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**Original Research Paper**

# Protection of Rebar Concrete by Means of Inhibitor Admixture

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## ABSTRACT

This paper deals with the effectiveness of nitrite based and amine based inhibitors in protecting steel rebar against corrosion due to aggressive environment. The suitability of the inhibitor was evaluated by carrying out flexural tests. Inhibitors were admixed during casting and the concentration of inhibitor was varied from 3% to 5%. The corrosion of reinforcement is accelerated by chemical and electrochemical techniques. Amine based inhibitor delays the onset of corrosion. Further, EIS studies were performed to study the effectiveness of amine based inhibitor.

## INTRODUCTION

Concrete, as a material of construction, even for structures situated in the severe environment of the ocean, has been expected for long time serviceability. Steel is an essential part of reinforced and prestressed concrete and the corrosion of steel is identified as the single largest factor responsible for its deterioration. The alkalinity of concrete, which protects the steel, may be affected either by carbonation of the concrete or by ingress of chloride ions. These may arise from sea salts or environmental corrosives. Work on rebar corrosion problem in concrete goes back to more than 75 years. The severity of the problem in the past few decades has prompted considerable acceleration of research. One of the major factors contributing to this deterioration process is the environmental and climatic condition to which a concrete structure is exposed. Investigations revealed that the most influential cause of rapid deterioration of marine concrete structure is high salinity and high oxygen content. Chloride ions and dissolved oxygen penetrate through the cement and attack the embedded steel when concrete permeability is increased due to biodeterioration. Boring organisms and sponges are found to be main cause of biodeterioration (Jadkowski & Wiltsie 1985).

When the severity of environment is compounded with poor quality concrete and/or defective design and construction practices, the process of deterioration becomes interactive, cumulative and very rapid, and a cancerous growth that cannot be easily stopped. Corrosion of reinforcing steel probably is the most widespread damage mechanism to which reinforced concrete structures are subjected, demanding significant amounts for repair and rehabilitation (Batis & Pantazopoulou 2003). Due to carbonation and chloride penetration the passive layer around the reinforcing steel is destroyed, leaving the steel bar unprotected to the effect of corrosion.

Several solutions of this problem have been proposed and tested, yet to date no ideal solution has been found. Some of these methods involve increasing the concrete cover over the rebar, reducing w/c ratio, using denser concrete, using latex or polymer modified concrete overlays adding waterproofing membrane with asphalt, overlay, coating the rebar with epoxy or zinc and cathodic protection. In last few decades, new admixture types have been developed in order to reduce the risk of steel corrosion in reinforced concrete. Many substances have been evaluated as inhibitors against the corrosion of reinforcing steel rebars (Griffin 1975, Treadaway 1966, Slater 1983, Berke 1991, Treadaway & Russel 1968, Rosenberg et al. 1977, Hope 1989). Some corrosion inhibitors can be mixed within the fresh concrete, while other types of corrosion inhibitors can be applied on the surface of existing concrete structures. The advantage of using corrosion inhibiting admixtures are:

1. The admixture is uniformly distributed throughout the concrete; therefore all of the steel in the structure is equally protected.
2. The use of the admixture does not need skill development; it only requires addition of critical amount of admixture.
3. Construction quality control generally is not a concern with admixture as it is with other method (i.e., damaging of epoxy coatings, difficulty of working with low w/c ratio or low slump concrete mixes).
4. There is no maintenance required with an inhibiting admixture system.

The objective of the present investigation is to design a suitable novel corrosion inhibiting admixture system to increase the corrosion resistance of steel embedded in concrete. In this study three types of inhibitors such as dicyclo hexyl ammonium nitrite, sodium nitrite and condensation product of octylamine and formaldehyde were evaluated in reinforced concrete specimens under accelerated and free corrosion conditions in laboratory by carrying out flexural test.

## MATERIALS AND METHODS

**Specimen details:** Reinforced concrete beam specimens of 500mm length, 100mm width and 100mm depth were cast. $M_{20}$ grade concrete was designed using OPC-43 grade cement, river sand 20mm aggregates and potable water. One mild steel reinforcement rod of 8mm dia was placed concentrically at the tensile zone and a clear cover of 20mm was maintained as shown in Fig. 1. In all cases, reinforcing steel bars were cleaned using pickling solution. These bars were weighed accurately. The ingredients of concrete used for casting were mixed thoroughly by hand. The inhibitor as per Table 1 was admixed during casting. The specimens were cast properly by vibrating the concrete on vibration table. After 24 hours the specimens were demoulded and left in potable water for curing.

In this study, three systems were evaluated. In system-1 the specimens were cured in potable water for 28 days. In system-2 specimens were cured in potable water for 7 days and then cured in 3.5% sodium chloride solution for 21 days. This is to chemically accelerate the corrosion of reinforcement. In system-3 the embedded steel reinforcement was subjected to accelerated corrosion by external applied anodic current of 500mA. The idea was to electrochemically accelerate the corrosion of reinforcement. In system-3, the specimen were initially cured in potable water for 7 days and subjected to accelerated corrosion for 21 days. Control specimens were cast without any inhibitors. The inhibitor admixed specimens were cast by varying the concentration of inhibitor from 3% to 5%. Triplicate beam specimens were prepared for all the systems. After evaluation of the specimens, flexural test was conducted. The maximum load carrying capacity was determined and tabulated in Tables 2, 3 and 4.

**Flexural testing:** The specimens were tested in universal testing machine. Central point load was applied. Maximum failure load, deflection were noted using a deflectometer of least count of 0.01mm.

**Inhibitors in solution:** The screening of inhibitors based on the film forming property at the steel surface was evaluated with amine based inhibitors to obtain its critical concentration level. Four organic amine based commercial inhibitors were evaluated in saturated calcium hydroxide and 3.5% sodium chloride solution. With these solutions the inhibitors were added at different proportions. EIS measurements were performed using three electrode system. The steel specimen of area 1 $cm^2$, polished with different emery paper up to 1200 grade washed with distilled water, degreased and dried with acetone was used as working electrode. A platinum electrode and a saturated calomel electrode (SCE) were used as counter and reference electrodes respectively. The pH values were recorded for all the concentrations of inhibitors added to saturated $Ca(OH)_2$ solution and 3.5% NaCl solution. Figs. 5, 6, 7 and 8 show the Nyquist plot for inhibitor added solution. The critical concentration of all the inhibitors was noted based on $R_{CT}$ values.

## RESULTS AND DISCUSSION

Table 2 shows the behaviour of sodium nitrite admixed specimens. Higher flexural strength was observed when sodium nitrite was admixed in the concrete. At higher dosage lesser strength was observed. In case of the anodically polarized specimens the flexural strength increased with respect to dosage. Lesser flexural strength was observed in specimens cured in 3.5% NaCl solution when compared with control specimens.

The performance of dicyclo hexyl ammonium nitrite admixed concrete specimens is given in Table 3. The flexural capacity of the concrete admixed with dicyclo hexyl ammonium nitrite increased when the dosage increase. The same trend was observed when the embedded steel anodically polarized for 21 days by applied voltage method. In case of the specimens immersed in 3.5% NaCl solution reduction in flexural behaviour was found when the dosage increases.

Table 4 shows the behaviour of amine based product admixed in concrete specimens. The flexural

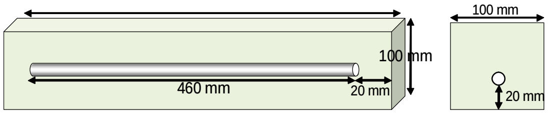

Fig.1: Schematic representation of specimen.

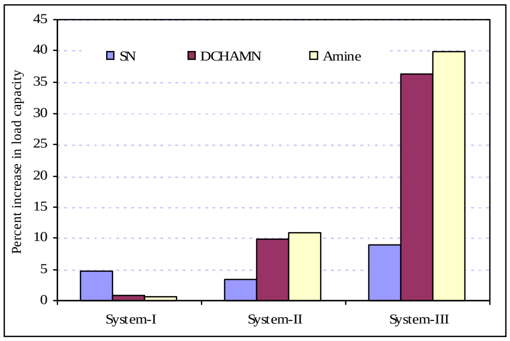

Fig. 2: Comparison of incremental load bearing capacity at 3% inhibitor concentration.

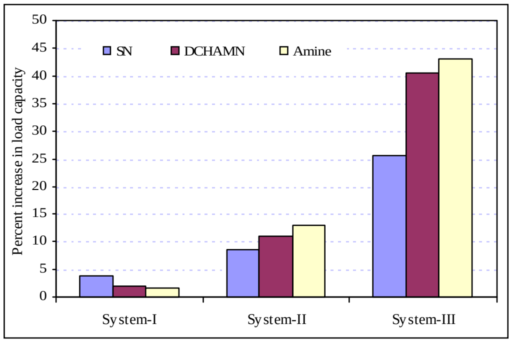

Fig. 3: Comparison of incremental load bearing capacity at 4% concentration of inhibitor.

Table 1: Concentration of inhibitors of corrosion.

| Sl. No. | Type | Dosage<br>1 | <br>2 | <br>3 |
|---|---|---|---|---|
| 1 | Dicyclo hexyl ammonium nitrite | 3% | 4% | 5% |
| 2. | Sodium nitrite | 3% | 4% | 5% |
| 3. | Amine based product | 3% | 4% | 5% |

Table 2: Flexural load capacity of sodium nitrite (SN) admixed concrete.

| Sl. No. | Inhibitor Concentration | System I<br>Maximum Load (KN) | <br>% increase in Load | System II<br>Maximum Load (KN) | <br>% increase in Load | System III<br>Maximum Load (KN) | <br>% increase in Load |
|---|---|---|---|---|---|---|---|
| 1. | 0% | 18.90±0.9 | - | 16.15±0.25 | - | 12.55±0.95 | - |
| 2. | 3% | 19.80±0.3 | 4.76 | 16.70±0.20 | 3.41 | 14.15±0.35 | 8.98 |
| 3. | 4% | 19.61±0.2 | 3.76 | 17.54±0.11 | 8.61 | 15.75±0.25 | 25.50 |
| 4. | 5% | 19.30±0.3 | 2.11 | 18.25±0.25 | 13.0 | 17.30±0.20 | 37.85 |

Table 3: Flexural load capacity of dicyclo hexyl ammonium nitrite (DCHAMN) admixed concrete.

| Sl. No. | Inhibitor Concentration | System I<br>Maximum Load (KN) | <br>% increase in Load | System II<br>Maximum Load (KN) | <br>% increase in Load | System III<br>Maximum Load (KN) | <br>% increase in Load |
|---|---|---|---|---|---|---|---|
| 1. | 0% | 18.90±0.90 | - | 16.15±0.35 | - | 12.55±0.95 | - |
| 2. | 3% | 19.05±0.50 | 0.80 | 17.75±0.25 | 9.91 | 17.10±0.15 | 36.25 |
| 3. | 4% | 19.30±2.11 | 2.11 | 17.93±0.17 | 11.02 | 17.65±0.13 | 40.64 |
| 4. | 5% | 19.70±0.40 | 4.23 | 17.65±0.35 | 9.29 | 17.68±0.15 | 40.88 |

Table 4: Flexural load capacity of amine based inhibitor admixed concrete.

| Sl. No. | Inhibitor Concentration | System I<br>Maximum Load (KN) | <br>% increase in Load | System II<br>Maximum Load (KN) | <br>% increase in Load | System III<br>Maximum Load (KN) | <br>% increase in Load |
|---|---|---|---|---|---|---|---|
| 1. | 0% | 18.90±0.9 | - | 16.15±0.25 | - | 12.55±0.95 | - |
| 2. | 3% | 19.00±0.6 | 0.53 | 17.90±0.20 | 10.84 | 17.55±0.17 | 39.84 |
| 3. | 4% | 19.20±0.7 | 1.59 | 18.25±0.25 | 13.00 | 17.95±0.25 | 43.03 |
| 4. | 5% | 19.36±0.7 | 3.42 | 18.37±0.27 | 13.75 | 18.10±0.15 | 44.22 |

Table 5: Comparison of load bearing capacity.

| Sl. No. | Inhibitor Concentration | System I<br>SN | <br>DCHAMN | <br>Amine | System II<br>SN | <br>DCHAMN | <br>Amine | System III<br>SN | <br>DCHAMN | <br>Amine |
|---|---|---|---|---|---|---|---|---|---|---|
| 01. | 3% | 4.76 | 0.80 | 0.53 | 3.41 | 9.91 | 10.84 | 8.98 | 36.25 | 39.84 |
| 02. | 4% | 3.76 | 2.11 | 1.59 | 8.61 | 11.02 | 13.00 | 25.50 | 40.64 | 43.03 |
| 03. | 5% | 2.11 | 4.23 | 2.43 | 13.0 | 9.29 | 13.75 | 37.85 | 40.88 | 44.22 |

strength was increased when the dosage increased in control specimens. The same trend was observed in accelerated corrosion evaluation and the specimens cured in 3.5% NaCl solution.

Table 5 gives the comparison of load bearing capacity of all the three inhibitors in systems I, II

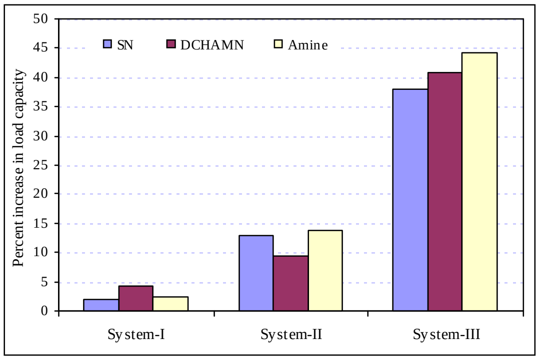

Fig. 4: Comparison of incremental load bearing capacity at 5% inhibitor concentration.

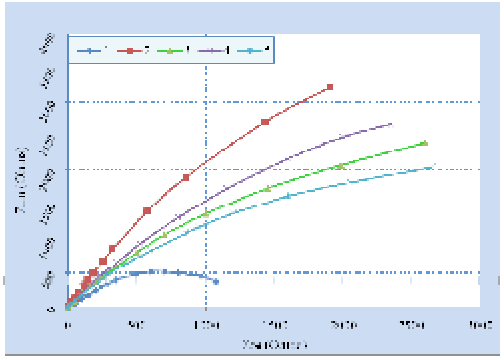

Fig. 5: Nyquist plot showing the effect of monoethanolamine in saturated $Ca(OH)_2$ with 3.5% NaCl solution. 1. Control, 2. Control+1% inhibitor, 3. Control+3% inhibitor, 4. Control+5% inhibitor, 5. Control+10% inhibitor

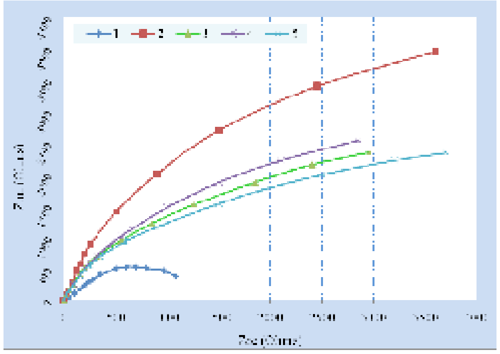

Fig. 6: Nyquist plot showing the effect of diethanolamine in saturated $Ca(OH)_2$ with 3.5% NaCl solution. 1. Control, 2. Control+1% inhibitor, 3. Control+3% inhibitor, 4. Control+5% inhibitor, 5. Control+10% inhibitor

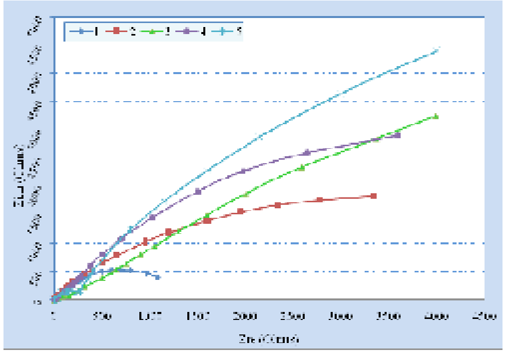

Fig. 7: Nyquist plot showing the effect of triethanolamine in saturated $Ca(OH)_2$ with 3.5% NaCl solution. 1. Control, 2. Control+1% inhibitor, 3. Control+3% inhibitor, 4. Control+5% inhibitor, 5. Control+10% inhibitor

and III. It is evident that at 5% concentration, the amine based inhibitor in system III almost restores its original load capacity.

Figs. 2, 3 and 4 show the incremental load bearing capacity of inhibitors at 3%, 4% and 5% concentration. It was observed that in system III, the amine based inhibitor at all the concentrations exhibits higher incremental load capacity compared to nitrite inhibitors.

From the Nyquist plot (Figs. 5, 6, 7, 8), it was observed that the different concentrations of inhibitor such as 1%, 3%, 5% and 10% were added in the aqueous solution of saturated calcium hydroxide with 3.5% sodium chloride media. The study shows 1% monoethanolamine, 1% diethanolamine, 3% triethanolamine and 5% melamine have higher charge transfer resistance in which corrosion protection efficiency can be obtained. The higher $R_{CT}$ value infers the lower corrosion rate under chloride contaminated environment.

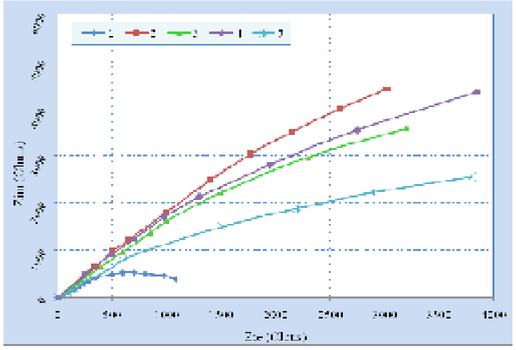

Fig. 8: Nyquist plot showing the effect of melamine in saturated $Ca(OH)_2$ with 3.5% NaCl solution. 1. Control, 2. Control+1% inhibitor, 3. Control+3% inhibitor, 4. Control+5% inhibitor, 5. Control+10% inhibitor

## CONCLUSION

In order of efficiency based on percentage increase in load bearing capacity; amine based inhibitor > dicyclo hexyl ammonium nitrite > sodium nitrite. It is evident from the flexural test results, that increased percentage of sodium nitrite has reduced corrosion effect and better load bearing capacity. In case of DCHAMN and amine type inhibitor, optimum concentration is 4% beyond which there is no appreciable effect. Amine based inhibitor performs better in all the systems. At 5% concentration, the amine based inhibitor almost restores the original load bearing capacity of un-corroded concrete. Obviously, amine based inhibitors are most efficient than the other two inhibitors.

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