Synergistic Effect of Electrochemistry and Water Treatment Agents in Cooling Water System

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Abstract. The electrochemical device was combined with the water treatment agent to investigate the scale removal, and corrosion inhibition, because it was found through experiments that the descaling ability of the electrochemical device is related to the voltage of the device, and the distance between the plates, and the hardness of the water body which is the synergistic descaling rate of the electrochemical device with 2-phosphonic acid butane-1,2,4-tricarboxylic acid and sodium molybdate was 79.23%, and the scale inhibition rate was 87.34%, and the inhibition rate was 89.94% by controlling the operating conditions of the electrochemical device, the concentration factor of the system can be improved, and an effective method for saving water and energy in the circulating cooling water system is provided.

Keywords: Circulating cooling water, Electrochemistry, Descaling, Concentration factor

The circulating cooling water system mainly faces problems such as scaling, corrosion and microbial growth [1]. At present, chemical methods are commonly used to solve these problems, including corrosion inhibitors, scale inhibitors, bactericidal algacides, etc. [2]. But the use of chemical agents is simple and effective, but there are also some problems, such as high cost of drugs and high operating costs, as the domestic and foreign research has been done to solve the problem of circulating water by other feasible methods to assist or replace chemical dosing [3]. Electrochemical method is one of the directions.

Electrochemical circulating cooling water treatment technology is a new water treatment technology developed after the 1970s [4], it only needs to consume a proper amount of electric energy during use, and it is a clean and pollution-free water treatment process. The Electrochemical method has a good anti-scaling, descaling, bactericidal and algae-killing function, because the electrochemical method does not have the corrosion inhibition property to the metal material, it is limited in practical use, and the treatment agent solves the problem of corrosion and scaling encountered in circulating water.
1. Experimental Part

1.1 Test materials
Experimental instrument: DC stabilized power supply, Wuxi Qiaowei Electronics Co., Ltd.; the size of the electrolytic cell is length × width × height = 50mm × 55mm × 150mm, the effective volume is 200mL, the plate area is 0.004m², and the anode plate is Liao titanium plate. The cathode plate is metal titanium; 722S spectrophotometer, Shanghai Precision Scientific Instrument Co., Ltd.; constant temperature water, Shanghai Yukang Science and Education Instrument Equipment Co., Ltd.

Figure 1 Schematic diagram of the experimental device
Experimental reagents: calcium chloride, sodium hydrogencarbonate, zinc sulfate, anhydrous magnesium sulfate, sodium chloride, sodium molybdate, analytical grade, Sinopharm Chemical Reagent Co., Ltd.; cycloalkyl amphiphilic imidazoline (KLSS-A), Dongying Keling Chemical Co., Ltd.; 2-phosphonic acid butane-1,2,4-tricarboxylic acid (PBTCA), Nantong Lianphosphine Chemical Co., Ltd.

1.2 Test methods
Determination of descaling performance of electrochemical devices
Analytical pure CaCl2 and NaHCO3 were prepared in pure water with a molar ratio of 1:2 to obtain the experimental water, and the hardness ranged from 200 mg/L to 1000 mg/L (calculated as CaCO3). The electrochemical device control voltage range was 5V to 15V. The spacing is 10 mm to 50 mm; after the formulated water is treated by the electrochemical device for 5 hours, the hardness of the water body and the weight increase of the cathode surface are measured. According to "Determination of Calcium and Magnesium Ion in Industrial Circulating Cooling Water - EDTA Titration Method" (GB/T 15452-2009), is the total hardness in water which is determined to obtain the hardness removal rate of water sample. The effects of voltage, plate spacing and hardness on hardness removal rate and cathode deposition rate were studied by single factor experiment, and the hardness removal rate is the hardness removal amount divided by the raw water hardness, and the cathode deposition rate is the surface area weight per unit area.

1.3 Determination of scale inhibition performance
In order to solve the problem of scaling in high temperature which is part of the heat exchanger, this paper discusses the scale inhibition performance which is determined according to the "Measurement of scale inhibition performance of water treatment agent - calcium carbonate deposition method" (GB/T 16632-2008).

1.4 Determination of corrosion inhibition performance
According to the "Measurement of Corrosion Inhibition Performance of Water Treatment Agent - Rotating Hanging Method" (GB/T 18175-2014) to determine the corrosion inhibition performance of the electrochemically combined water treatment agent, the test time is 72h, and the experimental water is the standard preparation water.

Table 1 Standard water quality indicators

| index | pH | Conductivity (μs/cm) | Total alkali (mg/L) | Total hardness (mg/L) | Cl- (mg/L) |
|-------|----|---------------------|--------------------|----------------------|----------|
| Standard formulated water | 8.05 | 2290 | 200 | 680 | 740 |
1.5 Determination of limit concentration multiple
The limit concentration of multiple experiment [5] uses tap water in Shanghai area, and the water body is 1L, and evaporates and also concentrates at a water bath temperature of 80 °C. The total hardness and Cl- concentration are measured during the experiment, and the constant volume is replenished. When the difference between the concentration ratio of total hardness and the concentration ratio of Cl- exceeds 0.2, that is, when KCl–K total hardness is >0.2, it is considered that the limit concentration factor is reached.

| Index | pH | Conductivity (μs/cm) | Total Alkalinity (mg/L) | Total Hardness (mg/L) | Cl- (mg/L) |
|-------|----|----------------------|-------------------------|-----------------------|-----------|
| Standard formulated water | 7.5 | 361 | 85 | 134 | 68 |

2. Results and Discussion

2.1 Study on descaling performance of electrochemical devices

2.1.1 Effect of voltage
According to 1.2.1, 1L of experimental water with a hardness of 400mg/L was prepared, and the distance between the plates of the electrochemical device was set to 20mm, and the voltages were 5V, 7.5V, 10V, 12.5V and 15V respectively. The experimental results are shown in Fig. 1.

Figure 1. Effect of voltage on hardness removal rate and cathode deposition rate
Within a certain range, as the voltage increases, the electrolysis reaction rate increases, which promotes the migration of Ca2+ to the negative electrode, and the alkalinity of the cathode region increases, so that the scale-forming ions are rapidly deposited and the hardness removal rate is gradually increased, when the voltage exceeds 10V, the hardness removal rate begins to decrease, which is the main reason of the higher the voltage, the more intense the hydrogen evolution reaction. The high voltage makes the disturbance caused by the floating of the gas interfere with the migration and deposition of scale ions [6, 7], so the hardness of the removal rate is reduced. The voltage is lower, the water hardness removal effect is poor, the hardness removal rate and the cathode deposition rate
are lower; when the voltage is too high, the removal rate of the scaled ions is affected, and the electric energy cost is relatively increased. It can be seen from Fig. 1 that when the voltage is 10V, the water body hardness removal rate reaches the maximum, and the hardness removal rate is 85.41%. Considering the water hardness removal rate and the cathode deposition rate, the optimal voltage of the electrochemical device is 10V.

2.1.2 Influence of plate spacing
According to 1.2.1, the hardness of 400 mg/L of experimental water was set to 1 L, and the electrochemical device voltage was set to 10 V. The plate spacing is 10mm, 20mm, 30mm, 40mm, 50mm, and the experimental results are shown in Figure 2.

![Figure 2](image_url)  
**Figure 2.** Effect of plate spacing on hardness removal rate and cathode deposition rate

It can be seen from Fig. 2 that as the distance between the plates increases, the hardness removal rate decreases continuously, and the cathode sedimentation rate has a maximum value at 20 mm. This is because the distance between the plates is too small, resulting in a large current, and the consumption is large, the severe disturbance of the water body makes the scale layer generated on the electrode plate thin, and the later scaling is not easy to form on the electrode plate; the distance between the plates is from 20mm to 50mm, and the hardness removal rate drops rapidly, which is the spacing of the plates that is more Large, the smaller the current density, which is not sufficient to remove most of the hardness of the water body. Therefore, the optimum plate spacing should be 20mm.

2.1.3 Effect of water hardness
According to 1.2.1, 1 L of experimental water was prepared, and the voltage of the electrochemical device was set to 10 V, and the distance between the plates was 20 mm. The hardness of the experimental water was 200 mg/L, 400 mg/L, 600 mg/L, 800 mg/L, and 1000 mg/L (calculated as CaCO3).
Figure 3. Effect of hardness on hardness removal rate and cathode deposition rate

It can be seen from Fig. 3 that the hardness removal rate of water body is higher than the hardness when the water body hardness is lower than 400 mg/L. When the hardness exceeds 400 mg/L, the hardness removal rate begins to decrease, and the cathode deposition decreases, this is because the hardness is too high, and the proportion of cathode deposition is far behind the increase in hardness, and the hardness increase is too large, so the hardness removal rate is correspondingly reduced, and the descaling effect is most pronounced when the water body hardness is 400 mg/L.

In summary, the electrochemical device has a high hardness removal rate and a cathode deposition rate at a voltage of 10 V and a plate pitch of 20 mm, so when the water body hardness is 400 mg/L, the hardness removal rate is the highest, reaching 85.41%.

2.2 Study on the performance of electrochemical device combined with water treatment agent

2.2.1 Effect of combined scale inhibitor on scale inhibition performance

The electrochemical device voltage was set to 10 V and the plate spacing was 20 mm. The experimental results are as follows:

Figure 4. Effect of PBTCA on scale and scale inhibition performance

Descaling and scale inhibition are not completely opposite processes. Descaling refers to fouling on an electrochemical device under an applied electric field, and scale inhibition refers to the surface of pipes and heat exchangers when adding and not adding chemicals. In the case of scaling, the locations of the two are different, and the way of investigation is also different, it can be seen from Fig. 4 that after adding 2mg/L to 10mg/L PBTCA, the scale inhibition rate does not change much, the descaling rate decreases with the increase of PBTCA concentration, and the concentration of PBTCA is 2mg/L. The descaling rate of the equipment and the scale inhibition rate of the medicament are
maintained at a relatively high value, so that the scale removal requirement of the water body can be satisfied, and the scale inhibition effect at the high temperature portion of the system can be ensured.

2.2.2 Effect of corrosion inhibitor on corrosion inhibition performance
The water was configured according to the 1.2.3 configuration standard, and the changes of dissolved oxygen and residual chlorine in the water were measured in the presence of an electrochemical device. The results are shown in Table 3.

Table 3. Changes in dissolved oxygen and residual chlorine during electrolysis

| Item          | 24h   | 48h   | 72h   |
|---------------|-------|-------|-------|
|               | Electrochemistry | Electrochemistry | Electrochemistry |
|               | Margin  | Margin  | Margin  |
| Dissolved oxygen (mg/L) | 5.1    | 10.1   | 5.3    | 10.6   | 5.1   | 10.7   |
| Residual chlorine (mg/L)  | 0      | 10.0   | 0      | 15.0   | 0     | 20.0   |

* Blank indicates the experimental data without electrochemical device

As can be seen from Table 3, the dissolved oxygen content of the water having the electrochemical device is higher than that of the water without the electrochemical device. Under the action of the electrochemical device, a certain amount of residual chlorine is generated in the water body, and the residual chlorine has good sterilization and algae-killing performance [8], so the problem of microbial growth in the circulating water can be alleviated.

A drug was selected from each of the adsorption film type, the precipitation film type, and the passivation film type corrosion inhibitor to investigate the effect of the type of the agent on corrosion inhibition.

![Figure 5](image_url)

Figure 5. Effect of drug type on corrosion inhibition
It can be seen from Fig. 5 that the addition of electrochemistry is disadvantageous to corrosion
inhibition in most cases, but the corrosion inhibition performance of the passivation film type corrosion inhibitor is improved. This is due to the addition of electrochemistry, which increases the dissolved oxygen in the residual chlorine in the water and promotes the formation of a passivation film type corrosion inhibitor.

For different concentrations of molybdate corrosion inhibitors, the absolute corrosion rates are as follows:

![Graph showing the effect of drug concentration on corrosion inhibition](image)

**Figure 6.** Effect of drug concentration on corrosion inhibition

It can be seen from Fig. 6 that the corrosion rate decreases with the increase of the concentration of molybdate added when no electrochemical device is added, which is due to the higher film forming concentration of sodium molybdate on the surface of carbon steel [9]. When the concentration reaches a certain value, it will have a good corrosion inhibition effect; when the electrochemical device is added, the corrosion rate will decrease at a lower concentration than the concentration, because the addition of the electrochemical device provides a good aerobic environment which makes the sodium molybdate able to form a good film and improve the corrosion inhibition rate. When the concentration is 200mg/L, the absolute corrosion rate is significantly increased when it is added to the electrochemical device, which is caused by cracks after the passivation film grows to a certain thickness [10]. At higher concentrations, the faster the passivation film grows, the faster the crack will be generated and expanded. At this time, the corrosion resistance of the passivation film does not increase, but decreases, and the corrosion inhibition performance begins to decrease. Therefore, the electrochemical device combined with the optimal sodium molybdate concentration is 100 mg/L.

### 2.2.3 Effect of combined scale and corrosion inhibitor on comprehensive performance

Considering descaling, corrosion inhibition and scale inhibition, the electrochemical device, 2mg/L PBTCA and 100mg/L sodium molybdate were finally combined to investigate the descaling, scale inhibition and corrosion inhibition performance. The results are shown in Table 4. Shown.

**Table 4.** Determination of performance of electrochemical combined scale and corrosion inhibitor

| Item       | Descaling rate (%) | Scale inhibition rate (%) | Corrosion rate (%) | Corrosion inhibition rate (%) |
|------------|--------------------|----------------------------|--------------------|-------------------------------|
| Margin     | /                  | /                          | 0.5239             | /                             |
| Composite result | 79.23         | 87.34%                      | 0.0527             | 89.94                         |

* Blank indicates experimental data when the single electrochemical device is not added
It can be seen from Table 4 that when the optimal ratio is applied to carbon steel, the corrosion rate of carbon steel is only 0.0527, which is less than 0.0750 mm/a in the Industrial Design Code for Cooling Water Treatment (GB 50050-2007). At this time, the descaling rate reached 79.23%, the scale inhibition rate reached 87.34, and the corrosion inhibition rate reached 89.94%, which shows that the composite formula has good descaling, scale inhibition and corrosion inhibition effect.

2.2.4 Effect on the limit concentration multiple
Since the electrochemical device combined with a small amount of agent can solve the problem of descaling and corrosion inhibition well, the most important function of applying it to the site is to increase the concentration factor. The experiment was carried out according to the experimental conditions of 1.2.4. After the end of the experiment, the hardness and chloride ion in the water were measured. The measured limit concentration is shown in Table 5.

| Device                  | Multiple Limit concentration |
|-------------------------|-----------------------------|
|                         | Tap water                   | Tap water, 2mg/L PBTCA | Tap water, 2mg/L PBTCA, 100mg/L Sodium molybdate |
| No electrochemistry     | 2.86                        | 3.15                    | 3.75 |
| Electrochemical         | 3.14                        | 3.29                    | 3.95 |

As can be seen from Table 5, the tap concentration limit is increased after the addition of the electrochemical device, the combination of tap water, PBTCA and sodium molybdate in the case of electrochemistry has a limit concentration factor of 1.38 times that of the limit of concentration without chemical and electroless, which indicates that the operating conditions of the electrochemical device can be controlled reasonably, and the system can be effectively concentrated and improved.

3. Conclusion
The descaling ability of the electrochemical device is related to the voltage of the device, and the distance between the plates, and the hardness of the water body, when the voltage of the electrochemical device is 10V and the plate spacing is 20mm, the electrochemical device has the highest removal efficiency of hardness, and in the electrolysis process, the hardness of the water body is 400 mg/L, the highest hardness removal rate is 85.41%.

It was also found through experiments that the electrochemical device, 2mg/L PBTCA and 100mg/L sodium molybdate synergistically, and the descaling rate was 79.23%, the scale inhibition rate was 87.34%, and the corrosion inhibition rate was 89.94%. Combining electrochemical device, 2mg/L PBTCA and 100mg/L sodium molybdate can increase the limit concentration of tap water in Shanghai by 1.38 times, which provides an effective method for water saving and energy saving of circulating cooling water.

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