Journal of Environmental Protection, 2013, 4, 671-675
http://dx.doi.org/10.4236/jep.2013.47077 Published Online July 2013 (http://www.scirp.org/journal/jep)

Experimental Study on a New Corrosion and Scale Inhibitor

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Received February 5th, 2013; revised March 6th, 2013; accepted April 5th, 2013

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ABSTRACT

The mixture consisted of benzotriazole (BTA), chitosan (CTS), polyacrylic acid and zinc salt has been investigated as a corrosion and scale inhibitor of A3 carbon steel in cooling water. The scale and corrosion inhibition efficiency was evaluated by static anti-scaling teat together with rotary coupon test. Compared with the phosphorus corrosion and scale inhibitor, the corrosion inhibition rate and scale inhibition rate of it increased respectively by 2.51% and 1.16%. As the corrosion and scale inhibitor is phosphate-free, it won't cause eutrophication, considering the product performance and environmental influence, the phosphate-free corrosion and scale inhibitor is superior to the traditional one.

Keywords: Corrosion and Scale Inhibitor; Scale Inhibition Performance; Corrosion Inhibition

1. Introduction

With the development of economy, the consumption of industrial cooling water is increasing rapidly. Because of evaporation, concentration, temperature rise and other reasons in the process of operation, dissolved salts will be separated out from cooling water and it can adsorb in pipe wall and equipment in the form of scale, the metal surface may form electrochemical corrosion because of irregularity, both of them will affect the equipment, service life of pipelines and use efficiency. Therefore people have to pay more attention to the treatment of the circulating cooling water [1,2].

Recently, dosing reagents into circulating cooling water is the most common method, and through the role of the pharmacy, the corrosion and scaling problem in the pipes will be solved effectively [3-6]. Now, phosphorus products are widely used in cooling water system. Because they can easily cause environmental pollution, an intense research effort is being undertaken to look for the replacement of phosphorus products by more environmentally friendly products [7-12]. The previous work has shown that Chitosan is a natural polymer material which has good resistance scale effect; benzotriazole and zinc salts both have corrosion inhibition effect.

The present work aims to study the performance of a new corrosion and scale inhibitor mixed by chitosan (CTS), polyacrylic acid, benzotriazole (BTA) and zinc salt in cooling water. The best formula has been found and it has obvious economic and environmental benefits.

2. Experimental

2.1. Materials and Instruments

Test specimens were 50 × 25 × 2 mm sheets prepared from A3 carbon steel. The exposed surfaces degreased with acetone. The corrosion products were eliminated by HCL at 10% for 3 minutes before tested.

The chitosan was made from shrimp. After removing impurities, cleaning the selected shrimp by water, soaking it into 10% hydrochloric acid for 3 days in order to remove the calcium in it. After filtration and washing, placed it into 10% NaOH, heated it to boiling for 3 hours, oxidated it with 4% $KMnO_4$ for 2 hours, then added 0.2% $NaHSO_3$ in order to fade the colour of $KMnO_4$ completely. Finally dry it to get white flakes of chitin. Placed 5 g chitin into a three-necked flask equipped with 50 mL 50% sodium hydroxide solution, keeping the temperature 100˚C, stirring speed 50 r/min, stirring time 50 min under the conditions of the deacetylation reaction, then filtration, washing and drying to get chitosan products, finally taking the chitosan products to prepare CTS working fluid of 0.02%.

2.2. Experimental Methods

2.2.1. Rotating Hanging Plate Experiment

Corrosion inhibition efficiency was determined by weight loss of the tested specimens using rotating hanging plate method [13], afterward, the instruments used was RCC-type I rotate hang piece of test, the experiment was achieved in laboratory configuration water (**Table 1**) at temperature 45˚C ± 1˚C, time 72 h and rotation speed 75 r/min. The corrosion rate X and corrosion inhibition rate η were calculated respectively by Types (1) and (2):

$$X = \frac{87600\left(m_1 - m_2\right)}{s\rho t} \quad (1)$$

where m_1 and m_2 were the quality of A3 carbon steel before and after the test respectively. s is the surface area, cm^2; ρ is the density. g/cm; t is the experimental time, h

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

where X_0 and X_1 were the corrosion rate without and with the corrosion and scale inhibitor.

2.2.2. Static Scale Inhibition Experiment

Scale inhibition efficiency was tested by "Calcium carbonate deposition method" [14]. The principle was to heat water samples with and without the scale and corrosion inhibitor, then determined the concentration of Ca^{2+} and calculated the inhibition rate. The experiment was achieved at temperature 80˚C ± 1˚C and time 10 h. Scale inhibition rate η was calculated by Type (3):

$$\eta = \frac{\rho_1 - \rho_0}{\rho_2 - \rho_0} \times 100\% \quad (3)$$

where ρ_0 and ρ_1 were the Ca^{2+} concentration without and with corrosion and scale inhibitor ,while ρ_2 was Ca^{2+} concentration before experimenting.

3. Results and Discussion

3.1. Best Formula of the New Phosphate-Free Corrosion and Scale Inhibitor

Adequate experimental studies have been made to determine the preliminary formula. In this paper, **Table 2** shows the four factors and their levels .The final formula would been determined by further experiments.

The best formula would be determined through orthogonal experiment used calcium carbonate deposition method (GB/T16632-2008). The initial Ca^{2+} concentration was 240 $mg \cdot L^{-1}$, scale inhibition rate was calculated by Type (3). **Table 3** shows the importance of factors as polyacrylic acid > CTS > BTA > zinc salt, the best formula was $B_3C_2A_2D_2$.

Table 1. Water quality index.

Ca^{2+}/ mg/L	conductance/ μS/cm	total hardness/ mg/L	total alkalinity/ mg/L	pH	Cl^-/ mg/L
134	357	7.8	7.3	7.5	221

3.2. Corrosion Inhibition Performance Analysis

Table 4 contains the corrosion inhibition efficiency of A3 carbon steel samples in colling water with 0PPM, 10 PPM, 20 PPM, 30 PPM and 40 PPM corrosion and scale inhibitor .In all cases the typical behavior was observed, corrosion inhibitor rate of the phosphorus—free corrosion inhibitor increased as the concentration elevated. The corrosion inhibition rate could reach 96.14% when the dosage was 30 PPM .

3.3. Scale Inhibition Performance Analysis

Table 5 shows the scale inhibition performance respectively with 0 PPM, 10 PPM, 20 PPM, 30 PPM and 40 PPM corrosion and scale inhibitor. The scale inhibition rate increased with the concentration elevated. The scale inhibition rate could reach 94.48% when the dosage was 30 PPM.

Table 2. Factors and levels of orthogonal experiment.

Experiment factors	Level		
	1	2	3
BTA (A)	0.05	0.10	0.15
Polyacrylic acid (B)	2	4	6
CTS (C)	8	10	12
Zinc salt (D)	0.8	1.0	1.2

Table 3. Orthogonal experiment of L_9 (3^4).

Sample	Level				Average scale inhibition rate
	A	B	C	D	
1	1	1	1	1	82.34%
2	1	2	2	2	91.23%
3	1	3	3	3	93.32%
4	2	1	2	3	92.26%
5	2	2	3	1	84.40%
6	2	3	1	2	92.93%
7	3	1	3	2	84.43%
8	3	2	1	3	87.28%
9	3	3	2	1	91.15%
k1	88.96%	86.34%	87.51%	85.96%	
k2	89.86%	87.63%	91.54%	92.36%	
k3	87.64%	92.49%	87.38%	90.95%	
R	2.22%	6.15%	4.16%	1.41%	
Factor	3	1	2	4	

Table 4. Results of corrosion inhibition rate.

Ethephon concentration (ppm)	Hanging plate number	Quality before experiment m_1 (g)	Quality after experiment m_2 (g)	Average weightlessness (g)	Corrosion Inhibition rate (%)	Corrosion rate (mm/a)
0	1	18.2532	17.9579	0.2954	0.00	1.6336
	2	18.2367	17.9412			
10	3	17.5180	17.4707	0.0382	87.10	0.2112
	4	17.4332	17.4041			
20	5	18.1130	18.0853	0.0225	92.38	0.1244
	6	19.3213	19.3040			
30	7	17.1954	17.1839	0.0114	96.14	0.0630
	8	18.1873	18.1760			
40	9	17.1854	17.1736	0.0116	96.07	0.0641
	10	18.1754	18.1634			

Table 5. Test results of scale inhibition.

Ethephon concentration (mg/L)	Ca^{2+} concentration before experiment (mg/L)	Ca^{2+} concentration after experiment (mg/L)	Scale inhibition rate (%)
0	240	157.23	0
10	240	229.45	87.25
20	240	234.56	93.43
30	240	235.43	94.48
40	240	232.23	90.61

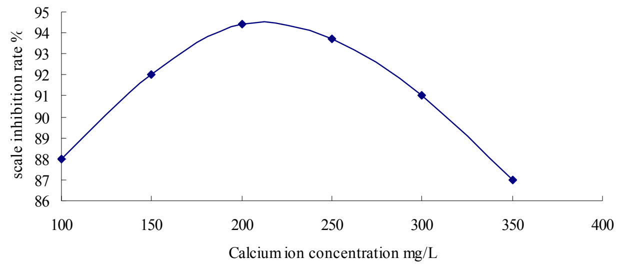

Figure 1. Influence of Ca^{2+} Concentration to scale inhibition rate.

3.4. Effect of Ca^{2+} Concentration

The relateship between inhibition rate and Ca^{2+} concentration was tested at scale inhibitor concentration 30 PPM, pH 7, temperature 80˚C and heating temperature 10 hours. **Figure 1** showed that scale inhibition rate increased with Ca^{2+} concentration elevated in the scope of 100 $mg·L^{-1}$ to 220 $mg·L^{-1}$, so this corrosion and scale inhibitor was applied to the system of Ca^{2+} concentration in 100 to 220 $mg·L^{-1}$.

3.5. Effect of pH Values

The curves included in **Figure 2** allowed to evaluate pH related to corrosion and scale inhibition. Calcium carbonate deposition method (GB/T16632-2008) was used. **Figure 2** showed that pH had great influence on corrosion and scale rate. Scale inhibition rate was less than 93% when pH was less than 7, it could reach 94.48% while the pH value was between 7 and 8, after PH researched 8, scale inhibition rate declined. In alkaline system calcium carbonate will generated Ca $(HCO_3)_2$ and OH^-, they would make scale inhibition rate declined. In acidic condition, a protective and dense calcium carbonate scale layer could not been easily formed on surface of A3 carbon steel, zinc salt would sediment and influence the corrosion inhibition rate on alkaline conditions when pH was greater than 8 [15-17]. This showed the corrosion inhibitor was applicable to the system in which pH value was between 7 to 8.

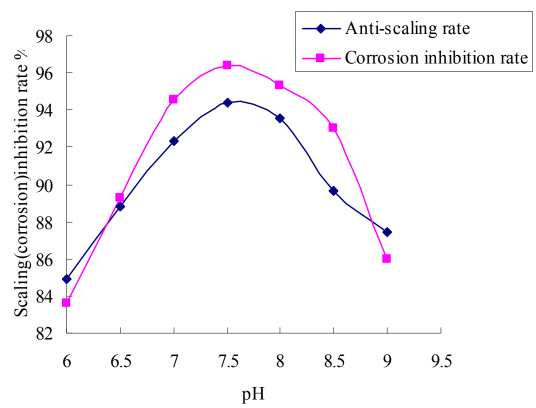

Figure 2. Influence of pH to corrosion and scale inhibition rate.

Table 6 showed the comparisons between the new and traditional corrosion and scale inhibitors were showed the corrosion inhibition rate and scale inhibition rate of the optimum formula increased respectively by 2.51% and 1.16%. It is an ideal corrosion inhibitor with phosphorus—free and would not cause water eutrophication.

4. Conclusions

From the whole set of datas obtained in this study, it can

Table 6. Comparisons between the new and traditional corrosion inhibitors.

Number	Corrosion inhibition rate (%)	Scale inhibition rate (%)	Optimal dosing quantity (ppm)	Cost (yuan/t)
Optimum formula	96.14	94.48	30	0.42
Traditional corrosion and scale inhibitor	93.63	93.32	40	0.42

be concluded that a phosphorus-free corrosion and scale inhibitor consist of benzotriazole (BTA), chitosan (CTS), polyacrylic acid and zinc salt showed a better performance than the traditional one.

Scale and corrosion inhibition rates could reach respectively 96.14% and 94.48% when dosage was 30 ppm. The phosphorus-free corrosion and scale inhibitor can apply to system at pH between 7 and 8.1 and Ca^{2+} concentration between 100 and 220 $mg \cdot L^{-1}$.

Compared with the traditional one, the corrosion inhibition rate and scale inhibition rate increased respectively by 2.51% and 1.16%. As the corrosion and scale inhibitor was phosphate-free, it wouldn't cause eutrophication, considering the economic cost, product performance and environmental influence, the new phosphate-free corrosion and scale inhibitor was significantly superior to the traditional one and had obvious environmental benefits.

5. Acknowledgements

This project was supported by Ministry of Science and Technology in China of SME Technology Innovation Foundation and Department of Science and Technology in Hubei Province, China of Science and Technology Research Foundation, express our thanks to those provided guidance and assistance.

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