Corrosion Inhibition of Carbon Steel in Open Recirculating Cooling Water System of Petroleum Refinery by Thiourea and Imidazole in Presence of Zinc (II) Sulphate

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Abstract

The inhibiting action of thiourea and imidazole towards corrosion for carbon steel in open recirculating cooling system (ORCS) of Numaligarh Refinery Limited (NRL) , Golaghat , Assam,India has been studied in presence of Zn^{2+}(as $ZnSO_4.7H_2O$) by weight loss and potentiodynamic polarization methods. The values of inhibition efficiency from weight loss method are in good agreement with those obtained from polarization studies. Polarization study indicates that imidazole retards the cathodic corrosion reaction where as thiourea inhibits anodic corrosion reaction in these particular blends of inhibitors. SEM and EDS study confirm the formation of an adsorbed protective film on the carbon steel surface.

Keywords: Thiourea, Imidazole, Zn^{2+}, Weight loss method, Potentiodynamic polarization method, SEM and EDS

1. Introduction

In open recirculating cooling water system (ORCS) of a petroleum refinery, carbon steel corrosion is a major problem. The make up water used in ORCS are either from river, sea or underground sources. The presence of large amount of total dissolved solids, total suspended solids, total hardness, microorganism and dissolved gases, such as, O_2 and CO_2 in the makeup water are responsible for scaling, fouling, under deposit and microbiological corrosion in the various equipments of cooling water system. Due to such corrosion the tubes of heat exchanger, an important part of ORCS get damaged easily, which affect the productivity and profitability. To minimize the adverse effect of corrosion, various protective methods have been adopted, one of the frequently used measure is the use of organic compounds containing nitrogen and sulphur atoms (Al-Faiyz YSS *et al*., 2006, Hossini *et al*., 2009 and Shetty *et al*.,2006). These compounds either can form strong co-ordination bond with metal atom or form passive film on the surface (Hassan *et al*., 2009). There is still a continuous search for better inhibitors or blend of inhibitors to meet the demand of the industry. The selection criteria for various inhibitors include low concentration, stability in recirculation, cost effectiveness and low operational hazard. There are reports of use of several substituted thiourea with increased electron densities at donor sites (Shetty *et al*., 2006).

We report here the effect of addition of thiourea and another electron donor imidazole in presence of Zn^{2+} as corrosion inhibitor in ORCS of petroleum refinery and evaluation of their optimum ratio to give the most effective blend for inhibition of corrosion, scale formation and microbiological problems.

2. Experimental procedures

Experiments were carried out by weight loss and potentiodynamic polarization methods.For performing these experiments, blends of imidazole (AR, Merck,25 ppm to150ppm) thiourea (AR,Merck,25 ppm to 150 ppm) and Zn^{2+}as $ZnSO_4.7H_2O$ (AR,CDH,50 ppm) of different concentrations were prepared separately. Table-1 gives the details of these blends.

2.1 Weight loss method

Carbon steel specimens of C-1010 coupons of known composition (S, 0.05; P, 0.04; Mn, 0.306, C; 0.08-0.13; Al, 0.03; Si, 0.21and Fe remainder) and size (1.0×1.0×0.15 cm) were used for weight loss study. All these strips were mechanically polished, degreased with acetone and finally dried in an oven at 105°C before and after each experiment. The weight of the test coupons were recorded and tests were carried out in a constant temperature bath of cooling water used in ORCS of NRL, Golaghat, Assam, India in absence and in presence of various blends of inhibitors separately for 15 days at temperature of 30±1°C.The various parameters of cooling water was analyzed by using standard method (Andrew *et al.,* 1995) (Table-2). Strips were then kept in a moisture free desicator for conditioning. After conditioning, coupons were weighed. From the weight difference the corrosion rate (CR) and percentage of inhibition efficiency (%IE) were calculated by using the equations 1(AN 116, Corrosion rate calculations from coupons. Rohrback Cossack Systems 11841 E. Smith Avenue, Santa Fe Springs, CA 90670 USA.) and 2 (Quraishi *et al.,2005)* respectively.

$$CR = \frac{3{,}650 \times \text{Weightloss (grams)}}{\text{Metal density (g/cm}^3) \times \text{Coupon area} \times \text{time (T)}} \quad \ldots\ldots\ldots\ldots (1)$$

Where CR is expressed in mm/year, weight loss in grams,corrosion period (T) in days and coupon area in cm^2.

$$IE\% = R_0 - R \times 100 / R_0 \quad \ldots\ldots\ldots (2)$$

Here R_0 and R are the corrosion rates in absence and in presence of inhibitors respectively.

2.2 Electrochemical studies

For electrochemical studies a carbon steel rod of same composition as those of the coupons used in weight loss studies, embedded in teflon with an exposed area of $0.05cm^2$ was used as a working electrode. A platinum foil was used as a counter electrode and the reference electrode was a silver-silver chloride electrode. In the electrochemical study, tests were carried out in a three electrode cell assembly at room temperature (30°C) using a potentiostate of model 600C of CH instrument. The studies were made in the scan rate of 0.05v/s. Before starting the polarization scan, a minimum of thirty minutes was given to stabilize the open circuit potential (OCP) within ±10 mv. The plot of E (potential) versus log I was drawn and from this the corrosion kinetic parameters such as corrosion potential (E_{corr}) and corrosion current (I_{corr}) were evaluated (Poongothai N *et al.,* 2007).The percentage of inhibition efficiency (%IE) can be calculated from the equation 3 (Taha K K *et al.,* 2006)

$$\% IE = (i_{corr} - i_{o\ corr}) \times 100 / i_{corr} \quad \ldots\ldots\ldots\ldots (3)$$

Where I_{corr} and $i_{o\ corr}$ are corrosion current densities in absence and in presence of inhibitors respectively.

3. Scanning electron micrograph

Samples of carbon steel specimen for scanning electron micrographs were prepared by treatment with cooling water used in NRL,Golaghat,Assam , India in absence and in presence of inhibitors (blend of SET-I-100 was taken)for 5 days separately. The SEM and EDS of theses samples were recorded at CIF, IIT, Guwahati,Assam,India which are shown in Figure 1, Figure 2 and Figure 3 respectively.

4. Results and discussion

From the weight loss study (Table-3) it is found that in case of the inhibitor blends of SET-I (SET-I includes SET-I-25, SET-I-50,SET -I-100, SET-I-150),the percentage of inhibition efficiency increases on increasing the imidazole concentration from 25ppm to100 ppm at constant Zn^{2+} and thiourea concentration (Zn^{2+}=50ppm and thiourea =50ppm), which does not increase on increasing the imidazole concentration beyond 100 ppm. This is also explainable with the help of polarization study.In polarization study the corrosion current density value decreases from the blank value of 10.96 $\mu A/cm^2$ to 2.04$\mu A/cm^2$ (Table-4) on increasing the imidazole concentration from 25ppm to 100 ppm (the inhibition efficiency increases from 42.42% to 81.38%), after that it increases on increasing the imidazole concentration from 100 to 150 ppm. The E_{corr} values shifted from the blank value of -195.2 mv to -247.4 mv (Figure 4) on increasing the imidazole concentrations i.e. slightly towards the negative side, which implies that imidazole works as a cathodic inhibitor in these blends of inhibitors (Achary *et al*., 2007). Similarly in case of the inhibitor blends of SET-II (SET-I1 includes SET-II-25, SET -II-50, SET -II-100, SET-II-150), the percentage of inhibition efficiency increases on increasing the thiourea concentration from 25ppm to100 ppm at constant Zn^{2+} and imidazole concentration (Zn^{2+}=50ppm and imidazole =50ppm) but beyond 100ppm of thiourea concentration there is no corresponding increase in corrosion inhibition. In using SET-II inhibitors, the corrosion current density value decreases from the blank value of 13.80$\mu A/cm^2$ to 2.75 $\mu A/cm^2$ on increasing the thiourea concentration from 25ppm to 100 ppm , implying increase in inhibition efficiency from 38.33% to 80.07 %. The corrosion current density increases on increasing the thiourea

concentration beyond 100 ppm , indicating decrease of inhibition efficiency (Vishnudevan M *et al*.,2007). The corrosion potential values (E_{corr}) shifted from the blank value – 229.0mv to -154.6mv (Figure 5) on increasing the thiourea concentrations, implying the anodic character (Hossini SMA *et al*.,2009) of thiourea as well as bond formation or physical adsorption.

The SEM micrograph of the test coupon (Figure 2) taken after treatment with inhibitors, shows smooth surface in comparison with the SEM micrograph of untreated coupon (Figure 1), indicating the formation of an adsorbed film of the inhibitors on the metal surface. EDS analysis of the specimen surface (Figure 3) showed presence of carbon, oxygen, nitrogen, zinc, sulphur, and iron after immersion in the solution containing the blended mixture, further corroborates the adsorption of zinc, imidazole and thiourea on the metal surface.

5. Conclusion

The present study shows that zinc and imidazole in presence of thiourea in respective ratio of 1.0:2.0:2.0 gives the most effective blend of inhibitors for corrosion, scale formation and microbiological growth of carbon steel in ORCS. The Polarization study indicates that imidazole retards the cathodic corrosion reaction whereas thiourea inhibits anodic corrosion reaction. The inhibition of corrosion is due to formation of an adsorbed passive film on the metal surface as observed from SEM and EDS results.

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Table 1. Composition of various inhibitors

Blends	Zn^{2+}(ppm)	Thiourea (ppm)	Imidazole (ppm)
SET-I-25	50	50	25
SET-I-50	50	50	50
SET-I-100	50	50	100
SET-I-150	50	50	150
SET-II-25	50	25	50
SET-II-50	50	50	50
SET-II-100	50	100	50
SET-II-150	50	150	50

Table 2. Parameters of cooling water used

P^H	Turbidity (NTU)	Conductivity ($\mu s/cm^2$)	TDS (ppm)	Total hardness (ppm)	Ca Hardness (ppm)	SiO_2 (ppm)
7.5	0.37	207.0	136.6	54.0	46.0	2.36

Table 3. Corrosion parameters obtained from weight loss measurements for carbon steel at various concentrations of inhibitors at 30^{o}C

Blends	Weight loss (gm)	Corrosion rate (mmpy)	Inhibition efficiency (%)
BLANK	0.0178	0.2120	-
SET-I-25	0.0082	0.0976	53.96
SET-I-50	0.0072	0.0857	59.57
SET-I-100	0.0059	0.0702	66.88
SET-I-150	0.0062	0.0738	65.18
SET-II-25	0.0075	0.0898	57.64
SET-II-50	0.0068	0.0815	61.56
SET-II-100	0.0052	0.0619	70.80
SET-II-150	0.0057	0.0685	67.69

Table 4. Inhibition efficiency of various blends of inhibitors by potentiodynamic polarization method

Blends	-E_{corr} (mv)	I_{corr} ($\mu A/cm^2$)	IE (%)
BLANK-I	195.2	10.96	--
SET-I-25	222.2	6.31	42.42
SET-I-50	258.1	3.31	69.80
SET-I-100	279.9	2.04	81.38
SET-I-150	247.4	2.34	78.64
BLANK-II	229.0	13.80	-
SET-II-25	217.3	8.51	38.33
SET-II-50	205.4	7.94	42.46
SET-II-100	187.8	2.75	80.07
SET-II-150	154.6	4.36	68.40

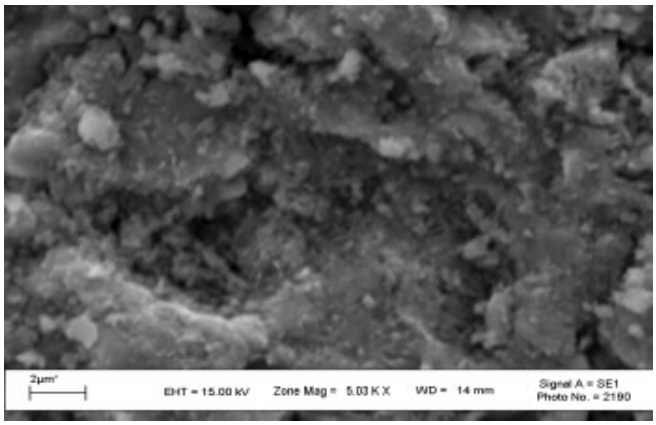

Figure 1. SEM micrograph of carbon steel after 5 days of treatment in absence of inhibitors

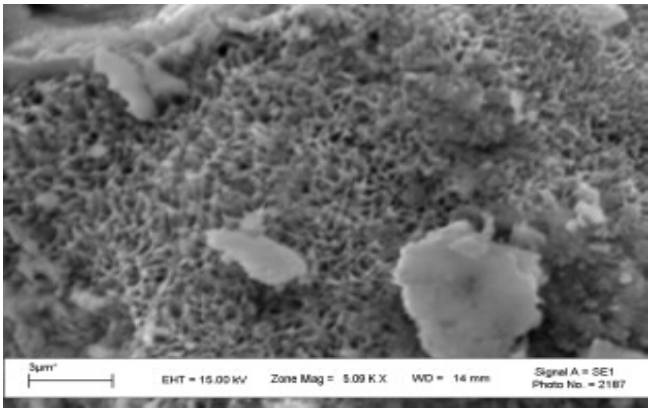

Figure 2. SEM micrograph of carbon steel after 5 days of treatment in presence of inhibitors

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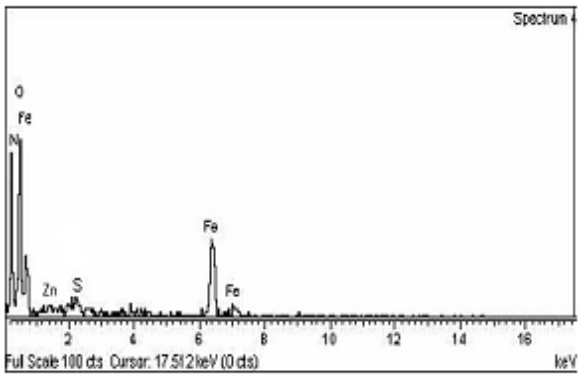

Figure 3. EDS analyses of carbon steel after 5 days of treatment in presence of inhibitors

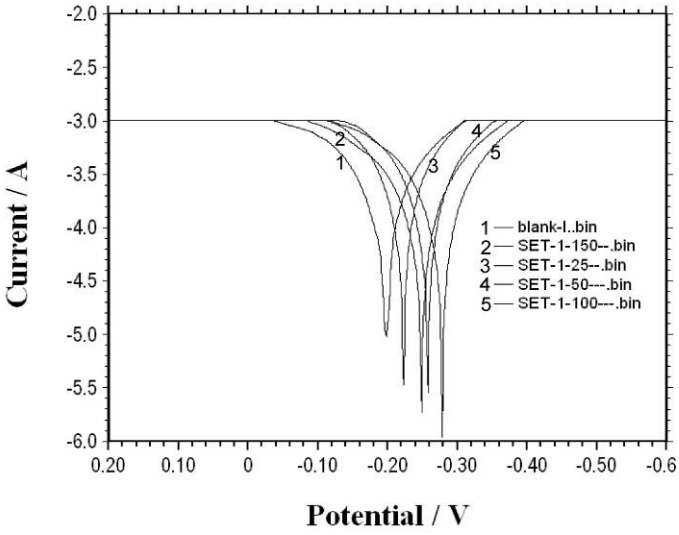

Figure 4. Potentiodynamic polarisation curves for the blends of SET-I

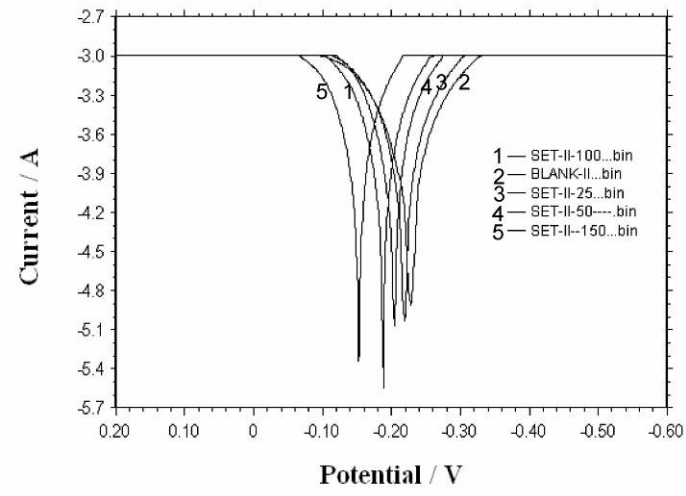

Figure 5. Potentiodynamic polarisation curves for the blends of SET-II