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Effects of Corrosion Inhibitors on the Critical Chloride Threshold of Thermo-Mechanically Treated (TMT) Steel

Vibha VENKATARAMU[1], Jayachandran KARUPPANASAMY[2], Arun KISHORE[3], and Radhakrishna G. PILLAI[4]*

[1]*Senior Engineer (Civil), Larsen & Toubro Construction, Chennai, India*
[2]*Ph.D. Student, Dept. of Civil Engg., Indian Institute of Technology Madras, Chennai, India*
[3]*B.Tech. Student, Dept. of Civil Engg., National Institute of Technology, Thiruchirappalli, India*
[4]*Asst. Professor, Dept. of Civil Engg., Indian Institute of Technology Madras, Chennai, India*
*(*Communicating Author: pillai@iitm.ac.in*)

ABSTRACT

The critical chloride threshold (Cl_{th}) is defined as the concentration of chloride ions required at the surface of embedded reinforcement to initiate corrosion. This is an important parameter in determining the service life of reinforced concrete structures exposed to chloride environments. An increase in Cl_{th} indicates an increase in corrosion resistance and service life of structures. Now-a-days, corrosion inhibitors (say, calcium nitrite and bipolar inhibitors) are used to increase the corrosion resistance of reinforced concrete structures exposed to chloride environments. Nevertheless, the manufacturers recommend a wide range of dosage of corrosion inhibitors (e.g., 10 to 30 litres of calcium nitrite inhibitor per m^3 of concrete). In addition, the quality control may be poor leading to a significance difference between the prescribed and actual concentrations of corrosion inhibitor used. Also, the effect of changes in the dosage of various types of corrosion inhibitors on Cl_{th} is not well understood. In addition, corrosion resistant steels (say, TMT steel) are also widely used with enhanced corrosion resistance in mind. However, very little information is available on the Cl_{th} of TMT steels used in India.

This paper will present the Cl_{th} of TMT steel embedded in mortar with various dosages of two types of corrosion inhibitors. The experimental program used a recently developed accelerated chloride threshold test method in which the corrosion rates are measured by linear polarization resistance technique. In this test, the potential application and corrosion rate measurement are performed in a cyclic manner until the corrosion initiation occurs. After the initiation of corrosion, the test specimen is autopsied and the chloride concentration in the mortar adjacent to the steel surface is determined. This is recorded as Cl_{th} values of the embedded steel specimen. Using this method, the Cl_{th} of TMT steel embedded in mortar with five different dosages of the calcium nitrite [$Ca(NO_2)_2$] and bipolar corrosion inhibitors were determined. The various dosages tested are R-20%, R-10%, R%, R+10%, and R+20%, where R is the average dosage recommended by the manufacturer.

Keywords: Concrete, chloride threshold, TMT steel, corrosion inhibitor, calcium nitrite, bipolar inhibitor

INTRODUCTION

Chloride-induced corrosion is one of the most widespread deterioration mechanisms in reinforced concrete structures. In general, structures along the coastal regions are experiencing premature deterioration due to the high concentrations of chlorides in surrounding air and soil in these regions. Delaying the initiation of corrosion of the steel reinforcement and the resulting reduction in the cross-sectional area of steel and structural capacity is a challenging task that civil engineers are facing. The maintenance and repair costs of these structures are sometimes so high, that demolition and reconstruction becomes the only viable option. Hays (2004) reported that India's total corrosion cost was INR 36,000 crores/year (USD 1.23 billions/year) approximately. Based on Koch et al. (2001), 16.4% of total corrosion cost can be attributed towards infrastructure (major portion being highways and bridges). Assuming this to be 15% and using the information from Hays (2004), the cost of corrosion attributed towards the infrastructure systems was INR 6120 crores/year (USD 1.23 billions/year) approximately in 2004. Such huge money spent on repair and maintenance of infrastructure systems can be minimized by taking appropriate measures during the design and construction phases. To achieve this, durability criteria can be incorporated during the structural design and materials selection processes. Quantitative information on the parameters such as critical chloride threshold (Cl_{th}) of steel, diffusion coefficient of chlorides in concrete, corrosion rate etc. are needed for performing durability-based design. This paper will focus on the Cl_{th} of TMT steel embedded in cementitious systems with varying dosages of corrosion inhibitors. The performances of two types of corrosion inhibitors that are available in the market have been presented.

The critical chloride threshold (Cl_{th}) of steel is defined as the chloride concentration at the surface of the embedded reinforcement to initiate corrosion. The Cl_{th} in this context is 'the minimum concentration of chlorides to be present at rebar level to overcome passivity and initiate corrosion in the reinforcing steel even in high pH environment' [Taylor et al. 1999]. In marine environment, chloride ions can ingress through the cover concrete, reach the steel reinforcement surface in sufficient quantity, and damage the passive film – resulting in corrosion. Chlorides can damage the passive films, which are stable at high pH, and initiate corrosion [Gaidis 2004, Ann 2007, Xu et al. 2010]. Literature shows that significant amount of research has been done to quantify the Cl_{th} of various types of steel reinforcement embedded in concrete. However, a compilation of the same shows that there exists a huge scatter in the Cl_{th} values reported for the same type of steel. This may be attributed to the variations in the influencing factors like the microstructural characteristics of steel and concrete, concrete mixture proportions, characteristics of steel-concrete interface, and experimental procedures. In addition, the experimental and human errors can contribute significantly to the scatter in the determined values of Cl_{th}. The authors believe that the Cl_{th} should be considered as a random parameter (due to both aleatoric and epistemic uncertainties).

MATERIALS

Thermo-mechanically-treated (TMT) steel

Recently, TMT steel is extensively used in the reinforced concrete structures in India, mainly to improve the earthquake resistance. The peculiar feature of TMT steel is that it has a harder periphery and softer core. The TMT steel can have approximately 15 to 20% elongation, which makes it suitable for use in earthquake resistant structures. The Cl_{th} of TMT steel embedded in cementitious system is necessary to determine the service life and/or assess the durability. The authors could not find reasonably accurate estimations on the Cl_{th} of TMT steel. Therefore, there is a dire need for determining Cl_{th} of TMT steel embedded in concrete such that we can predict service life with reasonable accuracy.

Corrosion inhibitors

The corrosion inhibitors offer a relatively economical as well as flexible way to increase the Cl_{th} of steel (Gaidis 2004, Ormessel et al. 2006, Morris and Vazquez 2002). However, very limited quantitative information is available on the effect of various types of corrosion inhibitors in increasing the Cl_{th}. In this study, calcium nitrite [$Ca(NO_2)_2$] and bipolar corrosion inhibitors are considered. Although, calcium nitrite is widely used and various authors have reported that it provides good corrosion resistance in alkaline environments compared to other corrosion inhibitors, a firm conclusion about its performance could not be found in the literature. Typically, a wide range of dosage (e.g., 10 to 30 litres of calcium nitrite inhibitor per m^3 of concrete) is prescribed by some manufactures. In addition, it should be noted that the actual dosage of the corrosion inhibitor can vary (although the manufacturer might have recommended a particular dosage) due to poor quality control, which may be prevailing at the site. Therefore, it is important to investigate the effect of the dosage of corrosion inhibitor on the Cl_{th} of steel.

Mechanism of action of calcium nitrite based corrosion inhibitors

When calcium nitrite corrosion inhibitor is used as an admixture, the nitrite ions (NO_2^-) compete with the chloride ions (Cl^-) to react with the ferrous ions (Fe^{2+}) at the steel-cementitious interface. This reaction produces γFeOOH (i.e., passive film), as shown in Equation (1) [Gaidis 2004, Ormellese et al. 2006].

$$Fe^{2+} + OH^- + NO_2^- \rightarrow NO + \gamma FeOOH \tag{1}$$

However, in the presence of chlorides the reaction in Eq. (1) is much faster than the transport of ferrous ions via chloride ion complex formation (i.e., the chloride-induced corrosion process). Therefore, it is seen that the presence of nitrite ions help in the production of a stable passive layer even when the chlorides are present. However, there exist contradictory or mixed opinions on the effectiveness of calcium nitrite corrosion inhibitor in the presence of chlorides. Rincon et al. (2002) reported that the effectiveness of calcium nitrite corrosion inhibitor is seen only in concrete with low water to binder ratio (i.e., less than 0.5). He has also stated that, the calcium nitrite inhibitors cannot effectively repassivate the severely corroded steel.

Rincon et al. (2002) also found that the calcium nitrite corrosion inhibitors are ineffective when NO_2^- to Cl^- ratio is less than 1. Ann et al. (2006) has also stated in their paper that calcium nitrite corrosion inhibitors are considered not suitable for immersed conditions of concrete. This is because the nitrite ions can leach out of the concrete and hence reduce the nitrite ion concentration inside the concrete. Although there are ambiguities relating to the performance of calcium nitrite corrosion inhibitor, it is the most widely used and the largest commercially available corrosion inhibitor till date. Therefore, a more intensive research in this regard is needed to accurately determine the effectiveness of the calcium nitrite based corrosion inhibitor, in mitigating the steel corrosion in reinforced concrete. The assessment of the effect of bipolar corrosion inhibitor on Cl_{th} of steel equally required, to compare two or more types of inhibitors for their performance. The objective of this work is to determine the effect of various dosages of calcium nitrite corrosion inhibitor and bipolar corrosion inhibitor on Cl_{th} of TMT steel embedded in mortar.

ACCELERATED CHLORIDE THRESHOLD (ACT) TEST METHOD

The ACT test, developed by Trejo and Miller (2002), is a method to quantitatively determine the Cl_{th} value of the steel reinforcement embedded in various types of cementitious materials. The schematic of ACT test specimen is shown in Figure 1. The inset at the top right corner of Figure 1 shows various parts of an ACT test mould. A 100 mm diameter Polyvinyl chloride (PVC) cylinder (Item 8 in Figure 1) is the mould for holding cementitious material. A 50mm diameter PVC cylinder (Item 2) on the top of the main cylinder acts as chloride reservoir containing 3.5% sodium chloride solution. Following is a brief description of the ACT test procedures and its features. The ACT test system consists of four independent test systems, explained as follows: (1) Chloride acceleration system, (2) Corrosion measurement system, (3) Corrosion initiation system, and (4) Chloride testing system. A brief discussion on each of these four systems is presented in the subsequent sections of this article.

Chloride acceleration system

The system consists of an anode, a cathode (Items 10 and 4, respectively in Figure 1), connected to an external power source, providing an absolute potential difference of 20 V. The anode and cathode are made of Nickel-chromium wire mesh and copper rod assembly (Nickel chromium mesh with 20 x 20 wires per square inch, wire diameter: 0.35 mm and Copper rods of diameter 3mm with necessary arrangements for holding the mesh). The anodic wire mesh is installed in the cylindrical mould before placing the cementitious material. After casting and curing the specimens, a fixed quantum of constant potential difference (say 20 V) is applied across the anode (at 0V) and cathode (at −20V) for a fixed amount of time (say, 10 hours). The application of potential difference leads to gradual increment in the chloride concentration near the steel specimen. The cyclic application of potential difference and measurement of corrosion rate (see System 2) is performed until a significant increase in corrosion rate is observed.

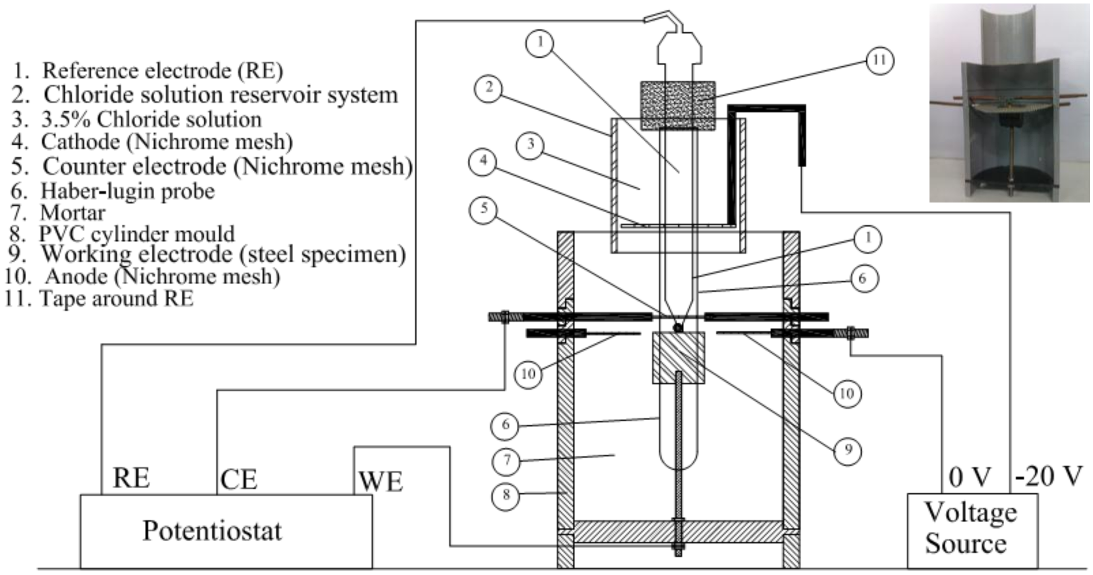

Figure 1 The Accelerated Chloride Threshold (ACT) test layout [Inset: An ACT test mould] (adapted from Pillai 2003)

Corrosion measurement system

Corrosion measurement system is the second system of ACT test method. It consists of four necessary components required to perform linear polarization resistance (LPR) measurements and sequentially to calculate the inverse polarization resistance $\left(\frac{1}{R_P}\right)$. It consist of: (i) a working electrode or the steel specimen; Item 9, (ii) a counter electrode (i.e., 25mm×25mm Nickel-chromium mesh; Item 5), (iii) a reference electrode (i.e., Saturated Calomel Electrode; Item 1), and (iv) a potentiostat attached with a computer.

After applying the external potential, the specimens are allowed to rest for a minimum fixed duration (say 42 hours) for the restoration of the open circuit potential (OCP). After the rest period, the OCP and the LPR were measured on each specimen using a potentiostat (Solartron Model - SI 1287).

The instantaneous overvoltage (E) versus instantaneous current (I) is measured to obtain linear polarization curve. A typical linear polarization curve obtained for one of the specimen in the experiment is shown in Figure 2. The slope of the linear portion of this curve, when it crosses the zero current (I) axis (i.e., when the current changes from negative to positive value), is called polarization resistance.

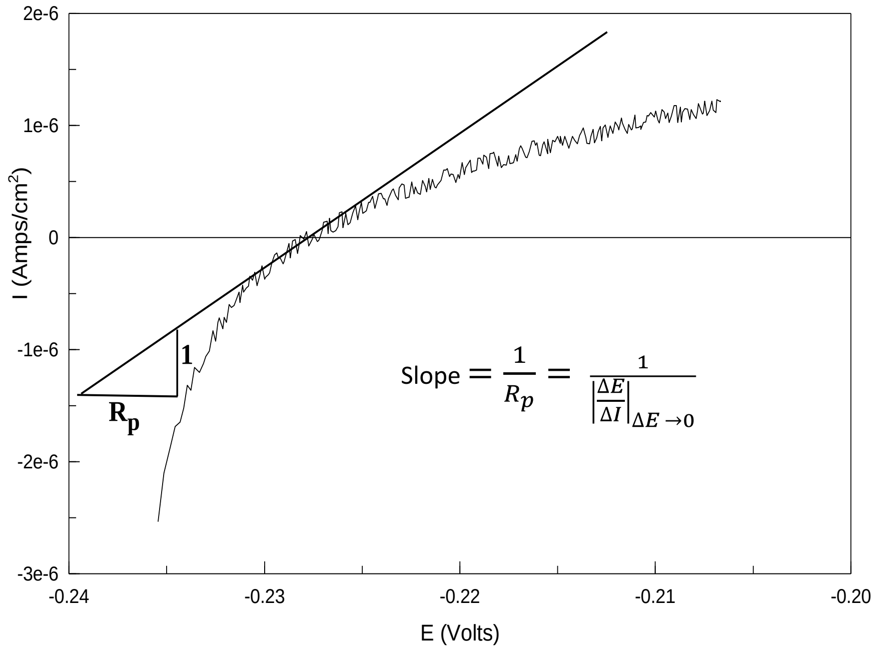

Figure 2 Typical linear polarization resistance (LPR) curve

Corrosion initiation system

The corrosion initiation system in ACT test method uses a statistical analysis approach to predict a new $\frac{1}{R_P}$ value, for the next cycle of voltage application, using the previous $\frac{1}{R_P}$ values recorded. Then, the predicted value is compared with the actual $\frac{1}{R_P}$ value measured after the subsequent cycle of voltage application. Figure 4 (a) and (b) show the recorded $\frac{1}{R_P}$, and OCP respectively for a single specimen, plotted as a function of the duration of applied voltage. The plot shows the deviation in corrosion rate after 100 hours of voltage application. Similar plots were obtained for the entire experimental program for monitoring the corrosion initiation. Using these plots and the statistical model developed, the variation in the $\frac{1}{R_P}$ value is monitored. If the newly measured $\frac{1}{R_P}$ is greater than 3σ of all the previously measured $\frac{1}{R_P}$, then the corrosion is considered to be initiated. In addition to this, a comparison of variation in the past and current OCP values has been performed to validate the corrosion initiation.

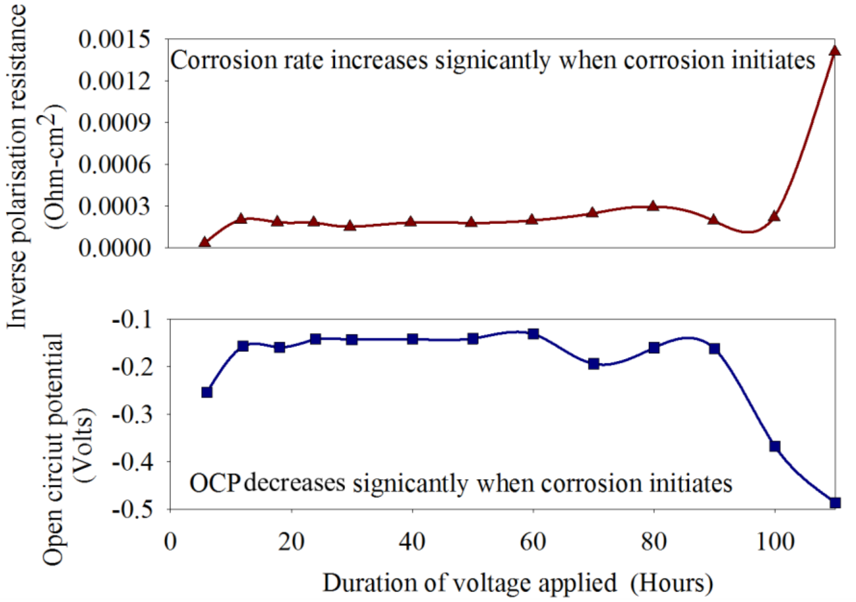

Figure 3 Variation in (a) inverse polarization resistance [top] and (b) open circuit potential [bottom] as a function of duration of applied voltage.

Chloride testing system

A chemical analysis has been performed to quantify the chloride concentration near the exposed part of the reinforcement [SHRP-S-330 (1992) *Standard test method for chloride content in concrete using the specific ion probe*]. After detecting the initiation of corrosion as explained in the previous sections, the specimens were autopsied as shown in the Figure 4.

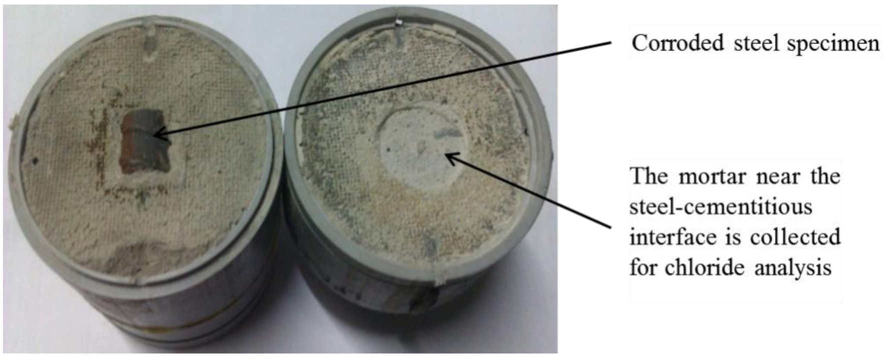

Figure 4 ACT test specimen autopsied across the steel-mortar interface

The mortar adjacent to the steel surface was collected in a fine powdered form. The chloride content in the collected mortar powder was determined using the SHRP-S-330 procedure. The chloride concentration determined as explained above was reported as the Cl_{th} of the steel specimen. Additional details of the ACT test procedures are provided in Pillai (2003) and Trejo and Pillai (2003, 2004).

EXPERIMENTAL PROGRAM

An ACT test program was conducted to determine the critical chloride threshold (Cl_{th}) value of TMT steel in cementitious environment and determine the effect various dosages of calcium nitrite corrosion inhibitor on Cl_{th} of TMT steel embedded in mortar.

The dosages of calcium nitrite (CN) corrosion inhibitor and bipolar (BP) corrosion inhibitor considered for the study were 0%, R-20%, R-10%, R, R+10%, R+20%. The term 'R' represents the upper limit of the dosage range recommended by the manufacturer (say, 30 ml per kilogram of cement). Five ACT specimens each were prepared with mortar containing various dosages of corrosion inhibitor. The mortar was prepared with Grade – III sand (size between 500 and 90 µm), OPC cement (53 Grade) and distilled water. The cement mortar mix with proportion as Water: Cement: Sand ratio of 0.5:1:2.25 was used to prepare the ACT test specimens.

Table 1 provides the fresh and hardened properties of the mortar used. The workability/flowability of the mortar was determined using the inflow table test (ASTM C230). In this test, the diameter of mortar spread in two perpendicular directions after 10 jolts are measured. The test results shown in Table 1 indicate that the flow of mortar increases as the actual dosage is either increased or decreased from the recommended dosage.

Table 1. Fresh and hardened properties of mortar used in ACT test

Corrosion inhibitor (ml/kg of cement)	Diameter of spread on flow table (mm)		7-day compressive strength (MPa)	
	Average	Standard deviation	Average	Standard deviation
None/control	151	3	30.7	3.38
CN_R-20%	163	2	32.4	1.35
CN_R-10%	154	2	32.6	1.81
CN_R	155	2	35.4	1.80
CN_R+10%	140	0	36.0	1.00
CN_R+20%	143	2	35.1	1.20
BP_R-20%	158	1	20.81	1.16
BP_R-10%	157	1	20.85	0.58
BP_R	158.67	1.15	17.97	0.69
BP_R+10%	159.67	1.52	18.93	1.50
BP_R+20%	164	1	18.94	0.85

In a controlled environment of 25±1ºC and 65±2% RH, the ACT specimens and mortar cubes (50 x 50 x 50 mm) were cast and then cured using the warm water curing method specified in the ASTM C684 for 24 hours. Then all these specimens were cured under normal curing conditions for 7 days. As shown in Table 1, the 7-day compressive strength of cubes with calcium nitrite corrosion inhibitors was slightly higher than that of cubes with no corrosion inhibitors. On the other hand, the cubes with bipolar inhibitor show reduction in strength with increase in dosage. It is also noted that the scatter in the observed compressive strength is reduced with an increase in the dosage of corrosion inhibitors. Additional testing is required to understand the mechanisms behind the reduction in the scatter.

RESULTS

Figure 5 shows the Cl_{th} values of thermo-mechanically treated (TMT) steel embedded in mortar with various dosages of calcium nitrite corrosion inhibitor. The horizontal line at the middle of the box in each column of data indicates the mean values. The specimens of the group CN_R, with the recommended dosage of calcium nitrite corrosion inhibitor (i.e., 30 ml per kg of cement) showed an average Cl_{th} of 0.55 kg/m^3. The hollow circles in second and third columns indicate the outliers. The Cl_{th} of the steel with calcium nitrite dosage of CN_R+10%, CN_R+20% ranges between 0.44 kg/m^3 and 1.5 kg/m^3, 0.4 kg/m^3 and 1.7 kg/m^3 respectively.

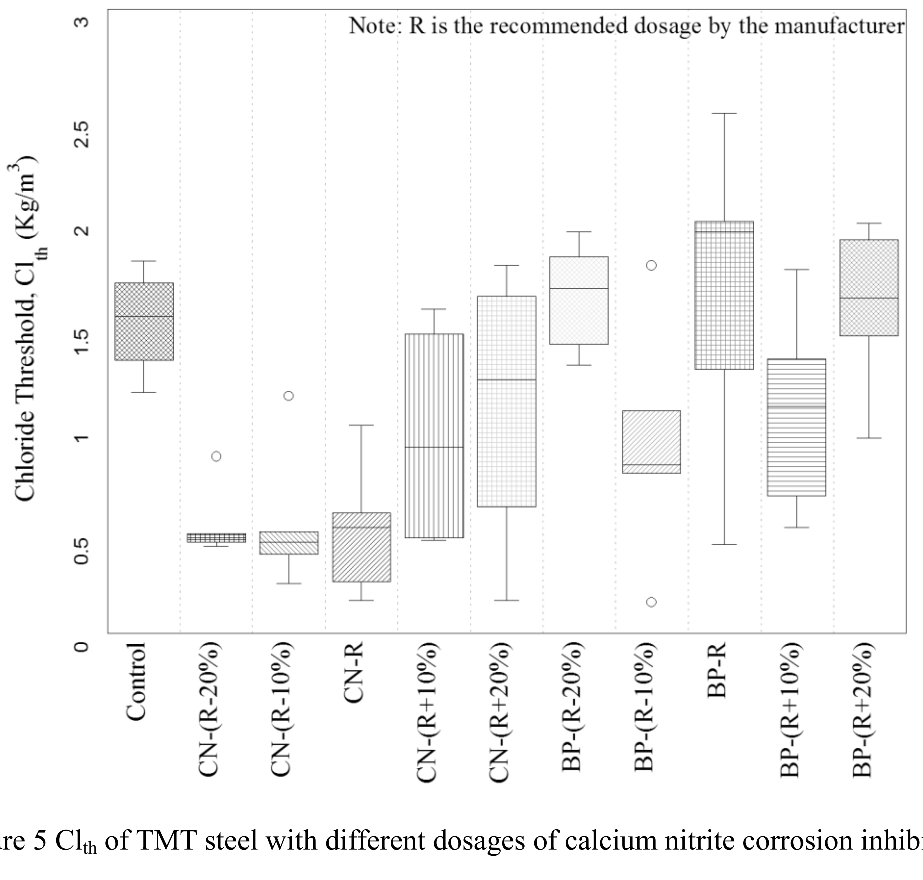

Figure 5 Cl_{th} of TMT steel with different dosages of calcium nitrite corrosion inhibitor

The results indicate that the calcium nitrite inhibitor failed to increase the Cl_{th} of the TMT steel. Rather, the specimens with calcium nitrite inhibitors exhibited lower Cl_{th} values than that of control specimens (i.e., specimens without any inhibitor dosage) in the first column. The specimens with bipolar inhibitor, Cl_{th} varies from 1.05 kg/m^3

to 2.15 kg/m^3 for recommended dosage (BP_R). The mean value of Cl_{th} increased when the dosage was increased.

Although these kinds of results are unexpected, other researchers have also observed a reduction in the corrosion resistance when calcium nitrite based corrosion inhibitors were added (Bhaskar 2013). However, it should be noted that the geometry of the test specimen and other experimental procedures and conditions might also have led to these unexpected results.

CONCLUSIONS

Based on the test data and analysis of Cl_{th} of TMT steel, the following conclusions are made.

- The TMT steel embedded in mortar with calcium nitrite corrosion inhibitor exhibited lower Cl_{th} values than specimens in mortar with no corrosion inhibitor or with bipolar corrosion inhibitor.
- The bipolar corrosion inhibitor showed better performance in inhibiting corrosion rates when compared to calcium nitrite inhibitor, in all the dosages considered.
- The accelerated chloride threshold test results in this test program do not indicate that the calcium nitrite corrosion inhibitor can significantly increase the Cl_{th} of TMT steel. However, it should be noted there may be the influence of experimental procedures on the results. Therefore, further tests are required to confirm this finding.

In this accelerated test procedure, the concentration of nitrites at the surface of the embedded steel might have been increased due to the application potential gradient during the test. The chloride/nitrite ratio might be a better parameter than the chloride concentration to assess corrosion initiation by accelerated tests, where potential gradients are applied.

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