# Friendly Inhibitor for Corrosion Inhibition of Copper in Sea Water

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Abstract: The inhibition and mechanism of corrosion of copper in sea water with and without inhibitors had been investigated by using weight-loss, electrochemical polarization and suface analysis technique SEM and XPS. It had been found that there was synergistic effect between BTA and sodium citrate. The inhibition efficiency was 96.0%, and corrosion rate was 0.00431 mm/a in the proportion of 2 mg·L$^{-1}$ BTA and 20 mg·L$^{-1}$ sodium citrate inhibitor. It was a mixture inhibitor. The SEM images show that the surface of copper without inhibitors which was heavily corroded, but the surface of copper with inhibitors remained shiny after immersed in seawater after 6 day. The results of the XPS spectrum of the surface of copper indicated that the compound inhibitor formed a Cu(I)-BTA and Cu(I)-complex film on copper surface. The film was insoluble and would block the Cu dissolving as $Cu^+$ and $Cu^{2+}$ ions in sea water.

Key words: copper; sea water; corrosion inhibitor
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Benzotriazole has been shown to be a good corrosion inhibitor for different metallic substrates including copper and copper alloys[1-6]. This work presents the results of a study of the corrosion inhibition of copper in seawater state by means of the addition of BTA and sodium citrate in different concentrations. The corrosion/inhibition mechanism and kinetics have been evaluated using electrochemical and surface analysis techniques (SEM, XPS).

## 1 Experimental procedures

### 1.1 Chemical and materials

The inhibitors used BTA and sodium citrates were chemically pure. Sea water was used as the test solution and typical analysis of this electrolyte is pH 8.1, Conductivity 700 000 (μs/cm), Cl$^-$ (18.12 g/L).

### 1.2 Weight loss method

Weight loss of rectangular copper specimens of size 5 cm × 2.5 cm × 0.2 cm in triplicate immersed in 500 mL of sea water with and without the inhibitors was determined after 6 days at 40℃.

### 1.3 Potentiodynamic polarization curves

The polarization curves were recorded by using computer controlled Gamry ZAHNER IM6/6e electrochemical system. The temperature of the electrolyte was maintained at 40℃.

### 1.4 Surface analysis

The specimens were examined for their structural and topographical features using Electron spectroscopy (SEM) for analysis of surface. The compounds formed on the copper surface were analysised by X-ray photoelectron spectroscopy (XPS) after 6 days in sea water with and without the addition of BTA and sodium citrate.

## 2 Results and discussion

### 2.1 Weight loss measurements

The results of experiment indicated that the inhibition efficiency increased with increasing benzotriazol (BTA) concentration, but the efficiency is over 90% until the concentration of BTA is 150 mg·L$^{-1}$. It had been found that there was synergistic effect between BTA and sodium citrate. The inhibition efficiency was 96.0%, and corrosion rate was 0.00431 mm/a in the proportion of 2 mg·L$^{-1}$ BTA and 20 mg·L$^{-1}$ sodium citrate inhibitor, and the cost of corrosion inhibitor for copper in seawater is decreased greatly (Fig. 1, 2).

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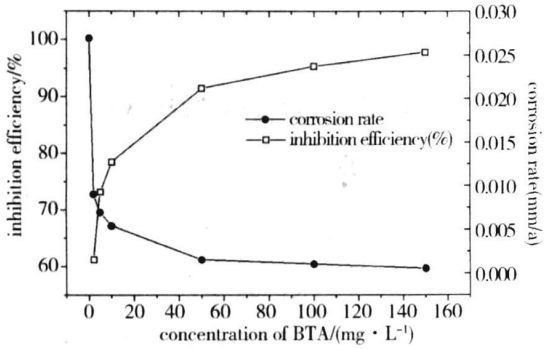


Fig. 1 Corrosion rate and inhibition efficiency of copper in seawater with and without BTA at 40℃

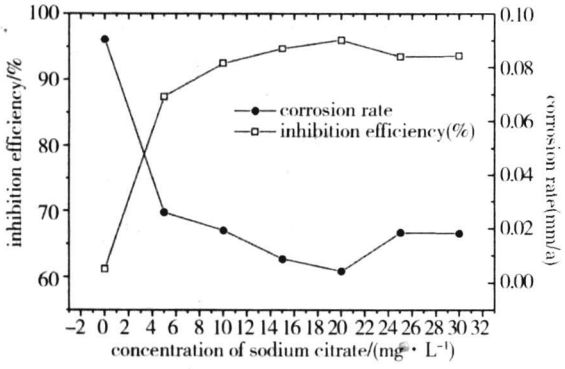


Fig. 2 Corrosion rate and inhibition efficiency of copper in seawater with and without sodium citrate at 40℃

## 2.2 Potentiodynamic polarization

Fig. 3 shows that the $E_{corr}$ with BTA 2 mg· $L^{-1}$ shifted to cathodic potentials, the inhibitors act as cathodic inhibitors; the polarization curves in seawater with BTA and sodium citrate compound inhibitors shift to positive and negative values, the BTA and sodium citrate compound inhibitor was a mixture inhibitor.

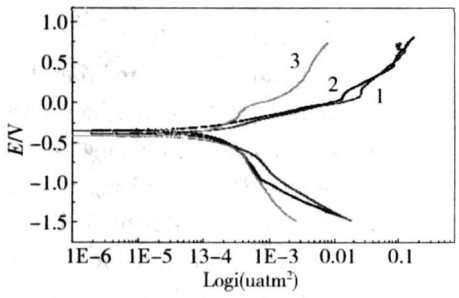


Fig. 3 Polarization curves for 1— blank; 2— 2 mg· $L^{-1}$ BTA; 3— 2 mg· $L^{-1}$ BTA + 20 mg· $L^{-1}$ sodium cirate

## 2.3 SEM analysis

Fig. 4 shows the SEM images of the surface of copper with or without inhibitors. The surface of copper without inhibitors which is heavily corroded, but the SEM image of the surface of copper with inhibitors shows little or no corrosion products and the surface remain shiny after immersed in seawater after 6 day.

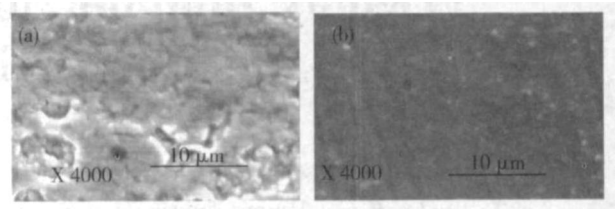


Fig. 4 Scanning electron micrographs of the surface of copper immersed in sea water after 6 days (a) without inhibitor (b) with 2 mg· $L^{-1}$ BTA and 20 mg· $L^{-1}$ sodium citrate inhibitor

## 2.4 Surface analysis of copper by XPS

The compounds formed on the copper surface were analysed by X-ray photoelectron spectroscopy (XPS) for the tests after 6 day of copper immersion in sea water with BTA and sodium citrate.

The results show that the inhibitive film formed on the copper surface contains Cu(Ⅰ)—BTA and Cu(Ⅰ)—sodium cirate complex. The film was insoluble and would block the Cu dissolving as $Cu^{+}$ and $Cu^{2+}$ ions in seawater.

# 3 Conclusions

(1) There was synergistic effect between BTA and sodium citrate. The inhibition efficiency was 96.0%, and corrosion rate was 0.00431 mm/a in the proportion of 2 mg· $L^{-1}$ BTA and 20 mg· $L^{-1}$ sodium citrate inhibitor, and the compound inhibitor was a mixture inhibitor.

(2) The SEM images show that the surface of copper without inhibitors which was heavily corroded, but the surface of copper with compound inhibitors remained shiny after immersed in seawater after 6 day. The results of the XPS spectrum of the surface of copper indicated that the compound inhibitor formed a Cu(Ⅰ)-BTA and Cu(Ⅰ)-complex film on copper surface. The film was insoluble and would block the Cu dissolving as $Cu^{+}$ and $Cu^{2+}$ ions in seawater.

## References:

[1] REDA Mahmoud, ALHAJJI R, JAMAL N. Effect of pre-extraneous ions of the corrosion of copper nickel alloys in sulfide-polluted artifical sea water[C]. J Univ Kuwait Sci, 1993, 14—19.

[2] LATHA G, RAJESWARI S. Diethyldithiocarbamate as a corrosion inhibitor for copper and brass in sea water[J]. Anti-Corrosion Methods and Materials, 1996, 43(1): 13—16.

[3] PATNAIK S R, VDAYABHANU G, RAWAT N S. E-

valuation of molybdate-polyvinyl alcohol mixtures as inhibitors for mild corrosion in synthetic seawater [J]. Bull Electrochem, 1993, 9 (2/3): 66—68.

[4] CELER E, AZAMBUJA D S. Corrosion inhibition of copper in chloride solution by pyrazole [J]. Corrosion Science, 2000, 42: 631—643.

[5] STATAKE M. Structure of benzotriazole films on metals [J]. Jpn Res Inst Adv Copper-Base Mater Technol, 2003, 42: 253—257.

[6] RAVICHANDRAN R, NANJUNDAN S, RAJENDRAN N. Effect of benzotriazole derivatives on the corrosion and dezincification of brass in neutral chloride solution [J]. Journal of Applied Electrochemistry, 2004, 34: 1171—1176.

# 海水介质中环境友好型紫铜缓蚀剂的缓蚀性研究

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摘　要：采用失重法、极化曲线、电镜扫描和 XPS能谱分析等方法对苯并三氮唑 (BTA) 及其复合缓蚀剂对海水中紫铜的缓蚀性能及缓蚀机理进行了研究。实验结果表明：单独使用 BTA浓度达到 150 mg·L⁻¹时，缓蚀率大于 90%；BTA与柠檬酸钠复配后，缓蚀率有了很大提高，当 BTA浓度为 2 mg·L⁻¹，柠檬酸钠浓度为 20 mg·L⁻¹时，缓蚀率达到 96.0%，腐蚀速率为 0.01014 mm/a，缓蚀剂成本大大降低。极化曲线试验结果表明，BTA缓蚀剂在海水中为阴极型缓蚀剂，BTA与柠檬酸钠复合缓蚀剂为混合型缓蚀剂。对添加了缓蚀剂的海水中的紫铜表面进行的扫描电镜测试及 XPS能谱分析的实验结果表明：添加了 BTA和柠檬酸钠缓蚀剂的紫铜表面光滑，基本没有腐蚀；且在试片表面形成了缓蚀剂各组分均参与成膜的非水溶性保护层，有效的抑制了紫铜在海水中的溶解腐蚀。

关键词：紫铜；海水；缓蚀剂；BTA；柠檬酸钠

中图分类号：TQ050.9