Experimental study on scale and corrosion inhibition of circulating cooling water in power plant

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Abstract: This paper introduced the research process of the static tests and the dynamic simulation tests for the circulating cooling water which used in a power plant. The appropriate scale inhibitor and the dosage were screened based on static tests (limited carbonate hardness test, pHc test, corrosion inhibition test, etc.), then the dynamic simulation test was used to simulate the practical system operation conditions, investigated the effect of scale inhibitor. The operating parameters obtained from the study are beneficial to water conservation, reduce the corrosion and scaling of the circulating water system, and have directive significance for the safe and economic operation and sustainable development for the power plant.

1. Introduction
In production process of thermal power plants, water is mostly used as the cooling medium for steam turbine exhaust, and the water consumption is very large, almost accounting for more than 97% of the total water consumption of the plant\textsuperscript{[1]}. In the situation of water shortage and environmental deterioration, increasing the concentration ratio of circulating water has great water-saving potential. In the circulating cooling water system, due to the concentration of salt, the decarbonization of cooling water and the rise of circulating water temperature in the operation process, fouling often forms in the condenser, which not only affects the heat transfer of the heat exchanger, blocks the pipeline, but also leads to under-deposit corrosion\textsuperscript{[2]}. Adding a certain amount of scale inhibitor\textsuperscript{[3]} to circulating water can take satisfactory scale inhibition effect. Different water quality and process require different scale inhibitors, so it is necessary to screen scale inhibitors according to the actual situation.

This paper is based on the actual situations of a power plant in Heilongjiang province. The static tests (the scale inhibiting test\textsuperscript{[4]}, the limited carbonate hardness test\textsuperscript{[5]}, the pHc test\textsuperscript{[6]}) were used to screening the scale inhibitor with good performance and the appropriate dosage was also determined. Then the practical operation and control indexes had been carried using the dynamic simulation test\textsuperscript{[7-9]}.

2. Test
2.1. Main parameters of circulating water system
The unit of the power plant in Heilongjiang is 300MW cogeneration units, the boiler is subcritical reheat natural circulation boiler, the steam turbine is single-shaft double cylinder double exhaust steam and double exhaust heat and condensate steam turbine, and the generator is hydrogen cooled generator.
The condenser type is n-17000-5, which is a single-shell, double-process and surface condenser, and the heat exchange pipe is made of stainless steel. Condensate pump is NLO250-370 x 8 (Ⅰ) vertical multistage centrifugal pump barrel bag type, flow rate of 419m³/h. The source of circulating water is river water, and the circulating water flow is 16236m³/h. During the actual operation of circulating water, the average temperature difference between condenser inlet and outlet is about 16.5℃, and the maximum temperature difference is 21℃.

2.2. The analysis of water
The trial water is the supplementary water used in the water circulating system witch provided by the power plant. The analysis results of the water are shown in table 1.

| Item | Outlook | pH | JD (mmol/L) | YD (mmol/L) | DD (μS/cm) | QG (mg/L) | Cl (mg/L) | Ca2+ (mg/L) |
|------|---------|----|-------------|-------------|------------|-----------|-----------|-------------|
| Unit | —       | 7.5| 2.31        | 2.52        | 319        | 262.0     | 17.71     | 81.3        |
| Data | clean   |    |             |             |            |           |           |             |

As can be seen in table 1, the alkalinity (JD) and hardness (YD) of the supplementary water was large. Due to the evaporation and other concentration process, the dissolved Ca²⁺ and Mg²⁺ forming calcium and magnesium carbonate, deposits on the metal surface will result in serious corrosion under the scale. Therefore, appropriate scale inhibitor should be used to improve concentration ratio and reduce scale deposition and slow down corrosion.

2.3. The scale inhibitors
The scale inhibitors used in the paper were provided by the power plant, named 1# and 2#. The properties are shown in table 2.

| Agents | Solid content (%) | pH | Density (g/m³) | Total phosphorus (%) |
|--------|------------------|----|----------------|---------------------|
| 1#     | 34.07            | 1.45| 1.220          | 0.33                |
| 2#     | 33.66            | 1.62| 1.215          | 0.40                |

2.4. The test equipments
The main equipment used in the test is rotation specimen tester(RCC-1) and dynamic simulation test device (WKMZ -II)

2.5. Test mental materials
Pipe: stainless steel, TP314
- Carbon steel specimens: A20, with an area of 28cm².
- Stainless steel specimens: TP314, with an area of 28cm².

3. Research process and result analysis
3.1. The static tests
In this part, comparative experiments were conducted to investigate the scale and corrosion inhibitors of the two scale inhibitors. And comprehensively analyzed the ultimate carbonate hardness, critical pH value and stable concentration rate of different agents with different dosages of different agents, and also the corrosion rates of stainless steel and carbon steel, the circulating water treatment agent witch suitable for this plant was screened out.

3.1.1. Scale inhibiting test. According to the standard"Guideline for anti-corrosion and anti-fouling of condenser tube in power pIant (DL/T300-2011)", when no chlorinated fungicides are used and water
quality is stabilized, $\Delta A$ is selected as the water quality stability index. When the $\Delta A$ is greater than 0.2, the water has a tendency to scale, and the operation conditions should be adjusted. Thereinto: $\Delta A = (c_{\text{circulating water}}/c_{\text{supplementary water}}) - (J_{\text{circulating water}}/J_{\text{supplementary water}})$.

The water samples (the circulating cooling water provide by the power plant) were added with different scale inhibitors, and then concentrated at the set temperature (45°C). Cl, YD, JD and Ca$^{2+}$ of concentrated water were detected during the concentration process and compared with supplementary water. According to $\Delta A$, determined the maximum stable concentration ratio that can be achieved at a given dosage. The concentration ratio (K) and $\Delta A$ were plotted with the 1.5 mg/L dosage of two agents, as shown in figure 1.

As can be seen in figure 1, if no scale inhibitor was used (figure. 1a), the circulating cooling water reached $\Delta A$ of more than 0.2 when the concentration ratio reached about 1.5, and the growth was fast, indicating that the circulating cooling water system was seriously scaling at this time. The using of the scale inhibitors (figure. 1b and figure. 1c) slowed down the scaling tendency of water. In addition, the scale inhibition performance of the two agents was different. Under the same dosage, the stable concentration ratio of 2# agent was 3.93, which was higher than 1#(3.20).

![Figure 1. The curve of concentration ratio (K) and $\Delta A$](image)

Next, the influence of scale inhibitors and dosages on scale inhibition rate was studied. We prepared the test water with concentration ratio of 3.5, adding different scale inhibitors with different dosages (from 0.5mg/L to 3.0mg/L). The scale inhibition rate are shown in figure 2.
According to figure 2, the scale inhibition effect of the two scale inhibitors was unsatisfactory when the dosages were less than 1.5 mg/L. The scale inhibition rate increased significantly when the dosages was more than 2.0 mg/L, while scale inhibitors 1# and 2# reached their maximum scale inhibition at 2.5 mg/L and 2.0 mg/L, respectively. The continuous increase of dosages had little effects on the scale inhibition rate, indicating that they had high efficient scale inhibition at low concentrations.

3.1.2. The limited carbonate hardness test. Different dosages of scale inhibitors were added to the supplementary water, circulating water was concentrated in a constant temperature water bath at \((45\pm1)\)°C, water quality was regularly analyzed, and water volume was timely replenished. The stable concentration ratio and ultimate carbonate hardness of the two agents at different dosages are shown in table 3.

Table 3. The results of limited carbonate hardness test

| Dosage | limited carbonate hardness (mmol/L) | K | △A   |
|--------|-------------------------------------|---|------|
| Item   |                                    |   |      |
| 0mg/L  | 1# 1.9                              | 1.6 | 0.23 |
| 0.5mg/L| 5.5 5.93                           | 2.45 2.8 | 0.25 0.27 |
| 1.0mg/L| 6.51 7.48                         | 2.82 3.39 | 0.27 0.27 |
| 1.5mg/L| 6.98 8.02                         | 3.2 3.93 | 0.26 0.28 |
| 2.0mg/L| 7.72 8.94                         | 3.53 4.09 | 0.27 0.30 |
| 2.5mg/L| 8.47 8.63                         | 3.81 3.80 | 0.28 0.26 |
| 3.0mg/L| 6.55 7.18                         | 2.95 3.26 | 0.28 0.26 |

The data in table 3 showed that with the increase of dosage, the stable limited carbonate hardness and stable concentration ratio of the two agents increased. Under the test condition, the maximum stable concentration rate of 1# was 3.81 when the dosage was 2.5 mg/L, and the limited carbonate hardness was 8.47. When the dosage of 2# was 2.0 mg/L, the maximum stable concentration rate was 4.09, and the limited carbonate hardness under this condition was 8.94.

3.1.3. The pHc test. Circulating water with concentration ratio of 3.5 was prepared, the pHc of circulating water without scale inhibitor (blank) was analyzed, contrasted with the pHc results of different agents and different dosages, as shown in figure 3.
It can be seen that the pHc value increased significantly after the addition of scale inhibitor, indicating that the addition of agent delayed the formation of precipitation. At the same time, compared with the results of scale inhibition rates, it was found that different kinds and dosages of scale inhibitors increased the pHc value to different degrees. The better the scale inhibition performance, the higher the pHc value, scale inhibitor 2# has better performance than 1#.

Figure 3. The effect of dosage on pHc

3.1.4. The Corrosion test The test was based on the standard "Determination of corrosion inhibition performance of water treatment agents-Rotation specimen method (GB/T18175-2014)". The experiment equipment was rotary specimens tester (RCC-I), and the dosage of scale inhibitor was 2.0mg/L. The test water was circulating water with the concentration ratio of 3.5, and was kept (45±1)℃. The test specimens were used A20 steel and stainless steel, the proportion of water volume and specimens area was 35mL/cm², with the rotation speed of 85r/min and 54h test time. At the end of the test, the specimens were taken out, and treated as required, dried and weighed, and the corrosion rate was calculated in table 4.

| Agents | Dosage   | Test specimens | Corrosion rate |
|--------|----------|----------------|---------------|
| 1#     | 2.0mg/L  | Stainless steel | 0.0007mm/a    |
|        |          | A20             | 0.044mm/a     |
| 2#     | 2.0mg/L  | Stainless steel | 0.0006mm/a    |
|        |          | A20             | 0.037mm/a     |

The surface of the stainless steel test specimens were smooth after the corrosion test, no pin-hole corrosion was found on the surface of the test specimens, and the corrosion rates of stainless steel were 0.0007mm/a and 0.0006mm/a, which were less than the specified value (0.005mm/a) in the standard "Code for design of industrial recirculating cooling water treatment (GB50050-2017)". A20 steel had a small amount of rust spots on the surface, and mostly found in the holes witch used for hanging. The calculated corrosion rates were 0.044mm/a and 0.037mm/a, which were less than the specified value(0.075mm/a).

Based on the comprehensive analysis of the above static tests, it was considered that scale inhibitor 2# had excellent scale inhibition performance, was selected with the dosage of 2.0mg/L for dynamic simulation test.
3.2. The dynamic simulation test
The test was carried out on the circulating water dynamic simulation test device according to the "Dynamic simulation method for cooling water (HG/T 2160-2008)". The test water quality are shown in table 5.

| Item | pH | DD μs/cm | JD (mmol/L) | YD (mmol/L) | Ca\(^{2+}\) (mg/L) | Cl\(^{-}\) (mg/L) |
|------|----|----------|-------------|-------------|----------------|----------------|
| Data | 7.86 | 377 | 2.28 | 2.79 | 84.57 | 20.67 |

Test conditions: Steam temperature was (100 ± 0.5) °C; Circulating water import temperature was (27 ± 0.5) °C; The circulating water flow rate is 175L/h, the length of the stainless steel test tube was 680 mm, and the effective heat transfer length was 500 mm. A20 steel and stainless steel specimens were placed at the import and export of the simulated heat exchanger.

Agent: 2#; Dosage: 2.0mg/L.

The results of dynamic simulation test are shown in table 6.

| Agent | Stable concentration ratio | Limited carbonate hardness | ΔA | pHc |
|-------|--------------------------|---------------------------|-----|-----|
| 2# 2.0mg/L | 5.11 | 11.26mmol/L | 0.35 | 11.37 |

In the dynamic simulation test, the concentration ratio of circulating water was higher than that obtained in the static test, which can reach 5.11. The limited carbonate hardness and pHc were improved to 11.26mmol/L and 12.37. In practical applications, 0.75-0.8 is usually multiplied on the basis of test data as a safer control value. Therefore, the concentration ratio is controlled to be less than 4.0. Also, the hardness and pH should be less than the limited values.

| Materials | Corrosion rate (mm/a) | The standard (GB50050-2017) |
|-----------|-----------------------|-----------------------------|
| A20 steel | entrance 0.0394        | <0.075mm/a                  |
|            exit 0.0427     | <0.075mm/a                  |
| Stainless steel test specimens | entrance 0.00015 | <0.005mm/a                |
|            exit 0.00046     | <0.005mm/a                  |
| Stainless steel test tube | 0.0017 | <0.005mm/a                |

The corrosion rates of specimens and stainless steel test tubes were measured and the results are shown in table 7. With changes in the operation of the circulating water quality, hardness and suspended state of impurity in the circulating water will gradually in the high heat load of condenser tube wall, which affects the condenser tube in heat efficiency, therefore the greater the fouling resistance of deposits on the inner wall of the condenser tube the more impurities, also explains the test sample in the dynamic test, the easier to form precipitation.
The transient heat resistance curve was shown in figure 4. The curve shows, there was an induction period at the initial stage of the system, during which the fouling deposition was very small, and the fouling resistance was very small at this time. With the growth of the dissolved salt crystal nucleus, the fouling gradually deposited, and the growth process of the fouling resistance shifted from the induction period to the constant growth and asymptotically balanced growth. During operation, the maximum of transient fouling resistance is $0.9622 \times 10^{-4} \text{m}^2 \cdot \text{K/W}$, then multiplied by 1.1, that is the annual fouling resistance is $1.1 \times 10^{-4} \text{m}^2 \cdot \text{K/W}$, this was less than the standard value $(3.44 \times 10^{-4} \text{m}^2 \cdot \text{K/W})$ in GB50050-2017.

According to the weight difference of stainless steel test tube before and after the dynamic simulation test, the inner fouling of stainless steel test tube was 55.8mg, and the basic properties of fouling are shown in table 8. Scale density was 0.558g/cm$^3$, average scale thickness was 0.0577mm, fouling deposition rate was 0.833mg/cm$^2$, and annual fouling thermal resistance was $1.1 \times 10^{-4} \text{m}^2$.

### 4. Conclusion

Combined with the water quality of the plant, the static test results showed that the scale inhibitor 2# had excellent efficiency in corrosion and scale inhibition, with higher stable limited carbonate hardness and pHc. According to the dynamic simulation test, the scale inhibitor 2# is optimized with the dosage of 2.0mg/L, and the concentration ratio of circulating water should be controlled below 4.0. Note that, in order to avoid or effectively slow down the scaling, corrosion and fouling deposition of circulating water system in actual operation, it is recommended to ensure the reliable service of rubber pellet scrubbing system. At the same time, the water quality of cooling water system (including supplementary water and circulating water) should be monitored regularly in daily operation.

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