Effectiveness of Inhibitors on Rebar Corrosion in Simulated Concrete

Shailesh Kumar Prasad[1] Monalisa Kundu[2] Virendra Kumar[3]

[1,2]Department of Chemistry [3]Department of Civil Engineering

[1,2,3]National Institute of Technology Jamshedpur

Abstract— Corrosion of reinforcing steel embedded in concrete is becoming a significant structural and financial problem worldwide as it leads to a significant loss of life and economy. Different methods have been proposed to combat reinforced corrosion in concrete structures. Corrosion inhibitors may be a good way to control reinforcing steel corrosion because they are easy to apply and less costly compare to other preventive techniques like coating, electrochemical chloride removal or cathodic protection. This paper studies the inhibitor efficiency of sodium nitrite (NaNO2) and aminoalcohol based inhibitors when they are used in reinforced cement mortars. Electrochemical monitoring of half-cell potential (HCP) and weight loss experiment were performed in 3.5% NaCl medium in order to obtain inhibitor information on the corrosion behavior of the reinforcing steel in cement mortar. Results showed better inhibitor efficiency in presence of inorganic sodium nitrite based inhibitor compare to organic aminoalcohol based inhibitor.

Key words: Corrosion inhibitor, Sodium nitrite, Aminoalcohol, Half cell potential, Weight loss method, Polarization Technique

I. Introduction

Corrosion of reinforcement in concrete is one of severe problems worldwide which requires a lot of attentions as it leads to a significant loss of life and economy. Service life of the structures is drastically reduced specially in the coastal areas where the corrosion is mainly attributed to the penetration of the chloride and sulfate ions into the hardened reinforce concrete [1]. Among several preventive methods, use of corrosion inhibitors seem to be attractive as they are cost effective and easy to handle compared to other preventive methods [2, 3]. A corrosion inhibitor is a chemical substance which, in the presence of corrosive agent, decreases the corrosion rate in a corroding system when used at suitable concentration [4, 5]. Traditional corrosion inhibitors are divided into inorganic (mainly nitrites) and organic (alkanolamine and their inorganic, organic acid salt mixtures) substances. Based on the mode of addition corrosion inhibitors are either admixture type or can be applied to the surface of the hardened concrete structures as migrating corrosion inhibitors (MCIs). Both the methods have certain discrepancies and certain advantages [6, 3]. From the action standpoint, inhibitors are either anodic inhibitors, such as calcium nitrite and sodium nitrite or cathodic inhibitors, such as phosphates and N, N-dimethylaminoethanol (DMEA) or mixed inhibitors which act on both anodic and cathodic sites. Amines and alkanolamines are the most commonly used mixed corrosion inhibitors [7]. Although nitrites are widely reported as an efficient corrosion inhibitor, due to its carcinogenicity and biological toxicity, it is forbidden in many European countries, i.e. Germany and Switzerland. On the other hand alcoholamine is a widely used organic corrosion inhibitor, however, there are still conflicting opinions about its effectiveness and different mechanisms are also reported [8]. In this paper the corrosion inhibitor properties of both the commercially useful inhibitors are tested in simulated concrete pore solution (SCP) as well as in cement mortar system.

II. Experimental

A. *Preparation of Concrete Blocks*

The test specimens were prepared with cement, (sand + gravel) and water in ratio 1:3:0.6. The formulation used for the reinforced concrete specimens in kg/m3 was cement-320, water-140, sand-700, and gravel-1150. The water/cement (w/c) ratio was 0.44. The cement type used was Ordinary Portland cement. Concrete blocks were used for the electrochemical monitoring experiment. Each block was admixed with 2% (by wt of cement) inhibitors and a fixed amount of 3.5wt% NaCl which was added to accelerate the corrosion of the embedded steel by providing increased chloride ions in the matrix and particularly around the steel-rebar.

B. *Casting of The Specimens*

The steel rebars considered for the present study were cylindrical 120 mm in height and 12 mm in diameter. Each contained one steel rebar in the position shown in Figure 1.The cement mortar constituents were mixed in a mortar mixer for approximately 5 minutes till a uniform consistency was achieved. The molds were filled with mortar and vibrated for consolidation using a vibrating table. Prior to the preparation, the steel surface was cleaned according to the ISO/DIS 8407.3 Standard [9]. Thereafter, the bars were placed in cylindrical moulds where the mortar was cast and stored at ambient conditions in the laboratory for 24 hours. After being demolded, the specimens were placed in water in curing room (RH > 98%, T = 20°C ± 1.5°C) for 24 hours and then kept for an additional 7 days at ambient temperature in a laboratory environment to stabilize internal humidity, followed by insulation with epoxy resin of the region shown in Figure 1[10]. Finally the specimens were partially immersed in 3.5 wt.% NaCl solution up to 20 mm from the bottom. The experimental duration of this study was 3 months.

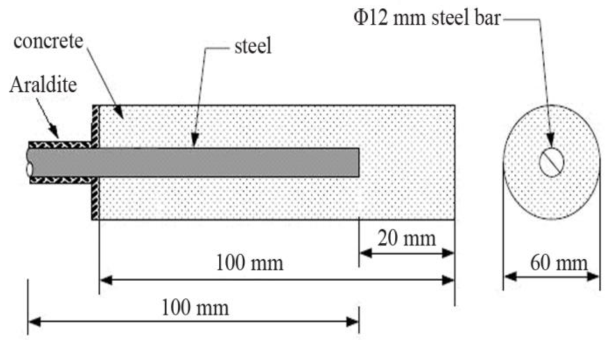

Fig. 1: Schematic representation of a reinforced mortar specimen

C. Half Cell Potential Measurement

During the exposure of the specimens in the corrosive environment the half-cell potential of steel rebars was periodically measured versus a saturated calomel electrode (SCE) and a high impedance multimeter. According to ASTM C876 Standard [11] corrosion potentials (Ecorr) more negative than −350 mV, with respect to SCE, indicate greater than 90% probability of active reinforcement corrosion. Values less negative than −200 mV SCE indicate a probability of corrosion below 5%, while those falling between −200 and −350 mV SCE indicate uncertainty of corrosion. The measurements were initially recorded on an everyday basis until equilibrium conditions were established and then they were recorded on a weekly basis.

D. Weight Loss Experiment

The corrosion rate of reinforcing steel was determined by measuring the mass loss of the steel bars in different times. The steel bars were cleaned from any corrosion products according to the ISO/DIS 8407.3 Standard [(9)] and were weighted to accuracy of 0.1mg. The average mass loss was calculated from the difference between the initial and the final weight of each steel bar according to the following equations:

$$\%\text{weight change} = \frac{(M_{initial} - M_{final})}{M_{initial}} \quad (1.1)$$

The corrosion rate was determined using the equations as follows which is,

$$\text{Corrosion rate (um/yr)} = \frac{8.76 * 10^7 * W}{A * T * D} \quad (1.2)$$

Where, W is the metal loss (g), A the rebars surface area (cm2), T the time of exposure (hr) and D the density of steel (g/cm3).

E. Polarization Technique

The corrosion of reinforced concrete is measured by polarization method to measure the corrosion rates over various time periods. Although the corrosion of steel in concrete is an electrochemical process and does not obey to Ohm's law it has been shown that Ohms's law will be approximately true if polarization applied to the steel does not exceed ±20 mV. Thus the resulting current is linearly plotted versus potential. The test setup for the polarization techniques included an EG&G Model 263 Potensiostat/Galvanostat. Additionally the computer program Softcorr III developed by EG&G Princeton Research was used for applying the potential scan, analyzing the parameters of corrosion current density (icorr)and polarization resistance (Rp). The corrosion current density was measured using the DC linear polarization resistance method. The resistance to polarization Rp (Ω•cm2) was determined by conducting a linear polarization scan in the range of 20 mV of the open circuit potential and the corrosion current density icorr [µA/cm2] was then calculated using the Stern-Geary equation which is given as follows,

$$I_{corr} = B / R_p \,.\, A \quad (1.3)$$

where B is a constant based on the anodic and cathodic Tafel constants where a value of 26 mV has been adopted for active corroding steel bars and 52 mV for passive conditions and A (cm2) is the exposed area of the rebar. This method has been considered to be a relatively simple and reliable technique to assess the rate of reinforcement corrosion in cement mortars. The corrosion level is considered negligible when icorr is less than 0.1 µA/cm2, it is considered low in the range between 0.1 and 0.5, moderate from 0.5 to 1 and high for values higher than 1 µA/cm2 [12].

III. RESULTS & DISCUSSION

A. Half-Cell Potential Measurements

In case of amino alcohol based inhibitor (Figure 2) the half-cell potential measurement of the specimens show an initial increase in the potential values towards more negative direction up to -270mv which indicates a primary increase in the corrosion rate. After that under the action of the inhibitor the potential value gradually changes to less negative direction attaining a value of around −195 mV during the first 90 days. Then again the potential decays to more negative value and finally reaches a steady state of potential around −170 mV due to the passivation of the reinforcing steel as a result of the formation of protective oxide layers even after 200 days of exposure. On the other hand in case of nitrite based inhibitor (Figure3) initially potential shifts to more negative direction to almost -600mv. The inhibitor shows slow start of its effect compare to the amino alcohol based inhibitor. However, under the action of the inhibitor the potential value decreases to -400mv during 55 days, and then reaches to the minimum of -75mv during 80 days. After that the potential again increases as the corrosion rate increases to almost -780mv and finally the passivity is attained during 125 days. The half-cell potential experiments show a clear difference between the inhibition efficiency as well as mechanism of action of both the inhibitors on the rate of corrosion of the reinforcing steel. Amino alcohol based inhibitor takes longer time to attain the passivity compare to the nitrite inhibitor.

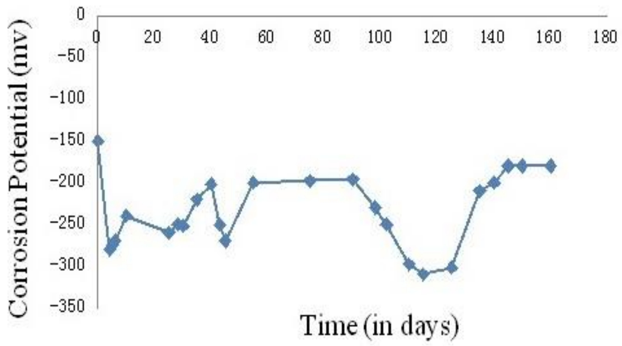

Fig. 2: HCP versus time of amino alcohol in cement mortar specimens in 3.5 wt% NaCl solution

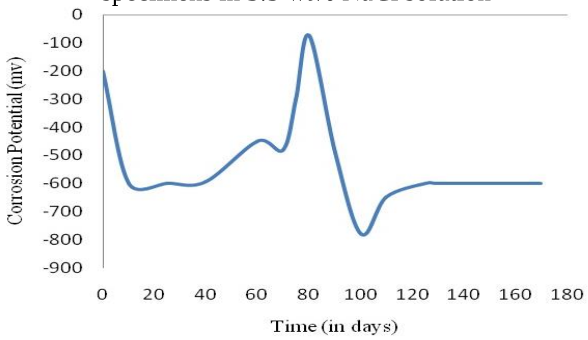

Fig. 3: HCP versus time of sodium nitrite in cement mortar specimens in 3.5 wt% NaCl solution

B. Weight Loss Experiment

Mass loss of all the specimens immersed in the corrosive environment was obtained at an interval of 90, 180 and 210 days (Figure 4). Control specimens demonstrated higher mass loss values at all intervals which showed that in the absence of inhibitors the corrosion activity strongly increased with time, leading to a higher mass loss. The specimens with addition of the corrosion inhibitor as admixture demonstrated lower mass loss versus time compare to the control specimen. The mass loss of the control specimens immersed into 3.5% NaCl solution was found to be dramatically higher than the mass loss of the specimens in presence of amino alcohol based inhibitor than sodium nitrite inhibitor under the same inhibitor concentration.

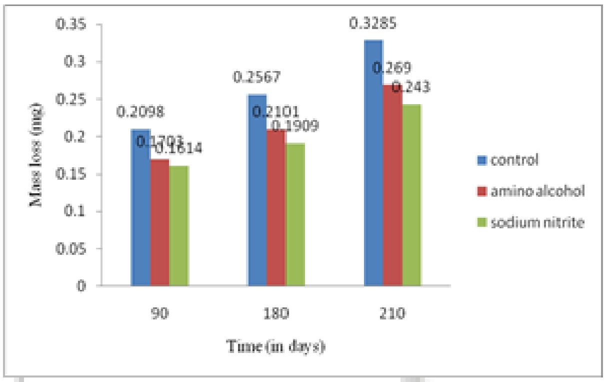

Fig. 4: Mass loss of reinforcing steel bars immersed in 3.5 wt% NaCl solution a) Control, b) Amino Alcohol,c) Sodium Nitrite

C. Polarization Method

Different previous electrochemical measurements showed that the inhibitor efficiencies of both amino alcohol based inhibitors and nitrite inhibitors when the steel was under corrosion attack [13-16]. Considering these results, the present work studied the ability of both amino alcohol based inhibitor and sodium nitrite inhibitor to resist the corrosion by measuring the corrosion current density in 3.5 wt% NaCl solution. (**Figure 5 & 6)** depicted the corrosion current density, i_{corr} on rebars immersed in SCP containing 3.5 wt% NaCl solution for 28 days in the presence of both amino alcohol based inhibitor and sodium nitrite inhibitor. The sample admixed with 2% amino alcohol corrosion inhibitor displayed the largest i_{corr} value, indicating that it exhibited a poor inhibition effect for the reinforcement steel in this corrosive environment whereas, in the presence of 2% sodium nitrite inhibitor, best inhibition effect was found with lowest i_{corr} value.

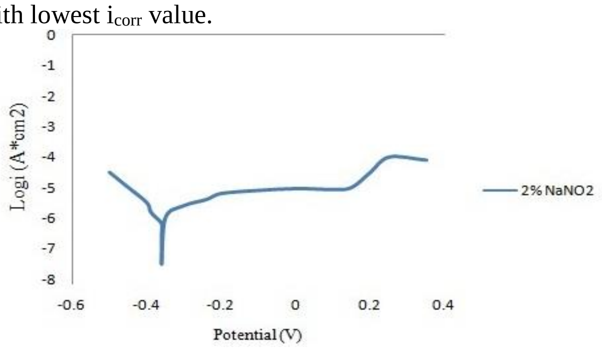

Fig. 5: Potentio-dynamic polarization curves of reinforcing steels in SCP solutions in the presence of NaNO2 corrosion inhibitors at 28day immersion ages

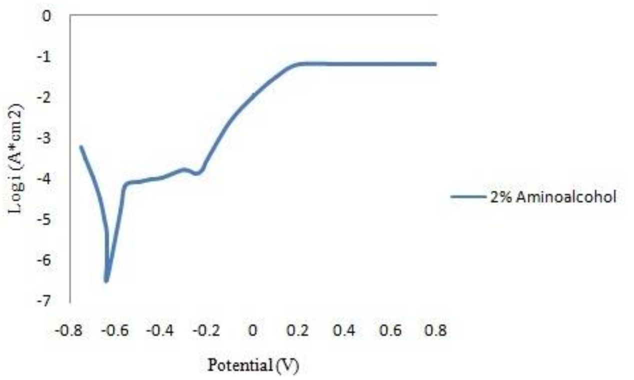

Fig. 6: Potentio-dynamic polarization curves of reinforcing steels in SCP solutions in the presence of aminoalcohol corrosion inhibitors at 28day immersion ages

IV. CONCLUSION

The following conclusions can be drawn from this investigation. Polarization studies showed that in SCP containing 3.5 wt% NaCl medium sodium nitrite showed better inhibition property compare to amino alcohol based inhibitor. Also in cement mortar specimens immersed in 3.5 wt% NaCl medium the admixed amino alcohol based inhibitor treated specimens demonstrated low corrosion inhibition property compare to sodium nitrite inhibitor. From the above, the goal of this paper to comparatively test the inhibitory action between the amino alcohol based inhibitor and sodium nitrite inhibitor under corrosive environment was achieved. However further in depth analysis are necessary regarding the mechanism of action of both the inhibitors under the presence of high chloride concentration and also to find out the characteristics of the passive film that is created by the inhibitor on the steel surface under various corrosive environments.

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