have similar trajectory. Even the corrosion current density values were almost same. When concentration of 4AP was 0.05M, the anodic curves are well inside passive region. There is hardly any difference in anodic curves at 240 hours and 120 hours which indicated that passive layer was probably formed between 72 and 120 hours of immersion. Anodic curve is even in more

passive region at 240 hours. From the Tafel plot the decrease in corrosion current density with time can be clearly seen. The anodic curve of plot was in less passive state at 24 hours than at 72 hours, 120 hours and 240 hours. But the difference in corrosion current difference values was negligible as trajectory of Tafel curves was almost similar.

The corrosion current density values of samples immersed in 4AP mixed solution was relatively higher than 2AP or 3AP mixed solution. When the concentration of 4AP was 0.01M, corrosion current density values were even higher than control samples in the beginning. But the inhibiting corrosion inhibiting effectiveness of 4AP increased with time. Out of the three investigated chemicals, 4AP was least effective in controlling corrosion as corrosion current densities were the highest in 4AP mixed solutions.

4.3.5 Effect of type of chemical on corrosion current density values

The effect of investigated chemicals on corrosion current density values at concentration 0.01M, 0.05M and 0.1M is provided in the form of bar graphs in Figures 4.14, 4.15 and 4.16 respectively.

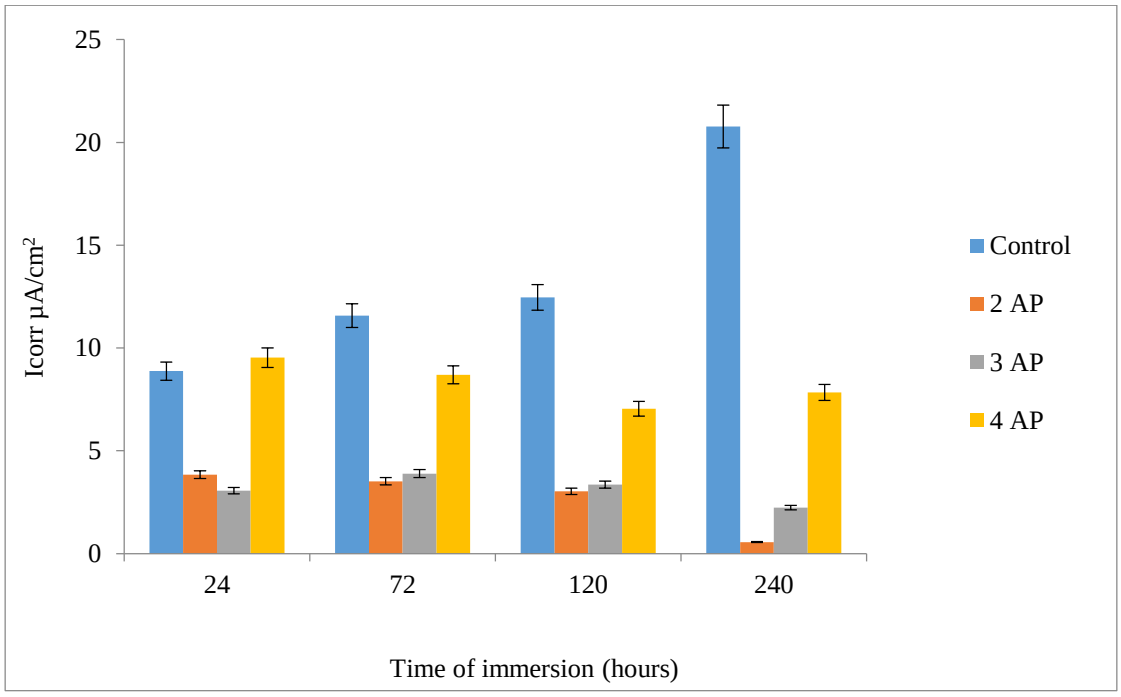


Fig. 4.14: Corrosion current density values of steel specimen in 0.01M chemical mixed solution

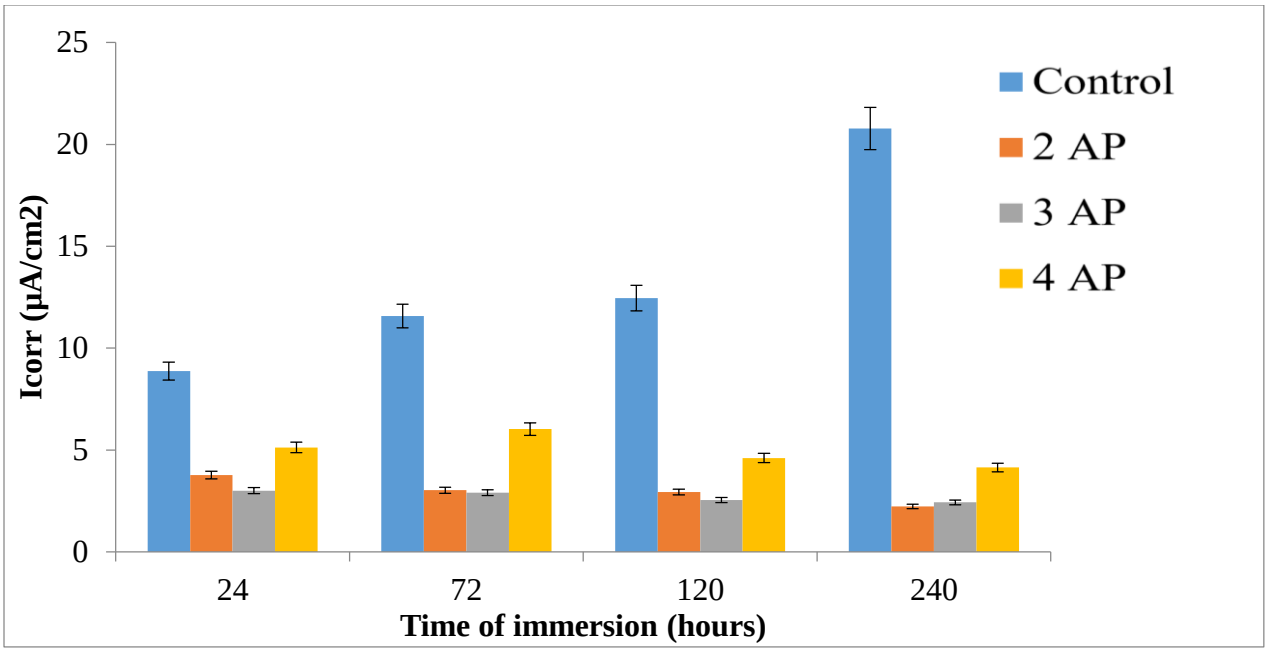


Fig. 4.15: Corrosion current density values of steel specimen in 0.05M chemical mixed solution

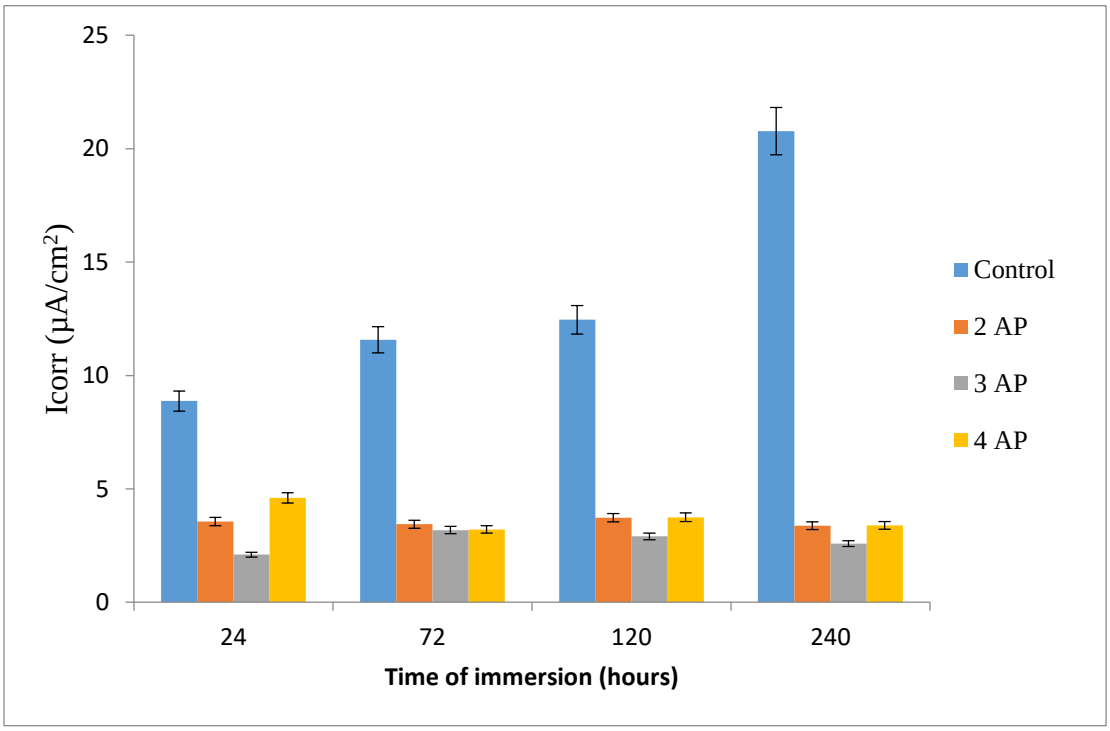


Fig. 4.16: Corrosion current density values of steel specimen in 0.1M chemical mixed solution

The corrosion current densities of samples immersed in control pore solution were high from the start of test only. However, increase of corrosion current densities with time was low initially. This could be due to formation of passive film on steel samples which inhibits further corrosion. But after 240 hours of immersion of samples in control pore solution, the corrosion current densities increased rapidly. This could be due to break down of passive layer on steel samples.

At 0.01M concentration, the effectiveness of 2AP and 3AP were identical initially but after 240 hours of immersion, 2AP was most effective in reducing probability of corrosion. At this concentration, 2AP was able to reduce corrosion current densities by 97% after 240 hours, while 3AP by 89%. 4AP at this concentration was not much effective initially but as time of immersion increased, the effectiveness of 4AP improved. After 240 hours, corrosion current densities were reduced by 62% in samples immersed in 4AP.

At 0.05M concentration, the effectiveness of 2AP and 3AP were similar initially but after 120 hours of immersion, 3AP was most effective in reducing probability of corrosion. Chemical 4AP was least effective in reducing corrosion current densities at this concentration as well. After 240 hours, corrosion inhibition efficiencies of 2AP, 3AP and 4AP were 89%, 88% and 80% respectively at 0.05M concentration. On an average, corrosion current densities were lower at 0.05M concentration than at 0.01M concentration for all three investigated chemicals.

At 0.1M concentration, all three chemicals were equally effective in controlling corrosion. However, initially 4AP was slightly less efficient than 2AP and 3AP. After 240 hours, corrosion inhibition efficiencies of 2AP, 3AP and 4AP were about 83%, 87% and 83% respectively at 0.1M concentration. There was no significant difference in corrosion current density values with increase in concentration from 0.05M to 0.1M.

From the above discussion following inferences can be drawn.

- All three chemicals, (Amino-phenols) regardless of the position of functional group ($–NH_2$ with respect to -OH) reduced the corrosion rate significantly. The effectiveness of alko-amines and amine based corrosion inhibitors in carbonated pore solution in carbonated pore solution was also confirmed by Kaur *et al*. (2016) *and* Ormellese *et al (2006).* However, contradictory results were reported by *Elsener et al. (1999)* .The efficiency of these chemicals (all three) in inhibiting corrosion rate improved with time. Chemicals were more effective after 240 hours than after 24 hours tests.

- Chemical 2AP seems to be the most effective inhibitor at 0.01M concentration and 3AP was the most effective at 0.1M concentration. At 0.05M concentration, initially efficiencies of 3AP and 2AP were identical but after 240 hours, 3AP performed slightly better than 2AP in controlling corrosion in steel specimen. Corrosion rates decreased significantly in most of the cases with increase in concentration of chemicals from 0.01M to 0.05M.
- Chemical 4AP was the least effective chemical among three in inhibiting corrosion of steel specimen. Concentration of 0.05M was observed to be optimum for all three chemicals as most of the values obtained at this concentration were less as compared to their corresponding values at concentrations of 0.01M and 0.1M. Although difference in values at 0.05M and 0.1M was insignificant but on an average, values at 0.05M were slightly less than values at 0.1M.

4.4 CHEMISTRY OF CHEMICALS IN PORE SOLUTION

All three investigated chemicals proved to be very effective in inhibiting corrosion in steel samples in pore solution. The effectiveness of these chemicals as corrosion inhibitors can be attributed to chemistry of Aminophenols in pore solution. Aminophenols belong to family of amino alcohols where alkyl group is attached to cyclic double bonded hydrocarbon which is benzene. The replacement of two hydrogen atoms of benzene ring from two different location by $–NH_2$ and –OH functional group makes it Aminophenol. The corrosion inhibiting action and efficiency of 2AP is very similar. Since they belong to family of amino-phenols, their mechanism in inhibiting corrosion should also be same as amino-alcohols.

The primary protective mechanism of amino-alcohol is by formation of protective layer by adsorbing on the surface of steel and secondary property is blocking the pores of concrete (*Soylev, 2008*). Chemical 2-Aminophenol was reported to be very effective in reducing corrosion rate in zinc pigment (*Muller et al. 1999*). The corrosion inhibiting property of 2AP on zinc blend was attributed to the fact that aromatic ring and –OH functional group can easily form chelate on the surface of metals as 2AP is a strong chelating agent (*Sims P et al, 1959*). As the valency of zinc and ferrous ions is same (that is 2), their behavior in terms of chemical reactions and bonding with other elements must be very similar. Therefore, reaction chemistry between zinc and amino-phenols must also be very similar to chemistry between iron and amino-phenols. The structure of chelate compound formed by 2AP is shown in Fig. 4.17 (*Howlader et al. 2008*).

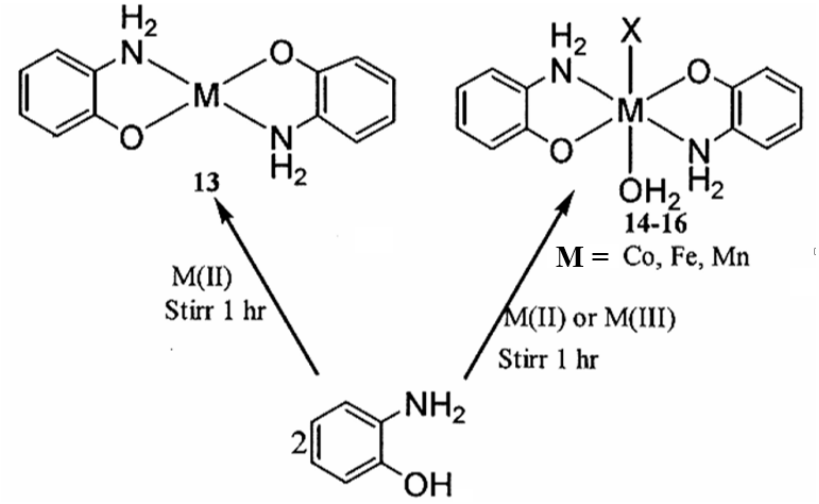


Fig. 4.17: Chelate formation by 2AP around ferrous and ferric ions

(*Howlader et al. 2008*)

Chemical 3AP was reported to form a layer of poly-3AP(*Bereket and Duran,2009*) which forms a chelate around around the cation The structure of poly-3AP is shown in Fig. 4.18.

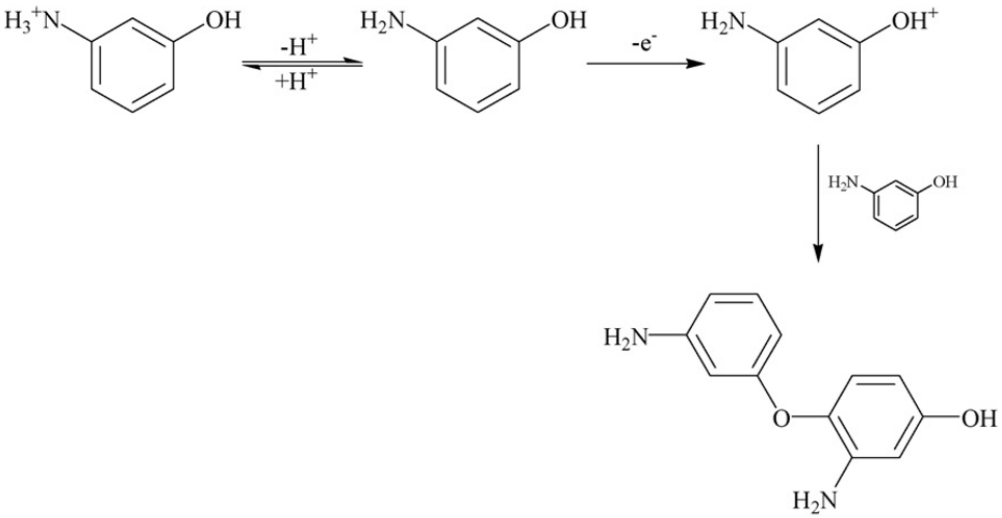


Fig. 4.18: Mechanism of formation of poly-3AP which forms a film on metal ion

(*Bereket and Duran 2009)*

Although 4-Aminophenol was also able to control corrosion but it was not as effective as other resonating structures. The relatively less efficiency of 4AP in inhibiting corrosion may be due to difficulty in formation of chelate complexes. The difficulty in formation of chelate complexes in

4AP can be due to more distance between two functional groups than 2AP and 3AP. Also, 4AP has a symmetrical structure and chemical stability of a symmetric structure is higher than that of asymmetric structures (*Dunitz, 1996*). Similar results were obtained in this research too. 2AP was better corrosion inhibitor of steel than 4AP.

4.5 CARBONATION DEPTH TEST

This test was performed to evaluate the pore-blocking property of chemicals on concrete and to find the effect of change in positioning of functional group on this property as discussed earlier in chapter 3.

In this test, cubes of size 100 mm were cast and cured by immersing in water for 14 days. After curing, 3 coats of chemical to be investigated as migratory corrosion inhibitor, was applied on one face of cube while rest of the faces were epoxy coated. The concentration of applied chemical was 1M in all the samples. Thereafter, samples were exposed to carbonation in carbonation chamber at RH 70% and CO_2 concentration 5% by volume. Carbonation depth of triplicate samples was determined after interval of 15 days upto 75 days. The depth of carbon-dioxide penetration in cubes was determined by using phenolphthalein indicator after splitting the samples. Table 4.6 presents average carbonation depth at different days of testing. The results are also presented in the form of bar graph in Fig. 4.19.

Table 4.6: Carbonation depth (mm) of treated and control samples at different days

Time of exposure	**Carbonation depth in mm**			
No of days	**Control**	**2AP**	**3AP**	**4AP**
15	8.44	7.665	5.77	2.72
30	11.33	8.44	7.55	7.77
45	12.99	11.1	9.55	8.11
60	14.77	14.3	12.86	12.53
75	17.1	16.4	15.33	13.26

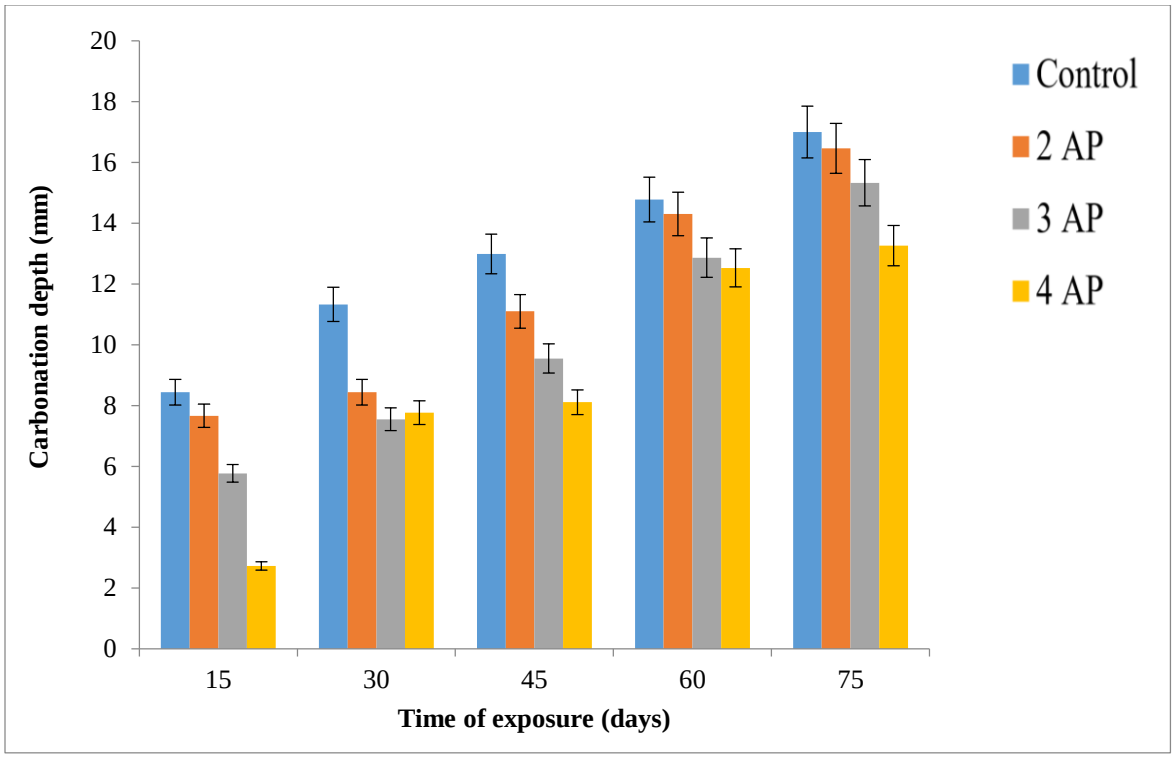


Fig. 4.19: Carbonation depth of chemical applied concrete samples and control samples at different days

Fig. 4.20: Carbonation depth results after 30 days of exposure to carbonation

Data in Table 4.6 clearly demonstrates that all the chemicals irrespective of the position of functional group were effective in reducing carbon-dioxide penetration in the concrete at all testing times. The difference in carbonation depths between control samples and treated samples can be

clearly seen in Fig. 4.20. The carbonation depth values in control samples after 75 days of exposure was 17.1 mm which was considerably high than that of treated samples. The effectiveness of Aminophenols can be due to pore-blocking effect which reduces the permeability of concrete which makes it resistant to carbon-dioxide penetration.

Further it can be seen that, 4AP was most effective in reducing carbonation depth in concrete samples. From Fig. 4.20, it can be seen that samples treated with 4AP have consistently lowest carbonation depth values at different days of testing. The carbonation depth value in samples treated with 4AP was only 13.26 mm. 3AP was second most effective chemical in reducing carbonation depth in concrete samples. After 75 days of exposure, the carbonation depth of samples treated with 3AP was only 15.33 mm. Out of three chemicals, 2AP was least effective in reducing carbonation depth. The carbonation depth of samples treated with 2AP was 16.4 mm after 75 days of exposure to carbon-dioxide contaminated environment.

The difference in effectiveness of three investigated chemicals can be due to difference in positioning of functional group. Chemical 4AP reduced permeability of concrete more effectively than 3AP and 2AP. Thus, it can be inferred that chemical 4AP was a better pore blocker than 3AP and 3AP was better pore blocker than 2AP.

4.6 SORPTIVITY TEST

Sorptivity test was done to detect the change in permeability and penetrability of moisture into concrete applied with chemical 2AP, 3AP and 4AP as compared to control concrete specimen. Triplicate cylindrical concrete samples of diameter 100 mm and height 50 mm were prepared and cured for 14 days in water tank for conducting sorptivity test. The samples were preconditioned in oven at 50^0C and relative humidity (RH) 80% for 3 days. After preconditioning, samples were applied with epoxy on curved sides of cylinder and a loose plastic sheet was tied on one of the face of sample. On the other face, three coats of chemical to be tested was applied. The concentration of applied chemical was 1M in all the samples. Prepared samples were transferred to a flat pan filled with water upto depth of 2 mm. The change in weight of samples was noted for 8 days at intervals described in ASTM C 1585-4. Average absorption of samples was calculated from cumulative weight of samples. From average absorption values initial and secondary sorptivity values were obtained. Average water absorption values of different samples obtained from this test are presented in Table 4.7. These values were used to compute sorptivity values for the samples.

Table 4.7: Average water absorption by samples (Average of 3)

Time		Average absorption I (mm)			
(Seconds)	**√Seconds**	**Control**	**2AP**	**3AP**	**4AP**
0	0	0	0	0	0
60	7	0.49	0.53	0.55	0.55
300	17	0.87	0.93	0.89	0.87
600	24	1.13	1.19	1.17	1.17
1200	34	1.42	1.66	1.55	1.59
1800	42	1.93	2.02	1.93	1.95
3600	60	2.61	2.8	2.61	2.71
7200	84	3.37	3.57	3.46	3.37
10800	103	3.99	4.05	3.9	3.99
14400	120	4.46	4.5	4.14	4.27
18000	134	4.84	4.61	4.33	4.42
21600	146	5.03	4.8	4.5	4.54
92220	303	5.22	4.88	4.63	4.62
193200	439	5.3	4.95	4.69	4.71
268500	518	5.39	5.01	4.74	4.77
432000	657	5.48	5.09	4.82	4.84
527580	726	5.54	5.16	4.88	4.92
622200	788	5.67	5.24	4.95	4.99
691200	831	5.75	5.29	4.99	5.05

As can be seen from Table 4.7, that during initial hours, difference between water absorption values of control samples as compared to samples treated with 2AP, 3AP and 4AP was not too significant. But with passage of time, there was considerable difference between absorption values of control specimen as compared to those treated with Aminophenols. Samples treated with aminophenol irrespective of postion of functional group absorbed less water than control samples. The difference in water absorption values between control sample and treated sample was more significant at later stage of testing. The difference in water absorption was the highest after 8 days.

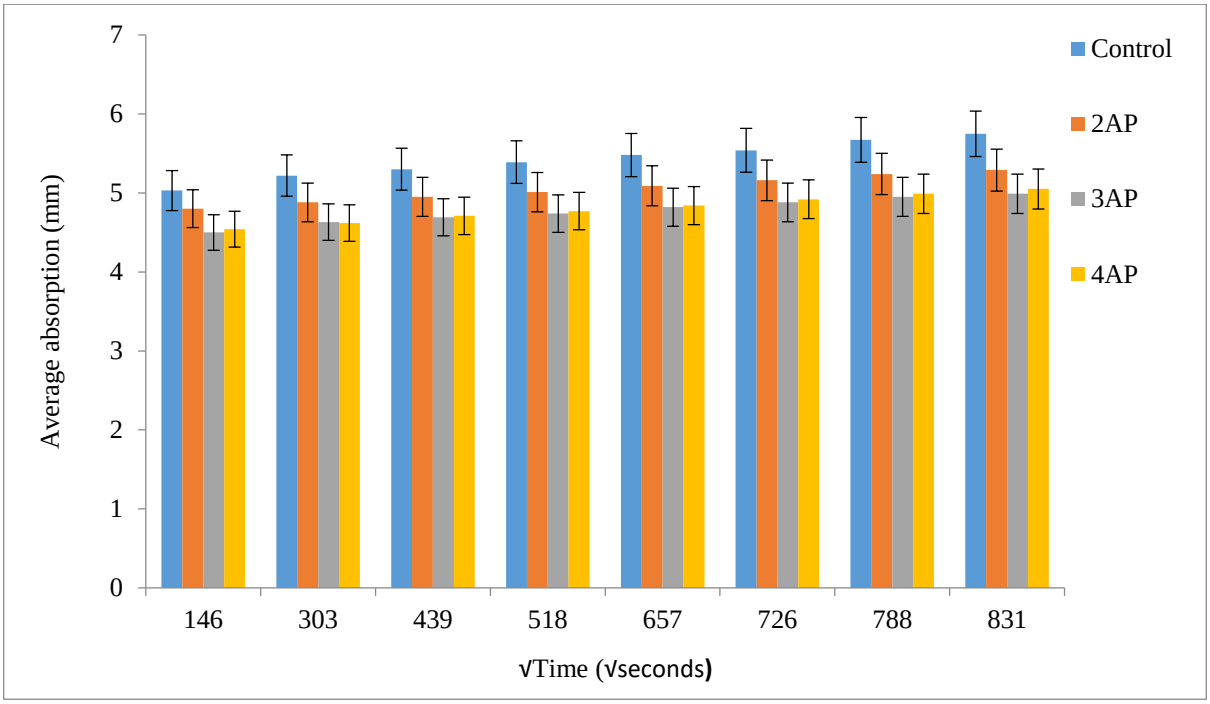


Fig. 4.21: Average cumulative water absorption values of concrete samples

Further, it can be seen from Fig. 4.21, that 3AP and 4AP were most effective in reducing water absorption. The water absorption values of samples treated with 3AP and 4AP were very similar. The application of 3AP on concrete surface reduced its water absorption by 13.21% while 4AP reduced it by 12.17% after 8 days. On the other hand, 2AP was slightly less effective in reducing water than 3AP and 4AP. Samples treated with 2AP absorbed 8% less water as compared to control samples after 8 days.

From the average absorption values, Initial and secondary sorptivity values of triplicate concrete samples according to ASTM C1585 – 4 were obtained. Initial sorptivity represents rate of increase of water absorption values of concrete sample with respect to square root of time up to first 6 hours of testing. Secondary sorptivity is rate of increase of water absorption values of concrete sample with respect to square root of time after first 6 hours of testing. The sorptivity values can be obtained by calculating the slope of best fit straight line graph to curve representing average water absorption by concrete samples with respect to square root of time. Table 4.8 presents the initial and secondary sorptivity values of untreated concrete samples as well as samples treated with chemicals 2AP, 3AP and 4AP.

Table 4.8: Initial and secondary sorptivity values of samples

For average of Triplicate samples	Control	2AP	3AP	4AP
Initial sorptivity s_i (mm/√s)	0.49	0.47	0.44	0.45
Secondary Sorptivity S_s (mm/√s)	0.088	0.07	0.062	0.07

From Table 4.8, it can be seen that, Initial sorptivity and Secondary sorptivity values were are clearly higher for control specimen than chemically treated samples in every case. This difference in values was more significant in secondary sorptivity.

From initial sorptivity values in Table 4.8, it can be seen that 3AP and 4AP were most effective in reducing initial sorptivity. There was negligible difference between sorptivity values of samples treated with 3AP and 4AP. 2AP was slightly less effective in reducing initial sorptivity values as compared to 3AP and 4AP. 3AP was most effective in reducing secondary sorptivity as well. 4AP and 2AP were equally effective in reducing secondary sorptivity values.

From sorptivity results, it can be inferred that all three chemicals viz. 2AP, 3AP and 4AP were able to reduce water penetration into concrete. This can be due to reduction in permeability of concrete with application of chemicals. These chemicals block the pore of concrete which reduced the permeability of concrete. Further, it can be concluded that chemicals 3AP and 4AP were better at reducing permeability of concrete than 2AP.

4.7 TEST RESULTS IN REINFORCED CONCRETE SAMPLES

Half-cell potential test and linear polarization resistance tests were conducted on steel embedded concrete samples. The experiment set up for both the tests was same as discussed in section 3.4.9. Cylinderical concrete samples of diameter 100mm and height 200mm were cast. Steel rod of 12mm diameter and 230mm was embedded in concrete at time of casting. Steel bar was covered with two coats of epoxy upto 50 mm from one end before casting of reinforced concrete sample. A clear cover of 20 mm was provided to steel rebar. The projected out steel rebar was covered with polythene before curing in water for 14 days. After air drying the samples, 1M of chemical to be investigated was applied on all the sides of cylindrical concrete samples in three coats. After

application of chemical, samples were kept in carbonation chamber where they were exposed to carbon-dioxide environment inside carbonation chamber. The concentration of CO_2 inside chamber was 5% by volume. Tests were conducted on same samples at an interval of 15 days upto 75 days. The results obtained from the tests are presented this section.

4.7.1 Half-cell potential test results in reinforced concrete samples

Half-cell potential test was conducted to determine before start of LPR test. The Half-cell potential values were recorded as the initial corrosion potential before start of potentio-dynamic test. The Half-cell potential values give an idea about probability of corrosion in sample as described by ASTM C 876-91 in Table 4.9.

Table 4.9 ASTM Interpretation of Half-Cell Potential values (*ASTM C 876 – 91*)

Half-cell potential values	Corrosion Condition
Less than -426 mV	Severe corrosion, corrosion induced cracking may occur
-426 mV to -276 mV	High risk, 90% probability of corrosion
-125mV to – 276mV	Intermediate risk, corrosion activity in reduction
More than -125mV	Low risk, 10% probability of corrosion

Table 4.10 Rest Potential values in steel embedded concrete samples

At 1M chemical concentration		Rest potential (mV/SCE)			
Sr no.	**Days**	**Control**	**2AP**	**3AP**	**4AP**
1	15	-107.13	-94.95	-48.915	-89.46
2	30	-112.64	-103.69	-110.04	-79.90
3	45	-439.41	-230.61	-167.05	-36.11
4	60	-291.94	-207.78	-93.436	-58.72
5	75	-462.69	-289.93	-90.755	-80.53

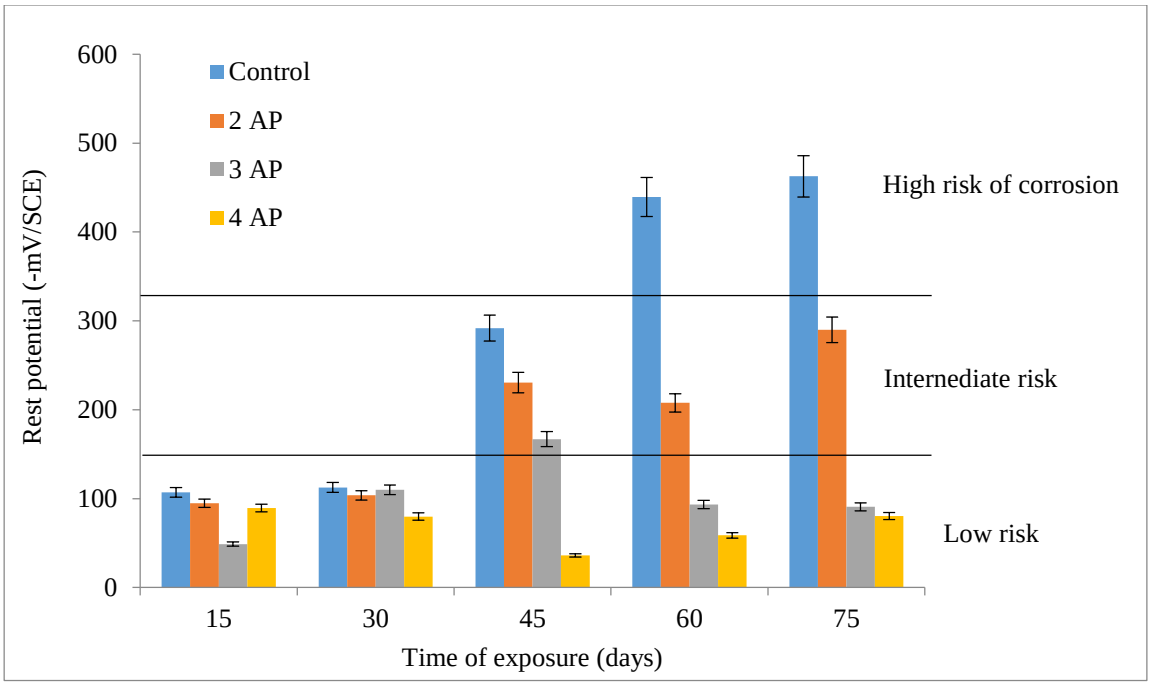


Fig. 4.22: Rest potential values (-mV/SCE) in Steel embedded Concrete samples

Corrosion probability was significantly higher in control reinforced concrete samples as compared to samples treated with investigated chemicals. According to standard Half-cell potential corrosion probability was more than 90% in control samples.

The Half-cell potential values obtained from the test are presented in Table 4.10 and in the form of bar graph in Fig. 4.22. Half-cell potential values indicate that Half-cell potential of untreated samples are more negative values than treated samples. The probability of corrosion of samples having more negative half-cell potential is higher than samples having less negative half-cell potential values.

The probability of corrosion in 4AP was less than 10% even after 75 days of exposure according to ASTM C 876 – 91. The half-cell potential values of samples treated with 4AP were least negative indicating that corrosion probability of the treated samples is least. Corrosion probability was very low (less than 10 %) in samples treated with 3AP. Corrosion probability in samples treated with 2AP was less than 10% during initial phase of testing but corrosion probability increased considerable with increase in time of exposure,.

4.7.2 Linear polarization resistance test in reinforced concrete samples

LPR test was conducted on cylindrical reinforced concrete samples which were subjected to carbonation environment for different durations. The start potential and end potential for this test were -25mV and +25mV respectively with scan rate of 10 mV/minutes on exposed area of 68.98 cm^2. The samples were treated with 2AP, 3AP and 4AP as discussed earlier in chapter 3. Tafel plots of steel embedded concrete samples obtained from which corrosion current density was noted. The Tafel plot of control samples and samples treated with 2AP, 3AP and 4AP at different days of testing are presented in Fig. 4.23 to Fig.4.26 respectively. The corrosion current densities obtained from test were compared with standard values presented by ASTM STP 1065 in Table 4.11. The I_{corr} values obtained from the test are shown in Table 4.12.

. Table 4.11 Typical corrosion rate of steel in concrete (ASTM STP 1065)

Rate of corrosion	Corrosion current density (I_{corr}) µA/cm^2
Very high	10-100
High	10-01
Low/moderate	0.1-10
Passive	< 0.1

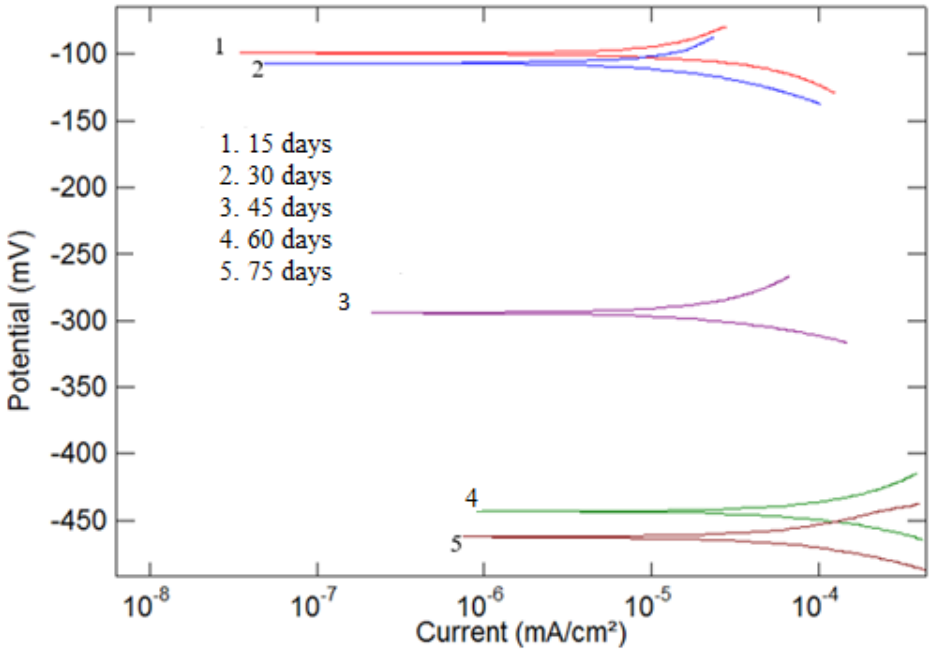


Fig. 4.23: Tafel plot for untreated concrete samples (control) exposed to carbonation

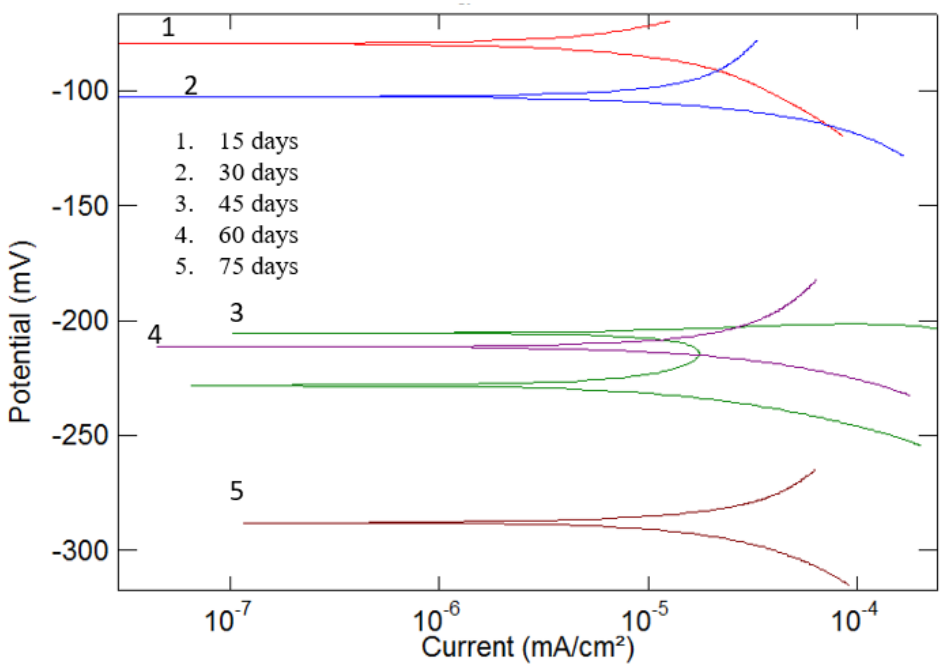


Fig.4.24: Tafel plot for concrete samples treated with 2AP and exposed to carbonation

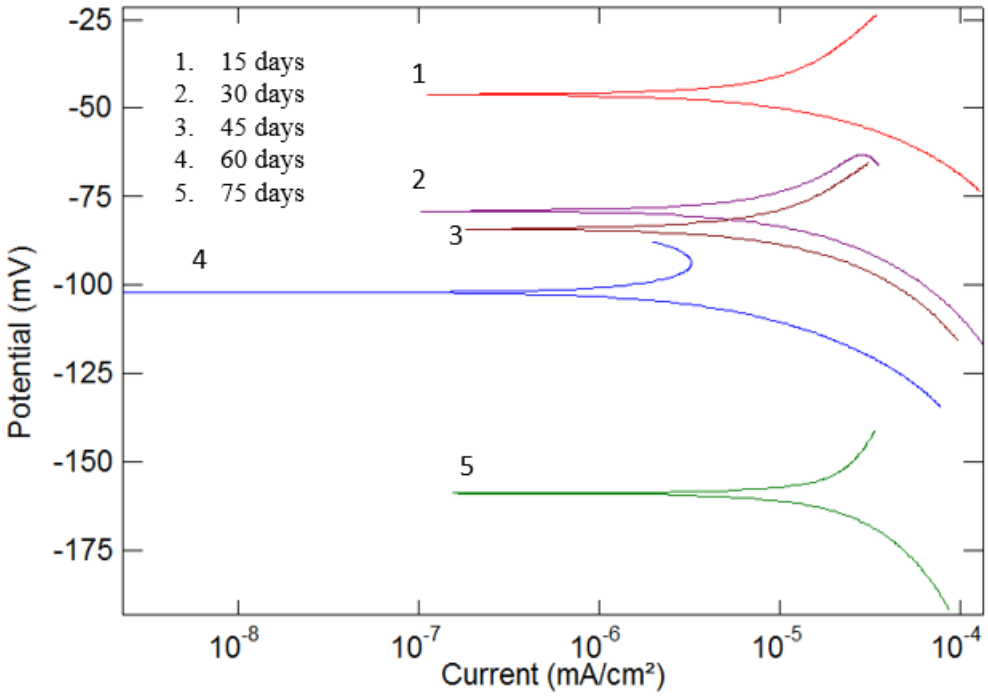


Fig.4.25 Tafel plot for concrete samples treated with 3AP and exposed to carbonation

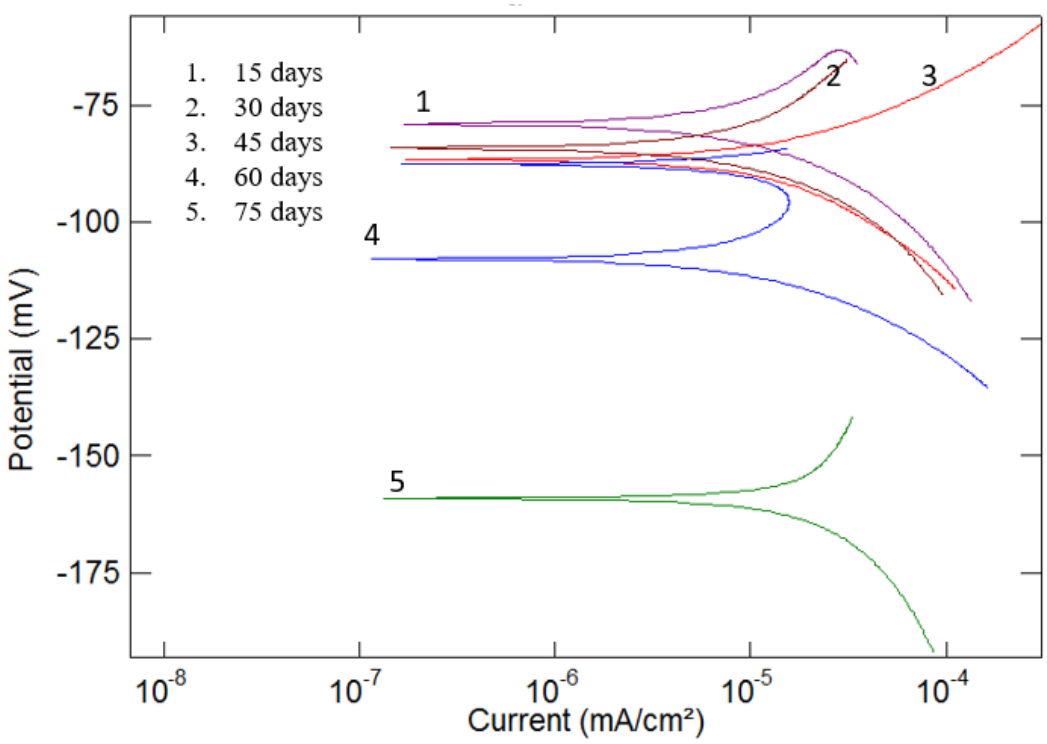


Fig.4.26: Tafel plot for concrete samples treated with 4AP and exposed to carbonation

Table 4.12: Corrosion Current Density values of chemically treated and control samples at different exposure times

Corrosion current density - I_{corr} (µA/cm^2)					
Sr no.	**Days**	**Control specimen**	**2AP**	**3AP**	**4AP**
1	15	0.00189	0.00136	0.00131	0.00036
2	30	0.00257	0.00143	0.00152	0.00175
3	45	0.00344	0.00204	0.00174	0.00128
4	60	0.00404	0.00276	0.00248	0.00235
5	75	0.00493	0.00317	0.00305	0.00299

By comparing I_{corr} values obtained from test with the standard values in Table 4.12, it can be inferred that samples were still in passive state. Even in control samples the corrosion current densities are very low.

The passive state of samples can be explained on the basis of the results of carbonation depth in Section 4.5, where it was observed that even after 75 days of exposure of samples, the carbonation depth had increased upto 17 mm into concrete which was less than the clear cover provided to rebars in cylindrical concrete samples in LPR test. This is the reason that corrosion current density was low even in control samples as the carbonation has not reached the steel bar and sample was still in passive state. However, from Tafel plot and Table 4.12, it can be seen that corrosion current density values of treated samples were lower than control sample. This shows that corrosion probability in control samples was more than treated samples. The corrosion current densities of all the samples were increased with time of exposure but rate of increase of corrosion current density values was more in control samples than treated samples.

4.8 INFERENCES

On the basis of discussion of tests in pore solution, it can be inferred that all three chemicals: 2AP, 3AP and 4AP were able to inhibit corrosion in steel samples. This can be due to chelate forming property of Aminophenols around metal surface which act as protective layer against corrosion. Among the three investigated chemicals, 2AP was most effective chemical and 3AP was second most effective chemical in controlling corrosion. This difference in effectiveness of chemicals can be due to extent of chelate formation in pore solution. Due to proximity in two functional groups in 2AP, chelate formation was easier as compared to 3AP. On the other hand, extent of chelate formation by chemical 4AP in pore solution was comparatively less because distance between two functional groups in 4AP structure was relative more than in 2AP and 3AP. Further, chemical 4AP has a symmetrical structure which a chemically stable configuration that makes chelate formation relatively difficult than other chemical. Hence, chemical 4AP was least effective in controlling corrosion in pore solution.

As surface-applied corrosion inhibitor, it can be inferred that all three chemicals: 2AP, 3AP and 4AP were able to migrate in concrete samples. Chemicals were able to reduce the permeability of concrete. Further, it was seen that 4AP was most effective chemical as seen from results in carbonation depth test, sorptivity test and half-cell potential test on concrete samples. It was also seen that 2AP was least effective pore blocker in concrete. The difference in effectiveness of chemicals can be due to difference in the positioning of functional group in their chemical structures. Chemical 4AP, which has a relatively stable symmetric structure was most successful as migratory corrosion inhibitor. In chemical structure of 2AP, two functional groups are very close to each other, were least effective as migratory corrosion inhibitors.

CHAPTER 5

CONCLUSIONS

Based on discussion in chapter, conclusions were drawn which are presented in this chapter.

- Amino-alcohols with aromatic ring can inhibit corrosion of steel significantly, when mixed in simulated concrete pore solution in carbon-dioxide contaminated environment.

- All the resonating structures of Aminophenols were able to inhibit corrosion of steel in pore solution effectively at all three concentrations: 0.01, 0.05M and 0.1M.
- Efficiency of Aminophenols increased with increase in their concentration from 0.01M to 0.05M in pore solution. There was not significant effect of further increase in concentration of Aminophenols on their effectiveness as corrosion inhibitors in pore solution.
- Among the resonating structures, 2-Aminophenol was observed to be most effective in inhibiting corrosion of steel in simulated concrete pore-solution under carbon–dioxide contamination, followed by 3-Aminophenol and 4-Aminophenol. After 240 hours, corrosion inhibition efficiencies of 2AP, 3AP and 4AP were 89%, 88% and 80% respectively at 0.05M concentration. This can be due to ease of formation of chelate rings around metal ions because of proximity between two functional groups in 2-Aminophenol.
- Aminophenols were also effective as surface applied corrosion inhibitors aswell. Amino phenols at 1M concentration can act as pore-blockers in concrete by reducing the permeability of concrete. Thus, the steel embedded in concrete remains safe from detrimental effects of adverse environment.
- There was a considerable effect on corrosion inhibiting properties due to difference in positioning of functional group in Aminophenol, when applied on surface of concrete.

  As migratory corrosion inhibitor, 4AP was most effective. Chemical 4AP reduced the carbonation depth by about 22% while 3AP and 2AP reduced it by about 10% and 4% respectively.

  Aminophenols were effective as corrosion inhibitors both in pore solution as well as surface applied inhibitors. In pore solution 2-Aminophenol was most effective while as surface applied, 4-Aminophenol was most successful to migrate in concrete pore structure.

SCOPE FOR FUTURE WORK

In this research, the effectiveness of resonating compounds in synthetic pore solution and as migratory corrosion inhibitor was determined. From the results, it was seen that with change in application of inhibitor, the effect of positioning of functional group on corrosion inhibiting property was also changed. Therefore more research is required which focuses on:

- Effectiveness of mixture of three chemicals as corrosion inhibitors.
- More electrochemical tests such electrochemical impedance spectroscopy (EIS) test to further confirm the effectiveness of inhibitors.
- Effect of these chemicals on fresh and mechanical property of concrete.
- Long term efficiency of Aminophenols as corrosion inhibitors in reinforced concrete.

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