

*Full Length Research Paper*

# Evaluation of corrosion inhibiting admixtures for steel reinforcement in concrete

Abdulrahman A. S.<sup>1,2\*</sup> and Mohammad Ismail<sup>1</sup>

<sup>1</sup>Faculty of Civil Engineering, University Technology Malaysia, 81310 UTM, Johor Bahru, Johor, Malaysia.

<sup>2</sup>Mechanical Engineering Department, Federal University of Technology, P. M. B. 65, Minna, Niger State, Nigeria.

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Inhibitors are added to concrete to improve its quality and integrity. The various inhibitors used in the construction industry to salvage the book or service life of steel reinforcement in concrete structures are broadly classified into organic and inorganic corrosion inhibitors and other methods which include cathodic protection, coatings to the reinforcement, penetrating sealers and chloride removal. In recent years, the use of these inhibitors in producing high performance concrete has increased significantly. Organic base (Amine) and inorganic base (Nitrite) have been known for protection of concrete structures but are not commercially indigenous to most developing economies due to manufacturing difficulties and are toxic to the environment. Also the inhibitors are not known to stop chloride attack in concrete. Hence, the objective of the present investigation was to study a novel, eco-friendly and hydrophobic green plant extracts inhibitor and compares its effectiveness with calcium nitrite and ethanolamine inhibitors. *Bambusa arundinacea* (Green plant extracts), calcium nitrite and ethanolamine corrosion inhibitors were selected for the present investigation. Compressive strength, electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR) technique were used for 180 days of exposure. The results of the inhibitors studied showed that *B. arundinacea* has superior compressive strength and the corrosion rate was the lowest compared to calcium nitrite and ethanolamine. *B. arundinacea* may be considered a better substitute for nitrite and amine- based corrosion inhibiting admixtures for durable concrete structures due to its hydrophobic effects and environmentally benign.

**Key words:** Concrete, chloride attack, inhibitors, steel reinforcement, green plant extracts.

## INTRODUCTION

The premature failure of reinforced structures is a serious problem for the developed and emerging economies. Corrosion of steel reinforcement is the major cause of these deterioration and early failure of reinforced concrete structures. The main cause of concrete contamination has been identified as chloride ions which depassivate otherwise passive alkaline concrete (Raafat et al., 2011; Ueli et al., 2011). Indrajit et al. (2011) 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.

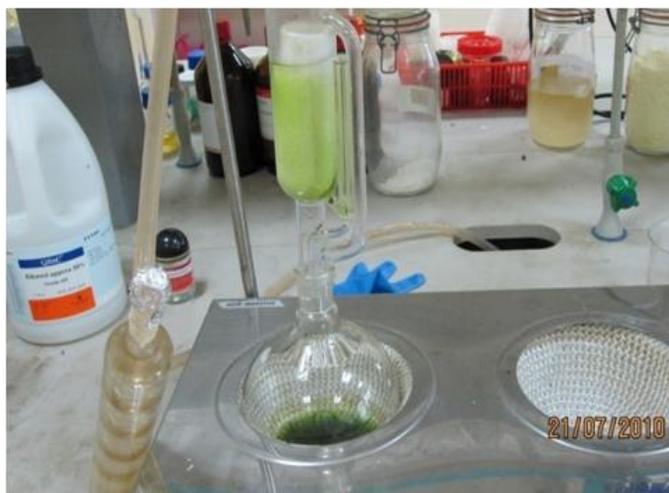
Over the years, a number of protection measures have been suggested by many researchers to delay, slow, or stop the corrosion process, thereby enhancing the service life of concrete structures. Some of the practical methods suggested for the control of steel corrosion in concrete were the uses of glass fibers, silica fumes and corrosion inhibitors either preventive or curative treatment (Morris and Vázquez, 2002; Ngala et al., 2002; Kondratova et al., 2003; Ngala et al., 2003; Berke and Hicks, 2004; Montes et al., 2004; Ann et al., 2006; Kubo et al., 2007; Saraswathy and Ha-Won, 2007; Benzina et al., 2008; Al-Mehthel et al., 2009; Ahmet et al., 2011; Saidi et al., 2011).

Most of these corrosion inhibitors which are presently in

\*Corresponding author. E-mail: [aspita2@gmail.com](mailto:aspita2@gmail.com).

**Table 1.** Concrete mix proportions.

Water-Cement ratio (w/c)	Water content (kg/m <sup>3</sup> )	Cement content (kg/m <sup>3</sup> )	Fine aggregate (kg/m <sup>3</sup> )	Coarse aggregate (kg/m <sup>3</sup> )
0.45	230	511	623	1016

**Figure 1.** Soxhlet extraction process.

use are not eco-friendly and biodegradable, hence the need to develop one which is sustainable. In this work, a green plant extract (*Bambusa arundinacea*) which has been proven to be biodegradable, cheap and environmentally benign (Abdulrahman et al., 2011a) was used to inhibit chloride induced corrosion of reinforcement in concrete.

## MATERIALS AND METHODS

Ordinary Portland cement (OPC) was used in this research. Chemical compositions accompanied by some important physical and mechanical properties of the cement are same as in the companion paper (Abdulrahman et al., 2011b). The chloride was admixed into the concrete as magnesium chloride of analytical reagent grade. The concentrations of magnesium chloride used were 1.5% by mass of cement and the corresponding chloride concentrations was 0.94%. Coarse aggregates of size 20 and 10 mm of quartzite origin were used in the ratio of 1.78:1 to satisfy the overall grading requirement of coarse aggregate (Pradhan and Bhattacharjee, 2009).

Land quarried sand passing through American Standards for Testing and Materials (ASTM) sieve No.(4.57 mm) 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 to 60 mm. The water content was kept constant to 230 kg/m<sup>3</sup> for the desired slump in all the mixes to have similar workability. The water-cement ratio (w/c) used was 0.45. The fresh density of concrete was then obtained as per guidelines specified by British method of mix selection of Department of Environment (DOE) to be 2380 kg/m<sup>3</sup>. Design mix is as presented in Table 1.

## Preparation of plant extracts

Fresh leaves of *B. Arundinacea* (Indian Bamboo) was washed under running water, shade dried and ground into powder (Mohammad et al., 2011). The extraction was done using soxhlet extraction process. 3 g of pulverized samples were placed in a porous container and allowing condensed solvent (ethanol) to extract continuously. The condenser function was to cool the solvent vapour and cause it to condense (turn back to liquid). Figure 1 shows a ring type of condenser which functions by increasing the surface area that can be used to transfer heat. The extracts from soxhlet apparatus were rotary evaporated to expel the ethanol.

## Preparation of concrete specimens for compressive strength test

100 × 100 × 100 mm concrete cubes were prepared using 1:1.2:2 mixes designed with a water/cement ratio (w/c) ratio of 0.45. Inhibitor admixtures, namely 2% of calcium nitrite, ethanolamine and green *B. arundinacea* were added on the basis of weight of cement. The concrete cubes were demoulded after 24 h of casting and subjected to water curing. The specimens were removed after 7, 28, 90 and 180 days of curing and subjected to compressive strength testing (as per British Standard BS1881: Part 116: 1983) using compression testing machine of 2000 kN capacity.

## Corrosion specimens

The corrosion behaviors 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).

**Table 2.** Compressive strength test (MPa).

System studied	7 Days	28 Days	90 Days	180 Days
Control	30.83	43.27	54.87	41.31
Contaminated by MgCl <sub>2</sub>	39.34	48.22	51.90	43.80
Ca(NO <sub>2</sub> ) <sub>2</sub> inhibitor	47.89	60.70	48.87	44.35
C <sub>2</sub> H <sub>7</sub> NO inhibitor	45.65	49.58	70.98	72.09
<i>B. arundinacea</i> inhibitor	47.29	51.91	68.40	78.09

Measurements were done at the corrosion potential; the amplitude of the sine wave perturbation was 10 mV in frequency range of 10 KHz to 10 mHz, 25 points sweep density per frequency decade were collected. The standard silver chloride electrode was used as reference, stainless steel disc as central and guard counter electrode. While 16 mm diameter mild steel was used as working electrode. EIS measurements were carried out after 180 days of exposure of wet and dry cycles. Initially the specimens were cured in seawater for 28 days at a laboratory temperature of 28°C after 24 h of casting. The polarization resistance ( $R_p$ ) (that is, charge transfer resistance) values obtained from Nyquist plot 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 ( $I_{corr}$ ) ( $\mu\text{A}/\text{cm}^2$ ) was calculated using Stern-Geary equation (Vishnudevan and 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  $b_c$

$$B = \frac{b_a \times b_c}{2.303(b_a + b_c)}$$

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

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

$$\text{The corrosion rate (mm/year)} = \frac{0.00327 \times a \times I_{corr}}{n \times D}$$

where  $I_{corr}$  = corrosion current density in  $\mu\text{A}/\text{cm}^2$ ; 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<sup>3</sup>). 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.

## RESULTS

### Compressive strength of concrete

The compressive strength of control, chloride contaminated

and inhibitor admixture concrete cubes tested after 7, 28, 90 and 180 days of exposure to water at 28°C are presented in Table 2.

### Linear polarization resistance (LPR) technique and electrochemical impedance spectroscopy (EIS) studies

The polarization resistance ( $R_p$ ), concrete resistivity ( $R_c$ ) and corrosion rate calculated from the LPR technique for control, contaminated and inhibitor admixture concrete are reported in Table 3. Also the double layer capacitance ( $C_{dl}$ ) that characterizes the charge separation between metal and electrolyte interface, polarization resistance ( $R_p$ ), corrosion rate calculated from EIS studies for all the samples were equally presented in Table 3 as derived from Nyquist plot as shown in Figure 2.

## DISCUSSION

### Compressive strength of concrete

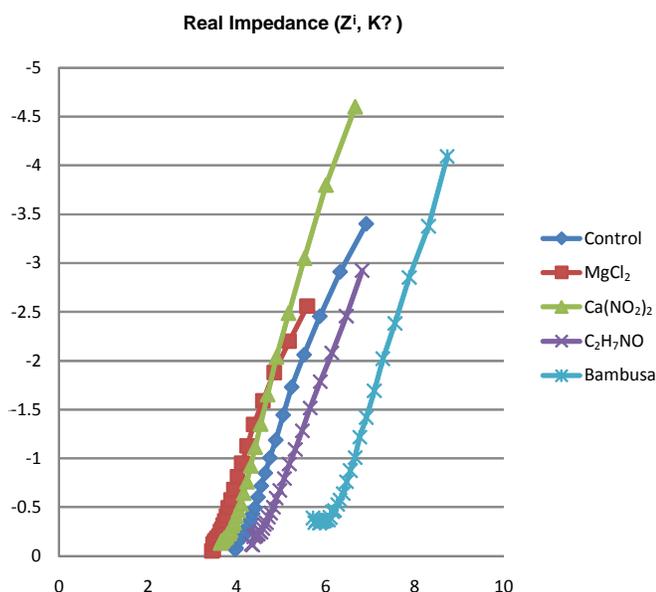
The results of the compressive strength test indicated that the additions of inhibitors increased the compressive strength of concrete when compared to the control specimen. These results show that there was an increase of 20 to 78% in the strength of concrete by adding *B. arundinacea* within the exposure period of 7 to 180 days. Ethanol amine (C<sub>2</sub>H<sub>7</sub>NO) inhibitor increased the strength by 16 to 64% for the same period. On the other hand, the addition of calcium nitrite (Ca(NO<sub>2</sub>)<sub>2</sub>) inhibitor shows initial increase of 22 to 26% between 7 and 28 days strength but declined to just 1.3% increase for 180 days strength. This trend in strength of (Ca(NO<sub>2</sub>)<sub>2</sub>) inhibitor addition to concrete is in line with earlier research reported by Kondratova et al. (2003).

### Linear polarization resistance measurements (LPR) and electrochemical impedance spectroscopic (EIS) study

The results of LPR and EIS tests in Table 3 shows that the concrete resistivity ( $R_c$ ) and polarization resistance ( $R_p$ )

**Table 3.** Measurement of corrosion rate by EIS and LPR technique.

System studied	Time (Days)	LPR				EIS				
		R <sub>c</sub> (KΩ)	R <sub>p</sub> (KΩ)	I <sub>corr</sub> (μA/cm <sup>2</sup> )	C.R (10 <sup>-3</sup> Mmpy)	C <sub>dl</sub> (mF)	R <sub>c</sub> (kΩ)	R <sub>p</sub> (kΩ)	I <sub>corr</sub> (μA/cm <sup>2</sup> )	C.R (10 <sup>-3</sup> Mmpy)
Control	180	4.10	170	0.1525	1.80	0.112	3.97	142	0.1883	2.19
Contaminated by MgCl <sub>2</sub>	180	3.42	130	0.2008	2.30	0.133	3.44	120	0.2179	2.50
Ca(NO <sub>2</sub> ) <sub>2</sub> inhibitor	180	3.46	226	0.1153	1.30	0.115	3.64	138	0.1883	2.19
C <sub>2</sub> H <sub>7</sub> NO inhibitor	180	4.41	136	0.1916	2.20	0.106	4.33	150	0.1735	2.02
<i>B. arundinacea</i> inhibitor	180	5.71	202	0.1285	1.50	0.080	5.73	198	0.1312	1.53

**Figure 2.** Nyquist plot of rebar embedded in concrete.

values were more higher for Ca(NO<sub>2</sub>)<sub>2</sub>, C<sub>2</sub>H<sub>7</sub>NO and *B. arundinacea* inhibitors admixture concrete as compared to the control and chloride contaminated concrete. R<sub>c</sub> is considered to be high if the value is greater than 4 kΩ. But *B. arundinacea* was outstanding compared with others two inhibitors. This might be due to its pore blocking effects which prevented the formation of differential aeration of cells that promote corrosion on the steel surface as a result of oxygen level. Also the lower value of double layer capacitance C<sub>dl</sub> of *B. 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. From Figure 2, the Nyquist plot shows the capacitive nature of the film (γ-Fe<sub>2</sub>O<sub>3</sub>) formed on the rebar surface with a large time constant indicative of passive steel as results inhibitors additions. The region of real impedance and imaginary impedance which increase continuously is known as Warburg impedance, which cause shielding or resistance

effect for the metal corrosion according to similar research by Ali et al. (2007). The observed impedance 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. In the contaminated concrete containing 0.94% chloride, the Nyquist plot yields a shorten curve indicating the break-down of dielectric film due to chlorides. 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 tricalcium aluminate (C<sub>3</sub>A) hydrate to form chloroaluminate (C<sub>3</sub>A.CaCl<sub>2</sub>.10H<sub>2</sub>O) which may contain 75 to 90% chloride (Indrajit et al., 2011). Since it has exceeded threshold chloride level, the protective passive layer would be destroyed. In general, the chloride threshold is taken to be 0.15% of the soluble chloride by weight of cement. So, 0.94% chloride has far exceeded the commonly accepted corrosion threshold in this work.

The R<sub>p</sub> is the rate determining resistance at the reinforcing steel corrosion; therefore, as the R<sub>p</sub> increases the corrosion rate decreases. This is evident in this work as inhibited contaminated concrete shows low corrosion rate. But *B. arundinacea* exhibited lowest corrosion rate as shown in Table 3.

## Conclusions

The following conclusions can be drawn from this work, in the abilities of calcium nitrite (Ca(NO<sub>2</sub>)<sub>2</sub>), ethanol amine (C<sub>2</sub>H<sub>7</sub>NO) and *B. arundinacea* to inhibit the initiated corrosion of steel embedded chloride contaminated concrete:

1. Inhibitors additions to chloride contaminate concrete have no harmful effects on the compressive strength, rather all the inhibitors increase the strength tremendously, except calcium nitrite (Ca(NO<sub>2</sub>)<sub>2</sub>) that showed reduction in strength over time. But *B. Arundinacea* inhibitor showed superior strength over and above ethanol amine and calcium nitrite inhibitors.
2. The polarization resistance, concrete resistivity and

double layer capacitance taken from impedance data can serve directly as an indicator of the corrosion behaviour of steel in concrete or contaminated concrete without need of their conversion into corrosion current density or corrosion rate.

3. *B. arundinacea* can be effective as mixed type corrosion inhibitor for steel reinforcement in concrete, when it is added to fresh concrete.

4. *B. arundinacea* is eco-friendly, which did not contain heavy metals, that is eliminating the fear of possible formation of dioxin from chlorine-containing water. Dioxin is persistent and accumulates in fatty tissue which is highly toxic to humans.

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## REFERENCES

- Abdulrahman AS, Mohammad I, Mohammad SH (2011a). Inhibiting Sulphate Attack on Concrete by Hydrophobic Green Plant Extract. *Adv. Mat. Res.*, 250-253: 3837-3843.
- Abdulrahman AS, Mohammad I, Mohammad SH (2011b). Inhibition of Corrosion of Mild Steel in Hydrochloric Acid by *Bambusa Arundinacea*. *Int. Rev. Mechanical Eng.*, 5(1): 59-63.
- Ahmet B, Celalettin B, Semsettin K, Ayhan S (2011). Effect of mineral admixtures on properties of lightweight pumice concrete. *Int. J. Phy. Sci.* 6(7): 1591-1603
- Al-Mehthel M, Al-Dulajjan S, Al-Idi SH, Shameem M, Ali MR, Maslehuiddin M (2009). Performance of generic and proprietary corrosion inhibitors in chloride-contaminated silica fume cement concrete. *Construction and Building Materials*, 23(5): 1768-1774.
- Ali GA, Kadriye K, Mehmet E (2007). The effect of thiosemicarbazide on corrosion resistance of steel reinforcement in concrete. *Construction and Building Materials*, 21: 669-676.
- Ann KY, Jung HS, Kim HS, Kim SS (2006). Effect of Calcium nitrite-based corrosion inhibitor in preventing corrosion of embedded steel in concrete. *Cement Concrete Research* 36: 530-535.
- Benzina MLL, Dhouibi M, Ben Oueddou ET, Zucchi F (2008). Investigation of the early effectiveness of an amino-alcohol based corrosion inhibitor using simulated pore solutions and mortar specimens. *Cement and Concrete Composites* 30(3): 167-173.
- Berke NS, Hicks MC (2004). Predicting long-term durability of steel reinforced concrete with calcium nitrite corrosion inhibitor. *Cement and Concrete Composites* 26(3): 191-198.
- Indrajit R, George CP, Julio FD (2011). Effect of Concrete Substrate Repair Methods for Beams Aged by Accelerated Corrosion and Strengthened with CFRP. *J. Aerosp. Eng. © ASCE*: 227-239.
- Kondratova IL, Montes P, Bremner TW (2003). Natural marine exposure results for reinforced concrete slabs with corrosion inhibitors. *Cement and Concrete Composites* 25(4-5): 483-490.
- Kubo J, Sawada S, Page CL, Page MM (2007). Electrochemical injection of organic corrosion inhibitors into carbonated cementitious materials: Part 2. Mathematical modelling. *Corrosion Science* 49(3): 1205-1227.
- Mohammad I, Abdulrahman AS, Mohammad SH (2011). Solid waste as environmental benign corrosion inhibitors in acid medium. *Int. J. Eng. Sci. Technol. (IJEST)* 3(No.2): 1742-1748.
- Montes P, Bremner TW, Lister DH (2004). Influence of calcium nitrite inhibitor and crack width on corrosion of steel in high performance concrete subjected to a simulated marine environment. *Cement and Concrete Composites* 26(3): 243-253.
- Morris W, Vázquez M (2002). A migrating corrosion inhibitor evaluated in concrete containing various contents of admixed chlorides. *Cement and Concrete Research* 32(2): 259-267.
- Ngala VT, Page CL, Page MM (2003). Corrosion inhibitor systems for remedial treatment of reinforced concrete. Part 2: sodium monofluorophosphate. *Corrosion Science* 45: 1523-1537.
- Ngala VT, Page CL, Page MM (2002). Corrosion inhibitor systems for remedial treatment of reinforced concrete. Part 1: calcium nitrite. *Corrosion Science* 44(9): 2073-2087.
- Pradhan B, Bhattacharjee B (2009). Performance evaluation of rebar in chloride contaminated concrete by corrosion rate. *Construction and Building Materials* 23(6): 2346-2356.
- Raafat EH, Amir M, Anna C, Sami R (2011). Effectiveness of Surface-Applied Corrosion Inhibitors for Concrete Bridges. *J. Mat. Civil Eng. © ASCE*: 271-280.
- Saidi M, Safi B, Benmounah A, Aribi C (2011). Effect of size and stacking of glass fibers on the mechanical properties of the fiber-reinforced-mortars (FRMs). *Int. J. Phys. Sci.*, 6(7): 1569-1582.
- Saraswathy V, Ha-Won S (2007). Improving the durability of concrete by using inhibitors. *Build. Environ.*, 42: 464-472.
- Ueli MA, Bernhard E, Claus KL, Oystein V (2011). Chloride induce reinforcement corrosion: Electrochemical monitoring of initiation stage and chloride threshold values. *Corrosion Science* 53: 1451-1464.
- Vishnudevan M, Thangavel K (2006). Evaluation of organic based corrosion inhibiting admixtures for reinforced concrete. *Anti-Corrosion Methods and Materials* 53(No. 5): 271-276.