



Trade Science Inc.

# Materials Science

*An Indian Journal*

---

## Full Paper

MSAIJ, 2(4-5), 2006 [142-147]

### A Comparative Study For The Effect Of $S^{2-}$ Ions On The Corrosion Of Cu, Cu-Zn And Cu-Ni In 3.4% NaCl In Presence Of Sodium Lauryl Sulfate As Inhibitor

Corresponding Author

H.A.El-Dahan  
Electrochemistry and Corrosion Lab.,  
National Research Center  
12622 Dokki, Cairo, (EGYPT)  
E-mail: hosnielldahan@hotmail.com

Received: 10<sup>th</sup> August, 2006

Accepted: 21<sup>st</sup> August, 2006

Web Publication Date : 14<sup>th</sup> November, 2006

#### ABSTRACT

A comparative study for the effect of sulfide ions concentrations on the corrosion of Cu, Cu-Zn (70/30) and Cu-Ni (90/10) in NaCl solution (3.4%) in presence of sodium lauryl sulfate (SLS) as inhibitor was studied using weight loss and potentiodynamic curves (Tafel lines). In low  $S^{2-}$  polluted salty water, the mean corrosion rate of the copper and its alloys increases, while in highly polluted salty water, the corrosion rate decreases. Generally the corrosion rates reveal good corrosion inhibition for Cu and its alloys in sulfide polluted salty water. The electrochemical corrosion parameters were obtained at different inhibitor concentrations. Tafel cathodic slopes in inhibited polluted salty water are considerable lower than those in uninhibited polluted salty solution. This points to cathodic control of the inhibitor. Moreover, the corrosion current density ( $I_{corr}$ ) decreased while the inhibition efficiency percent (I.E.,%) increased in presence of SLS. The inhibition effect of SLS was attributed to the adsorption of the inhibitor molecules on the coupons surfaces. © 2006 Trade Science Inc. - INDIA

## INTRODUCTION

Sulfide is usually introduced in sea water in many ways, such as from rotting vegetation and from industrial waste discharge. The mechanism of formation of sulfide in sea water has been discussed by many researchers (**Hack 1980; Francis 1990**). Most data indicated an acceleration of corrosion of copper and copper alloys in sulfide-polluted natural seawater, and similar effects were observed in synthetic seawater and even in aqueous solutions of sodium chloride (**Kato et al., 1984**). According to Syrett (**Syrett 1981**), sulfide interferes with the normal growth of the protective oxide film that forms on the surface of the copper alloys when exposed to seawater. Also, Syrett et al., (**Syrett et al., 1979**) concluded that the presence of sulfide, O<sub>2</sub> and oxidation products from the reaction between sulfide and O<sub>2</sub> (e.g. sulfure and polysulfide) lead to the accelerated attack and to the formation of thick, non protective, porous, cuprous sulfide which interferes with the normal growth of protective oxide film.

Organic inhibitors (e.g Benzotriazole, and its derivatives, Surfactants as Cetyltrimethylammonium bromide, Sodium Dodecyle Sulfate, etc.), has long been as an efficient inhibitor for copper and many of its alloys in a variety of environments (**Al-Kharafi et al., 2002, Youda et al., 1990, Xu et al., 1993, Tromans et al., 1998**).

The effect of surface-active agents (surfactants) on the corrosion behavior of copper was generally investigated from the point of view of corrosion inhibition. Studies have shown that sodium dodecyl sulfate (SDS) surfactant acts as an inhibitor for generalized corrosion of 304 stainless steel, nickel and aluminum in sodium chloride media as well as for copper in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution (**Villamil et al., 1999**). Based on preliminary results we recently showed that the addition of the sodium lauryl sulfate (SLS) surfactant in sulfide polluted salty water (3.4% NaCl) has a pronounced effect on the corrosion behavior of copper and its alloys. In the present study we compare data obtained on the effect of different concentrations of dissolved sulfide in presence of surfactant (SLS) as inhibitor on the corrosion rate of copper and its alloys (Cu-Zn, 70/30 and

Cu-Ni, 90/10) in sodium chloride solution (3.4% resemble sea water) by using electrochemical and weight loss techniques.

## EXPERIMENTAL METHOD

The apparatus for conducting the electrochemical measurements were, a saturated calomel electrode (SCE) used as the reference electrode and a platinum electrode as the counter electrode. All the potentials were measured with respect to the SCE. The tests were performed at 25±2°C in a three electrode cell with a separate compartment for the reference electrode with the main compartment via a Luggin capillary.

The copper electrodes and its alloys used in this study were prepared from cylindrical bars of the 98.87(wt.%) copper, 70/30 Cu-Zn and 90/10, Cu-Ni. The electrodes were rods of 0.5cm in diameter, sealed with epoxy resin leaving only the working area exposed. The surface of the specimens were polished with different grades of emery paper, degreased with acetone and rinsed with distilled water prior to each experiment.

The aggressive environment employed was 3.4% NaCl (simulated seawater) containing 5,10 and 20 ppm S(as Na<sub>2</sub>S) solution. The substances employed were analytical reagent grade and doubly distilled water.

The potentiodynamic current-voltage characteristics were recorded using potentiostat, model 273/81 at 0.2 mV/S scan rate under stirring conditions.

The action of sodium lauryl sulfate, (C<sub>12</sub> H<sub>23</sub> O<sub>5</sub> S Na) as inhibitor on the corrosion of, Cu, Cu-Zn and Cu-Ni has been examined in 3.4% NaCl solution containing different concentrations of S (5,10, 20 ppm) at room temperature using weight loss technique. Specimens 2.5 x 5 x 0.2cm were polished, degreased with ethanol and weighed before immersion in the corrosive solution for 30 days. In each experiment, two samples were supported by a glass hook and totally immersed in 250 ml solution and the results were averaged. The corrosion inhibition efficiency percent was calculated .

# Full Paper

## RESULTS AND DISCUSSION

### Gravimetric measurements

It is well known that some organic compounds will promote corrosion at certain concentrations, but then inhibit at another level. Further, both the pH of the corrodent and coupon exposure time can be important in deciding whether or not the compound will have practical application as an inhibitor.

The weight losses for coupons (Cu, Cu-Zn and Cu-Ni) exposed in sulfide polluted aqueous salty water (3.4% NaCl) with and without SLS were determined after exposure time (30 days). The average inhibition efficiencies over the period were then calculated using the expression:

$$I.E., \% = \frac{W_{uninh.} - W_{inh.}}{W_{uninh.}} \times 100$$

where  $W_{uninh.}$  and  $W_{inh.}$  are the weight losses for coupons in the absence and presence of the inhibitor respectively.

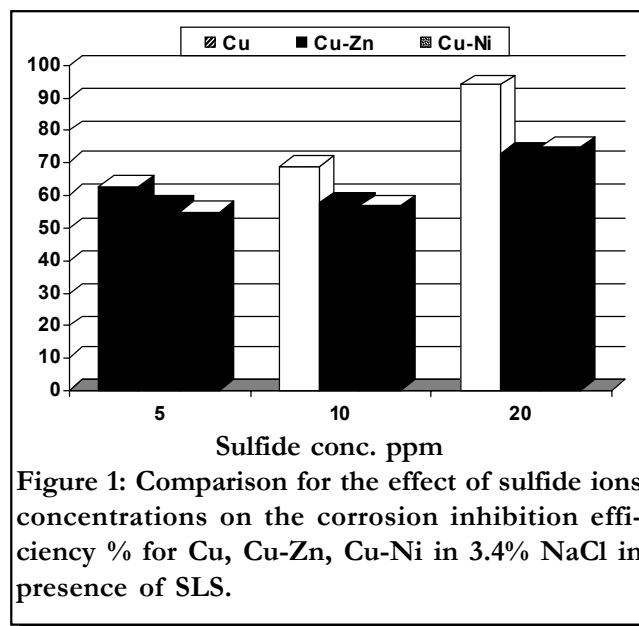
Firstly, the unpublished data show that after 10 days exposure, sodium lauryl sulfate (SLS-1000ppm) will not inhibit the corrosion of copper and its alloys (about 33% I.E, as example for Cu) and the I.E,% for SLS has increased from about 33 to 52% for 20 days exposure time. But for 30 days exposure time for SLS I.E,% reached to a maximum values.

Figure (1) shows the effect of sulfide concentrations on the corrosion inhibition % of Cu, Cu-Zn and Cu-Ni alloys in salty water (3.4% NaCl) in presence of 1000 ppm of SLS as inhibitor for 30 days at R.T. It is clear that the inhibition efficiency percent (I.E.%) for copper and its alloys are increased when the sulfide ions concentrations increased (up to 20 ppm S), this means that the corrosion rates of both Cu and its alloys are decreased and dependent of sulfide ions concentration. These data are in agreement with the data of Gudas and Hack (**Gudas et al., 1979**) in that the corrosion rate of Cu and its alloys increases at lower concentrations of sulfide.

Although surfactants have been widely used in the chemical and light industries and their properties have, also been a subject which has attracted many chemists attention, only a few studies focus on the application of surfactants and its mechanism

for corrosion prevention of metals and alloys as inhibitors.

Adsorption of inhibitors at the metal/solution interface is usually accepted as the formation of electrostatic or covalent bonding between the metal surface atoms and the adsorbates (**Trabanelli 1987, Luo, 1998**). Compared with common inhibitors, adsorption of surfactants at the metal surface seems to be much more complicated. In aqueous solutions, the surfactant molecules may adsorb on the solid surface through electrostatic attraction or chemisorption depending on the charge of the solid surface (**Miller et al., 1987**). Therefore, from the weight loss data we can concluded that under appropriate conditions, enough surfactant molecules (SLS) may adsorb to the solid surface forming an organized structure which can effectively prevent metals from corrosion in an aggressive environment.



**Figure 1: Comparison for the effect of sulfide ions concentrations on the corrosion inhibition efficiency % for Cu, Cu-Zn, Cu-Ni in 3.4% NaCl in presence of SLS.**

### Polarization Measurements

Coupons testing in salty water polluted with sulfide has shown that the exposure time is a crucial factor in deciding the worth of a compound (SLS) as an inhibitor. The compounds suitability as an inhibitor can also be evaluated by potentiodynamic polarization. Figures (2-4) illustrates the effect of sulfide ions and/or SLS on the polarization curves of Cu (Figure 2) alpha brass Cu-Zn, (Figure 3) and Cu-Ni (Figure 4) in 3.4% NaCl. A comparison of the curves clearly shows that the inhibitor slows down the cathodic reaction of the coupons. The cathodic curves

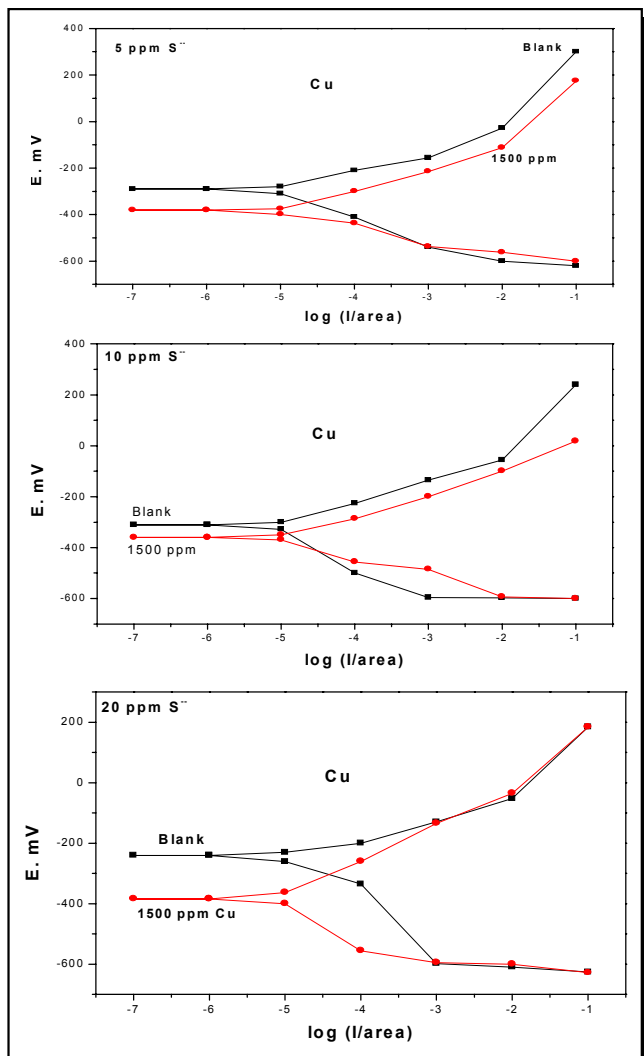


Figure 2: Polarization curves for comparison the effect of 5, 10, 20 ppm S on the Cu in 3.4 % NaCl in presence of SLS.

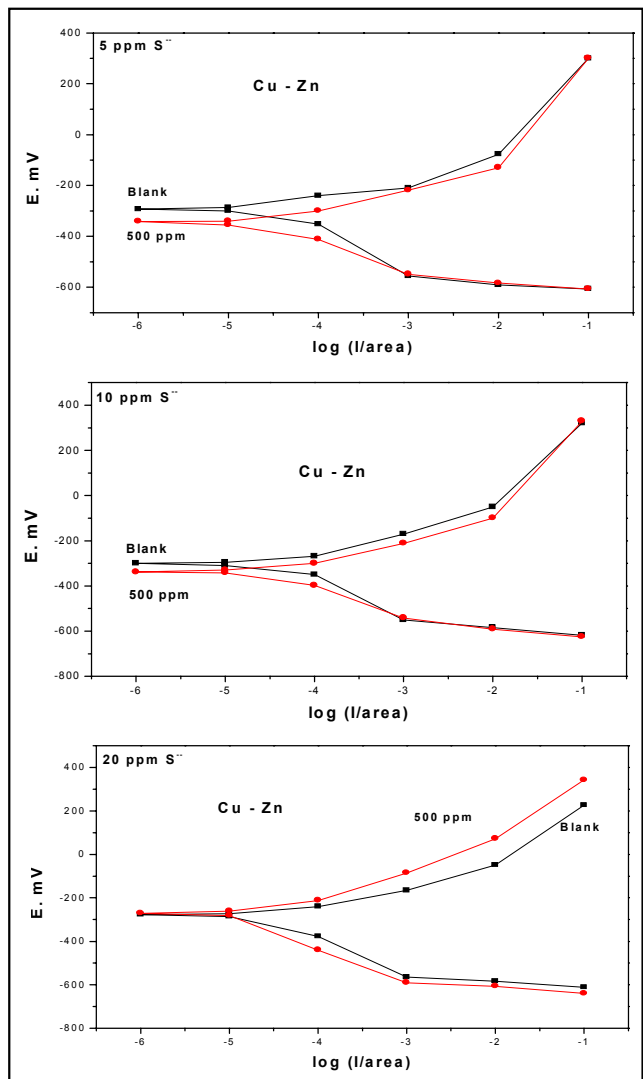
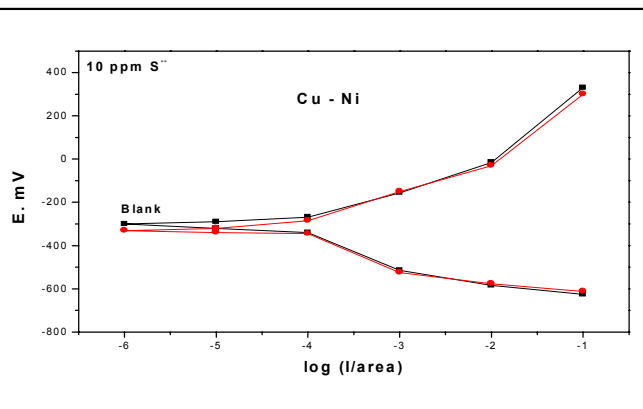
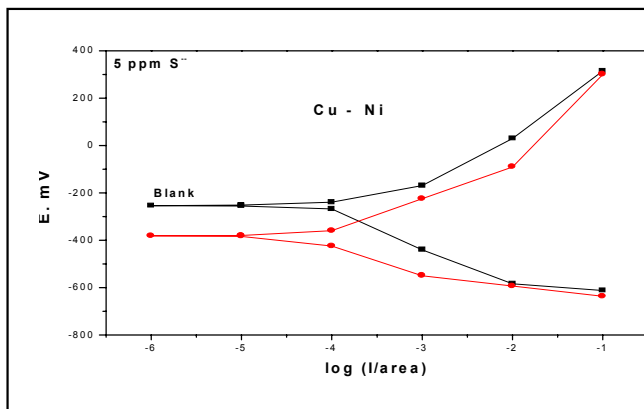


Figure 3: Polarization curves for comparison the effect of 5, 10, 20 ppm S on the Cu-Zn in 3.4 % NaCl in presence of SLS.



## Full Paper

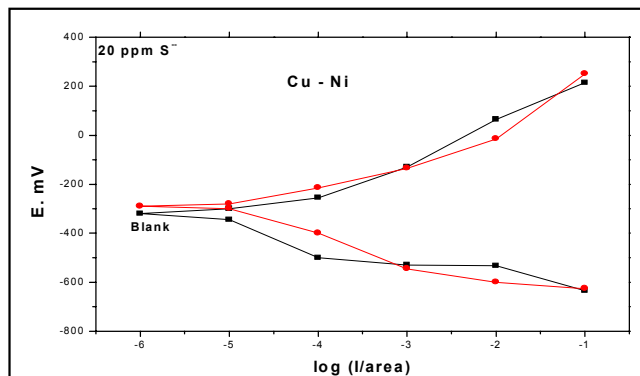


Figure 4: Polarization curves for comparison the effect of 5, 10, 20 ppm S on the Cu-Ni in 3.4 % NaCl in presence of SLS.

in presence of the additives are markedly shifted towards lower current density values with respect to that of the free system, indicating that the cathodic process is highly inhibited. The more important electrochemical parameters obtained from the polarization curves are listed in TABLE 1. These include corrosion potential ( $E_{\text{CORR.}}$ ), corrosion current density ( $I_{\text{CORR.}}$ ), anodic and cathodic tafel slopes  $\hat{a}_a$ ,  $\hat{a}_c$  and inhibition efficiency percent (I.E.%) calculated as the percentage reduction in the corrosion current density. The data depicted in TABLE 1 show that the I.E.% values are highly increased in inhibited system, compared to the free system meaning that the corrosion rates are highly decreased at the

different inhibitor concentrations. On the other hand,  $E_{\text{CORR.}}$  values are more negative in the inhibited system, compared to the free system. This means that, in sulfide polluted salty water, corrosion reaction of the Cu and its alloys were always under diffusion control and thus, cathodically controlled (Hajji et al., 1993). i.e the present compound (SLS) are mainly cathodic inhibitor. Tafel slopes values  $\hat{a}_a$  are slightly varied for inhibited polluted salty water solutions than uninhibited ones, while the variations in the cathodic tafel slopes in inhibited solution are considerably lower than uninhibited ones. This is confirmed a change in the cathodic reaction mechanism of the coupons, probably due to the adsorption of the inhibitor on the electrode surface forming complex. SLS like other adsorption inhibitors probably adsorbs inside the electrical double layer. The decrease in the corrosion rate with increasing concentration inhibitor can be correlated to the degree of surface coverage  $\theta$ . At room temperature ( $25^\circ\text{C}$ ) the inhibition efficiency attains highest values at the highest SLS concentrations.

In the light of the above mentioned results, information can be given which enables a conclusion regarding the mechanism of corrosion inhibition of Cu and its alloys in salty water (3.4% NaCl) polluted with sulfide.

The depends of the inhibitive effect of SLS on

TABLE 1: Comparison of the effect of different concentrations of sulfide ions on the electrochemical parameters of Cu, Cu-Zn, Cu-Ni. In 3.4 % NaCl in presence of SLS as inhibitor.

| 5 ppm S <sup>2-</sup>  |                     |                       |  |                            |                            |          |        |
|------------------------|---------------------|-----------------------|--|----------------------------|----------------------------|----------|--------|
| Sample                 | Inhibitor dose, ppm | $E_{\text{corr.}}$ mV | $I_{\text{corr.}}$ $\mu\text{A}/\text{cm}^2$ | $\hat{a}_a \times 10^{-3}$ | $\hat{a}_c \times 10^{-3}$ | C. R mpy | I. E % |
| Cu                     | Blank               | -284.2                | 16.31  | 107.6                      | 154.0                      | 14.87    | 98.6   |
|                        | 1500 ppm            | -377                  | 0.2265                                       | 87.54                      | 42.85                      | 0.2066   |        |
| Cu-Zn                  | Blank               | -287.6                | 50.18  | 156.0                      | 252.9                      | 47.8     | 93     |
|                        | 500 ppm             | -344.7                | 3.89   | 97.3                       | 79.8                       | 3.6      |        |
| Cu-Ni                  | Blank               | -259.6                | 288.4  | 151.0                      | 319.8                      | 263      | 92     |
|                        | 50 ppm              | -379                  | 23.0   | 128.0                      | 96.3                       | 21       |        |
| 10 ppm S <sup>2-</sup> |                     |                       |  |                            |                            |          |        |
| Cu                     | Blank               | -309.8                | 19.2   | 84.33                      | 245.6                      | 17.5     | 61     |
|                        | 1500 ppm            | -361.0                | 7.5  | 87.93                      | 108                        | 6.8      |        |
| Cu-Zn                  | Blank               | -301                  | 39.3   | 105                        | 230.8                      | 35.8     | 85     |
|                        | 500 ppm             | -338                  | 5.7  | 104                        | 86.3                       | 5.2      |        |
| Cu-Ni                  | Blank               | -300                  | 51.85  | 136                        | 147                        | 47.3     | 44     |
|                        | 1000 ppm            | -319                  | 28.85  | 122.9                      | 123                        | 26.3     |        |
| 20 ppm S <sup>2-</sup> |                     |                       |  |                            |                            |          |        |
| Cu                     | Blank               | -249.6                | 56   | 80.9                       | 286.7                      | 50.2     | 93     |
|                        | 1000 ppm            | -375.4                | 3.89   | 141                        | 113.8                      | 3.5      |        |
| Cu-Zn                  | Blank               | -280                  | 32.8   | 116.7                      | 231.7                      | 29.7     | 58     |
|                        | 1000 ppm            | -382                  | 13.8   | 84.9                       | 144                        | 12.6     |        |
| Cu-Ni                  | Blank               | -313.6                | 23.9   | 119.7                      | 282.9                      | 21.8     | 84     |
|                        | 1000 ppm            | -404.3                | 3.9  | 76.9                       | 60.8                       | 3.5      |        |

the immersion time indicates that from one side the adsorption of the surfactant SLS on copper surface and its alloys has a special influence on electrochemical behavior of the tested samples (Ma et al., 2001). The inhibition efficiency of SLS increased with the increase of the immersion time (30 days) and reached a maximum values, meaning that more SLS molecules adsorbed on tested samples and occupied more sites on the electrodes surfaces.

From the above findings we can concluded that, the inhibition effect of compound SLS can be attributed to adsorption process of the inhibitor molecules leading to a more homogenous coverage according to Horner's hypothesis (Horner, 1998). Moreover, the formation of Cu-chelates on the coupons surfaces which produce a barrier to the corrosive environment (Fox et al., 1979) is also expected since, the present compounds can form Cu-chelates via the interaction of C = O group of the inhibitor with the Cu-ions at the electrode-solution interface.

### CONCLUSION

The present work led to the following conclusions:

- 1 Sodium lauryl sulfate is effective in inhibiting Cu, Cu-Zn (70/30) and Cu-Ni (90/10) corrosion in sulfide polluted salty water (3.4% NaCl).
- 2 The corrosion rates obtained from weight loss method reveal that, in low sulfide polluted salty water, the mean corrosion rates of Cu and its alloys increases, while in highly sulfide polluted salty water the corrosion rates decreases.
- 3 The electrochemical parameters obtained from Tafel lines measurements show that the  $I_{\text{corr}}$  decreases, I.E.% increases and  $E_{\text{corr}}$  shifts to more negative values, which points to a cathodic control of the inhibitor.
- 4 The inhibition effect of SLS was attributed to the adsorption of the inhibitor molecules on the electrodes surfaces.

### REFERENCES

- [1] B.C.Syrett; Corros.Sci., **21**, 187(1981).
- [2] B.C.Syrett, D.D.Macdonald, S.S.Wing; Corrosion, **35**(9), 409 (1979).
- [3] B.C.Syrett, D.D.Macdonald; Corrosion, **35**, 505 (1979).
- [4] C.Kato, H.Pickering, J.Cartle; J.Electrochem.Soc., **131**, 1225 (1984).
- [5] C.A.Miller, S.Qututbuddin; 'Surfactant Science Series', Marcel Dekker, Inc., New York, **21**, 166, (1987).
- [6] D.Tromans; J.Electrochem.Soc., **145**, L42, (1998).
- [7] F.M.Al-Kharafi, B.G.Ateya; Journal of the Electrochemical Society, **149**(6), B206-B210 (2002).
- [8] G.Trabanelli; 'Corrosion Mechanism', F.Mansfeld Ed., Marcel Dekker Inc., New York, **119**, (1987).
- [9] H.Hack; Susceptibility of 17 machinery alloys for sulfide induced corrosion in sea water. Report A WFAL. TR-BI. 4019 Bethesda, MD, U.S.A. (1980).
- [10] H.Luo, Y.C. Guan, K.N.Han; Corrosion, **54**, 619 (1998).
- [11] H.Ma, S.Chen, S.Zhao, X.Liu, D.Li; J.of Electrochem. Society, **148**(11), B482-B488 (2001).
- [12] J.P.Gudas, H.P.Hack; Corrosion, **35**, 167 (1979).
- [13] J.N.Al Hajji, M.R.Redha; Corrosion, **49**, 10, (1993).
- [14] L.Horner; Chem., **Z100**, 247 (1976).
- [15] P.G.Fox, G.Lewis, P.J.Boden; Corros.Sci., **19**, 457 (1979).
- [16] R.F.V.Villamil, P.Corio, J.C.Rubin, S.M.L.Agostinho; J.Electroanal.Chem., **472**, 112 (1999).
- [17] R.Francis; 'Corrosion in Sea Water Systems', A.D. Mercer Ed., Ellis Horwood, Chichester, Ch.6, 65-75 (1990).
- [18] R.Youda, H.Nishihara, K.Aramaki; Electrochim.Acta., **35**, 1011 (1990).
- [19] Z.Xu, S.Lau, P.W.Bohn; Langmuir, **9**, 993, (1993).