

## CORROSION INHIBITION BY HEDP-Zn<sup>2+</sup> SYSTEM FOR MILD STEEL IN LOW CHLORIDE MEDIA

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The inhibition efficiency of HEDP - Zn<sup>2+</sup> system in controlling corrosion of mild steel in a neutral aqueous environment containing 60 ppm Cl<sup>-</sup>, a situation commonly encountered in cooling water systems, has been evaluated by weight loss study. Various concentrations of HEDP (10, 50, 100 ppm) and various concentrations of Zn<sup>2+</sup> (10, 50, 100, 150 ppm) have been used. A formulation is arrived at, which has 98% inhibition efficiency. The protective film has been analysed using X-ray diffraction, FTIR and uv-visible reflectance spectra. The protective film consists of Fe<sup>2+</sup>- HEDP complex and Zn(OH)<sub>2</sub>; free from any oxides of iron. The influence of a biocide, namely, N-cetyl-N, N,N- trimethylammonium bromide (CTAB), on the corrosion inhibition efficiency of HEDP-Zn<sup>2+</sup> system and also the influence of HEDP-Zn<sup>2+</sup> system on the biocidal efficiency of CTAB have been investigated.

Keywords: Biocide, corrosion inhibition, phosphonic acid, steel.

### INTRODUCTION

Phosphonates have been used as corrosion inhibitors, due to their scale inhibiting property, hydrolytic stability and ability to form complexes with metal ions [1-8]. The present work i) investigates the inhibition efficiency of various concentrations of HEDP-Zn<sup>2+</sup> system, in controlling corrosion of mild steel, immersed in a neutral aqueous environment, containing 60 ppm Cl<sup>-</sup>, a situation commonly encountered in cooling water technology, ii) analyses the protective film by x- ray diffraction, uv-visible reflectance and FTIR spectra, iii) investigates the influence of a biocide, namely, N-cetyl-N, N,N- trimethylammonium bromide (CTAB) on the corrosion inhibition efficiency of HEDP-Zn<sup>2+</sup> system and iv) the influence of HEDP-Zn<sup>2+</sup> system on the biocidal efficiency of CTAB.

### EXPERIMENTAL

#### Preparation of the specimens

Mild steel specimens (0.02 to 0.03% S, 0.03 to 0.08% P, 0.4 to 0.5% Mn, 0.1 to 0.2% C and the rest iron) of the dimensions 1 x 4 x 0.2 cm were polished to mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies.

#### Weight-loss method

Three mild steel specimens, were immersed in 100 ml of the solution containing various concentrations of the inhibitor in the absence and presence of Zn<sup>2+</sup>, for a period of seven days. The weights of the specimens before and after immersion were determined using a Mettler balance, AE-240.

#### Surface examination study

The mild steel specimens were immersed in various test solutions for a period of two days. After two days, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimens was analysed by various surface analysis techniques.

#### The UV-visible spectra

The uv-visible absorption spectra of solutions were recorded using Hitachi U-3400 spectrophotometer. The same instrument was used for recording uv-visible reflectance spectra of the film formed on the metal surface.

#### X-ray diffraction technique

The XRD patterns of the film formed on the metal surface were recorded using a computer controlled x-ray powder diffractometer, JEOL JDX 8030 with CuK<sub>α</sub> (Ni-filtered) radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at a rating of 40 kV, 20 mA. The

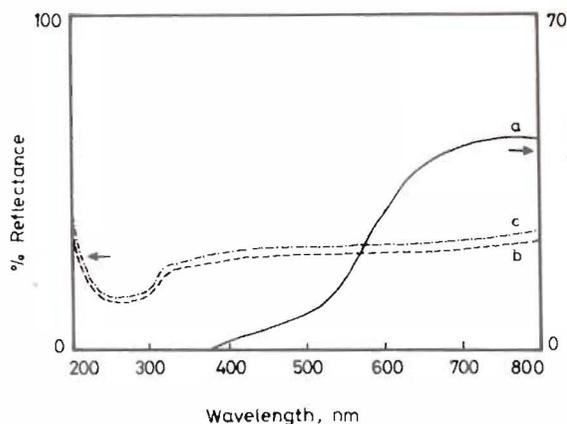


Fig.1: uv-visible reflectance spectra of mild steel surface immersed in various environments.

- (a) Cl<sup>-</sup> 60 ppm + Zn<sup>2+</sup> 50 ppm (b) Cl<sup>-</sup> 60 ppm + HEDP 50 ppm  
(c) Cl<sup>-</sup> 60 ppm + HEDP 50 ppm + Zn<sup>2+</sup> 50 ppm

scan rate was 0.05 - 20<sup>0</sup> per step and the measuring time was 1 sec per step.

#### Biocidal efficiency

The biocidal efficiency of the system was determined using Zobell medium and calculating the number of colony forming units per ml, using a bacterial colony counter.

### RESULTS AND DISCUSSION

#### Weight loss study

The corrosion inhibition efficiency offered by various HEDP- Zn<sup>2+</sup> systems to mild steel immersed in 60 ppm chloride environment for a period of seven days are given in Table I. It is observed that when the concentrations of HEDP and also that of Zn<sup>2+</sup> are less than 50 ppm, their combination does not show good inhibition efficiency (IE). However, when their concentrations are equal to and greater than 50 ppm, excellent inhibition efficiencies are noticed.

TABLE-I: Corrosion inhibition efficiencies (%) offered by HEDP - Zn<sup>2+</sup> systems to mild steel immersed in 60 ppm chloride medium for seven days

HEDP (ppm)	Zn <sup>2+</sup> (ppm)				
	0	10	50	100	150
0	-	10	-23	-35	-40
10	5	10	13	15	15
50	11	22	98	98	98
100	15	30	98	98	98
150	18	35	98	98	98

The formulation consisting of 50 ppm HEDP and 50 ppm Zn<sup>2+</sup>, for example, offers 98% IE. The surface of the metal was very bright. A thin interference film was observed.

#### FTIR spectrum

In the FTIR spectrum (KBr) of the film formed on the surface of the metal immersed in the environment consisting of 60 ppm Cl<sup>-</sup>, 50 ppm HEDP and 50 ppm Zn<sup>2+</sup>, the P-O stretching frequency of the phosphonic acid decreases from 1119 cm<sup>-1</sup> to 1048 cm<sup>-1</sup>. This shift is caused by the decrease of electron density of the P-O bond. The shift of electron density from the O atom to Fe<sup>2+</sup> suggests that the O atom of the phosphonic acid is co-ordinated to Fe<sup>2+</sup>, resulting in the formation of Fe<sup>2+</sup>-HEDP complex on the metal surface. The band at 1357 cm<sup>-1</sup> is due to Zn(OH)<sub>2</sub>. Thus FTIR spectrum confirms that the protective film consists of Fe<sup>2+</sup>-HEDP complex and Zn(OH)<sub>2</sub>.

#### UV-visible spectra

The uv-visible absorption spectrum of the solution containing 50 ppm HEDP and 100 ppm Fe<sup>2+</sup> shows peaks at 200 nm and 250 nm. This is due to Fe<sup>2+</sup>-HEDP complex in solution.

The uv-visible reflectance spectra of surface of mild steel immersed in various environments are given in Fig. 1. The spectrum of the film formed on the surface of the metal immersed in the environment consisting of 60 ppm Cl<sup>-</sup> and 50 ppm Zn<sup>2+</sup> shows wavelength transition at 550 nm. The film has a band gap of (E<sub>g</sub> = 239/0.55) 2.25 eV corresponding to oxides of iron having semiconducting property.

The uv-visible reflectance spectra of the films formed on the surfaces of the metal specimens immersed in the environment consisting of 60 ppm Cl<sup>-</sup> and 50 ppm HEDP, and also in the system, 60 ppm Cl<sup>-</sup> plus 50 ppm HEDP plus 50 ppm Zn<sup>2+</sup>, do not any wavelength transition at 550 nm indicating the absence of any kind of oxides of iron on these metal surfaces. Further, absorption peak at 260 nm indicates the presence of Fe<sup>2+</sup>-HEDP complex on these metal surfaces.

#### X-ray diffraction (XRD)

The various XRD parameters of surfaces of metal immersed in various environments are given in Table II. For polished metal the iron peaks appear at 2θ = 317.8, 338.1, 355.4 and 372.0 K. When the polished metal is immersed in the environment consisting of 60 ppm Cl<sup>-</sup>, iron peaks appear at 2θ = 317.7, 338.0 and 355.4 K. The peaks due to magnetite (Fe<sub>2</sub>O<sub>4</sub>) appear at 2θ = 303.1, 308.5 and 335.5 K.

The XRD patterns of the surfaces of the metal specimens immersed in the environment consisting of 60 ppm Cl<sup>-</sup> and 50 ppm HEDP, and also in the formulation, 60 ppm Cl<sup>-</sup> plus 50 ppm HEDP plus 50 ppm Zn<sup>2+</sup>, indicate the absence of any kinds of oxides of iron such α-FeOOH, γ-FeOOH and

TABLE.II: XRD parameters of mild steel surfaces immersed in various environments.

Environment	peak NO	Glancing Angle, 2θ, degree	Interplanar Spacing, d, Å	Intensity, I, cps	Relative, Intensity, I/I <sub>0</sub>
a) Polished metal	1	44.80	2.021	1919	100
	2	65.10	1.432	1252	65
	3	82.40	1.169	1317	69
	4	99.00	1.013	1136	59
b) Polished metal + Cl <sup>-</sup> 60 ppm	1	30.10	2.966	1106	63
	2	35.50	2.527	1191	68
	3	44.70	2.026	1753	100
	4	62.50	1.485	1180	67
	5	65.00	1.434	1358	77
	6	82.40	1.169	1300	79
c) Cl <sup>-</sup> 60 ppm + HEDP 50 ppm	1	44.50	2.034	470	100
	2	64.90	1.436	220	47
	3	82.30	1.171	275	59
d) Cl <sup>-</sup> 60 ppm + HEDP 50 ppm + Zn <sup>2+</sup> 50 ppm	1	44.50	2.034	473	100
	2	64.90	1.436	223	47
	3	82.30	1.171	279	59

Fe<sub>3</sub>O<sub>4</sub>. Only iron peaks appear at 2θ = 317.5, 338.9 and 355.3 K, in both the cases. That is, the surface of the metal is as bright as the polished metal. This is in agreement with visual observation, and uv-visible reflectance spectra.

#### Influence of a biocide on the corrosion inhibition efficiency of HEDP-Zn<sup>2+</sup> system

The influence of a biocide, namely, N-cetyl-N, N,N-trimethylammonium bromide (CTAB) on the corrosion inhibition efficiency (corrosion rate) of the HEDP (50 ppm) plus Zn<sup>2+</sup> (50 ppm) system is shown in Fig. 2. It is observed that the IE of the HEDP-Zn<sup>2+</sup> system is not altered upto a concentration of 100 ppm CTAB. But when the concentration of CTAB is greater than or equal to 150 ppm a decrease in IE (increase in corrosion rate) is noticed.

#### Influence of HEDP-Zn<sup>2+</sup> system on the biocidal efficiency of CTAB

The influence of HEDP-Zn<sup>2+</sup> system on the biocidal efficiency of CTAB is shown in Fig. 3. It is observed that when the concentration of CTAB is greater than or equal to 50 ppm, the formulations have 100% biocidal efficiency (nil colony forming units/ml).

### CONCLUSION

1. Excellent corrosion inhibition efficiencies are shown by HEDP- Zn<sup>2+</sup> systems when the concentrations of both the species are greater than or equal to 50 ppm.

2. The protective film consists of iron phosphonate complex and Zn(OH)<sub>2</sub>; it is free from any oxides of iron.
3. CTAB, upto a concentration of 100 ppm, does not reduce the corrosion inhibition efficiency of HEDP-Zn<sup>2+</sup> system.

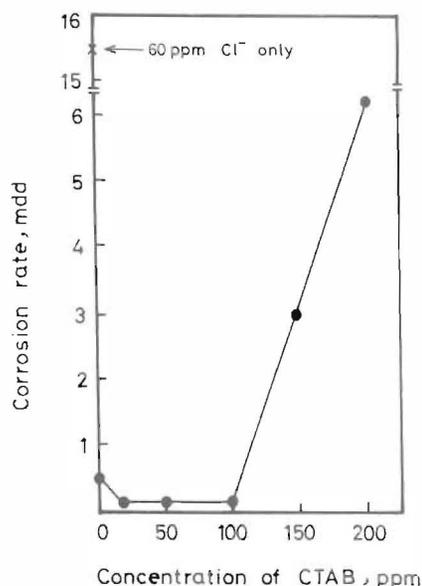


Fig.2: Corrosion rate of mild steel in a neutral aqueous environment (60 ppm Cl<sup>-</sup> + 50 ppm HEDP + 50 ppm Zn<sup>2+</sup>) as a function of concentration of the biocide - CTAB

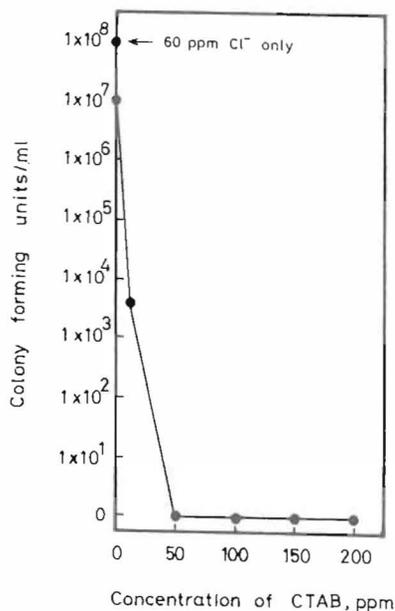


Fig.3: Number of colony forming units as a function of concentration of the biocide-CTAB system: Mild steel immersed in a neutral aqueous environment (60 ppm Cl<sup>-</sup> + 50 ppm HEDP + 50 ppm Zn<sup>2+</sup> CTAB)

4. HEDP-Zn<sup>2+</sup> system has no influence on the biocidal efficiency of CTAB.

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