Study on a solid slow dissolution sphere with corrosion inhibition

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Abstract. Many substances with excellent corrosion inhibition can’t be dissolved into aqueous solution according to the amount required by the formulation due to poor solubility, thus reducing the corrosion inhibition effect of the agent. Therefore, a spherical solid corrosion inhibitor has been developed. The effect of dosage and temperature on the corrosion inhibition rate was studied by corrosion test. The results showed that the best dosage of corrosion inhibition ball was 28.5mg/l, and the corrosion inhibition rate decreased with the increase of temperature. When the water temperature was 35 ℃, 45 ℃ and 55 ℃, the corrosion rates of carbon steel were 0.0243mm/a, 0.0306mm/a and 0.0559mm/a, which were lower than the national standard 0.075 mm / a indicating that the inhibitor has good corrosion resistance.

1. Introduction
Corrosion prevention of industrial circulating cooling system is the main aspect of water treatment. During the operation of circulating cooling water, there are several main corrosion phenomena, such as ion corrosion, cathodic corrosion, corrosion under scale and dissolved oxygen oxidation corrosion. The substances that can reduce, alleviate or even eliminate these corrosion phenomena are called corrosion inhibitors [1-3].

The inhibitor for water treatment is mainly composed of one or several substances with inhibition effect, and the water content of the product is 70-80%. Due to the different physical and chemical properties of the corrosion inhibitor, The solubility is very different, so many corrosion inhibitors can’t be prepared into aqueous solution at the required amount at the same time. That is to say, many excellent corrosion inhibitors cannot be prepared into solution at the desired amount. This kind of product reduces the corrosion inhibition effect [4-5]. Aiming at the above phenomena, in order to make full use of solid corrosion inhibitor with good corrosion inhibition effect and poor solubility and improve the corrosion inhibition effect, a solid-phase water treatment inhibitor was developed.
2. Experimental part

2.1. Water quality of experimental water sample
The experimental water sample is the make-up water of a chemical company in Cangzhou area, with pH = 7.8, calcium hardness of 128.5 mg / L, magnesium hardness of 106.4 mg / L, total alkalinity of 83.5 mg / L, conductivity of 469 μs / cm and chloride ion of 52.8 mg / L.

2.2. Reagents and instruments
Reagents: sodium tetraborate, sodium gluconate, EDTA, HEDP sodium salt, zinc sulfate, adhesive, additive, benzotriazole
Instruments: JA-4103 electronic balance, Shanghai balance instrument factory; SCRCC rotary coupon corrosion tester (10 holes); 724 spectrophotometer, Shanghai Optical Instrument Factory; A3 carbon steel test piece (50mm × 25mm × 2mm), Gaoyou Xinyou Instrument Factory

2.3. Inhibitor - Preparation of inhibitor solution ball
According to the characteristics, types, existing states of corrosion inhibitors and the principle of synergistic effect between them, and with reference to multiple corrosion tests, field applications and product prices, it is determined that the main ingredients of the formulation are sodium tetraborate, sodium gluconate, HEDP sodium salt and additives. According to the mass ratio of sodium tetraborate, sodium gluconate and HEDP sodium salt and additives, the formulation is 15 : 10:3:0.5 ratio for configuration, full mixing, mixing, pressure adjustment, through the thp-10 flower basket tablet press to produce water treatment inhibitor - Dissolution inhibition ball.

2.4. Evaluation method of corrosion inhibition performance
Weight loss method of rotating hanging piece [6]: GB / T 18175-2000 instrument: scrcc rotating hanging piece corrosion tester, test water: make-up water of a chemical company; A3 carbon steel sheet (50mm × 25mm × 2mm), test time: 72h; test temperature: 45 ℃; rotation speed: 75r / min, calculation formula of corrosion rate \( X_1 \) expressed in mm / A is:

\[
X_1 = \frac{87600 \times (m - m_0)}{s \cdot \rho \cdot t}
\]  

(1)

Where: \( m \) is the weight of the test piece before the test, g; \( m_0 \) is the weight of the test piece after the test, g; \( s \) is the surface area of the test piece, 28cm²; \( \rho \) is the density of the test piece, 7.850g/cm³; \( t \) is the test time of the test piece, 72h.

The calculation formula of the inhibition rate \( x_2 \) expressed in percentage is:

\[
x_2 = \frac{X_0 - X_1}{X_0} \times 100\%
\]  

(2)

Where: the corrosion rate of \( x_0 \) test piece in blank test, mm / a; the corrosion rate of \( x_1 \) test piece in reagent test, mm / a

3. Experimental results and discussion

3.1. Determination of inhibitor formula

3.1.1 test results of single component corrosion inhibition performance
The inhibition performance of sodium gluconate and sodium tetraborate was evaluated. The rotating hanging plate method is used, and the test water is 1.1 make-up water. See Table 1 and table 2 for the corrosion inhibition performance results of single components of sodium tetraborate and sodium gluconate, respectively.
Table 1. Corrosion inhibition performance of sodium gluconate

| Sodium gluconate (mg/L) | Weightlessness (g) | Corrosion rate (mm/a) | Corrosion inhibition (%) |
|------------------------|-------------------|-----------------------|--------------------------|
| 1                      | 0                 | 0.1727                | 0.9562                   | ---                       |
| 2                      | 100               | 0.0819                | 0.4533                   | 52.59                     |
| 3                      | 200               | 0.0662                | 0.3664                   | 61.68                     |
| 4                      | 300               | 0.0487                | 0.2696                   | 71.81                     |
| 5                      | 400               | 0.0376                | 0.2081                   | 78.24                     |
| 6                      | 500               | 0.0196                | 0.1085                   | 88.65                     |

Table 2. Corrosion inhibition performance of sodium tetraborate

| Sodium tetraborate (mg/L) | Sodium gluconate (mg/L) | Weightlessness (g) | Corrosion rate (mm/a) | Corrosion inhibition (%) |
|--------------------------|------------------------|-------------------|-----------------------|--------------------------|
| 1                        | 0                      | 0.1727            | 0.9562                | ---                       |
| 2                        | 75                     | 0.0783            | 0.4337                | 54.64                     |
| 3                        | 150                    | 0.0552            | 0.3054                | 68.06                     |
| 4                        | 200                    | 0.0288            | 0.1759                | 82.32                     |
| 5                        | 250                    | 0.0151            | 0.1085                | 91.27                     |
| 6                        | 300                    | 0.0132            | 0.0731                | 92.35                     |

It can be seen from table 1 and table 2 that the corrosion inhibition performance increases with the increase of agent concentration. If you want to get ideal corrosion inhibition effect by using alone, the agent quantity is large and the cost is high. From the experimental phenomenon, when the dosage is low, the surface corrosion is serious and the pitting corrosion is deep; when the concentration is high, the pitting depth is obviously reduced.

3.1.2 Compound formula screening

In order to reduce the amount of inhibitor, the synergistic inhibition performance between the two was measured first, and the results are shown in Table 3.

Table 3. Test results of synergistic corrosion inhibition performance of sodium tetraborate and sodium gluconate

| Sodium tetraborate (mg/L) | Sodium gluconate (mg/L) | Weightlessness (g) | Corrosion rate (mm/a) | Corrosion inhibition (%) |
|--------------------------|------------------------|-------------------|-----------------------|--------------------------|
| 1                        | 30                     | 40                | 0.0500                | 0.2770                   | 71.03                     |
| 2                        | 30                     | 50                | 0.0330                | 0.1824                   | 80.92                     |
| 3                        | 30                     | 60                | 0.0221                | 0.1223                   | 87.21                     |
| 4                        | 40                     | 40                | 0.0147                | 0.0816                   | 91.47                     |
| 5                        | 40                     | 50                | 0.0116                | 0.0644                   | 93.26                     |
| 6                        | 40                     | 60                | 0.0108                | 0.0597                   | 93.75                     |
| 7                        | 50                     | 40                | 0.0111                | 0.0614                   | 93.57                     |
| 8                        | 50                     | 50                | 0.0079                | 0.0431                   | 95.49                     |

It can be seen from table 3 that the corrosion inhibition performance of binary composite agent is significantly higher than that of sodium tetraborate and sodium gluconate alone. When the dosage of sodium tetraborate is 40mg/L, the dosage of sodium gluconate is 50mg/L, the inhibition rate is 93.26%. It can be seen that there is obvious synergistic effect between sodium tetraborate and sodium gluconate.

In order to save the cost of the agent, HEDP sodium salt with corrosion inhibition was introduced, and a ternary composite agent was prepared by using the synergistic corrosion inhibition among the
three agents. Considering the requirement of phosphorus content emission, the concentration of HEDP sodium salt in the formula is 3mg / L. The test results of corrosion inhibition performance of composite agent are shown in Table 4.

Table 4. Corrosion inhibition test results of ternary composite agent

| Reagent concentration (mg/L) | Weightlessness (g) | Corrosion rate (mm/a) | Corrosion inhibition (%) |
|-----------------------------|-------------------|-----------------------|--------------------------|
| Sodium tetraborate          | Sodium gluconate  | HEDP sodium salt      |                          |
| 1 10                        | 10                | 3                     | 0.0176                   | 0.0974                   | 89.81 |
| 2 10                        | 15                | 3                     | 0.0101                   | 0.0559                   | 94.15 |
| 3 10                        | 20                | 3                     | 0.0072                   | 0.0398                   | 95.84 |
| 4 15                        | 10                | 3                     | 0.0064                   | 0.0354                   | 96.30 |
| 5 15                        | 15                | 3                     | 0.0052                   | 0.0288                   | 96.99 |
| 6 15                        | 20                | 3                     | 0.0044                   | 0.0243                   | 97.46 |

It can be seen from table 4 that the addition of HEDP sodium salt makes the dosage of sodium tetraborate and sodium gluconate significantly reduced, and the synergistic effect of the three is significant. When the dosage of sodium tetraborate and sodium gluconate is 15mg / L and 10mg / L respectively, and the total dosage is 28mg / L, the corrosion inhibition rate is up to 96.30%, corrosion rate is 0.0354mm/a , lower than the allowable upper limit of corrosion rate of carbon steel pipe wall in code for design of industrial circulating cooling water treatment 0.075mm/a . From the experimental phenomenon, the corrosion trace on the surface of the test piece can hardly be seen by the naked eye.

In order to develop the inhibitor for dissolution ball, a certain amount of additives need to be added. The concentrations of fixed sodium tetraborate, sodium gluconate and HEDP sodium salt are 15mg / L, 10mg / L and 3mg / L respectively, and different additives are added. The test results are shown in Table 5.

Table 5. Formula test results

| code | Reagent concentration (mg/L) | Weightlessness (g) | Corrosion rate (mm/a) | Corrosion inhibition (%) |
|------|-----------------------------|--------------------|-----------------------|--------------------------|
| A    | 15 3 10 0.25               | 0.0076             | 0.0421                | 95.59                    |
| B    | 15 3 10 0.50               | 0.0052             | 0.0288                | 96.99                    |
| C    | 15 3 10 0.75               | 0.0058             | 0.0320                | 96.65                    |
| D    | 15 3 10 1.00               | 0.0064             | 0.0354                | 96.30                    |

From the data in Table 5, it can be seen that the addition of additives has little effect on the formula, and the corrosion rate of each formula is very small, and the corrosion rates of formula A, B, C and D are all over 95%. Considering the production process, operation cost and corrosion inhibition effect, formula B with lower total concentration was selected as the compound formula.

3.2. Study on the corrosion inhibition performance of corrosion inhibition ball

3.2.1 The effect of dosage on corrosion inhibition rate

After determining the formulation of the corrosion inhibitor, the effect of the amount of inhibitor on the corrosion inhibition rate is determined through the corrosion experiment, and the results are shown in the figure below.
It can be seen from the above figure that with the increase of the amount of inhibitor, the corrosion inhibition rate keeps increasing. When the amount of inhibitor is less than 28.5 mg / L, the effect of the corrosion inhibition rate is not good; when the amount of inhibitor is 28.5 mg / L, the corrosion inhibition rate is 96.8%, and the corrosion rate is 0.0306 mm/a. At this time, the corrosion inhibition rate of the agent has completely reached the national standard. The dosage continued to increase, and the corrosion inhibition rate tended to be stable. From the economic aspect, the concentration was 28.5 mg / L.

3.2.2 Effect of temperature on corrosion inhibition rate

Three different temperatures (35℃, 45℃ and 55℃) are used to represent the common temperature of circulating water. The amount of chemicals used is twenty-eight point five mg/L, see the table below for the experimental results.

| Temperature (℃) | Weightlessness (g) | Corrosion rate (mm·a⁻¹) | Corrosion inhibition (%) |
|-----------------|--------------------|--------------------------|--------------------------|
| 35              | 0.0044             | 0.0243                   | 97.46                    |
| 45              | 0.0055             | 0.0306                   | 96.80                    |
| 55              | 0.0101             | 0.0559                   | 94.15                    |

It can be seen from table 6 that as the temperature increases, the weight loss of the hanging piece increases in turn, the corrosion rate increases and the corrosion inhibition rate decreases. At three different temperatures, the corrosion rate of carbon steel is respectively 0.0243 mm/a , 0.0306 mm/a and 0.0559 mm/a , lower than the national standard 0.075 mm/a , the water temperature of circulating water in industrial enterprises is generally not higher than 55 ℃, indicating that the corrosion inhibitor has good corrosion inhibition effect on A3 carbon steel at different temperatures, reaching the specified standard.

4. Conclusion

The main components of solid corrosion inhibitor are sodium tetraborate, sodium gluconate, HEDP sodium salt and additives. The mass ratio of the four components is 15:10:3:0.5 The results show that at 45 ℃, the corrosion rate of carbon steel is 0.0306 mm / a and the amount of inhibitor is 28.5, which is superior to the national standard and has good synergistic effect.
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