Green Plant Extract as a passivation-promoting Inhibitor for Reinforced Concrete

Abdulrahman A. S.
Faculty of Civil Engineering, Universiti Teknologi Malaysia, 81310 UTM/
Mechanical Engineering Department, Federal University of Technology
Minna, Nigeria
asipita68@yahoo.com

Mohammad Ismail
Faculty of Civil Engineering
Universiti Teknologi Malaysia, 81310 UTM
Johor Bahru, Johor, Malaysia
mohammad@utm.my

ABSTRACT
The present corrosion inhibitors in market for the protection of steel reinforcement in concrete exposed to chloride attack are toxic to the environment and compromises sustainability drives. There is the needs to develop inhibitor that are eco-friendly and sustainable. In this work the ability of hydrophobic green plant extracts inhibitor (*Bambusa arundinacea*) to repassivates the chloride induced corrosion of steel was studied. Its efficacy and effectiveness was also compared with calcium nitrite inhibitor. Concrete mix was designed to 30MPa with 0.45 W/C ratios and 1.5% weight of cement content of chloride was added to initiate corrosion. Inhibitors additions were 2%. Electrochemical impedance spectroscopy, linear polarization resistance and Field emission spectroscopy (FESEM) were used to monitor corrosion behavior of steel at 180 days exposure period. Corrosion rate of the inhibitors studied showed that *Bambusa Arundinacea* is superior as compared to calcium nitrite as results of its high concrete resistivity, chloride binding property and polarization resistance. *Bambusa Arundinacea* may be considered a better substitute for nitrite based corrosion inhibiting admixtures for durable concrete structures due its versatility.

Keywords: Concrete; Chloride attack; Green plant extracts; Inhibitors; Carbon Steel

Introduction

Reinforcement steel in concrete normally acquires a permanent state of passivity due to the high alkalinity of the environment (Abd El Haleem et al. 2010a). pH values higher than 12 result from the liberation of $Ca(OH)_2$ and the presence of potassium and sodium hydroxides ensuring continuous protection of the steel (Abd El Haleem et al. 2010b; Abd El Haleem et al. 2010c). Presence of oxygen stabilizes the passive film on the surface of the embedded steel. Although the precise nature of the passive film is unknown, several views have been advanced in this context. A spinel α-Fe_3O_4–γ-Fe_2O_3 solid solution is proposed to form the passive film on steel (Batis and Rakanta 2005; Ann et al. 2010; Balafas and Burgoyne 2010). However, Contamination of concrete with ions like Cl^- causes breakdown of passivity and initiation of localized attack (El Hassan et al. 2010). Chloride ions can enter the concrete from de-icing salts, from sea water in marine environments, from chloride containing admixtures and/or from mixing water (Alvarez et al. 2011). Above a certain threshold chloride ion concentration, the passive layer on the reinforcing steel breaks down as a result of chloride induced pitting of steel (Berke 2005; Blau et al. 2007; Apostolopoulos and Koutsoukos 2008).

Over the years a number of protection measures have been suggested by many workers to delay, slow, or stop the corrosion process, thereby enhancing the service life of concrete structures. One of the practical methods suggested for the control of steel corrosion in concrete is the use of corrosion inhibitors either preventive or curative treatment (Trépanier et al. 2001; Tritthart 2003; Martínez and C. Andrade 2008; Tittarelli and Moriconi G. 2008; Tao et al. 2009; Tommaselli et al. 2009; Vedalakshmi et al. 2009; Yuan et al. 2009; Zhang et al. 2009; Zhang et al. 2009; Jing and Wu 2011).

Most of these corrosion inhibitors which are presently in 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. 2011b) was used to inhibit chloride induced corrosion of reinforcement in concrete. Hence in this work *Bambusa arundinacea* was used as a passivation- promoting inhibitor due its high content of alkali metals.

2.0 Materials and Methods

2.1 Materials used

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. 2011a). 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%.

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 was 0.45. The fresh density of concrete was then obtained as per guidelines specified by British method of mix selection (DOE) to be 2380Kg/m^3. Design mix is as presented in Table 1.

2.2 Preparation of plant extracts

Fresh leaves of *Bambusa Arundinacea* (Indian Bamboo) was washed under running water, shade dried and ground into powder. Details of the extraction process are as described in the paper (Mohammad et al. 2011).

2.3 Corrosion specimens

The corrosion behaviors of embedded steel in concrete were monitored by electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR) using the SRI-CM-III portable rebar corrosion meter. 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. The standard silver chloride electrode was used as reference, stainless steel disc as central and guard counter electrode. While 16mm 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^{o}C after 24h of casting. The surface morphologies and elemental analysis were observed by FESEM.

3. Results and Discussions

3.1 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 2. 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 2. The results of LPR and EIS tests shows that the concrete resistivity (R_c) and polarization resistance (R_p) values were more higher for $Ca(NO_2)_2$ and *Bambusa arundinacea* inhibitors admixture concrete as compared to the control and chloride contaminated concrete. R_c is considered to be high if the value is greater than 4 KΩ. But *Bambusa arundinacea* was outstanding compared with $Ca(NO_2)_2$ inhibitors. This is due to the present of high potassium which repassivates the concrete as evident in Figure 4 and Table 3. From Figure 1-3 there are presence of chloride which depassivate concretes and subsequently causes corrosion of the reinforcement, whereas in Figure 4 chloride disappeared as a result of passivating properties of *Bambusa arundinacea* inhibitor. This is a confirmation of low corrosion rate of 1.53 mmpy in Table 3 for *Bambusa arundinacea*.

Table 1. Concrete mix proportions

Water-cement Ratio (w/c)	**Water content (Kg/m^3)**	**Cement content (Kg/m^3)**	**Fine aggregate Content (Kg/m^3)**	**Coarse aggregate content (Kg/m^3)**
0.45	230	511	623	1016

Table 2. Measurement of corrosion rate by impedance and LPR technique

System studied	**Time Days**	**LPR**				**EIS**				
		R_c (KΩ)	**R_p (KΩ)**	**I_{corr} $\mu A/cm^2$**	**C.R (10^{-3}) mmpy**	**C_{dl} mF**	**R_c (KΩ)**	**R_p (KΩ)**	**I_{corr} $\mu A/cm^2$**	**C.R (10^{-3}) mmpy**
Control	180	4.10	170	0.1525	1.80	0.112	3.97	142	0.1883	2.19
Control with $MgCl_2$	180	3.42	130	0.2008	2.30	0.133	3.44	120	0.2179	2.50
$Ca(NO_2)_2$ Inhibitor	180	3.46	226	0.1153	1.30	0.115	3.64	138	0.1883	2.19
Bambusa Inhibitor	180	5.71	202	0.1285	1.50	0.080	5.73	198	0.1312	1.53

Table 3. Results of energy dispersive x-ray spectroscopy (EDS)

Sample	**Element Average weight (%)**										Corrosion Rate mmpy $\times 10^{-3}$
	C	**O**	**Al**	**Si**	**Cl**	**Ca**	**Mg**	**Fe**	**S**	**Total**	
Control	6.90	36.46	1.44	2.69	0.38	10.49	-	41.65	-	100	2.19
$MgCl_2$	6.90	42.99	3.20	2.67	1.03	21.04	-	21.36	0.85	100	2.50
$Ca(NO_2)_2$	6.58	41.80	2.4	5.82	0.69	18.50	0.29	23.92	-	100	2.19
Bambusa	5.98	37.97	1.48	4.04	-	14.15	0.28	36.11	-	100	1.53

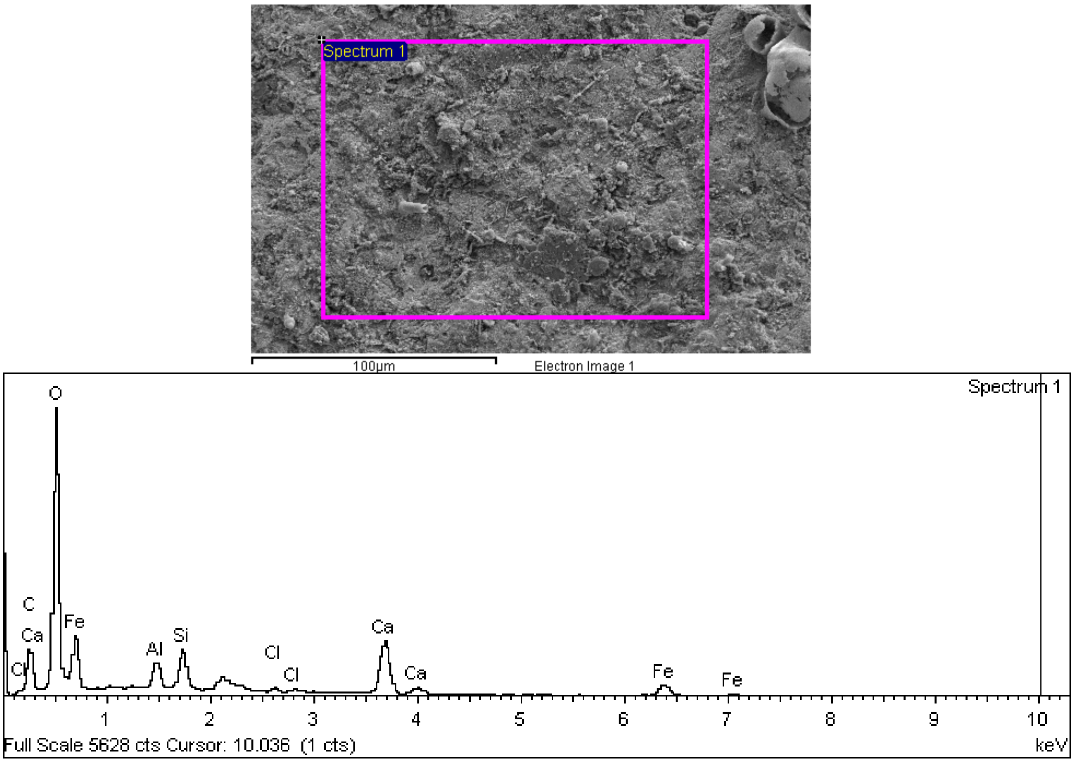

Figure 1: EDS for Control sample

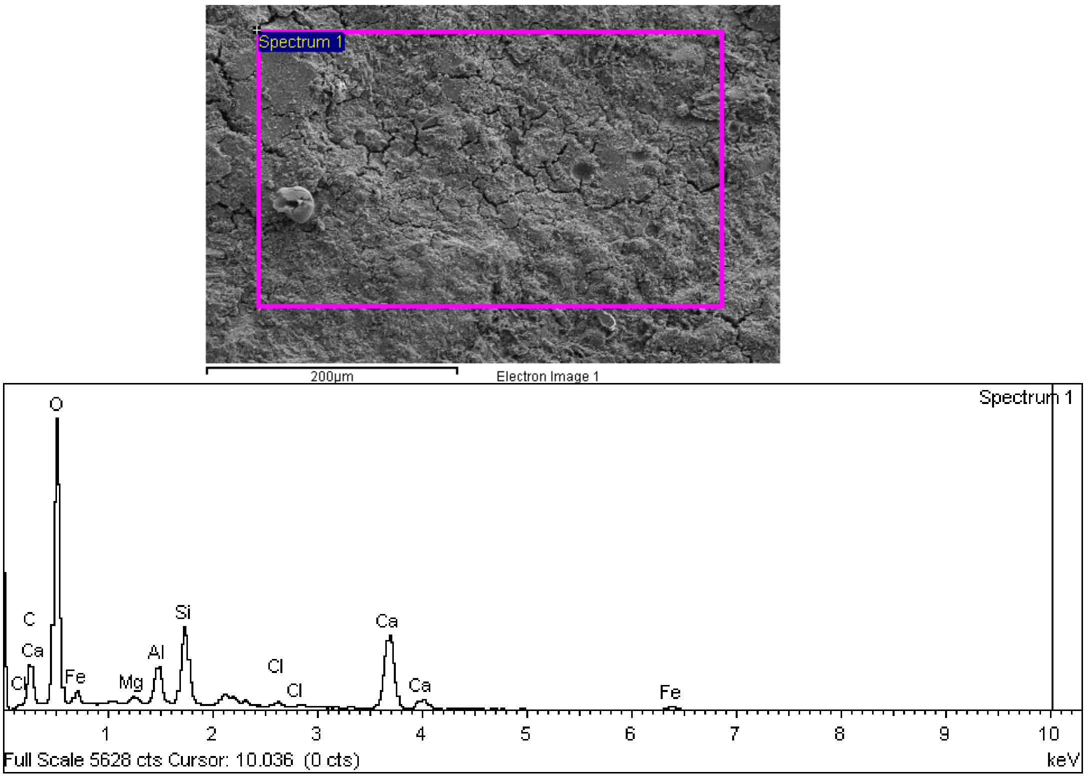

Figure 2: EDS for $MgCl_2$ salt contaminated sample

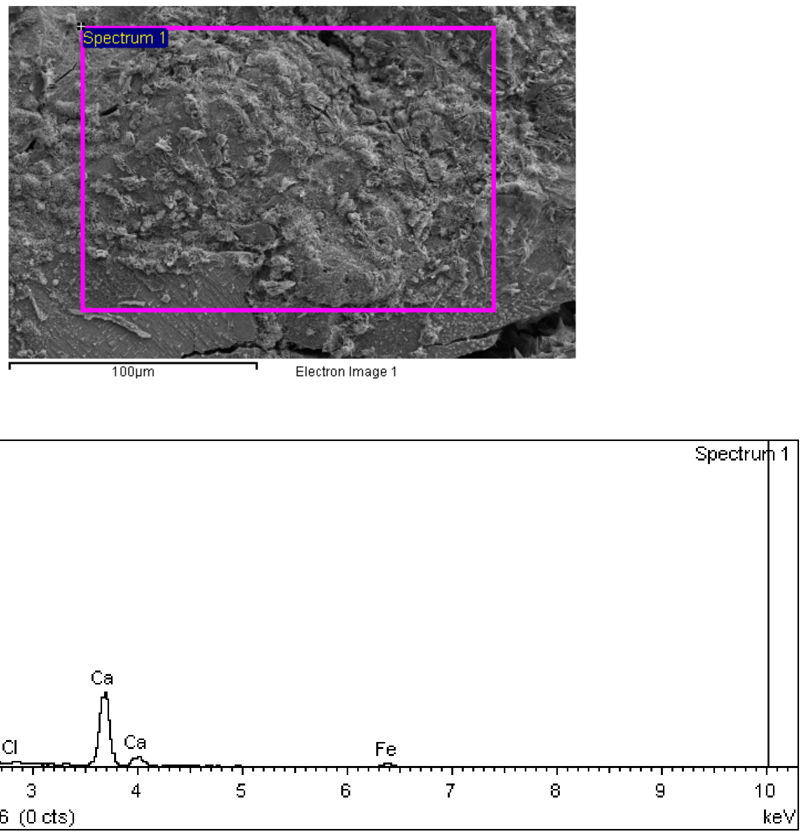

Figure 3. EDS for $Ca(NO_2)_2$ inhibited sample

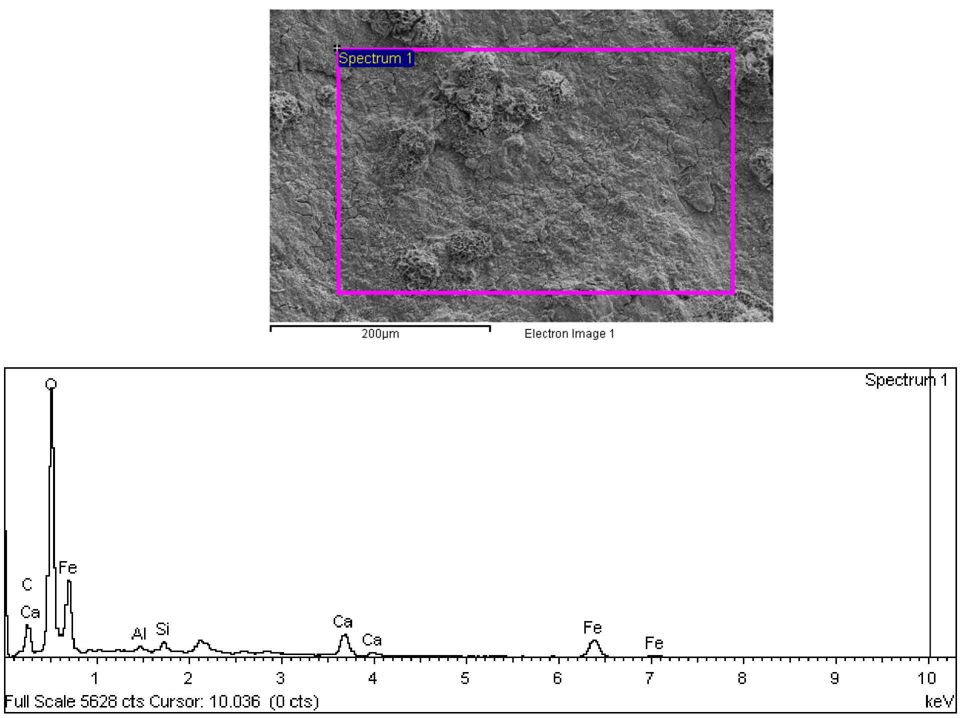

Figure 4: EDS for Bambusa inhibited sample

4. Conclusion

The following conclusions can be drawn from this work, in the abilities of $Ca(NO_2)_2$ and *Bambusa arundinacea* to inhibit the initiated corrosion of steel embedded chloride contaminated concrete:

1. 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.
2. *Bambusa Arundinacea* can be effective as mixed type corrosion inhibitor for steel reinforcement in concrete, when it is added to fresh concrete.

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References

[1] Abd El Haleem, S. M., E. E. Abd El Aal, S. Abd El Wanees and A. Diab (2010a). "Environmental factors affecting the corrosion behaviour of reinforcing steel: I. The early stage of passive film formation in Ca(OH)2 solutions." Corrosion Science **52**(12): 3875-3882.

[2] Abd El Haleem, S. M., S. Abd El Wanees, E. E. Abd El Aal and A. Diab (2010b). "Environmental factors affecting the corrosion behavior of reinforcing steel II. Role of some anions in the initiation and inhibition of pitting corrosion of steel in Ca(OH)2 solutions." Corrosion Science **52**(2): 292-302.

[3] Abd El Haleem, S. M., S. Abd El Wanees, E. E. Abd El Aal and A. Diab (2010c). "Environmental factors affecting the corrosion behavior of reinforcing steel. IV. Variation in the pitting corrosion current in relation to the concentration of the aggressive and the inhibitive anions." Corrosion Science **52**(5): 1675-1683.

[4] Abdulrahman, A. S., Mohammad Ismail and Mohammad Sakhawat Hussain (2011a). "Inhibiting Sulphate Attack on Concrete by Hydrophobic Green Plant Extract." Advanced Materials Research **250-253**: pp 3837-3843.

[5] Abdulrahman, A. S., Mohammad Ismail and Mohammad Sakhawat Hussain (2011b). "Inhibition of Corrosion of Mild Steel in Hydrochloric Acid by Bambusa Arundinacea." International Review of Mechanical Engineering **5**(No.1): 59-63.

[6] Alvarez, S. M., A. Bautista and F. Velasco (2011). "Corrosion behaviour of corrugated lean duplex stainless steels in simulated concrete pore solutions." Corrosion Science **53**(5): 1748-1755.

[7] Ann, K. Y., T. S. Kim, J. H. Kim and S. H. Kim (2010). "The resistance of high alumina cement against corrosion of steel in concrete." Construction and Building Materials **24**(8): 1502-1510.

[8] Apostolopoulos, C. A. and P. G. Koutsoukos (2008). "Study of the corrosion of reinforcement in concrete elements used for the repair of monuments." Construction and Building Materials **22**(7): 1583-1593.

[9] Balafas, I. and C. J. Burgoyne (2010). "Environmental effects on cover cracking due to corrosion." Cement and Concrete Research **40**(9): 1429-1440.

[10] Batis, G. and E. Rakanta (2005). "Corrosion of steel reinforcement due to atmospheric pollution." Cement and Concrete Composites **27**(2): 269-275.

[11] Berke, N. (2005). Environmental degradation of reinforced concrete. Handbook of Environmental Degradation of Materials. K. Myer. Norwich, NY, William Andrew Publishing**:** 165-177.

[12] Blau, P. J., J. J. Truhan Jr and E. A. Kenik (2007). "Effects of the exposure to corrosive salts on the frictional behavior of gray cast iron and a titanium-based metal matrix composite." Tribology International **40**(9): 1335-1343.

[13] El Hassan, J., P. Bressolette, A. Chateauneuf and K. El Tawil (2010). "Reliability-based assessment of the effect of climatic conditions on the corrosion of RC structures subject to chloride ingress." Engineering Structures **32**(10): 3279-3287.

[14] Jing, X. and Y. Wu (2011). "Electrochemical studies on the performance of conductive overlay material in cathodic protection of reinforced concrete." Construction and Building Materials **25**: 2655-2662.

[15] Martínez, I. and C. Andrade (2008). "Application of EIS to cathodically protected steel: Tests in sodium chloride solution and in chloride contaminated concrete." Corrosion Science **50**: 2948-2958.

[16] Mohammad, I., Abdulahman A. S. and Mohammad Sakhawat Hussain (2011). "Solid waste as environmental benign corrosion inhibitors in acid medium." International Journal of Engineering Science and Technology (IJEST) **3**(No.2): 1742-1748.

[17] Tao, Z. Z., Shengtao Li, Weihua Hou and Baorong (2009). "Corrosion inhibition of mild steel in acidic solution by some oxo-triazole derivatives." Corrosion Science **51**(11): 2588-2595.

[18] Tittarelli, F. and Moriconi G. (2008). "The effect of silane-based hydrophobic admixture on corrosion of reinforcing steel in concrete." Cement and Concrete Research **38**: 1354–1357.

[19] Tommaselli, M. A. G., N.A. Mariano and S.E. Kuri (2009). "Effectiveness of corrosion inhibitors in saturated calcium hydroxide solutions acidified by acid rain components." Construction and Building Materials **23**: 328–333.

[20] Trépanier, S. M., B. B. Hope and C. M. Hansson (2001). "Corrosion inhibitors in concrete: Part III. Effect on time to chloride-induced corrosion initiation and subsequent corrosion rates of steel in mortar." Cement and Concrete Research **31**(5): 713-718.

[21] Tritthart, J. (2003). "Transport of a surface-applied corrosion inhibitor in cement paste and concrete." Cement and Concrete Research **33**(6): 829-834.

[22] Vedalakshmi, R., SP. Manoharan, S. Ha-Won and N. Palaniswamy (2009). "Application of harmonic analysis in measuring the corrosion rate of rebar in concrete." Corrosion Science **51**: 2777-2789.

[23] Yuan, Q., C. Shi, G. De Schutter, K. Audenaert and D. Deng (2009). "Chloride binding of cement-based materials subjected to external chloride environment - A review." Construction and Building Materials **23**(1): 1-13.

[24] Zhang, X. L., Z. H. Jiang, Z. P. Yao, Y. Song and Z. D. Wu (2009). "Effects of scan rate on the potentiodynamic polarization curve obtained to determine the Tafel slopes and corrosion current density." Corrosion Science **51**(3): 581-587.

[25] Zhang, Z., S. Chen, Y. Li, S. Li and L. Wang (2009). "A study of the inhibition of iron corrosion by imidazole and its derivatives self-assembled films." Corrosion Science **51**(2): 291-300.