Lab Scale Evaluation of Circulating Cooling Water Hardness Removing Applied DSA Anode

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Keywords: Water Hardness Removing, Current Density, Inter-electrode Distance, Electrolysis, Dimensionally Stable Anode.

Abstract. In industrial production, calcium ions in water can cause scaling on the surface of heat exchanger in circulating cooling water system, resulting in problems such as reduced heat transfer efficiency, increased energy consumption and shortened service life of equipment. The surface of DSA electrode is coated with oxide coating, and its conductivity and catalytic performance are greatly improved compared with traditional electrode. The effects of current density, inter-electrode distance and electrolysis time on the hardness of circulating cooling water degraded by DSA electrodes were discussed. In the experiment, when the current density increases from 50A/m² to 250A/m², the removal rate of calcium ions increases continuously, with the highest removal rate of 53.7%. When the distance between anode and cathode plates increases from 2cm to 10cm, the removal rate of calcium ions decreases from 72.60% to 32.80%. When the raw water is electrolyzed for 10 minutes, the removal rate rises to 58.6%. As time goes on, the removal rate will not change. The experimental results provide valuable practical basis for the removal of calcium ions in circulating cooling water, and provide powerful data support for the optimal operation of the process.

Introduction

The most part of industrial cooling water contains and carbonate ions which are tend to induce scaling problems and serious failures such as efficiency decay of heaters or heat exchangers, pipe blocking, membrane clogging, etc.[1]. In order to prevent scaling, various methods just like chemical inhibition, chemical precipitation, acidification, ion exchange, and membrane technologies have been widely applied as a means of satisfied water softening[2,3]. However, all of these processes would result in harmful effects on environment, and some of these would require high power consumption and expenses to operate the treatment system.

In industry cooling water systems, the large submerged surfaces are present biofilms causing biofouling and microbially influenced corrosion, dramatically reduce the functionality of the cooling circuits[4,5]. Therefore, to reduce these problems, many biocides have been used in cooling water systems and its drainage also caused environmental problems[6].

In last few years, there appeared a kind of softening device for industrial cooling waters based on electrochemical methods[7-9]. A part of cycling water is piped into a series of electrolysers where electrical current passes between each set of electrodes. On the cathode of the electrolyser, the chemical and electrochemical reaction can be described as two elementary steps:

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

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

\[
\text{HCO}_3^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^{2-} \quad (3)
\]

\[
\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3 \quad (4)
\]
In this paper, simulative cooling water would be softened by Lab scale DSA anode experiment, related operational conditions would be evaluated at the same time.

Experiment

Experimental System
The experimental system consisted of a set of DC power and electrolysers. An electrode plate placement slot was provided every 1 cm in the length direction of the electrolyser to facilitate changing the inter-electrode distance. DC power supply (Yizhan Electronic Instrument Co., Ltd, Shenzhen of China) was used to supply power at a constant current intensity. The cathode was a 10 cm×10 cm titanium plated steel and the anode plate was a 10 cm×10 cm Ti/IrO\textsubscript{2}-RuO\textsubscript{2} electrode. The experimental system was shown as Figure. 1.

Raw Water
CaCl\textsubscript{2} and NaHCO\textsubscript{3} with certain weight were mixed into water to simulate hardness in certain concentration. The molar ratio between CaCl\textsubscript{2} and NaHCO\textsubscript{3} was 1:2. In addition, 2g of NaCl was added into a liter water to elevate the conductivity. The reagents used in the experimental were produced by Analytically pure Chemical Reagent Manufacturing Co., Ltd (Tianjin of China) were used in this experiment.

Analysis Methods
Water was sampled to determinate Ca\textsuperscript{2+} concentration by EDTA complexometric titration. Under each operational condition, three parallel samples were sampled during the experiment. The minimum detection concentration of this method is 0.05 mmol/L, and the repeatability deviation is ±0.04 mmol/L.

Results and Discussion

Current Density
Figure. 2 shown the change of hardness removal rate with time at different current intensity when using DSA electrode. Under the condition of 4cm electrode spacing and 10min electrolysis time, the hardness removal rate could reach 27.90% when the current density was 50A/m\textsuperscript{2}, and the hardness removal rate could reach 53.70% when the current density was 250 A/m\textsuperscript{2}. It could be observed that with the increasing of current density, the removal rate of hardness was higher, which meant that with the increase of current density, the effect of electrochemical action on water softening was better.
When the current density was greater than 200A/m², the hardness removal rate had little change with the increase of electrolysis time. Under the same experimental conditions, when the current density was 200 A/m², the hardness removal rate was 51.30%. Compared with the current density of 250A/m², the removal rate of hardness decreased by only 2.40%. The higher the current density, the higher the removal rate of electrochemical reaction, and the more OH⁻ produced by the reaction according to (1) and (2). When the current density was higher than 200A/m², excessive OH⁻ did not accelerate the formation of scaling. This might be explained by the fact that the rates of reaction (3) and (4) were limited by the convection-diffusion kinetics of calcium ions and bicarbonate ions to the reaction region[10].

When the current density was larger than 200A/m², the hardness removal rate tended to be stable, which meant that when the current density exceeded this value, a large part of the electric energy was consumed elsewhere, such as raising the water temperature. At the same current density, the hardness removal rate increased with the increase of electrolysis time, but the increase trend of hardness removal rate became more and more gradual, and finally reached a stable value. As the current intensity increased, the time required for the hardness removal rate to stabilize became shorter, and the stability value was also larger. At the beginning of electrolysis, the concentration of HCO₃⁻ and Ca²⁺ in the water was high, and the OH⁻ generated by the cathodic reaction rapidly reacted with HCO₃⁻ to form CO₃²⁻, so the hardness removal rate at the initial stage of electrolysis was high. With the prolongation of electrolysis time, HCO₃⁻ and Ca²⁺ in the water were continuously consumed by the reaction, which caused the concentration of HCO₃⁻ and Ca²⁺ to gradually decrease, resulting in a decrease for the chemical reaction rate, which slowed the growth rate of the hardness removal rate and finally reached a stable value.

**Inter-electrode Distance**

Inter-electrode distance was another important factor affecting electrochemical descaling of circulating cooling water. Fig.3 shown the change of hardness with time under different electrode plate spacing during electrolysis test with DSA electrode.
It could be seen that under the condition of the same current density and different plate spacing, the hardness removal rate varied greatly. This difference was more obvious when the plate spacing was small. When the electrolysis time was 10min, the hardness removal rate corresponding to the spacing of the plates were 72.60%, 59.40%, 48.40%, 38.50%, 32.80%, respectively. It was obvious that the hardness removal rate decreased with the increase of plate spacing. This was because the smaller inter-electrode distance, the larger the contact area between the solution and the plates, the more fully the electrochemical reaction was carried out, and the more OH$^{-}$ was generated at the cathode, thus improving the chemical reaction rate. Furthermore, when the plate spacing decreased, the Ca$^{2+}$ and HCO$_3^-$ present in the system could be diffused to the cathode reaction region more rapidly, where chemical reactions (3) and (4) could take place, thus making the Ca$^{2+}$ in the system more completely exhausted.

It was well known that the resistance of water and the energy loss due to ohmic drop were proportional to the distance between anode and cathode plates. For this reason, part of the current was consumed on the Ohm voltage drop without participating in the electrode reaction at a larger plate spacing, which led to a decrease in the electrolysis efficiency. Moreover, the larger the plate spacing, the lower the electrolysis efficiency. Regardless of the plate spacing, with the increase of electrolysis time, the increasing trend of hardness removal rate gradually decreased, and finally tended to be stable. Therefore, the smaller distance between plates, the better removal efficiency of scale in circulating cooling water.

**Electrolysis Time**

The degradation of pollutants in raw water by electrochemical experiments was studied under the conditions of plate spacing of 4cm, current density of 150A/m$^2$ and electrolysis time of 18 minutes. As could be seen from Figure 4, with the increase of electrolysis time, the hardness removal rate also increased, but the trend of hardness removal rate increased more and more gently, and the hardness removal rate finally reached a stable value. The hardness removal rate was 45.4% when the electrolysis lasted for 10 minutes.
With the extension of electrolysis time, the hardness removal rate basically did not change. With the prolongation of electrolysis time, on the one hand, the concentration of $\text{HCO}_3^-$ and $\text{Ca}^{2+}$ in water was gradually reduced, which led to the decrease of chemical reaction rate. On the other hand, the hydrogen evolution of the cathode in the electrolyzer led to less and less $\text{HCO}_3^-$ enriched to the cathode plate, which made the hardness removal rate increase steadily and finally reach a stable value.

**Conclusion**

In the current density range of 50A/m$^2$ to 250A/m$^2$, the hardness removal rate increases as the current density increases. When the current density is greater than 200A/m$^2$, the effect of the current density on the hardness removal rate is not obvious. This may be because the rate of scaling reaction is limited by the convection-diffusion kinetics of $\text{Ca}^{2+}$ and $\text{HCO}_3^-$ ions. The hardness removal rate is not linear with the change of electrolysis time, but with the extension of electrolysis time, the growth rate of hardness removal rate slowly decreases, and finally tends to be stable. The hardness removal rate decreases with the increase of plate spacing in the range of 2 cm to 10 cm. Under static test conditions, the optimum current density is 200A/m$^2$ and the optimum plate spacing is 2 cm.

**Acknowledgment**

The authors would like to express sincerely thanks for the financially support of Key Research and Development Project of Shandong Province (2016GSF117007), and sincerely express our gratitude for the constructive comments on the manuscript of reviewers and the Manuscript Editors.

**References**


