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Screening and Properties of Copper Corrosion Inhibitor in Circulating Cooling Water

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The corrosion behavior of four copper corrosion inhibitors benzotriazole (BTA), 2-mercaptobenzoxazole (MBO), methylbenzotriazole (TTA), and 5-carboxybenzotriazole (5-CBTA) at a concentration of 0.20 mmol/L to 3.5 % NaCl solution was studied. According to electrochemical test, soak test and corrosion morphology characterization analysis, the best corrosion inhibitor at the same concentration are screened out. The results of the electrochemical fitting test, static corrosion test, and metallographic micrograph all have suggested that the corrosiveness of the brass plate surface is significantly reduced after the addition of the high-concentration corrosion inhibitor. It can be obtained by means of a weight-loss method that, when the concentration of corrosion inhibitor is 0.20×10^{-3} mol/L, the minimum corrosion rate of BTA is 1.43×10^{-5} g/cm^2·d, metallographic micrographic characterization shows that BTA's inhibition effect is the best.

Keywords: electrochemical impedance spectroscopy, Tafel polarization, copper corrosion, corrosion inhibitors, electrochemical workstation.

1. INTRODUCTION

The circulating cooling water system is a major water consumer in industrial systems, and its stable operation is essential for ensuring safe and stable production in enterprises [1]. Currently, the main defects of circulating cooling water systems include scale deposition, metal corrosion, and the proliferation of bacteria and algae. The hazards of scaling include pipe blockage, reduction in the cross-sectional area of water circulation, increased flow resistance, and higher system transmission costs. The heat transfer resistance of heat exchanger tube walls is significantly increased, leading to increased energy consumption. Severe corrosion can occur beneath the scale, resulting in pipe perforation. The use of corrosion inhibitors increases the useful life of metals, significantly improves and conserves resource use, decreases environmental contamination, and lowers financial costs for businesses. The most effective way to prevent metal corrosion is generally to choose suitable corrosion inhibitors; however, different metal types have corresponding corrosion inhibitors of their own [2 – 5].

The dissolution and corrosion rates of copper are controlled by the anodic and cathodic reaction rates on its surface. The use of inhibitors is an effective method to reduce the corrosion rate of copper, which can be categorized into organic and inorganic inhibitors. Chromates, molybdates, and tetraborates are employed to decrease the corrosion rate of copper, but they pose certain challenges. For instance, chromates are toxic compounds that may increase the corrosion rate by accelerating the cathodic reaction rate. Due to the instability of the protective layer formed, molybdates and tetraborates cannot provide adequate corrosion inhibition in solutions containing corrosive anions. Most inorganic inhibitors exhibit relatively weak inhibition effects; thus organic inhibitors and their derivatives are commonly used to protect copper, as they offer higher inhibition efficiency [4].

Benzotriazole (BTA) [6] and its derivatives including 2-mercaptobenzoxazole (MBO) [7], methylbenzotriazole (TTA) [8], and 5-carboxybenzotriazole (5-CBTA) have been extensively studied as copper corrosion inhibitors. These compounds suppress corrosion by forming protective films on copper surfaces, playing critical roles across diverse industrial applications. However, their investigation in copper cooling recirculating water systems remains notably limited.

This study aims to investigate the effects of organic corrosion inhibitors like benzotriazole (BTA), 2-mercaptobenzoxazole (MBO), methylbenzotriazole (TTA), and 5-carboxylbenzotriazole (5-CBTA) on copper sheet surfaces in circulating cooling water. The inhibitors were evaluated by various electrochemical studies. The weight loss, EIS, potentiodynamic polarization, SEM, and XRD analysis were used to understand microbially induced corrosion inhibition processes.

2. EXPERIMENTAL

The copper samples were prepared by cutting, cleaning with tap water, and soaking in anhydrous ethanol for 3 minutes. Subsequently, they were rinsed sequentially with tap water and deionized water, dried, and left to stabilize until completely dry. The experiments were conducted using a CHI660C electrochemical workstation (Shanghai CH Instruments Co., Ltd.). The test specimens were subjected to Electrochemical Impedance Spectroscopy (EIS) and Tafel polarization curve measurements.

In this study, the electrochemical performance, static corrosion test results, and surface microstructure of copper sheets were comprehensively analyzed after the addition of

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BTA, MBO, TTA, and 5-CBTA at a concentration of 0.20 mmol/L.

A three-electrode system was employed, comprising platinum mesh (10 mm × 10 mm) as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and the copper sample had a contact area of 1 cm² as the working electrode. Open circuit potential (OCP) was measured over 600 seconds with a sampling interval of 1 second. For EIS measurements, the frequency range was set from 1 Hz to 1×10^5 Hz, with a sinusoidal perturbation amplitude of 0.01 V applied at the OCP value. The system was allowed to stabilize for 2 seconds before measurement, and automatic sensitivity settings were used. Tafel polarization curves were recorded at a scan rate of 0.001 V/s within ± 250 mV of the OCP. The scan duration was set to 1 segment, with a stabilization period of 2 seconds and automatic sensitivity adjustment. These procedures ensured accurate and reliable data collection while minimizing the load effect. This methodology provides a comprehensive approach to evaluating the corrosion resistance of brass materials under controlled conditions, facilitating further analysis and optimization of anti-corrosion strategies. The surface morphology of Cu in 3.5 % NaCl solutions with different corrosion inhibitors can indeed be observed by a metallurgical microscope MR2000 (Nanjing Jiangnan Novel Optics Co., Ltd.) to characterize the corrosion characteristics.

3. RESULTS AND DISCUSSION

The AC Electrochemical Impedance Spectra of BTA, MBO, TTA, and 5-CBTA at concentrations of 0.20 mmol/L and 3.5 % NaCl solution are shown in Fig. 1.

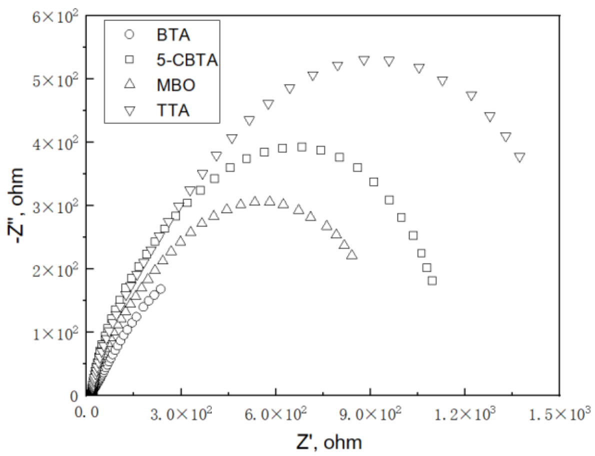


Fig. 1. Nyquist diagrams of copper sheets exposed to 3.5 % NaCl solution with various corrosion inhibitors

Fig. 1 shows that in all four solutions, the capacitive arcs of the copper plate exhibit dramatically flattened capacitive arcs along with powerful dispersion effects. For the copper electrode without different corrosion inhibitors, a high frequency semicircle was observed, followed by a straight line portion in the low-frequency (LF) region. The HF semicircle is attributed to the time constant of charge transfer and double layer capacitance for the resistance of the solution (R_s) enclosed between the working electrode and the counter electrode. The intercept of the HF charge transfer semicircle with the real axis gives the charge transfer resistance (R_t) value[9].

The arcs' departure from the expected semicircle shows that the oxide coatings and adsorbed substances on the electrode surface have an effect on the copper plates. Additionally, the reaction resistance of the copper hanging piece is maximum in MBO, lowest in 5-CBTA, and lower in TTA due to the direct association between the diameter of the semicircle and the reaction resistance.

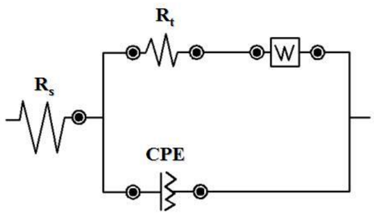


Fig. 2. The equivalent circuit

The information in Fig. 2 and Table 1 illustrates that whereas *CPE* and Z_w fluctuate somewhat, the values of R_s do not differ greatly from one another. The corrosion inhibitor TTA's R_t value was discovered to be the greatest when comparing charge transfer resistances, which suggests that the corrosion electrode reaction on the surface of copper is more challenging to take place. TTA has the best corrosion inhibition efficacy as a result. R_t size is arranged as follows: TTA>MBO>BTA>5-CBTA.

Table 1. The fitting parameters of EIS

Types	R_s, Ω	R_t, kΩ	Z_w, Ω	*CPE*, 10^{-6}×pF
BTA	13.2	1.2	6.8×10^{-5}	7.4×10^{-4}
MBO	14.5	1.3	2.7×10^{-5}	3.3×10^{-4}
TTA	14.4	1.9	2.5×10^{-4}	6.0×10^{2}
5-CBTA	12.8	0.7	2.9×10^{-4}	4.2×10^{-3}

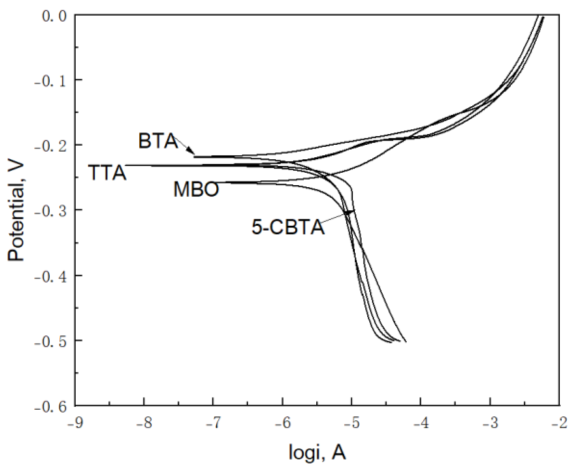


Fig. 3. Tafel diagrams of copper sheets exposed to 3.5 % NaCl solution with various corrosion inhibitors

Fig. 3 compares the polarization curves obtained from four corrosion inhibitors at doses of 0.20 mmol/L in a 3.5 % NaCl solution. Various corrosion inhibitors are depicted as curves in the picture.

Specifically, the anodic branch of copper in sodium chloride solution, shows three obvious regions. First, the current increases from the Tafel region at lower overpotential, and this increase continues until the peak current density is reached due to the dissolution of copper metal. The current increase at this stage is mainly due to the dissolution of copper. Secondly, the current enters the decreasing region until it reaches the minimum value. This decrease is due to the formation of $CuCl^+$. At this stage, the dissolution rate of copper gradually slowed down, forming a layer of CuCl film, which hindered the further dissolution of copper. Finally, the current density increases suddenly and reaches a limit value. This is due to the formation of $CuCl_2$, which is the main reason for the dissolution of copper. At this stage, the dissolution rate of $CuCl_2$ is faster, resulting in a significant increase in current density [10, 11]. Table 2 compares the Tafel curves corresponding to corrosion resistance parameters. Table 2 discovered that the E_{corr} did not alter considerably whereas the R_p varied dramatically from I_{corr}. The comparison of corrosion resistance parameters of the corresponding Tafel curve is shown in Table 2. It was found that the E_{corr} did not differ significantly, while the R_p fluctuated significantly. The I_{corr} of BTA was the smallest and the I_{corr} of IEI was also the smallest, indicating that BTA had the best corrosion inhibition effect. In summary, the corrosion behavior of copper in a 3.5 % NaCl solution is a complex electrochemical process involving multiple reaction stages and current changes. Through the study of potentiodynamic polarization curves, we can gain a deeper understanding of the corrosion mechanism of copper and provide a theoretical basis for the development of effective corrosion inhibitors.

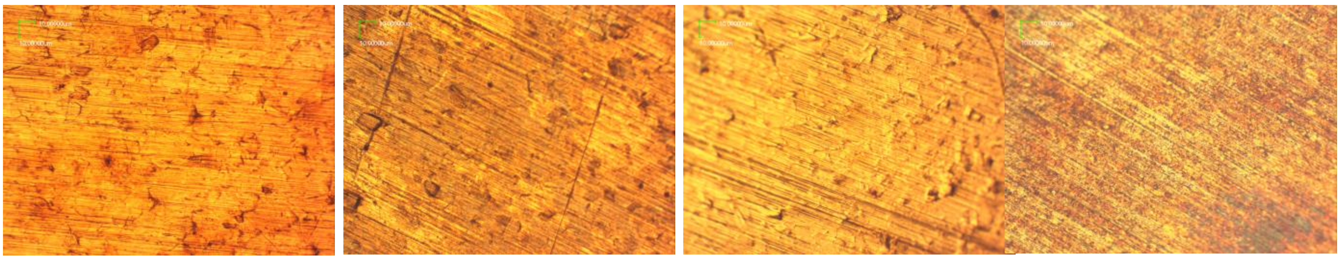
Fig. 4 illustrates the surface microstructure of copper hanging plates after static corrosion tests with BTA, MBO, TTA, and 5-CBTA added at concentrations of 0.20 mmol/L. The results indicate that BTA and TTA exhibit superior corrosion inhibition effects, as evidenced by the improved surface morphology and brighter color of the treated copper sheets. Conversely, MBO treatment resulted in an insufficiently smooth surface, while 5-CBTA led to significant corrosion covering the entire brass strip surface. This suggests that MBO and 5-CBTA failed to effectively suppress dezincification corrosion in the brass strips, highlighting their poor corrosion inhibition performance. The findings underscore the importance of selecting appropriate corrosion inhibitors to protect metallic surfaces in corrosive environments. Further research should focus on optimizing inhibitor formulations to enhance protection efficacy.

The average corrosion rates of four corrosion inhibitors in a 3.5 % NaCl solution at concentrations of 0.20 mmol/L are compared using the weight loss method. Different corrosion inhibitors are represented by the points on the curve in Table 3. Table. 3 demonstrated that each inhibitor's corrosion inhibition effects varied. The inhibitor's ability to prevent corrosion is worse the greater the average corrosion rate. It can be shown that BTA has the best corrosion inhibition effect because its average corrosion rate is the lowest and is closest to 0. The average corrosion rate of MBO is negative, which shows that corrosion products resulting from weight growth have not been entirely eliminated. Rust sticks to the brass sheet's surface as a result of dezincification corrosion, which takes place on the brass surface. The oxide film that forms on the copper surface at the start of corrosion causes some passivation to protect the copper sheet, therefore its ability to suppress corrosion is also effective.

It is important to note that during this process, the polymerization chain is joined by non-adjacent copper atoms and produces matching multi-layer protective coatings. The coordination bonds between the lone pair electrons on the nitrogen atoms in BTA molecules and copper efficiently attach them to copper. The corrosion inhibition mechanism of MBO is comparable to that of BTA, which prevents corrosion by forming a corrosion inhibition film by interacting with copper ions. The two, however, produce different protective films. TTA offers benefits in strength and density at a higher level.

Table 2. The fitting parameters of Tafel

Types	b_a, mV·dec^{-1}	b_c, mV·dec^{-1}	I_{corr}, μA·cm^{-2}	E_{corr}, V	I_{EI}, g/cm^2·d	R_p, kΩ
BTA	22.92	18.58	0.86	-261.25	0.010	5.16
MBO	40.94	33.13	1.04	-227.00	0.012	7. 68
TTA	45.43	25.95	1.72	-248.11	0.020	4.18
5-CBTA	28.91	14.05	2.21	-273.27	0.026	1.86



a b c d

Fig. 4. Metallographic graphs of copper hangers under four corrosion inhibitors: a – BTA; b – MBO; c – TTA; d –5-CBTA

Table 3. Average corrosion rates among different corrosion inhibitors

Corrosion inhibitor name	5-CBTA benzotriazole	2-mercaptobenzoxazole	Methylbenzotriazole	5-carboxylbenzotriazole
Average corrosion rate, g/cm^2·d	1.43×10^{-5}	-3.29×10^{-3}	5.71×10^{-5}	5.43×10^{-4}

TTA is an insoluble protective coating that is successfully produced on the copper surface through chemical adsorption and copper ions. The Cu_2O layer on the surface of 5-CBTA gradually thickens, and the film created by the electrode is the primary cause of this thickening and increase, which ultimately has the effect of inhibiting corrosion.

Corrosion inhibitors for copper function by reducing anodic or cathodic reactions, or both. Anodic inhibitors decrease the dissolution rate of copper in corrosive environments, forming protective films on the metal surface. Cathodic inhibitors slow down the reduction reactions of oxygen or hydrogen on the copper surface. Mixed inhibitors control both anodic and cathodic processes simultaneously. By adsorbing onto the copper surface or reacting chemically, these inhibitors form barriers that prevent corrosive species from interacting with the metal. This multifaceted approach ensures effective protection against corrosion, extending the lifespan and maintaining the integrity of copper materials in various applications.

3. CONCLUSIONS

The findings indicate that while all inhibitors exhibit some degree of corrosion suppression, BTA demonstrates superior efficacy in mitigating corrosion in copper sheets. Specifically, BTA significantly reduces corrosion rates and alters the surface microstructure to enhance protective properties. The electrochemical impedance spectroscopy (EIS) and polarization curves further support these observations, showing that BTA forms a more stable and effective protective film on the copper surface compared to other inhibitors. Therefore, BTA is identified as the most effective corrosion inhibitor among the tested compounds at this concentration. This conclusion underscores the importance of selecting appropriate inhibitors to optimize corrosion protection in practical applications.

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