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Study on an Eco-Friendly Corrosion and Scale Inhibitor in Simulated cooling water

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Abstract: In this study, a composite eco-friendly phosphate-free corrosion and scale inhibitor used in simulated cooling water has been developed by sodium polyacrylate, zinc sulfate, sodium tungstate, sodium gluconate and triethanolamine . The corrosion and scale inhibition rate were respectively evaluated by weight loss experiment , the static scale inhibition test and electrochemical test. The results indicated that the corrosion and scale inhibitor was consisted of polyacrylate 14ppm,zinc sulfate 3ppm,sodium tungstate 7ppm,sodium gluconate 2ppm and triethanolamine12ppm.The corrosion inhibition rate could reached 92.79%, and anti-scaling inhibition rate could reached 96.01%. The formula was efficient , phosphate-free and environmental, it would be widely used
.

Keywords: *Phosphate-free; scale inhibition; research; corrosion inhibition*

I. INTRODUCTION

The use of water as thermal fluid in cooling water system usually leads to three problems namely: corrosion ,scale and biological fouling processes .These phenomena are caused of the concentration of salts and suspended matters. [1-6] If these problems can not be solved timely, it will cause the production equipments of long period, full load and influence the safety and stable of equipments [4-7]. In order to limit the damage, many formulations have been developed to protect circuits, piping and materials structures against this scourge .Currently, agent used for simulated cooling water treatment are mainly phosphorus-containing formulas and they are easily to produce eutrophication and red tide phenomenon, so promoting a green chemistry and developing a phosphate-free water treatment agent have became the urgent matter. [8-12] In recent years ,phosphate-free corrosion and scale inhibitors are mainly molybdate salts, chromic acid salts, natural polymer and synthetic polymer , when they are used alone, the dosage is large and the cost is high , so they are not widely used. In this paper, a multi-component phosphate-free corrosion and scale inhibitor has been prepared by sodium polyacrylate, zinc sulfate, sodium tungstate, sodium gluconate and triethanolamine. The corrosion and scale inhibition rate were evaluated 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

II. EXPERIMENTAL DETAILS

The scale inhibition rate was tested by calcium carbonate deposition. The corrosion and scale inhibitor was infused into 500mL volumetric flask which containing 240 mg/L Ca^{2+}, 366mg/L HCO_3^- and 4 mg/L sodium borate . The mixture was incubated for 10h at 80°C. After the bath,taking 25mL filter liquor, adding 5 ml NaOH and a small amount of calcium indicator ,then titrated the filter liquor by ethylene diamine tetraacetic acid (EDTA) until the solution turned blue. The Ca^{2+} concentration after experiment was tested by

$\rho = \frac{V \times 40.08 \times c}{25}$. In this formula, v_0 is the amount of consumed EDTA, C is the concentration of EDTA .The static scale inhibition rate η was calculated by the Formula (1).

$$\eta = \frac{v_2 - v_1}{v_0 - v_1} \times 100\% \qquad (1)$$

In this formula, v_0 is the amount of consumed EDTA without the addition of corrosion and scale inhibitors before incubation, v_2 is the amount of consumed EDTA with the addition of corrosion and scale inhibitors after incubation, and v_1 is the amount of consumed EDTA without the addition of corrosion and scale inhibitors after incubation.

The dynamic corrosion inhibition rate was tested by weight loss experiment, which was conducted in the simulated cooling water at 45°C ± 1°C using a thermostat. Dried and accurately weighed the polished carbon steel sheets, then put the carbon steel sheets into beakers with 1 L simulated cooling water with and without corrosion and scale inhibitors. Distilled water was supplied for evaporating every 4 hours. After a period of 72 h, the carbon steel sheets were taken out, washed by ethanol, dried for 30 minutes, and then accurately weighed. The corrosion inhibition rate η was calculated by the Formula (2).

$$\eta(\%) = \frac{X_0 - X_1}{X_0} \times 100\% \qquad (2)$$

In this formula, X_0 and X_1 are the weight loss values of carbon steel after 72 hours being immersed in the simulated cooling water without and with corrosion and scale inhibitors. The electrochemical measurements were carried out in a cell with three-electrode mode; platinum sheet and saturated calomel electrode (SCE) were used as counter and reference electrodes. The 1 cm^2 steel sample was abraded, washed and finally immersed in the simulated cooling water. Polarization curves measurements were performed using k4291602 Electrochemical System. When polarization curve test was carried out, the potential scan rate was adjusted to 0.5mv/s. Polarization curves could be achieved after data process.

Double distilled water and analytical reagent-grade $CaCl_2$, $NaHCO_3$ were used for preparing the simulated cooling water and the characteristics of the simulated cooling water were given in Table 1.

Table 1. The characterization data of simulated cooling water

Parameter	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Cl^- (mg/L)	Total alkalinity (mmol/L)	Total hardness (mmol/L)
Value	7.3	105.36	65.45	254.35	4.36	4.90

III. RESULTS AND DISCUSSION

3.1. Confirming the best formula

Based on the principle of environment and economy, each component of the formula should be harmfulless or nontoxic, its concentration should be lower than the national standard requirements. From the aspect of economic benefits, its cost of the formula is lower than domestic phosphate corrosion and scale inhibitor, it will have market competitiveness and can be widely used.

Based on adequate experimental studies, the scale inhibitor formula was preliminary determined and it was consisted of sodium polyacrylate, zinc sulfate, sodium tungstate and sodium gluconate. The best proportion of them was determined by orthogonal test, table 2 showed the four factors and their levels .

Table 2 Factors and levels of orthogonal experiment

Level	Factor			
	polyacrylic acid (A/mg/L)	zinc salt (B/mg/L)	sodium tungstate (C/mg/L)	sodium gluconate (D/mg/L)
1	10	1	2	5
2	12	2	4	6
3	14	3	6	7

The data in table 3 indicated that the best scale inhibitor formula was A3D3B3C1 . it was consisted of sodium polyacrylate 14mg/L, Sodium gluconate 7 mg/L, zinc sulfate 3 mg/L and Sodium tungstate 2 mg/L.

Table.3 Design of orthogonal experiment L_9 (3^4) and experiment results

Table.3 Design of orthogonal experiment L_9 (3^4) and experiment results

sample	factor				Scale inhibition rate(%)
	A	B	C	D	
1	1	1	1	1	81.30
2	1	2	2	2	84.89
3	1	3	3	3	85.23
4	2	1	2	3	90.76
5	2	2	3	1	86.56
6	2	3	1	2	92.34
7	3	1	3	2	89.54
8	3	2	1	3	93.34
9	3	3	2	1	90.08
k1	83.81%	87.20%	88.99%	85.98%	
k2	89.89%	88.26%	88.58%	88.92%	
k3	90.99%	89.22%	87.11%	89.78%	
R	7.18%	2.02%	1.88%	3.8%	
influence factor	1	3	4	2	

Scale inhibition rate of the corrosion and scale inhibitor was shown in table 4 , scale inhibition rate reached 95.39% and it basically met the design requirements. Further measurement would be made to test corrosion inhibition rate.

Table 4 Results of scale inhibition rate

sample	the concentration of Ca^{2+} before experiment (mgL)	the concentration of Ca^{2+} after experiment (mgL)	Scale inhibition rate (%)
blank	240.00	66.53	—
1	240.00	232.01	95.39

Table 5 showed the corrosion inhibition rate only reached 89.62%, it couldn't meet the design requirements and further studies were needed.

Table 5 Results of corrosion inhibition rate

sample	corrosion rate (mm/a)	corrosion Inhibition rate (%)
blank	0.5879	—
1	0.0610	89.62

Through abundant tests before, triethanolamine was chosen to compound with the corrosion and scale inhibitor. The new formulas were given in table 6:

Table 6 Composition of new formula

sample	polyacrylic acid mg/L	sodium gluconate mg/L	zinc salt mg/L	sodium tungstate mg/L	Triethanolamine mg/L
2	14	7	3	2	8
3	14	7	3	2	10
4	14	7	3	2	12
5	14	7	3	2	14

Results in table 7 indicated that corrosion rate of formula 4 could reach 92.79% and it had good corrosion inhibition performance.

Table 7 Corrosion performance test

sample	corrosion rate (mm/a)	corrosion inhibition rate (%)
blank	0.5879	—
2	0.0610	89.62
3	0.0598	89.83
4	0.0424	92.79
5	0.0793	86.51

In table 8, the scale inhibition rate of formula 4 could reach 96.01%, it had excellent scale and corrosion inhibition performances, so formula 4 was designed as the best formula.

Table 8 Scale inhibition performance of formula 4

sample	the concentration of Ca^{2+} before experiment (mgL)	the concentration of Ca^{2+} after experiment (mgL)	Scale inhibition rate (%)
blank	240.00	66.53	—
4	240.00	233.08	96.01

3.2. Electrochemical analyses

The polarization curves of A3 carbon steel with and without formula 4 in the simulated cooling water were given in figure 1. The corrosion potential was shift to the positive after formula 4 was added and current density decreased, it indicated that the anode corrosion process was inhibited. sodium polyacrylate and sodium gluconate contains amount of hydroxy and carboxyl and they were hydrophilic groups. These molecules adsorbed on the active point or the entire metal surface, increasing the corrosion reaction activation energy, On the other hand, nonpolar groups of the corrosion inhibitor would form a layer of hydrophobic covered on the metal surface, it could obstacled charge or material transferred. So the efficient scale inhibitor was a anode type corrosion inhibitor[13,14].

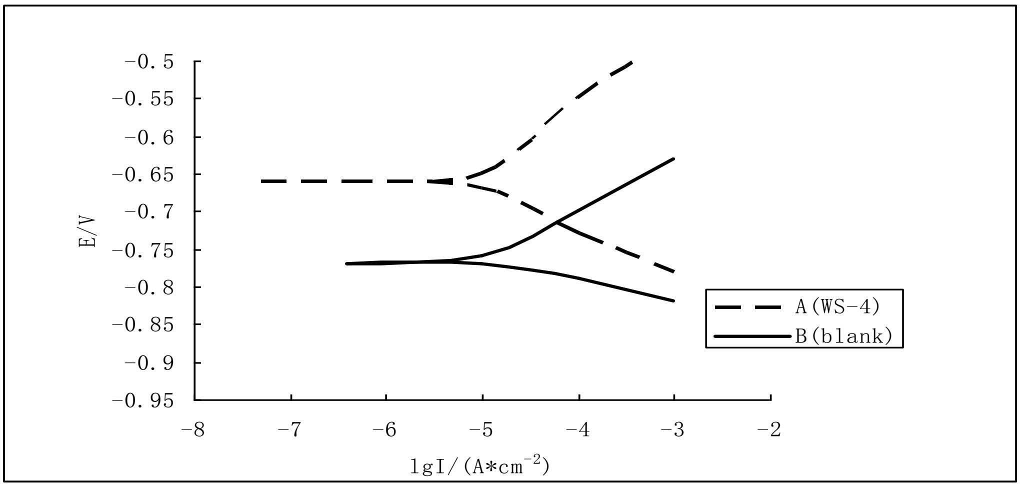

Figure 1 The polarization curve of the complex phosphate-free corrosion and scale inhibitors

3.3 Analysis of economic and environmental benefits

The phosphate-free corrosion and scale inhibitor was consist of sodium polyacrylate, zinc sulfate, sodium tungstate, sodium gluconate and triethanolamine . Each component of the formula was harmfulless or nontoxic, its concentration was lower than national minimum standards, it conformed to the requirements of environmental protection, at the same time, as the corrosion and scale inhibitor was phosphate-free, it would not cause eutrophication.Compared with other phosphate-free corrosion and scale inhibitors,this formula was of small toxicity, rich material sources, less dosage ,lower cost and better performance.From the aspects of economic benefits, the cost of the phosphate-free corrosion and scale inhibitor was lower than the cost of domestic phosphate corrosion and scale inhibitor, it will have market competitiveness and can be widely used

IV. CONCLUSIONS

A composite eco-friendly phosphate-free corrosion and scale inhibitor used in simulated cooling water has been developed by sodium polyacrylate 14ppm,zinc sulfate 3ppm,sodium tungstate 7ppm,sodium gluconate 2ppm and triethanolamine12ppm.The experimental results showed it was a kind of good corrosion and scale inhibitor whose corrosion inhibition rate and scale inhibition rate could reach 92.79% and 96.01%,respectively. Polarization curve test showed that the best formula was a kind of corrosion and scale inhibitor by mainly controlling anodic reaction and it was a anode type corrosion inhibitor.

V. ACKNOWLEDGEMENTS

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