Effect of operational parameters and material properties on hardness removal efficiency by electrochemical technique

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ABSTRACT

Electrochemical water treatment technology can be used for hard water softening, but its removal efficiency and energy consumption problems hinder its application. The effects of electrolysis voltage and cathode materials on efficiency, energy consumption and scale crystal form of electrochemical water treatment technology were studied experimentally. The experimental results show that electrochemical water treatment can effectively remove more than 40% of the TDS (total dissolved solids) in the influent. The electrolysis voltage has a great influence on the removal rate of hardness ions. The optimum electrolytic voltage for the titanium plate cathode is 25 V. At this electrolytic voltage, the treatment capacity of the titanium plate cathode is 16% higher than that of the copper plate cathode, and the energy consumption is 16% lower than that of the copper plate. Titanium plates are more efficient than copper plates and consume less energy. The effects of electrochemical water treatment on the scale crystal form were investigated by SEM (scanning electron microscopy) and XRD (X-ray diffraction). Electrochemical water treatment increases the mass fraction of aragonite in the calcium carbonate scale and changed the microscopic surface structure of calcium carbonate scale.

Key words | CaCO₃ scale, cathode materials, crystal composition, electrochemical water treatment, electrolysis voltage

HIGHLIGHTS

- The descaling efficiency of titanium plate as a cathode is higher than that of copper plate.
- The unit energy consumption of titanium plate is lower than that of copper plate.
- The best efficiency reduces the TDS by more than 40%.
- Electrochemical reaction makes the microstructure of calcium carbonate irregular.
- The crystal type of CaCO₃ will change from calcite to aragonite as the electrochemical reaction proceeds.
INTRODUCTION

Evaporative circulating cooling water systems are widely used in many industrial applications, such as power, metallurgical and petroleum industries, and usually have a high content of hardness ions. These high concentration hardness ions may form scale deposited on the surface of heat exchangers, resulting in increasing the resistance to flow, and causing a significant decrease in heat transfer efficiency (Hasson et al. 2010; Xu et al. 2020).

Various techniques are proposed and used to prevent scaling, such as chemical treatments including adding scale inhibitors (Zhi & Zhang 2014), and sulfuric acid addition to lower pH, which are not only laborious but also environmentally unfriendly due to generating a large volume of waste solutions of acids or salts. Physical treatments include electrochemical treatments (Jiang et al. 2018), reverse osmosis (RO) treatments (Pervov & Andrianov 2015), and ultrasonic treatments (Aghapour Aktij et al. 2020). Among the electrochemical treatments, electrochemical water softening has drawn wide attention in recent years; it has many advantages such as environmental friendliness, no additional chemicals, no brine production and convenient process control (Gabrielli et al. 2006). In the electrochemical water softening process, hydrogen evolution reaction occurs at the cathode and a large amount of OH$^-$ is produced at the same time, and then Ca$^{2+}$ reacts to form CaCO$_3$ and deposits on the surface of the cathode (Sanjúan et al. 2019). The hardness of the circulating cooling water and the probability of scale on the heat transfer surface are significantly reduced.

Although the electrochemical water softening technique has been reported widely, the application of this technology in industry has been limited. The major limitation of electrochemical water softening technology is the high cathode area requirement (Luan et al. 2019). For instance, it is necessary to precipitate at least 20 kg CaCO$_3$ per hour for one million cubic meters circulating water softening device. A typical precipitation rate attained is around 50 g CaCO$_3$ m$^{-2}$/h, so it requires at least a 400 m$^2$ cathode area. Therefore, it is necessary to improve the precipitation rate of electrochemical water softening technology (Hasson et al. 2010).

Electrolysis reaction and CaCO$_3$ deposition on the cathode surface are two main processes of electrochemical water softening (Piri & Arefinia 2018). The operational parameters (such as electrolytic voltage, current density and so on) and electrode properties such as material have been proved to have great influence on the performance of electrochemical reaction and crystal deposition behavior, which in turn affect the efficiency of electrochemical water softening technology (Lin et al. 2021). Rinat et al. found that the use of inexpensive materials with high surface area in an electrochemical device is useful for removing calcium carbonate from hard water (Rinat et al. 2009). Trinh et al. revealed that the Fe$_3$O$_4$ compositcd on rGO forms anchors to increase interfacial contact surface and decrease ion mass transfer resistance in electrodes and between electrodes and electrolytes (Trinh et al. 2016). The hardness removal of Fe$_3$O$_4$/rGO nanocomposite electrodes is 3 times higher than that of separate rGO electrodes. Marchesiello et al. studied the influence of the area of the electrode surface on the efficiency of the electrochemical water softening device and increased the softening power of the device by nearly 90% by a new device incorporating a fluidized bed constituted of 1 mm diameter 316 stainless steel balls (Marchesiello & Thivel 2018). In addition, when a mesh or plate electrode is used, the cathode area expansion can significantly increase the effective reaction area to facilitate the deposition of scale (Luan et al. 2019).

Furthermore, current density or electrolytic voltage has an important effect on the performance of electrochemical water softening technology. Zhang et al. revealed that the increase of current density can promote water softening efficiency (Zhang et al. 2014). With a certain range of current density, the higher the current density, the higher the mass transfer coefficient. When the current intensity was increased, the stabilization period was shorter, and the steady-state value of hardness abatement was larger. This effect was more pronounced for low currents (Gabrielli et al. 2006). Yu et al. found the precipitation rate variation with current density under different flow rates. As expected, the precipitation rate depended strongly on the current density (Yu et al. 2018a). Zeppenfeld revealed that the electric
current density initially augments the electrochemical precipitation of calcite, but at a sufficiently higher current density the precipitation rate tends to an asymptotic limit (Zeppenfeld 2011). Moreover, Yu et al. revealed that the current value affects the stable state of the cathode surface area and the crystalline morphology of scale formed (Yu et al. 2018c).

In the process of calcium carbonate crystallization, it is inevitable to go through two stages of induction and development (Shen et al. 2015). The crystallization induction period of electrochemical water softening process is shorter, and it is easily affected by electrolysis reaction and electric field intensity (Yang et al. 2012). Both in the induction period and the development period, the amount of precipitation and crystal morphology will be different under different voltages (Zhang et al. 2015).

In this research, the effects of electrolytic voltage and different cathode materials on the water softening performance of electrochemical method were studied. The crystallization process of calcium carbonate at the cathode will be further studied, and the morphology of the crystal will be observed by means of microscopic analysis.

EXPERIMENTAL APPARATUS AND METHODS

Principle of electrochemistry

The scale removal principle of electrochemical water softening technique is based on the creation of a high pH environment around the cathode by water and oxygen reduction reactions that release hydroxyl ions. In the alkaline environment, HCO$_3^-$ in the solution is converted to CO$_3^{2-}$ and reacts with Ca$^{2+}$ in the solution to form calcium carbonate crystals on the cathode (Sanjuán et al. 2019). The insoluble compounds are forced to deposit on the surface of the cathode through the transport and adsorption of ions by the electric field (Figure 1).

During water electrolysis, dissolved oxygen is reduced on the cathode in a large potential range by following the global electrochemical reaction (Hasson et al. 2012):

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (1)$$

when the applied potential is more negative than a value that depends on the substrate, water is directly reduced according to:

$$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 \uparrow + 2\text{OH}^- \quad (2)$$

The HCO$_3^-$ and Ca$^{2+}$ in the solution react in the alkaline environment at the cathode to form CaCO$_3$ and deposit on the surface of the cathode:

$$\text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^- \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O} \quad (3)$$

Experimental setup

The schematic diagram of the experimental apparatus is shown in Figure 2. The anode plate used in the experiment
was a titanium substrate plate coated with Ruthenium Iridium oxide and connected to the positive electrode of the power supply. The cathode plates were made of different materials and connected to the negative electrode of the power supply. The specifications of the two electrode plates were 100 mm × 100 mm and the plate spacing is 150 mm. The flow rate of the circulating pump is 60 L/h. The DC power supply (Maisen, China) outputs a constant voltage current, and its voltage can be adjusted within 0–30 V.

The solution used in the experiment was prepared by mixing sodium hydrogen carbonate (NaHCO₃) and anhydrous calcium chloride (CaCl₂) with distilled water. The molar ratio of sodium bicarbonate to anhydrous calcium chloride was 2:1. The hardness of the solution was 1,500 mg/L and the pH was 7.6–7.8.

**Experimental methods**

During the experimental process, the simulated circulating cooling water was added to the electrochemical water softening device. The circulating pump was turned on to circulate the water. As the electrolysis reaction began, the TDS value and conductivity of the aqueous solution were measured and recorded every hour. By analyzing the variation tendency of the TDS value and conductivity under different working conditions, the effects of electrode materials and applied voltages on the TDS removal and hardness reduction of electrochemical water softening were studied. The relationship between the power consumption during the experiment and the reduction of TDS was analyzed. Then SEM (scanning electron microscope) and XRD (X-ray diffractometer) technology were used to analyze the scale deposited on the cathode surface under different working conditions.

The TDS value and conductivity of the solution were measured using a TDS instrument (LICHEN, China). The solutions used in the experiments were prepared with chemically pure drugs in distilled water, and there was no interference from other substances during the experiment. Therefore, the TDS value and conductivity were inversely proportional to the removal rate of the fouling ions, so the descaling effect of the process could be characterized by online monitoring of changes in TDS and conductivity values.

The hardness was measured by using chrome black T as an indicator and titrating with an EDTA (ethylenediaminetetraacetic acid) standard solution. The SEM instrument was JSM-5510LV (JEOL, Japan), and the XRD instrument was D8 ADVANCE (Bruker AXS, Germany).

**RESULTS AND DISCUSSION**

**Effects of cathode materials**

The effects of electrolysis voltage applied and material of cathode on electrochemical water treatment performance was studied by setting the electrolysis voltage as 10 V, 15 V, 20 V, 25 V, 30 V and using titanium plate and copper plate as cathodes, respectively. The variation of the TDS of the solution after electrochemical treatment is shown in Figure 3, and the change in conductivity is shown in Figure 4.

When the experimental time is between 0 and 5 hours, the TDS and conductivity decrease significantly, and the removal rate of the scale-forming ions in the solution is faster. With the progress of the electrochemical reaction, the electrolysis reaction and the deposition of CaCO₃ on the cathode surface gradually coordinated, and the softening rate of electrochemical water gradually stabilized, but the hardness of the solution decreased continuously. With the surface of the cathode being covered by calcium carbonate crystals and the total hardness of the solution decreasing, the electrochemical reaction rate decreased continuously.

According to the law of conductivity decline, it can be divided into an induction period, a development period, and a stable period. During the induction period, the concentration of scale-forming ions in the solution is higher, and the fouling dissipation reaction near the cathode is severe. Moreover, because there is no calcium carbonate crystal attached on the surface of the cathode, the electrode activity is stronger, so the electrochemical water softening rate is higher. The scale-forming ions are quickly removed, and the TDS and conductivity values decrease rapidly. As the water treatment process progresses, the Ca²⁺ concentration in the solution gradually decreases, and a large amount of calcium carbonate scale is deposited on the surface of the cathode plate, so that the rate of electrolytic reaction in the solution...
and the deposition rate of the fouling on the cathode plate slow down (Yu et al. 2018b). The slower removal rate of scale-forming ions in the solution results in a slower decrease in the TDS and conductivity. During the stable period, the TDS and conductivity values of the solution are gradually stabilized. This is consistent with the effect of the experimental time reported in the related literature on the variation of TDS and conductivity (Ma et al. 2018). The TDS and conductivity values of the solution decreased more than 40%. These two values are positively correlated with the Ca²⁺ concentration in the solution, revealing that electrochemical water treatment can effectively remove Ca²⁺ from the solution.

When the electrolysis voltage is between 10 and 25 V, the decrease rate of the TDS and conductivity for
two different cathode plates increases with the increasing voltage. The amount of hardness removed from the solution decreases with the increasing voltage. When the electrolysis voltage exceeds 25 V, the decrease rate of the TDS and conductivity when the titanium plate is used as cathode decreases, and the value for hardness removed from the solution increases. The increase of voltage will aggravate the hydrogen evolution reaction near the cathode plate, and many bubbles will cause the flow field to be severely disturbed. They prevent calcium ions from depositing on the surface of the cathode as calcium carbonate crystals, which reduces the removal ratio of Ca$^{2+}$, resulting in an increase in the lower limit value of TDS and conductivity in solution. When the cathode is a copper plate, the decrease ratio of TDS and conductivity of the solution continues to

![Figure 4](image_url)
increase, and the lower limit value continues to decrease. The copper plate cathode will be slightly corroded, and the surface properties of the plate will be changed, resulting in a weakening of the hydrogen evolution reaction on the surface, a decrease in the number of bubbles and a weakening effect on the formation of CaCO₃ on the cathode.

Comprehensive analysis

Figure 5 shows the variation of TDS and conductivity in solution treated by electrochemical water treatment with different cathode materials when the electrolysis voltage is 25 V. Under the same applied voltage, when the cathode is a titanium plate, the rate of decrease of TDS and
conductivity in water is faster than when the cathode is a copper plate, and the lower limit value is lower. Because copper is more active than titanium, copper is constantly corroded in the electrochemical process (Figure 6), which impedes the nucleation of bubbles on the electrode surface and the nucleation of calcium carbonate crystals, resulting in increased energy consumption and a retarded rate of electrochemical water softening.

The water softening performance and energy consumption for removing unit hardness of the two different cathode materials are shown in Figure 7. When the titanium plate is used as the cathode, the TDS removal ratio is also higher than that of the copper plate cathode, and the energy consumption for removing the unit hardness is lower than that of the copper plate. This shows that when the titanium plate is used as the cathode, the water softening performance becomes better, and energy consumption is lower. The electrical conductivity of copper is better than that of titanium, so under the same voltage, the current value of the copper plate cathode is higher than that of the titanium plate cathode. Therefore, the power consumed by the copper plate as the cathode is higher than that of the titanium plate cathode. Moreover, the treatment effect of the titanium plate as the cathode is higher than that of the copper plate, so the energy consumption for removing the unit hardness of the titanium plate as the cathode will be significantly lower than that of the copper plate cathode. Therefore, the titanium plate is more suitable for an electrochemical water treatment device electrode than copper plate.

Microanalysis

When the electrolysis voltage is 25 V, the formation of CaCO$_3$ scale deposited on the titanium plate cathode is observed. The CaCO$_3$ scale formed under different conditions was analyzed by SEM and XRD. Figure 8 shows the
SEM images of calcium carbonate. The naturally occurring calcium carbonate scale crystals are mainly rhombohedral crystal forms of rhombohedral polyhedrons. Its shape is more regular and is cubic. Its size is mostly between 5 and 10 μm, and it is easy to form a hard fouling and adhere to the wall of the heat exchanger. The calcium carbonate scale crystal produced by electrochemical water treatment is mainly a bundle of crystals in which acicular particles are aggregated. Its shape is irregular, and its size is mostly between 20 and 30 μm. It is mainly a coarse-grained aragonite crystal with a small amount of calcite crystals.

Figure 9 shows the XRD diffraction spectra of calcium carbonate scale. The operating voltage of Figure 9(a) is 25 V and the experimental time is 5 hours. The operating voltage of Figure 9(b) is 25 V and the experimental time is 25 hours.

**Table 1** Mass percentages of calcite and aragonite

<table>
<thead>
<tr>
<th>Voltage/V</th>
<th>Time/h</th>
<th>Mass percentage of calcite/%</th>
<th>Mass percentage of aragonite/%</th>
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<tbody>
<tr>
<td>10</td>
<td>5</td>
<td>21.7</td>
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<td>15</td>
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<td>3.8</td>
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25 hours. In Figure 9(a), the diffraction angle $2\theta = 26.26^\circ$ mainly corresponds to the (111) crystal plane of the aragonite, and the diffraction angle $2\theta = 29.47^\circ$ mainly corresponds to the (104) crystal plane of the calcite. Except for the diffraction peaks of calcite and aragonite, the intensity of the diffraction peaks of other impurities is negligible. The angles of the main diffraction peaks in Figure 9 are identical. This means that the two samples contain the same type of composition, but the mass fraction of each component is different.

After the crystal form is determined, it is not difficult to find out from the SEM image that the crystals at the initial stage of crystallization are calcite. With the continuation of the experiment, aragonite began to form on the surface of calcite, showing the coexistence of calcite and aragonite.

![Figure 9(a)](image)

**Figure 9** | The diffraction angle $2\theta$ corresponding to the crystal plane.

![Figure 10](image)

**Figure 10** | Mass percentages of calcite and aragonite in the scale at different voltages. (a) Change of mass percentages of calcite and TDS. (b) Change of mass percentages of calcite, aragonite and TDS.
According to the ‘adiabatic method’ (Schreiner 2013), the mass fraction of calcite and aragonite in the sample can be calculated by the following formulas:

\[
W_C = \frac{I_{104}^C}{I_{104}^C + I_{111}^A} \times 100\%
\]

\[
W_A = 1 - W_C
\]

where \(W_C\) and \(W_A\) are the mass fraction of calcite and aragonite, respectively. \(I_{104}^C\) and \(I_{111}^A\) are the calcite (104) crystal plane and the aragonite (111) crystal plane in the XRD diffraction spectrum, respectively. \(K_A\) is the ratio of the RIR (Reference Intensity Ratio) of aragonite and calcite. According to the PDF (Powder Diffraction File) card, the RIR value of calcite (PDF#83-1762) is 3.25, and the RIR value of aragonite (PDF#75-2230) is 1.14. Based on this, the mass fractions of calcite and aragonite under each experimental condition are calculated as shown in Table 1.

In the process of CaCO₃ deposition, the duration of 5 hours is in the induction period and the duration of 25 hours is in the development period. The changes in calcite mass fractions at different electrolysis voltages are shown in Figure 10(a). In the induction period, it has reached the limit when the voltage is 20 V, and the increasing electrolysis voltage will not increase the calcite mass fraction. The change of TDS is opposite to the mass fraction of calcite, indicating that the decrease of TDS is mainly caused by the formation of calcite on the electrode surface. In the development period, it drops first and reaches a minimum at 15 V, then it continues to increase with the increase in voltage. When the voltage is increased from 25 to 30 V, it increases significantly while the TDS changes little. The disturbance of electric field and bubbles makes aragonite fall from the electrode surface, which leads to the decrease of aragonite content in the scale samples. The changes in aragonite mass fractions at different experimental voltages are shown in Figure 10(b). As the main two forms of calcium carbonate crystals, the change in aragonite is the opposite to calcite.

### CONCLUSIONS

The effects of operational parameters (such as electrolytic voltage) and material properties on hardness removal efficiency by the electrochemical technique are experimentally studied. The performances of electrochemical water softening technology were drastically dependent on materials, electrolysis voltage intensity, and electrolysis duration.

The TDS in the solution and the conductivity of the solution are effectively reduced by electrochemical water softening technology. More than 40% of the fouling-forming ions in the solution are removed.

The optimum electrolytic voltage for the titanium plate as the cathode is 23 V. Under this condition, the TDS removal rate is 16% higher than that of the copper plate as the cathode, and the energy consumption per unit hardness is 16% lower.

The mass fraction of the CaCO₃ scale formed by electrochemical water softening technology is higher than that of the CaCO₃ scale formed naturally. In the process, the mass fraction of aragonite is always much higher than the mass fraction of calcite. As the electrolysis voltage increases, the mass fraction of calcite decreases firstly and then increases to a limit and stabilizes. During the stable period of scale, the increase in voltage promotes the conversion of aragonite to calcite.

### ACKNOWLEDGEMENTS

This work Supported by Scientific Research Foundation of Wuhan Institute of Technology(K201630), Natural Science Foundation of China (50976080).

### DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 16 November 2020; accepted in revised form 29 March 2021. Available online 7 April 2021.