Evaluation of corrosion resistance of corrosion inhibitors in concrete structures by Impressed voltage test

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Abstract. There are several commercially marketed corrosion inhibiting admixtures for concrete, presently not tested adequately and lack long term performance results. In this study laboratory studies were conducted on two commercially available Corrosion inhibitors to determine the effectiveness and their corrosion resistance parameters of concrete with OPC and PPC. This study examined the durability parameters in concretes mixed with Anodic Inhibitor (Calcium Nitrite based) and Bipolar Corrosion inhibitor (amino alcohol-based). The Accelerated corrosion testing (Impressed voltage test) was conducted to determine the efficacy of inhibitors. For PPC mixes, the Calcium Nitrite Inhibitor has shown better results in reducing the rate of corrosion of the embedded steel reinforcement. For OPC mixes both the inhibitors have given better results compared to control mix in reducing the corrosion rate of embedded steel.

Keywords: Durability, Chloride induced corrosion, Anodic Inhibitor, Bipolar Corrosion inhibitor, accelerated corrosion testing, Impressed voltage test.

1. Introduction
Numerous options are available and new technologies continue to make an impact in the field of concrete protection. Environmental loading plays an important role in corrosion of reinforced concrete structures induced by the presence of chlorides. Chloride induced corrosion is predominant where the environmental loading exceeds the resistance of the structure against corrosion. For the protection of concrete structures, the environmental loading can be reduced or increased the resistance of the concrete or do a combination of both.

The primary deterioration mechanism in chloride-induced corrosion affects the reinforcement and damages the protective layer around the reinforcement. The physical applications over the concrete surfaces like barrier coatings prevent or delay the entry of chlorides, oxygen, and dampness through the concrete cover to the rebars. Admixtures, sealing compounds, overlays and protective coatings on steel reinforcing bars are being used in practice now. Membrane coatings made with materials such as resins and epoxies etc. like anti-carbonation coatings are used to prevent the ingress of harmful agents into the concrete.

In recent times, the utilization of corrosion inhibitors has become a lucrative solution for preventing or delaying the corrosion associated damage in reinforced concrete structures. There are several commercially marketed corrosion inhibiting admixtures for concrete available at present which have not undergone adequate testing and lack long term performance results to justify their use in important structures expected to serve for a longer period [1].

It has been proven that some admixtures, inhibit corrosion of the reinforcement in the chloride laden environment [2]. Calcium nitrate is one of the widely used corrosion inhibitors for concrete that is believed to be giving promising results [3]. Earlier studies focussed on various corrosion inhibition
admixtures with the primary attention on Potassium chromate, Sodium nitrite, Sodium benzoate and stannous chloride [4]. Corrosion inhibitors based on their action are categorized as anodic inhibitors, catholic inhibitors and Ambidic inhibitors.

Generally, the mechanism of an inhibitor can be explained in is one or more of the below-mentioned processes:

- The inhibitor is chemically adsorbed on the surface of the reinforcement and forms a protective layer with inhibitor effect
- The inhibitor forms a protective oxide layer on of the base metal;
- The inhibitor reacts with the corrosive component present in aqueous media and thereby forming a complex product.

![Figure 1. Mechanism of a conventional corrosion inhibitor](image)

2. Materials and Methods

Two commercially available corrosion inhibitors, Anodic inhibitor (Calcium Nitrite based) and Bipolar Inhibitor mixed (Amino alcohol-based) in concrete made from Portland pozzolana cement (PPC) and Ordinary Portland cement (OPC) are studied in terms of modification of the workability and compressive strength of concrete.

2.1 Materials

M 35 grade concrete using OPC and PPC was used to assess the effect of corrosion inhibitors in terms of corrosion resistance. The properties of each of these materials used in the concrete are tested and used for mix design of concrete. The materials are tested in conformation with the IS code. The materials used for this experimental work are:

- Cement: OPC & PPC
- Sand: Zone II
- Coarse aggregate: HBG 20 mm graded
- Water: Potable water
- Commercially available Anodic (Calcium nitrate based) corrosion inhibiting admixtures (CNIA)
- Commercially available Bipolar corrosion inhibiting admixtures (BIA)

2.1.1. Ordinary Portland Cement (OPC): 53 grade Ordinary Portland Cement conforming to IS 8112 is used in this study.

2.1.2 Portland Pozzolana Cement (PPC): PPC conforming to IS 1489 is used in this study

2.1.3 Anodic Corrosion inhibitors (Calcium Nitrite based): A commercially available corrosion inhibitor which works by anodic action Calcium Nitrite based inhibitor was used in this study. This is a chloride-free aqueous solution of calcium nitrate. Calcium nitrate is a component that chemically reacts to stop the corrosion caused by chlorides. Nitrites (Calcium or sodium salt) comes under anodic inhibitors, as they form ferric oxide film at the anode by attacking the chloride ions [5]. A major study examining the effects of calcium nitrite revealed that calcium nitrite significantly increased the resistance to pitting corrosion which is the quality of an anodic inhibitor [6].

The test parameters of the corrosion inhibitors are given in table 1.
Table 1. Test parameters of the corrosion inhibitors

| Sl. No. | Test Conducted                      | Calcium Nitrite Inhibitor | Bi-Polar Inhibitor |
|---------|-------------------------------------|---------------------------|-------------------|
| 1       | Dry Material content (by % weight)  | 31.78                     | 16.15             |
| 2       | pH                                  | 6.03                      | 8.17              |
| 3       | Ash content (by % weight)           | 15.55                     | 17.59             |
| 4       | Relative density                    | 1.18                      | 1.1               |
| 5       | Chloride (%)                        | Nil                       | Nil               |

2.2 Mix proportions

M35 grade concrete using OPC was used to assess the effect of corrosion inhibitors. Based on the properties of the ingredients, the mix was designed for M35 grade of concrete as per IS 10262:2009 [9]. The concrete specimens were cast to study the modification of the strength and durability parameters of concrete. The various mix proportions used in this study are given in table 2. The Calcium Nitrate Inhibitor is designated as CN and Bi-polar inhibitor is designated as BI.

Table 2. Details of Concrete mix proportions

| Sl. No. | Specimen Combination                  | Cement kg | Coarse Agg 20mm kg | Coarse Agg 12mm kg | Fine Aggregate kg | Water Litre | Inhibitor Litre | Remarks |
|---------|--------------------------------------|-----------|--------------------|--------------------|-------------------|-------------|----------------|---------|
| 1       | M35 Grade Concrete with (OPC)        | 360       | 690                | 460                | 710               | 167         | 0.00           | OPC Control Mix |
| 2       | M35 OPC + CN2%                       | 360       | 690                | 460                | 710               | 159.80      | 7.20           | 2% Inhibitor |
| 3       | M35 OPC + CN5%                       | 360       | 690                | 460                | 710               | 149.00      | 18.00          | 5% Inhibitor |
| 4       | M35 OPC + BI2%                       | 360       | 690                | 460                | 710               | 159.80      | 7.20           | 2% Inhibitor |
| 5       | M35 OPC + BI5%                       | 360       | 690                | 460                | 710               | 149.00      | 18.00          | 5% Inhibitor |
| 6       | M35 Grade Concrete with (PPC)        | 390       | 676                | 482                | 740               | 172         | 0.00           | PPC Control Mix |
| 7       | M35 PPC + CN2%                       | 390       | 676                | 482                | 740               | 164.20      | 7.80           | 2% Inhibitor |
| 8       | M35 PPC + CN5%                       | 390       | 676                | 482                | 740               | 152.50      | 19.50          | 5% Inhibitor |
| 9       | M35 PPC + BI2%                       | 390       | 676                | 482                | 740               | 164.20      | 7.80           | 2% Inhibitor |
| 10      | M35 PPC + BI5%                       | 390       | 676                | 482                | 740               | 152.50      | 19.50          | 5% Inhibitor |

2.3 Workability and Strength tests:

The slump cone test was conducted on all the mixes for determining the workability. Concrete cubes of size 150 × 150 × 150 mm were cast for M35 grade concrete using OPC cement. Both the inhibitors viz the anodic inhibitor (Calcium Nitrite based) and the Bipolar inhibitor in dosages of 2% and 5% by weight of cement are mixed in the concrete mixes and cubes were cast. These dosages are adopted based on the
literature review and the manufacturer’s dosage range. The cubes are cured underwater and are tested for determining the compressive strength at 3 days, 7 days and 28 days. The Testing of specimens for compressive strength was carried out according to IS: 516-1959 [10].

2.4 Accelerated Corrosion Testing (Impressed Voltage Test (ASTM-C876)).
Impressed voltage technique is used for accelerating the corrosion process of reinforcing steel in the laboratory. The impressed current technique is in vogue for laboratory studies for monitoring the effect of reinforcement corrosion on the deterioration of concrete.

2.4.1 Apparatus and procedure for Impressed Voltage Test (ASTM-C876) [11]: The Impressed voltage test is based on the principle of electrochemical polarization. To evaluate the corrosion resistance under accelerated test conditions, concrete cylinders of size 75 mm diameter and 150 mm length with a steel reinforcement bar of 16mm diameter is embedded centrally into it (refer schematic in figure 2). After curing, the dried cylinder specimens are immersed in a 3% Na Cl solution. The steel bar projecting out of the cylinder at the top is connected to the positive terminal of the power pack (anode) and the stainless steel plate is connected to the negative terminal (cathode). A constant voltage of 6 volts from the D.C power pack is supplied to the circuit. The applied voltage is maintained at a constant value and the variation of the current to time is monitored.

![Figure 2. Schematic of Impressed voltage technique](image)

![Figure 3. Experimental set up for impressed voltage test](image)

3. Results and Discussion
The results of workability, compressive strength and accelerated corrosion test are presented in subsequent sections

3.1 Strength Parameters:
There is no improvement in workability by the addition of corrosion inhibitors in concrete. A decrease in workability is observed by the addition of both Calcium Nitrite inhibitor and Bipolar inhibitor compared to control mix concrete. The results of the compressive strength are shown in figure 4. A rheological study is required to find out reasons for the decrease in workability.

For OPC mixes, by addition of 2% Calcium Nitrite inhibitor, there is an increase in compressive strength by 10% at 28 days. However, by addition of 2% Bipolar inhibitor, there is a very marginal increase in compressive strength by 2.5% at 28 days. Addition of Bipolar inhibitor at a dosage of 5% resulted in the reduction of compressive strength by about 33% to 36%. The reduction in compressive strength may be due to the hydrophobic nature of inhibitors which forms microbubbles making slightly porous and reducing the strength. For PPC Mixes by addition of 2% Calcium Nitrite inhibitor, there is a marginal increase in compressive strength by 3.4% at 28 days. Addition of Bipolar inhibitor at a dosage of 5% resulted in the reduction of compressive strength by about 3.5% at 28 days.
Figure 4: Graph showing the Compressive strengths of various mixes

3.2 Accelerated corrosion testing results

The corrosion of reinforcing steel was accelerated using the impressed voltage technique. The concrete cylinders of control mix and with admixed inhibitors were cast steel bar of 16mm diameter embedded centrally into it. The specimens were cured for 28 days and are dried for 24 hours before carrying out the impressed voltage test. The tested specimens showing the corrosion stains are shown in figure 5.

3.2.1 Impressed voltage test results for PPC mixes

Observations from figure 6:
- The results indicate that the maximum anodic currents are recorded to be 52, 35 and 50 mA for Control mix, 2% CN inhibitor and 2% BI inhibitor respectively (refer figure 6).
- 2% of CN has shown reduced anodic current measurements. Hence the time taken for the initial crack was prolonged.
- It was observed that the time for initiation of crack was found to be 132, 204 and 180 hours for Control mix, 2% CN inhibitor and 2% BI inhibitor respectively.
3.2.2 **Impressed voltage test results for OPC mixes**

**Observations from figure 7:**

- The results indicate that the maximum anodic currents are recorded to be 45, 40 and 40 mA for Control mix, 2% CN inhibitor and 2% BI inhibitor respectively (refer figure 7).
- 2% CN and 2% BI have shown reduced anodic current measurements. Hence the time taken for the initial crack was prolonged.
- It was observed that the time for initiation of crack was found to be 132, 204 and 180 hours for Control mix, 2% CN inhibitor and 2% BI inhibitor respectively.
4. Conclusions
1. There is no improvement in the workability of OPC concrete mixes or PPC concrete mixes by addition of both the Corrosion inhibitors. Lower dosage of Corrosion inhibitors i.e., @ 2% yielded better workability compared to higher dosages. The dosages recommended by the manufacturers also matches with the above result.
2. There is a very marginal increase in compressive strength by addition of both the inhibitors at 2% dosage, whereas there is a decrease in compressive strength by addition of inhibitors at 5% dosage.
3. From the Impressed voltage test results, the maximum anodic current measured was found to be 35 and 40 mA for the Calcium Nitrite Inhibitor. On the other hand, Bipolar inhibitor has shown the maximum anodic current as 45 and 40 mA.
4. For PPC mixes, the Calcium Nitrite Inhibitor has shown better results in reducing the effect of corrosion. For OPC mixes both the inhibitors exhibited better performance compared to control mix.

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