Research on Key Technology of Electrochemical Sterilization and Physical Application for Circulating Cooling Water

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Abstract. As a high-efficiency, low-cost, convenient and environmentally friendly sterilization technology, electrochemical disinfection has developed rapidly in recent years. Electrochemical sterilization is an environmentally friendly sterilization technology. The research progress of this technology in the recent 30 years in sterilization mechanism and electrode materials is summarized. The mechanism of electrochemical sterilization includes the chemical effects of active chlorine, active intermediates, copper or silver ions, and the physical effects of electric fields; the electrode materials used are titanium anode, carbon cathode, and anode. The article combined with electrochemical equipment in a thermal power plant cold open circulating cooling water treatment experiment. Experimental research found that under the conditions of current density of 120A/ m², residence time of 10s, and electrode spacing of 1.8cm, the bactericidal effect can reach 97%. Under certain experimental conditions and a certain period of time, the total number of heterogeneous bacteria in the circulating cooling water after treatment can be effectively inhibited.

Keywords: Electrode material, electrochemistry, sterilization, cooling water sterilization.

1. Introduction
The amount of water taken and consumed in the production process of thermal power plants is huge. For thermal power plants that adopt circulating cooling methods, the circulating water system is a major water and water consumer for the entire plant, and its water consumption usually accounts for more than 80% of the plant's wastewater discharge [1]. With the increasingly stringent requirements of the state and local governments on the water intake and drainage of industrial enterprises, including thermal power plants, the high-concentration operation of the circulating water system has become an effective means and inevitable requirement for optimizing the water use of the whole plant and reducing wastewater discharge. For a long time, the methods used for sterilization in the water treatment field are mainly chemical methods and physical methods. The chemical method points to the addition of chemical agents, such as \( \text{Cl}_2 \), \( \text{NaClO} \), \( \text{O}_3 \), \( \text{H}_2\text{O}_2 \) etc. to the aqueous solution to be treated,
among which $Cl_2$ is the most widely used. Chemical sterilization has low cost and good effect, but it is not friendly to the environment. The physical method refers to the method of sterilization using physical technologies such as ultraviolet rays and ultrasonic waves, which is environmentally friendly, but has no continuous sterilization effect and the effect is not ideal. In order to solve the problems of these two methods, since the 1970s, electrochemical sterilization has achieved rapid development in theory, technology and engineering. As a "clean technology", it has been widely used in many fields, especially environmental engineering.

2. **Electrochemical Treatment System**

2.1. **Technical principle**
The principle of electrochemical water treatment technology is to give full play to the oxidation and reduction reactions of the anode and the anode, and through the cross-action of the DC power supply sweep and mixing, the anode is oxidized to produce oxidizing substances such as OH, $H_2O_2$, $O_3$, $HCl$, and so on. Anti-corrosion and rust removal, sterilization and algae elimination; the cathode has a reduction effect.

(1) Scaling salts are directly precipitated from the cathode plate. $Ca^{2+}, Mg^{2+}$ in circulating water generally exists in the form of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. Under the action of a direct current electric field, cations such as $Ca^{2+}, Mg^{2+}$ will precipitate on the cathode plate to produce solids such as $CaCO_3$. The hardness of the circulating water decreases, which plays a role of anti-scaling and replaces the use of scale inhibitors [2]. The number of solids such as $CaCO_3$ is directly proportional to the hardness value, electricity amount, and energizing time.

(2) The bactericidal and algae-killing effect of strong oxidizing groups. Water can be ionized into $H^+$ and $OH^-$ under the action of direct current electric field,

$$H_2O \rightarrow H^+ + OH^- \quad (1)$$

Under the action of the electric field force, $OH^-$ moves towards the anode and discharges at the anode. A denser electron appears near the anode, and the following reaction occurs

$$4OH^- - 4e^- \rightarrow 2H_2O + 2[O] \quad (2)$$

Active oxygen atoms can be oxidized to ozone

$$3O \rightarrow O_3 \quad (3)$$

Ozone is extremely unstable and oxidizes to oxygen molecules

$$O_3 + O \rightarrow 2O_2 \quad (4)$$

At the same time, oxygen molecules can also be oxidized to

$$O_2 + e^- \rightarrow O_2^-$$
$$O_2^+ + e^- \rightarrow O_2^{2-} \quad (5)$$
$$O_2^+ + H^+ + e^- \rightarrow HO_2^-$$
$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
The above-mentioned $O_2^-, H_2O_2, OH^-, O_3, HO_2^-$ and so on are called linear oxygen. Linear oxygen has strong oxidizing properties, which can directly destroy the cell membrane of microorganisms and cause the death of microorganisms, thereby achieving better sterilization and algae killing effects.

(3) Remove $Cl^-$. Under the action of an electric field, $Cl_, HOCl, OCl^-$ will be generated at the electrode plate, which can not only reduce the $Cl^-$ in the water, but also make full use of the morphological changes of $Cl^-$ to play the role of sterilization and algae killing.

2.2. On-site experimental device and process flow

The electrochemical sterilization experiment device is shown in Figure 1. In the electrode area, metal oxide electrodes (DSA●) stainless steel (304) are used as anode and cathode respectively (the electrode area is 0.45m×0.40m, and a total of 19 anodes and 20 are used. Block cathode, the total effective electrode area volume is 0.144m$^3$, which is controlled by WWL-SS type steady current power supply [3]. The experimental device is placed near the 4# cooling water tower of Hebei Xibaipo Power Generation Co., Ltd. The submersible pump will raise the circulating cooling water to the electricity the chemical sterilization experimental device is discharged from the drainage pipe into the drainage channel after electrolysis treatment.

![Figure 1. Diagram of electrochemical sterilization experiment device](image)

2.3. Circulating water system

The circulating water system of a thermal power plant usually adopts the method of adding chemical agents to control and ensure the quality of circulating cooling water. In this pilot test, no chemicals were added, electrochemical treatment equipment was used to stabilize the circulating water quality, and the results were analysed and discussed on the water quality data of six months of operation. The electrochemical treatment equipment was put into operation on May 6, 2012 and ended on November 29. The parameters of the circulating cooling water system of the pilot plant are shown in Table 1, and the water quality indicators of the supplementary new water are shown in Table 2.

Table 1. Circulating cooling water system parameters of indirect cooling open system

| Item                        | Parameter |
|-----------------------------|-----------|
| Project circulating water volume/m$^3$/h | 1700      |
| Water retention/m$^3$/h     | 2000      |
| Sewage discharge/m$^3$/h    | 8.5       |
| Supplementary water/ m$^3$/h| 30.6      |
| Evaporation and wind loss/ m$^3$/h | 22.1      |
| Concentration rate/time     | 3         |
| Temperature difference/℃    | 8         |
| Material of heat exchange equipment | Brass, carbon steel, stainless steel |
Table 2. Supplemental new water quality indicators

| Item                                           | Numerical value |
|------------------------------------------------|-----------------|
| pH                                             | 8.12            |
| Total hardness (calculated as CaCO<sub>3</sub>) mg/L | 280.2           |
| Calcium hardness (calculated as CaCO<sub>3</sub>) mg/L | 145             |
| Alkalinity (calculated as CaCO<sub>3</sub>) mg/L       | 1171.8          |
| Cl/mg/L                                         | 115             |
| Conductivity/μS/cm                              | 1000            |

2.4. Test equipment

This test uses an electrochemical treatment equipment developed by an engineering company. The equipment is installed in a circulating cooling water pool and is not connected to a water pipeline. The effective current density is below 1mA/cm<sup>2</sup>, which is far lower than the human safe current density of 20mA/cm<sup>2</sup>. No harm to human body. The working principle of electrochemical equipment in the application of stable circulating cooling water quality can be summarized as anodizing reaction, cathodic reduction reaction and polar water molecule reaction [4]. The composition of the electrochemical equipment is shown in Table 3, and the installation diagram of the electrochemical equipment in the pool is shown in Figure 2.

Table 3. Composition of electrochemical equipment

| Item                                           | Quantity /set | Material                                      |
|------------------------------------------------|---------------|-----------------------------------------------|
| Multifunctional electrochemical water processor complete equipment | 16            | Stainless steel SUS304 and rare metals        |
| Matching rectifier cabinet and cable           | 8             | Carbon steel anti-corrosion of rectifier cabinet shell |
| Switch cabinet                                 | 1             | Carbon steel anticorrosion                     |
| Install the maintenance rack                   | 1             | Carbon steel anticorrosion                     |

Figure 2. Electrochemical equipment installed in the pool
3. Experimental results

3.1. Current density influence experiment
The current density influence experiment was carried out under the conditions of a flow rate of 50m$^3$/h, a distance between electrodes of 1.8cm, and a conductivity of 2.17mS/cm. The experimental results are shown in Figure 3.

![Figure 3. The influence of current density on the sterilization effect](image)

It can be seen from Figure 3 that as the current density increases, the sterilization efficiency continues to increase. When the current density is in the range of 0-60A/m$^2$, the sterilization efficiency increases significantly with the current density, but the total number of bacteria in the effluent is still around 104cfu/mL; when the current density is greater than 80A/m$^2$, the sterilization rate tends to a limit value [5]. At this time, the total number of bacteria in the effluent has all fallen below 2×10$^3$ cfu/mL. Combined with the above experimental results, on the one hand, as the current density increases, the active bactericidal substances produced in the water increase, and the bactericidal effect continues to increase. At this time, the electrochemical process is the control step of sterilization; on the other hand, when the current density increases to a certain level after the degree, the homogeneous reaction process between the bacteria and the active bactericidal substance is a control step, and has nothing to do with the current density.

3.2. Placement time experiment
Under different current densities, the effluent samples after electrochemical sterilization were exposed to the air and stirred with a magnetic stirrer for 1, 2, 3, 4, 5, and 6 hours. The total number of heterotrophic bacteria was determined by taking the water samples respectively. The experimental results as shown in Table 4. It can be seen from Table 4 that when the treated circulating cooling water is exposed to the air, the total number of heterotrophic bacteria increases with the storage time under low current density operating conditions (80A/m$^2$), and other higher currents The total number of heterotrophic bacteria remained basically unchanged with the storage time under the conditions of density operation. This shows that the circulating cooling water after electrochemical sterilization treatment still has certain continuous sterilization characteristics for a period of time [6]. The main reason is that, on the one hand, the cell membrane is ruptured due to the action of the electric field, and the metabolic process of the bacterial cell is disturbed by the electron transfer through the electrode. Eventually leading to bacterial death and limited proliferation; on the other hand, a variety of strong oxidants will be produced during the electrolysis process to have a continuous sterilization effect on circulating cooling water. For example, in the presence of chloride ions, electro-generated active chlorine has a strong sterilization effect.
Table 4. The effect of storage time of the treated water sample on the sterilization effect

| Current density (A/ m²) | 80  | 10  | 120 |
|------------------------|-----|-----|-----|
| Total number of heterotrophic bacteria in raw water (cfu/mL) | \(3.3 \times 10^4\) | \(2.1 \times 10^3\) | \(1.3 \times 10^3\) |
|                         | \(3.0 \times 10^3\) | \(2.6 \times 10^3\) | \(2.8 \times 10^3\) |
|                         | \(2.8 \times 10^3\) | \(1.7 \times 10^3\) | \(1.4 \times 10^3\) |
|                         | \(2.5 \times 10^3\) | \(1.8 \times 10^3\) | \(1.5 \times 10^3\) |
|                         | \(3.6 \times 10^3\) | \(1.7 \times 10^3\) | \(1.3 \times 10^3\) |
|                         | \(3.3 \times 10^3\) | \(1.9 \times 10^3\) | \(1.6 \times 10^3\) |
|                         | \(3.4 \times 10^3\) | \(2.2 \times 10^3\) | \(1.1 \times 10^3\) |

4. Conclusion

Current density, residence time, electrode spacing, and dilution ratio have a greater impact on the sterilization effect; under the conditions of current density 120A/ m², residence time 10s, and electrode spacing 1.8cm, the sterilization effect can reach 97%; under certain experimental conditions and within a certain period of time, the total number of heterotrophic bacteria in the circulating cooling water after treatment can be effectively suppressed. As an efficient and low-cost technology, electrochemical disinfection and sterilization technology is bound to have broader development prospects. Some researchers have suggested that because electrochemical reactions also produce a large amount of chlorine components, there may be the same shortcomings as chlorination disinfection. Therefore, whether electrochemical disinfection technology can completely replace chlorination disinfection remains to be verified. However, the incomparable advantages of electrochemical disinfection over other disinfection methods are still its most competitive bargaining chip. The three main problems currently existing in electrochemical sterilization technology are low current efficiency, cathode fouling, and sterilant concentration control. Some solutions have been developed. These measures need to be further improved in practical applications and are looking forward to development. New and more effective methods to solve these problems to promote the wide application of electrochemical disinfection technology.

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