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A New Molybdate-Based Inhibitor as a Replacement for Toxic Chromate Based Inhibitor in Cooling Water System

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Molybdate-based inhibitor is long known as an inorganic type inhibitor and is less toxic than chromate-based inhibitors, which are used in cooling water systems. Electrochemical techniques were used to study the inhibition effects on the general and pitting/crevice corrosion of mild steel, which is the main alloy of cooling water systems. In this study a molybdate-based inhibitor has been introduced with the composition of 40 ppm molybdate/15 ppm phosphate/40 ppm polyphosphate/10 ppm zinc. It has been compared with a low chromate and a commercial inhibitor. To study the inhibition effects of inhibitors on the uniform and pitting corrosion of mild steel, electrochemical techniques such as potentiodynamic, polarization and cyclic polarization, weight loss method and surface analysis techniques such as SEM and EDS microanalysis have been used. The results indicate that this molybdate-based inhibitor is as effective as the low chromate inhibitor and it is more effective than the commercial one.

Key Words: Inhibitor, Cooling water system, Molybdate, Polarization, SEM, EDS.

INTRODUCTION

The use of inhibitors in controlling corrosion in cooling water systems is an established technology. The toxicity of chromate-based inhibitors is a limiting factor in its use in this role. Molybdate-based inhibitor has been proposed as a possible replacement for chromate-based inhibitors in cooling water systems[1]. Molybdate has long been known as an inorganic (MoO_4^-) type corrosion inhibitor. Sodium molybdate, an anodic inhibitor, is effective for protecting mild steel in the pH range 5.8–8.5.[2–5] To act as an inhibitor, it requires the presence of oxygen. The presence of aggressive ions such as chloride anion (Cl^-) reduces the efficiency of molybdate and higher concentrations are necessary for corrosion inhibition[6–8], which is not economically favourable. In order to improve the action and to reduce the quantity of molybdate used to achieve good inhibition, especially in cooling water systems; other synergistic or complementary inhibitors have been employed. A mixture of inhibitors can give better inhibition protection than individual inhibitors.

Attempts have been made to improve the inhibition efficiency of molybdate by using it with organic compounds and with oxidizing agents such as nitrite (NO_2^-) etc.[9–15] Jefferies and Bucher[16] have investigated the addition of zinc to molybdate to improve its performance. Similarly, the ability of different compounds as additives to molybdate to hinder corrosion of mild steel in cooling water systems has been considered by several authors[17–24].

The objective of the present work was to investigate corrosion inhibition by new optimization molybdate-based (multinon-toxic inhibition) on mild steel in an artificial cooling water (ACW) which was composed of distilled water + 800 ppm (Cl^-) + 200 ppm (SO_4^{2-}).

EXPERIMENTAL

Mild steel specimens of the composition C = 0.05, Si = 0.4, Mn = 0.6 and remainder Fe with dimensions 7.62, 0.95, 10.16 cm were used for weight loss measurements. Mild steel cylindrical rods of the same alloy embedded in epoxy resin with an exposed area of 1 cm^2 were used for electrochemical measurements. Potentiodynamic and cyclic polarization curves were generated using a potentiostat (EG&G model 263A). The electrochemical tests were carried out using the following three-electrode assembly: Pt as counter electrode, saturated calomel electrode (SCE) as reference and mild steel as working electrode. Before each test, the specimens were prepared with silicon carbide paper to 300–600 grit, degreased in acetone and washed in distilled water. Testing solutions with different inhibitors (Table-1) were prepared by dissolving analytical-grade sodium molybdate ($NaMoO_4$), sodium polyposphate ($Na(PO_4)_4$), zinc sulphate ($ZnSO_4$), potassium chromate (K_2CrO_4) and sodium borate ($NaBO_3$).

Distilled water with 800 ppm sodium chloride and 200 ppm sodium sulphate was used as artificial cooling water (ACW). All tests were performed at 25°C. Before measurement of the polarization curves, a stabilization period of 1 h was observed which proved sufficient as indicated by open circuit potential (E_{oc}). All tests were carried out at a scan rate of 4 mV/s. Table - 1 shows the composition of the different inhibitors used in this work.

TABLE-1
COMPOSITION OF INHIBITORS

Inhibitor	Composition
1	1000 ppm molybdate
2	40 ppm molybdate + 40 ppm polyphosphate + 10 ppm zinc
3	40 ppm molybdate + 40 ppm polyphosphate + 15 ppm phosphate + 10 ppm zinc
4	5 ppm chromate + 40 ppm borate + 40 ppm polyphosphate + 5 ppm zinc
5	Commercial

RESULTS AND DISCUSSION

Electrochemical measurements

Polarization curves: The polarization curves for mild steel in ACW alone and with addition of 1000 ppm molybdate are shown in Fig. 1. Addition of 1000 ppm molybdate causes corrosion potential (E_{corr}) to increase and corrosion current density (I_{corr}) to decrease for mild steel. 1000 ppm molybdate reduces corrosion of mild steel in ACW but it is not suitable because its concentration is high. Therefore polyphosphate and zinc ion were added to molybdate to decrease its amount.

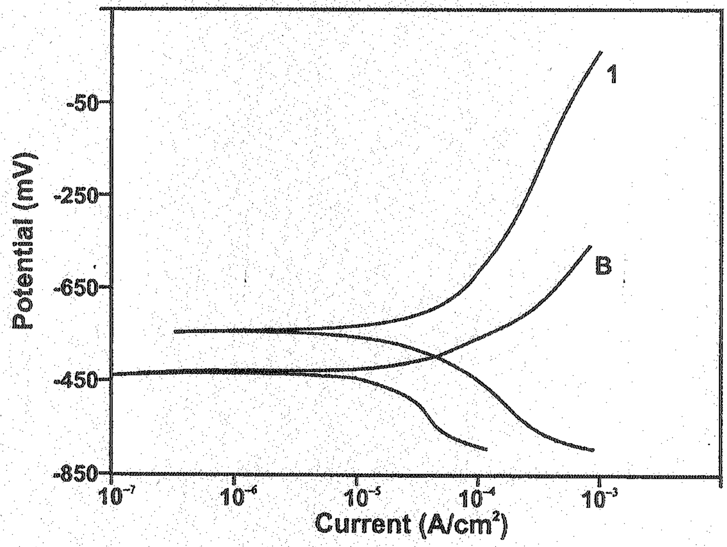

Fig. 1. Potentiodynamic polarization curves for mild steel in ACW (B) and 1000 ppm molybdate (1)

Fig. 2 shows polarization curves of mild steel in ACW with inhibitors 1 and 2. For inhibitor 2, corrosion potential is more negative and corrosion current density is lower than inhibitor 1.

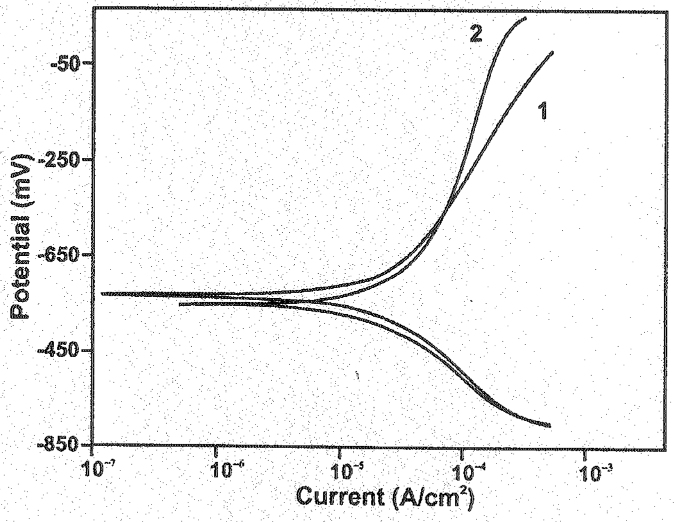

Fig. 2. Potentiodynamic polarization curves for mild steel in ACW with inhibitors 1 and 2

Figure 3 shows polarization curves for mild steel in ACW with inhibitors 2 and 3. The corrosion potential (E_{corr}) for inhibitors 2 and 3 is almost the same, but the passive regain of 3 is larger than 2.

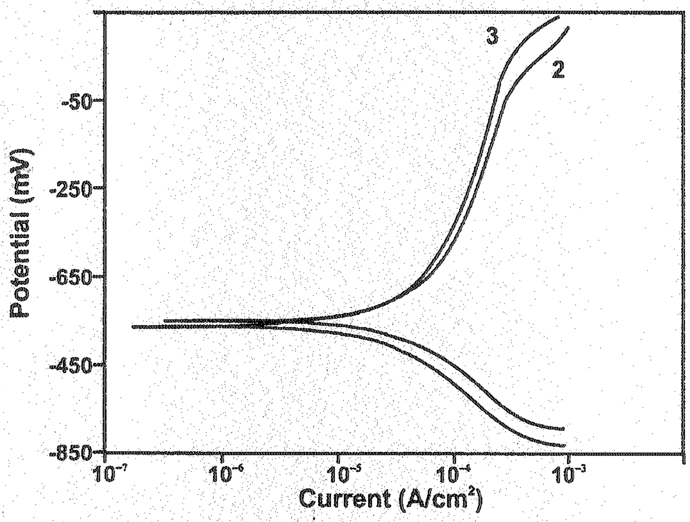

Fig. 3. Potentiodynamic polarization curves for mild steel in ACW with inhibitors 2 and 3

The electrochemical polarization results confirmed the generally accepted contention that inhibitor 1 affects the anodic corrosion process predominantly. Addition of polyphosphate and zinc to inhibitor 1 causes a slightly negative shift of potential in the cathodic curve suggesting that the action of polyphosphate was on cathodic sites.

Addition of phosphate and zinc to molybdate not only decreases the amount of molybdate but also improves its performance.

Fig. 4 shows polarization curves for mild steel in ACW with inhibitors 3 (molybdate-based), 4 (low chromate-based) and 5 (commercial).

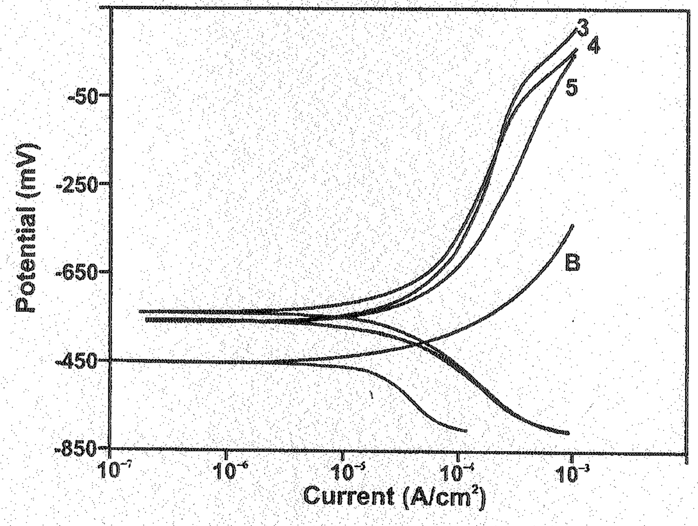

Fig. 4. Potentiodynamic polarization curves for mild steel in ACW (B) with inhibitor 3 (molybdate-based), 4 (chromate-based) and 5 (commercial).

Table-2 gives the values of inhibition efficiency η (%), corrosion current densities (I_{corr}) and corrosion potentials (E_{corr}) obtained from the polarization measurements of mild steel for different inhibitors in ACW. The inhibition efficiency is defined as:

$$\eta\ (\%) = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100$$

where I_{corr} and $I_{corr(i)}$ are the corrosion current density values without and with inhibitors respectively.

Regarding these results, it can be concluded that the value of corrosion current density of mild steel in ACW with addition of molybdate decreases and with addition of phosphate, polyphosphate and zinc ion to molybdate decreases more and its inhibition efficiency increases.

The electrochemical polarization results confirmed that the inhibitor 3 was of anodic type.

TABLE-2
ELECTROCHEMICAL POLARIZATION PARAMETERS FOR MILD STEEL IN ACW WITHOUT AND WITH DIFFERENT INHIBITORS

Inhibitor	E_{corr} (mV)	I_{corr} (μA cm^{-2})	η (%)
ACW(Blank)	–644.5	28.1	–
1	–550.4	7.1	71.30
2	–555.3	1.8	92.70
3	–551.7	1.8	92.70
4	–533.5	1.7	93.38
5	–553.5	9.1	92.80

Cyclic polarization curves: Cyclic potentiodynamic polarization measurements (pitting scans) were performed to determine the effectiveness of the inhibitors on susceptibility to localized corrosion (pitting and crevice corrosion) of mild steel.

This consisted of a forward scan and a reverse scan. The reverse scan was continued toward a more active potential until the forward and reversed scans intersected. The point of intersection was the protection potential (E_{prot}), meaning the potential of the material had to be above (E_{prot}) for existing areas of localized corrosion to propagate. Below (E_{prot}), all existing sites of localized corrosion would be passivated and will cease to propagate. The greater the difference between (E_{prot}) and the breakdown potential (E_b), the greater would be the tendency for pitting and crevice corrosion. The breakdown potential was part of the forward scan and indicated the potential value in which the protective surface film on the metal broke down and pits were formed. The possibility of pit initiation decreased with greater values of E_b.

Figs. 5, 6 and 7 show cyclic polarization curves of mild steel for inhibitors 3, 4 and 5 in ACW and Fig. 8 shows cyclic polarization curve of mild steel in ACW.

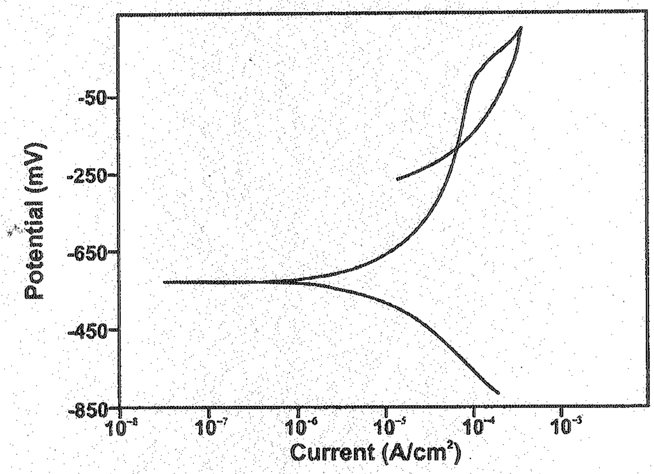

Fig. 5. Cyclic polarization curve of mild steel in ACW with inhibitor 3

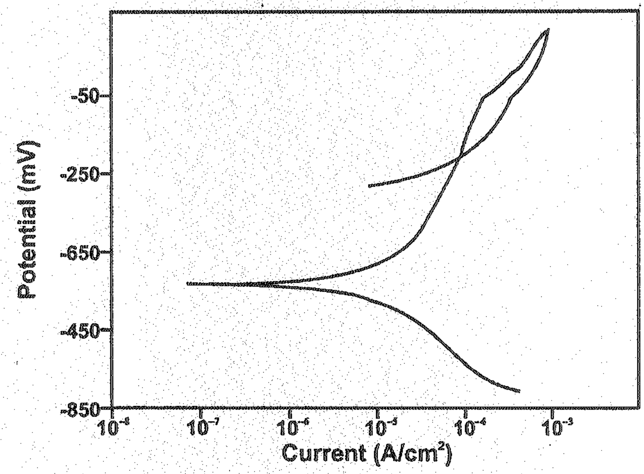

Fig. 6. Cyclic polarization curve of mild steel in ACW with inhibitor 4

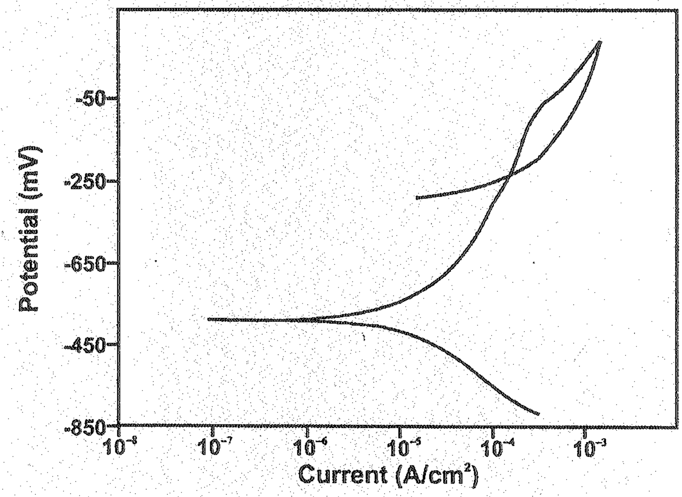

Fig. 7. Cyclic polarization curve of mild steel in ACW with inhibitor 5

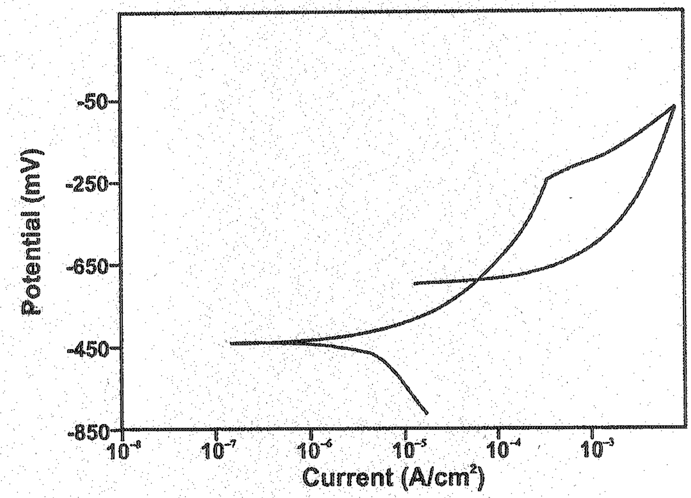

Fig. 8. Cyclic polarization curve of mild steel in ACW

For comparison, the values of the pitting potential (E_{pit}) and protection potential (E_{prot}) obtained from cyclic polarization measurements of mild steel in ACW for inhibitors 3, 4 and 5 are shown in Fig. 9.

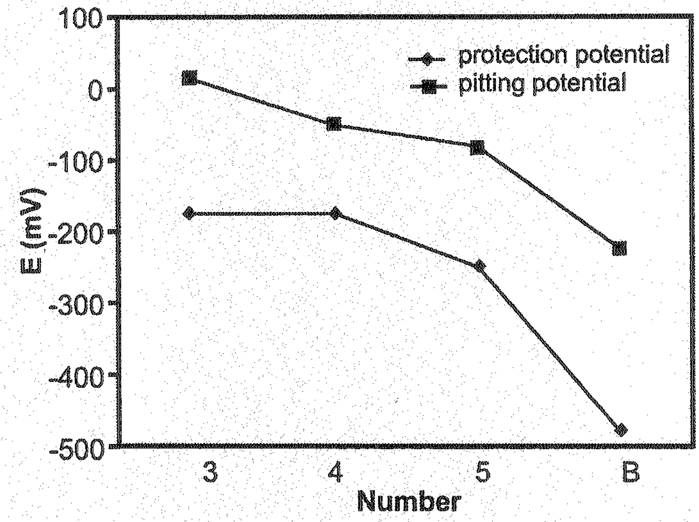

Fig. 9. Pitting and protection potential for mild steel in ACW(B) and inhibitors 3, 4 and 5

Pitting and protection potential of mild steel in solution with inhibitors 3, 4 and 5 are more positive than the solution without inhibitor ACW. Protection potential for inhibitor 3 is the same as 4 but pitting potential for inhibitor 3 is more positive than 4 and 5.

As the protection and pitting potential increases, this indicates that the possibility of pitting and crevice corrosion decreases.

The presence of phosphate-ion with molybdate causes the molybdate's conversion to hetero-polymolybdate which is a strong oxidizing agent and combines with ferro-ion and an insoluble precipitate of iron molybdate forms. The precipitation reduces the susceptibility to pitting and crevice corrosion[16].

Weight loss measurement: The weight loss of samples after 21 d exposure to solution ACW without and with different inhibitors were measured. Regarding experimental weight loss data, inhibition efficiencies (77%) were calculated classically as follows:

$$\eta\ (\%) = \frac{W_0 - W_i}{W_o} \times 100$$

where w_0 and w_i are the weight loss observed in the absence and in the presence of inhibitor respectively. Values of η (%) and rate of corrosion (mdd) for mild steel in ACW and with different inhibitors are summarized in Table-3. The results obtained from the polarization curves are in agreement with those from the corrosion weight loss tests.

TABLE-3
WEIGHT LOSS DATA OF MILD STEEL IN ACW AND WITH DIFFERENT INHIBITORS

Number	Rate of corrosion (mdd)	η (%)
ACW (Blank)	65.16	–
1	19.51	70.71
2	7.15	89.03
3	3.25	95.01
4	3.57	94.51
5	24.14	62.92

Surface analysis techniques

SEM test: SEM micrographs of samples after 21 d exposure to solution ACW (a) and with inhibitor 3 (b) are shown in Fig. 10; as observed, the surface patterns are different.

Fig. 10b exhibits a layer with a uniform adherent and continuous structure, while Fig. 10a shows crystal growth of iron oxide on the surface and its non-continuous structure. The surface roughness of mild steel exposed to solution ACW is higher than mild steel exposed to solution ACW with inhibitor 3.

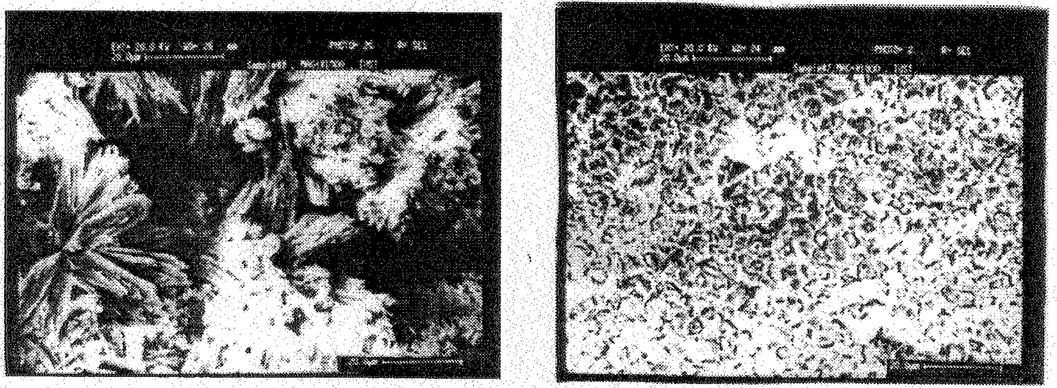

Fig. 10. SEM micrograph of mild steel surface in ACW (a) and with inhibitor 3 (b)

EDS tests: X-ray EDS of samples after 21 d exposure to solution ACW and inhibitor 3 (molydate-based inhibitor) are shown in Fig. 11. The presence of C, Si, Mn and Fe elements could be observed in Figs. 11a–b, but the presence of Mo is only in Fig. 11(b) which indicates that molybdate oxide forms on the surface of the mild steel sample only in ACW with inhibitor 3.

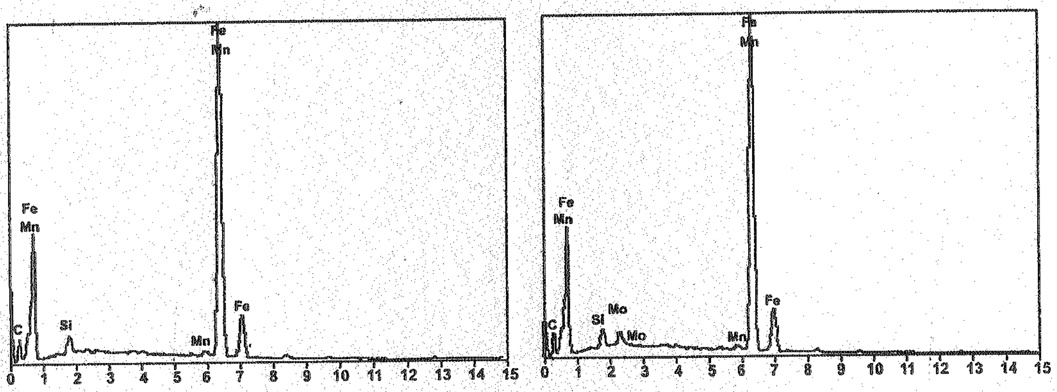

Fig. 11. X-ray energy dispersive spectrometry of mild steel in ACW (a) and with inhibitors (b).

A glance at the combinations, which are capable of inhibition corrosion, shows that addition of phosphate, polyphosphate and zinc ion have allowed reduction in the quantity of molybdate required for inhibition and increases its inhibition corrosion efficiency. The most important beneficial factor in using molybdate-based inhibitors is that they are not toxic and are suitable replacements for low chromate-based inhibitors.

Conclusion

1. Sodium molybdate with addition of phosphate, polyphosphate and zinc ion exhibits synergistic effect in protecting mild steel in cooling water systems.
2. The polarization curve indicates that inhibitor composition in molybdate-based inhibitors is of anodic type.
3. Cyclic polarization results indicate that pitting corrosion resistance of mild steel for molybdate-based inhibitors is similar to low chromate-based inhibitors and higher than commercial inhibitors.
4. Molybdate-based inhibitors exhibit corrosion inhibition efficiency similar to low chromate-based inhibitors and higher than commercial inhibitors.
5. The results of weight loss test exhibit good correlation with data obtained form the polarization curves.
6. Surface analyses indicate that molybdate-based inhibitors could form a relatively steady, complete, compact and uniform protective film on the surface of mild steel.

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