Research Article

Study on the Corrosion and Scale Inhibition Mechanism of the Thiourea-Modified Polyepoxysuccinic Acid (CNS-PESA)

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In this paper, thiourea-modified polyepoxysuccinic acid (CNS-PESA) was synthesized and used as a corrosion and scale inhibitor for the circulating cooling water system of the factory. Polyepoxysuccinic acid (PESA) has been widely used in industrial water treatment due to its good corrosion inhibition and scale inhibition performance. It also acts as a reliable material for dispersion of iron oxide, good biodegradation efficiency, and phosphorus-free content. The scale inhibition performance for calcium carbonate and calcium phosphate scale with corrosion inhibition performance using different inhibitor concentrations, temperatures, pH, and calcium ion concentration on scale inhibition efficiency were studied. The scanning electron microscope (SEM) analysis on the scale and corrosion of carbon steel with two methods as GB/T 18175-2000 “Measurement of inhibitors in water treatment: rotation coupon method” and electrochemical method for CNS-PESA and PESA were utilized. Compared to using CNS-PESA and PESA for calcium carbonate and calcium phosphate, the scale inhibition rates were increased by 6% and 18.7%, and the corrosion inhibition rate increased by 22.4%. The scale inhibition efficiency of CNS-PESA is best when the calcium ion concentration is less than or equal to 350 mg/L. Moreover, the thiourea-modified polyepoxysuccinic acid (CNS-PESA) was phosphorus-free corrosion and scale inhibitor and minimizes environmental pollution problems.

1. Introduction

Industrial water consumption is increasing rapidly due to the accelerated development of industrial production. Industrial cooling water accounts for more than 60%-70% of the industrial water. The industrial cooling water causes corrosion, scaling, and microbial slime problems for the equipment as well as the pipeline, thereby reducing their service life without treatment [1–3]. Mineral ions in cooling water systems of industry, such as bicarbonate and calcium, may settle to form scale in heat transfer equipment, for example, heat exchangers, evaporators, and condensers. Numerous chemicals such as polyepoxysuccinic acid and polyaspartic acid have been utilized extensively in the cooling water systems to control the formation of scale in the pipelines and equipment [4, 5]. Moreover, corrosion is also a primary concern for cooling water systems as consequences of corrosion could lead to loss of reliability, contamination of the process, diminished system performance, increased maintenance cost, or unscheduled shutdown [6, 7]. The two main operating problems of the cooling water system are corrosion and scale formation because of the electrochemical oxidation reduction reaction and the sedimentation of metal salt on the metal surface. Consequently, various inhibitors have been consumed to solve these problems of the cooling water systems [8, 9].

The concept of a green water treatment agent and green chemistry was deeply seated in the hearts of people during the time of the world’s environmental conservation laws and regulations [10]. Traditional and natural scale and corrosion inhibitors have problems such as high operating costs and considerable usage of the drug in substantial use. Moreover, phosphorus-containing corrosion and scale inhibitors have inferior scale inhibitory effects on calcium phosphate,
zinc scale, and iron oxide precipitation which are easy to hydrolyze. Polyepoxysuccinic acid (PESA) and polyaspartic acid (PASP) are currently identified as environmentally friendly scale and corrosion inhibitors for cooling water treatment in many countries [11, 12]. Polyepoxysuccinic acid (PESA) is a new environmentally safe green water treatment agent with nonphosphorus and nonnitrogen. It will not cause the trouble of eutrophication of the water environment in prolonged use [10, 11, 13, 14]. Conventional natural polymer corrosion and scale inhibitors have problems such as high treatment cost and intensive usage of chemicals in actual treatment [11].

Polyepoxysuccinic acid (PESA) is originally advanced as a scale and corrosion inhibitor. It has strong inhibition ability for calcium ion, magnesium ion, and iron ion, which makes it applicable for water treatment with tremendous amount of hardness and alkalinity. PESA without phosphorus and nitrogen is recognized as a green water treatment agent. Besides, PESA has a good treatment effect on pipeline scale problems, corrosion, and other problems and biodegrade itself. These advantages do not retain in conventional corrosion and scale inhibitors. Though some defects of PESA are apparent, the functional group of PESA is unattached, while the range of application is desperately limited. Consequently, many researchers have introduced experimental research on modification of PESA [11, 15–21].

The present research work was aimed at studying the chemical modification of polyepoxysuccinic acid (PESA) with thiourea. The branched chain is connected with thiourea because the existence of thiourea can improve the corrosion and scale inhibition performance of polyepoxysuccinic acid (PESA) to a certain extent. Therefore, polyepoxysuccinic acid was modified and synthesized, and its scale and corrosion inhibition mechanism are investigated in order to further improve the scale and corrosion inhibition performance and reduction of the cost performance in this study.

2. Materials and Methods

2.1. Water Sample. The water sample used in this experiment is the circulating cooling water sample from the factory. The water quality indexes are shown in Table 1.

2.2. Main Instruments. Constant temperature water bath (HH-8, Beijing Zhengkai Instrument Co., Ltd.), the rotary hanging film instrument (RCC - III type, Gaoyou Motian Electronic Instrument Co., Ltd.), pH meter (PHS – 3G, Youlaibo Technology Co., Ltd.), the electrothermostat (DHG – 9040A, Beijing Syntax equipment Co., Ltd.), electronic analytical balance (YP1002, Shanghai Chuyan Laboratory Equipment Co., Ltd.), Fourier infrared spectrometer (PX-1), electrochemical workstation (CHI660D, Shanghai Chenhua Instrument Co., Ltd.), and scanning electron microscope (JSM5610LV, Nippon electronic Co., Ltd.) were used in this research.

2.3. Main Materials. Sodium hydroxide (granular), borax, anhydrous calcium chloride, sodium bicarbonate, maleic anhydride, sodium tungstate, 30% hydrogen peroxide, calcium hydroxide, and thiourea were used in this experiment. All the above chemicals used in this experiment were analytical grade pure. Polyepoxysuccinic acid (Changzhou Jianghai Environmental Protection Co., Ltd., solid content of 40%) and modified polyepoxysuccinic acid (produced in the laboratory) were also used in this work.

2.4. Experimental Procedures

2.4.1. Synthesis of Epoxysuccinic Acid (ESA). Some amount of maleic anhydride was weighed by using an electronic balance and dissolved in deionized water. Then, a certain amount of sodium hydroxide was added to adjust the pH of about 9. The oil bath temperature was regulated at 60°C under the condition of heating and stirring. A certain amount of 30% hydrogen peroxide was added after heating and stirring to a certain extent. After that, the reaction temperature was adjusted to 80°C. Finally, sodium tungstate was used as the catalyst to cause an epoxidation reaction after a period of reaction time to obtain epoxysuccinic acid (ESA) [11]. The reaction equation for the synthesis of epoxy succinic acid (ESA) was shown in Figure 1.

2.4.2. Synthesis of Thiourea-Modified Polyepoxysuccinic Acid (CNS-PESA). A certain amount of thiourea (thiocarbamide) was weighed and put into epoxysuccinic acid. The oil bath temperature was adjusted to 100°C, and the stirring speed was kept at 150 rpm/min. The reaction time lasted for 2.5 hours. The thiourea-modified polyepoxysuccinic acid (CNS-PESA) was obtained after a period of reaction. The reaction equation for the synthesis of modified polyepoxysuccinic acid is shown in Figure 2 [11].

2.4.3. Experimental Procedure for Calcium carbonate Scale Inhibition Method. To determine the 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. Thiourea-modified polyepoxysuccinic acid (CNS-PESA) and polyepoxysuccinic acid (PESA) 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 cooled 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 [22, 23]:

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

where

\[ \rho_2 : \text{The value of the concentration of calcium ions (Ca}^{2+}\text{)} \]

with the addition of corrosion and scale inhibitor (mgL⁻¹),
The value of the concentration of calcium ions (Ca\(^{2+}\)) without the addition of corrosion and scale inhibitor (mgL\(^{-1}\)), 0.204: The value of the concentration of calcium ions (Ca\(^{2+}\)) in the test solution prepared before the test.

2.4.4. Experimental Procedure for Calcium Phosphate Scale Inhibition Method. The GB/T 22626-2008 method was used to determine the calcium phosphate scale inhibition. The water sample was prepared in the laboratory with the concentration of Ca\(^{2+}\) in 100 mg/L and the concentration of PO\(_4^{3-}\) in 5 mg/L. Thiourea-modified polyepoxysuccinic acid (CNS-PESA) and polyepoxysuccinic acid (PESA) were added to the 500 mL of water samples, respectively. The water samples with water 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 [22, 23].

2.4.5. 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 reference 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 thiourea-modified polyepoxysuccinic acid (CNS-PESA) and polyepoxysuccinic acid (PESA) was 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 addition 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 X1 (mm/a) can be calculated as follows [22, 23]:

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

where
\(m\): Quality of carbon steel hanging plate before experiment (g),
\(m_0\): Quality of carbon steel hanging plate after experiment (g),
\(s\): Corrosion area of hanging plate (mm\(^2\)),
\(\rho\): Density of carbon steel hanging plate (g/cm\(^3\)),
\(t\): Duration of experiment (h)
2.4.6. Experimental Procedure for the Determination of Corrosion Inhibition Performance with Electrochemical Test Measurement. The main performance of electrochemical testing is to study the basic processes of the electrode by testing the two physical quantities of potential and current of various kinds of dynamic information in the electrode process and study their changes under the action of various polarization signals and the relationship between these two processes. The electrochemical test instrument used in this paper is CHI660D electrochemical workstation. CHI660D series of electrochemical workstation for common electrochemical test system, by the microcomputer, electrochemical workstation, and three-electrode system, integrated with most of the electrochemical testing technology, including constant current, constant voltage, potential scanning, electricity rates jump, scanning electric current, pulse, current step, AC voltammetry, square wave, coulomb method, AC impedance and potential method, and fluid mechanics adjustable voltammetry, can be for a variety of electrochemical constant testing. The electrochemical test system used a conventional three-electrode system, namely, the working electrode, the reference electrode, and the auxiliary electrode. In this paper, the electrochemical test was used in the reference electrode as saturated calomel (SCE), auxiliary electrode as platinum electrode, and working electrode as self-made A3 carbon steel (standard A3 carbon steel is cut into 1 cm × 1 cm small test piece, one side of which is welded with a copper wire). Then, insert a small piece of copper wire into a section of PVC water pipe. The side without copper wire is level with one of the opening of the PVC pipe. This side is placed vertically down and filled it with epoxy resin AB glue from the top end to leave a piece of copper wire. Before each experiment, the surface of the working electrode was polished to bright step by step with 600#, 800#, 1000#, 1200#, and 1500# metallurgical sandpaper and then cleaned with distilled water, anhydrous ethanol, and acetone in turn. Then, the treated working electrode was soaked into the electrolytic cell as soon as possible with 3.5% NaCl solution as the electrolyte for electrochemical test [24].

\[ \eta = \frac{X_0 - X_i}{X_0} \times 100\% \]  

where

- \( X_0 \): Corrosion rate of hanging plate (blank test) (mm/a),
- \( X_i \): Corrosion rate of hanging plate (mm/a).

3. Results and Discussion

3.1. Infrared Spectra of CNS-PESA and PESA. Figure 3 shows the comparison graph of infrared spectra of CNS-PESA and PESA. In the infrared spectrum of the PESA, 3443.68 cm\(^{-1}\) is the O-H stretching vibration absorption peak of the –COOH group, 1619.27 cm\(^{-1}\) is the COO- stretching vibration absorption peak, and 1115.36 cm\(^{-1}\) is the C-O-C stretching vibration absorption peak. In the infrared spectrum of thiourea-modified polyepoxysuccinic acid (CNS-PESA), the N-H stretching vibration in the amide bond has a wave number of 3275.83 cm\(^{-1}\). The C-O-C stretching vibration absorption peak has a wave number of 1092.57 cm\(^{-1}\). These all proved the existence of thiourea-modified polyepoxysuccinic acid [11, 25].

3.2. Performance Evaluation of Thiourea-Modified Polyepoxysuccinic Acid

3.2.1. Determination of Calcium Carbonate Scale Inhibition Performance of PESA and CNS-PESA. The inhibition efficiency of the calcium carbonate scale for PESA and CNS-PESA is shown in Figure 4. The calcium carbonate scale inhibition efficiency was investigated by changing the concentration of PESA and CNS-PESA inhibitors. When the dosage of inhibitors was 1 mgL\(^{-1}\), the scale inhibition rate of PESA and CNS-PESA were 27.3% and 28.7%, respectively. It is seen that the scale inhibition efficiency keeps increasing with the increasing dosage. The scale inhibition efficiency of PESA and CNS-PESA decreased when the dosage of 5 mgL\(^{-1}\) for PESA and 4 mgL\(^{-1}\) and 7 mgL\(^{-1}\) for CNS-PESA. When the added dosage was from 1 mgL\(^{-1}\) to 4 mgL\(^{-1}\), there was not much difference in scale inhibition rate between PESA and CNS-PESA. However, the scale inhibition performance of CNS-PESA is obviously better than that of PESA when the dosage reached 5 mgL\(^{-1}\). The scale inhibition efficiency of CNS-PESA reached 95.7%, while the scale inhibition efficiency of PESA was 89.7% at the dosage of 11 mgL\(^{-1}\). The increased percentage of PESA and CNS-PESA was 6% in comparison. This is due to the presence of polar groups such as amide and amino groups in CNS-PESA, which enhances its electrostatic attraction and chelation process with calcium ions in water. Thus, it forms a stable calcium ion complex in water and reduces the formation of sediment so that the scale inhibition efficiency is further improved [20, 25, 26].

3.2.2. Determination of Calcium Phosphate Scale Inhibition Performance of PESA and CNS-PESA. Figure 5 shows the calcium phosphate scale inhibition efficiency of PESA and CNS-PESA. The calcium phosphate scale inhibition efficiency was investigated by changing the concentration of PESA and CNS-PESA inhibitor. It can be seen from the figure that PESA and CNS-PESA have a poor inhibition performance on calcium phosphate scale than calcium carbonate scale. The scale inhibition efficiency of PESA and CNS-PESA was 21.5% and 27.2% at 1 mgL\(^{-1}\), respectively. However, the scale inhibition rate of PESA and CNS-PESA increased continuously with the increasing dosage. When the dosage of PESA and CNS-PESA was 10 mgL\(^{-1}\), the scale
The scale inhibition rate of PESA and CNS-PESA was basically permanent after adding this dosage. The scale inhibition performance of CNS-PESA was 18.7% higher than that of PESA. These results indicate that CNS-PESA has better inhibition efficiency than PESA for calcium phosphate scale.

3.2.3. Effect of Calcium Ion (Ca^{2+}) Concentration on Scale Inhibition Performance of PESA and CNS-PESA. The effect of calcium ion (Ca^{2+}) concentration on scale inhibition efficiency is demonstrated in Figure 6. The scale inhibition efficiency of PESA and CNS-PESA gradually decreased with the increased concentration of calcium ion (Ca^{2+}). When the Ca^{2+} concentration was 300 mgL^{-1}, the scale inhibition efficiency of PESA and CNS-PESA was 79.5% and 93.5%, respectively. The scale inhibition rates of PESA and CNS-PESA decreased substantially when the calcium ion (Ca^{2+}) concentration was greater than 300 mgL^{-1}. The scale inhibition rates of PESA and CNS-PESA were 34.2% and 57.3% when the calcium ion (Ca^{2+}) concentration was 600 mgL^{-1}. The scale inhibition efficiency decreased, while the calcium carbonate scale increased with the increased concentration of calcium ions. However, the scale inhibition rate of CNS-PESA was still much higher than that of PESA. This effect may be the graft copolymer of the functional groups in thiourea introduced into the side chain and enhances the complex ability of CNS-PESA to calcium ions [27]. Figure 6 also indicates that CNS-PESA and PESA are suitable for the treatment of industrial wastewater with relatively low concentration of calcium ions, while wastewater with high calcium ions content needs to be diluted [28–30].

3.2.4. Corrosion Inhibition Performance of PESA and CNS-PESA. The corrosion inhibition performance of PESA and CNS-PESA by varying the concentration of inhibitors is shown in Figure 7. It can clearly indicate that the corrosion inhibition efficiency of PESA and CNS-PESA was continuously increased with the increased dosage starting from 8 mgL^{-1}. Their corrosion inhibition performance improved with the increased quantity of inhibitors. When the dosage
of PESA and CNS-PESA was 16 mgL⁻¹, the corrosion inhibition rates reached 73.2% for PESA and 95.6% for CNS-PESA. The corrosion inhibition efficiency gradually stabilized as the increased dosage of 18 mgL⁻¹. The corrosion inhibition performance of CNS-PESA was 22.4% higher than that of PESA. At the dosage of 20 mgL⁻¹, the corrosion inhibition efficiency of PESA and CNS-PESA slightly decreased. The grafting of thiourea group into polyepoxysuccinic acid improves its corrosion inhibition performance. Moreover, thiourea itself has a good corrosion inhibition performance on metal. Due to the sulfur (S) atoms in the thiourea-modified polyepoxy succinic acid, it is easier for the modified polymer to form the oxide film on the surface of the metal and give better prevention to metal [31, 32]. Therefore, it can be concluded that the corrosion inhibition efficiency of thiourea-modified polyepoxy succinic acid (CNS-PESA) is better than that of polyepoxy succinic acid (PESA).

3.2.5. Effect of Different Reaction Temperature on Scale Inhibition Performance for PESA and CNS-PESA. Figures 8(a) and 8(b) indicate the effect of different reaction temperature on calcium carbonate (CaCO₃) and calcium phosphate [Ca₃(PO₄)₂] scale inhibition efficiency for PESA and CNS-PESA. This experimental reaction is carried out at different reaction temperatures from 60°C to 95°C. The scale inhibition performance for CNS-PESA was better than that of PESA at different reaction temperature. It can be seen from Figure 8(a) that the calcium carbonate (CaCO₃) scale inhibition efficiency for PESA and CNS-PESA continuously increased from the temperature starting from 70°C. The highest scale inhibition rate for CNS-PESA reached 96.1% for calcium carbonate scale and 87.23% for calcium phosphate scale at 90°C. As for the PESA, the highest scale inhibition rate reached 90.1% for calcium carbonate scale and 68.42% for calcium phosphate scale at 90°C. The decomposition of the thiourea occurred as the increased reaction temperature and generated the materials such as hydrogen sulfide (H₂S) and ammonia (NH₃). These generated materials reduced the reaction rate of the inhibitors and caused the breaking of the main chain of polyepoxy succinic acid. Therefore, the scale inhibition efficiency of thiourea began to decrease [33].

3.2.6. Effect of pH on Scale Inhibition Performance for PESA and CNS-PESA. The effect of pH on calcium carbonate (CaCO₃) and calcium phosphate [Ca₃(PO₄)₂] scale inhibition efficiency for PESA and CNS-PESA is shown in Figures 9(a) and 9(b). As can be seen from the figure, scale inhibition rates of CNS-PESA and PESA were less than 90% at the pH value of less than 7. The best scale inhibition efficiency reached between the pH values of 7 and 8. The inhibition rates of CNS-PESA reached 95.6% for calcium carbonate scale and 87.27% for calcium phosphate scale, while the scale inhibition rates of PESA were 89.61% for calcium carbonate scale and 68.54% for calcium phosphate scale. The rate of scale inhibition decreased when the pH value greater than 8. The calcium carbonate scale produced Ca(HCO₃)₂ and OH⁻ in alkaline conditions. These substances create to slow down the scale inhibition efficiency of inhibitors. Therefore, it can be concluded that thiourea-modified polyepoxy succinic acid (CNS-PESA) was applicable between the pH values of 7 and 8 [34, 35].

3.2.7. Effect of Corrosion Inhibition Performance on Different Reaction Temperature and pH for PESA and CNS-PESA. Figures 10(a) and 10(b) show the effect of corrosion inhibition performance on different reaction temperatures and pH for PESA and CNS-PESA. Temperature can greatly influence the behavior of corrosion for materials. Because of its severe effects on physicochemical and electrochemical reaction rates, temperature is one of the imperative environmental parameters in studies of corrosion [36, 37]. According to Figure 10(a), the corrosion inhibition rate gradually
increased with the increasing temperature. The best corrosion inhibition performance reached 95.6% for CNS-PESA and 78.32% for PESA at 90°C. The corrosion inhibition rate declined as the temperature was more than 90°C. The reaction activity of thiourea and polyepoxysuccinic acid decreased when the temperature continued to increase. So, the temperature has a substantial effect on the development of corrosion processes [38].

Figure 8: Effect of scale inhibition performance of PESA and CNS-PESA for (a) calcium carbonate and (b) calcium phosphate scale at different reaction temperatures.
The effect of different pH values on corrosion inhibition performance for PESA and CNS-PESA is shown in Figure 10(b). The corrosion inhibition efficiency slightly increased when the pH values lower than 7. The corrosion inhibition rate was between 50% and nearly 90% at the pH lower than 7. The highest corrosion inhibition rate obtained the pH values between 7 and 8. The corrosion inhibition rate for CNS-PESA was 95.58% and for PESA was 78.27%. In an alkaline condition of pH greater than 8, the corrosion inhibition efficiency gradually decreased. The reaction efficiency of thiourea and polyepoxysuccinic acid decreased with the increasing pH values of greater than 8. It can be concluded that the maximum corrosion inhibition performance of CNS-PESA and PESA on temperature was 90°C and on pH values was between 7 and 8. The corrosion inhibition efficiency of CNS-PESA was more effective than PESA. Therefore, CNS-PESA was an effective corrosion and scale inhibitor for circulated cooling water system.

3.2.8. Self-Corrosion Potential with Electrochemical Test Measurement. Self-corrosion potential $E_{\text{corr}}$ refers to the stable potential of metal in solution, which changes with the state of metal surface, composition of solution, temperature, pH value, and other conditions, and is an important electrochemical parameter. Before the electrochemical test, the working electrode was first immersed in the solution for a
period of time, until the self-corrosion potential reaches stability, and then, the test is performed. This period of time was the potential stability time (t). After the electrode was treated in the solution, it was immediately immersed in 3.5% NaCl solution, and the self-corrosion potential with time was tested without corrosion inhibitor and with the concentrations of 10 mg/L, 20 mg/L, and 30 mg/L of thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor. The change curve of electrode potential (E) of carbon steel electrode relative to saturated calomel electrode with time t is shown in Figure 11. The change of potential decreased gradually after a period of time. Potential achieved stability about 30 minutes, and the electrodes were determined in electrochemical soaking time for 30 minutes before the test. In addition, with the increased concentration of the thiourea-modified polyepoxysuccinic acid (CNS-PESA), the $E_{corr}$ value gradually moved to a positive direction, and it can be preliminarily concluded that thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor has an inhibitory effect on the anodic corrosion reaction of A3 carbon steel [39].

3.2.9. Polarization Curve Measurement for Corrosion. Analyzing polarization curve is one of the methods to reveal the law and mechanism of metal corrosion and to discuss how to control corrosion problems. According to the change

![Figure 10: Effect of corrosion inhibition performance for PESA and CNS-PESA on (a) different reaction temperatures and (b) different pH.](image1.png)

![Figure 11: Corrosion potential curve with time.](image2.png)
of corrosion potential and polarization curve after adding corrosion and scale inhibitor, the mechanism of electrode reaction can be determined. In this experiment, 3.5% NaCl solution and different concentrations (10 mg/L, 20 mg/L, and 30 mg/L) of thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor were used as the system to test the polarization curve. The polarization curve test results are shown in Figure 12. As can be seen from Figure 12, the self-corrosion potential of the electrode in the polarization curve moved to a positive direction with and without the addition of the thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor in comparison. The cathodic and anodic polarization currents are inhibited to varying degrees with the addition of the thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor. The slope of anode polarization curve increased obviously, while the anode current decreased obviously. But the slope of cathode polarization curve changed little and the cathode current decreased not clearly. This indicates that the thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor is a kind of corrosion inhibitor which mainly inhibits anode polarization. With the increase of the concentration of the thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor, the self-corrosion potential of the electrode gradually moved to the positive direction, and the self-corrosion current density gradually decreased. This indicates that the thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor has a certain inhibition effect on the cathode of the electrochemical corrosion process, while the anode inhibition effect on the corrosion process is gradually enhanced.

3.3. Electrochemical Impedance Spectroscopy (EIS) of the Thiourea-Modified Polyepoxysuccinic Acid (CNS-PESA).

Electrochemical impedance spectroscopy (EIS) refers to applying a small amplitude alternating potential wave with different frequencies to the electrochemical system and measuring the change of the ratio of alternating potential to current signal (the ratio is the system’s impedance) with the sine wave frequency, or the change of the phase angle of impedance with the wave frequency [40, 41]. Then, the kinetics of electrode process, double electric layer, and diffusion are analyzed, and the mechanism of electrode material, solid electrolyte, conductive polymer, and corrosion protection is studied. An electrochemical system is regarded as an equivalent circuit, which consists of basic components such as inductance (L), capacitance (C), and resistance (R) combined in different ways such as series and parallel. By means
Figure 14: SEM analysis images of calcium carbonate scale (a) without CNS-PESA and (b) with adding CNS-PESA.

Figure 15: Bode diagram of carbon steel electrode in 3.5% NaCl solution with different concentrations of thiourea-modified polyepoxysuccinic acid (CNS-PESA).

Figure 16: SEM analysis images of calcium phosphate scale (a) without CNS-PESA and (b) with CNS-PESA.
of EIS, the composition of the equivalent circuit and the size of the basic elements can be measured, and the structure of the electrochemical system and the properties of the electrode process can be analyzed by using the meaning of these basic elements in the aspect of electrochemistry [40, 41].

Corrosion inhibitor itself does not participate in the electrode reaction, but the change of coverage caused by its adsorption and desorption on the metal surface will affect the process of electrode reaction. In this section, 3.5% NaCl solution and the addition of different concentrations of thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor were used to conduct electrochemical impedance test. This test was performed to discuss the corrosion inhibition mechanism of thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor. Thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitors with concentrations of 10 mg/L, 20 mg/L, and 30 mg/L were added to 3.5% NaCl solution at room temperature of 25°C, and the test was started after soaking for 30 minutes. The electrochemical impedance test results of Nyquist diagram are shown in Figure 13.

As can be seen from Figure 13, under the condition of thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor with different concentrations, the obtained impedance patterns have similar characteristics. The solution resistance was very small. In the range of high frequency region, the data points are relatively dense, showing a small curve arc. With the decrease of AC frequency, the data points continued to rise, and two maximum points appeared, with two semicircular characteristics of different degrees. This indicates that there are two capacitive reactance arcs, which are the general characteristics of impedance spectrum in corrosion inhibition and adsorption system. The radius of the semicircle increases with the increase of the concentration of the thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor. In addition, the dispersion effect appears in the low frequency region of the impedance pattern, which is related to the existence of Cl−, the surface roughness of the electrode, and the uneven current distribution. In the two capacitive reactance arcs of the Nyquist plot of electrochemical impedance spectroscopy, the chord length from the semicircle in the high frequency region to the real axis Z' corresponds to the charge transfer resistance Rct. For the corrosion inhibition system, Rct reflects the resistance of the coating layer of corrosion inhibitor on the metal surface to the metal ionization process, or it reflects the speed of corrosion reaction. The higher the value of Rct, the greater the resistance of metal ionization and the lower the corrosion rate of metal. As can be seen from Figure 15, the value of Rct increases with the increase of the concentration of the thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor. It indicates that the thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor can inhibit the corrosion of A3 carbon steel.

The Bode diagram of carbon steel electrode in 3.5% NaCl solution with different concentration thiourea-modified polyepoxysuccinic acid (CNS-PESA) formula is shown in Figure 14. As can be seen from Figure 14, two peaks appear in the phase frequency diagram, indicating that they are controlled by two time constants, one representing the electrode process and the other representing the adsorption process. According to the distribution of the data and the trend of the curve presented in the above Nyquist and Bode diagrams, the basic process involved in the system of this electrode reaction can be preliminarily inferred. The basic processes that may be involved are (1) the process of surface film formation, (2) the reaction process of charge transfer, and (3) adsorption process of thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor.

3.4. SEM Characterization of Calcium Carbonate (CaCO₃) and Calcium Phosphate [Ca₃(PO₄)₂] Scale Inhibition Performance. The water samples were drained from water bath after 10 hours at 80°C. The scanning voltage was set as 25 kV, and the magnification was 1000 times in the scanning electron microscopy experiment of calcium carbonate and calcium phosphate scale samples. Therefore, the mechanism of scale inhibition efficiency is observed and analyzed.

Figures 15(a) and 15(b) show the SEM images of calcium carbonate scale crystals without adding CNS-PESA and with adding CNS-PESA. It can be seen from Figure 15(a) that the crystal shape is hexahedral calcite structure with regular arrangement. The crystal was compact and has large volume which is easy to form calcium calcite [42]. Figure 15(b) shows the calcium carbonate scale crystal generated after the addition of CNS-PESA. It can be seen from these figures that the calcium carbonate crystal is not a regular rhombohedral structure but has crystal distortion. Therefore, the sheet and flocculent loose aragonite formed.

Figures 16(a) and 16(b) show the SEM images of calcium phosphate scale crystals without adding CNS-PESA and with adding CNS-PESA in the water sample. The crystals present regular shapes and are arranged in a relatively orderly manner according to Figure 16(a). Figure 16(b) shows the calcium phosphate scale crystal in the water sample with the addition of CNS-PESA. It can be found that the crystal shape is deformed. The regular cube shape of the crystal is almost disappeared, but the crystal is formed into a sheet, which changes the looseness of the crystal.

The carbonate and phosphate ions in the water sample continuously collide with calcium ions to form regular
diamond-shaped crystals. However, after adding CNS-PESA, the combination and collision of these ions in the water are destroyed, making it impossible to move in the original direction. Growth in turn makes the combination of carbonate ions and phosphate ions and calcium ions deformed [26, 42, 43].

The electronegative groups increased such as the amide and amino groups in the CNS-PESA molecule, and the CNS-PESA molecule adsorbs to the crystal surface to form an electric double layer. The charge state of the crystal surface changes, and the particles interact electrostatically with each other. Repulsion frees calcium ions in the water and plays a role of scale inhibition.

3.4.1. X-Ray Diffraction (XRD) Analysis of Calcium Carbonate (CaCO₃) Scale. In order to study the scale inhibition mechanism of the thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor on calcium carbonate scale, X-ray diffraction (XRD) method was used to conduct on the calcium carbonate scale samples obtained without the addition of corrosion and scale inhibitor and after the addition of the thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor. The results are shown in Figure 17. It can also be seen from the figure that the diffraction peak intensity of calcium carbonate (CaCO₃) scale sample formed with the addition of thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor was lower than that without the addition of thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion and scale inhibitor. This indicates that the addition of thiourea-modified polyepoxysuccinic acid (CNS-PESA) corrosion inhibitor and scale inhibitor reduced the integrity degree and order degree of CaCO₃ crystal growth and crystallinity. Therefore, the growth of CaCO₃ crystal inhibited [17].

3.5. SEM Characterization of Corrosion Inhibition Performance Analysis of Carbon Steel. The corrosion inhibition performance of CNS-PESA was tested by rotating hanging plate method. Figure 18(a) is the A3 carbon steel before the experiment, and it can be seen that the surface of carbon steel is smooth, with mechanical scratches and neat texture. Figure 18(b) shows the blank control of carbon steel without CNS-PESA in the rotary hanging plate experiment. After 72 hours of the test, the surface of the carbon steel appeared obvious corrosion phenomenon. The corrosion pits appeared on the surface of the carbon steel and grain also became disorderly. Figure 18(c) is an image of a carbon steel with the addition of CNS-PESA. From this figure, it can see that the mechanical grain of the carbon steel is relatively obvious. Compared with the carbon steel in Figure 18(b), the corrosion degree is lower and the corrosion pits are fewer. All these findings indicate that CNS-PESA form a layer of corrosion inhibition film on the surface of A3 carbon steel, which protects the carbon steel and reduces the corrosion degree of the carbon steel [18, 29, 39].

Figure 18: SEM images of corrosion inhibition performance analysis of carbon steel (a) before experiment, (b) without adding CNS-PESA, and (c) with adding CNS-PESA.
Table 2: Technical and economic indexes of CNS-PESA and PESA.

| Scale inhibitor | Calcium carbonate scale inhibition efficiency (%) | Calcium phosphate scale inhibition efficiency (%) | Corrosion inhibition efficiency (%) |
|-----------------|--------------------------------------------------|--------------------------------------------------|-------------------------------------|
| CNS-PESA        | 95.7%                                            | 87.3%                                            | 95.6%                               |
| PESA            | 89.7%                                            | 68.6%                                            | 73.2%                               |

3.6. Technical and Economic Indexes of CNS-PESA and PESA. The technical and economic comparison results for CNS-PESA and PESA are shown in Table 2. It can be seen from Table 2 that the performance of scale inhibition rate of the thiourea-modified polyepoxysuccinic acid (CNS-PESA) is increased by 6% for calcium carbonate scale and 18.7% for the calcium phosphate scale, and the corrosion inhibition rate is increased 22.4% than PESA. The cost is reduced 0.09 USD per ton. The reaction efficiency of CNS-PESA was greater than the traditional corrosion and scale inhibitor. Therefore, thiourea-modified polyepoxysuccinic acid (CNS-PESA) has great corrosion and scale inhibition performance and cost-effective among other corrosion and scale inhibitor.

4. Conclusion

This study focused on the evaluation of the thiourea-modified polyepoxysuccinic acid (CNS-PESA). The performance evaluation of scale inhibition rate of the thiourea-modified polyepoxysuccinic acid (CNS-PESA) is increased by 6% for calcium carbonate scale and 18.7% for the calcium phosphate scale, and the corrosion inhibition rate is increased 22.4% than PESA. According to the scanning electron microscope (SEM) experiment, it can be seen that the mechanism of CNS-PESA in scale inhibition was through the destruction of anions and cations. The crystals are distorted to generate irregular calcium scales to reduce the formation of precipitates as a result. And in terms of corrosion inhibition, CNS-PESA will form a protective film on the surface of carbon steel to reduce metal corrosion. Moreover, the thiourea-modified polyepoxysuccinic acid (CNS-PESA) lessens the pollution to our environment. Therefore, the thiourea-modified polyepoxysuccinic acid (CNS-PESA) was environmental friendly phosphorus free corrosion and scale inhibitor and had excellent corrosion and scale inhibition performance for circulating cooling water from factory.

Data Availability

The data used to support the findings of this study are cited at relevant places in the text as references.

Conflicts of Interest

We have no conflicts of interest to disclose.

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