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The Preparation and Performance Study of a Phosphate-Free Corrosion/Scale Inhibitor

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ABSTRACT

By using acrylic acid copolymer, sodium citrate, hydrolyzed polymaleic anhydride (HPMA), corrosion inhibitor D and Zn^{2+} synergist as raw materials, a multi-component phosphate-free corrosion and scale inhibitor was developed. The performance of the composite phosphate-free corrosion and scale inhibitor was evaluated using the rotary hanging sheet corrosion test, the static scale inhibition test and the corrosion electrochemical test. And the surface morphology of the carbon steel was observed by scanning electronic microscope (SEM). Orthogonal experiment results indicated that the optimal mass ratios of amino acid: Zn^{2+} synergist: HPMA: corrosion inhibitor D: acrylic acid copolymer was 0.5:10:12:1:8. It was also observed that phosphate-free corrosion and scale inhibitor based on an anodic reaction through the electrochemical corrosion experiment, its annual corrosion rate and scale inhibition rate reached 0.0176 $mm \cdot a^{-1}$ and 98.3%, respectively, showing excellent corrosion and scale inhibition performance.

Keywords: Phosphate-Free Corrosion/Scale Inhibitor; Static Scale Inhibition Method; SEM; Electrochemical Corrosion

1. Introduction

Industrial recirculating cooling water accounts for 60% - 70% in the industrial water, it will result in corrosion, scaling and microbial slime of the equipment and the pipeline as well as reduce their service life without treating. Thus, to treat recirculating cooling water has aroused the concern from the whole society.

Organophosphorus compound was a type of corrosion inhibitor extensively used since 1980s. However, it's diminishing because of its toxic effects on aquatic and other life [1]. Therefore, the public began to focus on the development of low phosphorus, non-phosphorus and heavy nonmetal salt corrosion and scale inhibitors. On one hand, low phosphorus corrosion and scale inhibitor is developing rapidly, such as 2-phosphono-1,2,4-tricarboxylic acid butane (PBTCA) and hydrolyzed polymaleic anhydride (HPMA) [2]. On the other hand, the non-phosphorus corrosion and scale inhibitor has also obtained new achievements.

In this paper, a multi-component phosphate-free corrosion and scale inhibitor blend composed of acrylic acid copolymer, sodium citrate, hydrolyzed polymaleic anhydride (HPMA), corrosion inhibitor D and Zn^{2+} synergist was prepared [3-7]. The recirculating cooling water was obtained from water treatment plant. The performance of the phosphate-free corrosion and scale inhibitor was eva-

luated by rotary hanging sheet corrosion test and static scale inhibition test. The mechanism of corrosion and scale inhibition was preliminarily investigated by corrosion electrochemistry test and scanning electron microscope (SEM) techniques [8-11].

2. Experimental

2.1. Main Materials

Acrylic acid copolymer, sodium citrate, hydrolyzed polymaleic anhydride (HPMA), sodium citrate, Zn^{2+} synergist and anhydrous alcohol. All chemicals were of analytical reagent-grade.

2.2. The Rotary Hanging Sheet Corrosion Test

The corrosion rate of A3 type carbon steel was determined by weight loss test. The carbon steel sheets were polished with different grades of emery paper, degreased with anhydrous alcohol, and rinsed with distilled water. Having been dried by electric dry oven and accurately weighed by electronic balance, the carbon steel were immersed in a beaker with water sample and with or without inhibitors. And the quality index of water sample was presented in **Table 1**. The beakers were put into the rotary hanging piece corrosion test instrument. Experimental conditions as follows: 1) constant temperature was $45°C \pm 1°C$; 2) rotating speed was 75 $r \cdot min^{-1}$; 3)

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Table 1. Water quality index.

Project	Analysis value
pH value	7.24
calcium ion/(mg·L^{-1})	92.57
magnesium ion/(mg·L^{-1})	61.28
chloride ion/(mg·L^{-1})	397.5
total hardness/(mmol·L^{-1})	4.54
total alkalinity/(mmol·L^{-1})	4.37
potassium ion/(mg·L^{-1})	15.24
conductivity/(μs·cm^{-1})	925
total dissolved solids content/(mg·L^{-1})	606

experimental period was 72 hours. After 72 hours, the carbon steel sheets were taken out, washed, dried and accurately weighed. Each set of experiments was repeated three times at least to ensure reproducibility. According to Technical Conditions of Standard Corrosion Spool of Chemical Treatment in Cooling Water (HG/ T3523-2008), A3 type carbon steel with a size of 50 mm × 25 mm × 2 mm and an area of 28 cm^2 in the experiment.

The annual corrosion rate and corrosion inhibition efficiency was calculated by formulae (1) and (2), respectively [12]:

$$K_a = \frac{87600(m_0 - m)}{s \rho t} \qquad (1)$$

where K_a is the annual corrosion rate, mm·a^{-1}; m_0 is the weight of the carbon steel before experiment, g; m is the weight of the carbon steel after experiment, g; s is the surface area of the carbon steel, cm^2; ρ is the density of the carbon steel, g·cm^{-3}; t is the test time, h.

$$K = \frac{(K_0 - K_1)}{K_0} \times 100\% \qquad (2)$$

where K is the corrosion inhibition efficiency; K_0 and K_1 are the values of the weight loss of carbon steel after being immersed in solutions without and with inhibitors, respectively, mm·a^{-1}.

2.3. The Static Scale Inhibition Test

The mechanism of scaling inhibition mainly included lattice deformation, complexation, dispersion effect and dispersive active [13,14]. In the experiment, 0.5 L·min^{-1} of nitrogen was ventilated to the bottom of the container with adding 30 mg·L^{-1} of inhibitor at 45˚C. The experiment was ceased after six times diluted concentration.

$$\eta_K = \frac{C_2 - C_1}{K \times C_0 - C_1} \times 100\% \qquad (3)$$

where C_2 is determined mass concentration of calcium

ion after adding chemicals, mg·L^{-1}; C_1 is determined mass concentration of calcium ion without chemicals, mg·L^{-1}; C_0 is initial mass concentration of calcium ion without chemicals, mg·L^{-1}; K is the concentration multiple in the determined conditions of C_2 and C_1.

2.4 .Corrosion Electrochemical Experiments

Corrosion electrochemical methods consulted the research methods and measurement techniques in other fields. According to the characteristics and requirements of corrosion metal electrodes, it has become a significant method for the research and measurement of corrosive electrochemistry with improvement and modification. In particular, the dynamic potential polarization is the common method that evaluates inhibition efficiency of corrosion inhibitor [15]. Polarization curve obtained from the dynamic potential polarization extrapolates corrosion potential to obtain corrosion current density I and *Tafel* parameters. The shape of cathode and anodic polarization curve intuitively reflects the corrosion inhibition mechanism of corrosion inhibitors, which is the main research and evaluation method of corrosion inhibitors.

Electrodes were connected by three electrodes polarization method in the experiment. A3 carbon steel was used as the working electrode, saturated calomel electrode (SCE) as the reference electrode and platinum sheet as the auxiliary electrode. The sample was immersed in a 3.5% (w/w) NaCl solution for 30 min. When polarization curve test was carried out, the potential scan rate was adjusted to 0.01 v·s^{-1}. Polarization curves could be achieved after data process.

2.5. Scanning Electronic Microscopy (SEM)

Corrosion crystal morphology on the surface of A3 carbon steel was observed by JSM5610LV type SEM. In this experiment, A3 carbon steel was immersed in water sample with and without phosphate-free scale and corrosion inhibitor, respectively. Afterwards the test coupon was washed with 98% (w/w) anhydrous alcohol and treated for vacuum drying. Accelerating voltage of the JSM5610LV type SEM was 25 kV, amplification factor was 2000.

3. Results and Discussion

3.1. Rotating Hang-Parcel Weight-Loss Experimental Performance Analysis

The inhibitor in this experiment composed of A (sodium citrate), B (Zn^{2+} synergist), C (HPMA), corrosion inhibitor D and E (acrylic copolymer). L16 (4^5) orthogonal table was used to arrange experiment.Corrosion rate of the carbon steel was determined after 72 hours, the final result was the average values of three replicates. The re-

sults were showed in **Table 2**.

As shown in **Table 2**, the sequence of the influencing factors was corrosion inhibitor D > Amino acid > Zn^{2+} synergist > acrylic copolymer > HPMA in order of importance to the corrosion rate. According to orthogonal experiment results, the optimum formula was $D_4A_4B_4E_1C_1$ on corrosion inhibition. Based on the optimum formula, the weight loss experiment was carried out. The mass ratios of amino acid, Zn^{2+} synergist, HPMA, corrosion inhibitor D and acrylic copolymer was 0.5:12:0:1:8 in the optimum formula. The results were presented in **Table 3**.

The corrosion inhibition efficiency of optimized formulation reached 96.6% (**Table 3**), showing good corro-

sion inhibition effect.

3.2. Static Scale Inhibition Performance Analysis

Comparison experiments were conducted with and without inhibitors. The relationship between the concentration of Ca^{2+}, HCO_3^- and cycle of concentration was showed in **Figure 1**.

When the solution concentration was concentrated by 1 - 1.8 times, the concentration of Ca^{2+} and HCO_3^- showed linear change, illustrating that Ca^{2+} and HCO_3^- were unsaturated in solution. The concentration of HCO_3^- appeared increases linearly with the inhibitor,

Table 2. Design of orthogonal experiment L16 (4^5) and experiment results.

Numbers	Experimental factor					Average corrosion rate/mm·a^{-1}
	A Amino acid /mg·L^{-1}	B Zn^{2+} synergist/ mg·L^{-1}	C HPMA/mg·L^{-1}	D Corrosion inhibitor/ mg·L^{-1}	E Acrylic copolymer/ mg·L^{-1}	
1	0.3	9	10	0.8	5	0.0245
2	0.3	10	11	0.9	8	0.0225
3	0.3	11	12	1	7	0.0239
4	0.3	12	13	1.1	6	0.0214
5	0.4	9	11	1	8	0.0221
6	0.4	10	10	1.1	7	0.0260
7	0.4	11	13	0.8	6	0.0299
8	0.4	12	12	0.9	5	0.0230
9	0.5	9	12	1.1	6	0.0234
10	0.5	10	13	1	5	0.0229
11	0.5	11	10	0.9	8	0.0288
12	0.5	12	11	0.8	7	0.0310
13	0.6	9	13	0.9	7	0.0211
14	0.6	10	12	0.8	8	0.0205
15	0.6	11	11	1.1	5	0.0197
16	0.6	12	10	1	6	0.0271
17	0	0	0	0	0	0.5215
i/5	0.1064	0.1059	0.0921	0.0923	0.0901	
ii/5	0.0953	0.0954	0.0919	0.1010	0.1029	
iii/5	0.0908	0.0960	0.1023	0.1061	0.1010	
iv/5	0.0943	0.0905	0.0926	0.0884	0.0918	
R	0.0156	0.0154	0.0104	0.0207	0.0128	
factors	2	3	5	1	4	

Table 3. Optimizing formula experimental results.

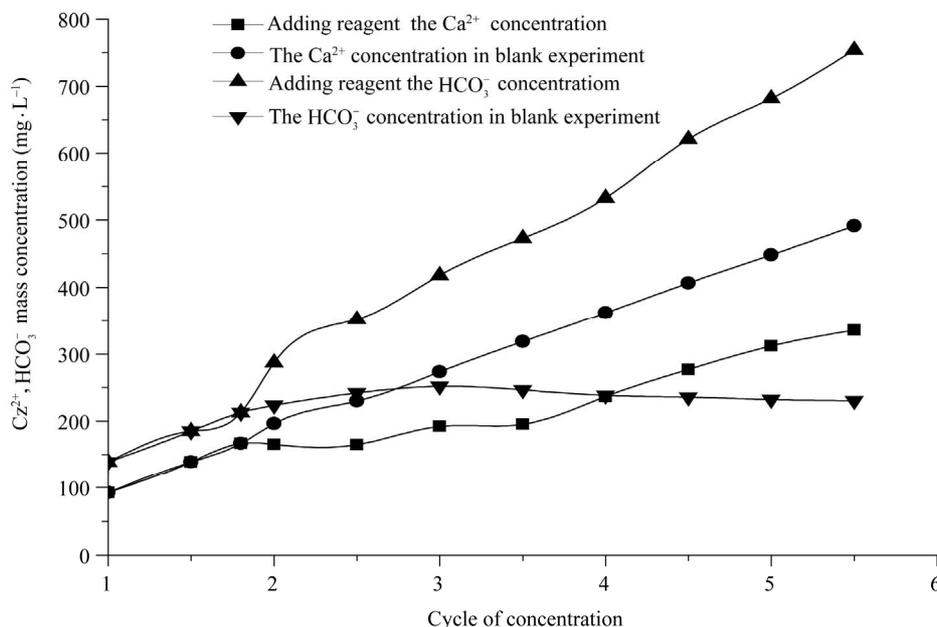| Experiment	Hang-parcel number	Quality of hang-parcel before experiment/g	Quality of hang-parcel after experiment/g	Weight loss/g	Annual corrosion rate /mm·a^{-1}	Inhibition efficiency/%
Optimized formulation	1152	19.2498	19.2465	0.0033		
	1153	19.1601	19.1567	0.0034	0.0176	
	1154	19.0684	19.0655	0.0029		
	1155	19.8299	19.7576	0.0945		96.6
Blank	1156	19.2922	19.2204	0.0940	0.5208	
	1115	19.3625	19.2941	0.0938		

Figure 1. Ca^{2+}, HCO$_3^-$ concentration and concentration multiple relationship chart.

while it increased slowly and even tended to decrease without the inhibitor. And the concentration of Ca^{2+} basically showed increases linearly with and without inhibitor, respectively. Experimental results showed that the concentrations of Ca^{2+} and HCO$_3^-$ in the solution were stabilized after adding inhibitor.

According to the results of **Table 4**, the average scale inhibition efficiency with phosphate-free corrosion and scale inhibitor reached 98.3%, showing good scale inhibition performance.

3.3. Corrosion Electrochemistry Results Analysis

Two specimens were immersed in 3.5% NaCl solution with and without inhibitor, respectively. Then the test method of electrochemical polarization curve was conducted. The results were presented in **Table 5** and **Figure 2**. And the inhibition efficiency of the inhibitor for the carbon steel corrosion was calculated by formula (4):

$$\eta = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100\% \tag{4}$$

In **Figure 2**, the corrosion potential was shift to the positive after adding the inhibitor. The increasing in anodic current density indicated that the dissolution of the anode materials. **Figure 2** showed the anode I_{corr} was reduced from 201 µA·cm^2 to 21 µA·cm^2 after adding the inhibitor. It indicated that the anode corrosion process was inhibited. And the anode inhibition was more significantly than the cathode with the inhibitor. **Table 3** and **Table 5** showed the consistent results with electrochemical test.
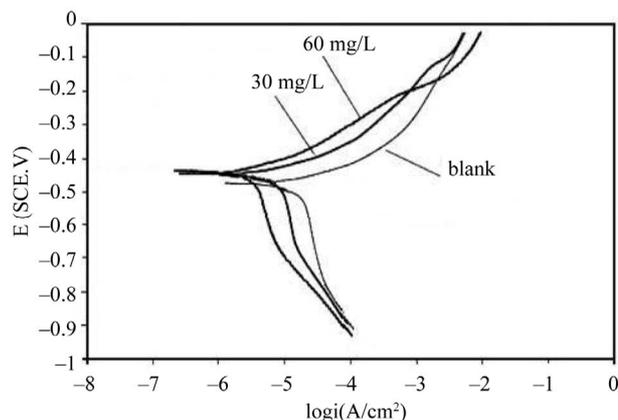

Figure 2. The polarization curve of blank and adding phosphate-free scale corrosion inhibitor treated samples in 3.5% NaCl solution.

3.4. SEM Structure Analysis

The experimental conditions as followed: the bath temperature was maintained at 50°C for 48 h, the flow rate of solution and the cycle of concentration were adjusted to 0.01 m·s^{-1} and 1.8 times, respectively. The concentration of phosphate-free corrosion and scale inhibitor was 30 mg·L^{-1}. **Figures 3(a)** and **(b)** were corrosion crystal on A3 carton steel surface with and without phosphate-free corrosion and scale inhibitor, respectively.
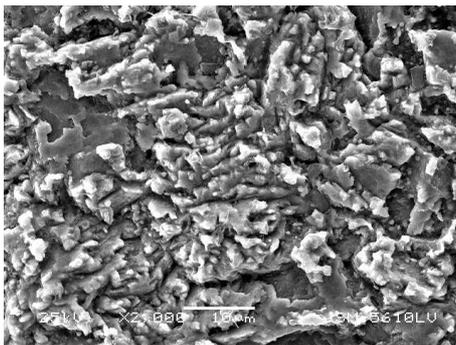
Figure 3 showed that the carbon steel was corroded severely without the inhibitor, many apertures appeared on its surface and some corrosion products deposited on the surface with uplift shape. In comparison, the surface of the carbon steel with 30 mg·L^{-1} of phosphate-free

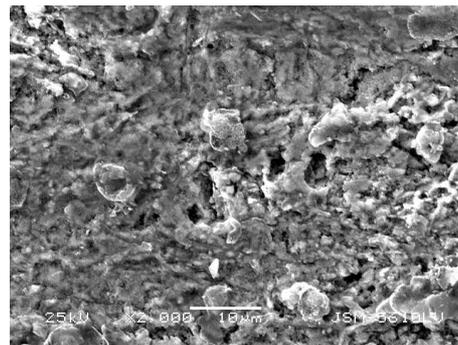**Table 4. Scale inhibition efficiency with different concentration multiple.**

Concentration multiple/K	Theoretical value $Ca^{2+}/(mg \cdot L^{-1})$	Without chemicals $Ca^{2+}/(mg \cdot L^{-1})$	Adding chemicals $Ca^{2+}/(mg \cdot L^{-1})$	Scale inhibition efficiency $\eta_k/\%$
2.5	231.4	166.7	230.8	99.1
3	277.7	180.1	271.0	98.2
3.5	324.0	195.2	320.6	98.5
4	370.1	236.7	368.1	98.3
4.5	416.5	270.1	415.1	98.7
5	462.8	308.2	460.2	99.1
5.5	509.1	330.2	504.2	98.0
Average				98.3

Table 5. Electrochemical parameter with different concentrations of corrosion inhibitor in 3.5% NaCl solution.

Concentration of corrosion inhibitor/mg·L^{-1}	E_{corr} (vsSCE)/mV	$I_{corr}/\mu A \cdot cm^2$	Corrosion rate $\eta/\%$
0	−482	201	0
30	−443	21	89.56
60	−435	19	90.55

(a)   (b)

Figure 3. The corrosion crystal on A3 carton steel surface.

corrosion and scale inhibitor was flat and smooth. It caused some damage and few corrosion products accumulation on the surface of the carbon steel because of polishing hang-parcel. But there were basically no corrosion marks. Results illustrated that a complete compact protective film formed on carbon steel surface after adding phosphate-free corrosion and scale inhibitor. It effectively cut off contact between the corrosive medium and carbon steel surface so as to significantly inhibit the corrosion of carbon steel in water sample.

4. Conclusions

1) A phosphate-free corrosion and scale inhibitor composed of A (sodium citrate), B (Zn^{2+} synergist), C (HPMA), corrosion inhibitor D and E (acrylic copolymer). The optimized mass ratio of amino acid: Zn^{2+} synergist: HPMA: corrosion inhibitor D: acrylic acid copolymer was 0.5:10:12:1:8.

2) Annual corrosion rate tested by optimized rotating

hang-parcel corrosion experiment was 0.0176 mm·a^{-1} which was lower than 0.075 mm·a^{-1} of industry standard according to Code for Design of Industrial Recirculating Cooling Water Treatment (GB50050-2007). The experimental results showed that the phosphate-free corrosion and scale inhibitor was a kind of good corrosion and scale inhibitor whose corrosion inhibition rate and scale inhibition rate surpassed 96% and 98%, respectively.

3) Polarization curve test showed the phosphate-free corrosion and scale inhibitor was a kind of corrosion and scale inhibitor that mainly caused anode type reaction. Based on the surface morphology of the carbon steel was observed by SEM, it showed that a protective film was formed on the surface of A3 carbon steel with optimized phosphate-free corrosion and scale inhibitor.

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