

CORROSION COUPON TESTING OF COMMERCIAL INHIBITOR IN SIMULATED COOLING WATER

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:

In maintaining cooling systems, one of the biggest challenges is to control the corrosion process. Various corrosion inhibitors are often used for this purpose. Which type of corrosion inhibitor will be chosen depends on the material from which the plant has made. The main causes of corrosion in these systems are: pH, dissolved gas, ammonia, temperature and microbiology. In this paper it was studied the efficiency of two multicomponent commercial corrosion inhibitors based on phosphates and one of which containing zinc chloride. For the purposes of research, the pilot plant of open recirculation cooling system is constructed and made of stainless steel (EN 1.4301) and copper (EN 13601). Experiments were performed in a simulated cooling water with recirculated for 3.5h. For the purpose of accelerating corrosion processes, it was added a corrosion activator (5% NaCl). It was monitored the corrosion rate of the mentioned materials in the cooling water with the corrosion activator, with and without inhibitor. Corrosion rate is determined by using corrosion coupons according standard ASTM D2688 and by analyzing physical-chemical parameters of cooling water. The results showed it was achieved higher protection efficiency for copper and stainless steel by using an inhibitor containing zinc chloride in addition to phosphate.

KEYWORDS: pilot plant, corrosion rate, stainless steel, copper.

INTRODUCTION

The corrosion in a cooling water system is defined as the electrochemical degradation of a metal that is in contact with cooling water. This process degrades the metal, reduces its strength, thickness, and in some extreme cases, creates pits and then holes in the material. At some point in the corrosion process, the metal can no longer do its job as a system component [1].

Circulating cooling water used to supply the cooling systems usually contains calcium and magnesium ions at concentrations of 10 to 600 ppm, in addition to these, there are bicarbonate ions. Because of continuous recycling, the water quality of cooling water becomes more concentrated leading to corrosion, fouling, scale forming and microbial breeding, which results in lower heat transfer efficiency of heat exchangers, corrosion and perforation of metal pipelines, and safety issues. In order to avoid this, cooling water is usually chemically treated with inhibitors and biocides to avoid corrosion, formation of scaling and fouling. It is common to use scaling inhibitor like phosphates, polyphosphates, and organophosphonates, and corrosion inhibitors such as zinc sulphate and azoles. Generally, chlorine and or sodium hypochlorite are

the most widely used as antifouling biocide in cooling systems [2, 3, 4].

Different types of commercial multicomponent corrosion inhibitors are most commonly used to protect industrial cooling systems. Which inhibitor will be used to protect the system from corrosion depends on the plants construction materials, the quality of used supply water, the cost of the inhibitor and its environmental toxicity.

It has been experimentally confirmed that many organic and inorganic compounds containing heteroatoms of nitrogen, phosphorus, sulfur and oxygen with double or triple bonds in their structures are effective in protecting metals from corrosion. Phosphonates were developed and extensively used as scale and corrosion inhibitors in a variety of fields including circulating cooling systems in power plants, industrial equipment cleaning, industrial water treatment, corrosion inhibitors in concrete, coating, rubber blends, acids cleaners and anti-freeze coolants. Most of the inhibitors used in cooling water nowadays are based on phosphonates, either alone or in combination with one or more other corrosion inhibitors. Phosphonates give better inhibition efficiencies when used in combination with zinc salts [5-9].

A numerous of research has focused on the problem of corrosion in cooling systems, as well as the application of phosphonate-based inhibitors, alone or in combination with metal cations. Two commercial corrosion inhibitors were used in this paper, and both of them have 2-phosphonobutane 1,2,4-tricarboxylic acid (PBTC) in their composition.

Nessren i Wisam examined the efficiency of PBTCA as a carbon steel corrosion inhibitor in cooling water and found that the efficiency of a corrosion inhibitor increased with increasing its concentration [8]. A series of PBTC modified hydroxyl terminated hyper-branched structure (HBPs) with hydroxyl and carboxyl were successfully prepared and used for scale and corrosion inhibition in the research of Wang et al. They concluded that increasing the concentration of the scale inhibitor will improve the effect of scale inhibition [10]. A similar research was conducted by Huang *et al.* New type of the scale and corrosion inhibitors with HBPs has been developed in this study to improve the scale and corrosion inhibition efficiency of existing scale inhibitors for industrial water. The experimental results show that the HBPs provides high scale inhibiting efficiency for CaCO₃ and CaSO₄ (96.7% and 93.9% at 20mg/L, respectively). HBPs inhibition effect on carbon steel corrosion in 3wt% NaCl medium was investigated. By the weight loss test it was obtained that corrosion inhibition efficiency depends on its concentration and reaches 91.3% [11].

The combination of zinc salts with carboxylic acid derivatives has proven to be effective in protecting the heat exchanger of industrial cooling systems [12]. By adding smaller amounts of zinc compounds to phosphate-based corrosion inhibitors, good corrosion protection is achieved, which is environmentally acceptable. In research of Jin *et al.* environmentally friendly inhibitor was designed (12.5% PBTC, 21.8% ZnSO₄, 18.7% PASP, 9.4% HPAA, 18.8% AA-ATMP-HPA polymer, and 18.8% HPMA) and it was examined its application in a pilot-scale cooling system with reclaimed wastewater. A protective film formed by the adsorption of inhibitor onto the surface of the carbon steel prevented corrosion and the inhibition efficiencies of carbonate scale and corrosion were 93.3 and 94.4%, respectively. [13].

EXPERIMENTAL

For the purposes of research, recirculation cooling pilot plant was constructed, designed as a real plant. During construction of the plant, attention was paid that a suitable heater (heat exchanger simula-

tion) would be provided for the defined water flow, which would heat the water to the desired temperature, as well as the cooling tower height and fan strength, which would cool the water. The materials from which the construction of the plant is made are stainless steel EN 1.4301 and copper EN 13601. Schematic view of the pilot plant is given in Figure 1.

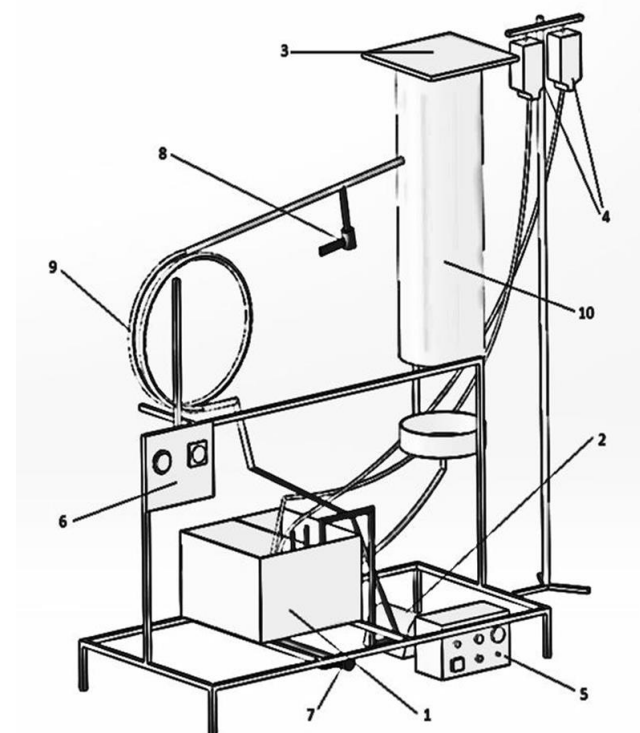


Figure 1. 3D model of open recirculation cooling system 1. Trunk with thermostat and heater, 2. Peristaltic pump, 3. Fan, 4. Dosing system for ammonia and sodium hypochlorite, 5. Control console for the pump, 6. Fan and heater control console, 7. Valve drain 8. Sampling valve, 9. Copper tube heater representing heat exchanger simulation and 10. Cooling tower

The parameter values of some parts of the plant are given in the Table 1.

Table 1. Parameters of a pilot plant

Parameter of Pilot plant	Value
Trunk	18 L
Peristaltic pump	1.1 L/min
Fan	410 m ³ /h
Heater	0.25 kW
Height of the cooling tower	0.8 m
Height of cooling pad	0.15 m

The standard physical-chemical methods [14], as well as some specific methods [15], used to determine the physical-chemical quality of cooling

and raw water. In addition to the physical-chemical analysis of water, a corrosion coupon analysis was performed, (gravimetric mass loss of corrosion coupons) before and after immersion in cooling water, in accordance with standard method [16]. Raw water was used to supply this pilot plant, which is a mixture of tap water (90%) and distilled water (10%). Used corrosion coupons used are shown in Figure 2.



Figure 2. Corrosion coupons made of stainless steel and copper

Three commercially available inhibitors KURITA S-6300 and HEMOD MS 1E were used. The amount of corrosion inhibitor was evaluated based on the total phosphate content. Based on real industrial systems, the total phosphate content was from 3 to 4 mg/L. This scope was the manufacturer's recommendation for all three of the mentioned corrosion inhibitors, so in this paper no corrosion inhibitory efficiency at various concentrations of the corrosion inhibitor was examined. Following table (Table 2) shows amount of inhibitors that should be dosed to achieve the required values.

Table 2. The amount of dosed corrosion inhibitors depending on the total phosphate content

Corrosion inhibitor	Amount of dosed inhibitor per liter of cooling water (mL/L)	Total phosphate content (mg/L)
KURITA S-6300	0.20	3.27
BWT CS-1006	0.08	3.97
HEMOD MS 1E	0.15	3.17

Following tables (3, 4) shows the physical-chemical composition of the corrosion inhibitors given in their accompanying MSDS.

Table 3. Chemical composition of corrosion inhibitor KURITA S-6300 [17]

Name of the compound	%
zinc chloride	5-10
sulfuric acid (96-98%)	5-10
2-phosphonobutane-1,2,4-tricarboxylic acid	1-5
1-hydroxyethylidene 1,1-diphosphoric acid	1-5

Table 4. Chemical composition of corrosion inhibitor HEMOD MS 1E [18]

Name of the compound	%
Sodium hydroxide	10-15
2-phosphonobutane-1,2,4-tricarboxylic acid	20-25

In order to avoid the growth of microbiological processes in the cooling water, $\omega = 3\%$ sodium hypochlorite solution was dosed, maintaining the residual chlorine content within the range of 0.1 - 0.2 mg L⁻¹. Since the corrosion processes are very slow, in addition to the corrosion inhibitor, corrosion activator is also dosed into cooling water to accelerate the corrosion process. As a corrosion activator 5% aqueous solution of NaCl was used. The pH was maintained in the range of 8.8 – 9.2 by dosing a $\omega = 5\%$ NH₄OH aqueous solution. All used chemicals are p.a. The cooling water recirculation time in the pilot plant was 3.5 h, during which time all water was circulated through the system for a ten times.

RESULTS AND DISCUSSION

The experimental results can be divided into two parts. First, the impact of inhibitor addition on cooling water quality was examined, and then the effect of chloride addition (as a corrosion activator) and water recirculation in the system on cooling water quality was examined.

Physical-chemical analysis was performed on five different samples:

- *Raw water* (without the addition of inhibitors and corrosion activators),
- *Raw water + KURITA S-6300* (without corrosion activator, and this water recirculated for 3.5 hours on a pilot plant),
- *Raw water + KURITA S-6300 + NaCl* (water with the corrosion inhibitor and the activator, and which recirculated for 3.5 hours on a pilot plant),

- Raw water + *HEMOD MS 1E* (without corrosion activator, and this water recirculated for 3.5 hours on a pilot plant) and
- Raw water + *HEMOD MS 1E* + NaCl (water with the corrosion inhibitor and the activator, and which recirculated for 3.5 hours on a pilot plant).

Physical-chemical analysis of raw water and cooling water with the addition of activator and corrosion inhibitors is given in Table 5.

Table 5. Physical-chemical composition of raw water and cooling water after 3.5 h recirculation using a corrosion inhibitor in 5% chloride solution

Parameter	Raw water	Raw water + KURITA S-6300	Raw water + KURITA S-6300 + NaCl	Raw water + HEMOD MS 1E	Raw water + HEMOD MS 1E + NaCl
pH	7.61	8.88	8.89	8.92	8.96
TDS	208	211	42800	295	42700
conductivity ($\mu\text{S}/\text{cm}$)	325	457	66900	461	66767
SiO ₂ (mg/L)	2.83	2.89	2.81	2.96	2.91
total hardness (TH) (mgCaCO ₃ /L)	176.8	181	276.8	190.3	266.6
calcium hardness (CaH) (mg/L)	132.2	132.1	155.7	160.3	127
p- alkalinity (mgCaCO ₃ /L)	0	45	82	30	159
m- alkalinity (mgCaCO ₃ /L)	155	181	276	190.3	266.6
Cl (mg/L)	3.5	23.1	>500	8.6	>500
SO ₄ ²⁻ (mg/L)	22.3	50.6	53.9	22.8	21.6
PO _{4,ortho} ³⁻ (mg/L)	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
PO _{4,total} ³⁻ (mg/L)	< 0.5	3.1	3.1	3.17	3.1
Cu ($\mu\text{g}/\text{L}$)	4	395	1081	25	1150
Fe ($\mu\text{g}/\text{L}$)	13	91.8	4150	46.7	4238
Zn (mg/L)	< 0.1	2.61	0.16	< 0.1	< 0.1
Cl _{residual} (mg/L)	0.3	0.2	0.2	0.2	0.1
carbonate hardness (CT) (mgCaCO ₃ /L)	155	181	276	190.3	266.6
NH ₃ (mg/L)	< 0.02	108	111	70.8	69.9
O ₂ (mg/L)	5.89	4.69	4.56	4.55	4.59

Addition of the *KURITA S-6300* in raw water results increase in the sulfate content, because sulfuric acid in the composition of this inhibitor. Also there is observed an increase in the zinc content of cooling water. Zinc content is increased because inhibitor contains zinc chloride. By adding corrosion activator and after recirculating cooling water, zinc-ammonia complex is formed, separated in the form of a precipitate, which result by reducing the zinc content in cooling water.

It can also be seen that both samples with *HEMOD MS 1E* have a slight increase in ammonia content, compared with samples with inhibitor *KURITA S-6300*. A slight increase in ammonia content occurs because sodium hydroxide is in

composition of the *HEMOD MS 1E*, and therefore an aqueous solution of ammonia is required in less dosage to achieve a pH of 8.8 – 9.2.

The addition of corrosion activator accelerates corrosion processes in open recirculation cooling systems. This can be seen based on chemical composition, where is considerable increase in amount of Fe and Cu when the corrosion activator is added. The smaller separation of copper ions occurs because only one smaller part of the plant is made of copper (the pipe section around which the heater is located, which is a simulation of a heat exchanger), while the rest of plant is made of stainless steel.

The addition of the *KURITA S6300* increases the zinc content, because the inhibitor contains zinc

chloride in its composition. It is also seen that the addition of corrosion activators leads to a decrease in the zinc content. Zn^{2+} is the most investigated cation for synergistic effect with metal corrosion inhibitors probably due to the ease of being replaced by a cation high up in the electrochemical series. It was supposed that in aqueous solution particularly alkaline and neutral solutions, Zn^{2+} -inhibitor complex forms in the solution. On the surface of the metal, the Zn^{2+} -inhibitor complex is converted into the metal-inhibitor complex, so the protective film consists principally of M^{2+} -inhibitor complex and $Zn(OH)_2$, the reason for the remarkable improvement in inhibition efficiency [9].

The efficiency of corrosion inhibitors on steel and copper was determined by placing corrosion coupons in a pilot plant during recirculation of 3.5 h. First, corrosion rate of steel and copper was determined in a 5% NaCl solution without the presence of corrosion inhibitors, and after that with the application of corrosion inhibitors (Figures 2 and 3).

Based on mass loss method, a *negative mass corrosion index* can be calculated according to the following equation:

$$K_m^- = \frac{m_0 - m_1}{S_0 \cdot \tau} \quad (\text{g/m}^2\text{h}) \quad (1)$$

where:

m_0 – mass of corrosion coupon before corrosion process (g),

m_1 – mass of coupon after corrosion process, after removing of corrosion products (g),

S_0 – surface of corrosion coupon (m^2)

τ – time of corrosion process.

Based on *negative mass corrosion index* it can be calculated corrosion rate by following equation:

$$\pi = \frac{K_m^- \cdot 8,76}{d_{Me}} \quad (\text{mm/year}) \quad (2)$$

where:

π – thickness (length) of duct resulting from corrosion (mm/year),

K_m^- – negative mass corrosion index ($\text{g/m}^2\text{h}$) and

d_{Me} – density of metal.

Based on the obtained results, it can be seen both inhibitors achieved the same inhibitory efficiency on stainless steel (Figure 3), while higher inhibitory efficiency on copper was achieved with KURITA S-6300 inhibitor (Figure 4). However, based on the physicochemical composition of the cooling water

(iron and copper content), we can see that better results are achieved on both materials by using the KURITA S-6300 inhibitor (Table 3).

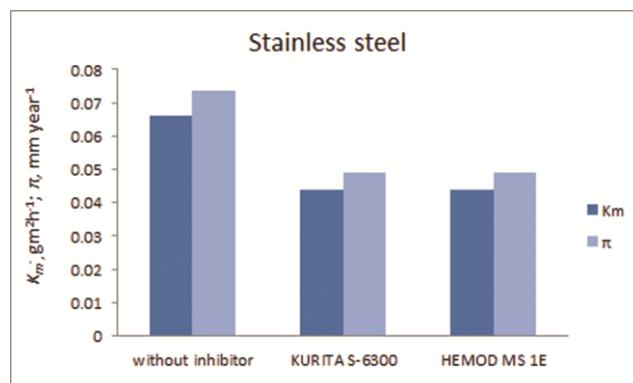


Figure 3. Corrosion inhibitor efficiency on stainless steel (EN 1.4301)

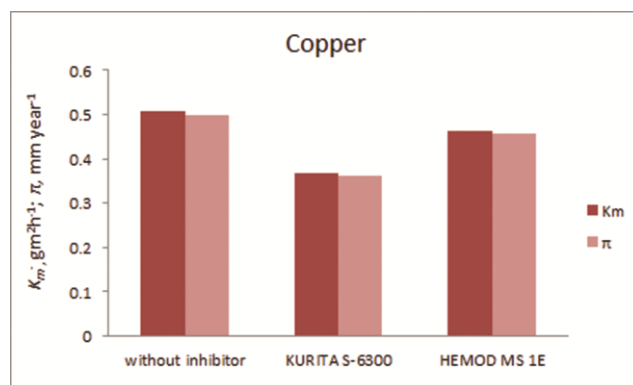


Figure 4. Corrosion inhibitor efficiency on copper (EN 13601)

CONCLUSION

The safe operation of the cooling system depends on the physical-chemical composition of the cooling water, as well as its quality monitoring. The use of proper quality cooling water slows down corrosion processes and prevents the separation of mineral and microbial deposits in the cooling systems, which results in an extended life of the plant.

The obtained results, based on the physicochemical analyze of the cooling water and weight loss method, shows that by use of KURITA S-6300 corrosion inhibitor in simulated cooling water better results are achieved in protection of stainless steel (EN 1.4301) and copper (EN 13601).

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