Research on Performance of a Kind of Compound-type Corrosion-Inhibition Bactericide

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Abstract. In the experiment, rotative weight loss method, electrochemical polarization, MPN, etc. were used to investigate the corrosion inhibition and bactericidal performance of compound-type corrosion-inhibition bactericide composed of phosphono- and carboxyl quaternary ammonium salt, etc. on A3 carbon steel in industrial recycling cooling water. The experimental test results showed that when the content of compound agentia reached 100 mg. L⁻¹, the corrosion rate of it on A3 carbon steel was 0.0366 mm. a⁻¹, superior to relative standard regulations, less than 0.075 mm. a⁻¹. While metallographic-phase microscopy test showed that there is a layer of protective film on the surface of A3 carbon steel, which indicated that compound agentia had relatively better corrosion-inhibition effect on A3 carbon steel; when the content of compound agentia reached 80-100 mg. L⁻¹, the sterilizing rate of compound agentia on heterotrophic bacterium and sulfate reducing bacteria were up to more than 99%, which indicated that compound agentia had good bactericidal performance.

1. Introduction

In electric power, metallurgy and chemical engineering industry, recirculating cooling water system for central air-conditioning is mainly composed of pipe and devices mainly made of carbon steel. When it is used in high-temperature circulating water with higher concentration ratio, oxygen absorption corrosion of metal and microbiological corrosion mainly caused by total general bacteria (TGB) and sulfate reducing bacteria (SRB) can be generated [1-2]. In actual application, chemical agentia is added to effectively resolve such problem. Single agentia only has single role, while different agentia mixing can decrease respective effect. Therefore, it is of great significance to studying the compound agentia with multiple functions.

The organic phosphonate with phosphono (-CPO₃H) can chelate with multiple metal ions in the water, to form the metal chelates, and its C-P bond with high chemical stability can’t be easily hydrolyzed [3]; carboxyl quaternary ammonium salt has the bactericidal performance due to containing the positively-charged quaternary ammonia ions [4]. In the paper, we especially investigated the corrosion inhibition and bactericidal performance of compound-type corrosion-inhibition bactericide composed of phosphono- and carboxyl quaternary ammonium salt on recirculating cooling water system for central air-conditioning.

2. Experiment

2.1. Preparation of Compound Agentia

Compound agentia is the quaternary ammonium salt composed of phosphono (-CPO₃H) 2-
Phosphonobutane-1,2,4-tricarboxylic acid and carboxyl quaternary ammonium salt.

Preparation of phosphono organic phosphonate
Add 3 times (molar ratio) of solid chloroacetic acid into the bisphenol A hot alkaline solution of 90℃ gradually, after reflux reaction for 2h, cooling, acid pickling and filtering were performed, the filter cake was recrystallized by acetic acid, to get the 2-Phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) [5] with purity of 98%.

Preparation of Carboxyl Quaternary Ammonium Salt
Weigh and add certain amount of tetradecyl methyl carbonate trimethyl quaternary ammonium salt and solvent ethyl alcohol into a 250ml four-neck flask, heat it under continuous agitating to the set temperature of 130℃, after completely dissolved, certain volume of acetic acid was added through a pressure equalizing dropping funnel. At this temperature, agitating was done for 2-3h, then the pale yellow liquid was got. After decompressed and solvent was removed in a rotary evaporator, the crude product was got. The crude product was recrystallized by ethyl acetate for 5 times, and dried for 6-8h in vacuum circumstance, then, the white solid product tetradecyl trimethyl ammonium acetate (TTAA) [6] with purity of 98% was got.

Formula of Compound-type Corrosion-inhibition Bactericide
Benzotriazole (BTA) 10 mg. L⁻¹ + 30 mg. L⁻¹ polymaleic acid (PMA) + 50 mg. L⁻¹ 2-Phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) + 500 mg. L⁻¹ tetradecyl trimethyl ammonium acetate (TTAA).

2.2. Corrosion-inhibition Experiment
Corrosion inhibition of compound agentia was tested by weight loss method. Instrument: RCC-l rotary coupon corrosion test instrument, material: A3 carbon steel standard test piece, specification: 50mm×25 mm×2mm, precision: 0.1mm, hanging hole: φ4.0±0.1mm, surface area: 28cm²: experiment medium: recirculating cooling water system for central air-conditioning indicated in table 1 of Item 1.6, test piece was completely immersed, experiment temperature: 50±2℃, experiment period: 72h. After experiment, test piece surface was cleaned with a scrubbing brush, and washed with acid, tap water, alkali, deionized water and absolute ethyl alcohol successively, dried to constant weight, and placed for 24h, then weighed, to calculate the corrosion rate [7].

2.3. Electrochemical Test
Electrochemical test was performed to investigate the corrosion inhibition of compound agentia. Instrument: CS dual unit electrochemical workstation, three-electrode system: auxiliary electrode is platinum electrode, reference is electrode saturated calomel electrode, research electrode is small cylinder of surface 1 cm² made of A3 carbon steel, the non-working surface is sealed with epoxy resin. Experiment medium is recirculating cooling water system for central air-conditioning, experiment temperature: room temperature.

2.4. Mirror Test
The blank sample solution and A3 carbon steel test piece in 80 mg/L compound agentia were longitudinally cut, inlaid, polished and eroded, thickness of film of A3 carbon steel test piece surface was tested in accordance with operation requirements of metallurgical microscopy and test requirements of this experiment. Test was done with a AE2000MET digital inverted metallurgical microscopy, with magnification of 400X.

2.5. Bactericidal Experiment
TGB and SRB in recirculating water at production site were used for enrichment culture of strains, bacteria quantity: TGB of 10⁵~10⁷个/ml; SRB of 10²~10⁶/ml. According to GB/T 22595-2008[8] and GB/T 14643.5-2009[9], number of TGB and SRB in recirculating cooling water before and after adding compound agentia was determined respectively.

2.6. Experiment Medium
The recirculating cooling water for central air-conditioning of Crowne Plaza was used as the experiment
medium, its main parameters are as shown in table 1:

**Table 1. Main Parameters of Recirculating Cooling Water (mg. L⁻¹).**

| Parameter Index | Ca²⁺ | Hardness | Alkalinity | Cl⁻ | Fe²⁺ | pH  |
|-----------------|------|----------|------------|-----|------|-----|
| Parameter data  | 108  | 360      | 203        | 40  | 0.5  | 7.3 |

3. Results and Discussions

3.1. Corrosion Inhibition of Compound Agentia

Corrosion inhibition results of different-concentration compound agentia on A3 carbon steel in recirculating cooling water refer to table 2.

**Table 2. Corrosion Inhibition Role of Compound Agentia on A3 Carbon Steel in Recirculating Cooling Water.**

| Concentration of compound agentia (mg.L⁻¹) | Corrosion rate (g.m⁻².h⁻¹) | Inhibition efficiency (%) |
|------------------------------------------|-----------------------------|----------------------------|
| 0                                        | 0.2167                      | -                          |
| 20                                       | 0.1426                      | 34.2                       |
| 40                                       | 0.1281                      | 37.4                       |
| 60                                       | 0.0979                      | 54.8                       |
| 80                                       | 0.0747                      | 65.5                       |
| 100                                      | 0.0326                      | 85.0                       |

Note: temperature is 50°C, soak period is 72h.

Seen from table 2: the inhibition efficiency of compound agentia increases along with increase of its concentration, its corrosion inhibition is especially apparent. When its concentration reaches 100 mg. L⁻¹, the inhibition efficiency is 85%, when the corrosion rate of A3 carbon steel reduces to 0.0366 mm/a, far below the value less than 0.075 mm. a⁻¹ specified in GB/T 50050-2017 Code for Design of Industrial Recirculating Cooling Water Treatment [10]. This indicated that the compound agentia with the structure of phosphono- and carboxyl quaternary ammonium salt has relatively better corrosion-inhibition effect on A3 carbon steel.

3.2. Electrochemical Behavior of Compound Agentia

3.2.1. Polarization Curve of Different-concentration Compound Agentia

Potentiodynamic scan curve of A3 carbon steel in recirculating cooling water with concentration-compound agentia refer to figure 1.

**Figure 1. Polarization Curve of A3 Carbon Steel in Different-concentration Compound Agentia Solution.**
Seen from figure 1: cathodic polarization and anodic polarization of polarization curve of A3 carbon steel in recirculating cooling water with compound agentia apparently increase, indicating that the compound agentia can apparently inhibit the cathodic and anodic polarization process of electrode, and belongs to the mixed-type corrosion inhibitor. The lower-concentration compound agentia can mainly inhibit the cathodic polarization process, while high-concentration one is of higher effect in inhibiting the anodic polarization process.

3.2.2. Corrosion Potential of Different-concentration Compound Agentia

Corrosion potential of A3 carbon steel in recirculating cooling water with different-concentration compound agentia refers to table 3.

Table 3. Corrosion Potential of Different-concentration Compound Agentia on A3 Carbon Steel.

| Concentration of compound agentia(mg.L⁻¹) | 0   | 20  | 40  | 60  | 80  | 100 |
|------------------------------------------|-----|-----|-----|-----|-----|-----|
| E(mV)                                    | -653| -517| -501| -485| -469| -452|

Seen from table 3, it can be seen that the compound agentia can make the corrosion potential apparently positively shifted, when its concentration is up to 100 mg. L⁻¹, positively shifted potential is about 200 mV. By comprehensively analyzing such electrochemical experiment data and weight loss experiment results, we find that the significant positive shift of corrosion potential and increased cathodic/anodic polarization can greatly decrease the corrosion rate of A3 carbon steel in industrial recycling cooling water.

3.2.3. Surface Appearance

Figure 2 refers to the appearances of blank A3 carbon steel coupon not provided with compound agentia and A3 carbon steel coupon provided with compound agentia. It can be seen that the surface of blank A3 carbon steel coupon not provided with compound agentia is in coarse and dark black color. While the surface of A3 carbon steel coupon provided with compound agentia of 80 mg/L is in original carbon steel metal luster.

![Figure 2. Surface Appearances of Blank A3 Carbon Steel Coupon Not Provided with Compound Agentia and Coupon provided with Compound Agentia of 80 mg. L⁻¹.](image)

3.2.4. Test on Surface Film

Figure 3 and 4 refer to the metallographs of cross sections of blank A3 carbon steel coupon and A3 carbon steel coupon provided with compound agentia of 80 mg. L⁻¹.
From the metallographic microstructure test results of A3 coupon cross section, it can be seen that surface of A3 carbon steel coupon in blank sample solution (figure 3) has no film, its appearance is dark and coarse. A3 carbon steel in compound agentia sample solution has a layer of even and compact film with uniform thickness of about 18.11 μm. After treated by compound agentia, the film is in bright color and metal luster, apparently, its corrosion resistance is greatly enhanced than that not in the compound agentia sample solution.

3.3. Bactericidal Performance of Compound Agentia

Experimental strains are TGB and SRB enriched-cultured in recirculating cooling water at the production site. Experimental results were got by the principle of dilution-to-extinction method. The bactericidal experiment results of compound agentia refer to table 4 and table 5.

Table 4. Rate of Sterilizing TGB after Adding Compound Agentia for 24h.

| Compound agentia(mg.L⁻¹) | 80   | 100  |
|--------------------------|------|------|
| Survived bacteria(pieces/ml) | $1.5 \times 10^3$ | $0.2 \times 10^2$ |
| Sterilizing rate(%)       | 99.4 | 99.992 |

Note: initial bacteria number is $2.5 \times 10^5$/ml.
Table 5. Rate of Sterilizing SRB after Adding Compound Agentia for 24h.

| Compound agentia(mg.L⁻¹) | 80    | 100   |
|--------------------------|-------|-------|
| Survived bacteria(pieces/ml) | 1.5×10³ | 0.3×10² |
| Sterilizing rate(%)       | 99.75 | 99.995 |

Note: initial bacteria number is 6.0×10⁵/ml.

The experimental results of table 4 and 5 indicated that after the compound agentia acts for 24h, its sterilizing rates on TGB and SRB are up to more than 99%. The compound agentia is of the molecular structure with positively-charged quaternary ammonium cations, which can change the osmotic pressure of cell wall by being absorbed onto the negatively charged bacteria surface, making the thalli ruptured. In addition, hydrophobic group and hydrophilic group in compound agentia can penetrate into the lipoid layer and protein of bacteria cell, to result in enzyme inactivation, protein denaturation and death [4], thus, the compound agentia has good bactericidal performance.

4. Analysis on Principle of Corrosion-Inhibition Bactericide

Compound agentia contains phosphono- and carboxyl quaternary ammonium cation and hydrophobic alkyl long-chain group, its synergistic effect can realize the corrosion inhibition on metal carbon steel and sterilizing effect on TGB and SRB. Phosphonyl functional groups (-CPO₃H) can chelate with Fe²⁺, Ca²⁺, Mg²⁺ and other ions [11] in recirculating cooling water, then, the generated chelates can cover the surface of carbon steel metal. The positive charges carried by ammonium cation carboxylate group can be absorbed at the cathode region of metal carbon steel surface by the electrostatic attraction. Additionally, the non-polar hydrophobic alkyl long-chain group can be vertical to metal carbon steel surface and stretched into the solution, then, the formed water-repellent layer can hinder contact of solution with carbon steel surface. Thus, under the joint action of functional groups in compound agentia, a layer of complete compound protective film can be formed on the carbon steel surface, to inhibit anodic stripping of carbon steel and cathode diffusion of dissolved oxygen in the water, to realize better corrosion inhibition. The weight loss test indicated that when the concentration of compound agentia reaches 80-100 mg/L in recirculating cooling water, the surface of carbon steel coupon is in even and apparent metal luster, without rustiness. The appearance photos and cross section metallographic tissue test experiment performed on blank A3 carbon steel experiment coupon not in the compound agentia and A3 carbon steel experiment coupon in 80 mg/L compound agentia also verified such viewpoint.

5. Conclusion

In this research, the weight loss and electrochemical test results indicated that the compound-type corrosion-inhibition bactericide can inhibit the cathodic and anodic reactions during A3 carbon steel corrosion, corrosion rate on A3 carbon steel was up to 0.0366 mm/a, inhibition efficiency was up to 85 %, superior to the corrosion indexes specified in relevant standards. The metallographic test on surface film also indicated that the compound agentia can form a layer of compact and even film on A3 carbon steel surface, to greatly enhance the anti-corrosion performance of carbon steel. The bactericidal test results indicated that sterilizing rate of compound-type corrosion-inhibition bactericide on SRB and TGB were up to more than 99%.

The compound-type corrosion-inhibition bactericide has better corrosion inhibition and bactericidal performance. It can be widely applied to corrosion resistance and sterilization on recirculating cooling water system pipe network and carbon steel equipment of electric power, chemical engineering industry, metallurgy and central air-conditioning.

References

[1] Dong Q Y and Zhang Q 2004 Corrosion and Protection Synergistic Effect of Carboxylic Acid Copper Corrosion Inhibitor and Benzotriazole in Seawater 25 426-28.
[2] Li Y 2015 *Cleaning World* Corrosion Properties and Corrosion Inhibition Mechanism of Bis-quaternary Ammonium Compound Inhibitors 31 24-9.

[3] Kalman E, Karman F H, et al. 1993 *Corros. Sci.* Inhibition efficiency of N-containing carboxylic and carboxy-phosphonic acids 35 1477-82.

[4] Zhang S C, Wu Z L and Chen J P 2001 *Industrial Water Treatment* Researches on the Performance and Corrosion Inhibiting Mechanism of Corrosion Inhibitor and Germicide, PS-12 21 16-8.

[5] Jia F C 2008 *J. Henan Mech. Electric. Eng. College* Performance Measurement of DG4 Corrosion and Scale Inhibitor and Bactericide 16 10-1.

[6] Yan H C 2012 Synthesis and Properties of Quaternary Ammonium Salts with Carboxylate Counterions, China Research Institute of Daily Chemical Industry.

[7] GB/T 18175-2014 2014 Determination of Corrosion Inhibition Performance of Water Treatment Agents - Rotation Specimen Method.

[8] GB/T 22595-2008 2008 Test Method for Efficacy of Antimicrobials - Aerobic Bacteria [S].

[9] GB/T 14643.5-2009, Industrial Circulating Cooling Water - Sulfate - Reducing Bacteria - MPN Test. 2009.

[10] GB/T 50050-2017, Code for Design of Industrial Recirculating Cooling Water Treatment. 2017.

[11] Ma W J and Tang L Q, et al. 2016 *Corrosion Protection Petrochem. Industry Res.* Progress of Bactericide with Corrosion Inhibition Performance 13 1-5.