Application of polyaspartic acid derivative in circulating cooling water system with high concentration multiple

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Abstract. The polyaspartic acid derivative compound was applicated in circulating cooling water system with high concentration multiple with the water quality of circulating cooling water system was characterized by higher hardness, higher alkalinity and higher corrosive ion content in order to solve the problem of scale and corrosion of the circulating cooling water system. The formulation of the polyaspartic acid derivative compound was determined to be PASP-AESA-ASP, ZnSO4, HPAA and BTA with the mass ratio of 15:4:6:0.1. The polyaspartic acid derivative compound had a good protective effect on A3 carbon steel in high-concentration-salt-water and good biodegradability.

1. Introduction

The different industrial enterprise has taken different countermeasures to realize reuse of cooling water. Most industrial enterprise adopt the method of increasing the concentration multiple of circulating cooling water system to realize it and has achieved some benefits in the actual production [1,2]. However, with the increase of concentration multiple, the water quality of circulating cooling water system was characterized by higher hardness, higher alkalinity and higher corrosive ion content. In order to make the system operate safely under this high salt water quality condition, it is the key to solve the problem of scale and corrosion of the circulating cooling water system. At present, the general scale and corrosion inhibitor in the market has a smaller scope of application, and the majority of them are phosphorus containing, toxic, non biodegradable products, which will cause red tide damage or pollute the soil environment after discharge [3].

In terms of the whole corrosion inhibitor field, its development speed is very fast, and many series have been formed [4,5]. Its research, application and development have made remarkable achievements, forming a series of corrosion inhibitors, such as chromate, zinc salt, borate, phosphate, silicate, nitrate, nitrite, all organic phosphine system, molybdate, tungstate and organic carboxylic acid, organic aldehydes, organic amines, etc. However, due to higher corrosion ions and scaling ions, many kinds of microorganisms and large organisms in high content salt water system, so the corrosion inhibition effect of these inhibitors on metals in high salt water medium is not ideal.

The first report about the corrosion inhibitor of high salt water medium was by Clay proposed formaldehyde as the corrosion inhibitor of seawater medium in 1946 [6]. Many foreign researchers...
conducted a lot of research on the corrosion inhibitors in the seawater medium in the 1950s-1960s, and found that chromate, dichromate and sodium nitrite had better corrosion inhibition on carbon steel and non-ferrous metals in the seawater medium. But the required amount of the corrosion inhibitors was higher, reaching thousands of mg/L. In this period, the main purpose of the study of corrosion inhibitors is to improve the efficiency of corrosion inhibitors, without considering the environmental pollution. Researchers developed a low phosphate and high pH of alkaline water treatment method in the early 1970s, which was applied to the treatment of circulating cooling water. The composition of corrosion inhibitors transformed from inorganic phosphate to organic polyphosphate ester and organic polyphosphonic acid, and then further developed 2-hydroxyphosphonic acid with lower phosphorus emission. Although researchers have made some researches on the corrosion inhibition of some organic matters and natural products in the 1980s, the components of corrosion inhibitor involved in the process of compounding are not all non-toxic, and it is proposed that there are few green corrosion inhibitors. The research on green corrosion inhibitors began to be active after the 1990s [7,8], and the research direction began to develop in the direction of no pollution or low pollution to the environment, such as polyaspartic acid, gluconate, molybdate, tungstate, zinc salt, aluminum metal salt, etc. It is of great significance for the effective utilization of high salt water to seek for the development of environmentally friendly composite inhibitor products suitable for high salt water system. We have synthesized polyaspartic acid derivative that has been reported in Desalination [9]. In this paper, polyaspartic acid derivative was used in circulating cooling water system with high concentration multiple.

2. Experimental

2.1. Preparation of the polyaspartic acid derivative compound

The compound of polyaspartic acid derivative (PASP-AESA-ASP), zinc sulfate heptahydrate (ZnSO₄), 2-hydroxyphosphonoacetic acid (HPAA) and benzotriazole (BTA) was optimized. The mass ratio of PASP-AESA-ASP, ZnSO₄, HPAA and BTA was 15:4:6:0.1, and the polyaspartic acid derivative compound inhibitor was obtained.

2.2. Weight loss measurement of the rotating hanging coupons test

Corrosion inhibition behavior of the corrosion inhibitor on carbon steel in the high-concentration-salt water using weight loss measurement were assessed in accordance with Chinese Standard GB/T 18175-2014. A XYZK-A type rotating hanging coupon test device was used for measuring weight loss. The test conditions are as follows: The dimensions of carbon steel samples was 50mm×25mm×2mm. The experimental temperature ranges were 40°C, 50°C and 60°C. The rotating speed of the rotating axis was 75 rpm. The experimental period lasted 72 h. The corrosion rate of the steel sample was calculated with Equation 1.

\[
X = \frac{8760 \times 10 \times (W_0 - W)}{A \times D \times T} = \frac{87600 \times (W_0 - W)}{28 \times 7.85 \times 72}
\] (1)

Where \(X\) is the average corrosion rate of carbon steel in the high-concentration-salt water, mm/y; the 8760 and 10 are conversion factors for number of hours in a year and dimensional (cm to mm) conversion respectively; \(W_0\) and \(W\) are the weights of the test samples prior to and after testing, g; \(A\) is the steel sample surface area, 28 cm²; \(D\) is the density of the steel samples, 7.85 g/cm³; \(T\) is test time, 72 h.

Corrosion inhibition efficiency of the polyaspartic acid derivative compound was calculated from Equation 2.

\[
\eta = \frac{(X_0 - X)}{X_0} \times 100\%
\] (2)
Where \( \eta \) is the corrosion inhibition efficiency of the corrosion inhibitor, \%; \( X_0 \) is the annual corrosion rate of carbon steel in the high-concentration-salt water, mm/y; \( X_1 \) is the annual corrosion rate of carbon steel in the presence of the high-concentration-salt water, mm/y.

2.3. Test of biodegradability

The biodegradability test was carried out by the method of microbial shaking table. The specific steps were as follows: 500 mL of nutrient solution containing the polyaspartic acid derivative compound (concentration of 100 mg/L) was added into the conical flask. Then 1.0 mL of inoculum was added into the conical flask, and shaked on the shaking table at room temperature. The COD of the sample was measured at the 1st, 7th, 14th, 21st and 28th days of the experiment. The degradation rate of the polyaspartic acid derivative compound is calculated as follows.

\[
D = \left(1 - \frac{C_t - C_{bt}}{C_0 - C_{b0}}\right) \times 100 \%
\]

(3)

Where \( D \) is the degradation rate of the polyaspartic acid derivative compound, \%; \( C_0 \) is the average initial concentration of COD measured in the inoculated reaction solution containing the polyaspartic acid derivative compound, mg/L; \( C_t \) is the average value of COD concentration measured in the reaction solution containing the polyaspartic acid derivative compound in \( t \) time, mg/L; \( C_{bt} \) is the average value of COD initial concentration measured without the polyaspartic acid derivative compound, mg/L; \( C_{b0} \) is the average value of COD concentration measured without the polyaspartic acid derivative compound in \( t \) time, mg/L.

3. Results and discussion

3.1. The relationship between corrosion inhibition performance and dosage of the polyaspartic acid derivative compound

The corrosion rate and corrosion inhibition rate of environmental protection composite inhibitor with different dosage are determined by rotating hanging coupons test, which was shown in Table 1. The experimental temperature was 40°C.

| Dosage (mg/L) | Corrosion rate (mm/a) | Corrosion inhibition rate (%) |
|--------------|-----------------------|-----------------------------|
| 0            | 0.7141                | /                           |
| 25           | 0.4699                | 34.20                       |
| 50           | 0.2481                | 65.26                       |
| 75           | 0.1705                | 76.12                       |
| 100          | 0.0452                | 93.67                       |
| 125          | 0.0379                | 94.69                       |
| 150          | 0.0348                | 95.13                       |

It can be seen from table 1 that the corrosion inhibition performance of the polyaspartic acid derivative compound for A3 carbon steel with the increase of the dosage. When the dosage of the polyaspartic acid derivative compound was 25 mg/L, the corrosion inhibition effect on A3 carbon steel was basically not effective. When the amount of inhibitor increased to 75 mg/L, the corrosion inhibition performance of A3 carbon steel was enhanced, but it still failed to meet the national standard, and the corrosion inhibition rate was about 78%. When the dosage was 100 mg/L, the corrosion rate of carbon steel was 0.0452 mm/a, which is up to the national standard of 0.075 mm/a. When the dosage continues to increase to 150 mg/L, with the increase of concentration, the corrosion inhibition rate of the inhibitor to the A3 carbon steel did not increase significantly.
3.2. The relationship between the corrosion inhibition rate and experimental temperature

The results of the rotation coupon test at different experimental temperatures and dosages were shown in Table 2.

| Temperature (°C) | Dosage (mg/L) | Corrosion rate (mm/a) | Corrosion inhibition rate (%) |
|----------------|---------------|-----------------------|-----------------------------|
| 40             | 0             | 0.7141                | /                           |
|                | 50            | 0.2481                | 65.26                       |
|                | 100           | 0.452                 | 93.67                       |
|                | 150           | 0.0348                | 95.13                       |
|                | 0             | 0.8192                | /                           |
| 50             | 50            | 0.2937                | 64.15                       |
|                | 100           | 0.0585                | 92.86                       |
|                | 150           | 0.0431                | 94.74                       |
| 60             | 50            | 0.3202                | 63.87                       |
|                | 100           | 0.0689                | 92.23                       |
|                | 150           | 0.0537                | 93.94                       |

It can be seen from Table 2 that at 40, 50 and 60 °C, the corrosion inhibition rate of the polyaspartic acid derivative compound for A3 carbon steel increased with the increase of inhibitor dosage. When the inhibitor dosage was 100 mg/L, the corrosion rates of A3 carbon steel at 40, 50 and 60 °C were respectively 0.0452 mm/a, 0.0585 mm/a and 0.0689 mm/a, which were less than the national standard of 0.075 mm/a. It can be seen from Table 2 that when the dosage of the inhibitor was the same, the corrosion inhibition rates of A3 carbon steel decreased with the increase of the experimental temperature, but the decrease range was very small, indicating that the polyaspartic acid derivative compound has good corrosion inhibition effects on A3 carbon steel at different temperatures, and the performance is stable.

3.3. Biodegradability of the polyaspartic acid derivative compound

According to the biological shaking table test method and the oxygen demand (COD) method, the biodegradation performance of the polyaspartic acid derivative compound was determined. The results were shown in Figure 1.

Figure 1. Biodegradability of the polyaspartic acid derivative compound

It can be seen that the COD of the polyaspartic acid derivative compound gradually decreases with the extension of time, and the degradation rate gradually increases from Figure 1. On the 7th day of the experiment, the COD was 10.8 mg/L, and the biodegradation rate was 61.5%; on the 28th day of the experiment, the COD was 4.2 mg/L, and the biodegradation rate was 84.8%, indicating that the polyaspartic acid derivative compound had excellent biodegradation performance.
3.4. Study on corrosion inhibition mechanism of the polyaspartic acid derivative compound

3.4.1. Surface observation and analysis of test coupons. After the rotating hanging coupons test, the corrosion coupons were photographed. When the experimental temperature was 40 °C, the results were as shown in Figure 2.

![Blank and 100 mg/L inhibitor photos](image1)

Figure 2. The photos of the corrosion coupons

It can be seen from the pictures in Figure 2 that there was a thick layer of corrosion products on the surface of A3 carbon steel test piece in high-concentration-salt water without adding inhibitor, which was very serious. The corrosion degree of the surface of the test coupon was far less than that of the blank high-concentration-salt when 100 mg/L the polyaspartic acid derivative compound was added. The surface of the test coupon was smooth, and no corrosion trace can be seen basically. This showed that when the polyaspartic acid derivative compound reached a certain amount, it had a good protective effect on A3 carbon steel in the high-concentration-salt water system, so the surface of the A3 carbon steel can be protected from the corrosion of high-concentration-salt water.

3.4.2. SEM of test coupons. After the rotating hanging coupons test, the test coupons were cleaned and observed by SEM.

![Blank (before cleaning), blank (after cleaning), 100 mg/L inhibitor (after cleaning) SEM photos](image2)

Figure 3. The SEM photos of the corrosion coupons

It can be seen from the SEM photos of Figure 3 that after the rotating hanging coupons test, if the surface of the test coupon was not cleaned, the surface of the test coupon was directly scanned with SEM, and the surface of the test coupon was covered with a layer of scale (mainly calcium carbonate scale), which fully showed that if the polyaspartic acid derivative compound was not added in the high-concentration-salt water, the corrosion under the scale of the test coupon will be aggravated. It can be seen from the SEM photo of the cleaned test coupon that the corrosion electrode was severely corroded and the corrosion pit was very deep. However, after adding the polyaspartic acid derivative compound, the SEM photo of the cleaned test coupon showed that the original texture of the test coupon was very clear and the corrosion was not serious. This showed that the polyaspartic acid
derivative compound had a good protective effect on A3 carbon steel in high-concentration-salt water, and the developed polyaspartic acid derivative compound was suitable for circulating cooling water system with high concentration multiple.

4. Conclusions
The formulation of the polyaspartic acid derivative compound was determined to be PASP-AESA-ASP, ZnSO₄, HPAA and BTA with the mass ratio of 15:4:6:0.1. The results showed that the corrosion rates of A3 carbon steel was 0.0452 mm/a when the temperature was 40 °C and the dosage was 100 mg/L. The polyaspartic acid derivative compound has good biodegradability, and the biodegradation rate can reach 84.8% on the 28th day of experiment. The developed polyaspartic acid derivative compound was suitable for circulating cooling water system with high concentration multiple.

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