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INTERFERENCE BETWEEN BIOCIDES AND INHIBITORS IN COOLING WATER SYSTEMS

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Most of the industries are adding biocides and inhibitors at the same point in cooling water systems. Inhibitors are added continuously and biocides are added weekly once or once in fifteen days. It is not known as to whether interference effect between biocides and inhibitors will lead to any adverse effect. The present study has been undertaken to know the influence of biocides on corrosion. Besides, to avoid the interference between biocides and inhibitors, some experiments have been carried out. Formaldehyde, Ethylene diamine tetra acetic acid (EDTA) and Cetryl trimethyl ammonium bromide (CTAB) have been evaluated for their biocidal efficiency. Further, the role of biocides on corrosion in the presence of inhibitors (morpholine phosphate + Zinc) has been investigated. From the corrosion point of view, morpholine phosphate with zinc acts as "very good mixed inhibitor". Morpholine phosphate when used alone acts as a good biocide, but when combined with zinc, the killing efficiency was nil. Results suggest that bacteria should be killed first and inhibitors should be added later for getting higher efficiency and for avoiding the interference between biocides and inhibitors.

Keywords: Biocides, inhibitor, biocidal activity, mixed inhibitor, interference.

INTRODUCTION

Fouling and corrosion are two important operational problems in heat exchangers and associated cooling water system pipelines. pipelines are known to be particularly susceptible to fouling induced corrosion due to their basic design characteristics and recirculation of water. Though biocides and inhibitors are used, problems have been noticed in various cooling water systems. The problems included flow blockage of pipes, pipe punctures and unacceptable general corrosion rates of the system components.

For controlling fouling and corrosion, inhibitors are added continuously and biocides are added weekly once or once in fifteen days. Hence, it is quite essential to study the interference between biocides and inhibitors for cooling water system. It was decided to evaluate three biocides along with one inhibitor system.

Though several studies on the use of phosphonic acid Viz. aminotrimethlene phophonic acid (ATMP), hydroxyethylidene diphosphonic acid (HEDP), hydroxy phosphonoacetic acid (HPA) etc. as corrosion inhibitor have been reported [1-4], the effect morpholine phosphate with zinc as inhibitor in the cooling water system pipelines has not been studied yet.

In the present study morpholine phosphate was used as inhibitor while biocides viz. formaldehyde, ethylene diamine tetra acetic acid (EDTA) and cetyltrimethyl ammonium bromide (CTAB) were used to study their interference effect on corrosion process. Formaldehyde is a protein soluble biocide, EDTA is a very good chelator and CTAB is a cationic biocide [5].

Materials and methods

Mild steel specimens (composition of sulphur 0.02 -0.3%, phosphorous 0.03 -0.08%, manganese 0.4 -0.5%, carbon 2.0% and iron the rest) of dimensions 1 x 4 x 0.2 cm and 1 cm^2 were cut mechanically and polished to nearer finish mechanically using emery fine grade paper and decreased with trichloroethylene. Side of 4 x 0.2 cm^2 specimens used for weight loss studies and 1 cm^2 specimen used for polarization studies.

Inhibitors and Biocides used

Morpholine phosphate with zinc was used as inhibitor system. Formaldehyde (HCHO), Ethylene diamine tetra acetic acid (EDTA) and Cetyl trimethyl ammonium bromide (CTAB) were used as biocides.

Corrosion studies — Weight loss Data

Initial weight of the mild steel specimen before corrosion test was noted. Mild steel specimens in triplicate were immersed in the test solution for a period of seven days. After seven days, specimens were pickled and washed in water and air dried. The loss in weight was determined and efficiencies assessed for the following four systems.

System I

To assess the influence of biocides in corrosion inhibition process, formaldehyde (125 ppm), EDTA (150 ppm) and CTAB (25 ppm) were added in pond water and weight loss data were obtained after seven days.

System II

To assess the inhibitor efficiency, of morpholine phosphate (200 ppm) with zinc (25 ppm) was used as corrosion inhibitor.

System III

To assess the influence of biocides (formaldehyde, EDTA and CTAB) and inhibitor (morpholine phosphate + zinc) and the interference effect between biocides and inhibitors on corrosion process, this system has been studied. Biocides and inhibitors were added at the same time and corrosion inhibition efficiencies were calculated.

System IV

Biocides were added in pond water to kill bacteria. After 24 hours, inhibitor was added in the same pond water and subsequently coupons were immersed for seven days to find out the weight loss.

Electrochemical Measurements

A three electrode cell assembly was used. 1 cm^2 mild steel specimen was used as the working electrode, large platinum foil as counter electrode and saturated calomel electrode (SCE) as reference electrode respectively. Polarisation studies were carried out using EG&G PAR model 173 potentiostat in combination with model 175 universal programmer and X-Y recorder. Potential (E) Vs log current (i) plots were recorded at a sweep rate of 1 mV/sec. Corrosion potential (E_{corr}), tafel slopes ba and bc were determined from the plots. For electrochemical study, systems III and IV were used.

TABLE I: Physical and chemical characteristics of pond water

Parameter	Value
*p*H	8.2
Conductivity (μ ohms/cm)	980
Alkalinity mA/K	250
Total hardness (ppm)	216
Ca-hardness (ppm)	130
Mg-hardness (ppm)	86
Chloride (ppm)	160
Sulphate (ppm)	114
Total solids (mg/l)	736
Dissolved solids (mg/l)	539
Suspended solids (mg/l)	197

Chemical and Biological analysis of water

Chemical characteristics of the pond water used in the investigation were analysed by standard analytical method [6]. The pelagic bacterial population of pond water was enumerated using nutrient agar adopting pour plate technique. The chemical characteristics of pond water are presented in Table I.

RESULTS

Weight loss data

The corrosion rate of mild steel in pond water in presence of biocide and inhibitor are presented in Tables II-V.

Biocides on corrosion (System I)

Table II brings out the influence of biocides on corrosion. The tested biocides did not contribute to corrosion but showed corrosion inhibition in the range between 33% and 39%

TABLE II: Corrosion rate of mild steel in pond water in presence and absence of biocide for 7 days (system I)

Biocide	Concn of biocide (ppm)	Corrosion rate (mmpy)	Efficiency (%)
Control	—	1.14990×10^{-4}	—
HCHO	125	7.64380×10^{-5}	34
EDTA	150	7.51850×10^{-5}	35
CTAB	25	7.05115×10^{-5}	39

TABLE III: Corrosion rate of mild steel in pond water in presence of inhibitor for 7 days (system II)

Inhibitor	Concn of inhibitor (ppm)	Corrosion rate (mmpy)	Efficiency (%)
Morpholine phosphate	200	7.9067×10^{-5}	31
Morpholine phosphate + zinc	200 + 25	4.4226×10^{-6}	96

Inhibitor on corrosion (System II)

Influence of inhibitor on corrosion is presented in Table III. Morpholine phosphate also slightly inhibited corrosion and the corrosion inhibition efficiency was about 31%. While adding Zn, morpholine phosphate drastically decreased (4.4226×10^{-6}) the corrosion rate and it showed a high inhibition efficiency of 96%.

Biocides and inhibitor on corrosion (Systems III and IV)

In system III, biocides and inhibitors (Morpholine phosphate+Zn) were added at the same time and corrosion efficiency was calculated. The inhibition efficiency is given in Table II. In the presence of formaldehyde with inhibitor, the efficiency was about 34%. In the presence of EDTA and CTAB with inhibitor, the efficiency was about 35% and 31% respectively.

In system IV, after killing of bacteria by biocides, in presence of formaldehyde the corrosion inhibition was about 92%. While adding EDTA and CTAB the inhibition efficiencies were about 85% and 94% respectively.

Electrochemical study

The potentiostatic polarisation data of mild steel immersed in pond water for systems III and IV are given in Table VI.

TABLE IV: Corrosion rate of mild steel in pond water in presence of inhibitor + biocides for 7 days (system III)

Inhibitor	Biocide	Concn of inhibitor & biocide (ppm)	Corrosion rate (mmpy)	Efficiency (%)
MPO_4+Zn	HCHO	200+25+125	7.6438×10^{-5}	34
MPO_4+Zn	EDTA	200+25+150	7.5185×10^{-5}	35
MPO_4+Zn	CTAB	200+25+25	7.9313×10^{-5}	31

TABLE V: Efficiency of inhibitor after killing bacteria by addition of biocides for 7 days (system IV)

Biocide addition	Inhibitor addition after 2nd day	Corrosion rate (mmpy)	Efficiency (%)
HCHO	MPO_4 + Zn	8.8453×10^{-6}	92
EDTA	MPO_4 + Zn	1.6953×10^{-5}	85
CTAB	MPO_4 + Zn	1.3711×10^{-6}	94

In system III, the inhibition efficiency with formaldehyde was about 75%, the OCP was about -685 mV. In presence of EDTA the inhibition efficiency was about 80% and the OCP was on positive side by about 100 mV when compared to control. CTAB with inhibitor gave corrosion efficiency of about 78% but OCP was more or less same as with control.

In system IV, the corrosion inhibitive percentage was higher when compared to system III. In presence of formaldehyde, the efficiency was about 99.9% and OCP was -676 mV. Inhibitor with EDTA shifted the OCP to negative side to about -729 mV when compared to control and system III. The inhibition efficiencies of EDTA & CTAB were about 99.95% and 99.87% respectively in these systems.

TABLE VI: Corrosion rate of mild steel in pond water in presence and absence of biocides by polarisation method

System	OCP (mV vs SCE)	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	Corrosion rate (mmpy)	Efficiency (%)
Control	-653	-670	4.000	90.87020	—
III. Mixing of biocide + inhibitor (system III)					
X	-685	-745	1.000	22.71760	75.00
Y	-560	-610	1.100	24.98930	80.00
Z	-652	-692	0.900	2.44580	78.00
IV. Inhibitor addition after killing bacterial by addition of biocide (system IV)					
X	-676	-720	0.004	0.09087	99.90
Y	-729	-635	0.002	0.04544	99.95
Z	-652	-693	0.005	0.11360	99.87

X = HCHO + MPO_4 + Zn; Y = EDTA + MPO_4 + Zn
Z = CTAB + MPO_4 + Zn

Bacterial killing efficiency

The bacterial killing efficiency of biocides along with inhibitor is presented in Table VII. A bacterial activity of about 10^1 was observed in 125 ppm of formaldehyde. In presence of EDTA the bacterial count was about 102, and in presence of CTAB the bacterial count was nil. It is indicated that CTAB acts as a very good biocide even at 25 ppm. The killing efficiency of morpholine phosphate was 100% but a large number of unshaped dead cells efficiency of morpholine phosphate was 100% but a large number of unshaped dead cells were observed in petridishes. When morpholine phosphate was combined with zinc, the bacterial growth was about 3.2 x 10^5. While the biocides formaldehyde and EDTA in combination with the inhibitor system, the bacterial count was very high, in presence of CTAB with inhibitor, the bacterial count was about 102. The variation in the *p*H value of pond water in various systems is shown in Table VIII.

DISCUSSION

Historically phosphates and chromates have been used as scale and corrosion inhibitors in cooling water systems [7-11]. Since phosphates act as good nutrients [12] for bacteria and inhibitor like chromate is toxic to environment, development of chemicals replacing phosphates and chromates are needed. Polyphosphates have easily hydrolyzable P-O bonds resulting in the formation of ortho phosphates. The ortho phosphates are not good corrosion inhibitors but good feed for bacteria and alagae resulting in biofouling effects, phosphates as such are not good corrosion inhibitors but in presence of zinc Ions they function as good corrosion inhibitors.

TABLE VII: Bacterial density (Pelagic bacteria)of pond water in various systems for 24 hours

System	Concentration (ppm)	Bacterial count (CFU/ml)
Control (PW)	—	5.7 x 10^6
HCHO	125	1.3 x 10
EDTA	150	5.2 x 10^2
CTAB	25	Nil
MPO_4	200 + 25	Nil
MPO_4 + Zn	200	3.2 x 10^5
MPO_4 + Zn + HCHO	200 + 25 + 125	5.2 x 10^6
MPO_4 + Zn + EDTA	200 + 25 + 150	5.4 x 10^6
MPO_4 + Zn + CTAB	200 + 25 + 25	5.4 x 10^2

CFU = Colony forming unit

Corrosion

It is observed from the results that the combination of morpholine phosphate with zinc acts as a good inhibitor (96%). It is also found that the biocides reduce the inhibition efficiency while combining with inhibitor. Besides, in system IV, the inhibitor gives higher efficiencies and indicates that interference between biocides and inhibitor is very low.

The inhibition may be due to the formation of zinc phosphate or zinc hydroxide on metal surface [11]. But in system III, the biocides formaldehyde, EDTA and CTAB complex may disturb the absorption of zinc phosphate and zinc hydroxide which may interfere with the action of inhibitor. But in system IV, within 24 hours biocides killed the bacteria and interference between biocides and inhibitor was least.

While adding morpholine to pond water, *p*H was about 9.62, and 7 days the *p*H decreased to 8.46. But the *p*H of the morpholine phosphate was about 7.86 on 1st day and 7th day, when morpholine phosphate combined with zinc, the *p*H was about 5.76 on 1st day and 6.15 on 7th day. However, the biocides did not influence the *p*H of the morpholine phosphate along with zinc. It indicates that *p*H influenced the activity of biocides and inhibitor. Adsorption of zinc phosphate or zinc hydroxide may be disturbed by biocides.

In system IV, after addition of formaldehyde and CTAB, the *p*H was in the neutral range. But in presence of EDTA the *p*H was about 4.83 on first day and while adding inhibitor the *p*H was about 7.23 on 7th day. It can be inferred that the inhibitor was working well in neutral *p*H and gave higher inhibition efficiency (95%).

The *p*H data suggest that mixing of inhibitor and biocides at the same time reduces the *p*H of the electrolyte which in turn may reduce the inhibition efficiency. On the other hand by adding biocides first and inhibitor subsequently the influence of *p*H on corrosion was found to be the least. It may be due to the higher *p*H on the 7th day. Potentiostatic polarisation results also indicate that the corrosion efficiency was low in presence of both inhibitor and biocides. While adding biocides first and inhibitor subsequently, the efficiency was improved. It also indicates that the interference between biocides and inhibitor was the least in system IV. The nature of curves also explain that morpholine phosphate + zinc along with biocides act as "mixed inhibitor".

Bacterial killing efficiency

The killing efficiency of biocides (formaldehyde, EDTA and CTAB) with and without inhibitor are presented in Table VII. The bacterial density of about 101, 102 and nil were observed in presence of above biocides respectively. Besides, the inhibitor morpholine phosphate also acts as a

TABLE VIII: *p*H of the pond water in various systems for 7 days

System	Initial *p*H (1st day)	Final *p*H (7th day)
Control (PW)	7.90	7.50
HCHO	6.61	8.00
EDTA	3.74	6.20
CTAB	5.41	8.49
Morpholine	9.62	8.46
MPO_4	7.86	7.87
MPO_4 + Zn	5.76	6.15
MPO_4 + Zn + HCHO	5.76	6.52
MPO_4 + Zn + EDTA	5.60	6.46
MPO_4 + Zn + CTAB	5.75	6.00
Inhibitor addition after killing bacteria by addition of biocide		
MPO_4 + Zn + HCHO	6.67	7.80
MPO_4 + Zn + EDTA	4.83	7.23
MPO_4 + Zn + CTAB	7.09	8.19

very good biocide. Formaldehyde kills the bacteria by solubilization of protein in phospholipid molecules. EDTA enhances the killing efficiency by chelating the trace metals present inside the bacteria. Eventhough, bacteria effectively utilize morpholine, CTAB acts as good biocide by disturbance of the arrangements of phospholipid molecules in the cell of the bacteria as the energy source and able to grow in high concentration of morpholine. Accumulation of ammonia inhibit the growth of bacteria [4]. Conversion ratio of morpholine to ammonia was reported as 1:0.82 by Pseudononas sp. Morpholine phosphate when combined with zinc chloride gave low killing efficiency. This reduction in killing tendency may be due to the formation of morpholinium chloride which may not be easily degradable. Because, the process of degradation may be very slow, requiring 235 to 300 hrs for complete removal of morpholine from the electrolyte [4,13].

When biocides and inhibitors were simultaneously injected the bacterial killing efficiency of biocides was not found effective. Probably, biocides lost their activity against bacteria. Hence it is suggested that biocides and inhibitor should be added separately for getting higher efficiency.

The present investigation has clearly shown that CTAB and inhibitor combination acts as good system for bacterial control, when compared to other biocides. The bacterial count was below the limiting level.

CONCLUSION

* From the corrosion point of view, morpholine phosphate with zinc acts as a very good mixed inhibitor system.
* Bacterial killing efficiency of biocide CTAB along with inhibitor appears to be better than another systems.
* It is not advisable to inject biocide and inhibitor at the same time. Bacteria should be killed first and inhibitor should be added later for getting higher efficiency.

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