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The influence of sodium hypochlorite biocide on the corrosion of carbon steel in reclaimed water used as circulating cooling water

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ABSTRACT

In this paper, we investigated the influence of sodium hypochlorite (NaClO) biocide on the corrosion of carbon steel in four different conditions during one dosing cycle. The results from the polarisation curve and electrochemical impedance spectroscopy (EIS) indicated that NaClO could affect the activity of microorganisms, leading to corrosion inhibition. The equivalent circuits had two time constants in the presence of biocide, which suggested that an oxide layer of NaClO was formed on the carbon steel surface. Environmental scanning electron microscopy (ESEM) and energy dispersive spectroscopy (EDS) were both employed to demonstrate that NaClO produced a good antibacterial activity, thereby indirectly retarding corrosion while simultaneously inhibiting scaling.

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1. Introduction

To make better use of limited water resources and relieve the serious fresh water resource crisis, the reclamation and reuse of wastewater have gained considerable interests in recent years [1,2]. Open recirculating cooling water systems that reuse cooling water are frequently used at large electric utility plants. Using reclaimed water as one of the unconventional water sources, these plants can reduce their use of water from other higher-quality sources. As a result, the high-quality water can be reserved for other purposes, such as supplying municipal drinking water [3–5]. However, reclaimed water inevitably contains organic matter and nutrients, such as nitrogen and phosphorus. In addition, abundant dissolved oxygen combined with an appropriate temperature and pH in the open system can easily result in the problem of microbe multiplication [6]. Microorganisms tend to form and grow biofilms – complex communities of microorganisms attached to surfaces by means of self-produced extra polymeric substances (EPS), leading to a reduction of the efficiency of the heat exchanger [7]. What is more, the production of hydrogen sulphides is enhanced, and the intrinsic heterogeneity established drastically changes the electrochemical conditions, such as the concentrations of ions, pH, and oxygen levels at the metal/solution interface, and finally leads to critical localised corrosion processes [8–13]. Consequently, adding biocide is considered a reliable approach to addressing microbe multiplication [14].

Most previous studies investigated the antibacterial activity of biocide and the effect on water quality [15], but overlooked its influence on corrosion. Only a small number of researchers have conducted experimental investigations of new antimicrobial corrosion inhibitors. For example, El-Shamy [16] studied how a new biocide – an antimicrobial corrosion inhibitor named HQS influenced mild steel dissolution in a saltwater environment through weight loss measurements and electrochemical and microorganism tests. The results obtained from the above study indicated that HQS could decrease corrosion and microbial growth under the conditions tested. In addition, scanning electron microscopy (SEM) images revealed that the corrosion inhibition by the HQS on the mild steel surface was significantly improved in the presence of the biocide.

Currently, oxidising biocide is the type of biocide that is widely used. In this study, actual circulating cooling water of four concentrations were used, and the microbial group was taken as the research object aiming at exploring the influence of the oxidising biocide on the corrosion of carbon steel in reclaimed water used as the circulating cooling water. Potentiodynamic polarisation (PP) measurement, electrochemical impedance spectroscopy, and environmental scanning electron microscopy were used to compare the different corrosion rate of carbon steel with and without microorganisms or biocide and to assess the influence of NaClO on the corrosion of carbon steel. Moreover, this study provided theoretical support for the addition of biocide in power plants.

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2. Experimental procedure

2.1. Material

The specimens used in the electrochemical experiment were L-shaped Q235 carbon steel. The steel's composition (wt%) was 0.20 C, 0.55 Mn, 0.30 Si, <0.050 S, <0.045 P and Fe balance. To create working electrodes (WE), only a circular surface of 0.5 cm in diameter of the specimen was in contact with the circulating cooling water, and the rest was sealed by epoxy resin. The working face was abraded using a series of silicon carbide papers of 500, 800, 1000 and 1200 grit, rinsed with distilled water, degreased ultrasonically in ethanol and acetone, and subsequently dried in room temperature.

2.2. Electrochemical studies

The electrochemical experiments were performed using impedance equipment (CorrTest CS2350). All of the tests were conducted in a standard three-electrode cell with a platinum sheet as a counter electrode, a saturated calomel reference connected to the reactor through a Luggin capillary filled with a salt bridge, and a carbon steel sample as a working electrode. The experimental water was obtained from a water reclamation plant in northern China and later concentrated up to four times, which has the best water-saving effect in actual production. The water quality of the cooling water is presented in Table 1.

Four experimental runs were performed under various operating conditions as follows: (I) carbon steel in regular circulating cooling water without NaClO; (II) carbon steel in circulating cooling water with NaClO; (III) carbon steel in sterile circulating cooling water with NaClO; (IV) carbon steel in sterile circulating cooling water without NaClO.The treatment methods are shown in Table 2.

According to prior experimental results, each electrochemical parameter fluctuated considerably when the new carbon steel electrodes were immersed in the circulating cooling water at the primary stages, which would reach steady values after 48 h. Consequently, the carbon steel electrodes were immersed in the circulating cooling water for 2 d before they were used to simulate rusty carbon steel in the actual conditions followed by sterilisation. Next, the three-necked flasks of these four groups with different water and electrodes were placed in a water bath at 40 ± 1 °C. The choice of this temperature is justified by the fact that it is the temperature of cooling water circulation. Considering that the dosing cycle of the biocide is usually 15 d in actual use, the electrochemical tests were conducted at 6 h, 2 d, 4 d, 8 d and 15 d.

Electrodes that required sterilisation (including counter electrode, reference electrode and working electrode) were exposed to ultraviolet light for 30 min prior to use. Sterile water was prepared four times using the following methods: regular four times circulating cooling water was injected into a conical flask and later sterilised in a vapour pressure cooker for 20 min at 121 °C. The same parameter was used for three-necked flasks.

There were five working electrodes of each group immersed in the same environment for the tests of polarisation curves. Only one electrode was used for testing each time and each electrode was only used once to ensure the electrodes were not affected by prior tests.

In this study, the polarisation was started at a scan rate of 0.10 mV/s over a range of −70 mV to 70 mV around E_{corr} after attaining a steady open circuit potential (OCP) at the frequency of 2.0 Hz. Cview 2.0 was used for the analysis and calculation of the potentiodynamic polarisation curve data. The EIS measurement was performed on a steady-state OCP driven at an applied ac signal of 10 mV and a frequency ranging from 100 kHz to 10 mHz. Zview was used to collect the EIS data.

2.3. Surface analysis

Environmental scanning electron microscopy (ESEM) and energy dispersive spectroscopy (EDS) techniques were used to examine the surface characteristics and corrosion features of the carbon steel electrodes after 15 d of exposure to circulating cooling water under the four different conditions.

3. Results

3.1. Polarisation curves

The potentiodynamic polarisation behaviour of carbon steel in the absence and the presence of biocide or microorganism is shown in Fig. 1(a)–(d) at 40 ± 1 °C. The electrochemical corrosion kinetics parameters, i.e., corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic and cathodic Tafel slopes (b_a, b_c), as well as corrosion rate obtained from the Tafel extrapolation of the polarisation curves, are presented in Table 3. In addition, polarisation resistance R_p obtained from R_p fit is also shown in the table.

As indicated in Table 3, the E_{corr} values of these four groups all shifted toward more positive values, demonstrating that the corrosion resistance of carbon steel was improved over time. Besides, the addition of NaClO in circulating cooling water significantly reduced i_{corr}, which indicated its corrosion inhibition properties for carbon steel. The polarisation resistance R_p represents the slope of tangent line at the point of E_{corr} on the polarisation curves [17]. The corrosion rate in (II) circulating cooling water with NaClO was smaller than those in (I) regular circulating cooling water without NaClO. In other words, the corrosion rate became lower in the presence of

Table 1
Water quality index of the recirculating cooling water.

Index	pH	Electrical conductivity (μs cm^{-1})	Hardness as $CaCO_3$ (mg/L)	Alkalinity as $CaCO_3$ (mg/L)	Cl^- (mg/L)	SO_4^{2-}(mg/L)
Value	9.34	4552	586.27	280.36	852.08	808.99

Index	COD_{Cr}(mg/L)	Total phosphorus(mg/L)	Total nitrogen(mg/L)	Turbidity(NTU)	Bacteria(CFU/mL)
Value	67	3.160	9.003	1.25	10^5

Table 2
Treatment method of each item.

	Water quality	Dosage of NaClO	Electrode	Three-necked flask
I	Regular circulating water	0 mg/L		
II	Regular circulating water	8 mg/L		
III	Sterile circulating water	8 mg/L	Ultraviolet sterilisation	High temperature sterilisation
IV	Sterile circulating water	0 mg/L	Ultraviolet sterilisation	High temperature sterilisation

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