The Scale and Antiscale Study of the Reclaimed Water Re-used in Industrial Recycling Cooling System

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ABSTRACT
The reclaimed water of municipal sewage reused in industrial recycling cooling system is an effective approach to save water resource and improve the ecological environment. One of its critical factors is controlling scale formation in recycling cooling system. In this paper, the scale formation and antiscale influence factors of the reclaimed water reused in Beijing thermoelectric plant were investigated. The scale of the reclaimed water was measured by SEM, XRD and XRF techniques. Through the static and dynamic simulation test, we obtained an optimum composite antiscale. Furthermore, the effects of ion components, COD and turbidity of the reclaimed water on the scale inhibition efficiency were examined. This can provide a useful information basis for controlling and estimating risks of the reclaimed water reused in industrial recycling cooling system.

Keywords: reclaimed water; scale formation; scale inhibition efficiency

1. INTRODUCTION
Water pollution has become more and more serious with the increase of industrial water consumption, resulting in water resource shortage. The situation is especially in northern China where water shortage is restricting the development of the industry (Yu et al., 2002). Industrial recycling cooling system consumes large quantities of water during its continuous run. Since its demand for water quality is not extremely high, the reclaimed water from municipal sewage can be used to resolve the problem of water shortage (Li et al., 2001). Using reclaimed water in industrial cooling system could be an effective approach to save water resource, improve the ecological environment and realize the benign circulation of water ecology. Such kind of reclaimed water reuse has been reported in many countries such as America, Britain, South Africa and so on where water shortage problem is serious (Schweitzer, Strittmatter, Humphris, 1997). At present, the reclaimed water reuse in industrial cooling system is gradually promoted and expanded in China, mainly in thermal power plants (Fang et al., 2004; Carlson et al., Liu, 2008; Song, Wang, 2006; Wu, Liu, 2009). Because of the different sources and various treatment processes, the suitability of the reclaimed water quality to industrial reuse becomes an issue of wide concern. One problem related to this is scaling in the cooling system.

Scaling may cause under-deposit corrosion which may bring about serious damage of the cooling system, but also waste energy. In the past years, lots of research work against scaling, scale inhibition and scale cleaning (Yue et al., 2010). Beijing thermoelectric plant is one of the plants which have used the
reclaimed water as cooling water for a long time. In order to investigate the scaling problem related to the reclaimed water reuse, the authors established a dynamic cycle simulation system which uses the reclaimed water as make-up water and conducted a series of experiments. Part of the experimental work is reported in this paper dealing with the characteristics of scale and anti-scale in two condensers.

2. EXPERIMENTAL

2.1 Experimental Facility

The structure analysis of scale was carried out by DMAX-RA Rigaku X-ray diffractometer (XRD) with Cu Kα radiation operated at 40 kV and 100 mA.

The element analysis of scale was performed on Rigaku ZSX Primus I I X Ray Fluorescence (XRF).

A dynamic simulation experimental facility (Dynamic simulation method for cooling water HG/T 2160-2008) was established in Beijing thermoelectric plant. Because the scaling rate relates to the heat transfer area and the surface energy (Tsibouklis et al., 1999; Pereni et al., 2006; Watkinson et al., 1974; Yang et al., 2000; Zhang et al., 2008), so select two condensers of 304 stainless steel and HSn70-1A brass for study.

2.2 Experimental Condition

Table 1 The main water quality index of reclaimed water in Beijing thermoelectric plant

<table>
<thead>
<tr>
<th>Element</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>HCO$_3^-$</th>
<th>SO$_4^{2-}$</th>
<th>PO$_4^{3-}$</th>
<th>NH$_4^+$</th>
<th>NO$_3^-$</th>
<th>NO$_2^-$</th>
<th>COD</th>
<th>Turbidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content(ppm)</td>
<td>72.0</td>
<td>35.4</td>
<td>217.1</td>
<td>60.0</td>
<td>0.2</td>
<td>0.9</td>
<td>20.0</td>
<td>0.86</td>
<td>67.7</td>
<td>0.97NTU</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

3.1 The Analysis of the Scale

Figure 1 and Figure 2 show the XRD results of scale in 304 stainless steel tube and HSn70-1A brass tube respectively. From the XRD results, we found that the main component of the scale is magnesium calcite (Ca, Mg)CO$_3$ which resulting from the ions in reclaimed water (Zhang et al., 2007). Also, there is trace of quartz scale. A part of quartz scale might
be formed by the polymerization of silica gel, and the others might come from the sedimentary sand which accompanied with the cooling water accessing into the condensers. Besides, trace ferric scale was found in stainless steel condenser which arising from the corrosion of recycling cooling pipes to stainless steel condenser, but no ferric scale in the brass condenser.

**Figure 1**  XRD result of scale in 304 stainless steel tube

**Figure 2**  XRD result of scale in HSn70-1A brass tube

**Table 2**  The XRF result of scale
Element composition of the condenser:

<table>
<thead>
<tr>
<th>Element</th>
<th>O</th>
<th>Ca</th>
<th>C</th>
<th>Fe</th>
<th>Mg</th>
<th>Si</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>45.100</td>
<td>39.200</td>
<td>9.2400</td>
<td>1.4400</td>
<td>1.4200</td>
<td>1.2600</td>
<td>0.8190</td>
</tr>
<tr>
<td>Brass</td>
<td>47.300</td>
<td>36.500</td>
<td>8.9100</td>
<td>0.2610</td>
<td>1.4600</td>
<td>1.1500</td>
<td>0.4750</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Cr</th>
<th>S</th>
<th>Sr</th>
<th>K</th>
<th>Ni</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>—</td>
<td>0.4310</td>
<td>0.3600</td>
<td>0.1700</td>
<td>0.1210</td>
<td>0.0930</td>
<td>0.0757</td>
</tr>
<tr>
<td>Brass</td>
<td>0.1550</td>
<td>—</td>
<td>0.3750</td>
<td>0.1450</td>
<td>0.0611</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Ti</th>
<th>P</th>
<th>Zn</th>
<th>Mn</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>0.0708</td>
<td>0.0654</td>
<td>0.0505</td>
<td>0.0474</td>
<td>0.0274</td>
</tr>
<tr>
<td>Brass</td>
<td>—</td>
<td>0.0760</td>
<td>3.1600</td>
<td>—</td>
<td>0.0241</td>
</tr>
</tbody>
</table>

The XRF result of scale is shown in Table 2. The XRF result shows that the scale components of stainless steel condenser are similar to brass condenser. The scale composed of O, Ca, C and Mg, which was in accordance with the XRD results. The surface of stainless steel and brass tubes has equivalent siliceous scale. The Fe content in the stainless steel surface scale is higher, but the Cu and Zn contents in the brass surface scale are higher, which indicates that both stainless steel surface and brass surface has occurred certain corrosion leading to scale. In addition, the scale contains trace of S, P, Sr, Al, Cl and K. The existence of S, P indicates that cooling water system also contain a few sulfate scale and phosphate scale. Sr also generates the homologous carbonate scale, sulfate scale and phosphate scale which is similar to Ca and Mg. Cl and K might come from the soluble-salt adsorbed in the crystals. The stainless steel surface scale also contains trace of Cr, Ni, Na, Ti and Mn, which might result from the corrosion of stainless steel itself. The quantity of scale indicates that the scale products by stainless steel are obviously less than that by brass.

### 3.2 The Effects of Water Components on Antiscalant in Cooling System

#### 3.2.1 The effect of calcium ion

In the experiment, use calcium chloride to prepare the calcium ion solution of certain concentration. Control different concentrations of calcium ion by adding different amounts of prepared solution.

Figure 3 shows that the inhibition efficiency decreases with the increase of Ca$^{2+}$ concentration. The inhibition efficiency falls faster when above 1.5 times concentrate ratio (108ppm) and begins to falling down slowly when achieves 4 times concentrate ratio (288ppm). Ca$^{2+}$ is one of the important factor for scale and antiscalant in recycling cooling water (Maruthamuthu et al., 2010). With the increase of temperature and concentrate ratio, Ca$^{2+}$ and HCO$_3^-$ form precipitation:

$$\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 \downarrow + \text{CO}_2 \uparrow + \text{H}_2\text{O}$$

The maximum concentrate ratio in absence of inhibitor is 1.5 at 70°C (Zou and Yue, 2011), so it should be slightly below 1.5 at 80°C. Before the concentrate ratio reaches 1.5, very little amount of scale formed and inhibition efficiency falls not apparently. With the increase of Ca$^{2+}$, more and more scale formed, scaling rate accelerates and inhibition efficiency falls apparently. But when Ca$^{2+}$ concentration further increase, the scaling rate will decrease, because the total HCO$_3^-$ is constant, the demand of HCO$_3^-$ is increase. From the experiment result, Ca$^{2+}$ concentration should be controlled below 396ppm so as to prevent scaling.
3.2.2 The effect of magnesium ion

In the experiment, use magnesium chloride to prepare the magnesium ion solution of certain concentration. Control different concentrations of magnesium ion by adding different amounts of prepared solution.

Figure 4 shows that inhibition efficiency decreases slightly with the increase of Mg\(^{2+}\) concentration at first. The inhibition efficiency falls down from 62.9% to 61.3% when Mg\(^{2+}\) concentration changes from 35.4ppm to 70.8ppm. But the inhibition efficiency increases with the increase of Mg\(^{2+}\) concentration when it greater than 70.8ppm. This indicates that the existence of Mg\(^{2+}\) can prevent scaling. At home and abroad, documents have been reported that the existence of Mg\(^{2+}\) can reduce the scaling rate of CaCO\(_3\). Many researchers thought the reason why the existence of Mg\(^{2+}\) can retarded the growth of CaCO\(_3\) crystal is that the Mg\(^{2+}\) gather on the given high potential site of CaCO\(_3\) surface which leads to the distortions of CaCO\(_3\) lattice, then the speed of nucleus growth slows down (Bischoff, 1968; Epstein, 1978; Pytkowicz, 1965; Soror, 2009). The experimental result shows that when the concentration of Mg\(^{2+}\) achieves to 177.0ppm, it still has very good antiscale effect. In the reclaimed water, the content of Mg\(^{2+}\) less than the content of Ca\(^{2+}\), so needn’t do special treatment and control for Mg\(^{2+}\).

3.2.3 The effect of bicarbonate radical

In the experiment, use sodium bicarbonate to prepare the bicarbonate radical solution of certain concentration. Control different concentrations of bicarbonate radical by adding different amounts of prepared solution.

Figure 5 indicates that the Ca\(^{2+}\) concentration falls very fast with the increase of HCO\(_3^-\) concentration in the sample water without adding scale inhibitor. The concentration of Ca\(^{2+}\) drops 94ppm from 214ppm to 120ppm. A complex reaction of Ca\(^{2+}\) and scale inhibitor (Ca\(^{2+}\) + nL\(^-\) = CaL\(_n\)^{2-n}) first appeared when adding scale inhibitor into the sample water, at this time the Ca\(^{2+}\) is rare in the solution and HCO\(_3^-\) is rare too, the Ca\(^{2+}\) forms little scale, so at the start the concentration of Ca\(^{2+}\) almost unchanged (Shakkthivel and Vasudevan, 2006). But with the increase of HCO\(_3^-\), the concentration of Ca\(^{2+}\) falls slowly. It drops 18ppm from 258ppm to 242ppm. Therefore, on the one hand the inhibition is very obvious when adding scale inhibitor into sample water; on the other hand even with the existence of scale inhibitor, a little quantity of scale still formed. So we
should keep looking for new better scale inhibitor for improving inhibition effect.

![Figure 4](image1.png)
**Figure 4** The effect of Mg$^{2+}$ on scale inhibition

![Figure 5](image2.png)
**Figure 5** The effect of HCO$_3^-$ on scale inhibition

3.2.4 The effect of sulfate radical

To test the effect of sulfate radical on the inhibition efficiency, using sodium sulfate to prepare the sulfate radical solution of certain concentration. Control different concentrations of sulfate radical by adding different amounts of prepared solution.

Figure 6 shows that the inhibition efficiency of cooling water nearly unchanged with the increase of SO$_4^{2-}$. The un-dissolving sulfates are CaSO$_4$, SrSO$_4$, BaSO$_4$, and PbSO$_4$. Their solubility product constant are listed in Table 3 (Lide, 1990~1991).

The smaller solubility product constant is, the easier scale forms. SrSO$_4$, BaSO$_4$, and PbSO$_4$ are easy scaling owing to their relatively small solubility product constant. But because of Sr$^{2+}$, Ba$^{2+}$, Pb$^{2+}$ belong to trace elements, so they form very little scale. Although mass of Ca$^{2+}$ in the sample water, because of the solubility product constant of CaCO$_3$ is $4.96 \times 10^{-9}$ much smaller than the solubility product constant of CaSO$_4$, mass of Ca$^{2+}$ prior forms CaCO$_3$ deposits and the Ca-SO$_4$ deposits are very little. The XRF analysis
result shows that besides a large number of Ca\(^{2+}\) in the scale, a small quantity of S (0.36\%) and Sr (0.17\%) also exist in the scale. The result indicates that the sulfate scale is so little in the sample water, so the SO\(_4^{2-}\) has very little effect on scale and antiscale when the re-claimed water reused in cooling water system.

![Figure 6](image_url)  
**Figure 6** The effect of SO\(_4^{2-}\) on scale inhibition

<table>
<thead>
<tr>
<th>Un-dissolving sulfates</th>
<th>CaSO(_4)</th>
<th>SrSO(_4)</th>
<th>BaSO(_4)</th>
<th>PbSO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility product constant(25°C)</td>
<td>7.10×10(^{-5})</td>
<td>3.44×10(^{-7})</td>
<td>1.07×10(^{-10})</td>
<td>2.53×10(^{-8})</td>
</tr>
</tbody>
</table>

3.2.5 The effect of phosphate radical

In order to simulate the effect of phosphate on the inhibition efficiency in cooling water system, using sodium phosphate to prepare the phosphate radical solution of certain concentration. Control different concentrations of phosphate radical by adding different amounts of prepared solution.

Figure 7 shows that the inhibition efficiency decreases with the increase of PO\(_4^{3-}\) concentration which descends from the initial 80.5\% to the finally 70\%. In the beginning, the concentration of PO\(_4^{3-}\) is lower and the downtrend is accordingly slower, but when the PO\(_4^{3-}\) concentration is greater than 0.5ppm, the antiscale efficiency falls significantly. PO\(_4^{3-}\) is one of the main anions for scale in the cooling water, the solubility product constant of Ca\(_3\)(PO\(_4\))\(_2\) (2.07×10\(^{-33}\)) is far less than the solubility product constant of CaCO\(_3\) (4.96×10\(^{-9}\)), so the formation of Ca\(_3\)(PO\(_4\))\(_2\) is easier than that of CaCO\(_3\) in the cooling system. At first, the concentration of PO\(_4^{3-}\) is very low and the scale is very little, so the effect of PO\(_4^{3-}\) on the inhibition efficiency is little too. With the increase of PO\(_4^{3-}\), the content of Ca\(_3\)(PO\(_4\))\(_2\) also increase, and the crystal nucleus formed in front plays a induction role in the formation of precipitate, this accelerates the formation of Ca\(_3\)(PO\(_4\))\(_2\). At the same time, the reduction of inhibitor resulted from the adsorption of the suspended Ca\(_3\)(PO\(_4\))\(_2\) leads to the inhibition efficiency falling further. So suggest that the PO\(_4^{3-}\) concentration should be controlled lower than 0.5ppm in the cooling water system.
3.2.6 The effect of ammonia nitrogen

In order to research the effect of ammonia nitrogen on the inhibition efficiency in cooling water system, using ammonium chloride to prepare the ammonia nitrogen solution of certain concentration. Control different concentrations of ammonia nitrogen by adding different amounts of prepared solution.

Figure 8 shows that the inhibition efficiency increases slowly with the increase of NH$_4^+$ concentration at first. It changes from 65.6% to 68.3% when the NH$_4^+$ concentration changes from 0.9ppm to 4.05ppm, so it has little effect on the inhibition efficiency when the NH$_4^+$ concentration is lower. But the inhibition efficiency increases significantly when the NH$_4^+$ concentration was greater than 4.05ppm. This indicates that large amount of NH$_4^+$ can suppress the formation of CaCO$_3$. In water, the NH$_4^+$ can disintegrate out H$^+$ (NH$_4^+$→NH$_3$+H$^+$), with the increase of NH$_4^+$, the concentration of H$^+$ increases accordingly.

The reaction of HCO$_3^-$ and H$^+$ (HCO$_3^-$+H$^+$→H$_2$CO$_3$) results in the decrease of HCO$_3^-$ which suppress the formation of CaCO$_3$. Furthermore, the nitrification of ammonia nitrogen also can produce acidic materials which lead to the acidity further raise in actual cooling water system, thus further suppress the formation of CaCO$_3$. 

![Figure 7](image_url) The effect of PO$_4^{3-}$ on scale inhibition

![Figure 8](image_url) The effect of NH$_4^+$ on scale inhibition
3.2.7 The effect of COD

The organic composition in water is quite complex. Some researchers made their antiscale experiment with the water in primary setting tank and secondary setting tank, but the results showed that the organic had little effect on the performance of scale inhibitor (Dong et al., 2004). Someone else once made his antiscale experiment with glucose and the result showed that the inhibition efficiency decreased slightly with the increase of glucose (Wang, 2006). In this experiment, using potassium hydrogen phthalate to control the organic matter concentration.

Figure 9 shows that potassium hydrogen phthalate has little effect on the inhibition efficiency. So the organic doesn’t react with ions to form scale. Some organics can also antiscale, all kinds of organic inhibitors for example. But organic matter is the main source of nutrition for biological fouling, so from the perspective of reducing total fouling, the organic matter should be controlled in cooling water.

![Figure 9](image_url)

**Figure 9** The effect of COD on scale inhibition

3.2.8 The effect of turbidity

In order to research the effect of turbidity on the inhibition efficiency, in the experiment control different turbidities by adding different amounts of turbidity agent.

Figure 10 shows that the Ca\(^{2+}\) concentration decreases slowly at lower turbidity (< 2NTU) and decreases apparently at higher turbidity (2~5NTU), but with the further increase of turbidity (> 5NTU), it decreases slowly again. In cooling water system the scale formation must meet three conditions: solution reaches supersaturated status, the formation of crystal nucleus, the growth of crystal. If change one of the conditions, it will affect the formation of scale. The increase of turbidity equivalents to the increase of crystal nucleus, this prompts the growth of crystal and the increase of scale, so the inhibition efficiency reduces significantly. But with the decrease of Ca\(^{2+}\) concentration, the supersaturated status of the solution begins to reduce, so the crystallization rate declines and the downtrend of inhibition efficiency reduces. Turbidity is the important factor for scaling, so suggest control it below 2NTU.
3.2.9 The effect of nitrite ion and nitrate radical

In this experiment, using sodium nitrite and sodium nitrate to prepare the nitrite and nitrate radical solution of certain concentrations. Control different concentrations of nitrite and nitrate radical by adding different amounts of prepared solution.

Figure 11 and Figure 12 show that the content of NO$_2^-$ is very low in the reclaimed water but the content of NO$_3^-$ relatively high. Although the large difference between their content, they are both have little effect on inhibition efficiency when the concentration ratio between one and five.

The inhibition efficiency varied between 64.2% and 65.7% for NO$_3^-$ and between 58.6% and 63.3% for NO$_2^-$, both of the change is not obvious. The NO$_2^-$ which is easy be oxidized less stable than NO$_3^-$, so it has a slightly fluctuation. The experimental results illustrate that NO$_2^-$ and NO$_3^-$ nearly have no effect on scaling.
CONCLUSIONS

The surface scale analysis of stainless steel condenser and brass condenser show that the scale of reclaimed water reused in industrial cooling system are mass of calcite, a few quartz and pipe corrosion products, so the key control object is calcium scale, then the quartz and corrosion scale.

The influence regularity of various components on scaling show that Ca$^{2+}$, HCO$_3^-$, PO$_4^{3-}$ and turbidity have negative effects on scale and antiscaling in cooling water system, so these components should be controlled; Mg$^{2+}$ and ammonia nitrogen have positive effect on scale and antiscaling, the existence of Mg$^{2+}$ could lead to distortion of CaCO$_3$ and decrease the formation of scale; the dissociation and nitrification of ammonia nitrogen increased the acidity of the solution, reduced the concentration of HCO$_3^-$ and increased the inhibition efficiency. SO$_4^{2-}$, NO$_2^-$, NO$_3^-$ and COD have little or no effect on scale and antiscaling.

From this study, many kinds of measures can be used to control the scaling problem for cooling system and promotes the widely use of reclaimed water in recycling cooling system.

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