34847

Available online at www.elixirpublishers.com (Elixir International Journal)



Corrosion



# Inhibitive Effect of New Class of Pyrazole Derivatives for the Control of Corrosion of Copper-Nickel Alloy in Marine Environment

N. Balamurugapandian<sup>1</sup> and R. Ravichandran<sup>2,\*</sup>

<sup>1</sup>Research & Development Centre, Bharathiar University, Coimbatore – 641 046, India. <sup>2</sup>Post Graduate & Research Department of Chemistry, Dr. Ambedkar Government Arts College, Chennai – 600 039, India.

# ARTICLE INFO

Article history: Received: 31 July 2015; Received in revised form: 29 August 2015; Accepted: 1 September 2015;

Keywords Copper-nickel alloy, Sea water, Pyrazole, Polarization, EIS. ICP-AES.

#### ABSTRACT

The corrosion behavior of copper-nickel alloy in the presence of two organic inhibitors that belong to the pyrazole derivatives namely 1,5-dimethyl-1H-pyrazol-3-yl)methylamine and 1,3-Dimethyl-1H-pyrazol-4-yl)acetic acid has been investigated in natural sea water. Weight-loss measurements, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were applied to analyze the effect of the organic compounds on the corrosion inhibition of copper-nickel alloy. Polarization studies showed that these inhibitors were found to act as mixed type for alloy in chloride solution. It suppresses the cathodic and anodic reactions rates and it renders the open circuit potential to more noble directions. Measurements of values of charge transfer resistance (Rct) and the double layer capacity (Cdl) have been carried out. Accelerated leaching studies revealed that the inhibitors control the dissolution of copper and nickel in the alloy.

© 2015 Elixir All rights reserved.

#### Introduction

Copper and its alloys, because of their excellent resistance to corrosion in neutral aggressive media and their ease of processing, they are widely used in industries, particularly as condensers and heat exchangers in power plants [1]. Coppernickel alloy has been widely used as tubing material for condensers and heat exchangers in various cooling water systems [2-4]. Due to the electrodissolution of copper in chloride solutions, there is a growing interest in inhibitors, for the application of copper or its alloys in marine environments. N-heterocyclic compounds have been widely used as corrosion inhibitors [5, 6]. Azoles have been widely used as corrosion inhibitors in several environments [7, 8]. Frignani et al. [9] investigated the influence of alkyl chain on the protective effects of benzotriazole towards copper in acidic chloride solution and concluded that the inhibitors effectively control corrosion. The chemisorption of the inhibitor on the surface gave enhanced resistance to atmospheric oxidation of copper [10]. The addition of BTA to aqueous acidic, neutral and alkaline solution is commonly used and has significantly reduced corrosion [11]. Walker [12] has shown that the addition of small amounts of 1,2,3-benzotriazole and 1,2,4-triazole inhibit the corrosion of brass in acidic, neutral and alkali solutions atambient temperature. Qafsaoui et al. [13] also reported that the growth of protective film on copper in the presence of triazole derivatives. Ravichandran et al. [14] investigated the effect of N-[1-(benzotriazol-1-yl) methyl] aniline (BTMA) and 1-hydroxy methylbenzotriazole (HBTA) on corrosion of brass in neutral aqueous NaCl solution. Ye et al. [15] studied the structure of the protective film of 1-phenyl-5-mercaptotetrazole (PMTA) formed by pre-filming the electrode by immersion in the PMTA solution. Geler and Azambuja [16] investigated the inhibiting effect of pyrazole on Cu anodic dissolution in 0.1 M HCl. Based upon the experimental results, the inhibition effect of pyrazole was related to an adsorption process which took place through

delocalized  $\pi$ -electrons of the pyrazole ring. Vera et al. [17] also investigated the ability of the tetradentate 1,5-bis(4dithiocarboxylate-1-dodecyl-5-hydroxy-3-methylpyrazolyl)pentane, on the inhibition of copper corrosion in 3.5% NaCl.

Although there is an extensive literature on the corrosion properties of triazole such as aninotriazole and benzotriazole on steel and copper, there are very few reports devoted to the various functional groups in pyrazole derivatives on the corrosion of copper-nickel alloy. In the cases where these pyrazole derivatives have been considered, they have first been introduced as effective corrosion inhibitors in marine environment. The present work was devoted to the investigation of the corrosion behavior of copper-nickel alloy in sea water. Further, the study was extended to understand the influence of various functional groups on pyrazole in the corrosion inhibition of copper-nickel alloy. The effect of the addition of pyrazole derivatives such as 1,5-dimethyl-1H-pyrazol-3-yl)methylamine and 1,3-Dimethyl-1H-pyrazol-4-yl)acetic acid as inhibitors on the corrosion behavior of copper-nickel alloy have been studied by the weight-loss method and some electrochemical methods, i.e. potentiodynamic polarization, potentiostatic current transient and electrochemical impedance spectroscopy.

#### Experimental Materials

In the present work, Cu-Ni (90/10) alloy was used as the material for corrosion studies. The elemental composition of the alloy was determined by optical emission spectrometer and is illustrated in the Table 1. The investigated pyrazole derivatives viz. (Sigma Aldrich) and absolute ethanol (Fischer) were used as received. The structures of pyrazole derivatives are shown in figure 1. The chemical composition of the natural seawater was analyzed by analytical technique, whose composition is given in Table 2. The pH of the seawater is 6.7.

#### Table 1. Chemical composition of Cu/Ni (90/30) (in wt.%)

Alloy	Cu	Ni	Al	Fe	Sn	Pb	Mn, As, Co & Sr
Composition	69.78	29.43	0.28	0.18	0.06	0.09	0.18

# Table 2. Composition of natural sea water

Species	Concentration (mg/lit)
Dissolvedoxygen	0.74
Chloride	30,327
Sulphate	463
Sulphide	23
Bicarbonate	71
Phosphate	0.84
Silicate	3.96
Nitrate	0.485
Nitrite	0.07

### Table 3. Weight loss measurements of copper-nickel alloy at different concentrations of DPMA and DPAC in sea water

Inhibitor Concentration (ppm)	Corrosion Rate x 10 <sup>2</sup> (mmpy)	Inhibition Efficiency (%)
Blank	9.46	-
DPMA		
10-5	3.532	62.66
10-4	1.962	79.26
10-3	0.612	93.53
10-2	0.435	95.40
DPAC		
10-5	3.374	64.33
10-4	1.756	81.44
10-3	0.474	94.99
10-2	0.318	96.64

 Table 4. Tafel polarization parameters for the corrosion of copper-nickel alloy in sea water at different concentrations of DBMA and DBAC

Inhibitor concentration (ppm)	I <sub>corr</sub> (µA cm <sup>2</sup> )	E <sub>corr</sub> (mV vs. SCE)	$ \begin{array}{c} \beta_a \\ (mV  de  c^4) \end{array} $	$\frac{\beta_c}{(mVdec^4)}$	Corrosion rate x 10 <sup>-2</sup>	In hibition efficiency
	-				(mmpy)	(%)
Blank	8.12	-275	69	-121	9.24	-
DPMA						
10-5	3.24	-245	78	-93	3.69	60.06
10-4	1.63	-223	94	-82	1.86	79.87
10-3	0.64	-214	126	-59	0.73	92.10
10-2	0.33	-208	122	-62	0.38	95.89
DPAC						
10-5	3.03	-236	83	-86	3.45	62.66
10-4	1.37	-227	99	-73	1.56	83.12
10-3	0.38	-212	131	-56	0.43	95.89
10-2	0.24	-203	130	-58	0.16	97.40

 Table 5. Electrochemical impedance data of copper-nickel alloy in seawater containing different concentrations of DPMA and DPAC

Inhibitor concentration (ppm)	R <sub>ct</sub> x 10 <sup>4</sup>	$C_{dl}$ (uF cm <sup>-2</sup> )	R <sub>F</sub> x 10 <sup>4</sup>	$C_{\rm F}$ ( $\mu \rm F \ cm^{-2}$ )	$\mathbf{n}_1$	<b>n</b> <sub>2</sub>	IE (%)
	$(\Omega \text{ cm}^2)$	() · · · /	$(\Omega \text{ cm}^2)$	Q. · · ·			
Blank	0.76	43.68	0.97	42.35	0.43	0.39	-
DPMA							
10-5	2.34	8.34	2.78	7.26	0.52	0.47	67.52
10-4	4.27	1.36	5.46	2.15	0.66	0.61	82.20
10-3	13.56	0.26	13.89	0.52	0.78	0.72	94.40
10-2	23.82	0.04	18.93	0.10	0.81	0.77	96.81
DPAC							
10-5	2.62	7.24	2.94	8.02	0.54	0.51	70.99
10-4	4.87	1.32	5.97	2.46	0.68	0.62	84.4
10-3	13.62	0.21	14.53	0.64	0.84	0.79	94.4
10-2	24.76	0.02	19.28	0.09	0.89	0.84	96.9

 Table 6. Effect of optimum concentrations of PBBT and OPBT on the Denickelification of cupro-nickel alloy in natural sea water.

	Solution analysis			Percent inhibition		
Inhibitors	Cu	Ni	Denickelification factor (n)	Cu	Ni	
	(ppm)	(ppm)		(%)	(%)	
Blank	0.978	11.46	27.78	-	-	
DPMA	0.054	0.243	10.67	94.47	97.88	
DPAC	0.031	0.179	13.68	96.83	98.43	



1,5-dimethyl-1H-pyrazol-3-yl)methylamine (DPMA)



1,3-Dimethyl-1H-pyrazol-4-yl)acetic acid (DPAC) Figure 1. Structure of pyrazole derivatives

# Methods

#### Weight-loss method

Weight-loss experiments were conducted with copper – nickel alloy specimens of dimension 5 cm x 3 cm x 0.3 cm. The panels were polished mechanically with silicon carbide papers from 120 to 1200 grit followed by 5  $\mu$ m diamond paste. The panels were degreased in acetone, thoroughly washed with double distilled water, dried and weighed. Then the panels were immersed in 300 ml of environment (natural sea water) with and without the addition of inhibitors. After immersion for a definite period (10 days) the panels were taken out, washed with distilled water, dried and the changes in weights were noted. Each experiment was repeated atleast three times to check the reproducibility.

#### **Electrochemical studies**

Electrochemical studies were carried out in a conventional three-electrode cell consisting of a platinum counter electrode, saturated calomel electrode (SCE) and the working electrode. The material was cut into  $1 \times 1 \times 0.3$  cm size for electrochemical studies. Each piece is attached with a brass rod using silver paste for electrical contact. Then, the samples were mounted on an epoxy resin in such a way that only one side with  $1 \text{ cm}^2$  surface area is exposed. The mounted samples were polished successfully upto 1200 grit silicon carbide emery paper and final polishing is done with 5 µm diamond paste. The samples were degreased with acetone and ultrasonically cleaned using deionized water. This served as the working electrode. The working electrode is connected to the brass rod of approximately 20 cm length and 0.3 cm diameter for introducing the electrode into the electrochemical cell.

#### **Polarization studies**

The polarization studies were carried out with brass strips having an exposed area of  $1 \text{ cm}^2$ . The cell assembly consisted of brass as working electrode, a platinum foil as counter electrode and a saturated calomel electrode (SCE) as a reference electrode with a Luggin capillary bridge. Polarization studies were carried out using the Electrochemical work station (Model: CHI 760C, CH Instruments, USA) at a scan rate of 1mV/s. The degreased working electrode is then inserted into the test solution and immediately cathodically polarized at -1.0 V (SCE) for 15 minutes to reduce any oxides on the alloy surface [18]. The cathodic and anodic polarization curves for copper-nickel alloy in the test solution with and without various concentrations of the inhibitors were recorded at a scan rate of 1 mV/s. The inhibition efficiencies of the compounds were determined from corrosion current densities using the Tafel extrapolation method.

#### Electrochemical impedance studies

A.C. impedance measurements were conducted at room temperature using an Polarization studies were carried out using the Electrochemical work station (Model: CHI 760C, CH Instruments, USA) at a scan rate of 1mV/s. The copper-nickel alloy specimen with an exposing surface area of 1cm<sup>2</sup> is used as the working electrode. A conventional three electrode electrochemical cell of volume 500 ml is used. A saturated calomel electrode (SCE) is used as the reference and platinum plate electrode is used as the counter. All potentials are reported vs SCE.

#### Potentiostatic current transient techniques

The current transient of copper – nickel alloy specimen as a function of immersion period in the natural sea water with and without the addition of pyrazole derivatives were recorded at a preset potential of -100 mV.

#### Solution Analysis by Inductively Coupled Atomic Emission Spectroscopy (ICP-AES)

ICP-AES is a spectroscopic technique with moderate to low detection. Samples are introduced into the system through a nebulizer with argon gas and are dissociated into its constituent atoms and ions. These are then excited by the plasma and a characteristic radiation is emitted for each element as it falls back to the ground state. The intensity of the emission is proportional to the concentration of the element and quantitative analysis is carried out by reference to calibration curves.

The elements detected by ICP-AES in this work are shown below along with the characteristic wavelengths chosen for each element viz Cu and Ni at 325 nm and 352.4 nm respectively. The concentration of Cu and Ni in the electrolytes, after the polarisation experiments in the presence and absence of 10<sup>-2</sup> M studied inhibitors, is determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES). An ICPAES (ARCOS from M/s. Spectro, Germany) is used to measure the amount of dissolution of nickel and copper from the alloy surface. The denickelification factor (n) is calculated using the equation [19].

$$n = \frac{[Ni / Cu]_{soln}}{[Ni / Cu]_{alloy}}$$

where,  $[C_{Ni}/C_{Cu}]_{sol}$  and  $[C_{Ni}/C_{Cu}]_{alloy}$  are the ratios between the concentrations of nickel and copper in the solution and in the alloy respectively.

# **Results and Discussion**

# Weight-loss measurements

The weight loss measurements are the best known and simplest of all corrosion monitoring techniques. The corrosion rates and inhibition efficiencies of copper-nickel alloy with different concentrations of DPMA and DPAC in natural sea water at room temperature (30°C) are given in Tables 3. The corrosion rate (CR) and percentage inhibition efficiency (IE %) were calculated using the following equation [20].

$$CR (mmpy) = \frac{87.6 \text{ x W}}{D \text{ x A x T}}$$
$$IE\% = \frac{CR_{(bl)} - CR_{(inh)}}{CR_{(bl)}} \text{ x 100}$$

where W is the weight-loss, D is the density, T is the immersion time, A is the area of the specimen and  $CR_{(inh)}$  and  $CR_{(bl)}$  are the corrosion rate of copper-nickel alloy in the presence and absence of inhibitors respectively. The corrosion rate decreases with increase in the concentration of the inhibitor. The inhibition efficiency increases with the increase in the concentration of the inhibitor up to the optimum level, thereafter it was found to

decrease slightly, which is due to the interaction between adsorbed molecules at the sites. The extent of inhibition depends on the nature and concentration of the inhibitor. The optimum concentration was evaluated on the basis of inhibition efficiency and it was found to be  $10^{-2}$  M for DPMA and DPAC in natural sea water. The inhibitors have shown the maximum inhibition efficiency of 95.40 and 96.64 respectively for DPMA and DPAC in natural sea water. It can be seen that the values of inhibition efficiency for copper-nickel alloy obtained using substituted pyrazoles in natural sea water follow the order.

DPMA > DPAC

Inhibition of corrosion of copper-nickel alloy in natural sea water can be explained in the following way. The adsorption of pyrazole derivatives on the surface of alloy leads to the formation of a protective layer of Cu(I)-chloride complex on the surface of alloy. Actually the formation of a pyrazole film starts with the chemisorption of the inhibitor molecule on to the slightly oxidized areas of the copper surface. The adsorption of pyrazole molecules on the oxidized parts of the copper surface was found to occur much faster than on bare metal zones. The film formed in this way has a limited hydrophobic action, which succeeds in protecting the alloy in the corroding medium by blocking main reaction centers on the metal surface.

#### **Polarization studies**

The cathodic and anodic polarization curves of coppernickel alloy in natural sea water containing different concentrations of DPMA and DPAC are shown in Figure 2 and 3. It is evident that in the presence of inhibitor, the cathodic and anodic curves were shifted towards noble direction and the shift was found to be dependent on inhibitor concentration. Tables 4 illustrate the corresponding electrochemical parameters. The  $E_{corr}$  values were shifted in the presence DPMA and DPAC, which clearly indicated that the inhibitors control the anodic and cathodic reactions and thus act as mixed-type inhibitors. The current density also decreased with increasing concentrations of the inhibitors. The corrosion rates and inhibition efficiencies were calculated from polarization curves using the following equation[21].

$$CR = \frac{3.27 \ x \ 10^{-3} \ x \ I_{corr} \ x \ EW}{IE\%} = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \ x \ 100$$

Where CR is the corrosion rate (mmpy), D is the density (g cm<sup>-3</sup>), EW is the equivalent weight of the specimen, IE is the inhibition efficiency and  $I_{corr (inh)}$  and  $I_{corr}$  are corrosion current density in the presence and absence of inhibitors respectively.

The values of cathodic Tafel slope ( $\beta_c$ ) and anodic Tafel slope ( $\beta_a$ ) of pyrazole derivatives are found to change with inhibitor concentration, which clearly indicates that the inhibitors controlled both the reactions. The inhibition efficiency of DBMA and DBAC in sea water attained a maximum value of 95.89% and 97.40% at 10<sup>-2</sup>M concentration respectively. The values of inhibition efficiency increase with increasing concentration of inhibitor, indicating that a higher surface coverage was obtained in the solution with the optimum concentration of inhibitor. The corrosion rate of copper-nickel alloy in sea water was found to be 9.24 x 10<sup>-2</sup> mmpy and it was minimized by adding the inhibitors to a lower value of 0.33 x 10<sup>-2</sup> mmpy and 0.24 mmpy due to the adsorption of DPMA and DPAC on the metal surface respectively.

A comparison of the values of inhibition efficiency obtained by weight loss measurements and polarization studies bring out clearly the fact that there is a fairly good agreement between these values. It is also found that all the compounds function more effectively on the corrosion inhibition of alloy in sea water.



Figure 2. Potentiodynamic polarization curves of copper-nickel alloy in sea water containing different concentrations DPMA



Figure 3. Potentiodynamic polarization curves of copper-nickel alloy in sea water containing different concentrations DPAC

# Electrochemical Impedance Spectroscopic Studies

Electrochemical Impedance Spectroscopic technique is a powerful tool in the investigation of the corrosion and adsorption phenomena. This method explains effectively the corrosion and passivation phenomena of metals and alloys. The impedance diagrams represented in Nyquist plot obtained at open-circuit potential after one hour immersion in seawater in the presence and absence of pyrazole derivatives are presented in Figure 5 and 6. The percent inhibition efficiency (IE %) of alloy was calculated as follows [22] :

$$IE \% = \frac{(R_{ct})^{-1} - (R_{ct(inh)})^{-1}}{(R_{ct})^{-1}} \times 100$$

Where,  $R_{ct(inh)}$  and  $R_{ct}$  are the charge-transfer resistance values with and without inhibitors respectively.

The calculated parameters obtained from equivalent circuit fitting analysis in the absence and presences of inhibitors in seawater are given in Table 5. The variation of  $R_{ct}$  values with different concentrations of inhibitor are presented in the Figure 4

and Figure 5. These Nyquist plots obtained for copper-nickel alloy in the presence of different concentrations of inhibitor exhibited different shapes, which indicated the change in corrosion mechanism due to the presence of inhibitors. It can be seen from the table that with increase in inhibitor concentration,  $R_{ct}$  value increased and  $C_{dl}$  value decreased. The decrease in  $C_{dl}$ value can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the pyrazole derivatives function by adsorption at the metal-solution interface. The decrease in  $\mathrm{C}_{\mathrm{dl}}$  value upon increase in inhibitor concentration was due to reduced access of charged species to the alloy surface, as inhibitor has adsorbed and a good persistent layer of the same was formed on the alloy surface. The change in  $R_{\rm ct}$  and  $C_{\rm dl}$  values was caused by the gradual replacement of water molecules by the anions of the NaCl present in seawater and adsorption of the organic inhibitor molecules on the metal surface, reducing the extent of dissolution [23].



Figure 4. Nyquist diagram of cupro-nickel alloy in natural sea water containing different concentration of DPMA.





The value of Faradic resistance  $(R_F)$  increases with increase in concentration showing that DPMA and DPAC stabilize the corrosion products on the metal surface. As the concentration of the inhibitor increases, the inhibitors get adsorbed effectively on the brass surface which increases the  $R_F$  values and decreases the  $C_F$  values.

The molecular structure normally determines the type of adsorption on copper-nickel surface. Pyrazole derivatives viz., DPMA and DPAC show differences in their inhibition efficiency due to the difference in their molecular structures, of the pyrazloe derivatives studied, DPAC has the highest inhibition efficiency and this corresponds well with the polarization measurements. The % IE calculated from EIS shows the same trend as those estimated from polarisation measurements i.e., polarization measurements and EIS study complement each other well.

#### Potentiostatic current transient techniques

Figure 6 shows the current-time relationship of the alloy specimen in sea water with and without the optimum concentration of DPMA and DPAC at the applied potential of -100 mV. During the initial 60 seconds, there was an abrupt decrease in the current and a slower decrease thereafter. After one minute there was no remarkable change in current and a steady value was obtained. Evidently, the intensity of metal dissolution was comparatively low in the presence of inhibitors. Among the inhibitors studied, DPAC shifted the corrosion current of Cu-Ni alloy to a lower value and thus effectively retards the metal dissolution sea water.



Figure 6. Current transient curves of copper-nickel alloy in sea water in the presence of optimum concentration of DPMA and DPAC. Accelerated leaching studies (ICP-AES)

The results of solution analysis and the corresponding denickelification factor (n) in the presence and absence of pyrazole derivatives at their optimum concentration level in natural sea water for cupro-nickel alloy are given in Table 6. The denickelification factor (n) was calculated using the relation.

n =

 $(NI/Cu)_{alloy}$ Where, the ratio  $(Ni/Cu)_{sol}$  is determined from solution analysis and  $(Ni/Cu)_{alloy}$  is the ratio of weight-percent in the alloy.

From the table, it can be observed that both copper and nickel were present in the solution whereas in the presence of inhibitors, which are able to minimize the dissolution of both copper and nickel. The data recorded in tables illustrate that the percent inhibition efficiency against the dissolution of nickel was correspondingly high as compared to the dissolution of copper. This indicates the excellent inhibition efficiency of inhibitors to prevent the denickelification of cupro-nickel alloy in natural sea water, which is also reflected in the values of denickelification factor. Among the inhibitors studied, DPAC shows highest inhibition efficiency in the dissolution of cupronickel alloy in natural sea water. The percent inhibition efficiency against the dissolution of Ni was correspondingly high i.e. 98.43% can be achieved in the presence of DPAC containing natural sea water for cupro-nickel alloy, indicating that the preferential dissolution of nickel was almost completely minimized.

#### Conclusion

The main conclusions are as follows:

1. All substituted pyrazole derivatives show good inhibition efficiency in sea water.

2. The polarization data indicate suppression of both the partial corrosion processes in the presence of pyrazole derivatives. These inhibitors behave as mixed type.

3. The inhibition is due to the adsorption of the pyrazole derivatives on the copper-nickel surface and blocking of active sites.

4. Electrochemical impedance spectroscopy shows that Rct values increase, while  $C_{dl}$  values decrease in the presence of pyrazole derivatives.

5. Solution analysis reveals that the pyrazole derivatives excellently prevent the denickelification of copper-nickel alloy. **References** 

[1] B. Todd and P. A. Lovett, "Marine engineering practice: selecting materials for seawater systems," Tech. Rep., Institute of Marine Engineers, London, UK, 1976.

[2] G. Petkova, E. Sokolova, S. Raicheva, P. Ivanov, Brit. Corros.J. 31 (1996) 55.

[3] R. Gasparac, C.R. Martin, E. Stupnisek-Lisac, Z. Mandic, J.Electrochem. Soc. 147 (2000) 991.

[4] P.T. Gilbert, Mater. Perform. 21 (1982) 47.

[5] Y.C. Wu, P. Zhang, H.W. Pickering, J. Electrochem. Soc. 140(1993) 2791.

[6] Qafsaoui, J. Roques, A. Srihiri, G. Mankowski, J. Appl.Electrochem. 31 (2001) 223.

[7] Rodrigues P.R.P., De-Andrade A.H.P. and Agostinho S.M.L. Br. Corros J.,33 (1998) 211.

[8]Villamil R.F.V., Corio P., Rubim J.C. and Agostinho S.M.L. J. Electroanal. Chem.,(1999) 472 112.

[9] A. Frignani, L. Tommesani, G. Brunoro, C. Monticelli, M.Fogagnolo, Corros. Sci. 41 (1999) 1205.

[10] L.Wang, Corros.Sci., 43 (2001) 2281.

[11] Y. Ling, Y. Guan, K.N. Han, Corrosion 51 (1995) 367.

[12] Qafsaoui, J. Roques, A. Srihiri, G. Mankowski, J. Appl.Electrochem. 31 (2001) 223.

[13] R. Walker, Corrosion 56 (2000) 1211.

[14] R. Ravichandran, N. Rajendran, Appl. Surf. Sci., 241(2005) 449.

[15] Ye, X. R., Xin, X. Q., Zhu, J. J. and Xue, Z. L Appl. Surf. Sci., 135(1998)307.

[16] Geler, E. and Azambuja, D. S. "Corrosion inhibition of copper in chloride solutions by pyrazole", Corros. Sci., 42 (2000) 631.

[17] Vera, R., Bastidas, F., Villarroel, M., Oliva, A., Molinari, A., Ramírez, D. and DelRío, R., Corros. Sci., 50 (2008)729.

[18]R. Ravichandran, S. Nanjundan, N. Rajendran, J. Appl. Electrochem., 34(2004)1171.

[19] K. Chandrasekaran, A. Jayasree, B.S. Alwar and R. Ravichandran, Corrosion, 69(2014) 22941.

[20] M. G. Fontana, "Corrosion Engineering," 3rd Edition, McGraw-Hill Book Company, New York, 1987.

[21] M. Bentis, M. Traisnel, M. Lagrenee, Brit. Corros. J. 35(2000) 315.

[22] M.A. Quraishi, R. Sardar, J. Appl. Electrochem. 33 (2003)1163.

[23] S. Muralidharan, K.L.N. Phani, S. Pitchumani, S. Ravichandran, J. Electrochem. Soc. 142 (1995) 1478.