Effect of fouling resistance in heat exchanger and the crystal form of CaCO₃ in hard circulating cooling water with electrostatic field and alternating current electric field

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ABSTRACT

The effect of high voltage electrostatic field and high voltage alternating current electric field on the heat exchanger surface fouling under the conditions of hard water was investigated. The Ca²⁺ concentration in two water conditions was 12 mmol/L. The Mg²⁺ concentration was 10 mmol/L and 12 mmol/L respectively. The HCO₃⁻ concentration changed with the Mg²⁺ concentration. X-ray diffraction and scanning electron microscope results confirmed that the main crystal phases of the scale samples consisted of calcite and aragonite. The high voltage electrostatic treatment can promote scale growth under both water quality conditions. However, the high voltage alternating current electric field treatment shows a good scale inhibition effect under both water quality conditions, and the scale inhibition effect is best when both Ca²⁺ and Mg²⁺ concentrations are 12 mmol/L, and the average scale inhibition rate reaches 47.58%. When the calcite content of the scale sample is significantly higher than that of aragonite, Mg²⁺ affects the growth and solubility of crystals. Conversely, the high voltage alternating current electric field treatment can effectively extend the fouling induction period of the adherent scale on the heat exchanger surface, which is favorable for heat exchanger fouling.

Key words: calcium carbonate, fouling resistance, high voltage alternating electric field, high voltage electrostatic field, magnesium ion

HIGHLIGHTS

- The scale inhibition experiments with different electric fields and Mg²⁺ concentrations were designed.
- Different electric fields have different treatment effects.
- The FIP can be used to evaluate the scale inhibition effect.
- The HVAC electric field treatment can enhance the inhibition effect of Mg²⁺ on crystal growth.
- After the HVAC electric field treatment, the calcite content in the scale sample increases.

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INTRODUCTION

Scaling is an inevitable problem in the heat exchanger of circulating cooling water in the industrial production process. Scales are formed when hard water is heated in heat transfer equipment such as heat exchangers, evaporators, cooling tower condensers, boilers, and tube walls. The formed deposits not only reduce the efficiency of heat exchangers but also increase energy consumption (Xing 2008; Tijing et al. 2010). Therefore, research on how to effectively control and prevent the scale on the surface of the heat transfer is very necessary.

At present, the scale inhibition methods include chemical and physical methods (Tijing et al. 2010). Chemical methods are not only costly and easy to pollute the environment, but also cause the solution to possibly contain substances harmful to organisms (Wang et al. 2018). To solve this problem, physical methods are used to treat scaling, such as electromagnetic fields (EMF), ultrasounds, catalytic materials, sudden pressure changes, and doping harmless elements (Tijing et al. 2010; Korchef 2019).

For physical methods, large numbers of studies have focused on electric fields, magnetic fields, and electromagnetic fields to treat scale. Firstly, these treatment methods could change the water quality parameters. Xing (2008) found that the precipitation process in solution is much faster and more effective by using the electromagnetic field generated by the pulse current effectively at low temperatures. For electromagnetic treatment, it could make a large number of crystals precipitate in the solution instead of adhering to the surface of the heat exchanger, pipe, or membrane, so as to reducing scaling (Alimi et al. 2007; Lin et al. 2020). Conversely, the treatment of the electromagnetic field not only affected the growth of scale in the heat exchanger but also changed the water quality parameters of the circulating water such as conductivity, pH, turbidity, etc. (Mosin & Ignatov 2015; Gao et al. 2020; Lyu et al. 2020). In 2020, Lyu et al. (2020) studied the effect of an alternating electromagnetic field on the thermal resistance, conductivity, pH, and dissolved oxygen of CaCO₃ solution and indicated that the fouling induction period can reach 10,000 minutes at 0.02 T, the scale inhibition effect is the best, and the conductivity can be used as a water quality indicator that reflects the change in fouling resistance. Moreover, the electromagnetic treatment also can affect crystal growth. Zhang et al. (2016a) found that electromagnetic treatment can reduce the fouling resistance on the heat exchanger surface and change the crystal grain size. Wang et al. (2018) also observed that the pulsed magnetic field is
more advantageous to restrain the formation of scale, and makes the grain size small and the non-adherent scale loose. Moreover, Lin et al. (2020) reviewed the potential economic savings of the EMF and indicated that more than 40% of total cost reduction by using EMF process.

Given this background, adding harmless ions into the solution effect of scale has been experimentally investigated by several groups. Tai & Chien (2002) found that Mg\(^{2+}\) has a complex effect on the formation of CaCO\(_3\). Different concentrations of Mg\(^{2+}\) have different inhibition and promotion effects on scaling with increasing MgCl\(_2\) in solution for up to \(\geq 696\) min, its transformation is retarded from amorphous calcium carbonate dispersed into crystalline calcium carbonate (Konrad et al. 2018). Researchers reported that Mg\(^{2+}\) can directly interact with CaCO\(_3\) crystals to affect its morphology, adsorbs on the surface of vaterite and calcite causing an increase in surface roughness (Zhang et al. 2016a, 2016b; Al-Gailani et al. 2020). By considering Mg\(^{2+}\) concentration with electromagnetic field or ultrasonic, they can improve the scale inhibition effect and make the CaCO\(_3\) particles gradually change into aragonite (Han et al. 2018). Gao et al. (2020) indicated that the scale inhibition under the electric field and Mg\(^{2+}\) is better than that under a single electric field.

Based on the above discussion, water quality and the Mg\(^{2+}\) concentration have a great influence on the scale inhibition effect of electromagnetic field. At present, most research has focused on the influence of electromagnetic field on the scale inhibition effect of low hardness water. Thus, it is necessary to design an experiment to further study the scale inhibition by considering electromagnetic fields on high hardness water containing different Mg\(^{2+}\) concentrations. In this study, the influence of high voltage electrostatic field and high voltage alternating current (HVAC) electric field on the surface fouling of the heat exchanger in high hardness circulating cooling water was analyzed. Four indicators were measured, including fouling resistance, average scale inhibition rate, scale inhibition rate by gravimetric method, and Ca\(^{2+}\) concentration. The crystal morphology of the scale samples was investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM) for adherent scale and non-adherent scale, respectively, to evaluate the scale inhibition effect.

**EXPERIMENT FACILITY AND METHODS**

**Facility**

The industrial circulating cooling water dynamic simulation test bench and flow chart are shown in Figure 1(a). The experiment equipment mainly consisted of eight parts, namely, water collecting tank, ion rod water processor, heat exchanger, cooling tower, constant temperature water tank, water supply system, automatic temperature acquisition system, and

![Figure 1](http://dx.doi.org/10.2166/wst.2021.344)

9. Temperature sensor  10. Interception net
power supply. In the experiment, the circulating cooling water is pumped out of the water collecting tank by a water pump and processed by the ion rod water processor, then arrives in the heat exchanger. Inside the heat exchanger, the direction of water in the constant temperature water tank is opposite to the circulating cooling water. The circulating cooling water runs through the tube and the heating water runs the shell. Finally, the circulating cooling water is cooled in the cooling tower and then returns to the water collecting tank, forming a closed cycle.

The ion rod water processor is shown in Figure 1(b). It mainly consisted of four parts, namely, ion bar, flow restraint pipe, metal pipeline cathode, and power supply. This study chose two power sources, respectively, high voltage DC power source and high voltage AC power source, both set to 6 kV. The flow restraint pipe ensures that the flow of cooling water in the ion rod processor chamber is equal to that of the external water pipe to avoid the experimental error caused by the sudden change of flow. The circulating cooling water enters from the lower water inlet and flows out from the upper water outlet. It flows in the cavity between the flow restraint pipe and the PTEF insulation layer.

Methods

In this study, analysis of pure (AR) grade CaCl₂, (AR) grade MgCl₂, and NaHCO₃ were used to prepare artificial hard water. The artificial hard water volume was 200 L. The temperature of the circulating cooling water was maintained at 30 °C ± 2 °C and that of the heating water was maintained at 90 °C ± 2 °C. The circulating water flow rate was kept at 1,000 L/h. In order to increase the artificial water hardness, the Ca²⁺ concentration was increased to 12 mmol/L, the Mg²⁺ concentration was increased to first 10 mmol/L and then to 12 mmol/L. Both the high voltage DC power source and the high voltage AC power source voltage were set to 6 kV, in order to study the combined effects from the high voltage electrostatic field, the HVAC electric field, and Mg²⁺, on scaling in the hard circulating cooling water. In this study, the ratio of the sum of Ca²⁺ and Mg²⁺ concentrations to the HCO₃⁻ concentration was about 1:1 (Table 1). In order to maintain the ion concentrations in the circulating cooling water and replenish ions lost to precipitation, two peristaltic pumps with a flow range of 0.001–380 mL/min were used to replenish the CaCl₂ and NaHCO₃ solution into the water collecting tank at a constant flow rate. CaCl₂ and NaHCO₃ were supplemented at flow rates of 1.32 mmol/L·h and 0.9 mmol/L·h, respectively. A water supply system is located above the water collecting tank with a volume of 50 L. When the circulating cooling water is reduced due to evaporation, the water inlet valve is opened to replenish water volume loss.

Four PT100-type temperature sensors were used to measure the inlet and outlet temperatures of the hot water and the circulating cooling water at both ends of the heat exchanger. The temperature was recorded by a software acquisition system every second and used as input to calculate fouling resistance.

In the course of the experiment, part of the scale was deposited on the copper tube surface of the heat exchanger, and the other part of the scale was washed into the interception net of the water collecting tank. At the end of the experiment, the adherent scale on the heat transfer surface of the heat exchanger and the non-adherent scale in the water collecting tank were collected. The scale was dried in an oven at 150 °C for 12 hours and stored in amber sample bottles. The adherent scale and non-adherent scale were weighed in order to calculate the scale inhibition rate by gravimetric method and to determine the rate of the total scale change. The scale samples were analyzed by SEM and XRD using an S4800 scanning electron microscope and PHILIPS APD-10 X-ray diffractometer.

The duration of each experiment was 12 hours. An appropriate amount of water sample was taken to measure the Ca²⁺ concentration every two hours during the experiment.

Table 1 | Ion concentration (mmol/L) in the circulating cooling water and the respective electric field

<table>
<thead>
<tr>
<th>Group</th>
<th>Electric field</th>
<th>CaCl₂</th>
<th>MgCl₂</th>
<th>NaHCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>High voltage electrostatic field</td>
<td>12</td>
<td>10</td>
<td>22</td>
</tr>
<tr>
<td>2#</td>
<td>High voltage alternating current electric field</td>
<td>12</td>
<td>10</td>
<td>22</td>
</tr>
<tr>
<td>3#</td>
<td>No field</td>
<td>12</td>
<td>10</td>
<td>22</td>
</tr>
<tr>
<td>4#</td>
<td>High voltage electrostatic field</td>
<td>12</td>
<td>12</td>
<td>24</td>
</tr>
<tr>
<td>5#</td>
<td>High voltage alternating current electric field</td>
<td>12</td>
<td>12</td>
<td>24</td>
</tr>
<tr>
<td>6#</td>
<td>No field</td>
<td>12</td>
<td>12</td>
<td>24</td>
</tr>
</tbody>
</table>
Calculating method of fouling resistance and scale inhibition rate

This study used the average scale inhibition rate and the scale inhibition rate by gravimetric method to evaluate the scale inhibition effect.

According to the thermal equilibrium conditions of heat transfer theory, fouling resistance can be used to evaluate the effect of scale inhibition (Zhao et al. 2014). Fouling resistance \( R_f \) is determined by the following equation:

\[
R_f = \frac{1}{K_t} - \frac{1}{K_{t=0}}
\]  

(1)

where \( R_f \) is the fouling resistance at time \( t \), \( K_t \) is the total transfer coefficient at time \( t \), \( K_{t=0} \) is the total transfer coefficient at the initial time.

The total heat transfer coefficient \( K \) can be defined by

\[
K = \frac{m_c c_{pc}(T_1 - T_2) \ln \left( \frac{T_3 - T_2}{T_4 - T_1} \right)}{A[(T_3 - T_2) - (T_4 - T_1)]}
\]  

(2)

where \( T_1 \) and \( T_2 \) are the inlet and outlet temperatures of circulating cooling water, respectively, \( T_3 \) and \( T_4 \) are the inlet and outlet temperatures of the heated water, respectively. \( A \) is the total heat transfer area, \( m_c \) is the mass velocity, \( C_{pc} \) is specific heat at the constant pressure.

The real-time scale inhibition rate \( \eta_t \) can be obtained by the experimental group and the control group fouling resistance:

\[
\eta_t = \left( 1 - \frac{R_{t, \text{experimental group}(t)}}{R_{t, \text{control group}(t)} - \frac{1}{C_{0}} \left( \frac{m_{\text{experimental group}}}{m_{\text{control group}}} \right) \times 100\%
\]  

(3)

where \( R_{t, \text{experimental group}(t)} \) is the fouling resistance of the experimental group, \( R_{t, \text{control group}(t)} \) is the fouling resistance of the control group.

Based on the above expression, the average scale inhibition rate \( \eta_{\text{average}} \) can be obtained by the following formula:

\[
\eta_{\text{average}} = \frac{\sum_{i=1}^{N} \eta_t}{N}
\]  

(4)

The scale inhibition rate by gravimetric method \( \eta_m \) is calculated by the following formula:

\[
\eta_m = \left( 1 - \frac{m_{\text{experimental group}}}{m_{\text{control group}}} \right) \times 100\%
\]  

(5)

where \( m_{\text{experimental group}} \) is the mass of the adherent scale of the experimental group, \( m_{\text{control group}} \) is the adherent scale mass of the control group.

The total scale change rate \( \eta_m' \) can be expressed as follows:

\[
\eta_m' = \left( 1 - \frac{m'_{\text{experimental group}}}{m'_{\text{control group}}} \right) \times 100\%
\]  

(6)

where \( m'_{\text{experimental group}} \) is the sum of the adherent scale mass and the non-adherent scale mass of the experimental group, \( m'_{\text{control group}} \) is the sum of the adherent scale mass and the non-adherent scale mass of the control group.

RESULTS AND DISCUSSION

Fouling resistance

Under different water quality conditions, the fouling resistance and its fitting curve obtained after the treatment of high voltage electrostatic field and HVAC electric field are shown in Figure 2. In this study, the changes in fouling resistance with time
can be clearly divided into three stages, namely, the initial stage (stage 1), the rising stage (stage 2), and the stable stage (stage 3). This is consistent with the results of Wang & Liang (2017) and Korchef (2019). In stage 1, the fouling resistance value is very small and does not change significantly. The research results indicated that if the fluid containing impurity ions contacts the heat exchanger surface, fouling will not immediately precipitate on the heat exchanger surface. This condition continues for a period of time. This period is called the fouling induction period (FIP), which is defined as the period from the time when the fluid passes the heat exchanger surface to the beginning of the growth of fouling resistance (Wang & Liang 2017).

As shown in Figure 3, fitting curves of FIP for six groups exhibit a gradually decreasing trend, so when the fouling resistance reaches the minimum value the FIP ended. Table 2 shows the linear equations for stage 1 and FIPs. All FIPs are small values and are correlated with the hardness of the artificial hard water. When the \( \text{Mg}^{2+} \) concentration is 10 mmol/L, the FIPs of group 1# treated with the high voltage electrostatic field is 28.83 min lower than that of the control group, and its fouling resistance curve is higher than that of the control group. Instead, the FIPs of 35.83 min for group 2# treated with the HVAC electric field is the largest, and its fouling resistance curve is lower than that of the control group.

When the concentration of \( \text{Mg}^{2+} \) is 12 mmol/L, the fouling resistance during the FIP of group 4# treated with the high voltage electrostatic field is higher than that of the control group, and its fouling resistance curve partially overlaps with the control group. In contrast, group 5# with the HVAC electric field treatment has the longest FIP (38.93 min) which is about two times that of the control group (18.25 min). Its fouling resistance curve is significantly lower than that of the other two groups.

![Figure 2](image-url) | Fouling resistance and its fitting curves for two different \( \text{Mg}^{2+} \) concentrations: (a) 10 mmol/L, (b) 12 mmol/L. Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/wst.2021.344.

![Figure 3](image-url) | Fitting curves of FIP for two different \( \text{Mg}^{2+} \) concentrations: (a) 10 mmol/L, (b) 12 mmol/L.
To sum up, when the Mg\(^{2+}\) concentration is 10 mmol/L and 12 mmol/L, the HVAC electric field can effectively prolong the FIP, correspondingly, the fouling resistance will be reduced. Instead, the high voltage electrostatic field can shorten the FIP and increase the fouling resistance. So, FIP can intuitively reflect the growth trend of the fouling resistance. That is, prolonging the FIP, delays the growth of crystals on the heat exchanger surface, reduces the fouling resistance, and results in scale inhibition. This suggests that the FIP can be used as an index to evaluate the scale inhibition effect, which is consistent with Xu et al. (2018). Conversely, different concentrations of Mg\(^{2+}\) will result in different FIPs in different electric fields, and also affect scale formation or inhibition on the heat exchanger surface. Likewise, Tai & Chien (2002) also found that Mg\(^{2+}\) in the solution will affect the FIP.

Stage 2 is the rising period following the FIP. During this period, both the fouling resistance and fouling rate will increase significantly. In this stage, the slopes of the six resistance curves initially increase and then decrease. The slopes of the curves representing the HVAC electric field treatment groups are the smallest. This trend indicates that the crystal growth rate on the heat exchanger surface is slower with the HVAC electric field treatment. In contrast, the slopes of the curves representing the high voltage electrostatic field treatment groups are the largest, that is, the crystal growth rate on the heat exchanger surface with high voltage electrostatic field treatment is the highest.

Finally, it enters stage 3, the stable period. The slopes of the curves gradually decrease and approach equilibrium. The fouling resistance gradually stabilizes, without any adherent scale formation on the heat exchanger surface.

**Scale inhibition rate**

**The real-time scale inhibition rate**

The real-time scale inhibition rate curves are shown in Figure 4. The four curves change significantly in the initial 2–4 hours and then stabilize, which supports the conclusion that the fouling resistance in stage 3 of crystal growth tends to remain stable. The real-time scale inhibition rates of the two groups with the high voltage electrostatic field treatment are mostly

### Table 2 | Linear equations of stage 1 and FIPs.

<table>
<thead>
<tr>
<th>Group</th>
<th>Stage 1</th>
<th>FIP (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>(y = -8.77E-10 + 2.62E-05)</td>
<td>28.83</td>
</tr>
<tr>
<td>2#</td>
<td>(y = -1.16E-09 + 1.13E-05)</td>
<td>35.83</td>
</tr>
<tr>
<td>3#</td>
<td>(y = -7.30E-11 + 1.84E-05)</td>
<td>30.50</td>
</tr>
<tr>
<td>4#</td>
<td>(y = -3.50E-09 + 5.17E-05)</td>
<td>32.30</td>
</tr>
<tr>
<td>5#</td>
<td>(y = -4.50E-09 + 2.89E-05)</td>
<td>38.93</td>
</tr>
<tr>
<td>6#</td>
<td>(y = -9.92E-09 + 5.42E-05)</td>
<td>18.25</td>
</tr>
</tbody>
</table>

![Figure 4](http://dx.doi.org/10.2166/wst.2021.344)
negative, and the real-time scale inhibition rates of the two groups with the HAVC electric field treatment are mostly positive. Test groups containing high Mg\(^{2+}\) concentrations exhibit better scale inhibition effects.

**The average scale inhibition rate and the scale inhibition rate by gravimetric method**

The average scale inhibition rate and the scale inhibition rate by gravimetric method under different conditions are listed in Table 3. When the Mg\(^{2+}\) concentration is 10 mmol/L, the average scale inhibition rate and the scale inhibition rate by gravimetric method for group 1# treated with the high voltage electrostatic field, are \(-38.48\%\) and \(-16.05\%\), respectively, which are both negative values and show the effect of promoting scaling. The average scale inhibition rate and the scale inhibition rate by gravimetric method for group 2# treated with the HVAC electric field are 28.98% and 39.28%, respectively, which are both positive values and show the scale inhibition effect.

When the Mg\(^{2+}\) concentration was increased to 12 mmol/L, the average scale inhibition rate and the scale inhibition rate by gravimetric method for group 5# treated by the HVAC electric field were 47.58% and 82.48%, respectively. Compared with the Mg\(^{2+}\) concentration of 10 mmol/L, there was a significant improvement. This indicates that higher Mg\(^{2+}\) concentrations enhance the scale inhibition effect of the HVAC electric field. The average scale inhibition rate and the scale inhibition rate by gravimetric method for group 4# treated with the high voltage electrostatic field, are \(-0.56\%\) and \(-11.33\%\), respectively. Although the high voltage electrostatic field treatment under these two water quality conditions shows the effect of promoting fouling, the average scale inhibition rate and the scale inhibition rate by gravimetric method for the group 1# with lower Mg\(^{2+}\) concentration are lower. The enhancement effect is more obvious, and the average scale inhibition rate at this time is closer to 0. These results indicate that the hardness of the water affects the treatment effect of the high voltage electrostatic field.

Previous studies have shown that the electrostatic field treatment of hard water with high levels of hard ions promotes scaling, while the electrostatic field treatment of artificial hard water with low levels of hard ions showed the effect of scale inhibition (Gao et al. 2020).

**The total scale change rate**

The mass of adherent and non-adherent scales are shown in Figure 5 so that the total scale change rate can be calculated and listed in Table 4. When the Mg\(^{2+}\) concentration is 10 mmol/L, the total scale change rate for group 1# is \(-45.94\%\), the

<table>
<thead>
<tr>
<th>Group</th>
<th>1#</th>
<th>2#</th>
<th>4#</th>
<th>5#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average scale inhibition rate</td>
<td>(-38.48%)</td>
<td>28.98%</td>
<td>(-0.56%)</td>
<td>47.58%</td>
</tr>
<tr>
<td>Scale Inhibition rate by gravimetric method</td>
<td>(-16.05%)</td>
<td>39.28%</td>
<td>(-11.33%)</td>
<td>82.48%</td>
</tr>
</tbody>
</table>

![Figure 5](http://iwaponline.com/wst/article-pdf/84/7/1608/948583/wst084071608.pdf)
Table 4 | The total scale change rate

<table>
<thead>
<tr>
<th>Group</th>
<th>1#</th>
<th>2#</th>
<th>4#</th>
<th>5#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total scale change rate</td>
<td>-45.94%</td>
<td>-24.90%</td>
<td>-21.26%</td>
<td>13.14%</td>
</tr>
</tbody>
</table>

average scale inhibition rate and the scale inhibition rate by gravimetric method are both negative, that is, the adherent scale and non-adherent scale quality of group 1# treated with the high voltage electrostatic field are both increased. The total scale change rate of group 2# is -24.90%, while the average scale inhibition rate and the scale inhibition rate by gravimetric method are both positive, that is, the quality of non-adherent scale increases after the HVAC electric field treatment, and the quality of adherent scale decreases. The AC voltage output from the high voltage AC power supply produces an electromagnetic field different from the electrostatic field around the ion rod, a phenomenon which can be explained by Maxwell’s equations. The energy of the electromagnetic field is transferred to the water to increase the collision probability of the positive and negative ions, so that the scaling ions form precipitation in the solution instead of growing on the surface of the heat exchanger, so as to achieve the effect of scale inhibition. This is consistent with the previous research (Alimi et al. 2007).

When the Mg$^{2+}$ concentration is 12 mmol/L, the total scale change rate (-21.26%) for group 4# is negative as the average scale inhibition rate and the scale inhibition rate by gravimetric method increase. However, the total scale change rate (13.14%), the average scale inhibition rate, and the scale inhibition rate by gravimetric method of group 5# treated with the HVAC electric field are all positive values, and both adherent and non-adherent scale decreased. This shows that under conditions of hard water quality, the HVAC electric field treatment does not only inhibit crystal growth on the heat exchanger surface, but may also affect the crystal precipitation of scaling ions in the solution. Previous studies have shown that Mg$^{2+}$ plays a role in scale inhibition by inhibiting the growth of crystals. Al-Gailani et al. (2020) suggested that Mg$^{2+}$ can inhibit the growth of crystals and the electromagnetic field generated by the HVAC electric field may enhance this inhibition effect more than the electrostatic field. The above studies show that the HVAC electric field treatment has an obvious scale inhibition effect, and the scale inhibition effect is better under the conditions of hard water. In addition, the HVAC electric field treatment may also change the crystal morphology, and the formed CaCO$_3$ scale is loose and easy to be washed away by water flow and peeled off the heat exchanger surface. These need to be further confirmed by SEM and XRD results.

**Ca$^{2+}$ concentration**

The main chemical reaction in circulating cooling water is as follows:

$$\text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$$  \hspace{1cm} (7)

The changing trend of Ca$^{2+}$ concentration with time when the Mg$^{2+}$ concentration is 10 mmol/L and 12 mmol/L is shown in Figure 6. The rates of Ca$^{2+}$ concentration change for the six groups are shown in Table 5.

The Ca$^{2+}$ concentration shows a decreasing trend in the first two hours, during which the ion consumption rate is greater than the replenishment rate. After two hours, Ca$^{2+}$ concentration gradually increases, and the slope of the line segment gradually increases, that is, the growth rate of the concentration of Ca$^{2+}$ gradually increases. During this period, the replenishment rate of ions is greater than the consumption rate. When the Mg$^{2+}$ concentration is 10 mmol/L, the Ca$^{2+}$ concentration in the three groups decreases at similar rates in the first two hours. At the end of the experiment, the Ca$^{2+}$ concentration change of group 2# (7.84%) with the HVAC electric field treatment was similar to that of the control group (9.80%). However, the change of Ca$^{2+}$ concentration in group 1# (3.92%) with the high voltage electrostatic field treatment was significantly smaller than in the other two groups. This behavior indicates that the high voltage electrostatic field treatment accelerates the consumption of Ca$^{2+}$ and promotes the scaling in solution, which is also consistent with the observation that group 1# has the smallest change in total scale and the most obvious fouling promoting effect.

When the Mg$^{2+}$ concentration is 12 mmol/L, the change of Ca$^{2+}$ concentration of group 4# and 5# is significantly higher than that of 10 mmol/L, and the change of the Ca$^{2+}$ concentration of group 5# with the HVAC electric field treatment is the largest. It is obvious that the total scale change of group 5# is the largest and positive, indicating that the HVAC electric field reduces the Ca$^{2+}$ consumption rate. Compared with group 2#, group 5# with a higher Mg$^{2+}$ concentration, exhibits more
obvious scale inhibition tendencies; the experimental conditions inhibit heat exchanger surface fouling, and also affect fouling in solution, and are consistent with the previous analysis of the scale inhibition rate.

**SEM and XRD analysis**

Calcite, aragonite, and vaterite are the three common crystal phases of CaCO$_3$. Calcite is the most thermodynamically stable crystal phase under standard conditions (room temperature and atmospheric pressure), while aragonite and vaterite are extremely unstable under standard conditions and are easily transformed to calcite (Wang *et al.* 2009). Zhang *et al.* (2007) studied the effect of scale inhibitors on the crystal form of CaCO$_3$, and found that the better the scale inhibition effect, the higher the vaterite content. Gopi *et al.* (2013) found that under different experimental conditions, the relative calcite, aragonite, and vaterite content varies. The crystalline composition of CaCO$_3$ is also one of the factors affecting scale formation. The XRD and SEM results of the collected adherent scale and non-adherent scale samples are shown in Figures 7 and 8.

Two crystal phases of calcite and aragonite were found in the XRD pattern. Calcite is a block-like hexahedral crystal (Figure 8(a)–8(c) and 8(g)–8(i)), and aragonite is a needle-like dense dendritic crystal (Figure 8(d)–8(f) and 8(j)–8(l)). In the experiment, the main crystal phase for non-adherent scale of all groups is calcite, and the main crystal phase of the adherent scale is aragonite, which is related to the crystallization temperature of CaCO$_3$. When the temperature was above 35 °C, aragonite is the main component, and below 35 °C, calcite was the main component (Xing 2008). Large numbers of studies have shown that needle-like aragonite is denser than calcite. It easily adheres to the heat exchanger surface and is difficult to remove. However, block-like calcite has lower adhesive properties than aragonite and can be washed away by water more easily (Xing 2008; Tijing *et al.* 2010; Gao *et al.* 2020). Therefore, if aragonite adhesion on the heat exchanger surface is reduced, scale formation inhibition is feasible. It is known that the (1 0 4) crystal plane (29.4°) is one of the main growth planes of calcite, and the (1 1 1) crystal plane (26.2°) is one of the main growth planes of aragonite (Gopi *et al.* 2013). Based on the K value method (Zhao *et al.* 2014), the relative mass fractions of calcite and aragonite in adherent and non-adherent scales are shown in Figure 9. For groups 3# and 6# (Figure 6(a) and 6(b)) without the high voltage electromagnetic field, the intensity of the calcite diffraction peaks of adherent scale is lower than that of the non-adherent scale. The diffraction peak intensity of group 6# with higher Mg$^{2+}$ concentration is the lowest. The intensities of the aragonite diffraction peaks of the adherent scale were all significantly stronger than that in the non-adherent scale, and the aragonite content in the
adherent scale and non-adherent scale for group 6# are higher than that of group 5# (Figure 9). This indicates that the aragonite from group 6# with high Mg\(^{2+}\) concentrations has a higher crystallinity and is difficult to remove when it adheres to the heat exchanger surface. Mg\(^{2+}\) can obviously promote the formation of aragonite, which is consistent with the results from previous research (Mejri et al. 2013). This also can be confirmed by the smallest FIP (Table 2), the largest fouling resistance.
Mg$^{2+}$ can obviously promote the formation of aragonite, which is consistent with the results from previous research (Mejri et al. 2013). Some studies have indicated that Mg$^{2+}$ inhibits the growth of calcite (Nielsen et al. 2013).

Based on the above analysis, when the Mg$^{2+}$ concentration is 12 mmol/L, the average scale inhibition rate of group 5# treated with the HVAC electric field is the largest, and the scale inhibition effect is the best. The SEM images show that the adherent scale of group 5# has a large particle size and a small amount of block-like calcite crystals (Figure 8 Mg$^{2+}$ = 12 mmol/L). The XRD pattern (Figure 7(c)–7(f)) also shows that the diffraction peak intensity of calcite in the adherent scale and non-adherent scale in group 5# is higher than in group 4#, which was treated by the high voltage electrostatic

(Figure 2), and the largest adherent scale mass (Figure 3). Mg$^{2+}$ can obviously promote the formation of aragonite, which is consistent with the results from previous research (Mejri et al. 2013). Some studies have indicated that Mg$^{2+}$ inhibits the growth of calcite (Nielsen et al. 2013).

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field. The results are consistent with the calculated relative mass fraction (Figure 9). The results obtained for group 5# with the smallest adherent scale quality and the best scale inhibition effect can be explained by the following mechanisms. The electromagnetic field promotes the collision of scale ions in solution, and calcite crystals are formed before the circulating water enters the heat exchanger. During the growth of calcite, Mg$^{2+}$ adheres to the growth surface of calcite, enters the calcite lattice structure, and occupies the original positions of Ca$^{2+}$ in the calcite lattice, making calcite unstable and inhibiting further growth of calcite crystals. The solubility of calcite increases (Berner 1975; Nielsen et al. 2013). These mechanisms might explain why the HVAC electric field treatment reduces the Ca$^{2+}$ consumption rate and the total scale in group 5#. In addition, the XRD spectra of (Mg, Ca)CO$_3$ and CaCO$_3$ are identical, supporting the hypothesis that Mg$^{2+}$ may enters the calcite lattice. This is consistent with the conclusion of Gao et al. (2020). Large amounts of calcite forming on the heat exchanger surface and in solution are beneficial to achieve scale inhibition. When the Mg$^{2+}$ concentration is 10 mmol/L, the aragonite content of the adherent scale of group 5# treated with the high voltage electrostatic field, is higher than that of the HVAC electric field treatment groups. This is consistent with the observation that group 2# promotes fouling significantly, with a negative average scale inhibition rate.

According to previous studies on electrostatic field effects and Mg$^{2+}$ on CaCO$_3$ scaling (Gao et al. 2020), the scale inhibition under electric field and Mg$^{2+}$ is better than that under a single electric field. When the Mg$^{2+}$ concentration is 4 mmol/L, the calcite content in adherent scale increases significantly after the electrostatic field treatment. In this study, under the two high hardness water conditions investigated, the combined scale inhibition effect of the electrostatic field and Mg$^{2+}$ is weakened and even promotes scaling. Zhang et al. (2020) studied the effect of alternating electric field and Mg$^{2+}$ on CaCO$_3$ scaling, indicated that Mg$^{2+}$ concentrations of 6 mmol/L have a potential scale inhibition effect after treatment in the HVAC electric field. Under the two different water conditions in this study, the HVAC electric field treatment also showed favorable scale inhibition effects.

**CONCLUSIONS**

The following conclusions were obtained in this study:

1. Under the two different hard water conditions, the high voltage electrostatic field appears to enhance scale formation. The HVAC electric field may also have a positive effect on scale inhibition. Scale inhibition in the HVAC electric field is optimum for both Ca$^{2+}$ and Mg$^{2+}$ concentrations of 12 mmol/L, with average scale inhibition rates reaching 47.58%.

2. The change of fouling resistance as a function of time can be divided into the initial stage (FIP), rising stage, and stable stage. Both the high voltage electrostatic field and the HVAC electric field influence the FIP. The HVAC electric field can prolong the FIP, which is favorable for reducing fouling on the heat exchanger surface. The FIP affects the fouling resistance and can be used as an index to evaluate the scale inhibition effect.

**Figure 9** | The mass fractions of calcite and aragonite in adherent scale and non-adherent scale for each group. Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/wst.2021.344.
Both the high voltage electrostatic field and HVAC electric field can promote the crystallization and precipitation of scaling ions in the solution. The electromagnetic field generated by the HVAC electric field can enhance the inhibition effect of Mg\(^{2+}\) on crystal growth and reduce the consumption rate of Ca\(^{2+}\) in the solution.

(4) The high concentration of Mg\(^{2+}\) enhances the crystallization of aragonite in the adherent scale on the heat exchanger surface. After the HVAC electric field treatment, the calcite content in the scale sample increases, but can be removed easily with water to achieve the scale inhibition effect.

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**DATA AVAILABILITY STATEMENT**

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

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