

EFFECT OF INHIBITORS ON THE CORROSION BEHAVIOUR OF CARBON STEEL REINFORCED IN CONCRETE.

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ABSTRACT

The effect of inhibitors on the corrosion behaviour of carbon steel reinforced in concretes exposed to 3.5% NaCl solution and tap water has been studied. Carbon steel was used as reinforcing bar for the experiment, calcium nitrite; sodium nitrite and bitter leaf (vernoniaamygdalina) extract were used as inhibitors. The corrosion behaviour was evaluated from potential and resistance readings using half-cell potential and concrete resistivity measurement techniques respectively. The results show that calcium nitrite and bitter leaf extract reduced corrosion rate in rebar compared to sodium nitrite. From the results, it is evident that the extract from vernoniaamygdalina (bitter leaf) acts as an excellent inhibitor for corrosion in reinforced concrete.

Keywords: *Corrosion, Inhibitor, Concrete, Carbon steel, Vernoniaamygdalina.*

1.0 INTRODUCTION

The degradation of reinforcing steel due to corrosion is prevalent in concrete structures all over the earth. Most structures are affected with chloride as a result of deicing and exposure to chloride laden environment such as structures for marine applications [1]. Corrosion effect causes weakening and rapid aging of structures [2]. Corrosion inhibitor is one of the most effective measures of corrosion mitigation in rebar embedded in concrete. Cost of inorganic inhibitor is relatively low, however some of them are very toxic (harmful to both human and environment) such as chromate, mercuride, arsenate etc. The use of inhibitors seem to be more promising due to their simplicity in application, and are relatively in-expensive. Inhibitors are generally classified according to which electrode reaction they influence. Al-Dulajjan et al [3] identified inhibitors as anodic, cathodic or mixed inhibitors. So far many investigations have been carried out on the effect of inorganic inhibitors on the corrosion of carbon steel in concrete. A.Krolkowski et al [4] studied nitrite as a penetrating corrosion inhibitor for steel in concrete. The study revealed that calcium nitrite was able to lower or inhibit the initiated localised corrosion of rebar steel chloride contaminated concrete. Calcium nitrite can inhibit the initiated, localised corrosion of reinforcing steel in solutions simulating chloride contaminated concrete, if it is present in sufficient concentration in early stages

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of the corrosion process. Soylev and Richardson [5] declare that nitrites (calcium or sodium salt) are anodic inhibitors, they compete with chloride ions for the ferrous ions at the anode to form a film of ferric oxide (Fe_2O_3).

The effects of plant extract as corrosion inhibitor in mild steel in acidic medium have been studied. It has been reported that *vernoniaamygdalina* (bitter leaf) and *Azadirachita* (Nee leaf) extract showed adequate corrosion inhibition in acidic media and that inhibition efficiency increases with increase in dosage. The inhibition mechanism of *vernoniaamygdalina* is related to their physical adsorption properties due to the presence of tannin, alkaloid and saponins [6,7,8]. The use of organic compound to reduce corrosion of mild steel has vital advantage due to their applications for corrosion prevention in different aggressive environments [9]. However, no cleared details in the past and present have shown the in-depth study of its potency in reinforcing steel bar in concrete exposed to both neutral and chloride environments. The present study was designed to identify and evaluate the behaviour of sodium nitrite, *vernoniaamygdalina* and calcium nitrite inhibitors on corrosion behaviour of carbon steel reinforced in concrete immersed in tap water and simulated seawater.

2.0 EXPERIMENTAL METHODS

2.1 Materials

The following materials were used for the study: substrates metal; carbon steel reinforcing bars, calcium nitrite, sodium nitrites and *vernoniaamygdalina* as inhibitors, cement, fine and coarse aggregates, tap water and 3.5% NaCl solution were used as test solutions.

2.2 Method

2.2.1 Sample preparation

The *vernonia amygdalina* leaves were acquired from the plant in the neighbourhood at Utama Pulai, Skudai and were thoroughly washed with water to remove unwanted materials and then weighed. The weighed amount (0.2kg) was put in a bottle container, methanol was added and the container was tightly covered to prevent evaporation. The mixture was left for 48 hours to allow proper removal and concentration of the extracts. Subsequently, the mixture was filtered to obtain a liquid residue containing methanol. The methanol was removed by heating the resulting solution over a water bath at 76^0C for 20 minutes in rotary evaporator model Buchi R-200.

2.2.1.2 Specimen dimension

Cylindrical concrete block with dimension 75mm diameter and 150mm height in accordance to ASTM C685M-11 was used. One plain carbon steel bar (grade 40) of diameter 10mm and length 170 mm was embedded at the centre of each concretes (lollipop).

2.2.1.3 Concrete sample making

Batching, mixing and casting of entire set of cylindrical concretes were done one day, so that the entire concretes specimen with inhibitors will have the same age. Prior to the day of casting, all the aggregates were weighed to the nearest kilogram (0.01). Calcium nitrite and the plant extracts inhibitor were measured volumetrically before the mixing in different containers. However, sodium nitrite was weighed in the weighing balance. Hand mixing was used in accordance to ASTM C685 (0.07m^3). The cement was premixed with the inhibitors before casting. Each concrete sample was mixed with $3\text{L}/\text{m}^3$ of calcium nitrite, *Vernonia amygdalina* and 1%wt sodium nitrite. But the controls were without inhibitors. Figure 2 shows the concrete specimens before demoulding after 24 hours

before curing. Curing was done at room temperature in water for 7 days before immersion in test solution.



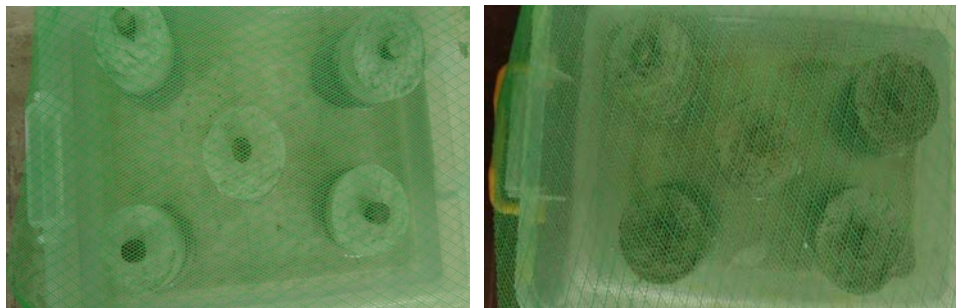
Figure 1: Concrete specimens in cylindrical mould.

2.2.2 Material characterization

The reinforcing steel bar chemical composition was analysed by Glow Discharge Spectrometer (GDS), model Leco 850A after proper grinding with emery paper of 220 grit size. The chemical composition wt% is as follows, C 0.032, Mn 0.193, P 0.012, S 0.014, Si 0.018, Fe 99.6.

2.2.3 Ponding (Immersion)

Concrete specimens which consist of the embedded carbon steel were partially immersed in a cycle of five days in solution in simulated sea water and tap water as shown in Figures 2 and two days out to accelerate the ingress of chloride ions. Five samples of different corrosion cells were immersed in each solution medium. Test was carried out at room temperature and the simulated solution used for the study was concentrated aggressive medium of 3.5% NaCl solution to simulate sea water concentration in real life situation and the other medium was normal tap water solution.



(a) Samples immersed in tap water (b) Sample immersed in 3.5%NaCl solution

Figure 2 : Plan view of immersed samples in tap water and 3.5% NaCl solution

2.2.4 Corrosion test

Corrosion test was conducted for the sample without concrete (bare samples) and sample with concrete as explained in sections 2.2.4.1 to 2.2.4.2.

2.2.4.1 Visual inspection

Visual inspection is a Non Destructive Evaluation method of corrosion monitoring. It is the simplest and the oldest inspection technique. This method is economical and fast. This simply involves most often the use of the human eyes to observe the surface morphology. Although this techniques has some limitations because it can only provide qualitative results but not quantitative and sometimes pitting corrosion can only be detected with

aided human eyes but it is always the first approach in corrosion inspection. In this study, the reinforcing steel bars were inspected prior and after immersion to examine surface appearances.

2.2.4.2 Half-cell potential measurement

In this study, copper-copper sulphate half-cell was used to measure the half-cell potentials of the steel rebar according to ASTM C 876-87 G3. Potential readings were taken by placing the copper-copper sulphate electrode (CSE) firmly on the surface of the concrete at portions of the cylinder block specimens (mapping) at close range interval, the measurement were carried out after the samples have been removed from immersion solutions for 2 hours to allow diffusion of air through concrete pores.



Figure 3 : Half-cell potential measurement set-up.

2.2.4.3 Concrete resistivity measurement

Wenner four probes resistivity measuring probe was used to measure concrete resistivity. This was done by placing the four probes in contact with the concrete directly above the reinforcing steel bar. Different readings were taken at different locations at the surface of the concrete. The average values of the readings were recorded

3.0 RESULTS AND DISCUSSION

3.1 Visual inspection

The reinforcing steel bars were removed by crushing the concrete specimens in compressive test machine at the end of the immersion time. The surfaces of the steel bar were observed visually. It was evident that corrosion products were deposited on the rebar without inhibitor as revealed in Figure 4a. However, there was no evidence of rust in the samples with inhibitors within this period.

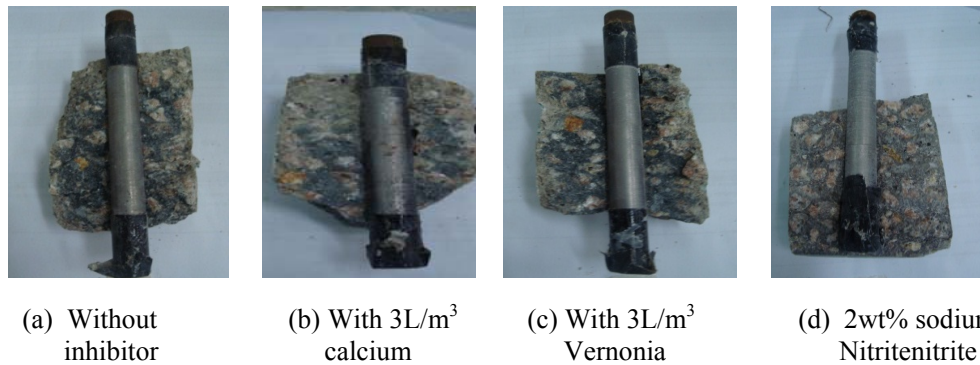


Figure 4: Reinforcing bar after immersion time in 3.5% NaCl solution.

3.2 Half-cell potential measurement

From Figure 4 and 5, it can be established that no pitting corrosion initiation is envisaged for all the samples with corrosion inhibitors at the end of the study, in an aerated concrete, corrosion potential range is usually from +100mV to -200mV SCE [10]. For low level of chloride content of about (0.3) % by mass of cement, corrosion potential of +250mV and below indicates that the chance of corrosion initiation is insignificant. However, there is the likelihood of corrosion initiation and propagation above this corrosion potential in chloride environment (Bertolini, 2004). However, the visual examination confirmed minute regions of pitting in the sample without inhibitor. Interestingly, all the curves show a down ward trend and with few erratic behaviour. In the absence of aggressive ions, a protective passive layer is formed on the reinforcing steel [12].

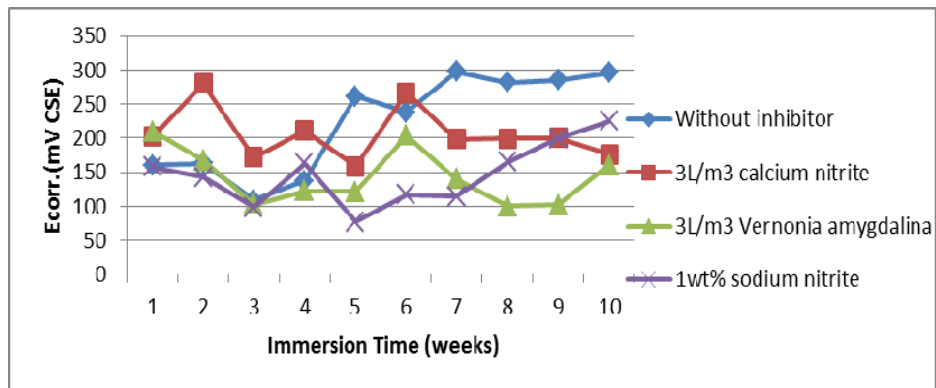


Figure 4 : Corrosion potential as a function of time for immersion samples in 3.5% NaCl solution.

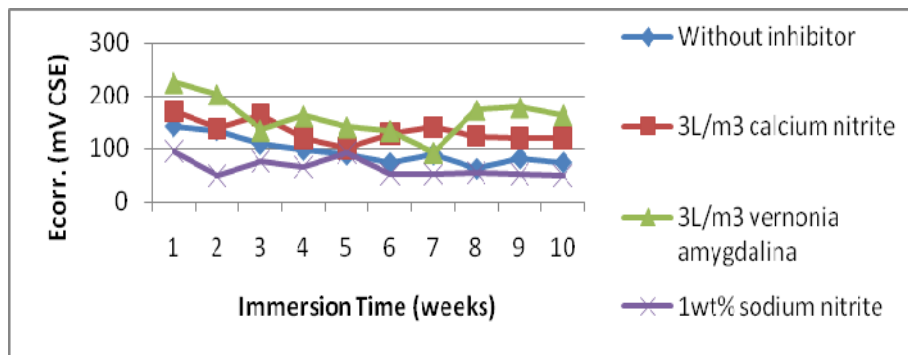


Figure 5 : Corrosion potential as a function of time for immersion samples in tap water

3.3 Concrete resistivity

Figure 6 and 7 show the plots of concrete electrical resistivity as a function of immersion duration for specimens immersed in 3.5% NaCl solution for 10 weeks. It can be observed that the curves follow the same upward drifts. However, sodium nitrite inhibitor assumed a lower resistance position. This is in accordance with the findings of Collepari et al, [13]. The lower resistivity is due to higher ions as a result of the presence of Na^+ and NO_2^- in the aqueous phase filling the pores capillary. According to (Morris et al, 2002), rebar are in active corrosion risk when concrete resistivity is lower than $10\text{k}\Omega\text{cm}$ and attain passivity at resistivity higher than $30\text{k}\Omega\text{cm}$. And as previously reported by Song and Saraswathy, [15], resistivity above $20\text{k}\Omega\text{cm}$ shows negligible corrosion risk while

between 10kΩcm to 20kΩcm suggests low corrosion risk. Calcium nitrite and the leaf extract show resistivity of 25kΩcm and 20kΩcm respectively, indicating negligible. Sodium nitrite shows the least because insufficient inhibitor accelerates corrosion.

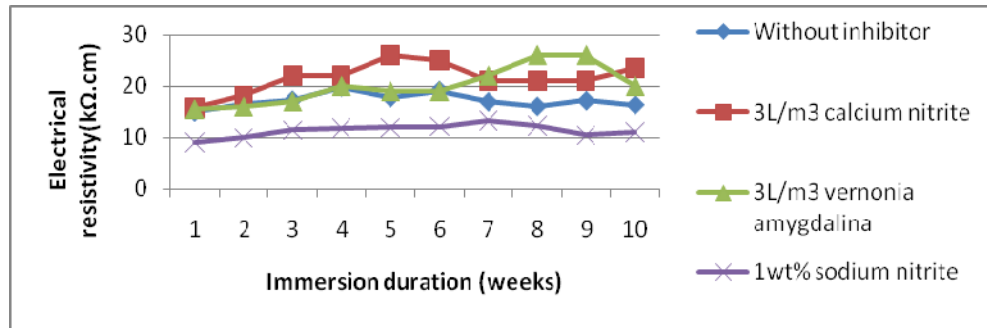


Figure 6: Concrete electrical resistivity versus immersion time in 3.5%NaCl solution.

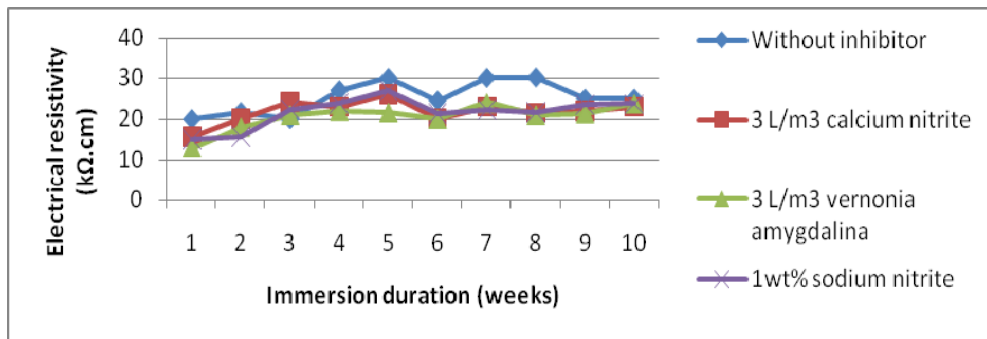


Figure 7 : Concrete electrical resistivity versus immersion time in tap water.

3.4.4 Corrosion rate

Sample without inhibitor shows corrosion rate of 0.006 mm/yr at the end of the study as shown in Figure 8. However, both calcium nitrite and vernoniaamygdalina reduced corrosion rate from 0.006mm/yr to 0.004mm/yr within 9 weeks of immersion. Corrosion rate was 0.009mm/yr for sodium nitrite at the end of the study. However, was relatively stable in samples immersed in tap water except for sample with sodium nitrite. The effectiveness of various corrosion inhibitions was more evident in samples immersed in 3.5% NaCl solution; this could be as a result of diffusion due to the difference in concentration gradient between the immersion solution and the concrete pore solution.

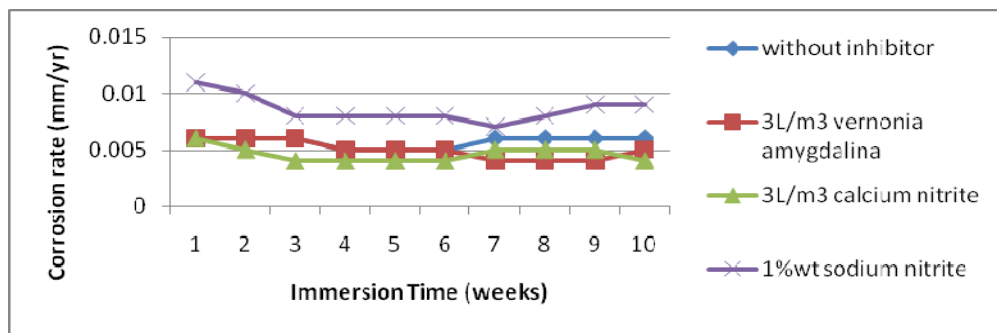


Figure 8 : Corrosion rates (mm/yr) versus immersion time for carbon steel in concrete immersed in 3.5% NaCl solution.

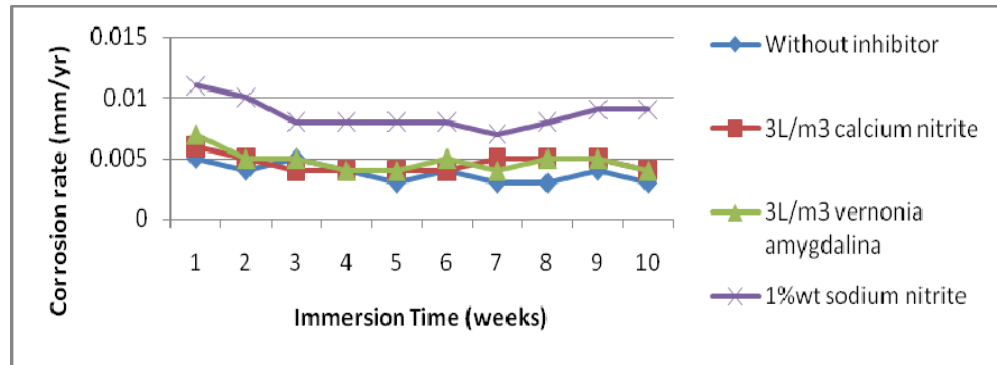


Figure 9 : Corrosion rates (mm/yr) versus immersion time for carbon steel in concrete immersed in tap water

4.0 CONCLUSIONS

- i. Vernoniaamygdalina (plant extract) inhibitor shows excellent E_{corr} of +150mV and calcium nitrite +125mV for 3L/m³ within the 10weeks of immersion. This shows that eco-friendly inhibitor can be harnessed for corrosion inhibition in reinforcing concrete in chloride laden environment.
- ii. The degree of reduction in corrosion rates in reinforcing carbon steel was slightly higher in calcium nitrite inhibitor. However, increase in vernoniaamygdalina inhibitor dosage could possibly improve corrosion inhibition efficiency.
- iii. Sodium nitrite inhibitor shows the lowest inhibition efficiency from the corrosion test compared to calcium nitrite and vernonia amygdalina.

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