CHAPTER 4

PROTECTIVE COATINGS AND CORROSION INHIBITORS

4.1 INTRODUCTION

Protective anticorrosive coatings to steel reinforcement before it is laid in concrete can guard against corrosion of steel rebars. Four different coating systems are available. They are metallic coatings which give sacrificial protection to steel reinforcement, insulating type of coating, passivating type of coating based on cement and barrier-cum-passivating-type of coating. Metallic coatings include hot dip galvanizing, copper and nickel coatings. Fusion bonded epoxy coating, chlorinated rubber coating, coal tar epoxy coating and asphalt coating are insulating type of coatings. Passivating type of coatings comprise of inhibited and sealed cement slurry and cement polymer anticorrosive coating. The cement polymer composite coating is a barrier-cum-passivating-type of coating. In the present investigation the performance evaluation of the following protective coating systems are studied.

- Inhibited and Sealed Cement Slurry Coating
- Cement Polymer Composite Coating
- Galvanization
- Cement Polymer Anticorrosive Coating
Inhibited cement slurry coating and cement polymer composite coating were developed by Central Electrochemical Research Institute (CECRI), Karaikudi, India. Hot dip galvanized coating were done on rebars as per the Indian Standards and cement polymer anticorrosive coating were developed by the author.

Corrosion inhibitors are effectively used to control corrosion of steel rebars in concrete. Sodium nitrite-based anodic mixed inhibitor was developed in the laboratory. The influence of inhibitor addition on the mechanical and durability properties of fresh and hardened concrete are studied in this chapter.

4.2 DEVELOPMENT OF PROTECTIVE COATING SYSTEMS

4.2.1 Inhibited and Sealed Cement Slurry Coating

(Corrosion Inhibitor-containing Cementitious Slurry Coating)

Steel reinforcements which are embedded in concrete are surrounded by an alkaline medium. So, a coating based on cement is expected to be more suitable. A cement coating of passivating type may have higher tolerance towards the defects. Galvanic effect is likely to be less pronounced because the surrounding concrete is alkaline in nature. In view of economy and efficiency, a coating based on Portland cement slurry admixed with special corrosion inhibitors was developed by Central Electrochemical Research Institute (CECRI), Karaikudi, India. The coating is made impermeable to salts by sealing treatment. Inhibited cement slurry coating was also known as corrosion inhibitor-containing cementitious slurry coating. Figure 4.1 shows the sequence of inhibited and sealed cement slurry coating process and Figure 4.2 shows the inhibited cement slurry coated bars in the water tank construction site.
Figure 4.1 Sequence of inhibited cement slurry coating process
Figure 4.2 Inhibited cement slurry coated bars in the water tank construction site

4.2.2 Cement Polymer Composite Coating
(Polymer-modified Cementitious Slurry Coating)

The base metal, namely, iron contains $\pi$ electrons which gets readily released in any corrosive environment leading to oxidation with the formation of $\text{Fe}_2\text{O}_3$ (rust), the principal deterrent. A surface coating capable of reacting and nullifying the released electron should be provided to prevent this oxidation. Further, prestressing and reinforcing steels exposed to an alkaline environment necessitates the introduction of top coat which should be compatible with the primer and the alkaline environment. To meet these two requirements suitable polymers are combined through the formation of a single phase in the polyblend. A rapid setting primer and cement polymer sealing coats are derived which offer the necessary mechanical and physical properties. This coating system was developed by CECRI, Karaikudi and was also known as polymer-modified cementitious slurry coating. Figure 4.3 shows the sequence of cement polymer composite coating process.
4.2.3 Cement Polymer Anticorrosive Coating

(Corrosion Inhibitor-containing Polymer-modified Cementitious Slurry Coating)

The process leading to corrosion control of steel in concrete goes beyond the minimum if the exposure conditions are particularly harsh and severe. These include both passive and active measures. Passive measures include the specification of high quality concrete produced by incorporation of various types of chemical admixtures and mineral admixtures. On top of that, the addition of corrosion inhibitors is significant. The use of coating the reinforcing bars such as epoxy coating, galvanizing, etc. has also become popular. However, the application of various special means to enhance the corrosion resistance of steel rebars in concrete requires caution. The special means are not to replace the standard requirements but rather

![Figure 4.3 Sequence of cement polymer composite coating process]

- Rusted rebar
  - Rust removal by sand blasting
  - Application of one coat of rapid setting primer
    - Drying time: 30 min
  - Application of one coat of cement polymer sealer coat
    - Drying time: 6 h
  - Treated rebar
    - Coating thickness: 150 ± 25 μm
    - Treatment duration: 8 h
additional to the standard. Thus the special means and standard requirements in the specifications are complementary to one another.

The maintenance of passivity on the steel rebar surface is vital for preventing corrosion. There is a need to evolve effective user friendly corrosion control measures which may be based on preserving passivating film on the steel at all times. This can be achieved by giving a permanent anticorrosive coating on the steel surface. The coating should have sufficient tensile strength, so that it does not develop cracks before yield stress.

Based on these requirements, a simple passivating type anticorrosive polymer solution was developed in the Strength of Materials Laboratory, College of Engineering, Guindy, Anna University, Chennai, India. The anticorrosive solution comprises of sodium nitrite, trace amount of sodium hydroxide and styrene-butadiene based polymer. Sodium nitrite stabilizes the passivating film by converting the ferrous oxide into stable ferric oxide, reduces the free chloride level due to charge similarity and thereby increases the threshold chloride level needed to initiate corrosion. The presence of sodium hydroxide increases the alkalinity of concrete and helps in preserving and stabilizing the passivation layer. Styrene-butadiene polymer impart improved tensile, flexural and waterproofing properties to the film. The corrosion protection mechanism of sodium nitrite and sodium hydroxide is detailed in the development of corrosion inhibitor.

This anticorrosive polymer solution is milky white in colour, pH around 12.50 and density of 1.03 g/cc. This solution is mixed with cement and applied over the rebar as coating. The overall alkalinity of the mix is 13. The cement content gives a barrier layer and offers a fair amount of toughness to the coating. The coating is well bonded to steel because of chemical composition similarity in the coating concrete interface. Even if the concrete cover gets carbonated and thereby the pH is reduced, the passivity of the steel
rebar remains unaffected. The estimated cost for application of this coating works out to about Rs. 2,000/- per M.T. of steel under Indian conditions. This is cheaper compared to other tested coating systems for corrosion protection. Hence this type of coating system is recommended not only in India but also globally. Cement polymer anticorrosive coating was also known as corrosion inhibitor-containing polymer modified cementitious slurry coating. Figure 4.4 shows the sequence of cement polymer anticorrosive coating process.

![Sequence of cement polymer anticorrosive coating process](image)

**Figure 4.4 Sequence of cement polymer anticorrosive coating process**
4.2.4 Galvanization

Zinc is an amphoteric metal which reacts with both strong acid and strong base solutions. The reaction will be more pronounced for pH value below 6 and pH value above 13. At intermediate pH ranges, the rate of attack on zinc is very slow due to the formation of protective surface layers. When embedded in concrete, zinc is passivated for pH values between 8 and 12.5, again due to the formation of a protective surface film of corrosion product which is insoluble below pH 12.5. Zinc reacts with wet cement, and the reaction ceases once the concrete has hardened and the barrier layer of calcium hydroxyzincate has formed.

Hydrated concrete is strongly alkaline with a pH in excess of 12.2 due to the presence of a saturated solution of Ca(OH)$_2$ filling the pore space. Corrosion of steel in concrete is usually caused by either a natural reduction in the pH of concrete through reaction with acidic gases such as carbon dioxide. Corrosion may also occur due to carbonation effect, or due to the presence of chloride ions above certain threshold levels at the depth of the reinforcement. Black steel in concrete typically depassivates below pH 11.5, or higher in the presence of chlorides, leading to the onset of corrosion. Zinc remains passivated at a pH of 9.5 thereby offering substantial protection against the effects of carbonation of the cover concrete. Zinc can also withstand exposure to chloride ion concentrations several times higher than that causes corrosion of black steel. The corrosion protection thus afforded by galvanizing is due to the combined effect of a substantially higher chloride threshold than black steel in concrete, and a complete resistance to the effect of carbonation of the concrete. Figure 4.5 shows the sequence of galvanization process and Figure 4.6 shows the view of various coated bars.
Rusted rebar

Rust removal by immersing the rebar in the derusting solution (HCl + water + inhibitor)
Duration: 15 – 30 min

Acid neutralization by cleaning with water
Duration: 5 min

Immersion in flux solution
(zinc chloride + ammonium chloride)
Duration: 5 min

Immersion in molten zinc(450°C)
Duration: 10 min

Quenching in sodium dichromate solution
Duration: 5 min

Galvanized rebar
Coating thickness: 100+25 μm
Treatment duration: 2 h

Figure 4.5 Sequence of galvanization process

Inhibited cement slurry coating
Cement polymer anticorrosive coating
Cement polymer composite coating
Galvanization

Figure 4.6 View of various coated bars
4.3 PROTECTIVE COATING MATERIALS

Table 4.1 shows the chemical products involved in the preparation of various coating systems with their requirement per metric ton of steel. The chemical products for inhibited cement slurry coating and cement polymer composite coating were procured from the CECRI licensed manufacturer. Hot dip galvanized coating were performed as per Indian Standard from an authorized coating company and cement polymer anticorrosive coating was developed by the author in the laboratory. Table 4.2 shows the general properties of various coating systems (Kumar et al. 1996, Rengaswamy et al. 1988, Thangavel et al. 1995).

Table 4.1 Chemical products involved in the preparation of various coating systems

<table>
<thead>
<tr>
<th>Type of coating</th>
<th>Chemical product</th>
<th>Quantity per M.T.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inhibited cement slurry coating</td>
<td>HCl based derusting solution</td>
<td>50 L</td>
</tr>
<tr>
<td></td>
<td>Manganese phosphating jelly</td>
<td>10 - 15 kg</td>
</tr>
<tr>
<td></td>
<td>Nitrite based inhibitor solution</td>
<td>20 - 25 L</td>
</tr>
<tr>
<td></td>
<td>Silicate based sealing solution</td>
<td>15 - 20 L</td>
</tr>
<tr>
<td></td>
<td>Cleaning powder</td>
<td>1.5 kg</td>
</tr>
<tr>
<td></td>
<td>Ordinary portland cement</td>
<td>50 kg</td>
</tr>
<tr>
<td>Cement polymer composite coating</td>
<td>Acrylic resin based rapid setting primer</td>
<td>10 L</td>
</tr>
<tr>
<td></td>
<td>Acrylic resin - cement based sealer coat</td>
<td>20 kg</td>
</tr>
<tr>
<td>Galvanization</td>
<td>Zinc</td>
<td>60-70 kg</td>
</tr>
<tr>
<td></td>
<td>HCl based derusting solution</td>
<td>50 L</td>
</tr>
<tr>
<td></td>
<td>Zinc chloride and ammonium chloride based flux solution</td>
<td>5 - 10 L</td>
</tr>
<tr>
<td></td>
<td>Sodium dichromate solution</td>
<td>5 - 10 L</td>
</tr>
<tr>
<td>Cement polymer anticroosive coating</td>
<td>Nitrite and styrene butadiene polymer based anticroosive polymer solution</td>
<td>15 - 20 L</td>
</tr>
<tr>
<td></td>
<td>Ordinary portland cement</td>
<td>50 kg</td>
</tr>
</tbody>
</table>
Table 4.2 Properties of coating systems

<table>
<thead>
<tr>
<th>Property</th>
<th>Inhibited cement slurry</th>
<th>Cement polymer composite</th>
<th>Galvanization</th>
<th>Cement polymer anticorrosive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating thickness (μm)</td>
<td>300±50</td>
<td>150±25</td>
<td>100+25</td>
<td>250±50</td>
</tr>
<tr>
<td>Behaviour under tension (direct tension test)</td>
<td>Fracture of coating beyond yield stress level.</td>
<td>No fracture of coating until rebar breaks</td>
<td>No fracture of coating until rebar breaks</td>
<td>Fracture of coating beyond yield stress level.</td>
</tr>
<tr>
<td>Tolerable limit for chlorides (ppm) (anodic polarization technique)</td>
<td>4500</td>
<td>&gt;10000</td>
<td>&gt;6000</td>
<td>5000</td>
</tr>
<tr>
<td>Impact resistance (9 Nm) (falling weight method) ASTM G 14-88</td>
<td>No coating failure around impact area</td>
<td>No coating failure</td>
<td>No coating failure</td>
<td>No coating failure around impact area</td>
</tr>
<tr>
<td>Bond strength to concrete IS 2770 – 1967</td>
<td>Excellent</td>
<td>Sufficient</td>
<td>Sufficient</td>
<td>Sufficient</td>
</tr>
<tr>
<td>Type of protection layer</td>
<td>Passivating</td>
<td>Passivating cum barrier</td>
<td>Barrier cum sacrificial</td>
<td>Passivating</td>
</tr>
<tr>
<td>Exposure to atmosphere (10 km from sea) (months)</td>
<td>3</td>
<td>10</td>
<td>&gt;12</td>
<td>10</td>
</tr>
<tr>
<td>Treatment duration (h )</td>
<td>60</td>
<td>8</td>
<td>2</td>
<td>12</td>
</tr>
</tbody>
</table>
4.4 DEVELOPMENT OF CORROSION INHIBITOR

The formation and stability of the passivating film on the steel rebar surface depend on the pH of the solution surrounding the steel. In the absence of interfering chloride or other ions, the passivating film formed indefinitely prevent the corrosion effectively if the pH is greater than 11.5. However, in practice and in the site conditions such favourable conditions may not exist and depassivation may occur due to change of pH level. The change in the pH may occur due to reaction with atmospheric carbon dioxide and penetration of chloride ions into the pore solution around the steel. Effective passivation could be obtained with conventional steel if the concentration of hydroxide ions in the pore solution of concrete around the rebar is high. The level of hydroxide ion concentration required to maintain passivation is not a constant and it varies with respect to the presence of other ions such as chloride ions.

Stabilization of passive film is referred to as conversion of ferrous oxide into more stable ferric oxide. Passivating film normally developed on the steel is either due to formation of ferrous (Fe$^{2+}$) or ferric oxide (Fe$^{3+}$) in nature. Both are chemically stable in the concrete in the absence of carbonation or chloride. But passivating film in the ferric oxide form is more resistant to chlorides than ferrous oxide films. Since chlorides react with the ferrous oxide to form a soluble complex as shown in equation (4.1) which dissolves in the presence of surrounding solution and thus could not provide protection. Moreover, neither ferrous nor ferric oxide films are protective if the OH$^{-}$ concentration is sufficiently low so that the pH is less than 11.50. At low concentration of OH$^{-}$, the oxides may be formed but do not adhere to the steel. Therefore under this condition it could not protect the steel rebars.

$$Fe(OH)_2 + Cl^- \rightarrow [FeCl]_x$$ (4.1)
The use of inhibitors in concrete is a common phenomenon for preventing corrosion of steel in concrete. The use of corrosion inhibitors in concrete has been attempted by many researchers (Omar et al 2003, Saraswathy and Song 2007). Corrosion inhibitors can either influence the anodic or cathodic reactions, or even both. Since the anodic and cathodic reactions should balance each other, a significant reduction in either or both will result in significant reduction in the corrosion rate. However, an anodic inhibitor is usually more effective than cathodic inhibitor, which enabled us to undertake anodic inhibitor for corrosion control. However, calcium nitrite was the first corrosion inhibitor used commercially on a large scale for reinforced concrete. Although sodium nitrite exhibited harmful effects on concrete strength, it is found to be the most effective corrosion inhibitor. The detrimental effects of sodium nitrite in plastic or hardened properties of concrete such as strength reduction can be compensated by using other additives.

Corrosion inhibitors are admixtures which usually do more than just inhibit corrosion. They may influence initial set, later strength gain or other properties. The effects they produce in the field depend on the site conditions, changes in the time of addition of an admixture or the order of addition of admixtures can give different set times.

Keeping these facts in mind, a simple sodium nitrite based anodic mixed inhibitor was developed in the Strength of Materials Laboratory, College of Engineering, Guindy, Anna University, India. Since the cost of sodium nitrite is cheaper compared to other corrosion inhibitors, it was chosen for the study as corrosion inhibitor. Further it is commercially available. The concentration of sodium nitrite was kept to a maximum of 1% by weight of cement. The anodic corrosion inhibitor mixture contains sodium nitrite, small amount of sodium hydroxide and sodium lignosulphonate. A trace amount
of sodium hydroxide was added to enhance the alkalinity of concrete. It has been reported that addition of sodium nitrite will have an appreciable effect in reducing the strength properties of concrete. Sodium lignosulphonate was added in small quantities to improve the strength properties. The colour of the corrosion inhibitor is dark brown with pH 11.10 and density 1.06 g/cc.

If chloride ions are present in the pores of concrete, they induce corrosion in the reinforcing bar at the location where ferrous oxide has not been converted into ferric oxide and resulted severe pitting corrosion. The process of local pitting corrosion competes with the passivation process, namely, conversion of ferrous oxide to ferric oxide. This will only proceed if the chloride content is high compared to the hydroxide ion content. Whereas sodium hydroxide may improve and maintains the required alkalinity around the rebars and helps in the formation of well established passive film. When nitrite ions are present in the inhibitor, it stabilizes the passivating film by involving in the corrosion reaction so that ferrous ions (Fe$^{2+}$) are further oxidized to produce more stable ferric oxide.

$$\text{Fe}^{2+} + \text{OH}^- + \text{NO}_2^- \rightarrow \text{NO} + \gamma - \text{FeOOH}$$ (4.2)

Chloride and nitrite ions compete at flaws in the passivating film for the same ferrous ions. The relative concentration of chloride and nitrite ions will determine the type of reaction that takes place. When chloride ion concentration is high large ratios of [Cl$^-$]/[NO$_2^-$] and/or [Cl$^-$]/[OH$^-$], the probability of chloride ion forming complex with ferrous ion is increased. This forms the basis for the concept of [Cl$^-$]/[NO$_2^-$] protection ratio, beyond which pitting corrosion is most likely. The ratio is in the range of 1 to 1.5 depending on the chloride content. From the macrocell corrosion studies, it has been found that inhibitor modification in concrete reduces the free chloride level in concrete up to 50%. This may be due to repulsion exists
between chloride and nitrite ions due to charge similarity. Thus, nitrite as an anodic inhibitor raised the threshold level of chloride needed to initiate corrosion.

Sodium nitrite is an anodic inhibitor because it functions at the anode. This quickly oxidized ferrous ions, the first product of corrosion, to ferric ions, which then precipitate in the alkaline pH of concrete. Studies revealed that the presence of nitrite modifies the oxide film on the steel bar to be more protective than the film that naturally forms in concrete.

4.5 MECHANISM OF CORROSION INHIBITION IN THE PRESENCE OF NITRITE

The corrosion activity of steel is strongly reduced by the presence of low concentration of nitrite. This is demonstrated unambiguously from the electrochemical measurements. Further, the amount of nitrite required to promote passivity is in proportion to the concentration of chloride ion present. The plausible pathway causing the corrosion inhibition in the presence of nitrite can be represented by the following chemical reaction (equation 4.3). The nitrite ions compete with chloride ions for ferrous ions produced in concrete and incorporates them into a passive layer, thus preventing further corrosion.

\[
\text{Fe}^{2+} + 2\text{OH}^- + 2\text{NO}_2^- \rightarrow 2\text{NO} + \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \tag{4.3}
\]

In concrete, two other reactions likely to occur are

\[
2 \text{NO}^- + \text{O}_2 \rightarrow 2\text{NO}_2 \tag{4.4}
\]

\[
2 \text{NO}_2 + 2\text{OH}^- \rightarrow \text{NO}_2^- + \text{NO}_3^- + \text{H}_2\text{O} \tag{4.5}
\]
The nitrite ions generated in equation (4.5) thus enabled the stability of ferric ions. Two other reactions of equal interest but do not proceed to any extent are

$$Fe + NO_2^- \rightarrow Fe + NO_2^- \quad (4.6)$$

$$Fe^{3+} + NO_2^- \rightarrow Fe^{3+} + NO_2^- \quad (4.7)$$

Thus the corrosion inhibition mechanism can be traced by considering both thermodynamic and kinetic properties of the system. There is a competition between corrosion and passivation reactions. The corrosion rate depends to a great extent on the pH of the solution. It is well understood that the nitrite ions act as anodic inhibitor by increasing the rate of formation of barrier oxide film. The protective action of the nitrite ions seemed to be more pronounced in highly corroding environment. This is due to the mechanism of inhibition, which uses the product of the unwanted corrosion reaction and converts it into a favourable passivating one.

It observed from earlier research studies that the threshold chloride content is 0.6 to 0.9 kg per cubic meter of concrete which is in the range of 3300 to 5000 ppm. It is evident that sodium nitrite ions are able to reduce the free chloride levels in concrete and thereby increase the threshold chloride level significantly to initiate corrosion process. The additional cost for production of inhibitor admixed concrete is about Rs.40/- per bag of cement under Indian conditions. The developed corrosion inhibitor was made in a liquid form and added at 4% by weight of cement such that it gives a nitrite concentration of 1% by weight of cement.
4.6 INFLUENCE OF INHIBITOR ON FRESH CONCRETE PROPERTIES

The following tests were conducted to study the influence of inhibitor addition on the fresh concrete properties such as setting time and workability.

- Test for initial and final setting time
- Slump test
- Compaction factor test
- Flow test

4.6.1 Initial and Final Setting Time

The setting time of cement was determined as per IS 4031-Part 5-1988. Table 4.3 shows the initial and final setting time values for control and inhibitor admixed cement. It can be observed that there is an increase in initial and final setting time values for inhibitor admixed cement compared to control concrete by 28.6% and 15.4% respectively. The presence of sodium lignosulphonate acts as a set retarder and influences in the increase in setting time values.

Table 4.3 Setting time values for control and inhibitor admixed cement

<table>
<thead>
<tr>
<th>Description</th>
<th>Type of cement</th>
<th>Percentage increase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control</td>
<td>Inhibitor admixed</td>
</tr>
<tr>
<td>Initial setting time (min)</td>
<td>105</td>
<td>135</td>
</tr>
<tr>
<td>Final setting time (min)</td>
<td>390</td>
<td>450</td>
</tr>
</tbody>
</table>
4.6.2 Slump Test

Slump test is the most commonly used method of measuring workability of concrete. The test was carried out as per IS 1199-1959. Table 4.4 shows the observation on slump test. It can be seen that the target slump of 20 – 50 mm was achieved with both the control and inhibitor admixed concrete for a water-cement ratio of 0.52 with a shear slump pattern. There is an increase in initial slump and slump retention values for inhibited admixed concrete due to the presence of sodium lignosulphonate which improved the workability of concrete and act as a retarder.

Table 4.4 Observation on slump test

<table>
<thead>
<tr>
<th>Type of Concrete</th>
<th>Slump (mm)</th>
<th>Slump retention (30 min) (mm)</th>
<th>Percentage slump retention</th>
<th>Slump pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control concrete</td>
<td>26</td>
<td>9</td>
<td>34.62</td>
<td>Shear</td>
</tr>
<tr>
<td>Inhibitor admixed concrete</td>
<td>50</td>
<td>26</td>
<td>52.00</td>
<td></td>
</tr>
</tbody>
</table>

4.6.3 Compaction Factor Test

Compaction factor test is one of the most efficient test for measuring workability. The test was carried out as per IS 1199-1959. Compaction factor refers to the ratio between partially and fully compacted concrete. Figure 4.7 shows the compaction factor test in progress. The compaction factor values for control concrete and inhibitor admixed concrete are 0.877 and 0.876 respectively. The compaction factor values observed for inhibitor admixed concrete are similar when compared with control concrete.
4.6.4 Flow Test

Flow test gives an indication of the quality of concrete with respect to consistency, cohesiveness and the proneness to segregation. This test was carried out as per IS 1199 - 1959. The flow of concrete is the percentage increase in the average diameter of spread from the base diameter of mould. Figure 4.8 shows the flow test set up.

\[
\text{Flow percentage} = \left(\frac{\text{spread diameter in cm} - 25}{25}\right) \times 100
\]

The flow percentage value for control concrete is 130.26. The value for inhibitor admixed concrete is 124.86. It can be concluded that addition of inhibitor appreciably increases the initial setting time, final setting time and slump retention values. Compaction factor and flow test results indicated an insignificant influence on workability properties due to inhibitor addition in concrete.
Concrete specimens were made with mix ratio 1: 2.18 : 2.84, with water-cement ratio of 0.52 and inhibitor was added at 4% by weight of cement. The following tests were conducted to assess the influence of inhibitor addition on the strength properties of cement concrete.

- Compressive strength test
- Flexural strength test
- Splitting tensile strength test

### 4.7.1 Compressive Strength Test

Compressive strength test was conducted as per IS 516 - 1968 to find the effect of inhibitor on the compressive strength behaviour of cement concrete. The size of the specimen is 150 mm cube. After 24 h, the cubes are demoulded and subjected to water curing. Compression testing machine of 2000 kN capacity was used for the test. The maximum load at which specimen failed was recorded.
Compressive strength = \( \frac{P}{A} \)

where \( P \) = Maximum load in Newton

\( A \) = Cross sectional area of specimen in mm\(^2\)

Figure 4.9 shows the comparison of compressive strength for control and inhibitor admixed concrete. It can be seen that there is an increase in compressive strength when the age of concrete was 1, 3 and 7 days for inhibitor admixed concrete. The increase is of the order of 70 – 32% compared to control concrete. But 28 day compressive strength test results showed a different behaviour for both control and inhibitor admixed concrete. It can be concluded that although addition of inhibitor improved the compressive strength at the early ages appreciably, there is a marginal decrease in the 28 day compressive strength as compared to control concrete.

**Figure 4.9** Comparison of compressive strength for control and inhibitor admixed concrete
4.7.2 Flexural Strength Test

This test was carried out as per IS 516 - 1968 to assess the influence of inhibitor addition on the flexural strength of concrete. The size of the beam is 500 × 100 × 100 mm. The test was carried out in the compression testing machine of 2000 kN capacity with additional fixtures to conduct flexure test. Figure 4.10 shows the flexural strength test in progress. The flexural strength of concrete is expressed in terms of modulus of rupture.

When the fracture initiates in the tension surface within the middle third of the span length, the modulus of rupture,

\[ R = \frac{PL}{bd^2} \]

where

- \( R \) - Modulus of rupture in N/mm\(^2\)
- \( P \) - Maximum applied load in Newton
- \( L \) - Span length in mm
- \( B \) - Average width of specimen in mm
- \( d \) - Average depth of specimen in mm

Figure 4.10 Flexural strength test in progress
Table 4.5 shows the flexural Strength test results at 28 days. It can be observed that for control and inhibitor admixed concrete specimens, the failure region was at the middle third span in the tension zone. Addition of inhibitor improves the 28 day flexural strength of concrete appreciably by 17% as compared to control concrete.

Table 4.5  Flexural strength test results at 28 days

<table>
<thead>
<tr>
<th>Description</th>
<th>Type of concrete</th>
<th>Percentage increase</th>
<th>Failure region</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control</td>
<td>Inhibitor admixed</td>
<td></td>
</tr>
<tr>
<td>Applied load (kN)</td>
<td>12</td>
<td>14</td>
<td>16.70</td>
</tr>
<tr>
<td>Flexural strength (N/mm²)</td>
<td>4.8</td>
<td>5.6</td>
<td>Middle third</td>
</tr>
</tbody>
</table>

4.7.3  Splitting Tensile Strength Test

The objective of this test is to assess the influence of inhibitor addition on the tensile strength property of cement concrete. The test was carried out as per IS 5816 - 1999. Cylinder specimens of size 160 mm diameter and 300 mm height were cast with control and inhibitor admixed concrete. Compression testing machine of 2000 kN capacity was used to conduct splitting tensile strength test. Figure 4.11 shows the splitting tensile test in progress. The splitting tensile strength,

\[ f_{ct} = \frac{2P}{\pi ld} \]

where \( f_{ct} \) - Splitting tensile strength in N/mm²
\( P \) - Maximum applied load in Newton
\( l \) - Length of the specimen in mm
\( d \) - Diameter of the specimen in mm
Table 4.6 shows the observation on splitting tensile strength test for cylinder specimens at 28 days. The addition of inhibitor improves the splitting tensile strength of concrete marginally of the order of 8% compared to control concrete. The presence of sodium lignosulphonate improves the workability and makes the concrete denser which results in the improvement of strength properties of inhibitor admixed concrete.

It can be concluded that there is an appreciable increase in flexural strength and splitting tensile strength properties for inhibitor admixed concrete where as the compressive strength reduced marginally.

Table 4.6 Observation on splitting tensile strength test

<table>
<thead>
<tr>
<th>Description</th>
<th>Type of concrete</th>
<th>Percentage increase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control</td>
<td>Inhibitor admixed</td>
</tr>
<tr>
<td>Applied load (kN)</td>
<td>280</td>
<td>302</td>
</tr>
<tr>
<td>Splitting tensile strength (N/mm²)</td>
<td>3.71</td>
<td>4.00</td>
</tr>
</tbody>
</table>
4.8 INFLUENCE OF INHIBITOR ON DURABILITY PROPERTIES

Concrete specimens were made with mix ratio 1: 2.18 : 2.84 and with water-cement ratio 0.52. Inhibitor was added at 4% by weight of cement. To study the influence of inhibitor on durability properties of reinforced concrete, the following tests were conducted.

- Water absorption test
- Chloride ion penetration test
- Test on alkalinity of concrete

4.8.1 Water Absorption Test

The objective of this test is to study the water absorption characteristics of cement concrete due to addition of inhibitor. Concrete cubes of size 100 mm were cast, moist cured for 28 days and subsequently dried in atmosphere for 24 h. Then the specimens were kept in an oven for 24 h at 100°C, cooled to room temperature and weighed. The water absorption characteristics was monitored at different time intervals for a period of 24 h. The change in weight expressed as the percentage of initial dry mass is the water absorption. Figure 4.12 shows the water absorption behaviour of control and inhibitor admixed concrete. It can be seen that there is a significant reduction in water absorption behaviour for inhibitor admixed concrete as compared to control concrete. Figure 4.13 shows the comparison of percentage water absorption for control and inhibitor admixed concrete at the end of test period. It can be seen that inhibitor admixed concrete reduces the water absorption of the order of 14.75% compared to control concrete.
Figure 4.12 Water absorption behaviour of control and inhibitor admixed concrete

Figure 4.13 Comparison of percentage water absorption for control and inhibitor admixed concrete
4.8.2 Chloride Ion Penetration Test

This test analyses the performance of inhibitor admixed concrete in resisting the chloride ion penetration. 100 mm concrete cubes were cast with and without inhibitor addition and cured in water for 28 days. The concrete cubes were applied with water proofing paint on the four vertical sides leaving the top and bottom surfaces free and immersed in 3% NaCl for 7 days. Then the specimens were split open into two vertical halves and sprayed with a solution containing 0.1% sodium fluorescein and 0.1 N silver nitrate. The depth upto which the colour changes to white indicates the chloride ion penetration depth. The remaining greenish area represents the unaffected area.

Figure 4.14 shows the view of chloride ion penetration in concrete with different measurement locations and Figure 4.15 shows the chloride ion penetration depth at different measurement locations. It can be seen that in all the measurement locations there is a reduction in chloride ion penetration for inhibitor admixed concrete as compared to control concrete. Figure 4.16 shows the comparison of chloride ion penetration depth for control and inhibitor admixed concrete. It can be seen that there is an appreciable reduction in chloride ion penetration characteristics for inhibitor admixed concrete of the order of 43% as compared to control concrete. Since nitrite and chloride ion contains highly negatively charged particles, there is repulsion between them which attributed to the reduction in chloride ion penetration depth in case of inhibitor admixed concrete.
Figure 4.14  View of chloride penetration in the concrete with different measurement locations

Figure 4.15  Chloride ion penetration at different locations
4.8.3 Alkalinity of Concrete

The object of this test is to assess the influence of inhibitor addition on the alkalinity of cement concrete. pH test was carried out on control and inhibitor admixed concrete at the age of 28 days. The core samples were collected, crushed to powder form and sieved through a 600 µm sieve. From the powder sample, 5% solution was prepared and the pH of the solution was determined using digital electronic pH meter. Figure 4.17 shows the comparison of pH value for control and inhibitor admixed concrete. It can be seen that the pH values observed for control concrete and the inhibitor admixed concrete are almost the same with a marginal decrease for specimens with inhibitor admixed concrete.

Figure 4.16 Comparison of chloride ion penetration for control and inhibitor admixed concrete
Figure 4.17 Comparison of pH for control and inhibitor admixed concrete

It can be concluded that addition of inhibitor does not have any adverse effect on the alkalinity of concrete. There is a remarkable reduction in chloride ion penetration depth and significant reduction in water absorption for inhibitor admixed concrete as compared to control concrete.

4.9 FOURIER TRANSFORM INFRARED TECHNIQUE AND X-RAY DIFFRACTION TECHNIQUE

Concrete cylinder specimens of 70mm diameter and 115 mm height with centrally embedded rebar were cast with and without inhibitor addition. The specimens were subjected to alternate wetting (3% NaCl) and drying cycle for a period of 360 days. At the end of test period, concrete specimens were broken and samples near the rebar were collected, powdered and sieved through 75 μm sieve. These powder samples were subjected to Fourier Transform Infrared (FT-IR) spectral analysis and X-Ray Diffraction Technique analysis.
Fourier transform infrared (FT-IR) spectra of the materials were recorded with a resolution of 2 cm\(^{-1}\) on a Nicolet (Avatar 360) instrument using the KBr pellet technique. About 15mg of the sample was pressed (under a pressure of 2 tons/cm\(^2\)) into a self-supported wafer of 13 mm diameter. This pellet was used to record the spectra in the region 4000 to 400 cm\(^{-1}\).

Figure 4.18 shows the Fourier Transform Infrared spectra of concrete powder samples with and without addition of inhibitor. The developed inhibitor consists of sodium nitrite, trace amount of sodium hydroxide and small amount of sodium lignosulphonate. Nitrites with the functional group O–N=O shows two strong stretching frequency in the region between 1680 to 1650 cm\(^{-1}\) and 1625 to 1610 cm\(^{-1}\) which corresponds to symmetric and asymmetric vibrations respectively. A strong intense peak at 1650 cm\(^{-1}\) is due to the –N=O stretching vibration in all the inhibitor admixed concrete samples both at the initial and at the end of exposure period. The spectral analysis revealed that there is presence of nitrite in the lattice of concrete composites with uniform distribution.

The powder X-ray diffraction (XRD) patterns of concrete powder samples were recorded in a PANalytical X’pert PRO diffractometer using nickel filtered CuK\(_\alpha\) (0.154 nm) radiation and a liquid nitrogen – cooled germanium solid state detector. The diffractograms were recorded in the 2\(\theta\) range 5\(^o\) to 80\(^o\) in steps of 1.2\(^o\) with a count time of 10 seconds at each point.

Figure 4.19 shows the XRD patterns of concrete powder samples with and without addition of inhibitor. In general XRD patterns confirm the crystallinity of the samples. The sharp and intense peaks revealed the crystalline nature of the sample. It can be seen that there is an increase in intensity values up to three times which may be due to increased crystallinity of the inhibitor admixed concrete.
Figure 4.18 Fourier transform infrared spectra of concrete powder samples with and without addition of inhibitor.

Figure 4.19 XRD patterns of concrete powder samples with and without addition of inhibitor.
The presence of strong intense peak at $2\theta = 26.7^\circ$ indicates the presence of sodium nitrite in the lattice of concrete composition irrespective of exposure period. For control concrete samples, no appreciable changes in the phases of crystalline hydration products such as portlandite, calcite and ettringite irrespective of exposure period. It can be noticed that inhibitor admixed concrete samples also exhibit the same phases of hydrated products as that of control concrete whereas the quantity of the phases were modified due to addition of inhibitor. The FT-IR and XRD results clearly evident that there is a strong presence of nitrite ions in concrete even after exposure to accelerated corrosion conditions. This shows the effectiveness of inhibitor in maintaining the passivity on steel rebar.