The Effect of Benzotriazole and Phenyl-amino-triazine-dithiol on Corrosion Inhibition of Copper in Low-conductivity Water

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Impedance measurements of copper electrodes in a low-conductivity water (less than $10 \mu\text{S/cm}$) with the addition of either benzotriazole (BTA) or phenyl-amino-triazine-dithiol (PTD) were performed. BTA inhibits copper corrosion better than PTD. Corrosion inhibition with PTD occurs only at concentrations above 10 ppm. A combination of BTA and PTD proved more effective than either used alone. The optimum ratio is 3 ppm BTA + 2 ppm PTD with the total amount of inhibitor 5 ppm.

Key words: copper corrosion inhibition, low-conductivity water, mixed inhibitor, impedance measurement

1. Introduction

Water cooled generators are widely used in power plants. Low-conductivity water (less than $10 \mu\text{S/cm}$) flows through hollow copper conductors as the cooling medium and causes corrosion of the conductors. Therefore, corrosion inhibitors are important to protect copper conductors against corrosion and to operate generators safely and economically. Impedance measurements are effective approaches to the study of corrosion inhibition.

There are several papers on impedance measurements with benzotriazole (BTA) as a corrosion inhibitor for copper in sodium chloride solutions^{1)~3)}. However, there have no impedance studies on the inhibitive action on copper in low-conductivity solutions. This paper studies the inhibition of copper corrosion with BTA and *N*-phenyl-6-amino-1,3,5-triazine-2,4-dithiol (PTD) in the low-conductivity solutions by impedance measurements.

2. Experimental

The chemical analysis of the low-conductivity solution is as follows; O_2 1.5~2 ppm, NH_3 <1

ppm, SiO_2 <20 ppb, and Na^+ <50 ppb. Fig. 1 shows the chemical structure of BTA and PTD. A 99.9% pure copper electrode was with a sur-

N-Phenyl-6-amino-1,3,5-triazine-2,4-dithiol
mono sodium salt

Fig. 1 Chemical structure of the inhibitors.

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face area of 1 cm^2 and reagents were of analytical grade. The pH of the solutions were adjusted with ammonia water and kept at 7.4, and except the 40 ppm PTD solution the conductivity of solutions was maintained at less than $10\text{ }\mu\text{S/cm}$. The use of ammonia water to adjust pH of solution is a common practice in most power plants in China. Since there was only a little amount of NH_4^+ in the solution, it did not accelerate copper corrosion with forming ammonium-copper complex. Before every run the electrode surface was abraded with emery papers No. 2, 3, 4, and 5. The electrode was washed, degreased with acetone, rinsed with deionized water, and immersed in the solution in a cell.

Impedance measurements were performed at the corrosion potential in a three-electrode electrochemical cell at 30°C with a Pt electrode as a counter electrode and a saturated calomel electrode as a reference electrode with a PARC M 273 potentiostat, PARC 5208 EC lock-in amplifier, and PARC M 378 software system over a frequency range of 0.05 Hz to 100 kHz.

3. Results and discussion

The equivalent circuit for the electrode system with corrosion inhibitors is shown in Fig. 2, where R_1 is the solution resistance, R the film resistance, C the film capacitance, and Z_w the Warburg impedance²⁾. The R and C values can be determined from Bode plots, where the R value can be calculated from the maximum phase angle, $\theta_{\max}$, and the corresponding value of the impedance modulus at $\theta_{\max}|Z|_{\theta_{\max}}$ according to

$$R = 2|Z|_{\theta_{\max}} \tan \theta_{\max}^{4), 5)} \quad (1)$$

Fig. 2 Equivalent circuit for the copper electrode in low conductivity solutions containing corrosion inhibitors.

Fig. 3 Bode plots for copper electrodes 30 min after immersion in low conductivity solutions with the addition of BTA at 30°C . BTA: 0 ppm ●, 2 ppm ▲, 10 ppm ■, 40 ppm ○

and the C values calculated from $|Z|_{\theta, \max}$ and the corresponding value of the frequency at $\theta_{\max}$, $f_{\theta, \max}$ according to the equation⁵⁾

$$C = \frac{1}{2\pi f_{\theta, \max} |Z|_{\theta, \max}} \quad (2)$$

Fig. 3 shows Bode plots for copper electrodes after 30 min immersion in low-conductivity solutions with various BTA concentrations. Both the impedance modulus $|Z|$ and $\theta_{\max}$ increases with BTA concentration. With increased BTA concentration, R increases and C decreases as shown in Fig. 4. In addition, both R and C change markedly with the BTA concentrations below 5 ppm.

Fig. 4 R and C vs. BTA concentration for copper electrodes after 30 min immersion in low conductivity solutions at 30°C.

Fig. 5 shows R and C vs. immersion time with the addition of 5 ppm BTA and that of 20 ppm PTD. With increased immersion time R increases and C decreases. The changes in R and C due to the addition of BTA are attributed to the formation of a CuBTA protective film^{6), 6), 7)}. The film becomes thicker and more protective as BTA concentration and immersion time increase.

Mori et al.⁸⁾ reported that PTD reacted easily with copper oxides in water, and the chemical formula of the surface films formed on copper oxides would mainly be $C_6H_5NH-C_3N_3S_2 \cdot 2Cu(I)$, as determined by infrared spectroscopy. For copper, and especially brass, PTD is an effective corrosion inhibitor^{9) ~ 11)}, and inhibition appears at concentrations above 10 ppm.

Fig. 6-a, b, c, and d show Nyquist plots for copper electrodes 24 hr after immersion in solutions containing 0, 5, 10, and 20 ppm, respectively. In the absence of PTD (Fig. 6-a), a high frequency semicircle and a straight line are observed. The straight line with the slope of about 45 degrees appears at low frequencies, which represents Warburg impedance due to the diffusion of dissolved oxygen in the solution. It implies that the corrosion reaction of copper in the absence of PTD is dominated by the diffusion of dissolved oxygen. The high frequency semicircle can be mainly attributed to the reference electrode system in the cell¹²⁾. (We are studying this phenomenon further and will publish results separately.) The impedance locus in Fig. 6-b is similar to that in Fig. 6-a. In Fig. 6-c, the second semicircle appears in

Fig. 5 R and C vs. immersion time for copper electrodes in low conductivity solutions with 5 ppm BTA and 20 ppm PTD at 30°C.

Fig. 6 Nyquist plots for copper electrodes after 24 hr immersion in low conductivity solutions with (a) 0 ppm, (b) 5 ppm, (c) 10 ppm, and (d) 20 ppm PTD.

the middle frequency range, corresponding to the charge transfer process at the CuPTD/solution interface.

Fig. 6-d shows a much larger semicircle for 20 ppm PTD, and the film resistance R , determined from the diameter of the semicircle, increases from $\sim 5 \times 10^3 \Omega \text{cm}^2$ to $1 \times 10^6 \Omega \text{cm}^2$ as PTD concentration increases from 10 ppm to 20 ppm. Therefore, the corrosion reaction of copper in the presence of 20 ppm PTD is controlled by the resistance of CuPTD film. It is noted in Fig. 6-d that the high frequency semicircle still remains and its enlarged diagram is exhibited in the inset of Fig. 6-d. The diameter of the high frequency semicircle decreases with increasing PTD concentration because of the increase in solution conductivity caused by PTD. As to the explanation of the high-frequency semicircle and the determination of solution resistance we shall write in a separate paper.

Table 1 shows the relationship between solution conductivity and PTD concentration. Unlike PTD even small amounts of BTA shows marked inhibitive action. Both $|Z|$ and $\theta_{\max}$ increase remarkably from 0.01 ppm to 0.1 ppm BTA. The addition of 0.1 ppm BTA in the solution makes $\theta_{\max}$ close to 40 degrees.

Fig. 7 shows R vs. concentrations of BTA and PTD. It is evident that BTA inhibits cor-

Table 1 Changes in solution conductivity with PTD concentration.

PTD concentration (ppm.)	0	5	10	20	40
conductivity ($\mu \text{ mho/cm}$)	4	5	6	8	12

Fig. 7 Influence of BTA and PTD concentration on R after 30 min immersion at 30°C.

rosion of copper better than PTD at concentrations up to 40 ppm. Experiments with a combination of BTA and PTD at a total concentra-

Fig. 8 R vs. PTD/BTA ratio for copper electrodes after 30 min immersion in low conductivity solutions at 30°C.

tion of 5 ppm, which is suitable for practical applications in water cooling generators, were made. The combination of BTA and PTD is more effective than either used alone.

Fig. 8 shows R vs. the PTD to BTA ratio. The maximum value of R is at the 2 ppm PTD to 3 ppm BTA ratio. The value at this ratio is about $10^6 \Omega\text{cm}^2$. The combination of BTA and PTD obviously improves the inhibitive action and shows a synergistic effect. BTA may spread over the surface of copper electrodes

and form a protective film consisting of a CuBTA polymeric network^{9),10)}. PTD may then plug defects in the network on Cu/Cu₂O by forming CuPTD film.

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