INFLUENCE OF CHEMICAL ADMIXTURES ON THE CORROSION OF REBARS IN CRACKED CONCRETE

Bhaskar Sangoju (1), Ravindra Gettu (2) and B. H. Bharatkumar (1)

(1) CSIR-Structural Engineering Research Centre, Chennai, INDIA
(2) Indian Institute of Technology Madras, Chennai, INDIA

Abstract

The paper discusses the results of limited laboratory studies on accelerated chloride-induced corrosion of reinforcement bars in concretes with selected chemical admixtures (polycarboxylic ether superplasticizer, PCE SP, and calcium nitrite inhibitor, CNI), as well as reference concrete. The effect of the crack and the crack width on corrosion is studied using U-shaped specimens with surface crack widths of 0.2 and 0.4 mm. The specimens were cast with a deformed bar of 12 mm diameter and 20 mm clear cover. They were subjected to 10V constant voltage for a specified duration while submerged in 3.5% NaCl solution. In the cracked specimens, rust stains were observed at the cracks followed by longitudinal cracking. In the case of uncracked specimens, rust stains were observed along the rebar followed by corrosion-induced cracking along the rebar. Visual observations indicated microcell corrosion in the uncracked specimens and macrocell corrosion in the pre-cracked specimens. After the longitudinal cracking, uniform corrosion was observed in both the uncracked and pre-cracked specimens because the corrosion cracks joined leading to a single longitudinal macrocrack along the reinforcement bar. The gravimetric weight loss in the rebars were determined; the results showed lower weight loss in the concrete with the PCE SP than that of the reference concrete whereas the rebar weight loss in the concrete with the CNI is higher.

Keywords: Concrete, durability, corrosion of reinforcement, PCE superplasticizer, calcium nitrite inhibitor

1. INTRODUCTION

The main limitation of concrete, even of good quality, is the presence of pores through which chlorides, CO₂, moisture, etc., can penetrate and attack the reinforced concrete (RC) structure. In addition to its chemical composition, the durability of concrete is mainly related
to its transport properties, which depend on the concrete penetrability and cracking, where penetrability is a function of the interconnectivity of pores and the pore size distribution. Experience shows that RC structures do not always have adequate resistance to aggressive environments and that corrosion of reinforcement is one of the main causes of deterioration. Though the steel embedded in concrete is normally protected against corrosion by the alkalinity of the pore water in the concrete, the ingress of aggressive agents, such as chlorides, CO₂, etc., through the cover causes a loss in the passivity, which results in corrosion [1]. Furthermore, RC structures under service generally develop cracks, which provide easier access for the aggressive agents [2].

Researchers like Beeby [3] observed that crack width does not play an important role for significant corrosion to occur in long term though chlorides penetrate rapidly through cracks [4]. Other findings showed that steel at crack intersections depassivate earlier than that in uncracked areas and that corrosion rates increase with an increase in crack width [5-6]. Most codes of practice specify maximum permissible crack widths from the durability point of view, which do not normally exceed 0.3 mm [7, 8]. It should be noted that ACI 224 [9] and ACI 318 [10] limit crack widths to 0.4 mm, and state that corrosion is not clearly correlated with surface crack widths and, therefore, concrete quality, adequate compaction, and ample concrete cover may be of greater importance for corrosion protection than the surface crack width.

Chemical admixtures such as superplasticizers and corrosion inhibitors [11] have been commonly used in RC construction for improving the durability of concrete structures. Researchers, like Dhir et al. [12], Swamy [13] and Roy and Northwood [14], have shown that the incorporation of superplasticizers reduces the porosity and penetrability, and refines the pore structure, thereby reducing the ingress of aggressive chemicals. It has been reported that polycarboxylic ether superplasticizers (PCE SP) provide better durability properties [15] than other products. Berke and Rosenberg [16] carried out pioneering research on corrosion inhibitors and stated that the calcium nitrite inhibitor (CNI) performs well for crack widths up to 0.25 mm. However, some research indicated detrimental effects of CNI on the properties of concrete as well as in preventing corrosion of rebars. Nmai and McDonald [17] found that CNI seems to be ineffective at reducing corrosion unless a large dosage is used. Though, considerable research has been carried out describing the influence of cracking on rebar corrosion in concrete with chemical admixtures, some aspects regarding the effect of the type of chemical used and the width of the pre-crack need detailed study.

Experimental studies on the chloride induced corrosion of steel in cracked OPC and PPC concretes have already been reported by the authors elsewhere [18]. These studies are extended here to evaluate the effect of cracking in concretes having PCE SP and CNI, and their corrosion resistance.

2. EXPERIMENTAL PROGRAM

2.1 Materials used

Ordinary portland cement (OPC), potable water, polycarboxylic ether superplasticizer (PCE SP) and calcium nitrite inhibitor (CNI) were used in the tests. River sand and graded crushed granite fractions with maximum sizes of 20 mm and 12 mm, in the ratio of 1.5:1,
were used as aggregates. Thermomechanically treated (TMT) bars of Fe 415 grade and 12 mm diameter were used as reinforcement.

ACI 211 and IS 456 [8, 19] guidelines were followed in the mix design of the concrete used; the composition is given in Table 1. A CNI dosage of 10 L/m³ (3.5 % by weight of cement) was used, which is in the range of 5 to 30 L/m³ indicated by the manufacturer. The water content of CNI (i.e., 65% by weight), was taken into account in the water added to the mix. A slump of 25 - 50 mm for the control concrete and concrete with CNI; and of 125 - 150 mm for the concrete with PCE SP were obtained. Standard specimens such as 150 mm cubes for compressive strength, cylinders of 150 mm diameter and 300 mm height for split tension and prisms of 100×100×500 mm for flexural strength tests were cast. 100×200 mm cylinders were also cast for the rapid chloride ion penetration test (RCPT) as per ASTM C 1202.

<table>
<thead>
<tr>
<th>w/c</th>
<th>Cement (kg)</th>
<th>Sand (kg)</th>
<th>Coarse Aggregate (kg)</th>
<th>Water (kg)</th>
<th>PCE SP (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.57</td>
<td>299</td>
<td>870</td>
<td>1056</td>
<td>170</td>
<td>0.90 (0.3%)</td>
</tr>
</tbody>
</table>

Different methodologies have been adopted for initiating cracks in specimens used for corrosion studies. In the present study, a U-shaped specimen is used for initiating flexural cracks of a required width [18]. After curing in water for 28 days, the specimens were air dried for 30 days. The tie rods of the specimens were stressed to produce cracks on the bottom, some of which were observed to reach the level of the reinforcement bars in all the specimens. Pre-crack widths of 0.2 and 0.4 mm (i.e., below and above, respectively, of the value of 0.3 mm specified by IS 456 and BS 8110) were considered.

2.2 **Accelerated corrosion test**

The corrosion process was accelerated by impressing an anodic potential between the rebar anode and steel plate cathode, and recording the variation of current with time [7]. Initially, the specimens were immersed in a 3.5% NaCl solution. After 24 hours, an impressed voltage of 10V was applied; the high voltage is used to accelerate the corrosion process and shorten the test period [20]. Fig. 1 shows a photograph of the accelerated corrosion test setup.

![Accelerated corrosion test setup](image)

3. **DISCUSSION OF TEST RESULTS**
3.1 Standard tests
The 28-day compressive, split tensile flexural and RCPT results are presented in Table 2. In each case, three specimens were tested and the average values were reported. It can be seen that the compressive, split tensile, flexural and RCPT results of control concrete and the concrete with PCE SP are nearly the same. There is a marginal reduction in strength with the CNI, which is in accordance with previous work [21], where change of pore ratios and diameters were observed due to the CNI. It should also be noted that others have reported that compressive strength increased with the incorporation of the CNI [22, 23]. The RCPT value of the concrete with CNI is about 1.6 times that of the control concrete, which can be attributed to the highly ionic nature of the CNI that leads to more charge passing through the concrete [24, 25].

Table 2 Parameters obtained for the different concretes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Control concrete</th>
<th>Concrete with PCE SP</th>
<th>Concrete with CNI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cube strength, MPa</td>
<td>33.2</td>
<td>32.9</td>
<td>25.6</td>
</tr>
<tr>
<td>Split tensile strength, MPa</td>
<td>2.4</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Flexural strength, MPa</td>
<td>4.1</td>
<td>4.0</td>
<td>3.2</td>
</tr>
<tr>
<td>RCPT, Coulombs</td>
<td>2600</td>
<td>2550</td>
<td>4500</td>
</tr>
</tbody>
</table>

3.2 Impressed voltage test
As described earlier, U-shaped specimens were subjected to impressed voltage test. The duration of the tests was estimated based on Faraday’s law, by which the loss of iron over time can be obtained from the area under the curve of corrosion current versus time, for a weight loss of 20% in the reinforcement bar. For the weight loss of 20% in the uncracked control concrete specimen, the time required as estimated as 22 days, and the same was adopted for all other series [18]. As is well known, the amount of corrosion is related to the electrical energy consumed and is a function of voltage, amperage and time interval. For determining this, the corrosion current was monitored and recorded every hour using an automatic data logger. The charges passed in all the tests are presented in Fig. 2; in each series, three specimens were used and the average values were reported. Note that the series are designated by the nomenclature ‘mix type-crack width’. It can be seen that the charge passed in the control concrete specimens is slightly higher than that of specimens of concrete with PCE SP. Again, the charge passed is more in the cracked specimens compared to their respective uncracked specimens; as the crack width increases, the total charge passed also increases. It is evident that any cracking facilitates the passing of charge through the concrete. It can also be seen that the corrosion current was higher for concretes with CNI (in other words, the corrosion resistance response was lower).
3.3 Visual observations
In the pre-cracked specimens, initially rust stains were observed at the pre-cracks (transverse cracks) and then corrosion induced (longitudinal) cracks developed. In the case of uncracked specimens, stains were observed along the rebar much later. Initially, it appears that corrosion is localized, especially in pre-cracked specimens, and later more generalized corrosion is observed because the corrosion cracks interconnect and a single longitudinal corrosion crack develops along the reinforcement. After completion of testing, the specimens are taken out from NaCl solution and cut over the middle 300 mm length, split open and the rebar is examined for corrosion. It was observed that more generalized corrosion was observed in the rebars of the uncracked specimens, and both localized and generalized corrosion was observed in the rebars of the precracked specimens. More corrosion damage in the form of localized corrosion (pitting) was observed in concretes with CNI.

3.4 Weight loss measurements on rebars
After each specimen was broken after testing, the rebar was cleaned to remove the rust, and the corrosion of the rebar was estimated by determining the gravimetric weight loss over the middle 300 mm length, which is taken to represent the average weight loss. The weight losses are presented in Table 3.

Table 3 Gravimetric Weight Loss (in %)

<table>
<thead>
<tr>
<th>Description</th>
<th>Control Concrete</th>
<th>Concrete with PCE SP</th>
<th>Concrete with CNI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncracked</td>
<td>18.5</td>
<td>17.3</td>
<td>40.3</td>
</tr>
<tr>
<td>0.2 mm-crack</td>
<td>30.2</td>
<td>28.8</td>
<td>44.8</td>
</tr>
<tr>
<td>0.4 mm-crack</td>
<td>33.4</td>
<td>31.6</td>
<td>46.1</td>
</tr>
</tbody>
</table>

The difference in weight loss is observed to be higher when the uncracked and 0.2 mm crack width specimens are compared than when the specimens with 0.2 and 0.4 mm crack widths are compared. This implies that the presence of the crack influences corrosion more than the crack width itself. This may be due to the effect of macrocell corrosion and a nonlinear relationship between the pre-crack width and degree of corrosion. The gravimetric
weight loss was more in concretes with CNI, compared to that of the respective control and concrete with PCE SP concretes, which is in accordance with the higher total charge passed.

Visual observations, the total charge passed and the gravimetric weight losses reveal that the specimens of concrete with CNI did not show any corrosion inhibition effect in the present tests, and rather aggravated the corrosion leading to higher corrosion damage in terms of gravimetric weight loss. The possible reasons could be due to inadequate/inappropriate dosage, higher conductivity of the pore solution and low concrete resistivity. Some researchers have reported that inadequate dosage can lead to pitting and be counterproductive in terms of corrosion inhibition [26-28]. From the chemistry, it is clear that the inhibitive action of calcium nitrite depends on its reaction with the ferrous ions (Fe^{2+}) leading to the formation of a stable passivating layer. In determining the minimum dosage of CNI to prevent corrosion, it has been reported the concentration ratio of NO_2^-/Cl^- plays an important role [28, 29]. From the above data, it can be inferred that the performance of CNI could also be affected by the impressed current during accelerated testing, which is a conventional testing method. This is corroborated by reports that the nitrites do not help in zones where the passivating oxide layer has been destroyed due to chloride ions, since they are consumed early due to the reaction with the anodic corrosion products [30]. Nevertheless, Song et al. [31] did observe good inhibition due to nitrites in accelerated impressed voltage tests. Such inconsistency in the performance as reported by various researchers [23-28], in addition to the results from the present study, warrants a cautious use of the CNI with prior study of the effectiveness at the type of exposure. This also emphasizes further detailed investigation before arriving at general conclusions regarding the benefits of incorporating a CNI in concretes prone to cracking and chloride ingress.

4. CONCLUSIONS

From the limited tests done on concretes with w/c =0.57 having a polycarboxylate based superplasticizer and a nitrite based corrosion inhibitor, the following conclusions are made, with reference to the materials and dosages used:

- The RCPT value of concrete with CNI was found to be more than that of other concretes, which may be due to high ionic nature of CNI that causes more charge to pass through the concrete.
- The difference in weight loss of the rebar embedded in the concrete is higher between the uncracked to 0.2 mm crack width specimens than between the 0.2 mm and 0.4 mm crack width specimens. This implies that the presence of the crack influences corrosion more than the crack width itself.
- The gravimetric weight losses show that the concrete with PCE SP performed much better compared to that of control concrete in terms of corrosion inhibition.
- On the other hand, the weight losses in concrete with CNI are higher than that in the control concrete, the reason for which has to be clarified with further detailed investigation.

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REFERENCES