ELECTROCHEMICAL ASSESSMENT OF CONCRETE TERNARY INHIBITORS USED IN RETARDING CORROSION OF STEEL REINFORCEMENT

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ABSTRACT
Corrosion of steel reinforcement in concrete is generally considered as an electrochemical process which reduces the service life of a structure exposed to chloride ions attack. Therefore, laboratory experiments were performed in order to ascertain the effectiveness and sustainability of ternary inhibitors (calcium nitrite, ethanolamine and eco-friendly green Bambusa Arundinacea) in protecting steel reinforcement in concrete from corrosion attack due to chloride. Concrete mix was designed to be 30MPa with 0.45 and 0.65 W/C ratios. Inhibitors additions were 2% and 4% by weight of cement. The specimens were subjected to various durability corrosion test (using; electrochemical impedance spectroscopy (EIS)) for 360 days. The results showed that Bambusa arundinacea has exhibited lowest corrosion rate, highest concrete resistance and highest polarization resistance (Rp) values for the period of exposure, compared to calcium nitrite and ethanolamine. Bambusa arundinacea may be considered a better substitute for nitrite and amine-based corrosion inhibiting admixtures for durable concrete structures due to its viability, versatility and eco-friendliness.

Keywords: steel reinforcement, concrete, corrosion, green Inhibitor, sustainability, EIS.

1. INTRODUCTION
Deterioration and collapse of reinforced concrete structures is due to corrosion and a major problem in the construction industry especially in the coastal region, which are characterized by high salinity. The cost of repairing or replacing deteriorated structures has become a major liability to government and the private sectors. The primary cause of this deterioration is the corrosion of steel reinforcement due to chlorides whose main source is the seawater and deicing salts (Abdulrahman et al., 2012; Jing and Wu, 2011; Królikowski and Kuziak, 2011; Ismail et al., 2010a).

In many countries with rapidly developing infrastructures, economies in construction have led to poor quality concrete and low concrete cover to the steel resulting in corrosion problems. Also, the developed economies are not left out of this endemic problem, according to Indrajit et al. (2011), who reported that one out of nine of existing concrete bridges in United States of America is deficient as a result of chloride ions from deicing salts on highway bridges exposed to freeze-thaw and dry-wet cyclic which translated to 31.7% of the nation’s 73, 800 structurally deficient bridges and this alone consumes 3.1% of their GDP.

Therefore, the major daunting challenge facing the civil engineering community is to execute projects in tandem with nature using the concept of sustainable development involving the uses of environmental benign materials produced at a reasonable cost. In the context of concrete, which is the predominant building material, it is imperative to identify corrosion inhibitor which is eco-friendly to salvage the life span of concrete structure exposed to harsh environments.

Several solutions to this problem have been proposed and tested, albeit to date no ideal solution has been found workable (Abdulrahman et al., 2011a; Boltryk et al., 2011; Rwamamara and Simonson, 2012). Thus, the principle of the corrosion inhibitor admixture is to prevent the chloride ions from reacting with the steel surface and also to increase the time needed for the chloride ions to penetrate through the concrete cover. Corrosion inhibitors are chemical substance which decreases the corrosion rate when present in the corrosion system at a suitable concentration without significantly changing the concentration of any other corrosive agent (Ismail et al., 2010b).

In recent studies (Abdulrahman et al., 2011b; Raja and Sethuraman, 2008; Uhlig, 2004) green inhibitors have proved more effective and environmentally benign than organic and inorganic inhibitors in chemical and petrochemical industries. Consequently, more work in this area is necessary in order to ascertain the compatibility and suitability of green inhibitor to reinforced concrete to minimize the risk posed by organic and inorganic inhibitors to environmental and sustainability.

2. EXPERIMENTAL PROCEDURE
2.1. Materials used
Ordinary Portland Cement (OPC) was used in this research. The chloride was admixed into the concrete as magnesium chloride of analytical reagent grade. The concentrations of Magnesium chloride used was 1.5% and 4.5% by mass of cement and the corresponding chloride concentrations were 0.94% and 2.82% respectively. Coarse aggregates of size 20 mm and 10 mm of quartzite origin were used in the ratio of 1.78:1 to satisfy the overall grading requirement of coarse aggregate (Ismail et al., 2011).
Land quarried sand passing through ASTM sieve no. (4.57mm) conforming to zone II classification of British standard was used as fine aggregate. The sand has a fineness modulus of 2.5. Tap water was used for the preparation of specimens. All the concrete mixes were designed for similar workability with slump of 30-60 mm. The water content was kept constant to 230 kg/m$^3$ for the desired slump in all the mixes to have similar workability. The water-cement ratio (w/c) used were 0.45 and 0.65. The fresh density of concrete was then obtained as per guidelines specified by British method of mix selection (DOE) to be 2380Kg/m$^3$. The design mix is as presented in companion paper (Abdulrahman et al., 2012).

2.2. Corrosion rate measurement

Corrosion behaviours of embedded steel in concrete were monitored by electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR) using the Shikoku Research Institute Portable Rebar Corrosion Meter (SRI-CM-III). Measurements were done at the corrosion potential; the amplitude of the sine wave perturbation was 10mV in frequency range of 10 KHz to 10 mHz, 25 points sweep density per frequency decade were collected. Standard silver chloride electrode was used as reference, stainless steel disc as central and guard counter electrode and 16 mm diameter mild steel was used as working electrode. EIS measurements were carried out after 360 days of exposure to wet and dry cycles. Initially the specimens were cured in seawater for 28 days at a laboratory temperature of 28°C after 24h of casting. Polarization resistance ($R_p$) (that is, charge transfer resistance) values obtained from Nyquist plot which was calculated from the diameter of the semi-circle extrapolated in the low frequency range between 10 KHz and 10 mHz. By assuming B as 26 mV, the corrosion current density ($i_{corr}$) ($\mu$ A/cm$^2$) was calculated using Stern-Geary equation in accordance with earlier work of Vishnudevan, Thangavel (2006).

\[ i_{corr} = \frac{B}{R_p} \]

Where B is a constant which is a function of the anodic and cathodic Tafel slopes, $b_a$ and $b_c$

\[ B = \frac{b_a \times b_c}{2.303(a + b_c)} \]

In this investigation B value of 26 mV was used for both active and passive state of rebar, since the system was premixed with magnesium chloride except control sample (Vishnudevan, Thangavel, 2006).

Corrosion rate (mmpy) of the exposed rebar is measured by using following formula:

\[ \text{Corrosion rate (mm/year)} = \frac{0.00387 \times a \times i_{corr}}{n \times D} \]

Where $i_{corr}$ = corrosion current density in $\mu$ A/cm$^2$, $a$ = atomic weight of iron, that is, 55.845 g/mol, $n$ = no. of electrons exchanged in corrosion reaction, that is 2 for iron, $D = $ density of steel (7.85 g/cm$^3$). The double layer capacitance was calculated from $R_p$ values using the formula:

\[ C_{dl} = \frac{1}{2\pi \times F_{max} \times R_p} \]

Where $F_{max}$ = frequency maximum, $R_p$ = polarization resistance.

For calculation of the corrosion current density for EIS, the assumed model for the steel/concrete interface is shown in Figure-1. Steel-concrete interface is represented by a simple equivalent electric circuit. The equivalent circuit consists of concrete resistance $R_c$ in series with the interface impedance. The interface impedance consists of polarization resistance $R_p$ in parallel with a double layer capacitance $C_{dl}$. Frequency dependent impedance $Z(\omega)$ of the electrical equivalent circuit shown in Figure-1 is given by the following expression:

\[ Z(\omega) = R_c + \frac{1}{(1 + \omega^2 R_p C_{dl})} \]

And at very high frequencies

\[ Z(\omega) \rightarrow \infty(\omega) = R_c \]

Therefore $R_c$ measured at high frequency can be subtracted from $R_p + R_c$ measured at low frequency to give a compensated value of $R_p$ free of ohmic interferences in high resistivity medium like concrete.
Impedance behaviour of an electrode may be expressed in Nyquist plots of \( Z' (\omega) \) (imaginary component) as a function of \( Z'' (\omega) \) (real component). The Nyquist plot would show a semicircle with frequency increasing in a counterclockwise direction. At very high frequency, the imaginary component \( Z' (\omega) \) disappears, leaving only the concrete resistance, \( R_c \). At very low frequency, \( Z'' (\omega) \) again disappears leaving a sum of \( R_c \) and \( R_p \). Thus the radius of the semi circle is \( \frac{R_p}{2} \).

3. RESULTS AND DISCUSSIONS

3.1. Corrosion potential (\( E_{corr} \)) of embedded steel

Corrosion potential (\( E_{corr} \)) monitoring and electrochemical impedance spectroscopy (EIS) was the techniques used for this study. These techniques have being extensively used in laboratory investigations of the corrosion behaviour of reinforced concrete exposed to chloride-containing environment (Ann et al., 2006; De-Schutter and Luo, 2004; Kondratova et al., 2003). EIS has the major advantage of providing the possibility of establishing a physical interpretation of the processes involved.

Figures 2-3 shows the typical corrosion potential (\( E_{corr} \)) behaviour, as a function of exposure time in days, of reinforced concrete with w/c ratio of 0.45 subjected to wet and dry cycle. Starting potential was 10 mV vs. Ag/AgCl electrode. Starting at approximately six months of exposure, potentials of reinforcing steel were not indicative of corrosion likelihood in the concrete mix according to ASTM C876-09.

Generally, going by the potential results of all the inhibitors, their inhibitions were adequate for 0.45 w/c ratios. But Bambusa arundinacea standout for excellent inhibition for both mixes as can be seeing in Figures 2-3. However, with increasing periods of exposure, the potential values tended to decrease (become more positive). This is due to the hydration process of cement paste which corresponds to the compressive strength values recorded. This work demonstrates that adequate good protection is already provided with 2% of inhibitor that is below the recommended amount (4%) (Pech-Canul and Castro, 2002).

3.2 Corrosion current

Corrosion current density (\( I_{corr} \)) represents instantaneous rate of corrosion at the particular time of voltage measurement, and changes frequently over time for specimen according to Raafat et al. (2011). \( I_{corr} \) values corresponding to reinforcement in the two mixes for this research are presented in Figures 4-5 as a function of exposure time. They are calculated from the polarization resistance values using a Stern-Geary constant of 26 mV.

Corrosion current density is most widely treated as an indication of the corrosion performance of steel in concrete. Its values from 0.1 \( \mu \text{A/cm}^2 \) to 0.5 \( \mu \text{A/cm}^2 \) were used as the borderlines between passive and active corrosion as was indicated in previous work by Królikowski and Kuziak (2011).

Starting with values in the order of 0.01 \( \mu \text{A/cm}^2 \) corresponding to steel in passive condition according to earlier research by Pech-Canul and Castro (2002), there was tendency of \( I_{corr} \) to increase beyond 0.2 \( \mu \text{A/cm}^2 \) for MgCl\(_2\) contaminated sample, 4% Ca (NO\(_2\))\(_2\) and 4% C\(_2\)H\(_7\)NO inhibited samples until 300 days exposure for 0.45 w/c ratios as evident in Figure-4. While 2% for all
three inhibitors, 4% *Bambusa arundinacea* and control sample were still within passive region for same exposure period. Also from Figure-5 only C₂H₇NO inhibitor and control sample were within passive region (that is, below 0.2 µA/cm²) for the first 300 days of exposure before the other inhibitors reduced to within the passive region at 360 days exposure as a result of complete cement paste hydration. This behaviour is not surprising and is in agreement with earlier report by other authors (Jamil et al., 2003; Dhouibi et al., 2002; Tommaselli et al., 2009; Pradhan, Bhattacharjee 2009).

3.3. Electrochemical impedance spectroscopy (EIS) measurements

EIS is a powerful technique for obtaining detailed knowledge of conductive anode system and used to monitor electrical properties (material behaviour) of reinforced concrete in aggressive environment. It provides information on a number of parameters, such as the presence of surface films, interfacial reaction and mass-transfer phenomena (Jing, Wu, 2011). Impedance spectra (in Nyquist representation format) of EIS data obtained before and after the additions of the three inhibitors at the different concentrations studied and used as corrosion inhibitors after 12 months of exposure in the corrosive medium (seawater) for wet and dry cycles are presented in Figures 6-9.
confirm that Icorr is dependent on frequency. Since the absence of double layer capacitance, then there will be surfaces. Vedalakshmi resistance ($R_c$) and polarization resistance ($R_p$) values were the same pattern of trends for the metal and the cement paste electrolyte.

The non-linear reactive part of the electrode impedence contains double layer capacitance ($C_{dl}$) and pseudo capacitance in the frequency measurement. In concrete, pseudo capacitance arises due to the adsorption of OH, K+, Na+ and Ca2+ ions on the reinforcement surfaces. Vedalakshmi et al. (2009) suggested that if there is absence of double layer capacitance, then there will be no frequency dependence. But data presented in Figures 6-7 confirm that $I_{corr}$ is dependent on frequency. Since the process may have large time constants, the reactive part of the impedance spectra cannot be eliminated completely. But at a lower frequency of 10 mHz, both passive and active conditions of reinforcement were fulfilled, ensuring that the measured current passes through the charge transfer resistance ($R_q$) rather than $C_{dl}$. The double layer capacitance reduces after adsorption of the inhibitors since the adsorbed film reduces the dielectric constant between the metal and the cement paste electrolyte.

From Figures 6 and 8, the Nyquist plots shows the same pattern of trends for the Bambusa arundinacea inhibitor efficiency 360 days exposure for inhibition of MgCl2 contaminated concrete containing 0.94% chlorides, even more than the control samples and other inhibitors. This might be attributed to the hydrophobic capacitive nature of the film ($\gamma$-Fe2O3) formed on the rebar surface with a large time constant indicative of passive steel. The region of real impedence and imaginary impedence which increase continuously is known as Warburg impedence, which cause shielding or resistance effect for the metal corrosion according to similar research by Ali et al. (2007). The observed impedence of the inhibitors is as a result of the slow diffusion of oxygen through the concrete matrix and the dielectric film component of solid hydroxide layer at the steel-concrete interface. These processes can be attributed to the electrochemical reaction on the electrode (film) surface and the associated charge-transfer resistance and double-layer capacitance which was also observed in previous work by Tommaselli et al. (2009).

On the other hand, in the contaminated concrete containing 2.82% chloride, the Nyquist plot yields a shortend curve indicating the break-down of dielectric film due to chlorides which can be observed in Figures 7 and 9. The addition of chloride decreases the charge transfer resistance which indicates the competition between the aggressive chloride ions and the passivating hydroxyl ions. Chloride ion might have reacted with hydrated tricalciumaluminate ($C_3A$) hydrate to form chloroaluminate ($C_3A.CaCl_2.10H_2O$) which may contain 75-90% chloride according to study by Indrajit et al. (2011). Since it has exceeded threshold chloride level, the protective passive layer would be destroyed as in the case of chloride contaminated samples. In general, the chloride threshold is taken to be 0.15% of the soluble chloride by weight of cement. So, 0.94% and 2.82% chloride has far exceeded the commonly accepted corrosion threshold in this work.

It is important to note that the three inhibitors exhibited almost the same behaviour during all the test times and for all the concentrations. The polarization resistance ($R_p$) of the steel surface representing the resistance to current flow across the steel-concrete interface at a corrosion potential, is dependent on the formation of passive film of iron hydroxides/oxides during the process of corrosion and is expected to decrease if this protective film is broken under certain conditions. $R_p$ which is the rate determining resistance at the reinforcing steel corrosion, therefore, as the $R_p$ increases the corrosion rate decreases and the capacitance of interface also decreases. This is evident in this work as inhibited contaminated concrete shows low corrosion rate. But Bambusa arundinacea exhibited lowest corrosion rate, $C_{dl}$ and highest $R_p$ values for the entire period of exposure. The large arcs observed from high to low frequencies in Figures 6-9, indicates that the polarization resistance, $R_p$, becomes dominant due to adsorption of inhibitors. Also the inhibition efficiency derived from the $R_p$ values of the impedance measurement shows that Bambusa arundinacea is consistently higher compared to other two inhibitors for 0.45w/c at 1.5% MgCl2 contamination. Only ethanolamine inhibition efficiency was adequate for
0.45 w/c at high 4.5% MgCl₂ contamination. Inhibition efficiency was derived from the below expression according to Cruz et al. (2004).

\[
\%IE \left( R_p \right) = \frac{R_p \left( C_{dl} \right) - R_p \left( inh \right)}{R_p \left( C_{dl} \right)} \times 100.
\]

Where \( R_p \) is the polarization resistance without inhibitor and \( R_p \left( inh \right) \) is the polarization resistance with inhibitor. Meanwhile the \( R_p \) values obtained from impedance measurements enable us to validate corrosion inhibition properties of these three inhibitors studied as a function of time.

**4. CONCLUSIONS**

In view of the outlined objectives earlier mentioned in this research work and subsequent series of investigations conducted as well as the results obtained, the following conclusions were drawn:

- The electrode potentials of reinforcing steel were not indicative of early corrosion likelihood in the concrete mix.
- The potential results of all the inhibitors and their inhibitions were adequate for 0.45 w/c ratios, but *Bambusa arundinacea* stand out for excellent inhibition.
- Corrosion current density (\( I_{corr} \)) which represents instantaneous rate of corrosion at the particular time of voltage measurement, increases beyond 0.2\( \mu \text{A/cm}^2 \) for MgCl₂ contaminated sample, 4% Ca(NO₂)₂ and 4% C₂H₇NO inhibited samples at age of 360 days exposure for 0.45 w/c ratios. While 2% for all three inhibitors, 4% *Bambusa arundinacea* and control sample were still within passive region for same exposure period.
- The pore blocking effects of *Bambusa arundinacea* prevented the formation of differential aeration of cells that promote corrosion on the steel surface as a result of oxygen level due to it high concrete resistance. Also, the lower value of double layer capacitance \( C_{dl} \) of *Bambusa arundinacea* could be associated with its adsorption mode. This confirmed its adsorbed molecules paralleled to metal surface, and decreased the number of surface active sites due to its hydrophobic characteristics. The double layer capacitance reduces after adsorption of the inhibitors since the adsorbed film reduces the dielectric constant between the metal and the cement paste electrolyte.
- The addition of chloride decreases the polarization resistance (\( R_p \)) which indicates the competition between the aggressive chloride ions and the passivating hydroxyl ions. *Bambusa arundinacea* exhibited lowest corrosion rate, lowest \( C_{dl} \) and highest \( R_p \) values for the entire period of exposure despite exceeding chloride threshold value.
- Nyquist plots shows the same pattern of trends for the *Bambusa arundinacea* inhibitor efficiency at 360 days exposure for inhibition of MgCl₂ contaminated concrete containing 0.94% chlorides, even more than the control samples and other inhibitors. This might be attributed to the hydrophobic capacitive nature of the film (\( \gamma - \text{Fe}_2\text{O}_3 \)) formed on the rebar surface with a large time constant indicative of passive steel, the region of real impedance and imaginary impedance which increase continuously cause shielding or resistance effect for the metal corrosion. The observed impedance of this inhibitor is as a result of the slow diffusion of oxygen through the concrete matrix and the dielectric film component of solid hydroxide layer at the steel-concrete interface.
- It was observed that corrosion rate is inversely proportional to concrete resistance. Thus resistance can be considered as general parameter for describing performance of reinforced concrete structures subjected to chloride contamination.

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