Research on the Influence of Circulating Cooling Water on Electrochemical Scale Inhibition

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Abstract. Electrochemical water treatment technology can effectively prevent the formation of scales. In this paper, the electrochemical workstation is used to explore the process of cathode scale formation and its influencing factors under different conditions. The results show that the electrochemical scale inhibition can effectively remove Ca²⁺ and Mg²⁺ in water. When it comes to scale inhibition, and it provides theoretical analysis and experimental basis for solving the scaling problem of the external cold spray water of the high-voltage DC valve cooling system.

1. Foreword
The spray water quality of the cooling tower outside the valve cooling system of the converter station of the DC project is poor, which can easily cause scaling of the cooling tower and seriously affect the cooling effect. Electrochemical water treatment technology (EWT) was developed in the 1970s. At present, many studies have shown that this technology is used in circulating cooling water systems, which can effectively prevent scale, sterilization and algae, and delay corrosion. It is a green circulating cooling water treatment method [1-3].

Electrochemical water treatment technology is that under the action of electrochemistry, the cathode will discharge water molecules, emit H₂, generate OH⁻, and at the same time scale ions migrate to the cathode, forming a precipitate in the cathode area. Physical method to remove it, so as to achieve the purpose of scale inhibition. Xu Hao et al [4-5] found that under the action of an electric field, scale ions are enriched at the cathode, and scale precipitation will be formed under the electrolytic reaction. In order to further explore the process of cathode fouling in electrolytic cells and its influencing factors, this paper carried out a dynamic experiment to explore the actual effect of electrochemical scale inhibition methods, and provided a theoretical analysis for solving the problem of scaling of external cold spray water in the high-voltage DC valve cooling system.
2. Experiment procedure

2.1. Basic principles of electrochemical scale inhibition
Adding a certain DC voltage between the two electrodes, the cathode will have the following electrode reactions:

\[
2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^- \\
2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \\
\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \\
\text{Mg}^{2+} + \text{OH}^- \rightarrow \text{Mg(OH)}_2 \downarrow \\
\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3 \downarrow
\]

At the same time, the inert metal anode will react as follows, and the generated active chlorine has a certain killing effect.

\[
\text{Cl}^- \rightarrow 2\text{e}^- \rightarrow \text{Cl}_2 \\
2\text{OH}^- \rightarrow 4\text{e}^- \rightarrow \text{O}_2 + \text{H}_2\text{O}
\]

2.2. Cathodic scaling experiment of electrolytic cell
Under the conditions of constant potential and constant current density, an electrochemical workstation and a three-electrode system were used to conduct electrochemical experiments. Among them, the electrolyte is 300 mg/L CaCO$_3$ experimental water, stainless steel cathode, titanium ruthenium as anode, cathode potential is -1.0V, -1.4V (vs. SCE), polarization time 0.5, 1, 2, 4 h, electrode. The cup was thermostatically stirred in a water bath at 25°C, and the changes in polarization current density and polarization potential with time were recorded.

3. Experimental results and discussion

3.1. Effect of CaCO$_3$ scale formation under constant pressure
Figure 1 is a graph of cathode current density with time under constant voltage conditions. When the polarization potential is -1.0 V, the current density decreases rapidly within 60 min; when the polarization potential is -1.4 V, the decline is slow. After 100 min, the current density is maintained at about 0.25 mA/cm$^2$. It is speculated that the scale of the cathode surface is different at different potentials. When the potential is lower than the hydrogen evolution potential, the reaction is the reduction of O$_2$ (see equation (1)). The surface of the electrode is covered with CaCO$_3$ crystals, resulting in a decrease in current density to 0. The scale inhibition effect disappears. When the potential is higher than the hydrogen evolution potential, the reaction is accompanied by a hydrogen evolution reaction (see equation (2)). H$_2$ precipitation will disturb the scale layer on the electrode surface and generate OH$^-$ which makes the scale layer loose or even falling off and leaving the cathode surface partially exposed, thus a stable current density can be maintained.

![Figure 1. Cathode current density changes with time under constant voltage](image-url)
3.2. Influence of CaCO$_3$ scale formation under constant current

Figure 2 shows the change in cathode potential with time under constant current conditions. It can be seen that the current is constant, and the cathode potential rises sharply with time and then drops sharply, and then rises slowly with time, with more obvious fluctuations. It is speculated that the scale layer does not completely cover the electrode, and there are still areas and channels that allow the cathode reaction to continue. This is because the H$_2$ generated by the cathode reaction makes the scale layer loose and even falls off, so that the electrode surface is exposed again and causing potential fluctuations and has declined.

![Figure 2](image.png)

**Figure 2.** Cathodic potential changes with time under constant current

3.3. Effect of current density and electrode spacing

Figure 3 shows the change of conductivity with time. The conductivity can reflect the deposition rate of the scale layer on the cathode surface. It can be seen from the figure that the rate of decrease in conductivity is different under different current densities. When the current density is 0.4 mA/cm$^3$ and 0.6 mA/cm$^3$, the rate of decrease in conductivity is slower. When the current density is 0.8 mA/cm$^3$, the rate of decrease is faster, but at 2 mA/cm$^3$, the rate of decrease does not change significantly. Studies have shown that [6] Ca$^{2+}$ is the reason for the decrease in conductivity, so the current density is controlled at 1 mA/cm$^3$.

![Figure 3](image.png)

**Figure 3.** The change curve of conductivity with time

3.4. Sample characterization

3.4.1. SEM characterization. Figure 4 is an SEM image of the scale layer on the surface of the electrode under constant pressure. A picture shows that when the polarization potential is -1.0 V, it can be seen that uniform fine CaCO$_3$ crystals are formed on the cathode surface. Figure b shows that when the polarization potential is -1.4 V, the electrode shows that the formed CaCO$_3$ crystal is loose and has obvious shedding, and the scale layer is not complete, thus exposing part of the electrode surface, the result is consistent with the speculation of 3.1.
Figure 5 is a SEM image of the scale layer under constant current conditions, showing the growth process of the scale layer on the cathode surface. It can be seen that at the beginning of the reaction, the surface of the cathode is covered with fine CaCO$_3$ crystals, at which time the cathode reaction is blocked. As the potential rises, the reaction proceeds, producing large-particle CaCO$_3$ crystals, but it cannot completely cover the cathode surface, with voids and pores. In figure d, dendritic CaCO$_3$ crystals are formed. This is because the OH$^-$ concentration near the pores increases, and Ca$^{2+}$ and HCO$_3^-$ crystals grow into dendrites in the solution, but these crystals are not dense and have large voids. The inference is due to breakage and caused by shedding. This is confirmed by the conclusion drawn in 3.2.

![Figure 4. SEM image of electrode surface under constant pressure](image)

![Figure 5. Microstructure of the scale layer on the cathode surface at different times, (a) 0.5 h, (b) 1 h, (c) 2 h, (d) 4 h](image)

4. Conclusion
In this paper, the electrochemical workstation was used to explore the process of the cathode structure of the electrolytic cell and its influencing factors under different conditions, and a dynamic experiment was carried out to obtain the following conclusions.

1) Electrochemical scale inhibition is based on the electrolytic reaction of circulating cooling water. The cathode reaction can produce OH$^-$, which generates CaCO$_3$ on the cathode surface with HCO$_3^-$ and Ca$^{2+}$, and removes Ca$^{2+}$ in the water, thereby playing the role of scale inhibition.

2) Under constant pressure, when the voltage is lower than the hydrogen evolution potential, the cathode scale layer is dense, which hinders the progress of the cathode reaction. When the voltage is higher than the hydrogen evolution potential, the cathode surface scale layer is loose due to the action of hydrogen bubbles. Maintain a large current density. Under constant current conditions, the scale layer does not completely cover the surface of the electrode, and there are...
still some voids and channels. The OH\(^-\) concentration near the channel increases. Ca\(^{2+}\) and HCO\(_3^-\) in the main solution crystallize near the channel and grow into dendrites. The cathode reaction also can continue.

3) The deposition rate of the scale layer on the cathode surface is mainly affected by the current density. Within a certain range, increasing the current density can increase the scale deposition rate. When the current density increases to a certain level, it is controlled by the mass transfer of Ca\(^{2+}\) and HCO\(_3^-\). The deposition rate is no longer greatly improved. It is more appropriate to control the current density at 1 mA/cm\(^3\).

Acknowledgments
The research was funded by the Guangzhou Science and Technology Plan Project (201710010186, 20180410147), the Guangdong Science and Technology Plan Project (2017A030223005), the National Natural Science Foundation of China (NSFC-51408256), Special Funds for Research from the Environmental Charity Project of South China Institute of Environmental Sciences (PM-zx703-201703-011, PM-zx703-202003-101).

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