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Synergistic Inhibition of Corrosion of Carbon Steel by the Ternary Formulations containing Phosphonate, Zn (II) and Ascorbic Acid

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Abstract

Studies on corrosion inhibition of carbon steel in low chloride aqueous environment using ternary inhibitor formulations based on phosphonates namely 1-Hydroxyethane-1,1-diphosphonic acid (HEDP) and Nitrilotris(methylenephosphonic acid) (NTMP) are presented. From these studies, an environmentally friendly organic compound namely ascorbic acid (AA) is proved to be an excellent synergist to the binary inhibitor formulations, HEDP – Zn^{2+} and NTMP – Zn^{2+} in corrosion control of carbon steel. Gravimetric studies infer that the required minimum concentrations of both the phosphonate as well as zinc ions for good corrosion inhibition could significantly be reduced by the addition of ascorbic acid. The minimum concentration of Zn^{2+} required for effective inhibition in case of HEDP – Zn^{2+} – AA and NTMP – Zn^{2+} – AA are 15 ppm and 20 ppm respectively. Further, still lower concentrations of Zn^{2+} are sufficient for the maintenance of the protective film in case of both the inhibitor formulations. Studies on effect of pH on corrosion inhibition indicate that both the ternary inhibitor formulations are effective in corrosion control in wide pH ranges. HEDP – Zn^{2+} – AA is effective in the pH range 5.0 to 9.0 and NTMP – Zn^{2+} – AA is effective in the pH range 4.0 to 10.0.

Keywords: Corrosion inhibition, carbon steel, phosphonate, ascorbic acid, synergism.

Introduction

Phosphonates in combination with zinc ions have been in use as effective corrosion inhibitors for carbon steel in cooling water systems for the past three decades[1–6]. The profound use of phosphonates is due to their hydrolytic stability, ability to form stable complexes with metal ions and low toxicity. Although several binary formulations containing phosphonate and Zn^{2+} were reported to be efficient corrosion inhibitors for carbon steel, they demand certain minimum levels of both Zn^{2+} and phosphonate in order to achieve an effective inhibition. But, the disposal of zinc salts in wastewaters at such levels has become unacceptable. The tolerance limit of zinc ions is restricted to about 2 mg dm^{-3} in industrial wastewaters[7]. Owing to these strict environmental restrictions on industrial wastewater disposal, research has been focussed in the direction to minimise the concentration of Zn^{2+} in the inhibitor formulations. An interesting method to decrease the concentration of Zn^{2+} in the phosphonate–Zn^{2+} inhibitor formulations is to add another non-toxic component of either organic or inorganic nature, which can synergistically act along with phosphonate and Zn^{2+}. A few of such ternary inhibitor formulations were reported in literature[8–10]. Thus, the focus has shifted to the search for effective "environmentally friendly ternary inhibitor formulations", with relatively low levels of Zn^{2+} and phosphonates. In the present study, two phosphonic acids namely, 1-Hydroxyethane-1, 1-diphosphonic acid (HEDP) and Nitrilotris(methylenephosphonic acid) (NTMP) have been chosen. Both these phosphonates have been extensively studied for their property of corrosion inhibition[1, 2, 11–17]. Also, these phosphonic acids have gained commercial importance in the cooling water systems over the past two decades. The organic additive chosen as second synergist in order to develop the ternary inhibitor formulations is ascorbic acid (AA), an environmentally friendly compound. A few studies on synergistic effect of ascorbate in combination with various phosphonate-Zn^{2+} systems have been reported by the authors of the present study[18–21]. The present study involves an extensive investigation of synergistic action of ascorbate in combination with the binary inhibitor systems viz., HEDP-Zn^{2+} and NTMP-Zn^{2+} in corrosion inhibition of carbon steel in an environment of 200 ppm of NaCl, using gravimetric method. Gravimetric method provides information on the amount of material attacked by corrosion over a specified period of time and under specified operating conditions[22]. This method gives relatively more reliable information on the loss of material on longer immersion times.The present investigation involves the determination of optimum concentrations of all the components of the inhibitor formulations to achieve an effective inhibition, minimum dosages for maintenance of the protective films and the effect of pH on inhibition efficiency of the ternary formulations.

Material and Methods

Specimens of the dimensions, 3.5 x 1.5 x 0.2 cm, taken from a single sheet of carbon steel with the following composition were used in the present study. C – 0.1 to 0.2 %, P – 0.03 to 0.08 %, S – 0.02 to 0.03 %, Mn – 0.4 to 0.5 % and the rest iron. Prior to the tests, the specimens were polished to mirror finish with 1/0, 2/0, 3/0 and 4/0 emery polishing papers respectively, washed with distilled water, degreased with acetone and dried.

HEDP ($C_2H_8O_7P_2$), NTMP ($C_3H_{12}NO_9P_3$), zinc sulphate ($ZnSO_4.7H_2O$), ascorbic acid (AA) ($C_6H_8O_6$) and other reagents were analytical grade chemicals. The molecular structures of the selected inhibitor molecules are shown in figure-1.

All the solutions were prepared by using triple distilled water. The pH values of the solutions were adjusted by using 0.01 N NaOH and 0.01 N H_2SO_4 solutions. An aqueous solution consisting of 200 ppm of NaCl has been used as the control because of the following reason. The water used in cooling water systems is generally either demineralised water or unpolluted surface water. In either case, the aggressiveness of the water will never exceed that of 200 ppm of NaCl.

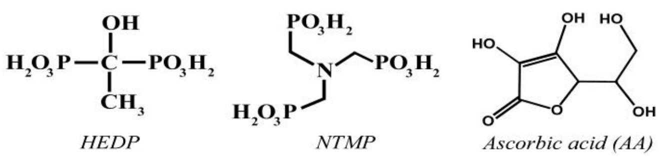

Figure-1
Molecular structure of the inhibitor molecules

In all the gravimetric experiments, the polished specimens were weighed and immersed in duplicate, in 100 mL control solution in the absence and presence of inhibitor formulations of different concentrations, for a period of seven days. Then the specimens were reweighed after washing, degreasing and drying. During the studies, only those results were taken into consideration, in which the difference in the weight-loss of the two specimens immersed in the same solution did not exceed 0.1 mg. Accuracy in weighing up to 0.01 mg and in surface area measured up to 0.1 cm^2, as recommended by ASTM G31, was followed[23]. The immersion period of seven days was fixed in view of the considerable magnitude of the corrosion rate obtained in the absence of any inhibitor after this immersion period.

The immersion period was maintained accurately up to 0.1 h in view of the lengthy immersion time of 168 h. Under these conditions of accuracy, the relative standard error in corrosion rate determinations is of the order of 2 % or less for an immersion time of 168 h[24]. Corrosion rates (CR) of carbon steel in the absence and presence of various inhibitor formulations are expressed in mmpy. Inhibition efficiencies (IE) of the inhibitor formulations were calculated by using the formula,IE (%) = 100 $[(CR)_o – (CR)_I] / (CR)_o$ where $(CR)_o$ and $(CR)_I$ are the corrosion rates in the absence and presence of inhibitor respectively.

Gravimetric studies were first carried out on the binary formulations containing the selected phosphonic acids and Zn^{2+}. The results of these studies were used to fix the concentration ranges of phosphonates and Zn^{2+} in the ternary inhibitor formulations. Gravimetric studies of the ternary formulations containing different phosphonates, Zn^{2+} and AA were carried out at pH 7.

The influence of pH on inhibition efficiency of the effective inhibitor formulations was also studied in wide pH ranges. Gravimetric experiments were also conducted with the specimens after the formation of the protective film in the inhibitor formulations, in order to arrive at the required minimum dosage of all the components for maintenance of the protective film in the chosen corrosive environment.

Results and Discussion

Corrosion inhibition efficiencies of the binary system, HEDP – Zn^{2+} at various concentrations of HEDP and Zn^{2+}, at pH 7.0 and an ambient temperature of 30 ^oC are presented in figure-2. These results indicate that HEDP alone in the concentration range of 30 – 60 ppm aggravates corrosion of carbon steel. As expected, addition of Zn^{2+} to HEDP offered good inhibition at optimum concentrations of each of the components, due to synergistic effect.

At any given concentration of HEDP, the inhibition efficiency increases with increase of concentration of Zn^{2+}, reaches a maximum at an optimum concentration and decreases on further increase of concentration. The highest inhibition efficiency of 95 % is obtained for the synergistic mixture containing 60 ppm of HEDP and 40 ppm of Zn^{2+}, corresponding to the molar ratio of $[HEDP]:[Zn^{2+}]$ as 1 : 2 at 3 x 10^{-4} M HEDP. At lower or higher molar ratios of [HEDP]: $[Zn^{2+}]$ than that mentioned above, the inhibition efficiencies are found to be less. These results indicate that the synergistic effect operating between HEDP and Zn^{2+} is the highest at a given molar ratio of $[HEDP]/[Zn^{2+}]$ in solution.

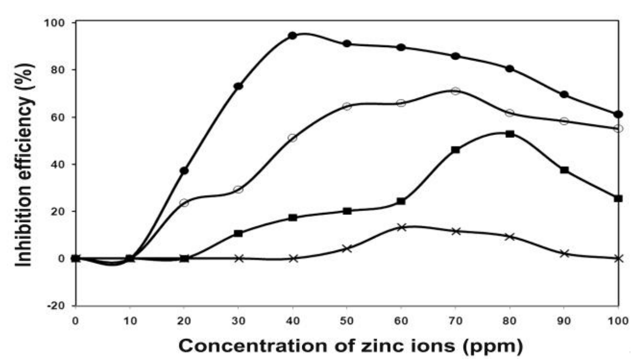

Figure-2
Corrosion inhibition efficiency of the binary system, HEDP – Zn^{2+}, as a function of concentration of zinc ions, at pH 7.0 and at different concentrations of HEDP: —✕—30 ppm; —■—40 ppm; —○—50 ppm; —●—60 ppm

Corrosion inhibition efficiencies of the binary system, NTMP – Zn^{2+} at various concentrations of NTMP and Zn^{2+} are presented in figure-3. These results indicate that NTMP alone in the concentration range of 30 – 50 ppm aggravates corrosion of carbon steel. Addition of Zn^{2+} to NTMP offered good inhibition at optimum concentrations of each of the components, due to synergistic effect. At 30 ppm as well as 40 ppm of NTMP, the inhibition efficiency increases with an increase in concentration of zinc ions. However, the highest inhibition efficiency is found to be only 70 % for the combination of 40 ppm of NTMP and 100 ppm of zinc ions. When 50 ppm of NTMP is considered, the inhibition efficiency increases with increase in concentration of Zn^{2+}, reaches a maximum of 97 % at 50 ppm of Zn^{2+} and decreases on further increase of concentration of Zn^{2+}.

The optimum concentrations of both NTMP and Zn^{2+} required for this highest inhibition efficiency, are 50 ppm each, corresponding to the molar ratio of 1:4.6 ([NTMP]:[Zn^{2+}]) at 1.7×10^{-4} M NTMP and at lower or higher molar ratios, the inhibition efficiencies are found to be less. These results indicate that the synergistic effect operating between NTMP and Zn^{2+} is the highest at a given molar ratio of [NTMP]:[Zn^{2+}] in solution.

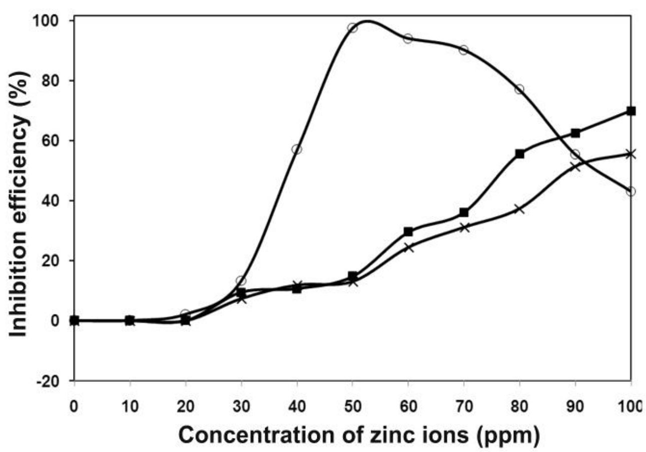

Figure-3
Corrosion inhibition efficiency of the binary system, NTMP – Zn^{2+}, as a function of concentration of zinc ions, at pH 7.0 and at different concentrations of NTMP: —×— 30 ppm; —■— 40 ppm; —○— 50 ppm

When AA is added as another additive to the mixtures of HEDP and Zn^{2+} as well as NTMP and Zn^{2+} at relatively low concentrations of each of them, corrosion rate of carbon steel is found to be reduced significantly. Hence, the ternary inhibitor formulations containing 20–40 ppm of HEDP and 10–15 ppm of Zn^{2+} as well as the formulations containing 20–40 ppm of NTMP and 10–20 ppm of Zn^{2+} are considered along with AA in the concentration range of 10 – 200 ppm. The results of these studies are shown in figures-4 and 5. In the presence of AA, in order to achieve an inhibition efficiency > 95 %, the required minimum concentrations of HEDP and Zn^{2+} are 20 ppm and 15 ppm, corresponding to 0.98×10^{-4} M and 2.3×10^{-4} M, respectively.

While the binary system consisting of 20 ppm of HEDP and 15 ppm of Zn^{2+} aggravated corrosion, the ternary inhibitor system containing 25 ppm of AA, 20 ppm of HEDP and 15 ppm of Zn^{2+}, afforded an inhibition efficiency of 96 %. Similarly, the ternary inhibitor system containing 25 ppm of AA and 20 ppm each of NTMP and Zn^{2+}, afforded an inhibition efficiency of 95 %. The synergistic effect of AA in the ternary systems is established by this result.

However, at the higher concentrations of AA such as 100 ppm and above, the inhibition efficiency is found to be reduced to less than 50 %. From these results, it can be observed that in case of the ternary inhibitor formulations, as the concentration of AA is increased, the corrosion rate decreases, reaches a minimum at an optimum concentration of AA and then increases.

Thus, in case of the ternary inhibitor formulations also, the mixtures containing optimum concentrations of each of the components give the highest inhibition efficiency. In other words, optimum amounts of each of the three components must be available in the solution, so that each one of them plays its own synergistic role in the formation of protective film covering the entire metal surface. It may be mentioned here that the molar ratio of HEDP: Zn^{2+} : AA is 1 : 2.3 :1.3 to exhibit excellent synergism with an efficiency > 95 %. In case of NTMP-Zn^{2+}-AA system, the molar ratio of NTMP: Zn^{2+} : AA is 1 : 4.6 :2 corresponding to an inhibition efficiency > 95 %.

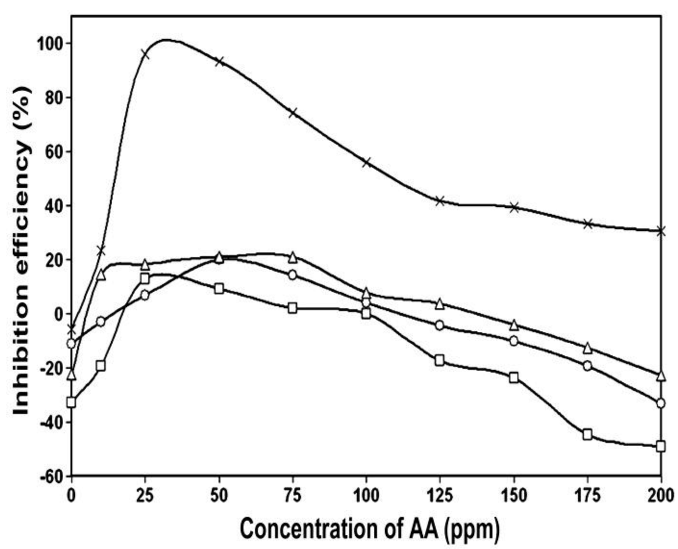

Figure-4
Inhibition efficiency of the ternary inhibitor formulation, HEDP-Zn(II)-AA, as a function of concentration of ascorbic acid, added to various combinations of HEDP and Zn^{2+} at pH 7 —○— HEDP (20 ppm) + Zn^{2+} (10 ppm); —△— HEDP (30 ppm) + Zn^{2+} (10 ppm); —□— HEDP (40 ppm) + Zn^{2+} (10 ppm); —×— HEDP (20 ppm) + Zn^{2+} (15 ppm)

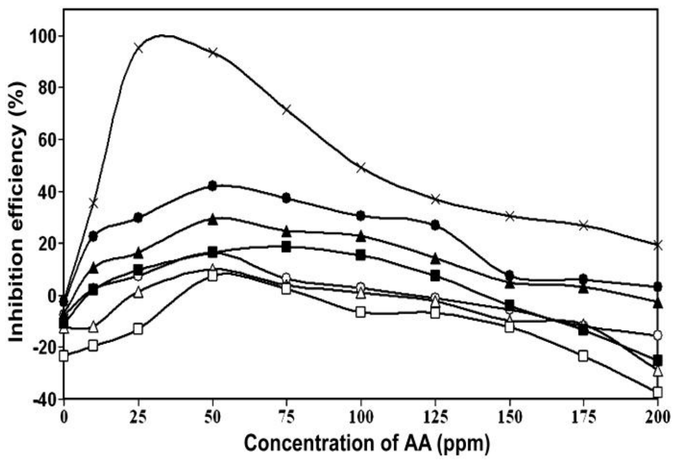

Figure-5
Inhibition efficiency of the ternary inhibitorFormulation, NTMP-Zn(II)-AA, as a function of concentration of ascorbic acid, added to various combinations of NTMP and Zn^{2+} at pH 7 —○—NTMP (20 ppm) + Zn^{2+} (10 ppm); —△—NTMP (30 ppm) + Zn^{2+} (10 ppm); —□—NTMP (40 ppm)+ Zn^{2+} (10 ppm); —●—NTMP (20 ppm) + Zn^{2+} (15 ppm); —▲—NTMP (30 ppm) + Zn^{2+} (15 ppm); NTMP (40 ppm) + Zn^{2+} (15 ppm); —×—NTMP (20 ppm) + Zn^{2+} (20 ppm)

The influence of pH on inhibition efficiency of the inhibitor system, HEDP (20 ppm) + Zn^{2+} (15 ppm) + AA (10 – 75 ppm) in the pH range of 4.0–10.0, is shown in figure-6 and that of the inhibitor system, NTMP (20 ppm) + Zn^{2+} (20 ppm) + AA (10 – 75 ppm) in the pH range of 3.0–11.0, is shown in figure-7.

The highest inhibition efficiency could be obtained by the formulation containing HEDP (20 ppm) + Zn^{2+} (15 ppm) + AA (25 ppm) in the pH range of 5.0 – 8.0. But when the pH is decreased from 5.0 to 4.0. The inhibition efficiency is reduced to 47 % and when the pH is increased from 8.0 to 9.0, the inhibition efficiency is reduced to 37.6 %. Interestingly, when the concentration of AA is increased to 50 ppm, the ternary formulation is found to show 97 % inhibition efficiency even at pH 9.0.

In case of the ternary formulation containing NTMP, Zn^{2+} and AA, the highest inhibition efficiency > 90 % could be obtained by the formulation containing NTMP (20 ppm) + Zn^{2+} (20 ppm) + AA (25 ppm) in the pH range of 4.0 – 8.0. But when the pH is decreased from 4.0 to 3.0, the inhibition efficiency is reduced to 15 % and when the pH is increased from 8.0 to 9.0, the inhibition efficiency is reduced to 27 %. However, when the concentration of AA is increased from 25 to 50 ppm, the ternary formulation is effective at pH 9.0 also. Similarly, when the concentration of AA is further increased to 75 ppm, the formulation is effective even at pH 10.0. Hence, both the ternary inhibitor systems are excellent inhibitors for cooling water systems as far as the effect of pH is considered.

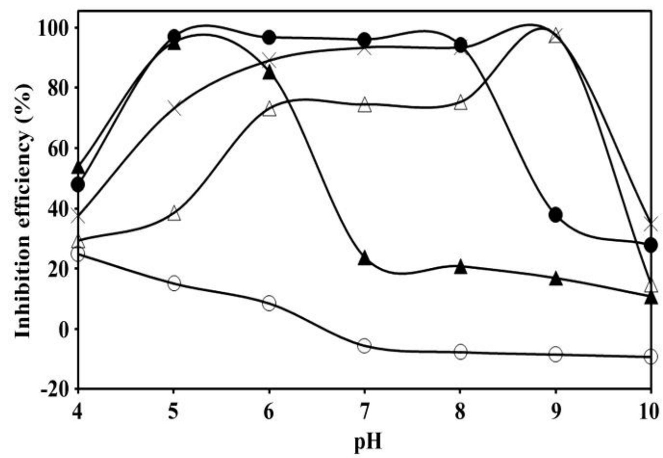

Figure-6
Corrosion inhibition efficiency of the ternary inhibitor system, HEDP (20 ppm) – Zn^{2+} (15 ppm) – AA, as a function of pH, at different concentrations of AA —○—0 ppm; —▲—10 ppm; —●—25 ppm; —×—50 ppm; —△—75 ppm

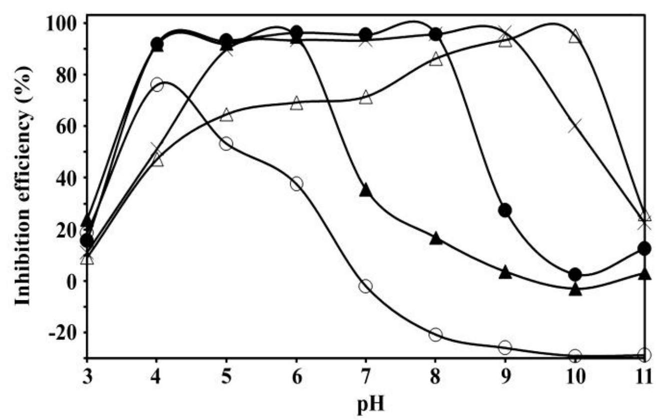

Figure-7
Corrosion inhibition efficiency of the ternary inhibitor system, NTMP (20 ppm) – Zn2+ (20 ppm) – AA, as a function of pH, at different concentrations of AA —○—0 ppm; —▲—10 ppm; —●—25 ppm; —×—50 ppm; —△—75 Ppm

The results of gravimetric studies carried out in order to determine the minimum concentrations of all the three components of the inhibitor formulations for maintenance of the protective films are shown in tables-1 and 2. The results (table-1) indicate that the inhibitor mixture containing only 15 ppm of HEDP, only 5 ppm of Zn^{2+} and 20 ppm of AA could maintain the protective film. The maintenance dosage of HEDP : Zn^{2+} : AA in terms of molar ratio is 1 : 1 : 1.4. The results shown in table-2 indicate that the inhibitor mixture containing 20 ppm of NTMP, 10 ppm of Zn^{2+} and 15 ppm of AA could maintain the protective film. The maintenance dosage of NTMP: Zn^{2+} : AA in terms of molar ratio is 1 : 2.3 : 1.

Table-1
Results of gravimetric studies of the inhibitor formulations containing HEDP, Zn^{2+} and AA for maintenance of the protective film

S. No.	Concentration of the inhibitor component for maintenance of the protective film (ppm)			Corrosion rate (mmpy)	Inhibition efficiency (%)
	HEDP	Zn^{2+}	AA		
1	0	0	0	0.08108	-
2	20	15	25	0.00316	96.10
3	20	10	25	0.00377	95.35
4	20	5	25	0.00558	93.11
5	15	5	25	0.00574	92.92
6	10	5	25	0.01661	79.51
7	5	5	25	0.03485	57.01
8	15	5	20	0.00682	91.59
9	15	5	15	0.01222	84.93
10	15	5	10	0.03146	61.20
11	15	5	5	0.04517	44.29

Table-2
Results of gravimetric studies of the inhibitor formulations containing NTMP, Zn^{2+} and AA for maintenance of the protective film

S. No.	Concentration of the inhibitor component for maintenance of the protective film (ppm)			Corrosion rate (mmpy)	Inhibition efficiency (%)
	NTMP	Zn^{2+}	AA		
1	0	0	0	0.08108	-
2	20	20	25	0.00385	95.25
3	20	15	25	0.00406	94.99
4	20	10	25	0.00434	94.64
5	20	5	25	0.03814	52.96
6	15	10	25	0.02520	68.91
7	10	10	25	0.05811	28.33
8	5	10	25	0.06521	19.57
9	20	10	20	0.00635	92.17
10	20	10	15	0.00662	91.83
11	20	10	10	0.03414	57.89
12	20	10	5	0.07081	12.66

Conclusion

Both the ternary inhibitor formulations viz., HEDP-Zn^{2+}-AA and NTMP-Zn^{2+}-AA are effective inhibitor systems for corrosion control of carbon steel in low chloride aqueous environment. These systems require very low concentrations of zinc ions in presence of ascorbic acid. The synergistic action of ascorbic acid in combination with phosphonate-Zn^{2+} is proved in the present study. The uniqueness of the inhibitor system, HEDP-Zn^{2+}-AA is that it requires only 5 ppm of Zn^{2+} in order to maintain the protective nature of the surface film. Both the formulations are effective in corrosion control in a wide pH range that includes pH range maintained in cooling water systems.

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