Study on the Performance Evaluation of Phosphorus-Free Composite Corrosion and Scale Inhibitor

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Abstract

The new type of phosphorus-free composite corrosion and scale inhibitor (FS) was prepared by using thiourea-modified polyepoxysuccinic acid (CNS-PESA), polyaspartic acid (PASP), hexamethylenetetramine, zinc chloride (ZnCl₂), hydrolyzed polymaleic anhydride (HPMA). This FS inhibitor was an environmentally friendly and phosphate-free inhibitor to solve the problems of corrosion and formation of scale in industrial circulating cooling water systems. The maximum corrosion and scale inhibition efficiency was 99.2% and 98.9% respectively. The FS inhibitor worked effectively with the pH between 6 to 8. Compared with other inhibitors, the composite corrosion and scale inhibitor had great performance on the inhibition of calcium carbonate and calcium phosphate scale inhibition. Moreover, the FS inhibitor could reduce the environmental pollution problems effectively.

Keywords: thiourea-modified polyepoxysuccinic acid (CNS-PESA), phosphorus-free composite corrosion and scale inhibitor, corrosion and scale inhibition efficiency

Introduction

Cooling water accounts for a large proportion of industrial water consumption. Almost all kinds of industrial enterprises need to use cooling water, and the consumption of cooling water in petroleum, chemical, electrical power, metallurgy and other industries accounts for more than 85% of the total water consumption [1-5]. The circulating cooling water system is mainly composed of heat exchanger equipment, cooling equipment, water pump and pipelines and other equipment. Circulating cooling system in industrial production can effectively save water consumption by increasing the ratio of concentration. Circulating cooling water usually contains a large number of incompatible cation and anion. Water temperature, the leakage of process medium and other comprehensive factors, the concentration of all kinds of cation and anion in cooling water will multiply with the increase of concentration ratio, and these cation and anion are easy to form inorganic salt scale attached to the pipe wall of circulating cooling water system. The scale attached to the pipe wall will affect the heat transfer efficiency of the heat exchanger and cause the blockage

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of the pipe. The long-term existence of the scale is a kind of consumption to the equipment and also affects the normal operation of the circulating cooling water system [6-11].

At the same time, the presence of dissolved oxygen in the water can corrode the metal in the system. Because the circulating cooling water system is generally a relatively closed system, the long-term operation of the system will lead to continuous accumulation of scale and metal corrosion, resulting in the gradual deterioration of water quality. Microorganisms in the circulating cooling system can also corrode the pipes due to the deterioration of water quality. The metabolites produced by these microorganisms in their life activities and the sludge in the cooling water will adhere to the metal surface. The existence of corrosion products will also accumulate on the surface of the pipeline, which will also cause scaling in the circulating cooling water system [12-13]. Dissolved salts will also be separated out from the cooling water because of evaporation, concentration, increasing temperature and other reasons in the process of operation, and it can adsorb in wall of pipes and equipment in the form of scale. The metal surface may cause electrochemical corrosion because of irregularity. Therefore, people have to pay more attention to the treatment of the circulating cooling water [14-15]. With the continuous strengthening of national environmental protection, phosphorus containing corrosion and scale inhibitor will be gradually eliminated with the development of society. So the development of environmental protection of new corrosion and scale inhibitor has become a trend. Phosphorus series and heavy metal-containing corrosion and scale inhibitors that do not conform to the national environmental protection development strategy will sooner or later be replaced by more environmentally friendly and efficient corrosion and scale inhibitors [16-18].

The present work focuses on the study of the performance evaluation of the prepared high efficiency composite corrosion and scale inhibitor (FS) without phosphorus on corrosion and scale inhibition of circulating cooling water systems. Consequently, the newly prepared composite corrosion and scale inhibitor (FS) without phosphorus have markedly environmental and economic benefits for circulating cooling water systems and deals with the corrosion and scale formation problems that existing in industrial production.

Material and Methods

Water Sample

The water sample used for this research work was taken from the circulating cooling water from the industry that located in Hubei, Wuhan, China. The characteristics of water sample are presented in Table 1.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Parameters</th>
<th>Numeric Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>pH</td>
<td>7.83</td>
</tr>
<tr>
<td>2.</td>
<td>Total Alkalinity (mgL⁻¹)</td>
<td>185</td>
</tr>
<tr>
<td>3.</td>
<td>Total Hardness (mgL⁻¹)</td>
<td>210</td>
</tr>
<tr>
<td>4.</td>
<td>Conductivity (µs/cm)</td>
<td>896</td>
</tr>
<tr>
<td>5.</td>
<td>Calcium ion concentration (mgL⁻¹)</td>
<td>170.25</td>
</tr>
</tbody>
</table>

Main Equipment

Constant temperature water bath (HH-8, Beijing Zhengkai Instrument Co., Ltd.), the hanging film instrument (RCC – III type, Gaoyou Motian Electronic Instrument Co., Ltd.), pH meter (PHS – 3G, Youlaibo Technology Co., Ltd.), the electro-thermostat (DHG – 9040A, Beijing Syntax equipment Co., Ltd.), electronic analytical balance (YP1002, Shanghai Chuyan Laboratory Equipment Co., Ltd.), and fourier infrared spectrometer (PX - 1) were used in this research.

Main Reagents and Materials

Sodium hydroxide (granular), borax, anhydrous calcium chloride, sodium bicarbonate, maleic anhydride, sodium tungstate, 30% hydrogen peroxide, calcium hydroxide, thiourea, sodium polyaspartic acid (PASP), hexamethylenetetramine, zinc chloride (ZnCl₂), and hydrolyzed polymaleic anhydride (HPMA) were used in this experiment. All the above chemicals used in this experiment were analytical grade pure.

Experimental Procedures

Synthesis of Phosphorus-Free Composite Corrosion and Scale Inhibitor

Firstly, the synthesis of thiourea-modified polyepoxy succinic acid (CNS-PESA) was carried out and to further improves its corrosion and scale inhibition performance by adding other corrosion and scale inhibitors. In addition to chemical modification of corrosion and scale inhibitor, another method is to mix the original corrosion and scale inhibitor with other corrosion and scale inhibitors by means of compound technology, so as to improve its corrosion and scale inhibition performance by playing the synergetic effect between substances. According to a large number of literature and experiments, it is found that polyaspartic acid (PASP), zinc chloride, hydrolyzed polymaleic anhydride (HPMA), hexamethylenetetramine and polyacrylic acid (PAA) have relatively excellent corrosion and scale inhibition performance. First of all, these substances were designed by orthogonal experiment in 5 factors and 4 levels, and their scale inhibition properties were measured by static scale inhibition method, so as to
obtain the best formula of corrosion and scale inhibition performance. The total dosage of the designed compound was 25 mg/L. The best formula of composite corrosion and scale inhibitor is selected as CNS-PESA: PASP: HPMA: ZnCl2; Hexamethylenetetramine = 9:6:4:5. The advantages for the synthesis of this composite corrosion and scale inhibitor (FS) are to improve the corrosion and scale inhibition performance with compound formula, to reduce the operation cost during treatment and to get good inhibition efficiency for the circulating cooling water system.

Experimental Procedure for Calcium Carbonate Scale Inhibition Method

The determination of calcium carbonate scale inhibition test, calcium chloride (CaCl2) solution and sodium hydrogen carbonate (NaHCO3) solution were used to prepare calcium carbonate (CaCO3) water sample following the GB/T 16632-2008 method. The concentration of Ca2+ is 250 mg/L and the concentration of HCO3- is 732 mg/L. The composite corrosion and scale inhibitor (FS) and other comparable inhibitors were added into 500 ml of water samples. The water samples added with water treatment agent and blank water samples were placed in a water bath at 80°C and heated for 10 hours. When the reaction was completed, the water samples were cool at room temperature. The supernatant from the water sample was titrated with EDTA solution after cooling to room temperature. The scale inhibition rate was calculated according to the titration data. The scale inhibition performance of water treatment agent (η) expressed as a percentage is calculated as follows:

\[ \eta = \frac{\rho_2 - \rho_3}{0.240 - \rho_3} \times 100 \]  

(1)

Where;
\( \rho_2 \) = The value of the concentration of calcium ions (Ca2+) with the addition of corrosion and scale inhibitor (mg/L-1)
\( \rho_3 \) = The value of the concentration of calcium ions (Ca2+) without the addition of corrosion and scale inhibitor (mg/L-1)
0.204 = The value of the concentration of calcium ions (Ca2+) in the test solution prepared before the test

Experimental Procedure for Calcium Phosphate Scale Inhibition Method

To determine the calcium phosphate scale inhibition test, the GB/T 22626-2008 method was used. The water sample was prepared in the laboratory with the concentration of Ca2+ in 100 mg/L and the concentration of PO43- in 5 mg/L. The composite corrosion and scale inhibitor (FS) and other comparable inhibitors were added to the 500 ml of water samples respectively. The water samples with treatment agent and blank water samples were placed in a water bath at 80°C and heated for 10 hours. After the heating process was completed, the water samples were allowed to cool at room temperature. The supernatant was titrated with ethylenediaminetetraacetic acid (EDTA) solution after the cooling process. The scale inhibition rate was calculated according to the titration data. The calculation method is similar to that of calcium carbonate scale inhibition test.

Experimental Procedure for the Determination of Corrosion Inhibition Performance

The specific steps of the rotary hanging plate test for corrosion inhibition performance were performed according to the method of GB/T 18175-2000 as the following procedure. A beaker marked with multiple concentrations was taken to prepare the standard corrosion test water samples. An equal amount of the composite corrosion and scale inhibitor (FS) and other comparable inhibitors were added to the beaker. Then the experimental water samples were placed into the volumetric flask to measure and poured into the beaker and then placed in a steady water tank. The weighed test piece is fixed on the hanging device with plastic screws and put into the test solution. The experimental time was recorded. The hanging machine rotation was paid attention to observing when the motor started working. The changing condition of the corrosion phenomenon was recorded. The test solution was continuously evaporated and concentrated after the beginning of the experiment. When the liquid level dropped 2/3 of the original volume, the liquid level was kept carefully with continuously adding deionized water or distilled water. The continuous adding of the deionized water or distilled water maintained the constant evaporation of the test solution and allowed it to keep near the 2/3 scale line of the total amount of the solution until the end of the experiment. The experiment was finished after 72 hours. The hanging plate samples were taken out from the solution, washed, dried, and weighed for observation and the test solution was analyzed. The corrosion rate XI (mm/a) can be calculated as follows:

\[ X_1 = \frac{8760 \times (m - m_0) \times 10}{s \cdot \rho \cdot t} \]  

(2)

Where;
\( m \) = quality of carbon steel hanging plate before experiment, g
\( m_0 \) = quality of carbon steel hanging plate after experiment, g
s = surface area of carbon steel hanging plate, cm²
\( \rho \) = density of carbon steel hanging plate, g/cm³
\( t \) = experimental duration time, h
8760 = hours in a year
10 = a number of millimeters corresponding to one centimeter
The calculation formula of corrosion inhibition rate $\eta$ (%) is as follows:

$$
\eta = \frac{X_0 - X_1}{X_0} \times 100 \%
$$

(3)

Where;

$X_0$ = corrosion rate of hanging plate (blank test), mm/a
$X_1$ = corrosion rate of hanging plate, mm/a

**Results and Discussion**

**Effect of pH on the Scale Inhibition Performance of Composite Corrosion and Scale Inhibitor (FS)**

The scale inhibition performance of composite corrosion and scale inhibitor (FS) changes with pH shows in Fig. 1. When the pH value reaches about 8, the scale inhibition rate of the composite corrosion and scale inhibitor reaches 98.1%. As the pH increases and the alkalinity of water increases, more HCO$_3^-$ and CO$_3^{2-}$ will be generated. These anions will precipitate with the Ca$^{2+}$ and Mg$^{2+}$ plasma in the water, and these precipitates will accumulate continuously to form scale. On the other hand, the FS inhibitor is generally acidic, and the constant increase of pH will affect the stability and scale inhibition performance of the inhibitor to some extent [19-20]. The prepared FS inhibitor maximizes scale inhibition performance when pH is around 6-8.

**Effect of Temperature on the Corrosion Inhibition Performance of Composite Corrosion and Scale Inhibitor (FS)**

The corrosion rate and corrosion inhibition efficiency of carbon steel changes with temperature was shown in Fig. 2. When the water temperature is 20°C, the corrosion rate of carbon steel reaches 0.0176 mm/a, and the corrosion inhibition rate of the FS inhibitor is 98.9%. However, with the continuous increase of temperature, the corrosion rate is also accelerating, and the inhibition efficiency of corrosion and scale inhibitor is also decreasing. When the temperature is lower, the activation energy of ions in water is lower and the corrosion rate is slower. When the water temperature increases to about 40°C, it not only accelerates the corrosion rate of carbon steel, but also the performance of corrosion and scale inhibitor activates to a certain extent, so that the prepared FS inhibitor is more likely to form precipitation film on the surface of carbon steel. This film protects the surface of the carbon steel from corrosion. However, with the further increase of temperature, the corrosion rate of carbon steel is also accelerating, and more and more uneven corrosion products are piled on the surface of the carbon steel. The uneven interface is formed on the surface of the carbon steel, which is easy to form more fine corrosive batteries. It also destroys the precipitation protective film formed by corrosion and scale inhibitor on the surface of carbon steel to a certain extent.

**Effect of Rotation Speed on the Corrosion Inhibition Performance of Composite Corrosion and Scale Inhibitor (FS)**

The effect of rotation speed on the corrosion inhibition efficiency of composite corrosion and scale inhibitor (FS) show in Fig. 3. In the circulating cooling water system, the corrosion of carbon steel is mainly caused by the polarization of oxygen. The diffusion rate of oxygen directly affects the corrosion rate of carbon steel. The metal corrosion in the circulating cooling water system was simulated by the corrosion experiment of the hanging plate. The rotating speed of the hanging plate was used to replace the flow speed. When the speed is at a low speed, the corrosion rate of carbon steel is relatively low, because the corrosion inhibitor and scale inhibitor can form a layer of corrosion inhibitor film uniformly on the surface of carbon steel due to the low speed of the hanging plate, which protects the metal to a certain extent and reduces the corrosion rate. However, when the rotating speed is increased from 40 r/min to 120 r/min, the corrosion rate of carbon steel increases and the corrosion inhibition efficiency decreases. The reason was the laminar layer of the medium contact surface and the carbon steel surface becomes thin with the continuous increase of the rotation speed, and the dissolved oxygen in the water fully contacts with the carbon steel and electrochemical corrosion occurs. On the other hand, the increase of rotation speed will also break the film formed by the corrosion inhibitor on the surface of carbon steel, making the metal lose their protection. When the
rotating speed is increased from 120 r/min to 160 r/min, it is found that the corrosion rate of carbon steel decreases and the corrosion inhibition efficiency of the inhibitor increased. This is because of the increase of speed, sufficient amount of dissolved oxygen will form a layer of oxide film on the metal surface. Therefore, the corrosion rate is reduced and the corrosion inhibition effect is increased. However, when the rotating speed is further increased, it is difficult for the composite corrosion inhibitor and scale inhibitor to form corrosion inhibitor film on the metal surface. Meanwhile, the oxide film formed by dissolved oxygen in water and carbon steel will also be destroyed due to the scouring of water. Therefore, the corrosion will continue to occur on the metal surface when it is exposed to water again [6, 21].

Comparison on the Calcium Carbonate Scale Inhibition Performance of Composite Corrosion and Scale Inhibitor (FS) and Other Inhibitors

In this experiment, the performance of composite corrosion and scale inhibitor (FS) on calcium carbonate scale inhibition was carried out in compared with CNS-PESA, PBPCA and polyacrylic acid (PAA). According to Fig. 4, it can be seen that the prepared FS inhibitor is significantly stronger than the thiourea-modified polyepoxy succinic acid (CNS-PESA), PBPCA and PAA in calcium carbonate scale inhibition performance. When the amount of the prepared FS is 4 mg/L, the inhibition efficiency can reach 67.9%, and the other three kinds of corrosion and scale inhibitors are obviously lower than that of the prepared FS inhibitor.
With the increase of the amount of inhibitor, the inhibition efficiency of the prepared FS inhibitor can reach 98.9% at the amount of 18 mg/L. It was much higher than that of PBTCAs as the inhibition efficiency of 88.6%. Compared with CNS-PESA, the prepared FS inhibitor is better in inhibition performance of calcium carbonate scale. This is because in the prepared FS inhibitor, CSN-PESA acts as the main body, and other corrosion and scale inhibitors have a synergistic effect with their compound, which further improves the chelation with metal ions in water, and makes metal ions and corrosion and scale inhibitor in water form a complex [1, 22]. Therefore, metal ions cannot precipitate and scale with HCO$_3^-$ and CO$_3^{2-}$ in the water.

Comparison on the Calcium Phosphate Scale Inhibition Performance of Composite Corrosion and Scale Inhibitor (FS) and other Inhibitors

According to Fig. 4, CNS-PESA, PBTCAs, polyacrylic acid (PAA) and composite corrosion scale inhibitor (FS) were compared with the experiment on the determination of various substances in the same experimental conditions for the performance of calcium phosphate scale inhibition. When the dosage was 4 mg/L, the calcium phosphate scale inhibition rate of the FS inhibitor reached 60.3%, CNS-PESA was 56.3%, PBTCAs was 64.5%, polyacrylic acid (PAA) was 42.2% respectively. When the dosage was relatively little, the calcium phosphate scale inhibition efficiency of PBTCAs was higher than that of the other three kinds of corrosion and scale inhibitors. However, the dosage of PBTCAs increased, the calcium phosphate scale inhibition efficiency of PBTCAs was higher than that of the other three kinds of corrosion and scale inhibitors. The inhibition rate of the FS inhibitor was higher than that of the other three kinds of scale inhibitors with the increased dosage. When the dosage was 18 mg/L, the calcium phosphate scale inhibition efficiency of FS inhibitor could reach 95.1%, which was significantly higher than that of the other three inhibitors.

Comparison on the Corrosion Inhibition Performance of Composite Corrosion and Scale Inhibitor (FS) and other Inhibitors

According to Fig. 5, it can be seen that when the amount of chemicals reaches 16mg/L, the corrosion inhibition performance of various chemicals did not significantly change. When the dosage of the inhibitors was 18mg/L, the corrosion inhibition efficiency of the prepared FS, CNS-PESA, PBTCAs and PAA were 99.2%, 97.6%, 89.2% and 78.2%, respectively. When the concentration or dosage of inhibitors continues to increase, the corrosion inhibition efficiency of inhibitors did not change significantly. Due to the presence of Zn$^{2+}$ in the FS inhibitor, this chemical and sodium gluconate can well play a synergistic effect with CNS-PESA, forming a more stable corrosion inhibition film on the surface of carbon steel, which inhibits the contact between the metal surface, oxygen, and water. Electrochemical corrosion on the surface of carbon steel is prevented to a certain extent [23-25]. Organic phosphonic acid (PBTCAs) is significantly worse than the prepared FS inhibitor in the performance of corrosion inhibition.

Performance of Composite Corrosion and Scale Inhibitor (FS) for Dispersion of Iron Oxide

Due to the existence of iron oxide in the circulating cooling water system, it is easy to accumulate and formation of scale at the bottom of the equipment and this scale which affects the normal operation of the equipment. The composite corrosion and scale inhibitor (FS) can disperse iron oxide to a certain extent and making it unable to deposit and form scale.
In this experiment, the dispersion ability of the FS inhibitor is determined according to the light transmittance of water. The lower the light transmittance is, the better the dispersion effect is; otherwise, the dispersion ability is poor. As can be seen from Fig. 6, the composite corrosion and scale inhibitor (FS) are increasing continuously. The light transmittance of the water begins to decrease because the iron oxide floats in the solution and blocking out the light [9]. When the FS inhibitor was added to 10 mg/L, the light transmittance was the lowest 52.3%. When the dosage increased continuously, the added inhibitor would form a gel to increase the light transmittance of the solution, and then its light transmittance would stabilize.

Environmental and Economic Benefits of Composite Corrosion and Scale Inhibitor (FS)

The composite corrosion and scale inhibitor (FS) developed in this paper is aimed at the market. In addition to having good corrosion and scale inhibition performance, it also has a certain cost advantage in the operation. The prepared FS inhibitor was compared with the low phosphorus corrosion and scale inhibitor JH-500 provided by Hubei Haili Chemical Technology Co., Ltd. According to Table 2, it can be seen that the prepared FS inhibitor is significantly better than low-phosphorus inhibitor JH-500 in corrosion inhibition performance, and its scale inhibition effect is also higher than that of low-phosphorus inhibitor JH-500. The costs of the operation are similar. The prepared FS inhibitor in this paper will not cause pollution to the environment because it does not contain phosphorus. Other corrosion and scale inhibitors used in circulating cooling water systems generally contain phosphorus, some contain organic phosphonic acid, and some contain inorganic phosphoric acid. When it is discharged directly into the water without treatment, it will destroy the surrounding aquatic environment ecosystem. It will inevitably increase the cost of the operation due to the treatment of the phosphorus removal.

Conclusions

In this paper, the performance evaluation affecting the corrosion and scale inhibition performance of the composite corrosion and scale inhibitor (FS) were analyzed. When the pH was between 6 to 8, scale inhibition performance of the prepared FS inhibitor can be better. When the temperature of the water is at 20°C to 40°C, the corrosion inhibition efficiency of the prepared FS inhibitor was 98.9% while the corrosion rate of carbon steel reaches 0.0176 mm/a. When the rotating speed is increased from 40 r/min to 120 r/min, the corrosion rate of carbon steel increases and the corrosion inhibition efficiency decreases. The rotating speed is increased from 120 r/min to 160 r/min, it was found that the corrosion rate of carbon steel decreases and the corrosion inhibition efficiency was increased. The prepared FS inhibitor was compared with thiourea-modified poly epoxy succinic acid (CNS-PESA), PBTCA, and PAA for their corrosion and scale inhibition performance. The inhibition efficiency

Table 2. Technical indexes of composite corrosion and scale inhibitor (FS) and JH 500.

<table>
<thead>
<tr>
<th>Name of chemical</th>
<th>Corrosion Inhibition Efficiency (%)</th>
<th>Scale Inhibition Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composite corrosion and scale inhibitor (FS)</td>
<td>99.2</td>
<td>98.9</td>
</tr>
<tr>
<td>JH - 500</td>
<td>96.3</td>
<td>93.7</td>
</tr>
</tbody>
</table>
of calcium carbonate scale performance found that FS>CNS-PESA >PBTCA>PAA. When the amount of FS was 18 mg/L, the inhibition efficiency to calcium carbonate scale reached 98.9%. The calcium phosphate scale inhibition performance of FS was greater than that of the other three kinds of comparable inhibitors. When the amount of the prepared FS inhibitor was 18 mg/L, the inhibition efficiency of the calcium phosphate scale can reach 95.1%. The corrosion inhibition performance of the FS could reach 99.2% in comparison with other inhibitors. The composite corrosion and scale inhibitor (FS) is also excellent in the performance of dispersing iron oxide. When the FS inhibitor was added to 10mg/L, the light transmittance was the lowest 52.3%. In comparison with low phosphorus inhibitor JH-500, the light transmittance was lowest 52.3%. The prepared FS inhibitor in this paper will not cause pollution to the environment. Therefore, it can be concluded that the synthetic FS inhibitor was superior in corrosion and scale inhibition performance. The inhibition efficiency of the calcium phosphate scale could reach 99.2% in comparison with other inhibitors. The composite corrosion and scale inhibitor (FS) is also excellent in the performance of dispersing iron oxide. When the FS inhibitor was added to 10mg/L, the light transmittance was the lowest 52.3%. The comparison with low phosphorus inhibitor JH-500, the light transmittance was lowest 52.3%.


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Conflict of Interest

The authors declare no conflict of interest.
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