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Electrolytic treatment of industrial circulating cooling water using titanium–ruthenium–iridium anode and stainless steel cathode

Guoqing Zhang[a,*], Yongping Qiu[a], Xiaoqing Yang[a], Xinxi Li[a], Huageng Pan[b]

[a]*School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, China, Tel. +8618924808351; email: pdzgq008@126.com (G. Zhang), Tel. +8615622108150; email: 765934259@qq.com.cn (Y. Qiu), Tel. +8613824470131; email: yxq-886@163.com.cn (X. Yang), Tel. +8618686468507; email: qingfeng2005168@163.com.cn (X. Li)*
[b]*Foshan Shunde Dowell Technological & Environmental Engineering Co. Ltd., Foshan 528300, China, Tel. +8613121398503; email: phg398@139.com.cn (H. Pan)*

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ABSTRACT

Electrolysis is an effective approach to solve the issues of scaling, corrosion, and microbiological slime, which are three major problems typically associated with industrial cooling water system. To further investigate the mechanisms and performance of electrolysis, a new electrolytic prototype device was developed. There are three tasks conducted in this study: (1) to analyze the composition and structure of the scale deposit; (2) to evaluate the ability and performance in the removal of several key substances; and (3) to investigate effects of sodium chloride concentration, duration, and current density on electrolysis. Scanning electron microscopy and X-ray diffraction results show that the scale deposited on the cathode surface was a layer of loose, fine granular calcium carbonate precipitation. Under the optimal condition of 15 min of electrolysis and current density of 10.7 mA cm^{-2}, the removal rate of bacteria, Ca^{2+}, and chemical oxygen demand is 99.99, 52.6, and 50.8%, respectively.

Keywords: Electrolysis; Circulating cooling water; Corrosion; Scale; Current density

1. Introduction

Water resource shortage in a lot of countries and regions is inevitable as a result of continuing population growth and the unprecedented development of modern industry in the coming decades [1]. Industrial circulating cooling water (or "Cooling water" for short in this paper) is widely used to decrease the consumption of fresh water. However, there are bacteria, calcium ion, chemical oxygen demand (COD), and other components in cooling water that cannot be untreated and ignored. With the continuous recycling of water in the cooling system, the bacteria population, calcium ion (Ca^{2+}) concentration, and COD will inevitably increase, causing three common issues: microbiological slime, scaling, and corrosion. These issues typically further lead to the loss of the capacity for thermal exchange and the corrosion of metallic surface, which usually occur simultaneously and ultimately cause a decrease of service life of the whole system [2–5]. Therefore, a comprehensive technology in treating water is urgently needed to remedy these issues. Ca^{2+} is the main scaling ion in circulating cooling water, so reducing the content of calcium ion is logically a reasonable approach to solve the issue of scaling. In addition, the degradation of COD and sterilization can

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*Corresponding author.

prevent corrosion and microbiological slime of cooling water system [6,7].

Most of the traditional methods of water treatment are chemistry based, which typically involve in adding acid or water quality stabilizer. These traditional methods not only require higher equipment investment, they also have two fundamental defects: pipeline corrosion and environmental pollution [8,9]. As a result, significant efforts have been made to develop new technologies to complement or even to replace the current methods.

Direct electrolysis of Electrochemical Oxidation Technology (EOT) has been developed as a promising method for the treatment of water containing toxic and bio-refractory organic compounds. Comparing with traditional chemical methods, electrolytic treatment has the advantages of lower cost and pollution free. Besides, it is highly efficient in de-scaling, sterilization, algae removal, and degradation of COD [10–13]. At present, direct electrolysis is widely used in the field of water treatment.

There has been little knowledge regarding the performances of comprehensive water treatment using EOT in circulating cooling water. Therefore, in this paper, direct electrolysis was applied in cooling water system to test its performance in resolving the three aforementioned issues: scaling, corrosion, and microbiological slime. The direct electrolysis was conducted using a novel electrolytic equipment designed and customized by the authors to achieve higher efficiency. Influencing factors, such as applied current density, sodium chloride concentration (C_{NaCl}), electrolytic time, and initial calcium ion (Ca^{2+}) concentration, were investigated to evaluate the water treatment performance. Furthermore, the mechanism of de-scaling and sterilization has also been discussed in this paper, and the self-cleaning feature of the electrolytic equipment was studied as well.

2. Methods

2.1. Experimental materials

The parameters of the simulated cooling water are shown in Table 1. The water quality parameters are set up based on two standards: "Water Quality Standards of National Circulating Cooling" and "Recycle Water of China Petroleum & Chemical Corporation" [14].

Using the formula $m = C·V$, the mass of each component required can be determined. In the formula, C is mass concentration of the target components, and V is the volume of solution—exactly 12 L of working volume in an electrolytic cell. After the calculation, the required quantity of each chemical component is as follows: 3.264 g of $CaSO_4$, so the calcium hardness of the cooling water is 80 mg L^{-1}; 1.02 g of potassium hydrogen phthalate, which was selected as the source of COD; 1.2 g of NaCl; 1.2 g of Na_2SO_4, and 4.8 g of $NaHCO_3$. Meanwhile, the initial pH was adjusted to 8.2 by adding appropriate amounts of dilute sulfuric acid or sodium hydroxide solution.

Table 1
Parameters of the circulating cooling water

Parameters	Values
COD (Potassium hydrogen phthalate mg L^{-1})	100
NaCl (mg L^{-1})	100
Na_2SO_4 (mg L^{-1})	100
$CaSO_4$ (mg L^{-1})	275
$NaHCO_3$ (mg L^{-1})	400
Concentration of bacteria (n mL^{-1})	5.6×10^5
pH	8.2

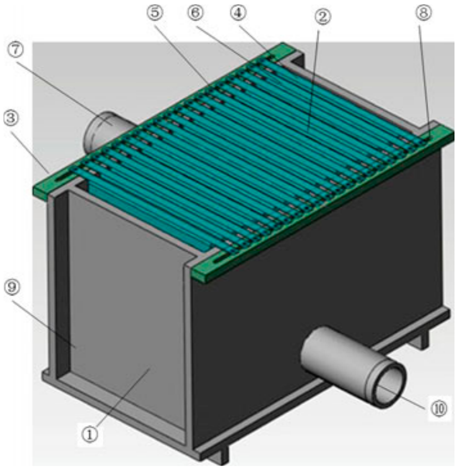
The bacterial concentration in the simulated water is approximately 5.6×10^5 mL^{-1}. The bacterium is *Escherichia coli* which was cultivated with nutrient agar in the laboratory. The total number of bacteria was detected by the standard Agar method (37℃, 24 h). The original cooling water was diluted by a factor of 10^4, and the test result revealed that the *E. coli* concentration is 56 bacteria per mL after dilution.

2.2. Experimental equipment

The electrolytic equipment was self-designed to achieve an optimal performance. The electrolytic cell has a working volume of 12 L, which was made from PVC plastic plate with a dimension of 300 mm × 180 mm × 300 mm. Meanwhile, a titanium plate coated with ruthenium and iridium and a stainless steel plate is selected as anode and cathode, respectively. Each electrode has a dimension of 200 mm × 150 mm × 0.6 mm, and they are manufactured in Baoji Ruicheng Titanium Industry Co., Ltd. The electrodes were packed with a fixed gap of 20 mm. Fig. 1 is a schematic diagram of the electrolytic cell. (The lip, the front slot wall, and some electrodes are not shown.)

2.3. Analytical methods

Scanning electron microscopy (SEM, S-3400N-II) and X-ray diffraction (XRD, D/MAX-Ultima IV) were used to characterize the composition and structure of the scale deposited on the cathode surface. Components of the cooling water, including Ca^{2+} concentration, COD, and the number of bacteria were



Description:
1. Bottom fixed plate
2. Electrode module
3. Interface between electrode module and electrolytic cell
4. Cathode
5. Set screws
6. Anode
7. Water outlet
8. Up fixed plate
9. Electrolytic cell
10. Water inlet

Fig. 1. The drawing of electrolytic equipment.

analyzed at time intervals following the standard method. EDTA titration method was used to monitor Ca^{2+} concentration, giving a margin of error of $\pm 1.6\,mg\,L^{-1}$; UV–visible light spectrophotometer (SP-754PC) and COD Digital Reactor Block (XJ-3) were used to monitor the change of COD by fast airtight catalysis. The number of bacteria was detected by standard AGAR method (37℃ train 24 h).

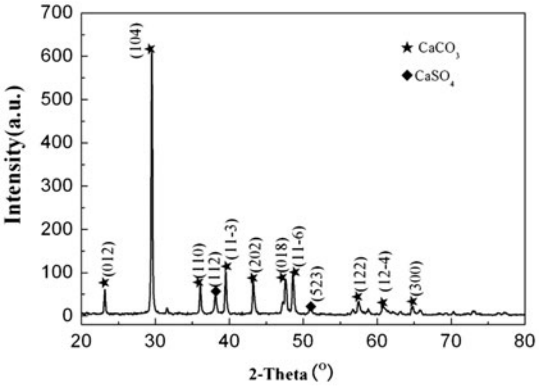


Fig. 2. XRD pattern of scale.

3. Results and discussion

3.1. The scale removal due to electrolysis

Calcium ion is the main scaling ion in cooling water system, so the removal of calcium ion should solve the scaling issue. Electrolytic treatment of cooling water was performed at a laboratory bench-scale at ambient temperature (25℃). After 20 h of electrolytic treatment, a layer of white scale was deposited on the cathode surface. Results of XRD analysis confirmed that the scale is $CaCO_3$ scale (Fig. 2).

The main mechanism of scaling can be illustrated by a series of chemical reactions, as summarized generically as follows [15,16]:

$$2H_2O + 2e \rightarrow H_2\uparrow + 2OH^- \quad (\text{On cathode}) \tag{1}$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \tag{2}$$

$$CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3\downarrow \tag{3}$$

Besides, the existence of $CaSO_4$ also has been detected; this is because $CaSO_4$ is used as the source of the calcium of the simulated water in this research, so a small trace of $CaSO_4$ left on the cathode surface is understandable.

The morphology of the scale was observed by SEM scanning, and the SEM images of cathode surface were all magnified by a factor of 1,000. It can be vividly seen that very few sediments were deposited on cathode surface before electrolysis (Fig. 3(a)). However, after electrolysis, a layer of loose fine-granular $CaCO_3$ scale was formed on the cathode surface (Fig. 3(b)).

Researchers have done a lot to analyze the crystallization of $CaCO_3$ scale formed in electrolytic process. Based on our previous experiments and confirmed by other publications, the crystallization shape of $CaCO_3$ scale without electrolysis is mainly rigid needle-shaped calcite, which adheres on the substrate surface firmly. This is the kind of scale deposited on pipelines and results in the scaling of cooling water system [17,18]. However, the crystallization of $CaCO_3$ scale

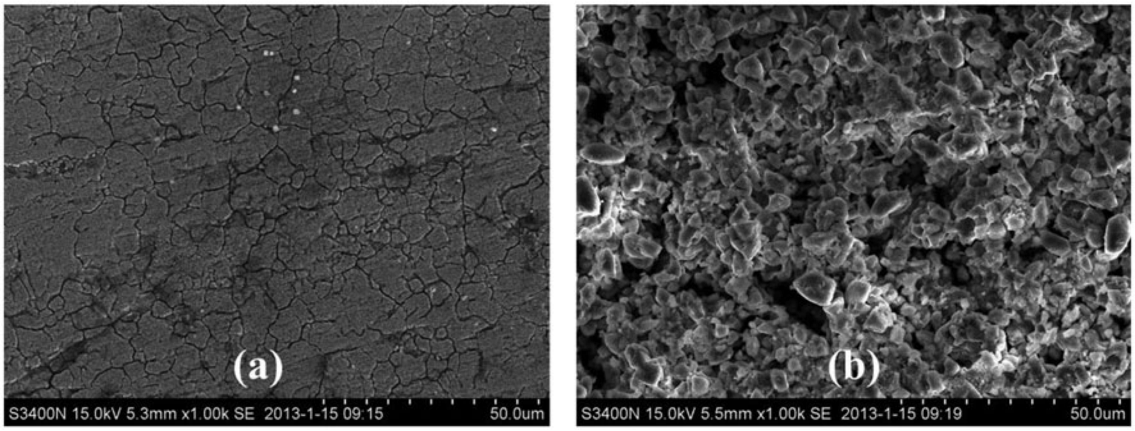


Fig. 3. SEM images of cathode surface (a) before and (b) after electrolysis.

formed during electrolytic process is a loose fine-granular aragonite, and a large quantity of the scale is left in water. The scale deposited on cathode surface would reduce the efficiency of water treatment. So how to remove the scale on the cathode is a pivotal problem that we have to tackle.

Switching electrodes and swapping the polarity of the cathodes and anodes can sweep away the scale on cathodes. The reason is that anodic oxidation was taken place on the surface of stainless steel, before the stainless steel plate was oxidized, oxygen gas and a little of chlorine gas was produced on the surface of stainless steel, which would make the calcium carbonate scale strip away from stainless steel surface. In order to avoid electrode dissolving and high energy consumption, the self-cleaning process was carried out at low current density of 3.0 mA cm^{-2} with 5 min of electrolysis. Fig. 4 demonstrates the self-cleaning effects. Fig. 4(a) is SEM images of cathode surface which has been used to treat industrial circulating cooling water for 60 h, but without self-cleaning. After 5 min of self-cleaning, the scale was swept away completely, SEM images were shown as Fig. 4(b). The removal of the scale restores the high efficiency, and the self-cleaning feature is an obvious advantage of our self-designed electrolytic equipment.

3.2. *The effects of current density and initial $CaSO_4$ concentration on de-scaling*

Fig. 5 depicts the Ca^{2+} removal rate ($R_{Ca^{2+}}$) at current densities ranging from 7 to 14 mA cm^{-2}, and initial $CaSO_4$ concentration ($C_{0\ CaSO_4}$) ranging from 200 to 450 mg L^{-1}. The initial temperature of the cooling water is 25.4℃, and each electrolysis takes 15 min.

As seen in Fig. 5, $R_{Ca^{2+}}$ is highly influenced by the applied current density. When $C_{0\ CaSO_4}$ is constant, $R_{Ca^{2+}}$ increases with the increase in current density. For example, when $C_{0\ CaSO_4}$ is 275 mg L^{-1}, $R_{Ca^{2+}}$ is only 30% at 7 mA cm^{-2}, while it increases to 52.6% at 14 mA cm^{-2}. Such increase is due the fact that a higher applied current density provides more electrons for Reaction (1) and then facilitates Reaction (2) and (3). Higher current density also leads to the rapid transfer of Ca^{2+} to the electrode surface under a strengthened electric field, thus, increasing $R_{Ca^{2+}}$ [19].

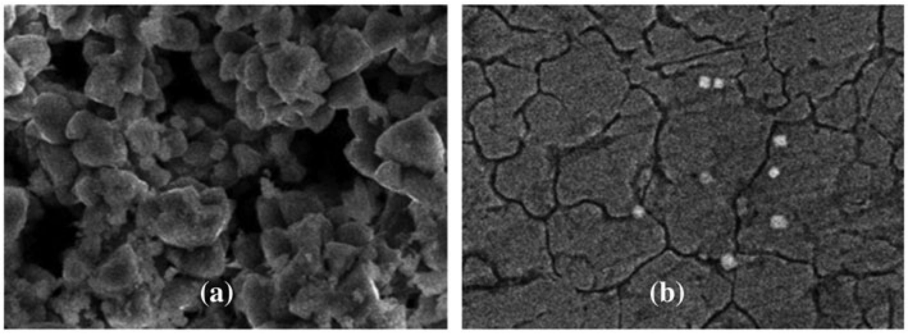


Fig. 4. SEM images of cathode surface: (a) before self-cleaning and (b) after self-cleaning.

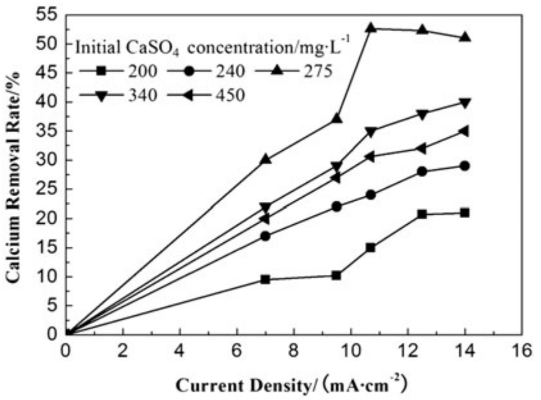


Fig. 5. Ca^{2+} removal rate curves of different current density and $C_{0\ CaSO_4}$.

On the other hand, with the increase of $C_{0\ CaSO_4}$, $R_{Ca^{2+}}$ increases initially and then starts decreasing. $R_{Ca^{2+}}$ reaches the highest value of 52.6% at 275 mg L^{-1}. The reason is that the increase of $C_{0\ CaSO_4}$ provides more Ca^{2+} for Reaction (3), thus, increasing $R_{Ca^{2+}}$. However, since the amount of CO_3^{2-} in cooling water is limited, the product $R_{Ca^{2+}}$ would reach its peak at equilibrium when no additional CO_3^{2-} is available. In addition, it can be observed that $R_{Ca^{2+}}$ decreases at a $C_{0\ CaSO_4}$ of 275 mg L^{-1} when the current density exceeds 12 mA cm^{-2}. This may be due to the dissolution of $CaCO_3$ scale caused by excessive current.

3.3. The effects of sodium chloride on sterilization

To study the effects of sodium chloride on electrolytic sterilization and its mechanisms, two kinds of cooling water samples have been treated. Sample I contains no NaCl, while Sample II contains 0.5 g L^{-1} NaCl. Both samples were treated by electrolysis under the same condition. The number of bacteria was detected by standard Agar method (37°C, 24 h). Fifty-six bacteria per milliliter were detected after diluting the original water by factor of 10^4, so the number of bacteria is 5.6×10^5 mL^{-1} in cooling water without electrolysis. The effects of the presence of sodium chloride on sterilization are shown in Fig. 6(a).

Fig. 6(a) shows that the bactericidal performance of Sample II was better than that of Sample I. After 15 min of electrolysis, the sterilization rate of Sample I and II was 96.68 and 99.99%, respectively.

Fig. 6(b) further illustrates the effects of sodium chloride concentration (C_{NaCl}) on sterilization. The bacterial number is 5.6×10^5 mL^{-1} in cooling water without electrolysis. The electrolytic time is 7 min in order to make the results more intuitive.

It can be seen from Fig. 6(b) that the number of bacteria drops sharply with the increase of C_{NaCl}. The number of bacteria declines from 5.6×10^5 to 1 mL^{-1} at 200 mg L^{-1}, the sterilizing rate reaches as high as 99.99%. To minimize the experiment error, each sample was diluted to different multiples factors (i.e. 10, 10^2, 10^3, 10^4) and the bacteria counts of two repeats were averaged for each dilution. Based on our previous experiments and supported by other publications, we conclude that the active chlorine can be electrogenerated on the anode. The reaction mechanisms are shown as follows [20,21]:

On anode:

$$2Cl^- \rightarrow Cl_2 + 2e \tag{4}$$

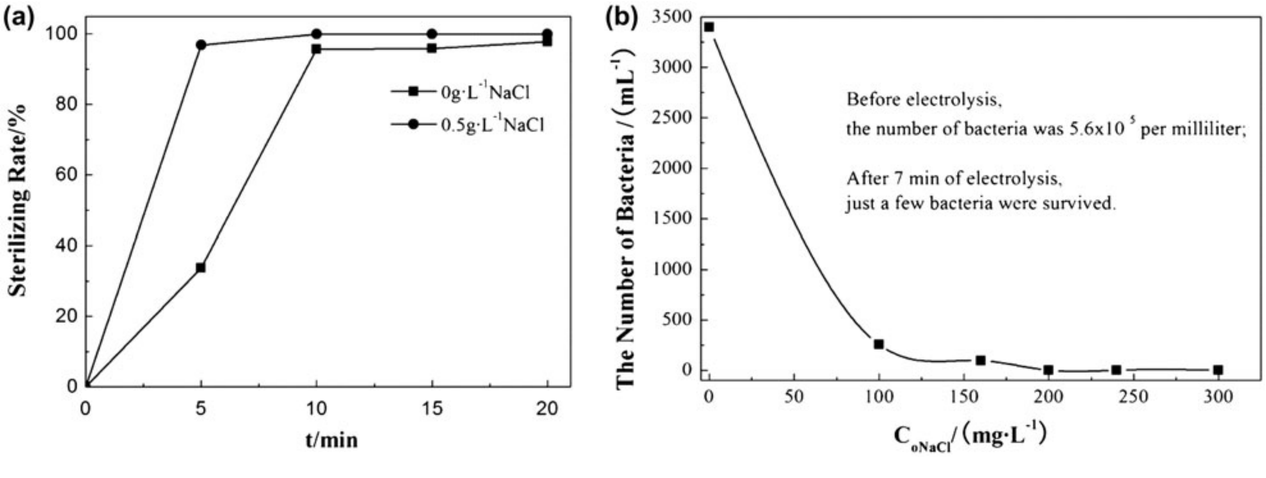


Fig. 6. (a) Effect of the presence of sodium chloride on sterilization and (b) effects of initial concentration of sodium chloride ($C_{0\ NaCl}$) on sterilization.

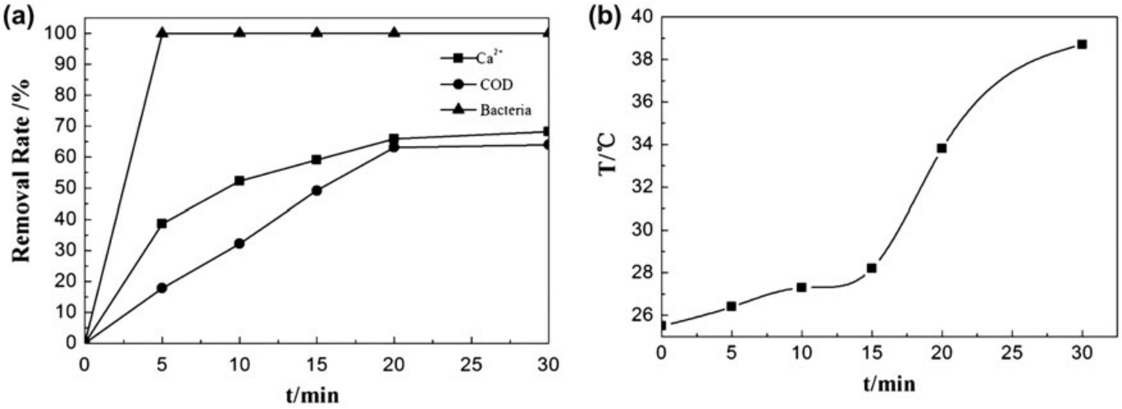


Fig. 7. (a) Comprehensive performances of electrolysis and (b) temperature curves of different electrolytic time.

In solution:

$$Cl_2 + H_2O \rightarrow ClO^- + 2H^+ + Cl^- \quad (5)$$

On top of the active chlorine, reactive oxygen species are also electrogenerated on the anode, including ·OH, O^-, and H_2O_2. The active substances and the electric field formed under the action of impressed current lead to the strong sterilizing effects of electrolytic treatment.

3.4. Comprehensive performances of electrolytic treatment

Electrolytic treatment not only has the abilities of sterilization and reducing the content of Ca^{2+}, it can also effectively degrade COD. Except active chlorine, reactive oxygen species are also electrogenerated on the anode, including ·OH, O^-, and H_2O_2. These active substances can degrade COD. Fig. 7(a) shows the comprehensive performances of electrolytic water treatment at initial water temperature of 25.0℃, and the current density of 10.7 mA cm^{-2}.

We can obviously see that the removal rate of Ca^{2+}, COD, and the sterilizing rate all increase with the increase of electrolytic time. Approximately 99.99% bacteria were killed after 5 min of electrolysis. The removal rate of Ca^{2+}, COD, and the sterilization rate is 52.6%, 50.8%, 99.99%, respectively with 15 min of electrolysis. The Ca^{2+} and COD removal rates continue to increase and reach plateau at 20 min of electrolysis. However, Fig. 7(b) shows that the water temperature rose dramatically after 15 min of electrolysis, which lead to extra energy consumption. Therefore, an optimal electrolytic time should be controlled strictly at 15 min, which yields high removal efficiency without excessive energy wasted.

4. Conclusions

We designed and tested a novel electrolytic equipment that can potentially serves as a complement to the traditional water treatment approach. Electrolytic treatment can effectively reduce the contents of calcium ion, COD, and bacteria in cooling water which solve the typical issues of scaling, corrosion, and microbiological slime associated with cooling water system. Additionally, the scale on cathode surface can be completely removed by switching electrodes for 5 min with an appropriate current density. This feature of the electrolytic process allows it to clean the electrolytic equipment itself and recover the efficiency.

In summary, electrolytic treatment of cooling water has great significance to promote the efficient use of water resources and environmental protection. The safety, de-scaling, sterilizing, and anticorrosive properties allow it to play an important part in the water treatment process.

Acknowledgments

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