"ASSESSMENT OF CORROSION AND RETROFITTING OF COLUMNS: A CASE STUDY ON THE BALANCE WORK OF NH-6 IN KHANDESH REGION"

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ABSTRACT

Concrete is the second most used construction material in world after water. Concrete may be considered as best construction material but its durability can adversely be affected by various means. Corrosion of steel present in reinforced concrete is most significant durability problem in the world of Civil Engineering.

Many Highway Projects have been stalled due to various issues leading to termination of Contracts. This results in partially completed structures which leads to corrosion of reinforcement exposed to atmosphere. Corrosion can cause reduction in strength, expansion or mass loss in concrete. Hence, many methods have been developed to reduce or prevent corrosion of steel in concrete. From all the methods available for corrosion protection, corrosion inhibitors sound very promising.

Inhibitors that are available in market usually have a tendency to protect against only one factor of corrosion i.e. either carbonation or chlorides along with the fact that commercially available corrosion inhibitors are very expensive and affect the total cost of structure. Due to which, there arises a need to find a cheaper replacement which can inhibit corrosion due to carbonation and presence chlorides.

In this study, assessment of corrosion of reinforcement in partially completed structures and retrofitting using corrosion inhibitors such as Picolinic Acid, 4-Aminobenzoic acid, 2-Salicylaldehyde and 2-Aminopyridine with 1% addition has been carried out.

Keywords: Concrete, Corrosion, Reinforcement, Civil, Highway, Inhibitors, Structures.

CHAPTER 1

INTRODUCTION

1.1 General

In India the percentage of people living in cities and urban area almost doubled to 27.78% in year 2001, which was low when compared to developed countries. However, the 28.53 crore urban population living in 27 metros, 396 cities and 4738 towns is more than the total population of developing and developed countries. The Parliament by the NHAI Act, 1988 has established National Highways Authority of India (NHAI). The NHAI Act, 1988 states that, "An Act to provide for the constitution of an Authority for the development, maintenance and management of national highways and for matter connected therewith or incidental thereto". It has been entrusted with National Highways Development Project, which alongwith other minor projects, has vested in it 50329 kms of National Highways for development, maintenance and management.[1]

NHAI is mandated to implement National Highways Development Project (NHDP) which is India's largest ever Highways Project in a phased manner. The National Highways have a total length of 1,32,499 (approx) km to serve as the arterial network of the country. Although National Highways constitute only about 2 per cent of the road network, it carries 40 per cent of the total road traffic. Rapid expansion of passenger and freight traffic makes it imperative to improve the road network in the country. Accordingly, Government of India launched major initiatives to upgrade and strengthen National Highways through various phases of National Highways Development Project (NHDP) and Bharatmala Pariyojana. Many Highway Projects have been stalled due to various issues leading to termination of Contracts. This results in partially completed structures which leads to corrosion of reinforcement exposed to atmosphere. Fig. 1.1 shows examples of partially completed structure in the project of four laning of Fagne- Maharashtra/Gujrat border section of NH-6 wherein reinforcing bars have been exposed to atmosphere.

Figure 1.1: Partially completed column structure of NH-6

Reinforced concrete is one of the most important construction material and is used for almost all types of construction purposes, for its proved durability and high structural performance.

The durability of concrete structures and their long-term performance have emerged over the last few decades as a primary concern for structural engineers, infrastructure owners, and consumers. Most reinforced concrete structures are expected to last at least 75 years. However, problems may start to occur within only a few years, not because of a structural problem, but because of a durability issue. The deterioration of a concrete structure may occur due to many processes, which act individually or combined. Some examples of processes that cause material deterioration include alkali aggregate reactivity, sulphate attack, freezing and thawing, and corrosion of reinforcement inside the concrete.

1.2 Corrosion

Corrosion is an expensive and severe material science crisis. Corrosion of metals is defined as the spontaneous damage of metals in the course of their chemical, electrochemical and biochemical exchanges with the surroundings. Thus, it is precisely the opposite of extraction of metals from ores. In the majority of environments the metals are not inherently stable, and most likely to revert to compounds which are more stable, a course of action which is called corrosion. Corrosion is also defined as worsening of intrinsic properties in a material due to its reactions with surroundings. It is the oxidation of metals reacting with water or oxygen. Corrosion is derived from the Latin word "Corrosus" meaning "gnawed away".

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Corrosion of reinforcing bars (rebars) inside concrete is one of the most important phenomenon that reduce the service life of a concrete structure, and it causes a huge load on the maintenance budget of the affected structure. Corrosion of reinforcement in concrete is an electrochemical process. Once initiated, corrosion products, which are having higher volume than that of the parent metal (around 5-7 times), will accumulate in the space between the rebar and concrete, and since there is almost no space in concrete to accommodate these products, cracking and spalling of the concrete cover will surely occur. If the rebar cross sectional loss is severe, structural problems may start to occur.

1.3 Classification of Corrosion

There is no universally accepted classification for corrosion, but the following classification is adapted:

1.3.1 Uniform or general corrosion

Uniform or general corrosion, as the name imply, results in a fairly uniform penetration (or thinning) over the complete exposed metal surface. The general attack results from local corrosion cell action, that is, multiple anodes and cathodes are operating on the metal surface at any given time. The place of the anodic and cathodic areas continues to move about on the surface, ensuing uniform corrosion. In this case the exposed metal/alloy surface area is entirely corroded in an environment such as a liquid

electrolyte (chemical solution, liquid -metal), gaseous electrolyte (air, CO_2, SO_2 etc.,) or a hybrid electrolyte (solid, water, biological organisms, etc.). Fig 1.2 shows an steel storage tank corroded uniformly over the whole outer surface.
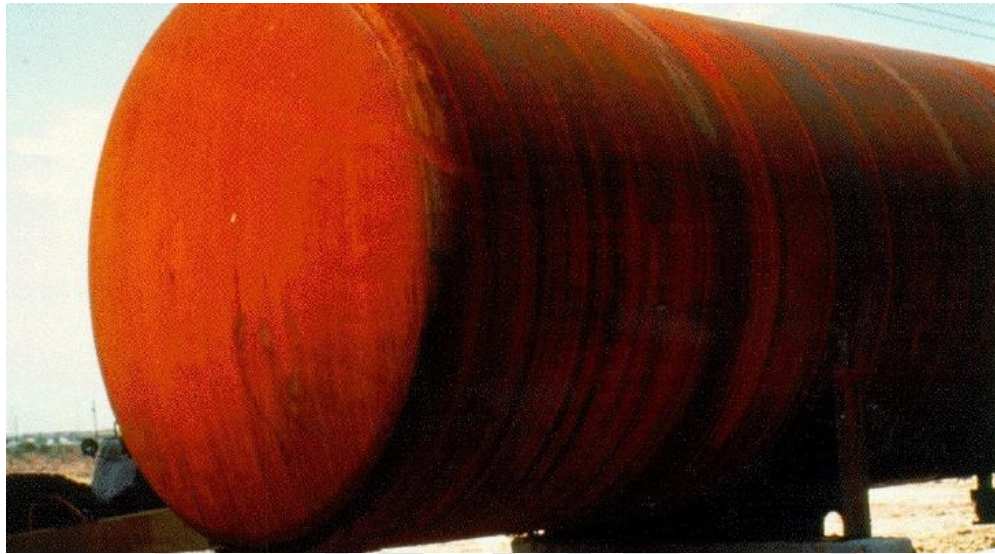

Figure 1.2: Uniform corrosion on a storage tank

(Source : http://chemblinks.blogspot.in)

1.3.2 Galvanic corrosion

Galvanic corrosion is an electrochemical action of two different metals in the company of an electrolyte and an electron conductive path. It occurs when dissimilar metals are electrically coupled in a common solution, the more negative (more active) metal will be the anode of the galvanic corrosion cell and its corrosion rate will increase. The more positive (more noble) metal will be the cathode and its corrosion rate will decrease and it is detectable by the presence of a build-up of corrosion at the joint between the dissimilar metals. For example when aluminium alloys or magnesium alloys are in contact with steel (carbon steel or stainless steel), galvanic corrosion can occur and accelerate the corrosion of the aluminium or magnesium. Fig. 1.3 shows an example of galvanic corrosion.
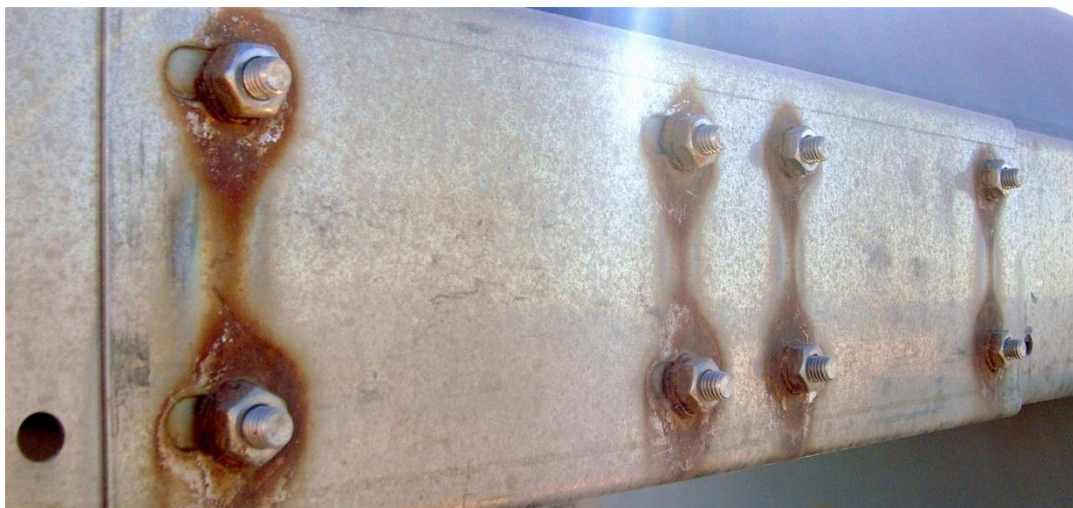

Figure 1.3: Galvanic corrosion

(Source : http://www.tecnoconverting.com)

1.3.3 Localized corrosion

This term implies that, specific parts of an exposed surface area corrode in a suitable electrolyte. This form of corrosion is more difficult to manage than the general corrosion. Localized corrosion can be classified as following:

1.3.3.1 Crevice corrosion

It is similar to pitting corrosion in a stagnant electrolyte after its initiation. This form of corrosion starts due to changes in local chemistry such as reduction of oxygen in the crevice, increase in pH with increasing hydrogen ion concentration and boost of chloride ions. Oxygen depletion implies that, cathodic reaction for oxygen reduction cannot be sustained within the crevice area and consequently metal dissolution occurs. Crevice corrosion may take place on any metal and in any corrosive environment. However, metals like aluminium and stainless steel that depend on their surface oxide film for corrosion resistance are particularly prone to crevice corrosion, especially in environments such as seawater that contain chloride ions. The material responsible for forming the crevice corrosion need not be metallic. Wood, plastic, rubber, glass, concrete, asbestos, wax and living organisms have been reported to cause crevice corrosion. It is frequently more intense in chloride environments. The mechanism of crevice corrosion is electrochemical in nature. It requires a prolong time to start the metal oxidation process, but it may get accelerated afterwards. Fig 1.4 shows an example of crecive corrosion.

Figure 1.4: Crevice corrosion on a stainless steel flange

(Source : http://www.cdcorrosion.com)

1.3.3.2 Filiform corrosion

It is basically a special type of crevice corrosion, sometimes termed as "under film" corrosion. This sort of corrosion takes place under painted or plated surfaces when moisture penetrates the coating. Lacquers and "quick-dry" paints are most susceptible to the problem. Their use should be avoided except absence of an adverse effect has been established by field experience. Fig 1.5 shows an example of filiform corrosion.
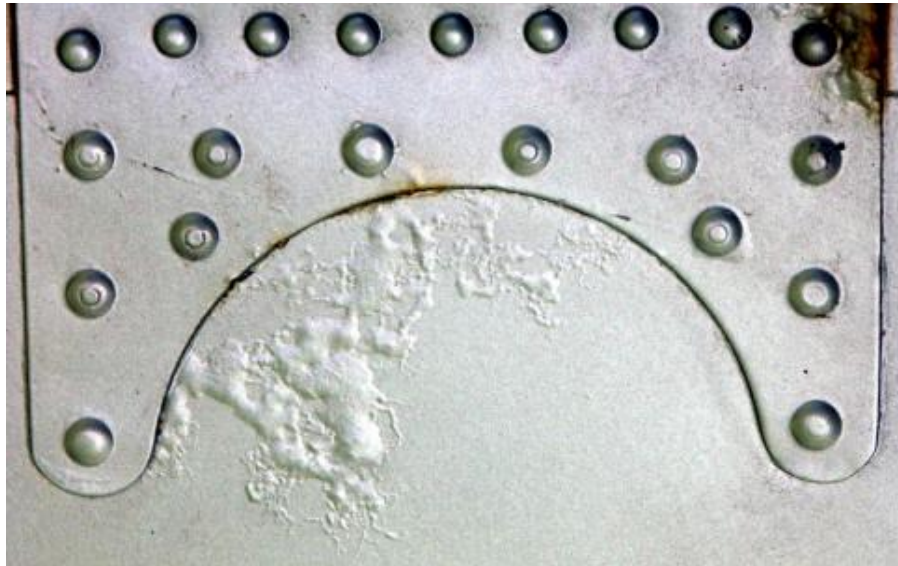

Figure 1.5: Filiform corrosion spreading beneath painted surface

(Source : www.nace.org)

1.3.3.3 Pitting corrosion

Pitting Corrosion is "self-nucleating" crevice corrosion, starting at occluded cells. Corrosion products frequently cover the pits, and might form "chimneys". Pitting is considered to be more risky than uniform corrosion damage because it is more complex to detect, predict and prevent. A small, narrow pit with negligible overall metal loss can escort to the failure of a complete engineering system. Once they start, both crevice and pitting corrosion can be explained with the help of differential concentration cells, cathodic reactions, i.e., oxygen reduction or hydrogen evolution may start in the crevice or the pits. Huge surface areas will turn out to be cathodic and pits or crevices will turn into anodic and corrode. Metal dissolution will thus be concentrated in tiny areas and will continue at much higher rates than with uniform corrosion. Large crevices are less expected to corrode because water movement causes mixing and replenishes oxygen, hydrogen ions, bicarbonate or hydrogen sulfide. Fig 1.6 shows an example of pitting corrosion.

Figure 1.6: Pitting corrosion on sink surface

(Source : http://www.amteccorrosion.co.uk)

1.3.3.4 Intergranular corrosion

Intergranular corrosion is a local type of corrosion. It is a preferential attack on the grain boundary phases or the zones straight adjacent to them. Little attack is experienced on the main body. This results in loss of strength and ductility. The attack is often quick, penetrating severely into the metal and leading to failure. Fig 1.7 shows an example of intergranular corrosion.
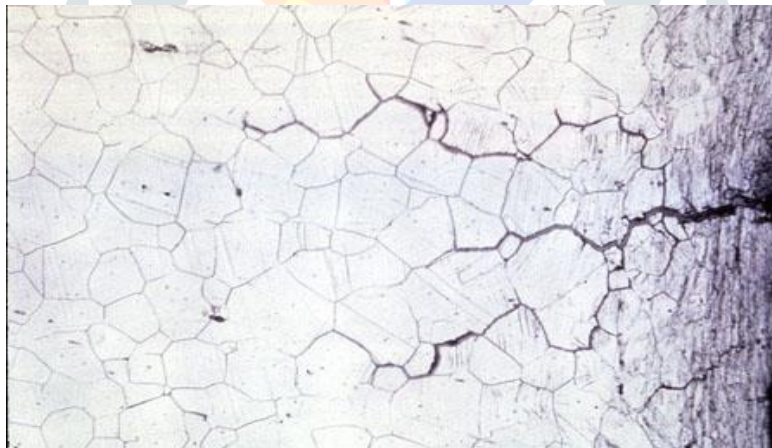

Figure 1.7: Intergranular corrosion of stainless steel

(Source: https://www.gewater.com/handbook)

1.3.4 Microbiologically Influenced Corrosion (MIC)

MIC refers to corrosion that is affected by the existence and activities of microorganisms (bacteria, fungi etc) and/or their metabolites. An aerobic bacterium produces highly corrosive type as part of their metabolism. Most resources, including metals, polymers, glass and ceramics can be degraded in this manner. The production of corrosive species such as minerals, organic acids, ammonia, sulphide and a variety of types of microbes tend to act synergistically in the corrosion of materials with their interactions characteristically being of a complex nature. Fig 1.8 shows an example of MIC corrosion.

Figure 1.8: MIC corrosion inside a fire sprinkler systems

(Source : http://www.croberts.com/erosion-corrosion.htm)

1.3.5 Erosion corrosion

The term "erosion" applies to deterioration due to mechanical power. When the factors contributing to erosion hasten the rate of corrosion of a metal, the attack is called "erosion corrosion". It is the effect of a combination of an aggressive chemical environment and elevated fluid surface velocities. This can be the effect of fast fluid flow past a stationary object, such as the case with the oilfield check valve, or it can be the outcome from the quick motion of an object in a stationary fluid, such as when a ship's propeller churns the ocean. Surfaces which have undergone erosion corrosion are usually fairly clean, unlike the surfaces from a lot of other forms of corrosion. In the Fig. 1.9, the red arrow points to pin holes in the pipe wall. Notice the crushed pipe wall which is much thinner than normal (blue arrow). Figure is a view of a section of the failed pipe showing the interior surfaces. The blue arrow in Figure points to the normal wall thickness of the copper tubing, while the red arrow points to an excessively thin wall area where pin hole leaks had occurred. This thinning of the copper pipe wall in new installations is characteristic of the phenomenon called erosion-corrosion. Due to turbulence and excessive water velocity, the passive corrosion protective film has been removed in some areas, causing accelerated corrosion of the pipe wall, thinning of the pipe wall and eventual water leakage.
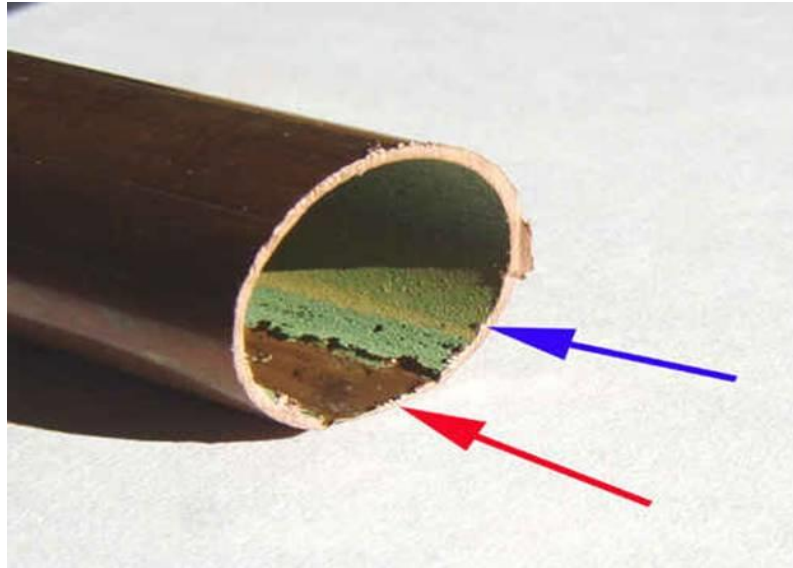
Figure 1.9: Erosion corrosion inside a pipe

(Source : http://www.croberts.com/erosion-corrosion.htm)

1.4 Corrosion Inhibitors

The use of chemical inhibitors to reduce the rate of corrosion processes is quite diverse. In the oil extraction and processing industries, inhibitors have always been considered to be the first line of defence against corrosion. A great number of scientific studies have been dedicated to the topic of corrosion inhibitors. Although, for the most part is known has been grown from trial and error experiments, both in the laboratories and in the field. Rules, equations, and theories to guide inhibitor growth or use are very restricted by definition, a corrosion inhibitor is a chemical substance that, when added in small concentration to an environment, efficiently decreases the corrosion rate. The competence of an inhibitor can be articulated by a measure of this improvement:

$$\text{Inhibitor efficiency (\%)} = 100 \; \frac{[CR(\text{uninhibited}) - CR(\text{inhibited})]}{CR(\text{uninhibited})}$$

where CR(uninhibited)=corrosion rate of the uninhibited system,

CR(inhibited)=corrosion rate of the inhibited system.

1.5 Classification of Inhibitors

The corrosion inhibitors can be classified based on physical mode of protection and mechanism of protection as follows:

1.5.1 Admixed inhibitors

Those compounds which are added to the fresh concrete at the time of mixing for new structures are known as admixed inhibitors. These compounds are added immediately after the addition of water to cement. Admixed inhibitor influence initial set, later strength gain or other properties i.e. hydration processes of cement. To overcome this, retarder was added to concrete mix which balances the acceleration of the inhibitors and provided a little more retardation. The inorganic compounds which are based upon calcium nitrite, sodium nitrite, sodium benzoate and sodium chromate are used as admixed inhibitors. Organic compounds based upon mixtures of alkanolamines, amines or amino-acids, or based on an emulsion of unsaturated fatty acid ester of an aliphatic carboxylic acid and a saturated fatty acid also proposed as admixed inhibitors.

1.5.2 Migrating inhibitors

These are the chemical which are applied on the hardened concrete surface and are able to diffuse through concrete to the underlying rebar where they act to suppress both the anodic and cathodic corrosion reactions by forming a monolayer film at the steel-concrete interface. According to physical mode of application, these types of inhibitors are also known as Surface applied corrosion inhibitors or Penetrating corrosion inhibitors. Use of migrating corrosion inhibitors are proposed in the last 15-20 years and are generally proposed for the repair works. These inhibitors are typically based either on mixtures of alkanolamines and amines or on inorganic compounds based upon Monofluro-phosphate.

In addition, nitrite ions can penetrate into concrete by absorption and diffusion if applied to the surface by spraying or ponding with aqueous solutions. Alkanolamines and amines have relatively high vapour pressure under atmospheric conditions, assisting diffusion and migration into concrete. Amino alcohols, such as ethanolamine and dimethylethanolamine, can act at the cathode and prevent oxygen reduction to hydroxyl ion by a blocking mechanism, following adsorbtion on the steel surface.

1.5.3 Anodic inhibitors

Anodic inhibitors form a protective oxide film on the surface of the metal leading to a large anodic shift of the corrosion potential. This leads to the shift of metallic surface into the passivation region. They are also called as passivators form time to time. Chromates, nitrates and tungstate are some basic instances of anodic inhibitors.

1.5.4 Cathodic Inhibitors

Cathodic inhibitors either slow down the cathodic reaction itself or selectively precipitating on cathodic areas to bound the diffusion of reducing species to the surface. Cathodic poisons can also be used to reduce the rate of cathodic reactions. However, cathodic poisons can also raise the vulnerability of a metal to hydrogen induced cracking as hydrogen can also be absorbed by the metal through aqueous corrosion or cathodic charging. Reduction in corrosion rate can also be done by the use of oxygen scavengers that react with dissolved oxygen. Sulphite and bisulphite ions are some examples of oxygen scavengers that can combine with oxygen to form sulphate.

1.5.5 Mixed Inhibitors

Mixed inhibitors work by reduction in both the cathodic and anodic reactions. The formation of precipitates takes place on surface blocking both anodic and cathodic sites indirectly as they are usually the film forming compounds. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal thus forming a protective film. The most common inhibitors of this sort are silicates and phosphates. Sodium silicate, for instance, is used in many household water softeners to avoid the occurrence of corrosive water. In aerated hot water systems, sodium silicate protects steel, copper and brass. However, protection is not at all times reliable and depends a great deal on pH. Phosphates also need oxygen for efficient inhibition. Silicates and phosphates do not afford the degree of protection provided by chromates and nitrites; however, they are very useful in situations where non-toxic additives are required.

1.5.6 Volatile inhibitors

Volatile corrosion inhibitors (VCIs) are also known as vapour phase inhibitors (VPIs). They are compounds which are moved to a closed environment to the place of corrosion by volatilization from a source. Morpholine is one of the volatile basic compounds which when transported with steam to stop corrosion in condenser tubes in boilers by counterbalancing the acidic carbon dioxide or by shifting the surface pH towards less acidic. If the corrosion product is volatile, it volatilizes as soon as it is created, thereby leaving the underlying metal surface uncovered for further attack. This causes fast and continuous corrosion leading to too much corrosion. For example, molybdenum oxide, the oxidation corrosion product of molybdenum is volatile. In closed vapor process (shipping containers), volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene amine are used as volatile corrosion inhibitors.

1.6 Objectives of the study

The objectives of the work are as follows:

- To understand the corrosion behaviour in partially completed structures of highway project,
- To study different standard methods of retrofitting of columns using corrosion inhibitors,
- To find the effective corrosion inhibitor to be used to improve the corrosion Resistance in partially completed structures.

1.7 Outline of the Report

The report consists of the following six chapters:

Chapter 1: Under the title *'Introduction'*, the chapter deals with the brief introduction of topic, brief details on corrosion, objectives and outline of the report. It illustrates the brief description of corrosion inhibitors.

Chapter 2: Under the title *'Literature Review'*, the brief details in respect of previous studies conducted by the different researchers has been mentioned.

Chapter 3: Under the title *'Study Area Details',* it emphasizes the details of the study area and project road. The brief of project road has been mentioned with various maps.

Chapter 4: Under the title *'Methodology',* an attempt has been made to elaborate the methods and technologies used to study corrosion behaviour of the partially completed structures. The thorough details in respect of methodology have been mentioned.

Chapter 5: Under the title *'Results and Discussions',* the results obtained from the tests conducted have been mentioned.

Chapter 6: Under the title *'Conclusions'*, the important conclusions as per the research work conducted, are given in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 General

The problems of corrosion of steel in concrete still exist despite the extensive research conducted over the last 20 years. The numerous factors involved in this type of corrosion instigate a number of studies to help understand the phenomenon and an equal number to bring about its prevention. This chapter includes the details of studies and data collected by different Researchers on experimentations conducted for the study of Corrosion resistance.

2.2 Reviews of Researchers on Corrosion Resistance

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

Monticelli et al. (2000) studied the inhibiting behaviour of many organic and inorganic substances against steel corrosion in an alkaline chloride solution constituted by a saturated calcium hydroxide solution containing 0.1 M chloride ions. Besides 0.05 M sodium nitrite (SN), among the tested substances, only 0.005 M 5-hexyl-benzotriazole (C6BTA), 0.05 M sodium β-glycerophosphate (GPH) and saturated dicyclohexylammonium nitrite (DCHAMN) were able to prevent pitting corrosion over 30-day exposures to the aggressive electrolyte.

Malik et al. (2004) investigated the performance of various surface applied corrosion inhibitors, viz., dimethyl ethanol amine-based, tri-ethanol amine-based and vapour based inhibitors. The condition of the exposed specimens was evaluated by physical examination of the rebar and also by carrying out electrochemical measurements. The electrochemical studies were consisted of open circuit potential and polarization measurements. The experimental data from the studies have been analyzed and the usefulness of MCI in protecting the rebar concrete was discussed.

M. Moreno et al. (2004) investigated the effects of the chloride concentration on both the polarization characteristics and the corrosion rate of as received reinforcing steel immersed in solutions simulating the pore liquid of alkaline and carbonated concrete, with particular reference to the critical chloride concentration. The electrochemical processes affecting rebar corrosion in concrete were analyzed by means of potentiodynamic polarization curves. The corrosion rate of steel was monitored in time by means of polarization resistance measurements. The effect of different levels of carbonate plus bicarbonate in the simulated pore solution was also evaluated.

Trabanelli et al. (2005) studied the effect of benzoic acid and its derivatives on protection against carbonation induced corrosion in solutions simulating the pore chemistry of carbonated concrete. Effectiveness of sodium monofluorophosphate as a corrosion inhibitor for concrete reinforcements and focuses on the understanding of MFP, in particular in terms of its potential penetration into concrete materials. Cylindrical mortar specimens with 35 mm diameter and 40 mm long, containing a centred mild steel of 6 mm diameter, were cast with ordinary Portland cement and a water-cement ratio of 0.5. All specimens were wrapped in an adhesive aluminium sheet, in order to reduce moisture loss, and then preserved for one year at 20ºC before the experimental campaign. Monofluorophosphate penetration profiles in carbonated or non- carbonated hardened cement pastes were calculated. These profiles were obtained at 7 and 28 days, after the application of MFP aqueous solution on the outside of cement paste specimens. A 5-mL volume of an aqueous MFP solution (20% by mass) was applied to one of the surfaces perpendicular to the axis of cylindrical cement paste specimens. (3cm diameter, 6cm high), either carbonated or not.

Heiyantuduwa et al. (2006) studied about the corrosion protection of steel with DMEA-based organic inhibitor. Methods used to assess cement mortar specimens performance included the measurement of corrosion potential, corrosion rate and mass loss. The corrosion potentials for each of the test specimens were recorded at regular intervals versus a saturated calomel reference electrode (SCE). The measurements were initially recorded on an everyday basis until equilibrium conditions were established and then they were recorded on a weekly basis. Fiber optical microscopic images were also taken. The corrosion potentials in cement mortar specimens contaminated with chloride ions shift to more negative values as the chloride concentration increases. On the other hand, when corrosion inhibitor is added, the corrosion potentials shift towards more positive values. The addition of 2% of cement DMEA inhibitor

decreases the mass loss of the steel rebar about 43%. The corrosion rate of steel reinforcement increases as chloride concentration increases. However, the corrosion rate of the rebars decreases as the concentration of the corrosion inhibitor increases.

Saraswathy et al. (2007) studied the performance of the anodic inhibitors (sodium nitrite and zinc oxide), cathodic inhibitors (mono ethanol amine, diethanol amine and tri ethanol amine) and mixed inhibitors to control rebar corrosion. Compressive strength test, tensile strength test, chloride diffusion test and macro cell corrosion test were conducted by varying the type of inhibitors and varying the concentration of inhibitors. The addition of inhibitors not only increased the compressive strength of the concrete but also improved the corrosion resistance properties.

Jitu K et al. (2011) studied the effectiveness of corrosion inhibitors in saturated calcium hydroxide solutions acidified by acid rain components. They analysed the effect of sodium nitrite and sodium molybdate as corrosion inhibitors in a saturated calcium hydroxide solution polluted with sulfuric and nitric acids (acid atmosphere) using Anodic Polarization curve and Impedence test. Both compounds showed significant inhibitory effects depending on the concentration. sodium molybdate showed an efficiency of approximately 67% whereas sodium nitrite showed an efficiency of 52% at low concentrations that is 0.013% total solution mass, but at 0.040% total solution mass (at high concentrations) their inhibitory effect was found to be similar.

Monticelli et al. (2011) have studied about two corrosion inhibitors, that is sodium 2-amino-benzoate (2AMB) and sodium glycero-phosphate (GPH), in a synthetic solution simulating the composition of the pore solution in a carbonated concrete, containing chlorides. Tests have been performed to verify if the simultaneous use of the two substances is compatible and if their addition can efficiently hinder the corrosion attack in the presence of both chlorides and carbonation. From this experiment, he concluded that in carbonated chloride-containing solution (from here on the blank solution) no significant variation of steel corrosion behaviour is achieved by prolonging the immersion period from 45 min up to 72 h. This suggests that the corrosion product film growing on the metal surface is not protective.

Kulwinder et al. (2016) inferred that a lot of research work has already been done on prevention of chloride induced corrosion by using corrosion inhibitors. However, research on the role of inhibitors on prevention of carbonation induced corrosion of rebar was still in initial stages. Moreover, the focus of previous research was on the use of inhibitors as admixed in concrete at the time of casting. The prime focus of the investigation was to evaluate the effectiveness of inhibitors when applied on the surface of concrete. Both commercially available amine group based inhibitors (already in use against prevention of chloride induced corrosion) and the generic chemicals having the amine group were tested for their effectiveness in prevention of carbonation induced corrosion in concrete.

Hilke Verbruggen et al. (2016) studied to evaluate different inhibitors for both types of corrosion that can occur in reinforced concrete: pitting corrosion (by chloride attack), and uniform corrosion (by a drop in pH). Depending on where the inhibitors act a distinction can be made between anodic inhibitors, which impede the oxidation reaction, cathodic inhibitors, which decrease the reduction reaction, or mixed inhibitors which act on both half-reactions. Consequently, the inhibition effectiveness depends on the corrosive environment and the metal surface it needs to act on. The following inhibitors were used: Sodium molybdate dehydrate ($Na_2MoO_4-2H_2O$) with a purity P=99.0%; Cerium nitrate hexahydrate ($Ce(NO_3)_3-6H_2O$) with a purity = 99.0%; 2,5-Dimercapto-1,3,4-thiadiazole (DT) with a purity P98.0%; 2-Mercaptobenzothiazole (MBT) with a purity P97.0%; 1H-benzotriazole (BTA) with a purity P98.0%.In this work, they defined three critical situation that can realistically occur in reinforced concrete and thus in which an inhibitor should act.

Ibrahim et al. (2017) stated that corrosion of reinforcing steel bars in concrete structure is a major challenge particularly in oil and gas and marine environments due to its high corrosiveness. Several corrosion mitigation methods such as protective coatings, cathodic protection, sealants are commonly employed but the use of corrosion inhibitors is becoming more attractive to researchers probably due to its economics and ease of application. Migratory corrosion inhibitors (MCIs) are effective in corrosion mitigation as it has ability to diffuse through the pores of the concrete and form a monomolecular layer between the steel bar and the concrete thereby delaying the initiation of corrosion of the steel bars; consequently, extending the services life of the concrete structures. The performances of selected migratory corrosion inhibitors either as admixture or apply on the surface of concrete has been studied and the evaluation of its effectiveness in the corrosion reduction of the steel bars is presented.

Zhijie Yuan et al. (2017) stated that corroded bridge piers are often subjected to dynamic axial loads, such as the vertical pounding that occurs during earthquakes or due to railway trains. Repeated axial loading was used to simulate this vertical pounding effect. Therefore, the seismic performance of corroded RC structures under repeated axial and horizontal cyclic loading is an urgent issue. To investigate the influences of steel corrosion and repeated axial loading on the seismic performance of a column pier, eight RC column specimens were experimentally investigated. The results indicated that corrosion significantly influences the yield strength and load bearing capacity of a column. The load bearing capacities of the corroded specimens decreased by 18.27% compared with noncorroded specimens when the longitudinal loss of steel mass was 7.16%. Repeated axial loading did not significantly influence the mechanical properties of the corroded RC piers. Cyclic tests were performed to validate a finite-element model that was used to assess the effects of corrosion level on the seismic performance of columns. The level of steel corrosion ranged from 0 to 28%. According to the finite-element analysis, the yield strength (35%) and ultimate displacement (34%) decreased with increasing corrosion.

Shiping Yin et al. (2019) evaluated the study for determining the bond properties between textile-reinforced concrete (TRC) which is a confined concrete and a corroded steel bar. Based on the results of electrochemical corrosion and pullout tests, the bond properties between concrete and a steel bar under unconfined and confined conditions were comparatively analyzed in terms of the corrosion-induced cracking, failure mode, bond-slip curve, bond strength, and bond failure mechanism. The empirical calculation formula of the ultimate bond strength between unconfined concrete and a corroded steel bar was obtained, and the confinement effects of TRC and fiber-reinforced polymer (FRP) were compared by collecting data from the relevant literature. The research results indicated that TRC confinement can effectively improve the bond properties between concrete and a corroded steel bar and limit the development of corrosion-induced cracks. Furthermore, TRC controlled any further crack expansion during the pulling out of the steel bar. After TRC confinement, the brittle failure characteristic of the bond behavior between concrete and a corroded steel bar was improved, and the failure mode was changed from splitting to splitting pullout. The confinement effect of TRC using a lower fiber-reinforcement ratio is similar to that of FRP.
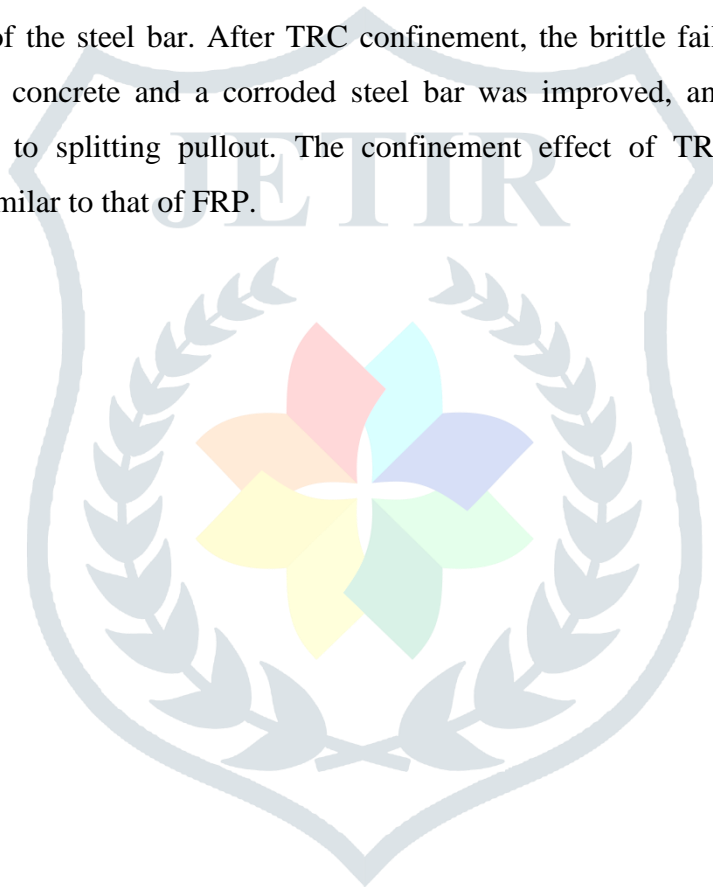
CHAPTER 3

STUDY AREA DETAILS

3.1 General

The main objective for road development is improvement in the economic conditions and social welfare of road users and nearby habitation area. Travel time and costs of vehicle use gets reduced due to increased road capacity and improved pavements. Other benefits such as increased access to markets, job opportunities, education and health service and reduced transport from the vehicle plying on the road can also be achieved by road development.

Improvement of the road project will have significant positive impacts, but they may simultaneously also bring significant negative impacts on nearby communities if proper precaution is not taken during design and implementation stage of the project. The people and properties may be in the direct path of road work and affected in major way. People may also be indirectly affected by the project, through the disruption of livelihood, loss of accustomed travel paths and community linkages, increase in noise levels and pollution. Roads bring people and people bring development. Roads are agents of change, which can bring both benefits and damage to the existing balance between the people and their environment. With the increasing pace of all round development activities in India, the intensity of traffic on Indian roads in general and particularly on highways has increased many folds thus rendering inadequate the existing roads capacity to contained this increased volume of traffic. To cope up with this challenge, Ministry of Road Transport and Highways, Government of India has entrusted the National Highway Corridors for augmenting their capacity adequately for safe and efficient movement of traffic. The Government has decided to convert some of the existing 2 lane highways into four lane highways. The project would envisage widening of existing 2 lane highways into four lanes with additional features such as provision of underpass, service roads, flyovers, Railway over bridge (ROB) and bridges, etc. so as to enhance operational efficiency and safety.

In this present study, an attempt has been made to study the project road details and the status of the work which may affect the structural strength and progress.

3.2 Description of the Study Area

The project road passes through Dhule and Nandurbar districts of Khandesh region of Maharashtra as shown in fig. 3.1.
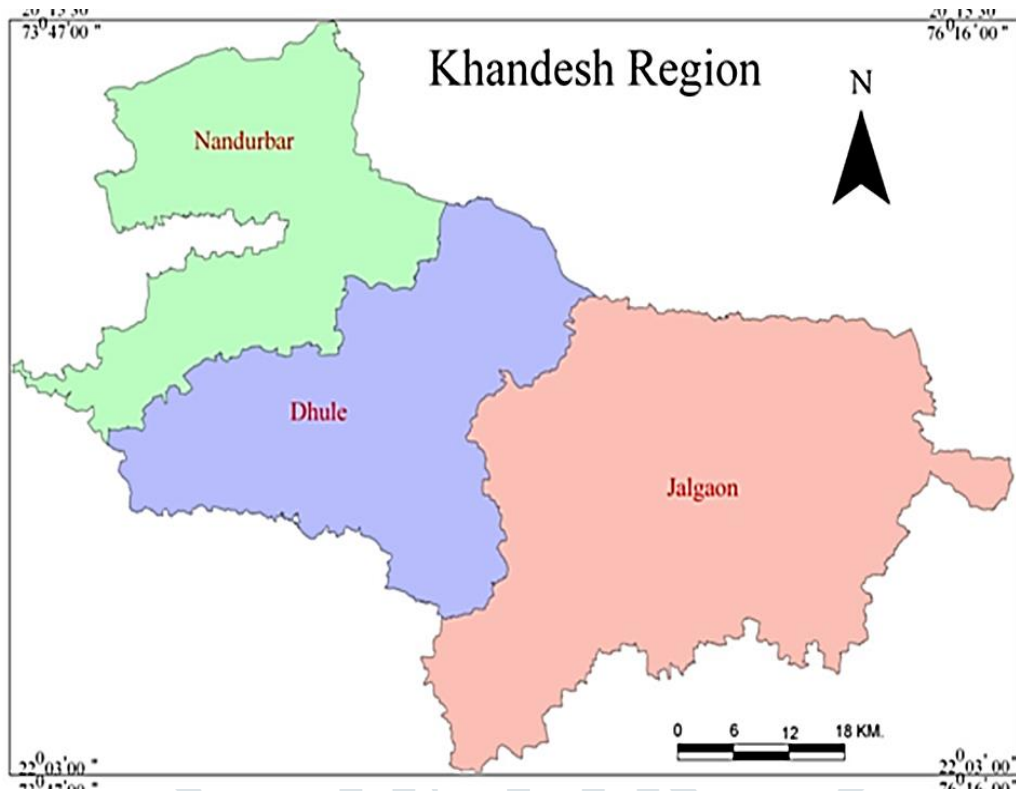
Figure 3.1: Khandesh region

(Source : Survey of India)

Khandesh region covers an area of three district of North Maharashtra i.e. Nandurbar, Dhule and Jalgaon. The national highway No.6 (NH-6) passes from these three districts. The extension of the Khandesh region is between latitudes $20^000'00''$N to $22°00'30''$N latitude and longitudes $73°31'00''$E to $76°28'00''$E.

Jalgaon district is the northernmost part of the State of Maharashtra. It covers an area of 11765 km^2. There are total 15 tehsils in the district. The average density of population of Jalgaon district is 313 persons/km^2. Jalgaon district was formerly known as East Khandesh district. It is located in the north-west region of the state of Maharashtra. The district has a population of about 4 million. It is abounded by many religious places and cultural establishments. It is bounded by Satpuda mountain ranges in the north, Ajanta mountain ranges in the south.

Dhule district is located in the northern parts of Maharashtra and lies on Latitude 20° 38' to 21° 61' N and Longitude 73°50' to 75°11' E. It is located on the merging point of three national highways namely NH-6 (Surat-Nagpur), NH-3(Mumbai-Agra) and NH-211 (Dhule-Solapur). Dhule district is bounded by Nandurbar district in the North-West, Nashik district in south and Jalgaon district in East. Dhule city is the Headquarter of district.

Nandurbar district is an administrative district in the north-west corner (Khandesh Region) of Maharashtra state in India. On 1 July 1998, Dhule was bifurcated as two separate districts now known as Dhule and Nandurbar. The district headquarter is located at Nandurbar city. The district occupies an area

of 5035 km². Nandurbar district is bounded to the south and south-east by Dhule district, to the west and north is the state of Gujarat, to the north and north-east is the state of Madhya Pradesh. The northern boundary of the district is defined by the great Narmada River.

Khandesh region has got pretty diverse climate. It is exceptionally hot and dry during summer with temperature reaching as high as 44°C. The present study is carried out over Khandesh region of Maharashtra which includes districts Jalgaon, Dhule and Nandurbar. It is roughly estimated that almost 85% of the total rainfall occur during rainy season of four months and the remaining spread over other months of each year. As per the IMD data, the average annual rainfall in the Khandesh region is 90cm. This is followed by pleasant temperature in winter. The climate of this Khandesh region is generally dry except in the monsoon. The year may be divided into four seasons. The cold season from December to February is followed by the hot season from March to May. The monsoon season is classified as June to September. In India, the post-monsoon season is from October and November. Along with other factors, temperature, humidity and air pressure are most important climate determining factors.

Khandesh region is well connected to the major cities of India Delhi, Pune, Nagpur, Durg, Raipur, Sambalpur and Kolkata, Bhopal, Mumbai, Nashik through National Highway No. 6 as shown in fig. 3.2.
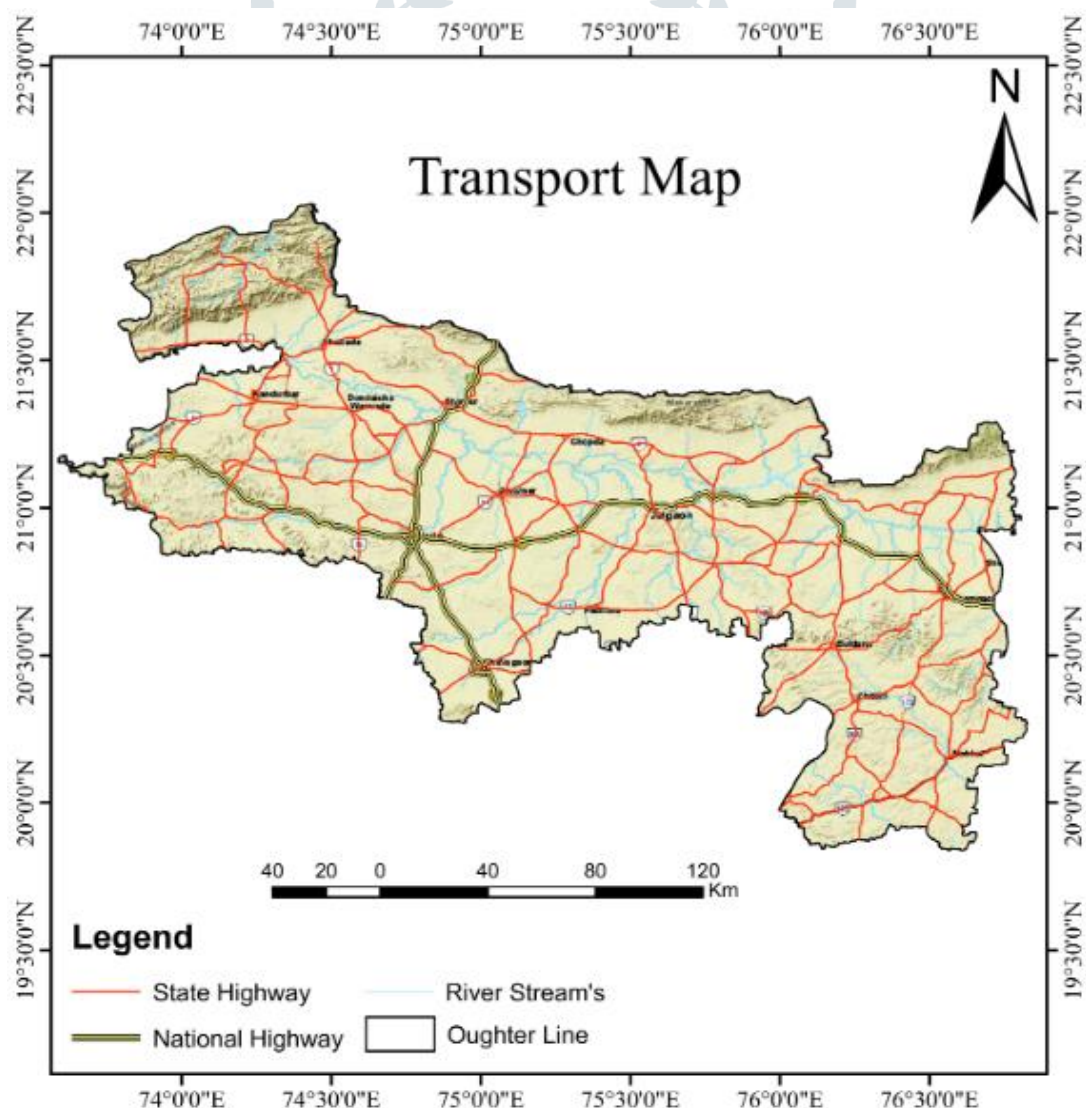

Figure 3.2: Transport map of Khandesh region

(Source: National Remote Sensing Centre, Hyderabad prepared on ArcGIS software)

3.3 Description of the Project Road

The project road corridor starts from Fagne in Dhule district at km 510.00 of NH-6 and ends at Maharashtra-Gujarat Border at km 650.79 of NH-6. The present configuration of the project road is mostly 2-lane except some stretches are two lane with paved shoulders and 4-lane (divide / undivided) in urban/ semi urban areas. Service road is not seen in built-up areas. The pavement type in all along project corridor is flexible. The project road has one existing bypass i.e. Dhule (connecting NH-3 to NH-6) and two level crossings are there in which one is narrow gauge at km 632.92 of NH-6 near Chinchpada and other at km 647.10 of NH-6 near Nawapur town. The length distribution of the project road in different districts is tabulated in table 3.1:

Table 3.1: District wise length of Project road

S. N.	District	Chainage	Length (km)	(%)
1	Dhule	km 510.00- km 606.00	96.00	68.19
2	Nandurbar	km 606.00- km 650.79	44.79	31.81
	Total		140.79	100%

The Right of Way (RoW) available with the NHAI for the entire length of corridor is about 24 m to 45 m for existing road alignment. The RoW is fairly clear except shops, houses and other structures on the both sides of the project road in the settlement areas. Presently, the project road is 2 lanes road and vehicle pressure on this road demands to widen existing two lane road into four lanes road. The main objective of the project is to widen the highways into 4 lanes with paved shoulder road to meet the traffic needs for the minimum next 15-20 years. On the basis of projected traffic growth, widening and strengthening of the project corridor to 4 lanes becomes essential. It is also proposed to add paved shoulder, earthen shoulder, proper drainage, Railway over Bridge (RoB), Bypasses small realignments utilities and amenities wherever required. Attention has been paid throughout the design to minimize resettlement problems, cutting of trees, shifting of cultural properties, etc., as far as possible through engineering design. The proposed widening and strengthening of the project road will not only improve the riding quality, journey speed but also cut the travel time and cost on the highway.

With the widening and improvements of the existing highway, the faster corridor will be established linking to east-west corridor of Khandesh region of north Maharashtra. The improvements will help

local population of Khandesh region to have better access to facilities of education, health care, family welfare, trade, commerce, market, employment etc. also the people inhabiting areas along to facilities of education, health care, family welfare, etc.

3.4 Development of the Project Road

The work of development of the project road starting from Fagne in Dhule district at km 510.00 of NH-6 and ending at Maharashtra-Gujarat Border at km 650.79 of NH-6 has been undertaken by National Highways Authority of India. It is an important East-West highway which is also called Great Eastern Road and also referred as Asian Highway-46 (AH-46). NH-6 starts from Kolkata and goes upto Hazira port. The highway is important for interstate connectivity between West Bengal, Jharkhand, Orissa, Chhattisgarh, Maharashtra and Gujrat. It is a part of New NH-53 which is important for port to port connectivity between Paradeep at Orissa to Hazira at Gujrat. The work of 4 laning of this project stretch was awarded to M/s. ILFS on BOT basis in the year 2016. However, due to the financial crisis of the Contractor M/s. ILFS, the Contract Agreement has been terminated by NHAI in the year 2019. At the time of termination of the Contract Agreement, about 65% of the physical progress had been achieved by the Contractor. This termination of the Contract has been resulted in partially completed structures at site.

The balance work of 4 laning of Fagne – Maharashtra / Gujrat border section of NH-6 has been awarded by NHAI to the Contractor M/s. J. M. Mhatre Infrastructure Pvt. Ltd. on EPC mode in the year 2020. The work is ongoing by the Contractor. The major challenge involved is retrofitting of the partially completed structures in the project highway. At the time of award of the work to the Contractor, about 90 structures were in partially completed state. The details of the structures to be constructed in the project road are as described in table 3.2 below:

Table 3.2: Details of Structure to be constructed in Project road

S. N.	Particular	Details
1	Interchange Dhule bypass	01 No.
2	Viaduct	01 No.
3	Major Bridges	10 Nos.
4	Minor Bridges	90 No.
5	Vehicular Underpasses	14 Nos.
6	Pedestrian Underpasses	10 Nos.
7	ROB	3 Nos.

The key plan of the project highway from Fagne to Maharashtra / Gujrat border section of NH-6 has been shown in fig. 3.3.
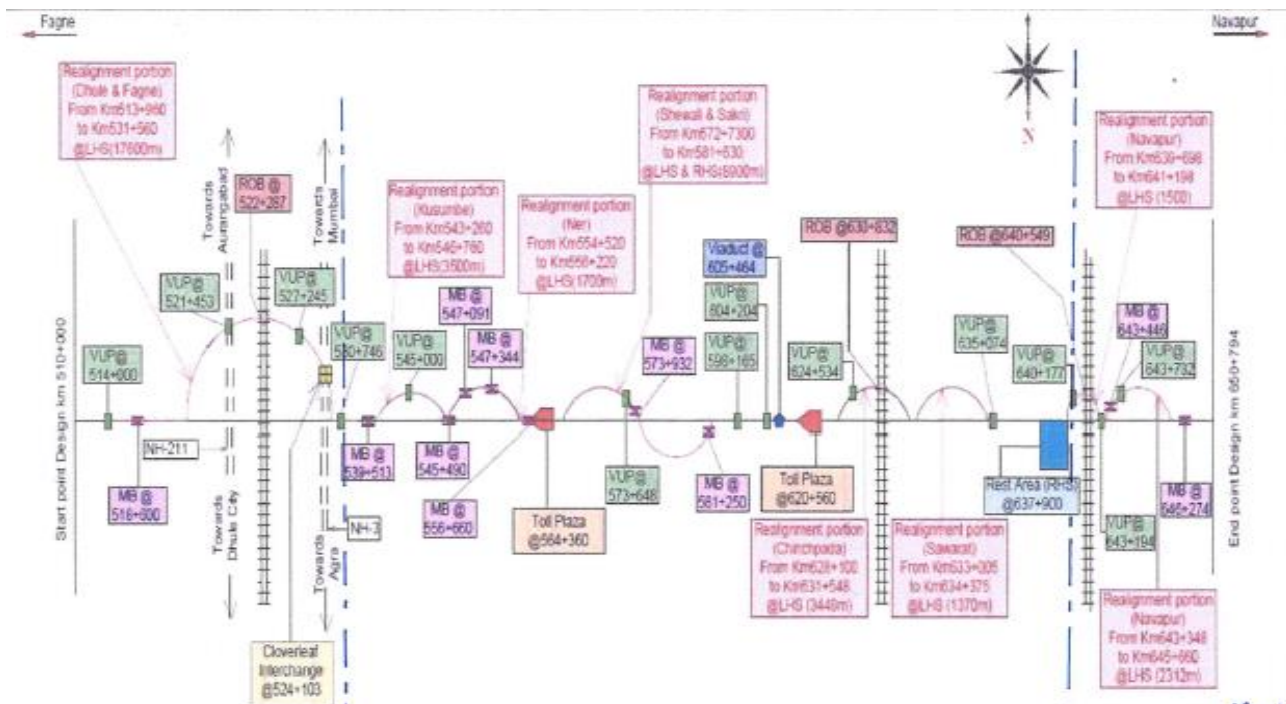

Figure 3.3: Key plan of the project road

CHAPTER 4

METHODOLOGY

4.1 General

In this chapter, the methodology used for the research work has been elaborated. The details in respect of collection of samples, tests conducted, procedures of testing, etc. have been mentioned in this chapter.

4.2 Collection of Samples

The Thermo Mechanically Treated (TMT) Steel bars of 1000mm in length and 20 mm in diameter have been obtained from partially completed structures from project road. The reinforcing bars have been cut using Gas cutter to obtain the test specimen of required dimensions. The samples have been taken from site as shown in fig. 4.1.

Figure 4.1: Collection of sample at site

4.3 Testing of samples for Chemical and Mechanical Properties

The Thermo Mechanically Treated (TMT) Steel bars of 1000 mm in length and 20mm in diameter and TMT bars of same dimensions obtained from partially completed structures from project road have been tested for analysis of chemical composition and mechanical properties.

The chemical parameters of samples analyzed are as given below in table 4.1:

Table 4.1: Chemical Composition parameter

S. N.	Test Parameter
1	Carbon
2	Sulphur
3	Phosphorous
4	Sulphur + Phosphorous

The mechanical parameters of samples analyzed are as given below in table 4.2:

Table 4.2: Mechanical property testing parameter

S. N.	Test Parameter
1	Yield Stress
2	Ultimate Tensile strength
3	Ratio of TS/YS
4	Elongation
5	Mass
6	Bend Test
7	Rebend Test

4.4 Methods of Testing of samples for Chemical and Mechanical Properties

The reference methods used for conducting various tests on samples and details of reference code used are given in table 4.3 below:

Table 4.3: Methods of testing and reference code

Test Parameter	Reference Test Method / code
Carbon	IS: 8811-1998, ASTM E 415
Sulphur	
Phosphorous	
Sulphur + Phosphorous	
Yield Stress	IS: 1608 (Part 01) - 2018
Ultimate Tensile strength	
Ratio of TS/YS	
Elongation	
Mass	IS: 1786-2008
Bend Test	IS: 1599-2019
Rebend Test	IS: 1786-2008

4.5 Corrosion Inhibitors

In this study, various types of chemical corrosion inhibitors were used to evaluate the corrosion resistance of TMT steel bars. The chemicals were selected upon their power of interrupting the corrosion process and their potential to be used as corrosion inhibitor. Various corrosion inhibitors that were used for the experiment purpose are listed in table 4.4.

Table 4.4: Chemical corrosion inhibitors used for experimental work

Chemical	Chemical Formula	Molar Mass (gm/mol.)	Appearance	Density (g/cm^3)
2-Aminopyridine	$C_5H_6N_2$	94.12	Colorless solid	1.21
2-Picolinic Acid	$C_6H_5NO_2$	123.11	White Solid	1.025
Salicylaldehyde	$C_7H_6O_2$	122.12	Dark Green Oil	1.146
4-Aminobenzoic Acid	$C_7H_7NO_2$	137.14	White Powder	1.374

To simulate the environment of media, pure $Ca(OH)_2$ was used. To attain an environment which simulated a concrete specimen under the influence of carbonation and chloride induced corrosion, pure NaCl and Carbon Dioxide gas from a standard CO_2 cylinder of 99% purity for the purpose of bubbling were respectively used. Fevitite Rapid is a two component multipurpose epoxy adhesive. It contains resin and hardener which is mixed in the ratio of 1:1 few seconds before it is used. In these experiments, it is used to prevent some part of steel bar from chemically reacting with the pore solution.

4.6 Preparation of specimen for Testing for Corrosion

Steel bars of 20 mm diameter are firstly cut into required lengths of 60 mm. These pieces of steel bars were drilled and threaded at one end according to the necessity of the electro-chemical cell and the various tests. The diameter of drill was kept as 3 mm and the depth was kept as 10 mm so that proper conductivity of electricity can be ensured.

Each piece of steel bar of length 60 mm was rubbed by wire brush and sand paper to remove any rust present on the surface. They were then further cleaned by soaking in analytical reagent grade hexane and allowed to air dry. After air drying the specimens for 24 hours, they were coated with one layer of epoxy

which is followed by another layer of epoxy having a time difference of minimum 1 hour between these two layers. The resulting specimens after epoxy coating were kept for 24 hours. Figure 4.2 shows the sample which is ready for experiment after coating. After that a nut with two bolts on it were screwed into the hole that was prepared and a copper wire is tightened between the bolts so as to ensure proper electrical conductivity. Figure 4.3 shows the line diagram of final steel specimen.
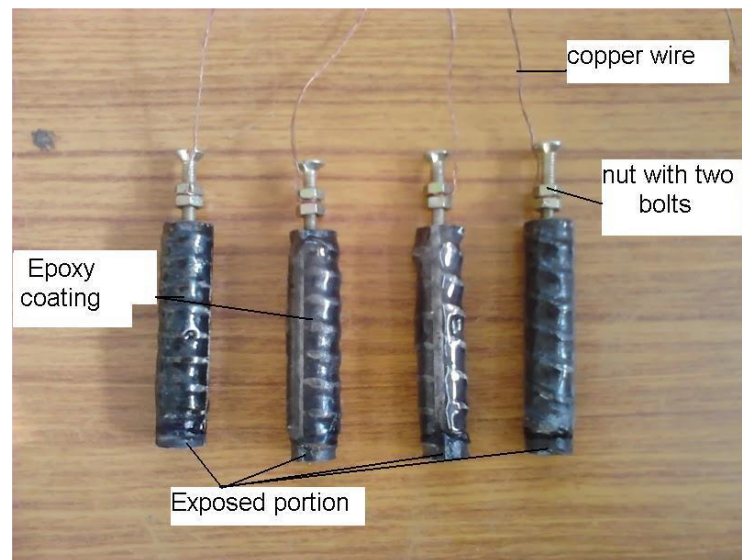

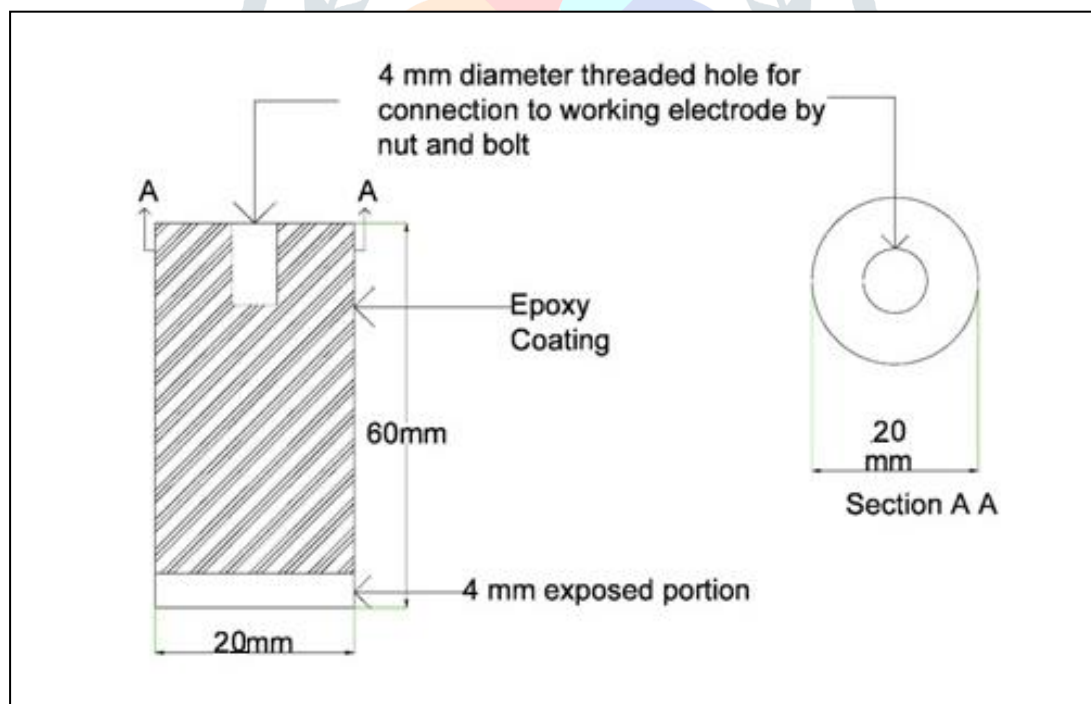Figure 4.2: Details of prepared steel specimen used for experimental works

Figure 4.3: Line diagram of prepared steel specimen

4.7 Preparation of Synthetic Pore Solutions

To obtain a pore solution whose pH ranges from 12-13, simulating freshly prepared concrete, saturated solution of $Ca(OH)_2$ is used. Calcium hydroxide solution is also known as lime water. A fully saturated

solution is prepared by taking 2.7gm/l (0.035M solution) of calcium hydroxide in de-ionized or distilled water (to ensure there will not be any foreign mineral or chemical that are present in tap water, which can affect the resultant pH of solution). This solution is then mixed properly and is left for at least 24 hours in a sealed container so that it doesn't absorbs any CO_2 from the atmosphere. After 24 hours, the resultant solution is then filtered through a filter paper in a sealed container. The exposure of solution to the atmosphere should be kept minimum so as to get optimum results.

To make a synthetic solution simulating to concrete which is under carbonation and chloride attack, the pH value of the saturated calcium hydroxide solution was decreased from 12 to around value of 7.4. To prepare the carbonated solution, Standard CO_2 of 99% purity was simply bubbled through the pore solution. Bubbling of CO_2 gas was done to achieve the carbonation condition in pore solution. Purpose of this process was to simulate corrosion prone carbonation state in the pore solution. The pH value of solution was reduced from 12 to 7.4 due to carbonation of calcium hydroxide. By reducing the pH value of solution to 7.4, a state of extreme carbonation in pore solution was achieved.

Table 4.5 shows the final pH of solutions in which steel specimens were kept. CO_2 reacts with calcium hydroxide present in lime water to produce calcium carbonate precipitates. This process is being monitored properly as the process converting calcium hydroxide into calcium carbonate while CO2 bubbling is very fast, an eye should be kept on the pH throughout the process. Pure NaCl was added into the resultant solution, at a quantity of 3.5% w/w. The resultant solution then should be filtered by filter paper. Figure 4.4 shows the Solutions of Chemical Inhibitors in Carbonated Saturated NaCl.

Table 4.5: Final pH of solutions in which steel specimens were kept.

Sr. No.	Abbreviations	Sample	pH value
1	Sol. 1	Saturated Ca(OH)2	12.4
2	Sol. 2	Carbonated and saturated chloride solution	7.4
3	Sol. 3	2-Amoinopyridine	9
4	Sol. 4	Picolinic Acid	7.1
5	Sol. 5	Salicylaldehyde	6.8
6	Sol. 6	4-Aminobenzoic Acid	6.9

Figure 4.4: Solutions of Chemical Inhibitors in Carbonated Saturated NaCl

4.8 Testing procedure for Corrosion

Six different steel bars of 20 mm diameter and 60 mm length are used. These steel bars are coated with one layer of epoxy along the length leaving a length of 4 mm from the bottom as discussed in the previous sections. After an hour when the first layer of epoxy has completely dried, another layer of epoxy is applied again, so as to ensure that epoxy layer doesn't breaks during the experiment. The bottom uncoated length of the six different steel bars, were submerged in four different corrosion inhibitors solution to understand their effectiveness to prevent corrosion. Along with this, two test specimens were submersed in control solutions, one of calcium hydroxide and other of carbonated solution along with chlorides to compare the results with un-carbonated and carbonated stages respectively. Figure 4.5 shows Final prepared specimens.

Various specimens were monitored for different periods of time i.e. 1 hour, 24 hour, 48 hours, 120 hours, 240 hours and 480 hours. 480 hours was the maximum time for which a specimen was being monitored. However, in all these tests, same working electrode was used. Due to this the solution was disturbed when the reading was taken. In order to avoid any error due to this, the system was kept untouched for 45 minutes prior LPR and OPC readings.
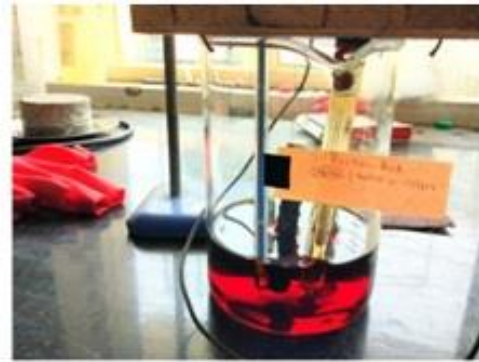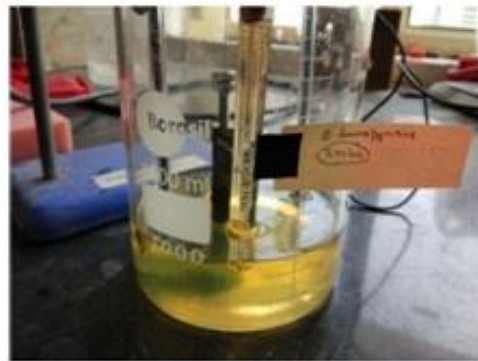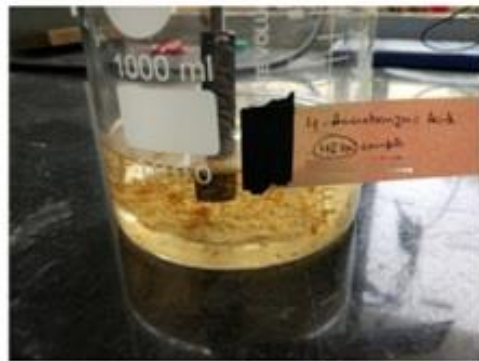
Figure 4.5: Final prepared specimens.

After preparing the solutions with corrosion inhibitors, steel specimens were placed in them. After the epoxy has dried properly and then monitored for corrosion and two electrochemical tests were conducted to monitor corrosion activity i.e. open circuit potential measurement and corrosion current density measurement. Corrosion monitoring was done by using ACM field machine.

ACM Model: Serial No. 1463 Field Machine was used for corrosion monitoring. ACM field machine provides many electrochemical techniques like current & voltage / time, long term-LPR sweep, long term-LPR step, Galvanostatic, AC impedance and Potentiostatic for corrosion monitoring. Current & voltage / time, long term-LPR sweep techniques were used for this experiment. ACM field machine used for the experiment is shown in figure 4.6 below:

Figure 4.6: ACM Model: Serial No. 1463 Field Machine

4.8.1 Half Cell Potential Measurements

Half -cell potentials is measured on the reinforcing steel bars. Half-cell potential readings are taken with respect to Saturated Calomel electrode as reference electrode (Potassium chloride). The value of half-cell potential obtained gives an indication of de-passivation of steel and hence the possibility of corrosion. In this study, the specimens were monitored at specific times by half-cell potential using a saturated calomel reference electrode (KCl) by placing the electrode in the solutions. The procedure followed by ASTM Standard. The half-cell potential measurement is the most common method used in the bridge deck corrosion surveys. An indication of the relative probability of corrosion activity can be empirically obtained through measurement of the potential difference between a standard portable half-cell placed on the surface of the steel rebar underneath. The ASTM interpretation of half-cell potential (SCE) is summarized in table 4.6.

Table 4.6: ASTM Interpretation of Half-Cell Potential Readings

Half Cell Potential values	Corrosion condition
< -426 mV	Severe corrosion, corrosion induced cracking may occur
< -276 mV	High risk, 90% probability of corrosion
-126mV to -275 mV	Intermediate risk, corrosion activity in reduction
0 to -125 mV	Low risk, 10% probability of corrosion

4.8.2 Linear Polarization Resistance (LPR)

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

The polarization resistance, R_p of the steel is then calculated from equation

$$R_p = \Delta E/\Delta I$$

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

$$I_{corr} = B/R_p$$

Where, B is the Stern-Geary constant and is given by $B = \dfrac{(\beta a \times \beta c)}{2.3\,(\beta a + \beta c)}$

β_a and β_c are anodic and cathodic tafel constants respectively. The value of B is taken as 26mV considering steel in active condition. R_p is the polarization resistance. A value of 26 mV has been adopted for active steel and 50 mV for passive steel. In order to determine the corrosion current density (i_{corr}) the surface area (A) of steel that has been polarized needs to be accurately known:

$$i_{corr.} = I_{corr.}/A$$

The present residual strength and, by extrapolation, the remaining service life of the structure can then be estimated. In this experiment, potentiostatic linear sweep test was carried out on bare steel specimens using the ACM Field Machine. The electrochemical cell consists of a 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, auxiliary electrode and noise reduction probe were attached to the electrochemical cell. The potentiostatic linear sweep test was carried out from -300 mV to 1500 mV with offset from corrosion potential at a sweep rate of 50 mV per minute.

CHAPTER 5

RESULTS AND DISCUSIIONS

5.1 General

In this chapter, the results obtained from the different tests conducted on the specimen, have been elaborated. The attempt has been made to discuss the results with standards of different IS codes and to study the comparison and effect on the performance of the structures. This chapter presents the experimental results with a discussion of their significance. As was discussed earlier, the main objective of this research was to study the corrosion resistance provided by the various corrosion inhibitors. The following sections discuss the results based on the data from OCP and LPR sweep tests.

5.2 Chemical Properties of the test specimen

The various chemical properties of TMT Fe500 steel bars used for the experimentation have been obtained using standard methods described in previous chapter. The chemical properties of the specimen are given in the table 5.1 below:

Table 5.1: Chemical properties of TMT Fe500 steel bars

Test Parameter	Test Result		Permissible limit as per IS 1786-2013
	New Steel bars	Collected from Partially completed structures	
Carbon (%)	0.23	0.192	Max. 0.25 ± 0.02
Sulphur (%)	0.024	0.028	Max. 0.040 ± 0.005
Phosphorous (%)	0.027	0.021	Max. 0.040 ± 0.005
Sulphur + Phosphorous (%)	0.051	0.049	Max. 0.075 ± 0.01

5.3 Mechanical Properties of the test specimen

The various mechanical properties of TMT Fe500 steel bars used for the experimentation have been obtained using standard methods described in previous chapter. The mechanical properties of the specimen are given in the table 5.2 below:

Table 5.2: Mechanical Properties of TMT Fe500 steel bars

Test Parameter	Test Result		Permissible limit as per IS 1786-2013
	New Steel bars	Collected from Partially completed structures	
Yield Stress (N/mm^2)	542	507	Min. 500
Ultimate Tensile strength (N/mm^2)	680.2	602	Min. 545
Ratio of TS/YS	1.25	1.19	Min. 1.08
Elongation (%)	18.5	20.50	Min. 16.00
Mass (kg/m)	2.47	2.445	$2.47 \pm 3\%$
Bend Test	No crack or	No crack or	There should be no

	rupture observed	rupture observed	any visible rupture or cracks
Rebend Test	No crack or rupture observed	No crack or rupture observed	There should be no any visible rupture or cracks

From the above tables, it can be observed that both the samples of TMT Fe500 steel bars shows the results which are under permissible limits as per respective IS codes, however, the strength has been decreased due to corrosion.

5.4 Testing for Corrosion

Linear Polarization Resistance sweep monitoring for corrosion measuring is an effective electrochemical method. Observing the relationship between electrochemical potential and current generated between electrically charged electrodes in a process stream that allows the calculation of the corrosion rate. LPR effectiveness in pore solutions is maximum and has confirmed to be a technique of rapid response. This measurement of the actual corrosion rate allows almost instant feedback to operators.

The linear sweep test has been conducted on bar steel specimen. Anodic polarization curve for Sol. 1 in calcium hydroxide saturated solution for 1hr and Sol. 2, after passing CO_2gas and saturating it with NaCl has been shown in fig. 5.1. This graph shows different zones of corrosion for the steel reinforcement which is indicated:

Active zone

It is the zone where the very little change in potential is promoted with the increase in current density, is significantly high.

Passive zone

It is the zone where the change in current density is relatively small with significant increase in potential. It lies above the active zone.

Pitting zone

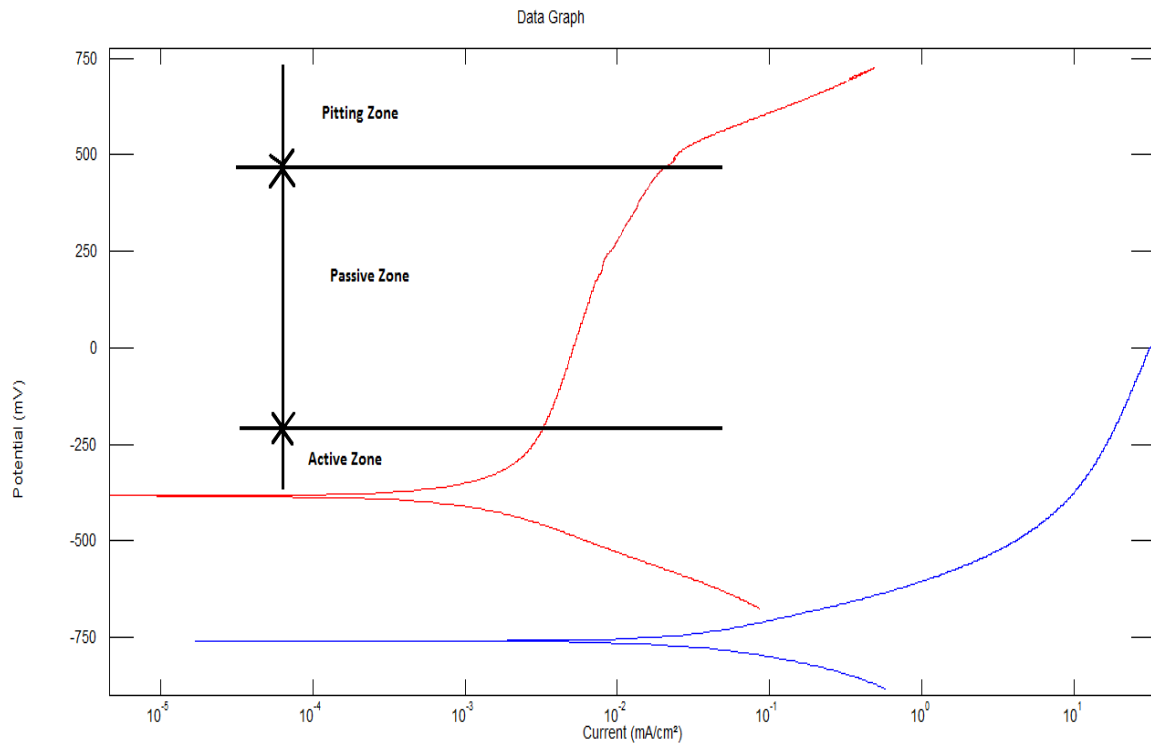The pitting zone with oxygen evolution lies above the passive zone.

Figure 5.1: Anodic polarization curve for Sol. 1 and Sol. 2

From the graph above, it can be seen that for Sol. 1, all the zones are well defined unlike Sol. 2. For Sol. 1, the active zone is which the steel bar is very resistant to the current density, which means there is no effect on the passive layer around the steel. The passive zone is well defined as the steel bar starts to resist the corrosion from current density between10^{-3} mA/cm^2 to 10^{-2} mA/cm^2 and the passive layer starts to deplete between 10^{-2} mA/cm^2 to 10^{-1} mA/cm^2 of current density and does enter into the pitting zone afterwards. For Sol. 2, as CO_2 gas is passed through calcium hydroxide after which 3.5% of NaCl is added into the solution, the graph did not showed any defined zones. In the initiation period or active zone for Sol. 2, starts to flow a very low potential when compared to Sol. 1. The passive zone which is the propagation period is small or does not exist as the passive layer is now deplete at very low potential or we can say steel did not prepare any passive layer as there is reduction in the pH of the solution. From comparing the both samples it can be said that CO_2 along with NaCl in the solution causes rapid deterioration of the steel bar due to carbonation and chloride induced corrosion. For the experiments different corrosion inhibitor have been added to the Sol. 2 to prevent corrosion and even understand their effectiveness.

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

Tafel plot gives variation of potential (mV) at Y-axis with respect to current density (mA/cm^2) at X-axis. Tafel plots give more precise values of I$_{corr}$. and corrosion rate by the use of Tafel extrapolation. Tafel ruler function in sequencer of ACM field machine can be used for Tafel extrapolation. Tafel rulers can only be used on potential v current graphs where the current axis is logarithmic. Three rulers are placed on the graph, a horizontal ruler which identifies the rest potential. The other rulers indicate Tafel slopes.

In order to compare the performance of chemicals as corrosion inhibitors, Tafel plots of the specimens immersed in these chemicals are compared with the Tafel plot of the specimen immersed in carbonated calcium hydroxide solution with NaCl (Sol. 2). Corrosion current density values less than 10^{-4} mA/cm^2 correspond to passive condition and corrosion current density values ranging between 10^{-4} mA/cm^2 and 10^{-3} mA/cm^2 correspond to moderate corrosion rate. Similarly corrosion current density values ranging between 10^{-3} mA/cm^2 and 10^{-2} mA/cm^2 and between 10^{-2} mA/cm^2 and 10^{-1} mA/cm^2 correspond to high and very high corrosion rate respectively.

5.5 Test Results of Various Specimens at different immersion times

Monitoring of corrosion as done at 1 hour, 24 hours, 48 hours, 120 hours, 240 hours and 480 hours of immersion

5.5.1 Test results after 1 Hour of immersion

After preparing steel specimens and placing them in the respective control and inhibitor solutions for a time of 1 hour, two tests were performed on each specimen i.e. Current and Voltage and LPR sweep, through which following results have been obtained.

The results obtained after a time of 1 hour are not much dependable as the time provided to inhibitors to prove their inhibiting qualities is not sufficient.

Table 5.3: Half-Cell potential and I$_{corr.}$ results after 1 hour of immersion

Sol. No.	Rp (-mV)	I$_{corr.}$ (mA/cm^2)
Sol. 1	390.5	0.057
Sol. 2	661	1.175
Sol. 3	655	1.323
Sol. 4	545	1.315
Sol. 5	663	1.031
Sol. 6	543	0.41

The difference between the half cell potential gives us an idea about the high probability of corrosion in the other specimens, and is generally due to the presence of chlorides and the lower pH of the solution.

The curve obtained is shown in figure 5.2 for steel in saturated $Ca(OH)_2$ solution vs carbonated saturated $Ca(OH)_2$ vs solutions with different corrosion inhibitors @1% inhibitor w/w, clearly shows that except 4-Aminobenzoic acid all of the inhibitor have shown their inhibiting quality . An active region, where the current density was lower than 10^{-3} mA/cm^2, was observed in the controlled specimen (Sol. 1) before the starting of breaking of passive layer. The major difference was a displacement of the curve towards lower potentials that was most probably associated to the lower pH of the carbonated $Ca(OH)_2$ solution and the presence of Cl$^-$ ions.
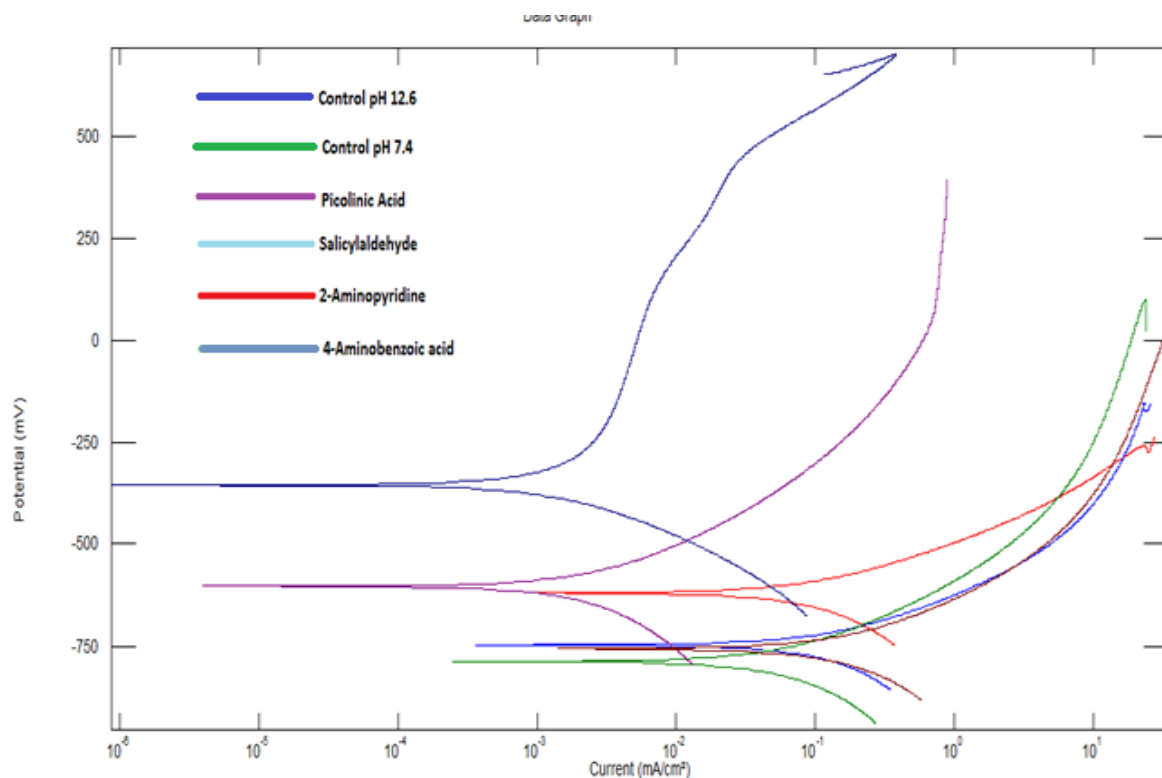

Figure 5.2: Tafel plot for various solutions immersed for 1 hour

5.5.2 Test results after 24 Hours of immersion

After preparing steel specimens and placing them in the respective control and inhibitor solutions for a time of 24 hours, two tests are performed on each specimen i.e. Current and Voltage & LPR sweep, through which following results have been obtained as shown in table 5.4.

Table 5.4: Half-Cell potential and $I_{corr.}$ results after 24 hour of immersion

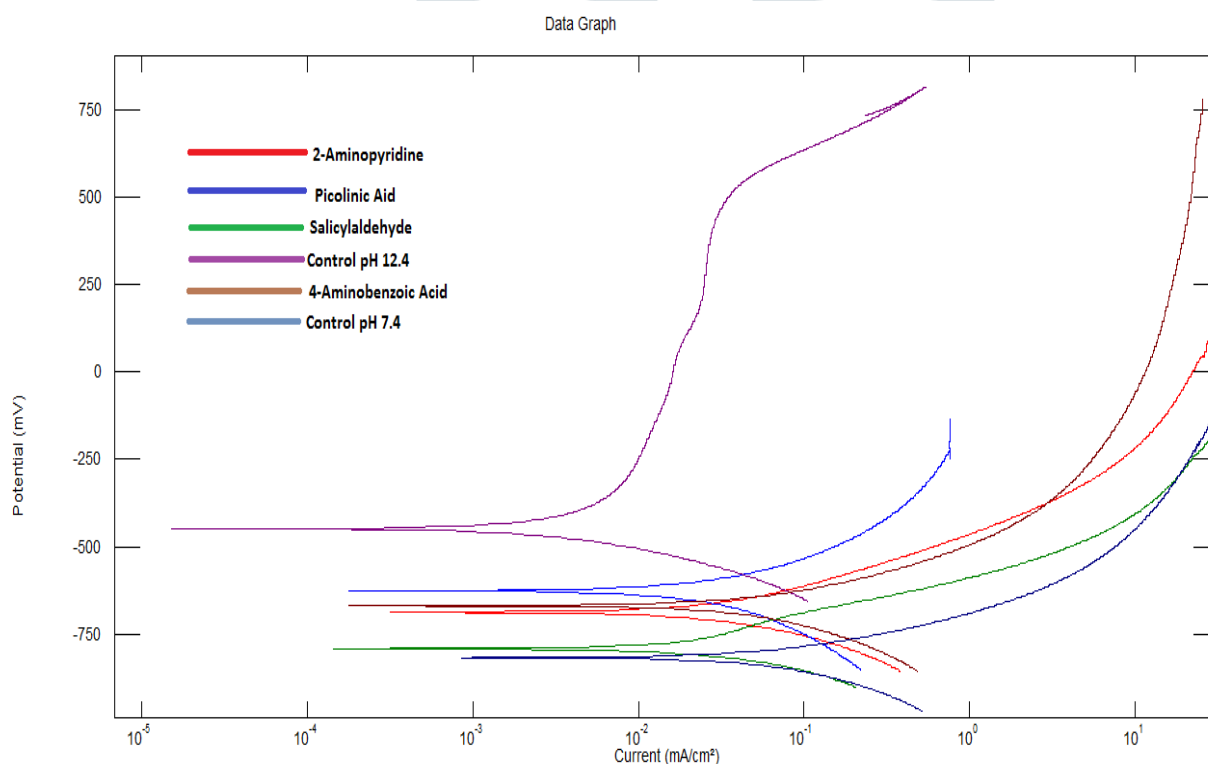| Sol. No.	Rp (-mV)	$I_{corr.}$ (mA/cm^2)
Sol. 1	472.5	0.04
Sol. 2	711.1	1.275
Sol. 3	588.5	1.204
Sol. 4	660.1	1.118
Sol. 5	656.2	1.175
Sol. 6	544.2	0.525

Figure 5.3: Tafel plot for various solutions immersed for 24 hour

From the values of half-cell potential obtained from current and voltage curves, it can be seen that the control solution with pH 7.4, have half-cell potential of -711mV which clearly depicts initiation of corrosion. From the values of I_{corr}, it is clear that the inhibitors have started working as compared to control Sol. 2.

The $I_{corr.}$ Value for 4-Aminobenzoic Acid is 0.525mA/cm^{2}which gives us an idea that in the initial stages, 4-Aminobenzoic acid has performed exceptionally well as compared to the other corrosion inhibitors. Along with it, Salicylaldehyde has also performed well as compared to other inhibitors.

5.5.3 Test results after 48 hours of immersion

After preparing steel specimens and placing them in the respective control and inhibitor solutions for a time of 48 hours, two tests are performed on each specimen i.e. Current and Voltage & LPR sweep, through which following results have been obtained as shown in table 5.5.

Table 5.5: Half-Cell potential and $I_{corr.}$ results after 48 hour of immersion

Sol. No.	Rp (-mV)	I_{corr} (mA/cm^2)
Sol. 1	511.78	0.045
Sol. 2	732.2	2.551
Sol. 3	648.30	1.841
Sol. 4	639.1	1.85
Sol. 5	680.2	1.12
Sol. 6	560	0.783

The values of $I_{corr.}$ and Rest potential obtained depicts that theSpecimen which was in Sol. 1 shows noble passive behaviour till now. A shift of $I_{corr.}$ value towards active zone was observed after 48 hours of immersion in Sol. 1, whereas the specimens in all the inhibitors have showen a huge rise in $I_{corr.}$value till now. Picolinic Acid proves to the worst inhibitor for a short period of time (upto 48 hours), whereas 4-Aminobenzoic Acid is the best among them.
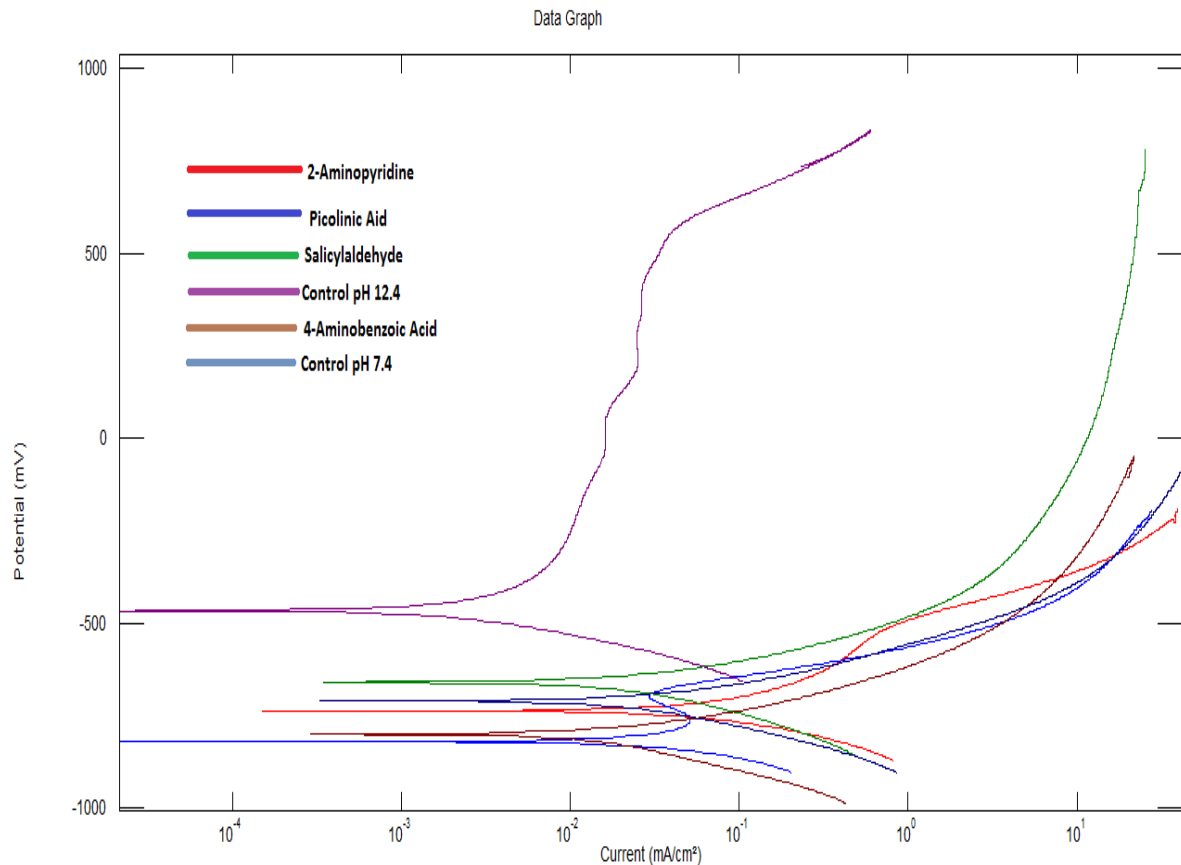
Figure 5.4: Tafel plot for various solutions immersed for 48 hour

Hence through these polarization curves, it can be concluded that after 48 hours of immersion except 4-Aminobenzoic acid, none of the chemical inhibitor has shown any remarkable progress in achieving passivation. All the specimen with corrosion inhibitors were having a rest potential of less than -600mV.

5.5.4 Test results after 120 hours of immersion

After preparing steel specimens and placing them in the respective control and inhibitor solutions for a time of 120 hours, two tests are performed on each specimen i.e. Current and Voltage & LPR sweep, through which following results have been obtained as shown in table 5.6.

Table 5.6: Half-Cell potential and $I_{corr.}$ results after 120 hour of immersion

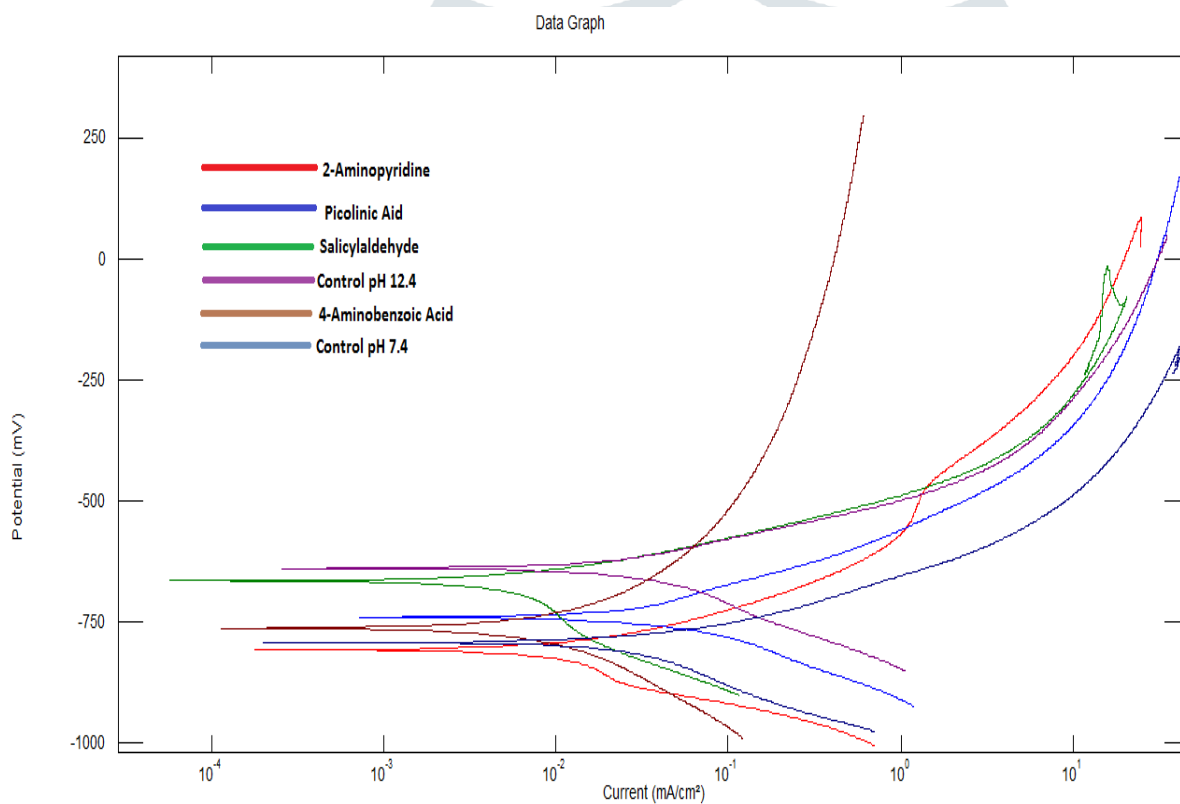| Sol. No.	Rp (-mV)	$I_{corr.}$ (mA/cm^2)
Sol. 1	705.5	0.38
Sol. 2	746.2	2.355
Sol. 3	674.6	1.751
Sol. 4	653.78	1.283
Sol. 5	649.5	1.552
Sol. 6	597.9	1.475

Figure 5.5: Tafel plot for various solutions immersed for 120 hour

Through the values of $I_{corr.}$ And Half cell potential it can be seen that the control specimen with pH 12.4 is now probable to corrode. 4-Aminobenzoic acid which has shown very promising nature has declined its performance.

As can be observed from Tafel plot of specimen in Sol. 1 shown in fig. 5.5, I_{corr} value shifts toward active zone showing no passive behaviour with increasing immersion time. I_{corr} value for this specimen was 0.057 at 1 hour of immersion which shifted to 0.38 at 120 hours.

Figure 5.6: Steel specimens after measuring Half-cell Potential and Linear Polarization Resistance, immersed in different solutions after 120 hours

In fig. 5.6, it can be seen that the specimen which was immersed in Sol. 2 has an absurd amount of corrosion on it. As we know the volume of corrosion rust is 3-7 times as iron, it can be seen in the figure that the volume expansion has caused cracking of the epoxy. When compared to other specimens, it is clearly shown that all the inhibitors are working with approximately equal effectiveness upto this point with 2-aminopyridine having an upper hand among all.

The specimen with salicylaldehyde may seems to have lesser rust on it but when the LPR Sweep is done for this sample, it has been found that the corrosion is present on it in sufficient quantity.

5.5.5 Test results after 240 hours of immersion

After preparing steel specimens and placing them in the respective control and inhibitor solutions for a time of 240 hours, two tests are performed on each specimen i.e. Current and Voltage & LPR sweep, through which following results have been obtained as shown in table 5.7.

Table 5.7: Half-Cell potential and $I_{corr.}$ results after 240 hour of immersion

Sol. No.	Rp (-mV)	$I_{corr.}$ (mA/cm^2)
Sol. 1	743.5	0.0255
Sol. 2	738.08	2.276
Sol. 3	665.2	0.77
Sol. 4	496.8	0.768
Sol. 5	700	1.049
Sol. 6	692.2	1.185

The values obtained of rest potential and $I_{corr.}$ is a clear proof that all the corrosion inbitors have inhibited specific amout of corrosion as compared to the control Sol. 2. Fig. 5.6 depicts that, specimen immersed in Sol. 5 shows passive behaviour at 240 hours of immersion. I_{corr} valuefor Sol. 5 shows a satisfactory shift towards passive zone at 240 hours of immersion.
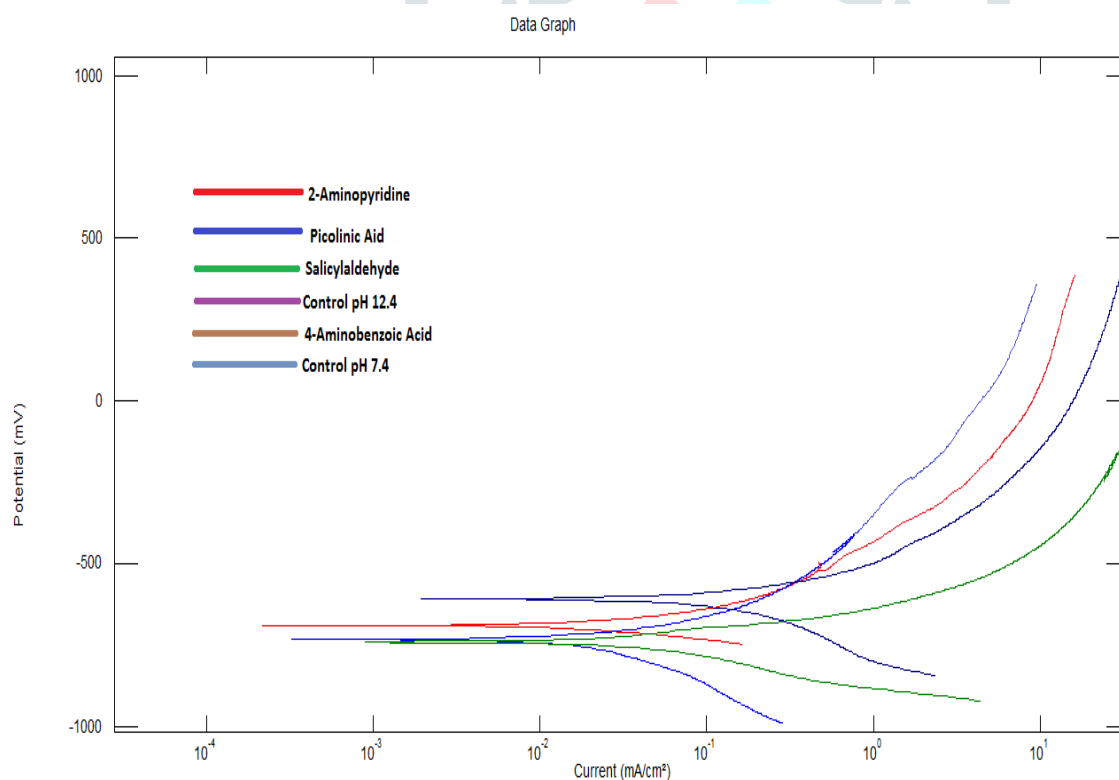

Figure 5.7: Tafel plot for various solutions immersed for 240 hours

Figure 5.8: Steel specimens after measuring Half-cell Potential and Linear Polarization Resistance, immersed in different solutions after 240 hours

From the figure 5.7 and 5.8 above, it is clear that 2-aminopyridine has performed best among all the inhibitors followed by 4-Aminobenzoic acid.

5.5.6 Test results after 480 hours of immersion

After preparing steel specimens and placing them in the respective control and inhibitor solutions for a time of 480 hours, two tests are performed on each specimen i.e. Current and Voltage & LPR sweep, through which following results have been obtained as shown in table 5.8.

Table 5.8: Half-Cell potential and $I_{corr.}$ results after 480 hour of immersion

Sol. No.	Rp (-mV)	$I_{corr.}$ (mA/cm^2)
Sol. 1	769.21	0.032
Sol. 2	739.2	2.030
Sol. 3	595.2	0.085
Sol. 4	400.5	0.179
Sol. 5	577	0.033
Sol. 6	568	0.058

The values of OCP and $I_{corr.}$ are showing variations from the start and after a time of 480 hours, the value of $I_{corr.}$ is very low as acompared to the control sample with pH=7.4, which indicates that all the corrosion inhibitors have performed as expected.

There are some variations in the results among the inhibitors itself, which shows that 2-Aminopyridine has performed best among all the inhibitors followed by salicylaldehyde.
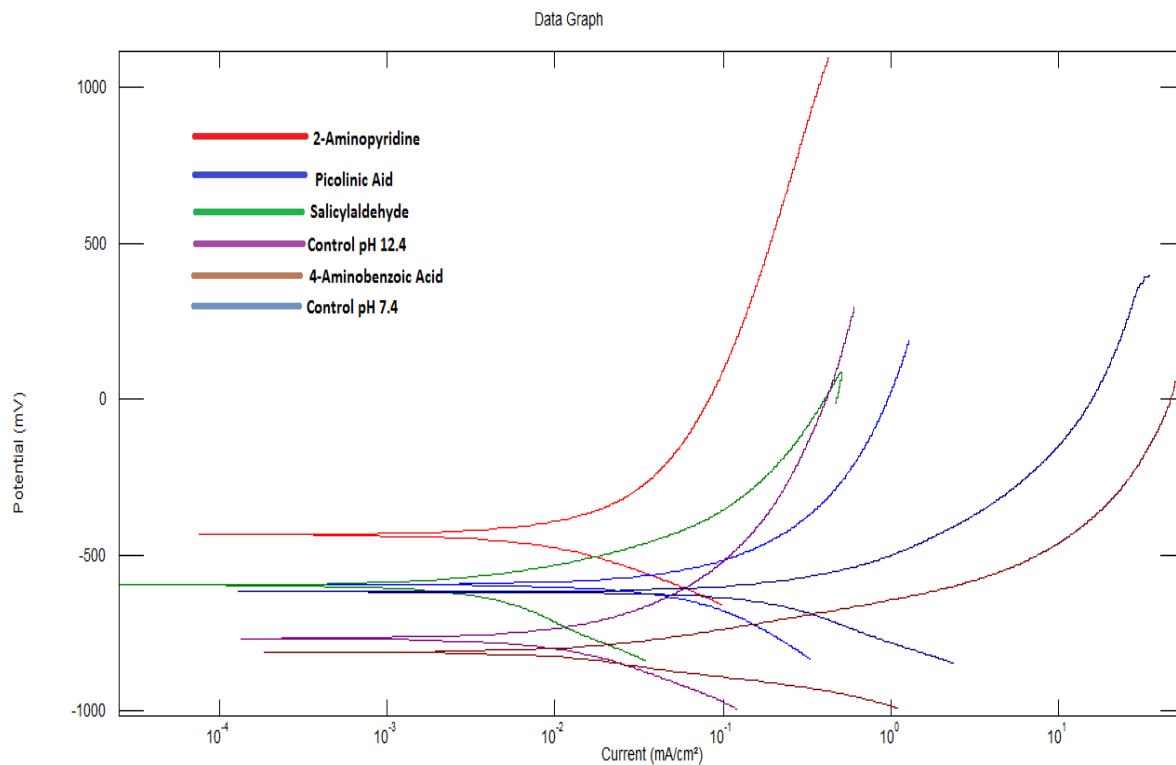

Figure 5.9: Tafel plot for various solutions immersed for 480 hour

Figure 5.10: Steel specimens after measuring Half-cell Potential and Linear Polarization Resistance, immersed in different solutions after 480 hours

From the figure 5.9 and 5.10 above, it can be concluded that each of the inhibitors have showen significant amount of inhibition as compared to the control specimen of pH=7.4. the specimen in Sol. 2 has been corroded very badly, all the steel part that has been exposed has corroded, and rust is falling off from the surface

5.6 Comparison of Corrosion Inhibitors with Control Solutions

The comparison of all the corrosion inhibitors used for the study with respect to the control solutions is described below:

5.6.1 Half cell Potentials Vs Time

The half cell potential readings just indicate the de-passivation of steel and hence the possibility of corrosion. This gives a rough idea of whether the corrosion has started or not. The half cell potential below -250 mV shows that the corrosion has not yet started.
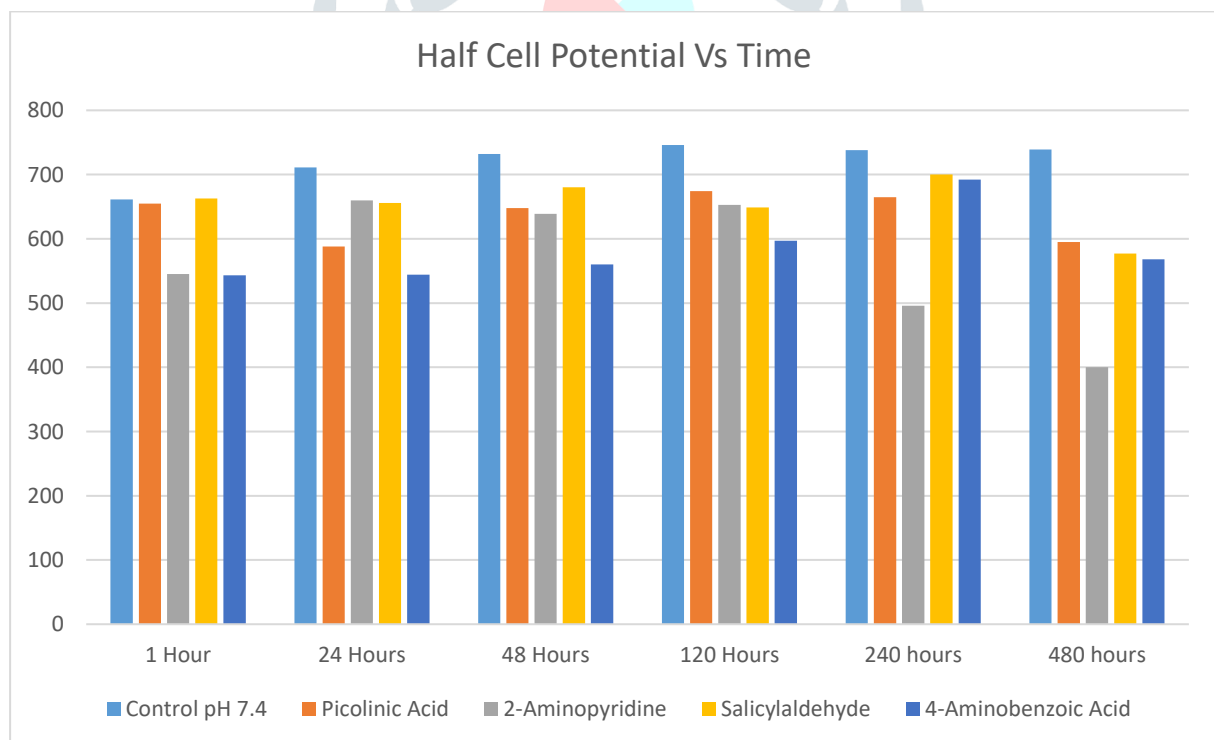

Figure 5.11: Variation of Half-cell potential (-mV) vs Time

The graph of HCP vs immersion time as shown in fig. 5.10 depicts the following:

- The value of half cell potential for Sol. 2 i.e. control solution of pH 7.4 is varying between 650-800mV which proves that the probability of corrosion is above 90% throughout, irrespective of the time variation.

- The half cell potential of 2-Aminopyridine is -400mV after 480 hours, where the probability of corrosion is much lesser. Even before 480 hours i.e. at 240 hours the 2-Aminopyridine shows the least half cell potential amongst all the inhibitors.

- The half cell potential of Picolinic Acid didn't varied much, as it remained around -600mV, which will keep an probability of corrosion

- Half cell potential of 4-Aminobenzoic acid has decreased upto an immersion time of 240 hours but after that it has shown a raise of 125mV.

5.6.2 Linear polarization resistance I_{corr} vs Time

Corrosion initiation described as the process by which chloride ions accumulate around the reinforcing steel, thereby breaking down passivity of the reinforcing steel and allowing corrosion to initiate. Half cell potential is effective only in monitoring the corrosion initiation. Therefore, LPR measurements are necessary as the values obtained from corrosion current density indicate the progression of corrosion in the propagation phase. The LPR readings were taken along with the half cell potential readings of each specimen.

The graph of I_{corr} vs immersion time as shown in fig. 5.11 depicts the following:

- At 48 hours of immersion, Sol. 2 showed max. value of I_{corr} i.e. $2.55mA/cm^2$.

- At earlier stages, 4-Aminobenzoic acid performance was remarkable, but after 120 hours its performance started declining. Hence it can be understood that 4-Aminobenzoic acid provided proper inhibition but only for short term span.

- 2-Aminopyridine may not have performed remarkably upto 48 hours but after that the reduction in the values of I_{corr} was maximum provided by 2-Aminopyridine.

- Picolinic acid and salicylaldehyde had same approach towards I_{corr} i.e. they both reduced the values of I_{corr} but were less effective from 4-Aminobenzoic acid and 2-Aminopyridine.
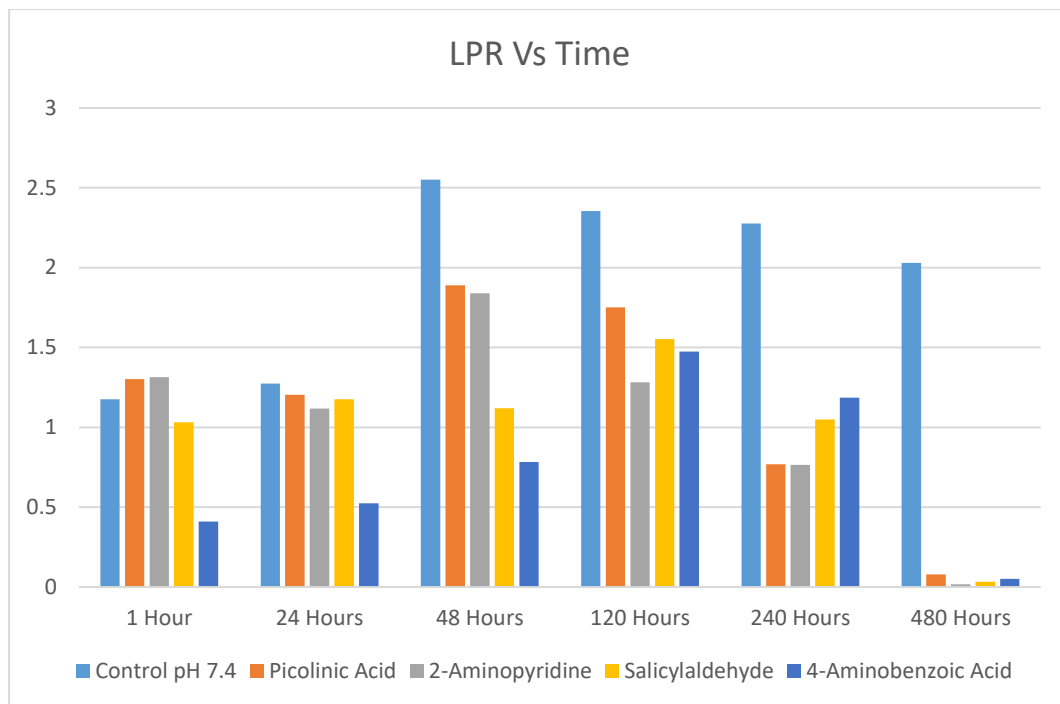
Figure 5.12: Variation of LPR $I_{corr.}$vs Time

CHAPTER 6

CONCLUSIONS

6.1 Conclusions

Based on research work carried out to study the corrosion behaviour of steel in partially completed structures and method to be used for retrofitting of columns using corrosion inhibitors for the project of NH-6 in the Khandesh region, the following conclusions are made:

1. The testing of TMT Fe500 steel bar samples have been carried out in respect of chemical and mechanical properties. From the experiments, it has been observed that both the samples of TMT Fe500 steel bars i.e. new bars and bars obtained from the partially completed structures, shows the results which are under permissible limits as per respective IS codes, however, the strength has been decreased due to corrosion.

2. To study the corrosion behaviour and retrofitting using corrosion inhibitors, Half Cell Potential Measurements and Linear Polarization Resistance (LPR) tests have been conducted using four chemical corrosion inhibitors viz. 2-Amoinopyridine, Picolinic Acid, Salicylaldehyde and 4-Aminobenzoic Acid.

3. 2-Aminopyridine has proven itself a very effective corrosion inhibitor of steel bar when mixed in carbonated calcium hydroxide solution with reduced alkalinity in the presence of NaCl. All the inhibitors have proven themselves in inhibiting the carbonation and chloride induced corrosion. Upto a time of 48 hours, $I_{corr.}$ And half cell potential has shown an increasing trend, but after that inhibitors came into action and the values of $I_{corr.}$ And half cell potential has started declining. 4-Aminobenzoic acid has performed well initially, but after 120 hours 2-Aminopyridine has performed better. After 480 hours the corrosion on control specimen with a pH of 7.4 (Sol. 2) is so absurd that the epoxy layer on the specimen has started to dissolve.

6.2 Future Scope

1. The present study has been conducted for the balance work of NH-6 in Khandesh region. The study can be conducted in various projects which are terminated in partial stage.

2. The study can also be conducted in various corrosion media by differentiating pH values of pore solutions depending upon the nature of environment in respective area.

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