

Non-Phosphorus Treatment Technology for Cooling Water Systems

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ABSTRACT

The combination of phosphorus and zinc is mainly used as the carbon steel corrosion inhibitor for cooling water systems in the industrial plants such as petroleum refining or petrochemical plants. Moreover, treatments with high-concentration phosphorous and zinc are also applied to inhibit initial corrosions when the industrial plants are started up. Recently in some countries such as China, using phosphorous is prohibited by the wastewater regulation because of increasing conscious for environment. Therefore, non-phosphorus treatments for cooling water systems are highly required.

In this presentation, new developed non-phosphorus treatments (initial and maintenance treatments) are introduced based on the laboratory and field tests.

(1) Initial treatment: The combination of a specific organic acid and zinc showed the same inhibition ability as that of high-concentration phosphorus and zinc treatments.

(2) Maintenance treatment: The combination of low-molecular weight polymers and zinc showed the same inhibition ability as that of phosphorus and zinc treatments. It was assumed that the polymers improve the corrosion inhibition abilities by dispersing zinc effectively.

Key words: Non-phosphorous treatment, corrosion inhibition, scale inhibition, cooling water treatment,

INTRODUCTION

For cooling water treatment chemicals, environmentally friendly chemicals should be developed continuously because huge amount of industrial water are used for cooling water systems and it is necessary to concern effect for environment. As carbon steel corrosion inhibitors for cooling water systems in the industrial plants such as petroleum refining or petrochemical plants, chromates treatments were prohibited. The combination of phosphorus and zinc is mainly used because the enforcement of various regulations limit the applicable chemical compositions.¹

Now it is necessary to develop non-phosphorus treatments because regulations of phosphorus discharge from cooling water is expanding globally to prevent ecosystem in environmental water from eutrophication. Especially, China and several parts of USA strictly regulate phosphorus discharge. Therefore, the using phosphorus for cooling water treatment is limited in these areas. Aside from regulations, using phosphorous for corrosion inhibitor in cooling water systems causes undesired issues such as the formation of calcium phosphate scales, increasing cyanobacteria and algae.¹ By using phosphorous as corrosion inhibitors, it is necessary to use scale and slim inhibitors.

Recently, several researchers were reported for non-phosphorus treatments.^{1,2,3,4,5,6,7,8,9} As organic acid, the corrosion inhibition abilities of gluconic acid or gluconate,^{5,6,7} combination of gluconate and molybdate,⁸ polyaspartic acid and polyepoxysuccinic acid⁹ were reported. Some of them reported that gluconic acid showed higher corrosion inhibition ability.

However, all of reports were focused on the maintenance treatment. There is no report for non-phosphorus initial treatments. Kowata and Takahashi reported the importance of the initial treatment for rusted surfaces because the surface of carbon steel tube in the actual plant system is formed with rust.¹⁰ They confirmed that combination of phosphorus and zinc treatment for 3 days showed significant change of elements in the rust.

Moreover, zinc dispersion ability of polymers was also reported to affect corrosion inhibition ability.¹¹ It was reported that corrosion rates were decreased with increasing the ratio of Film Formed Zinc (FFZ). If suitable polymers can be used, it is possible to inhibit corrosion with lower zinc concentration.

In this presentation, new developed non-phosphorus treatments (initial and maintenance treatments) are introduced based on the laboratory and field tests. It was found that superior chemicals for initial and maintenance treatments were different. It is necessary to select suitable chemicals for each treatment and combination of suitable treatments can provide environmentally friendly and higher stable plant operation.

EXPERIMENTAL PROCEDURE

Evaluation for Initial Treatments

Corrosion Test

In order to evaluate performance of initial treatments, liner polarization resistance measurements were conducted with a corrosion meter and a standard 3 electrodes ($\phi 10 \text{ mm} \times 30 \text{ mm}$) set up (working electrode was made of mild steel SS-400 (JIS G3101), counter and reference electrodes were made of stainless SUS-304 (JIS G4303)). Electrodes were immersed in the initial treatment water (1 dm^3) for 24 hours. After that, electrodes were immersed in the corrosive water (1 dm^3) for 3-20 hours. Test condition and properties of initial treatment and corrosive water were described in Table 1-3.

Evaluated chemicals were described in Table 4. As organic compounds, ethylenediaminetetraacetic acid (EDTA), gulonic acid (GA) and proprietary organic acid (POA) were evaluated. In order to compared with the performance of traditional initial treatment, combination of phosphoric acid and zinc treatment (P/Zn) was evaluated.

Table 1
Water Qualities for the Corrosion Test

Parameter	Unit	Initial Treatment	Corrosive water
pH	-	7.5	7.5
M-alkalinity	mg-CaCO ₃ /L	40	40
Ca hardness	mg-CaCO ₃ /L	40	40
Mg hardness	mg-CaCO ₃ /L	20	20
SiO ₂	mg-SiO ₂ /L	15	15
Cl	mg-Cl/L	20	100
SO ₄	mg-SO ₄ /L	20	100

Table 2
Initial Treatment Conditions for the Corrosion Test

Parameter	Unit	Organic Acid	P/Zn
Organic Acid	mg/L	50	-
T-PO ₄	mg-PO ₄ /L	-	100
Zn	mg-Zn/L	-	20

Table 3
Test Conditions for the Corrosion Test

Parameter	Unit	Initial Treatment	Corrosive water
Temperature	degree C	30	30
Rotation speed	rpm	300	300
Duration	hour	24	3-20

Table 4
Evaluated Chemicals for Initial Treatments

Abbreviation	Composition
EDTA	Ethylenediaminetetraacetic acid
GA	Gluconic acid
POA	Proprietary organic acid
P/Zn	Combination of phosphoric acid and Zinc

Potentiodynamic Polarization Measurements

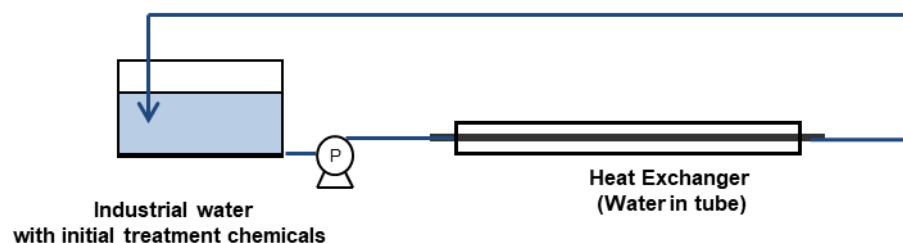
Electrochemical measurements were carried out in a conventional three electrodes set up. The working electrode was made of SS-400 ($\phi 10 \text{ mm} \times 30 \text{ mm}$). Ag/AgCl and carbon electrodes were used as the reference and auxiliary electrodes, respectively. Electrodes were immersed in the test solution at 30 degree C and under rotation at 300 rpm. Polarization curves were recorded at scan rate of 80 mV/min. Polarization resistance was defined as the slope of the polarization curve at E_{corr} . 0.8 V/SSE (anodic polarization) and -1.2V/SSE (cathodic polarization). Water quality of test water was same as the initial treatment in Table 1.

Field Heat Exchanger Test

The performance of POA initial treatment was compared with P/Zn treatment by utilizing industrial water in Japan. Initial treatment chemicals were added in the industrial water and circulated a carbon steel tube (STB 340, $19 \Phi \times 1,350 \text{ L} \times 2.3 \text{ t}$) at 0.5 m/s without blow down. The period of initial treatment was 2 days for POA treatment and 4 days for P/Zn treatment. In the case of P/Zn treatment, Kowata and Takahashi reported that more than 3 days are necessary because of significant change of elements in the rust¹⁰⁾. Therefore we selected 4 days for the treatment. In the case of POA treatment, we selected 2 days because we confirmed 1 day was enough. After initial treatments, the cooling water in the actual oil refinery plant with P/Zn maintenance treatment was passed through a heat exchanger. The cooling water was heated by steam and temperature of the inlet water of the heat exchanger was controlled 30 degree C and outlet was 40 degree C. The test period was 14 days (Figure 1, Table 5-7).

The corrosion inhibition ability was evaluated by the maximum pitting depth (mm/14 days), and scale inhibition ability was evaluated by the maximum scale formation rate (mg/cm²/month). The chemical composition of the silica scale samples was determined by wet chemical analysis.

a) Initial treatment



b) Maintenance treatment

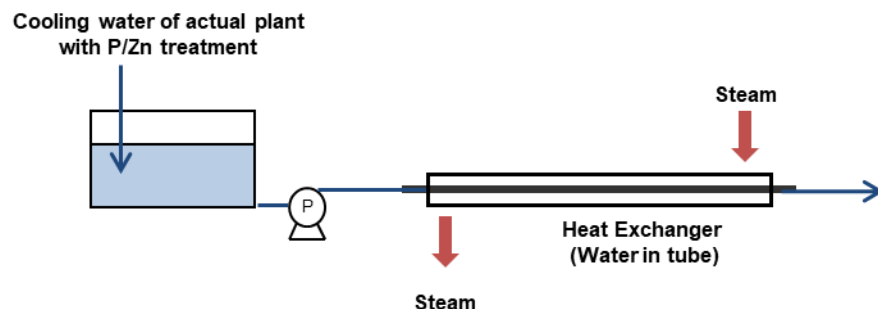


Figure 1: Flow diagram of the field heat exchanger system.

Table 5
Water Qualities for the Field Heat Exchanger Test

Parameter	Unit	Initial Treatment	Maintenance Treatment
pH	-	6.6-7.4	8.9-9.0
M-alkalinity	mg-CaCO ₃ /L	50-60	350-420
Ca hardness	mg-CaCO ₃ /L	45-55	300-390
Mg hardness	mg-CaCO ₃ /L	30-40	190-240
SiO ₂	mg-SiO ₂ /L	15-20	100-120
Cl	mg-Cl/L	35-45	200-270
SO ⁴	mg-SO ₄ /L	35-45	200-270

Table 6
Treatment Condition for the Field Heat Exchanger Test

Parameter	Unit	Initial Treatment		Maintenance Treatment
		POA	P/Zn	
POA	mg/L	50	-	-
T-PO ₄	mg-PO ₄ /L	-	100	4
Zn	mg-Zn/L	5	20	2

Table 7
Operation Condition of the Heat Exchanger System for the Field Heat Exchanger Test

Parameter	Unit	Initial Treatment		Maintenance Treatment
		POA	P/Zn	
Duration	Day	2	4	14
Velocity	m/s	0.5		0.5
Temp.(inlet of H/E)	degree C	30		30
Temp.(outlet of H/E)	degree C	30		40

Evaluation for Maintenance Treatments

Recirculating Test

In the case of maintenance treatments, the corrosion rate for long term (7 days) was compared by liner polarization resistance measurements with same set up as described in the corrosion test section. Figure 2 shows the flow diagram of the recirculating test. The test water was passed through electrodes at 0.5 m/s. The basin (100 dm³) was filled with test water from a reservoir vessel constantly. The hydraulic residence time (HRT) was set 80 hours. The temperature was controlled at 30 degree C by the chiller system. The corrosion rates were measured twice a day and the average of corrosion rates in 7 days were compared. Operation condition and properties of water were described in Table 8-10. The evaluated polymers were described in Table 11.

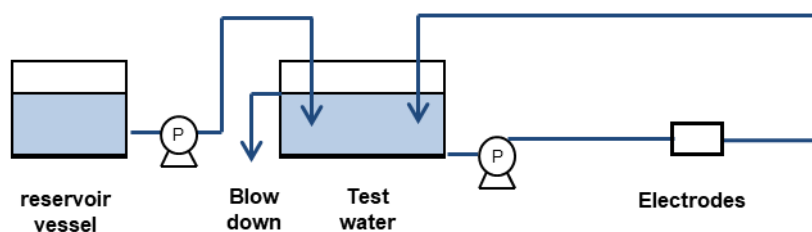


Figure 2: Flow diagram of the recirculating test.