

# An Efficient Phosphorus-Free Inhibitor for both Anti-corrosion and Anti-scaling in Circulation Cooling Systems

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**Abstract.** Properties and mechanism of a non-phosphorus inhibitor were studied, in the simulate condition of a circulation cooling system. The inhibitor enable control the corrosion of system containing both carbon steel and copper alloy, which is similar to a real circulation cooling system. Studies showed that the inhibitor showed excellently corrosion inhibition properties and protect metals well. Scale inhibition experiment showed that the rate of scale inhibition could reach up to 98%. Therefore, the environment-friendly inhibitor is an efficiency inhibitor and could control both corrosion and scaling for the circulation cooling conditions.

**Keywords:** Phosphorus-free, Inhibitor; Mechanism, Circulation cooling

## 1. Introduction

The main problems of water treatment in circulation cooling systems are corrosion and scaling, which involve deterioration and decrease the capacity of thermal exchange. And the problems of corrosion and scaling get more serious with cycles of concentration increasing. The best and economic way is adding inhibitor in water. Many inhibitors were studied in detail and have been used in cooling systems [1]. Various inorganic and organic inhibitors were successively developed and applied [2-3]. Phosphorus-free or low-phosphorus inhibitors have become the development trend. And complex inhibitors based on the synergistic effects of organic inhibitors and inorganic inhibitors have become a hotspot [4]. Therefore, a complex phosphorus-free inhibitor with synergistic effects was prepared and optimized to solve the main problem of scale and corrosion in circulation cooling system, in this paper. The properties and mechanism of the complex inhibitor were investigated.

## 2. Experiments

### 2.1. Preparation of Complex Phosphorus-free Inhibitor

The complex phosphorus-free inhibitor was prepared based on the synergistic effects of Gluconate, carboxyl, epoxy-, Zn ion, borate and surfactant. The inhibitor consisted of part A and part B. Part A was prepared by mixing Sodium Gluconate, Poly(acrylic acid) (35%), ZnSO<sub>4</sub>·7H<sub>2</sub>O and surfactant in 80ml deionized water, in a ratio of 10:5:5:(0~1). Part B was prepared by epoxysuccinic acid (50%), borax and BTA in 20ml ethanol, in a ratio of 10:10:1. And then mix these two parts to prepared final inhibitor.

### 2.2. Weight Loss Experiment

The experiments were taken in fresh water and fourth-time concentrated water of North China. The processes referred to Standard of GB/T 18175-2014.

### 2.3. Electrochemical Measurement

electrochemical measurements were taken out by VMP3 electrochemical station. And the tests were performed using a conventional three-electrode system assembly, and SCE was used as a reference. The working electrode was carbon steel or copper. All electrochemical tests were carried out in glass cell. EIS was conducted with a 10 mV peak-to-peak sine wave in the frequency range from 100 kHz to 10 mHz.

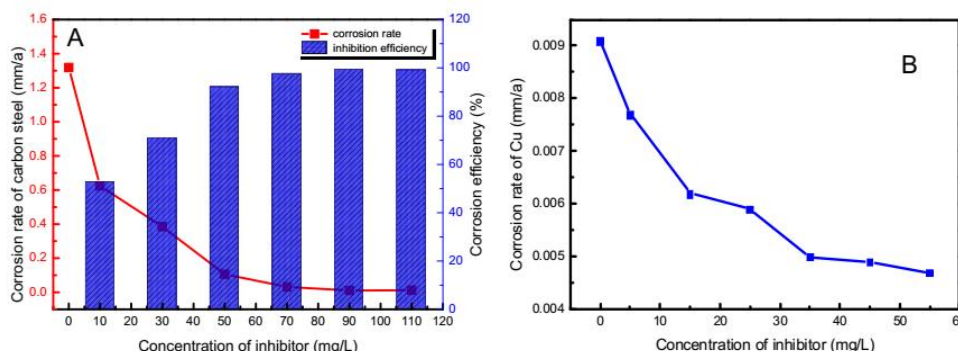
### 2.4. Scaling Inhibition Test

Ability of the complex inhibitor to inhibit calcium carbonate scale in forth-times concentration test was determined, comparing with that of free-inhibitor. The tests were taken by the static scale inhibition method refer to the National Standard of GB/T 34550.2-2017.

## 3. Results and Discussions

### 3.1. Weight Loss

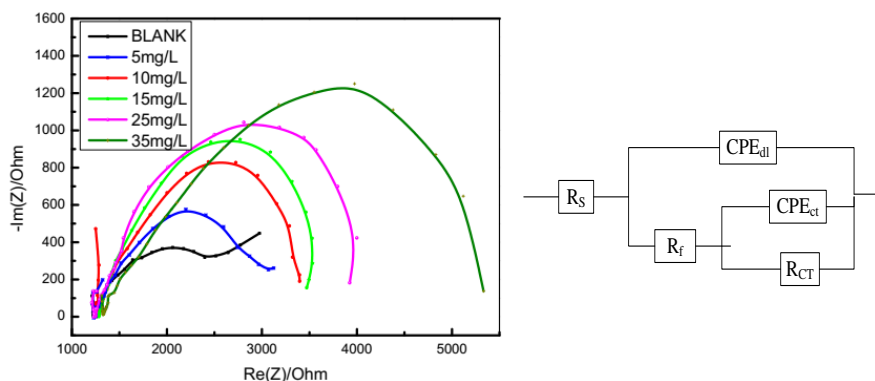
In this study, weight loss experiments were carried out with mixing samples of two carbon steels and one copper.



**Fig 1.** The corrosion rate and inhibition efficiencies of the inhibitor with different concentration (A: carbon steel; B: Cu)

The obtained experimental results were shown Fig.1. Results showed that the corrosion rate of the carbon steel reduced obviously in the presence of inhibitor, and decreased with the inhibitors concentration increasing. The corrosion rate could be reduced to 0.0317 mm/a at the concentration of 35 mg/L, and fall down to 0.0103 mm/a (with inhibition efficiency of 99.2%) at 45 mg/L. Then, it did not improve obviously anymore. In addition, the corrosion of Cu could be controlled (lower than 0.005 mm/a) by this inhibitor, when the inhibitor concentration was more than 35 mg/L, as shown in Fig.1B.

### 3.2. Electrochemical analyses



**Fig 2.** Nyquist plots and Equivalent circuits for 20# carbon steel

As analysis above, carbon steel was more prone to corrosion in the system containing both carbon steel and copper alloys, but was also the main beneficiary of the inhibitors. So, further investigations were carried out on carbon steel specimen.

EIS for carbon steel in the solution without and with inhibitors were investigated, after 1h immersion at open circuit potential (Fig. 2). Results showed that there was one depressed capacitive loop at the higher frequency range (HF) of blank sample, which ascribed to charge transfer resistance and double layer capacitance. And there was a straight line at low frequency (LF) range, which related to Warburg impedance.

Compared with comparative experiment, the diameters of Nyquist plots increased remarkably, indicating a high inhibitive ability of the inhibitor. The equivalent circuit calculated from Zview software fit well our experimental results. The impedance of the CPE was expressed as Eq.1 [3]:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \tag{1}$$

The values of n calculated from equivalent circuit were 0.5682 and 0.4705, indicating a nonhomogeneity surface, ascribed to the adsorption of inhibitor.

### 3.3. Scale Inhibition Properties

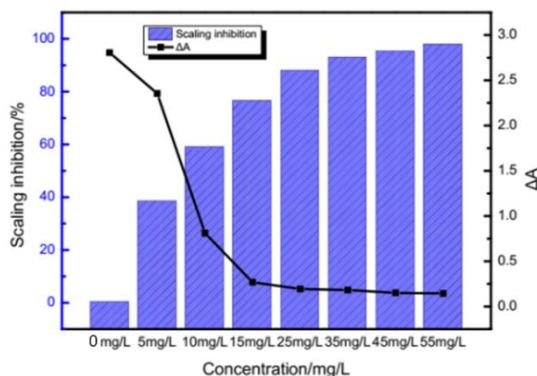
In order to study the scale inhibition properties, the samples contained 15 mg/L, 25 mg/L, 35 mg/L, 45 mg/L and 55 mg/L inhibitors were subjected to static scale inhibition tests. The scale inhibition efficiency and  $\Delta A$  were defined as Eq.2 and Eq.3.

$$\eta = \frac{\rho_{Ca3} - \rho_{Ca4}}{N\rho_{Ca2} - \rho_{Ca4}} \times 100\% \tag{2}$$

$$\Delta A = N - N_M \tag{3}$$

Where  $\rho_{Ca2}$  is the concentration of  $Ca^{2+}$  (mg/L) in the original solution,  $\rho_{Ca3}$  is the concentration of  $Ca^{2+}$  (mg/L) in the presence of inhibitor,  $\rho_{Ca4}$  is the concentration of  $Ca^{2+}$  (mg/L) in the absence of inhibitor,  $N$  is the concentration multiple of chloride ion,  $N_M$  is the concentration multiple of alkalinity, and  $\Delta A$  is the difference between  $N$  and  $N_M$ .  $\Delta A$  should not be greater than 0.2, according to the standard of GB/T 34550.2-2017.

The scale inhibition properties of the inhibitor with different concentration, in the fourth-times concentration experiment, were shown in Fig. 3. Result showed that in the range of 15mg/L and 35mg/L, the scale inhibition efficiency increased in pace with the dosage of inhibitor and even got up to 98%. Moreover, the values of  $\Delta A$  kept less than 0.2, when the dosages were more than 25 mg/L. These results indicated that the scaling could be controlled by the inhibitor effectively, in fourth-times concentration process.



**Fig 3.** CaCO<sub>3</sub> scale inhibition efficiency and  $\Delta A$  in the presence of various concentration of inhibitor

## 4. Conclusions

Focus on the corrosion and scaling problems of the cooling system with both carbon steel and copper alloys, a new phosphorus-free inhibitor was published. Weight lost tests showed that the corrosion of carbon steel and copper could be controlled efficiently, in the presence of inhibitor. Electrochemical tests showed that the impedance increased and the corrosion potentials shift towards positive (about 230 mV), in the present of inhibitors. In addition, adsorption isotherm was studied to further understand adsorption mechanism. Results indicated that Multi-Synergy adsorption was the main mechanism for the inhibitor, and the adsorption of inhibitor on metal surface was a mixed adsorption of physical and chemical adsorption. Fourth-times concentration enrichment experiment showed that the inhibitor could control scaling well. These results indicated that the inhibitor could control corrosion and scaling problems on metals' surface, which benefit for realizes the metal protection and water treatment in plant cooling system.

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