Research Progress of Electrochemical Water Softening Technology for Industrial Circulating Water

Yuhang Wei[1], Dongqiang Wang[1,*], Gangsheng Li[2], Xuewu Dong[1], Haiqin Jiang[1]

[1]School of Mechatronics Engineering, Zhongyuan University of Technology, Zhengzhou, 450007, PR China
[2]Department of Civil Engineering, Universiti Sains Malaysia, 11800, Minden, Pulau Pinang, Malaysia

*Corresponding author's e-mail:weiyuhang0927@163.com

Abstract. Problems such as scale formation, pipe corrosion, and sludge bacteria and algae in the circulating cooling water system have always restricted the heat exchange efficiency of heat exchange equipment, and high energy consumption has made it difficult for enterprises to improve production efficiency. The trendy new electrochemical water softening technology provides a new idea for the stable operation of industrial circulating water systems because of its environmental protection, high efficiency and low energy consumption. This paper reveals the mechanism of active descaling and sterilization of algae by electrochemical water softening technology, elaborates the composition of important core components of electrochemical equipment (selection and preparation of anode and cathode materials, power system), compares the types and installation modes of mainstream electrochemical equipment in the market, and analyzes the key factors affecting the efficiency of electrochemical descaling. Finally, the future development of this technology is summarized and prospected.

Keywords: Circulating cooling water; Electrochemical technology; Scale; Electrochemical equipment; Influencing factor.

1 Introduction

The stable operation of the circulating cooling water system has an important impact on ensuring the improvement of the production efficiency of the enterprise[1]. During the operation of circulating water, as the temperature rises, evaporates and concentrates, a large number of scale ions in the water are precipitated and attached to the inner wall of the circulating water pipeline, resulting in pipeline blockage and decreased thermal conductivity efficiency, which greatly limits the heat reduction efficiency of the circulating water for the pipeline system and increases energy consumption[2,3]. At the same time, the water temperature, PH and the presence of nutrient-rich substances of the circulating water also provide an extremely suitable environment for the growth of micro

A. E. Abomohra et al. (eds.), *Proceedings of the 2023 9th International Conference on Advances in Energy Resources and Environment Engineering (ICAESEE 2023)*, Atlantis Highlights in Engineering 29,
https://doi.org/10.2991/978-94-6463-415-0_28

organisms and various types of bacteria and algae, resulting in the production of biological slime inside the pipeline, and in serious cases, it will cause scale corrosion, causing great interference and economic losses to the production of enterprises[4].

For this reason, many researchers have adopted various methods to limit and solve such problems. These include chemical reagent method[5], ion exchange resin method[6], limestone softening method, membrane filtration method[7], ultrasonic method[8], electromagnetic method[9], and electrochemical water softening method. However, most technologies are limited by high economic costs, pollution and other reasons can not be widely used. The current emerging electrochemical water softening technology can separate the scale-forming ions in the circulating water to the surface of the cathode without adding chemical reagents on the original basis, and reduce the tendency of scale deposition from the source. Compared with other methods, the equipment used in this technology is simple to produce, low energy consumption, and excellent economic benefits[10-12].Combined with the current research status, this paper firstly systematically expounds the mechanism of electrochemical water softening technology, the core hardware of water treatment equipment, equipment types, installation system and other aspects, and then reveals the key factors affecting the descaling efficiency. Finally, the future development and application of this technology are summarized and prospected.

2 Electrochemical Water Softening Technology

Electrochemical water softening technology not only has excellent performance in descaling in circulating water system, but also has good effect in sterilization, algae removal and removal of organic matter in water. Descaling is mainly done in the cathode area, and sterilization and algae removal are mainly realized in the anode area. Its specific schematic diagram is shown in Figure 1.

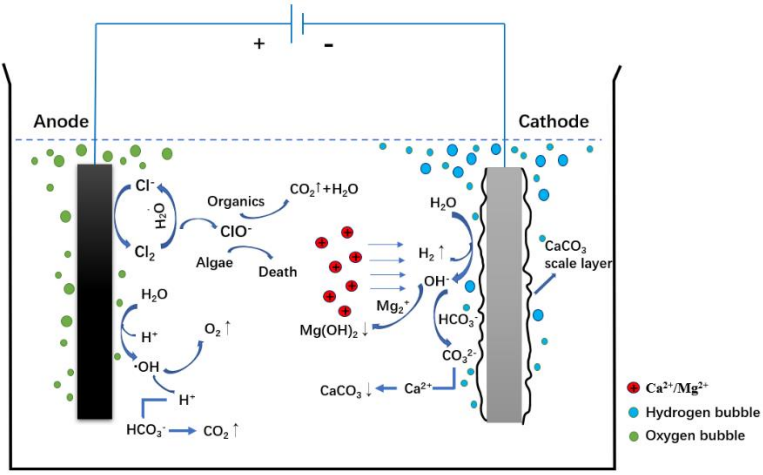

Fig. 1. Schematic diagram of electrochemical water softening technology

2.1 Cathode Region

In the cathodic polarization reaction, a large amount of OH^- will be generated near the cathode through the oxygen reduction process and hydrogen evolution process, forming a high alkalinity region with a pH of about 13[5,13,14]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

$$2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^- \quad (2)$$

In the actual reaction process, it can be seen that the hydrogen evolution process shown in formula (2) is more inclined to the main reaction process of generating OH^- by observing a large number of bubbles generated in the cathode region[10,15]. In addition, during the reaction, HCO_3^- in the electrolytic cell moves to the cathode surface region under the action of mass transfer and combines with the nearby OH^- to form CO_3^{2-}[12,14]:

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \quad (3)$$

At the same time, the high-hardness ions such as calcium and magnesium in the bulk solution also move to the cathode surface under the double push of electric field migration and mass transfer, and combine with CO_3^{2-} or OH^- to form scale attached to the cathode surface[16-18]:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \downarrow \quad (4)$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \downarrow \quad (5)$$

In this way, the effect of reducing the hardness of the water is achieved.

2.2 Anode Region

In the anodic electrocatalytic reaction, hydro electrolysis is the main reaction process. Through electrolysis of water and part of oxygen dissolved in water, short-life strong oxidizing substances such as hydrogen peroxide (H_2O_2) and ozone (O_3) are generated[19], and highly acidic regions are formed:

$$2H_2O - 2e^- \rightarrow H_2O_2 + 2H^- \quad (6)$$

$$H_2O_2 \rightarrow 2 \cdot OH \quad (7)$$

$$\cdot OH \rightarrow 1/2\, O_2 \uparrow + H^+ + e^+ \quad (8)$$

$$O_2 + 2OH^- - 2e^- \rightarrow O_3 + H_2O \quad (9)$$

These short-acting strong oxidizing substances can oxidize a variety of components in algae and microbial cells, thus achieving irreversible death[20-22].

At the same time, the HCO_3^- in the bulk solution migrates to the anode reaction area under the combined action of mass transfer and electric field force, and generates CO_2 gas in the highly acidic anode area, thereby reducing the alkalinity[23]:

$$HCO_3^- + H^+ \rightarrow CO_2 \uparrow + H_2O \tag{10}$$

If chloride ions are present in water, strong oxidizing OCl^- will be formed:

$$2Cl^- \rightarrow Cl_2 \uparrow + 2e^- \tag{11}$$

$$Cl_2 + H_2O \rightarrow Cl^- + OCl^- + 2H^+ \tag{12}$$

Different from the above-mentioned short-term strong oxidizing substances, OCl^- has strong oxidation stability in the solution, and it still has a certain bactericidal and algae killing effect even after leaving the electrochemical reaction cell[24].

3 Core Components of Electrochemical Devices

3.1 Cathode

Cathode plays an important role in electrochemical scaling. Its material type, surface structure and reaction area greatly affect the efficiency of scaling deposition and removal.

From the perspective of practical application, most metal materials that can conduct electricity can be used for the preparation of cathodes. For this reason, Jaouhari[25] et al. studied the effect of different cathode materials on scale deposition, and concluded that the scale performance of cathode materials is gold>bronze>stainless steel. The main reason for this phenomenon is that the oxides on the surface of different materials reduce the rate of oxygen reduction at different rates, which leads to different decreases in the nucleation rate of $CaCO_3$, which ultimately affects the deposition rate of scale on the cathode plate. However, considering the difficulty of obtaining materials and the cost of capital, stainless steel is still the first choice. According to Karoui[26] et al., unlike other materials, stainless steel can be used as an auxiliary driving force to accelerate the deposition of scale even under experimental conditions of higher PH interfaces caused by high temperature, higher cathode potential and low speed.

When conventional flat or mesh cathodes are used, the expansion of the cathode area can increase the contact area between water and the cathode, and increase the chance of Ca^{2+}/Mg^{2+} coming into contact with the cathode in solution, which is conducive to the precipitation reaction of $CaCO_3/Mg(OH)_2$[27]. Lin[28] studied the influence of different cathode structures (titanium plate, titanium mesh and copper plate) on the removal rate of water sample hardness during electrochemical treatment, and the results showed that in terms of overall water treatment performance, titanium mesh > titanium plate > copper plate. Li[29] et al. conducted a water treatment experiment by using a multi-layer coupled cathode composed of 20, 12, 8 and 50-mesh 304 stainless steel mesh, and found that the unique shielding and synergistic effect presented by the three-dimensional cathode system could not only effectively reduce the demand for cathode area, but also

improve the water softening efficiency and reduce the energy consumption of the system.

Under the condition that the structure of the cathode is determined, the state of the cathode surface also has a certain influence on the precipitation of hardness ions and the subsequent scale stripping. JIN[30] et al. explored the influence of cathode surfaces with different roughness on the deposition and denudation efficiency of $CaCO_3$, and the results showed that smooth cathode surfaces were not only conducive to the deposition of hardness ions, but also conducive to the spalling from the cathode plate. In addition, extending the cathode area can reduce the connection resistance of the cathode, thus reducing the voltage of the device under the same current condition, which is conducive to reducing the energy consumption of the system[29]. Xu[31] from Xi'an Jiao Tong University reproduced the classic cabinet-type electrochemical equipment through three-dimensional modeling. After continuous optimization and debugging, they found that the flat design of the external box of the equipment can maximize the available area of the cathode. It provides a good reference idea for the internal structure design of future cabinet-type electrochemical equipment.

3.2 Anode

3.2.1 Anode Material Selection.

At present, the common electrochemical anodes are graphite electrode, precious metal electrode, titanium oxide electrode (including Ti/PbO_2 electrode, Ti/Sb-SnO_2 electrode, Ti/RuO_2 electrode and Ti/Ti_4O_7 electrode, etc.) and boron-doped diamond electrode (BDD electrode). Among them, titanium used as substrate material is widely favored because of its high electrical conductivity and good electrochemical inertia.

3.2.2 Titanium-Based Monolithic Metal Oxide Anode.

Titanium-based monolithic metal oxide anode is formed by coating and firing a single metal oxide on a titanium substrate[32]. Among them, although Ti/IrO_2 has excellent stability in acidic solutions[33], it has low electrocatalytic activity and short service life. Although Ti/SnO_2 electrode is affordable and has excellent electrocatalytic performance, it is not suitable for working in circulating water with high chlorine content. Considering comprehensively, Ti/RuO_2 electrode is often used because of its stable size, high chemical resistance and high electrocatalytic activity[34]. In addition, commonly used monoary titanium-based metal oxides also include Ti/PbO_2. Ti/PbO_2 electrode is widely used in lead-acid batteries, ozone generation and oxidation of organic pollutants in wastewater due to its high peroxy potential, electrical conductivity and low cost, and the thermal expansion coefficient of Ti and PbO_2 is similar, which can be widely used in titanium coating materials[35]. However, the service life of the pure PbO_2 electrode is short and the electrocatalytic activity is low, so in order to improve the electrocatalytic activity and stability of the PbO_2 electrode, some solid solution intermediate layer is added between the Ti substrate and the PbO_2 coating[36], or some additives such as: F^-[37], Gd^{3+}, Co^{3+}[38], Eu^{3+}, etc. are incorporated into PbO_2 thin films to obtain Ti/PbO_2 electrodes with better performance.

3.2.3 Titanium-Based Multi-Element Metal Oxide Anode.

Titanium-based multi-metal oxide anode is composed of a mixture of two or more metal oxides coated on a titanium substrate[39,40]. By obeying the Hume-Rothery theory, these mixed metal oxides can form new stable compounds, and these newly formed compounds have a significant improvement in the stability and catalytic activity of their respective single metal oxides[41]. For example, RuO_2 is characterized by high catalytic activity and low stability, adding a second or third component to it can improve the stability of RuO_2 electrodes, so in order to increase the service life and improve electrode stability, adding IrO_2 to RuO_2 has become a common practice. In addition, in order to improve the economic benefit and stability of the titanium-based metal oxide anode, elements such as Sn, Ti, and Sb can also be doped into it to form a ternary or quaternary mixed metal oxide anode. For example, adding a certain Sn element to the Ru/Ir precursor solution can improve the long-term stability of the composite oxide coating electrode, adding a certain Ti element to it can reduce the amount of precious metals in the system and improve the adhesion of the oxide layer on the metal carrier[41]. For titanium-based mixed metal oxide anodes, the content of each metal oxide and the electrode preparation conditions can largely determine the stability and catalytic ability of the electrode.

3.3 Power System

In electrochemical water softening systems, the most common power supply methods are DC power supply (DC constant voltage, DC constant current) and pulse power supply (pulse constant voltage, pulse constant current)[10,21]. Ideally, the pulse power supply method is better than the DC power supply method, because the pulse power supply can well solve the problem of mass transfer and diffusion imbalance in the electrochemical reaction, and the energy consumption is relatively low. However, considering the investment and application stability, it is relatively better to take DC constant current power supply as the first choice. Of course, there are other power supply cases from the perspective of accelerating the shedding of cathode scaling and prolonging the deactivation time of cathode polarity. For example, Yu[42] et al. adopted a current pulsating electrochemical process to achieve the automatic detachment of the cathode scale layer, prolonging the inactivation time of the cathode electrochemical treatment. After parameter optimization, the total hardness removal efficiency and energy consumption were 17.8%~22.8% and 8.9~13.2 kW·h/kg $CaCO_3$, respectively. Jin[43] and Qian[44] et al reported the experiment of using polarity reversal technology (as shown in Figure 2) to promote the automatic stripping of cathode scale. The results show that although this technology can effectively remove the cathode scale and has a stable water softening effect, it is limited by the lifespan reduction caused by frequent polarity reversals. Therefore, Zhang[45] et al. studied a novel titanium-based electrode using a ternary mixture of iridium oxide, tantalum and rhodium (IrO_2-RhO_x-Ta_2O_5) as an active electrocatalyst film for frequent polarity reversal electrochemical water processing application.

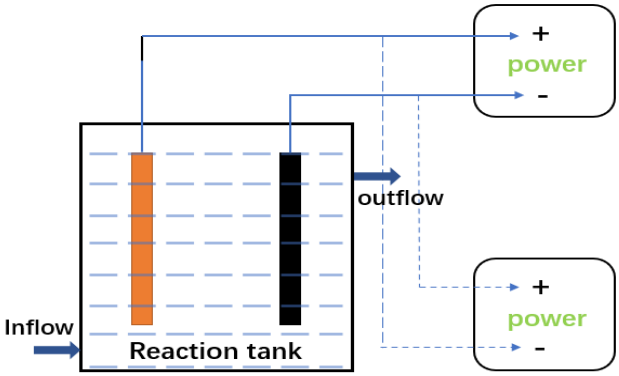

Fig. 2. Periodic interchange of anode and cathode current polarity

4 Electrochemical Device Type and Installation Mode

4.1 Manual Descaling Device

Currently common electrochemical descaling equipment is roughly divided into manual descaling and intelligent descaling. Manual descaling equipment does not have the function of automatic cleaning of scale layer. In the process of constant current power supply, when the internal voltage of the electrolyzer rises significantly or runs for a certain period of time, the reactor will be taken out or opened by the staff for manual cleaning (cleaning can be done by beating with sticks, washing with high pressure water gun, etc.), so that the scale layer deposited on the cathode network will fall off, which is convenient for subsequent use.

Figure 3 shows the cabinet-type manual descaling equipment, which has several staggered cathode and anode plates inside. When the circulating water flows in the interior, it can reach a turbulent state, which will be conducive to more full contact between the circulating water and the electrode, and the cross-baffling effect between the plates extends the residence time of the circulating water in the equipment, improves the descaling rate of the equipment, and reduces energy consumption[46].

Fig. 3. A typical cabinet manual descaling device (a) Before use; (b) After water softening treatment; (c) Manual descaling

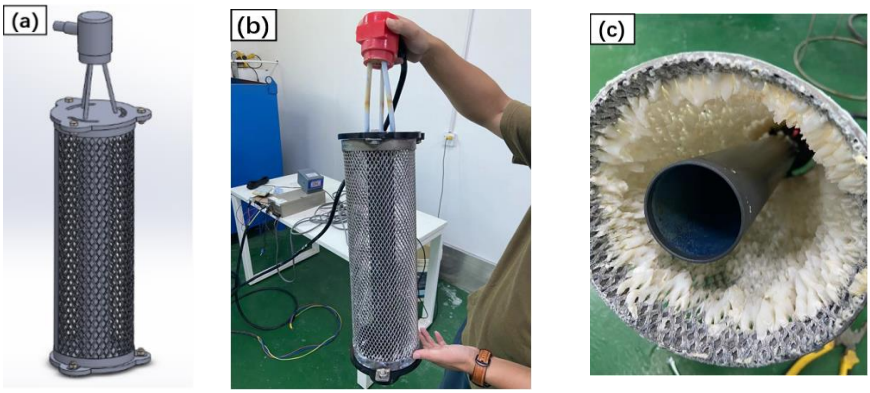

Fig. 4. Cage manual descaling device (a) Three-dimensional modeling diagram; (b) Physical drawings; (c) After water softening treatment

Figure 4 shows the cage type manual descaling equipment. The equipment is centered on the titanium-based composite metal oxide rod-shaped anode, and the outer ring is made of stainless steel mesh as the cathode. There are stable mass transfer channels and fixed reaction distances between the cathode and anode, which improves the descaling efficiency of the equipment and reduces energy consumption. When we put this equipment into actual engineering projects, we found that the cage descaling equipment is time-consuming and labor-intensive, and has low economic benefits. When using, it is necessary to appropriately increase or decrease the number of equipment according to the on-site circulating water volume and water quality, and the cathode grid will inevitably be deformed or even damaged after manual descaling, so it is not suitable for the application of large-scale water treatment systems.

4.2 Intelligent Descaling Device

The intelligent descaling equipment has an automatic descaling device inside, which avoids the waste of human resources caused by manual descaling. A typical smart descaling device is shown in Figure 5. The equipment is equipped with a scraper between the anode and cathode, and the external is controlled by the electric control cabinet. When the system runs to the specified working condition, the internal scraper rotates under the drive of the motor to mechanically scrape off the cathode scale, and cooperate with the subsequent cleaning process to effectively restore the cathode activity. However, because the presence of the scraper affects the setting of the distance between the electrodes, reducing the effective cathode area, it is necessary to optimize the internal spatial structure of the intelligent device in exchange for maximizing the available cathode area.

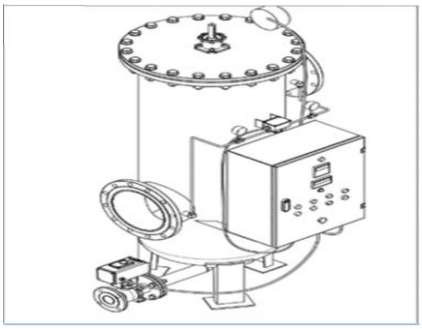

Fig. 5. A typical electrochemical water softening intelligent scale removal device

4.3 Installation Mode

Throw-in type and external connection type are two commonly used installation methods for electrochemical water treatment equipment[10].The throw-in type is to put the shell-less electrochemical descaling equipment (the descaling cage shown in Figure 4) directly into the cooling tower as shown in Figure 6, and select the amount of input according to the appropriateness of the circulating water volume on site. After a period of reaction, it is taken out manually, and the scale layer attached to the cathode net is cleaned. The disadvantage is that it is time-consuming and laborious, the service life is short, and it is only suitable for small circulating water system. The external type means that the circulating water is imported into the shell type electrochemical reactor through the pump, and then returned to the cooling tower through the pipe at the other end after softening treatment (as shown in Figure 6). Compared with the throw-in installation method, the external connection type requires additional components such as pipes, water pumps, and valves, which will undoubtedly increase the cost. For small circulating water systems, it seems more reasonable to use throw-in installed water treatment equipment.

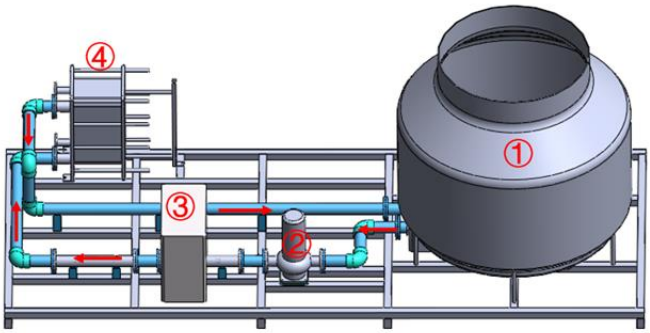

Fig. 6. External connection diagram of electrochemical descaling equipment of circulating water system:①Cooling tower;②Water pump;③Electrochemical device;④Heat exchanger

5 Influencing Factors of Electrochemical Descaling

5.1 Current Density

According to many experimental studies, current density is one of the most critical factors affecting the electrochemical water softening efficiency. The research group of Xu[10,31,47,48] from Xi 'an Jiaotong University studied the influence of different current densities on the descaling efficiency of electrochemical systems under the condition that other conditions remain unchanged. The results show that when the current density increases, the removal rate of hardness and alkalinity is increased. The reason is that when the current density increases, the alkali production reaction of equation (1)-(2) is intensified, thus indirectly accelerating the scale deposition reaction (4)-(5). At the same time, they also found an interesting phenomenon that as the current density increased, the actual amount of fouling in the final cathode decreased. The reason is that when the current density increases, the cathode hydrogen evolution reaction will also intensify, and a large number of hydrogen bubbles will disturb the migration process of Ca^{2+} and HCO_3^- to the cathode during the accumulation and floating process, resulting in the inability of hardness ions to fully deposit on the cathode. In addition, according to Jin[43] et al. the increase of current density is accompanied by the increase of precipitation rate and energy consumption. However, due to the restriction of effective mass transfer of Ca^{2+} from bulk solution to cathode reaction zone, when the current density is too large (no matter how large it is), the cathode precipitation rate tends to reach a horizontal progressive value, and the excess energy consumption is wasted. This results in a decrease in current efficiency. In addition, when Zeppenfeld[49] and Sanjuán[16] et al. studied the effect of current density on the precipitation rates of Ca^{2+} and Mg^{2+} respectively, they found that the precipitation rate of Ca^{2+} would have a gradual value with the increase of current density, but there was no specific boundary for the growth of the precipitation rate of Mg^{2+}. Different from the two-step chemical reaction (3)-(4) required to generate $CaCO_3$, Mg^{2+} in solution can directly react with OH^- to generate $Mg(OH)_2$. In addition, the radius of Mg^{2+} is smaller than that of Ca^{2+}, which is less affected by the convection and diffusion limitation caused by the deposition of scale layer[14,50].

5.2 Reaction Time

The reaction time refers to the time that the circulating water stays in the electrochemical reactor. When the internal volume of the electrolytic cell is constant, it can be expressed by the flow rate. The reaction time is inversely proportional to the flow rate. Guo[51] et al used four peristaltic pumps with different speeds (6, 10, 20, 40 rpm) to equivalently replace different reaction times (5 min 55 s, 3 min 48 s, 1 min 50 s and 58 s), and then studied the influence on the electrochemical treatment effect. The results showed that hardness, alkalinity and TDS removal rate all decreased with the increase of peristaltic pump speed. This is consistent with the research results of scholars such as Sanjuán[16] and Lee[52]. They all believe that with the decrease of residence time of circulating water in the electrolytic reactor, the scale ions are not transferred enough to

the cathode surface under the disturbance of high flow rate, resulting in the decrease of hardness removal rate. In addition, YU's[30,42,43,50] research group found through further experiments that with the increase of circulating water flow, scale precipitation rate and current efficiency increased, but the total hardness removal rate and energy consumption decreased. The reason is that when the flow rate increases, the water solution treated in the electrolytic chamber becomes more per unit time, and more scaling ions can be quickly deposited, so the current efficiency and precipitation rate will increase. However, due to insufficient deposition reaction, the total hardness removal rate is reduced. And higher flow rate is accompanied by more scale-forming ions, which leads to lower energy consumption per unit mass of $CaCO_3$ removal. The above results show that we should fully integrate all the influencing factors, select the best circulating water flow and determine the optimal reaction time in the practical application of engineering.

5.3 Water Quality Parameter

Water quality parameters of circulating water also affect the effect of electrochemical water treatment to some extent. This includes the hardness value of the circulating water to be treated, the ratio of hard alkalinity, and the content of special ions. Guo[51] et al. concluded that with the increase of the hardness value of circulating water, the hardness, TDS removal rate and unit scaling energy consumption showed a downward trend, while the alkalinity removal rate and unit scaling amount increased Xu's[10,31,47,48] research group found that the difference in the proportion of hardness and alkalinity in circulating water has a certain impact on the effect of water treatment. With the decrease of the hardness-alkalinity ratio, the hardness removal rate and the actual amount of deposits both increased, which indicated that the increase of the alkalinity played a positive role in promoting the electrochemical water softening process. The research group of Gabrielli[14,53] studied the influence of the presence of SO_4^{2-} and Mg^{2+} on the morphology and process of calcium carbonate scaling. It was found that in the absence of magnesium, sulfate ions are conducive to the precipitation of calcium carbonate in the form of vanadite, and the transformation of vanadite to aragonite is accelerated when magnesium exists. And it should be noted that when sulfate ions coexist with magnesium, the proportion of aragonite increases significantly. According to Hasson[12] et al. the increase of Ca^{2+} in solution can improve scale deposition and reduce energy consumption. The reason is that the presence of high-hardness ions can increase the conductivity of circulating water, and the high-conductivity solution can enhance the conversion of electrical energy, thereby reducing energy consumption. However, in practical applications, if the hardness of circulating water is too high, it will lead to insufficient processing capacity of electrochemical equipment, and the final descaling effect is not up to standard. Therefore, in engineering applications, considering the large differences in water quality parameters in different places, it is extremely important to do a good job of water quality-related research in advance.

5.4 Electrode Spacing

Under the premise that the internal space volume of the electrolytic cell is determined, the appropriate electrode spacing can weaken the mass transfer limitation and be more conducive to the precipitation reaction. Sanjuán[16] et al. under the premise of constant current density, flow rate and initial hardness, changed the electrode spacing to explore its influence on the descaling effect. The experiment found that when the distance between cathode and anode is reduced, both the deposition rate and the total hardness removal rate are significantly improved. This is consistent with the results proposed by Gabrielli[14]. The reason for this phenomenon is that when the electrode spacing is reduced, the calcium and bicarbonate in the bulk solution can diffuse more rapidly to the active region of the cathode, promoting the precipitation reaction (4) in the region. In addition, under the appropriate current density, the buoyancy generated by the hydrogen and oxygen precipitation in the anode and cathode regions can also enhance the mass transfer to a certain extent. However, for the same volume of treated water, the reduction of electrode spacing will lead to larger electrode area and higher manufacturing cost. Therefore, it is not a wise choice to blindly reduce the electrode spacing, and the electrode spacing should be selected according to the actual situation.

6 Summary

The importance of maintaining stable industrial circulating water quality is self-evident for the improvement of enterprise production efficiency. The electrochemical water softening technology reported in this paper has shown good results in active scale removal, sterilization and algae elimination, water quality improvement, water saving and emission reduction. However, there are still some defects, and further improvements need to be made in the future in terms of instability, processing limitations and high costs. The subsequent development of electrochemical water softening technology is multi-directional. It can not only improve the problem of processing limitations by seeking methods in combination with other technologies, but also develop new long-acting composite electrodes for the problem of high electrode manufacturing costs, reduce production costs and extend service life. In addition, the existing automatic cathode descaling technology will cause damage to the cathode and shorten the service life, so the development of new automatic descaling technology in the future is also an important development trend.

Reference

1. Yifei G, Zhicheng X, Siyuan G, et al. (2022) Practical optimization of scale removal in circulating cooling water: Electrochemical descaling-filtration crystallization coupled system[J]. Separation and Purification Technology, 284: 120268.
2. Yang Q, Xu L, He Q, et al. (2022) Reduced cathodic scale and enhanced electrochemical precipitation of Ca2+ and Mg2+ by a novel fenced cathode structure: Formation of strong alkaline microenvironment and favorable crystallization[J]. Water Research, 209: 117893.

3. Wang X, Tang R, Chen Z, et al. (2023) Influence of pulse current on the electrodeposition behaviors of CaCO3 scale in the industrial circulating water system[J]. Desalination, 554: 116495.
4. Yan Z, Zhu Z, Chang H, et al. (2023) Integrated membrane electrochemical reactor-membrane distillation process for enhanced landfill leachate treatment[J]. Water Research, 230: 119559.
5. Hasson D, Cornel A (2017) Effect of residence time on the degree of CaCO3 precipitation in the presence of an anti-scalant[J]. Desalination, 401: 64-67.
6. Fischer L, Hartmann S S, Maljusch A, et al. (2023) The influence of anion-exchange membrane nanostructure onto ion transport: Adjusting membrane performance through fabrication conditions[J]. Journal of Membrane Science, 669: 121306.
7. Khan I A, Lee Y S, Kim J-O (2023) Chemically enhanced pretreatment (CEPT) to reduce irreversible fouling during the clean-in-place process for membranes operating under constant flux and constant pressure filtration[J]. Desalination, 549: 116313.
8. Qu Z, Wu L, An Y, et al. (2019) A descaling methodology for a water-filled pipe based on leaky guided ultrasonic waves cavitation[J]. Chemical Engineering Research and Design, 146: 470-477.
9. Kamar N, Le Page Mostefa M, Muhr H (2022) Scaling control of gasketed plate heat exchanger by using very low frequency electromagnetic resonance fields[J]. Chemical Engineering Science, 262: 118040.
10. Xu H, Xu Z, Guo Y, et al. (2020) Research and application progress of electrochemical water quality stabilization technology for recirculating cooling water in China: A short review[J]. Journal of Water Process Engineering, 37: 101433.
11. Khan Z U, Moronshing M, Shestakova M, et al. (2023) Electro-deionization (EDI) technology for enhanced water treatment and desalination: A review[J]. Desalination, 548: 116254.
12. Hasson D, Lumelsky V, Greenberg G, et al. (2008) Development of the electrochemical scale removal technique for desalination applications[J]. Desalination, 230(1): 329-342.
13. Sanjuán I, García-García V, Expósito E, et al. (2019) Paired electrolysis for simultaneous electrochemical water softening and production of weak acid solutions[J]. Electrochemistry Communications, 101: 88-92.
14. Gabrielli C, Maurin G, Francy-Chausson H, et al. (2006) Electrochemical water softening: principle and application[J]. Desalination, 201(1): 150-163.
15. Zhi S, Zhang S (2014) A novel combined electrochemical system for hardness removal[J]. Desalination, 349: 68-72.
16. Sanjuán I, Benavente D, García-García V, et al. (2019) Electrochemical softening of concentrates from an electrodialysis brackish water desalination plant: Efficiency enhancement using a three-dimensional cathode[J]. Separation and Purification Technology, 208: 217-226.
17. Rousseau C, Baraud F, Leleyter L, et al. (2010) Calcareous deposit formed under cathodic protection in the presence of natural marine sediments: A 12 month experiment[J]. Corrosion Science, 52(6): 2206-2218.
18. Jin H, Yu Y, Chen X (2020) Membrane-based electrochemical precipitation for water softening[J]. Journal of Membrane Science, 597: 117639.
19. Ke S, Li S, Ma J, et al. (2023) Three-dimensional Electrolysis-A/O-Ozone Process for Treatment of the Leachate in the Later Stages of Landfills[J]. China Water & Wastewater: 1-7.
20. Liang S, Lin H, Habteselassie M, et al. (2018) Electrochemical inactivation of bacteria with a titanium sub-oxide reactive membrane[J]. Water Research, 145: 172-180.

21. Jiani L, Zhicheng X, Hao X, et al. (2020) Pulsed electrochemical oxidation of acid Red G and crystal violet by PbO2 anode[J]. Journal of Environmental Chemical Engineering, 8(3): 103773.
22. Guo W, Xu H, Yan W (2015) Ex-situ Electrochemical Disinfection with the PbO2 Anode[J]. International Journal of Electrochemical Science, 10(11): 9605-9620.
23. Kaur R, Kushwaha J P, Singh N (2019) Amoxicillin electro-catalytic oxidation using Ti/RuO2 anode: Mechanism, oxidation products and degradation pathway[J]. Electrochimica Acta, 296: 856-866.
24. Shao D, Yan W, Cao L, et al. (2014) High-performance Ti/Sb–SnO2/Pb3O4 electrodes for chlorine evolution: Preparation and characteristics[J]. Journal of Hazardous Materials, 267: 238-244.
25. Jaouhari R G, Benbachir A, Guenbour A, et al. (2000) Influence of Water Composition and Substrate on Electrochemical Scaling[J]. JOURNAL OF THE ELECTROCHEMICAL SOCIETY, 147: 2151-2161.
26. Karoui H, Riffault B t, Jeannin M, et al. (2013) Electrochemical scaling of stainless steel in artificial seawater: Role of experimental conditions on CaCO3 and Mg(OH)2 formation[J]. Desalination, 311: 234-240.
27. Luan J, Wang L, Sun W, et al. (2019) Multi-meshes coupled cathodes enhanced performance of electrochemical water softening system[J]. Separation and Purification Technology.
28. Lin W, Yuan J, Xu J, et al. (2019) Effect of cathode material and structure on electrochemical water treatment performance[J]. Industrial Water Treatment, 39(07): 81-84.
29. Li X, Wang L, Sun W, et al. (2020) Study on electrochemical water softening mechanism of high-efficient multi-layer mesh coupled cathode[J]. Separation and Purification Technology, 247: 117001.
30. Yu Y, Jin H, Meng P, et al. (2018) Electrochemical water softening using air-scoured washing for scale detachment[J]. Separation and Purification Technology, 191: 216-224.
31. Xu H, Yuan M, Luo Q, et al. (2019) Experimental study on pilot test of electrochemical scale removal technology[J]. Industrial Water Treatment, 39(07): 37-41.
32. Ajab H, Isa M H, Yaqub A (2020) Electrochemical oxidation using Ti/RuO2 anode for COD and PAHs removal from aqueous solution[J]. Sustainable Materials and Technologies, 26.
33. Silva L M d, Santos G O S, Pupo M, et al. (2018) Influence of heating rate on the physical and electrochemical properties of mixed metal oxides anodes synthesized by thermal decomposition method applying an ionic liquid[J]. Journal of Electroanalytical Chemistry, 813: 127-133.
34. Kaur R, Kushwaha J P, Singh N (2019) Electro-oxidation of amoxicillin trihydrate in continuous reactor by Ti/RuO2 anode[J]. The Science of the total environment, 677: 84-97.
35. Fu F, Yang W H, Ke C Y (2018) Structure dependent electrochemical performance of PbO2 thin-film electrode[J]. Materials Chemistry and Physics, 220: 155-160.
36. Santos T É S, Silva R S, Jara C C, et al. (2014) The influence of the synthesis method of Ti/RuO2 electrodes on their stability and catalytic activity for electrochemical oxidation of the pesticide carbaryl[J]. Materials Chemistry and Physics, 148: 39-47.
37. Yu Q Y, Jiang Z Y, Yin J L, et al. (2022) Unraveling the Role of F in Electrochemical Ozone Generation on the F-Doped PbO2 Electrode[J]. Journal of Physical Chemistry C, 126(45): 19397-19408.
38. Dai Q, Zhou J, Weng M, et al. (2016) Electrochemical oxidation metronidazole with Co modified PbO2 electrode: Degradation and mechanism[J]. Separation and Purification Technology, 166: 109-116.

39. Vasconcelos V M, Gonzaga I M D, Dória A R, et al. (2020) Effects of temperature and heating method on the performance of Ti/Ru0.25Ir0.25Ti0.50O2 anodes applied toward Bisphenol S removal[J]. Electrochimica Acta, 364: 137273.
40. Gonzaga I M D, Doria A R, Castro R S S, et al. (2022) Microwave-prepared Ti/RuO2-IrO(2)anodes: Influence of IrO2 content on atrazine removal[J]. Electrochimica Acta, 426.
41. Santos G O S, Silva L R A, Alves Y G S, et al. (2019) Enhanced stability and electrocatalytic properties of Ti/RuxIr1-xO2 anodes produced by a new laser process[J]. Chemical Engineering Journal, 355: 439-447.
42. Yang Y, Huachang J, Jin X, et al. (2018) Current Pulsated Electrochemical Precipitation for Water Softening[J]. Industrial & Engineering Chemistry Research, 57: 6585-6593.
43. Jin H, Yu Y, Zhang L, et al. (2019) Polarity reversal electrochemical process for water softening[J]. Separation and Purification Technology, 210: 943-949.
44. Qian K, Hu J (2020) Influence of electrolysis parameters on the treatment of circulating cooling water and the descaling effect of reversing electrodes[J]. Industrial Water Treatment, 40(01): 83-86.
45. Jin H, Zhang Y, Zhang X, et al. (2021) High-Performance Ti/IrO2–RhOx–Ta2O5 Electrodes for Polarity Reversal Applications[J]. Industrial & Engineering Chemistry Research, 60: 4310-4320.
46. Hu F, Zhang X, Pan Y (2021) Flow field distribution and optimization of different configurations of electrochemical descaling equipment[J]. Journal of Xiangtan University(Natural Science Edition), 43(03): 17-25.
47. Xu H, Yan W, Tang C (2009) Technology and Mechanism of Water Scale Removal by Electrochemical Method[J]. Journal of Xi'an Jiaotong University, 43(05): 104-108.
48. [48] Xu H, Yan W (2013) Effect of Cathode Current Density on Scale Generated by Electrochemical Scale Removal Technique[J]. Journal of Xi'an Jiaotong University, 47(07): 47-51.
49. Zeppenfeld K (2011) Electrochemical removal of calcium and magnesium ions from aqueous solutions[J]. Desalination, 277(1): 99-105.
50. Yu Y, Jin H C, Quan X J, et al. (2019) Continuous Multistage Electrochemical Precipitation Reactor for Water Softening[J]. Industrial & Engineering Chemistry Research, 58(1): 461-468.
51. Guo Y, Xu Z, Guo S, et al. (2021) Selection of anode materials and optimization of operating parameters for electrochemical water descaling[J]. Separation and Purification Technology, 261: 118304.
52. Lee S H, Cho Y I (2002) Velocity effect on electronic-antifouling technology to mitigate mineral fouling in enhanced-tube heat exchanger[J]. International Journal of Heat and Mass Transfer, 45(20): 4163-4174.
53. Tlili M M, Benamor M, Gabrielli C, et al. (2003) Influence of the interfacial pH on electrochemical CaCO3 precipitation[J]. JOURNAL OF THE ELECTROCHEMICAL SOCIETY, 150(11): C765-C771.