

Effect of Molybdate, Nitrite and Zinc Ions on the Corrosion Inhibition of Mild Steel in Aqueous Chloride Media Containing Cupric Ions

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Abstract

An investigation has been conducted on the corrosion inhibition of mild steel by molybdate, nitrite and zinc ions in aqueous chloride media containing cupric ions. Molybdate inhibits mild steel corrosion in near neutral and alkaline (pH 6 and above) chloride media and accelerates corrosion in acidic media (below pH 6) both in the presence and absence of cupric ions. Nitrite inhibits mild steel corrosion in chloride media at pH 4.5 and above, but accelerates corrosion below pH 4.5 both in the presence and absence of cupric ions. Molybdate and nitrite act as a synergistic corrosion inhibitor in chloride media with or without cupric ions at pH 4.5 and above. In the acidic region between pH 3 and 4.5, the combination can decrease corrosion with a low concentration of molybdate and high concentration of nitrite. These concentrations depend on the relative amounts of molybdate and nitrite present in the system. Zinc ions inhibit mild steel corrosion only in acidic chloride media. Based on the experimental results, mechanisms of action of molybdate, nitrite and zinc ions on mild steel corrosion in aqueous chloride media with or without cupric ions have been proposed.

Keywords: Molybdate; Nitrite; Mild steel; Corrosion rate; Synergistic corrosion inhibitor.

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1. Introduction

Mild steel and steel alloys have wide range of applications. However, corrosion is the severe problem for mild steel in aqueous media. In many cases copper and copper based alloys are used with steel in industries. It is, however, known [1, 2] that trace amount of copper in the aqueous medium can accelerate the corrosion of the mild steel. Many methods such as coating, phosphating, anodic or cathodic controls, use of inhibitors, etc are adopted to minimize the corrosion damages of steel. Among them only the use of inhibitor is convenient and economic for controlling aqueous corrosion of boiler, condensers and pipelines carrying cooling water, petroleum and natural gas. The corrosion

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inhibition of mild steel in chloride media in presence of cupric ions has not yet been systematically investigated.

'Nowadays' there are hundreds of corrosion inhibitors but none of them equals to chromate and dichromate based inhibitors in efficiency. The strong objection against the use of chromate and dichromate inhibitors is their toxicity. Molybdate has long been known as an inorganic XO_4^{n-} type corrosion inhibitor [3-5]. It is a nontoxic chemical [6], easily available, and cheap. However, investigations have shown that molybdate is not as effective as the toxic chromate and dichromate based inhibitors. Pryor and Cohen [7] have reported that the low inhibition efficiency of molybdate is a result of its weak oxidizing power and acts only in the presence of dissolved oxygen. Lizloves [8] have investigated the corrosion inhibition behavior of molybdate in the presence of aggressive chloride and sulfate ions, and reported its efficiency in the presence of oxygen. There have been extensive researches on the improvement the inhibition efficiency of molybdate in actual situation. Farr and Saremi [9] have investigated the effect of immersion time on the corrosion inhibition efficiency of molybdate and the effect of citric acid as a primary film former. Nitrite is an oxidizing agent with corrosion inhibitive properties. It has been used [10] for improving the corrosion inhibition efficiency of molybdate.

Most investigators have been used electrochemical technique for the evaluation of the inhibitive action of molybdate. However, determination of the corrosion rate of steel by electrochemical technique is a highly tedious and difficult procedure, especially when the surface is covered with an oxide layer. The present investigation has been carried out by solution analysis due to corrosion. The aim of the present study is to investigate the effect of molybdate, nitrate, and zinc ions on the corrosion inhibition of mild steel in chloride media containing cupric ions.

2. Experimental Procedure

Commercial grade mild steel coupons ($40 \times 40 \times 0.5 \text{ mm}^3$ in size) were used in all experiments. Both sides of the coupons were abraded with various graded waterproof silicon carbide paper, and polished on a polishing wheel using Griffin's fast cutting alumina powder (grade 5/50). The polished coupons were washed with tap water followed by distilled water and finally rinsed with acetone. These were then dried in the open air, and stored in a desiccator over silica gel before being used in experiments.

The aqueous solution for corrosion rate study was prepared by dissolving appropriate amounts of NaCl and CuCl_2 in distilled water. The inhibitor solution was prepared by dissolving appropriate amounts of sodium molybdate / sodium nitrite / zinc chloride or sodium molybdate and sodium nitrite together in chloride and cupric media. The pH values of the solutions were measured by a Corning 7A model pH meter and adjusted by the addition of dilute solutions of HCl or NaOH. All reagents used were of reagent grade. Each mild steel coupon was immersed in 200 mL of stagnant solution contained in a 250 mL glass beaker. The coupon was suspended in the solution by a fine cotton thread from a glass rod placed across the top of the beaker. Care was taken so that the coupon was fully immersed in the solution and did not touch the side walls or bottom of the beaker. The

immersion period was 4 days in all experiments. After the expiry of the immersion period, any rust adhering to the coupon was carefully removed with a camel brush into the solution. Concentrated HCl (10 mL) and HNO₃ (1 mL) were added into the solution and the solution was then boiled to dissolve all solid corrosion products and to oxidize ferrous ions to ferric state.

The concentration of Fe³⁺ in the solution was determined by the thiocyanate method [11] at 480 nm using a WPA S104 spectrophotometer. The corrosion rate of mild steel in mg dm⁻² day⁻¹ (mdd) was calculated according to the relation:

$$\text{Corrosion rate} = \frac{\text{amount of iron in the solution}}{\text{surface area of the coupon} \times \text{immersion time}}$$

where the amount of iron is expressed in mg, surface area is expressed in dm², and immersion time is expressed in day.

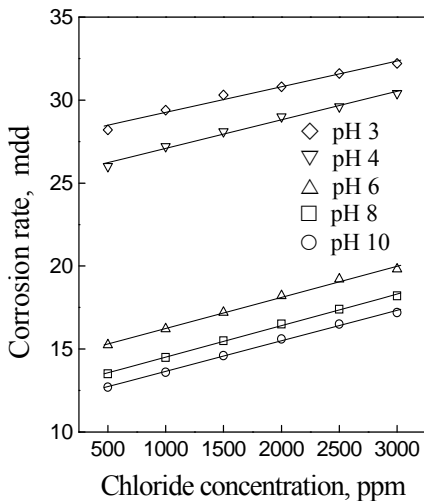


Fig. 1. Effect of chloride ions concentration on corrosion rate of mild steel in different pH media.

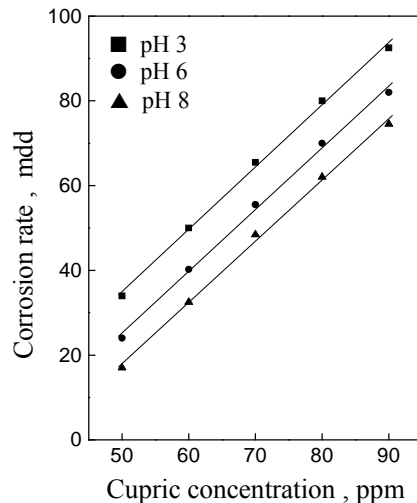


Fig. 2. Effect of cupric ions concentration on corrosion rate of mild steel in 500 ppm chloride ions at different pH media.

3. Results and Discussion

The variation of corrosion rate of mild steel with chloride ions concentration in acidic, near neutral and alkaline solution is shown in Fig. 1. Corrosion rate of the mild steel increases with the increase of chloride ions concentration at all pH values. However at constant chloride ions concentration the minimum corrosion rate of mild steel is observed at the highest and maximum at the lowest value of pH. It is known that chloride ions are highly aggressive for mild steel due to very high solubility of iron chloride. In the absence of chloride ions, hydrous oxide layer of the composition FeOOH exists on the iron surface

in near neutral and alkaline media. However in the presence of chloride ions, the mechanism of corrosion could be due to the exchange reaction as suggested elsewhere [12, 13] to produce ferric oxychloride according to the reaction:



The ferric oxychloride so produced possesses higher solubility, and as a result it removes the oxide layer very easily and corrosion goes on unhindered.

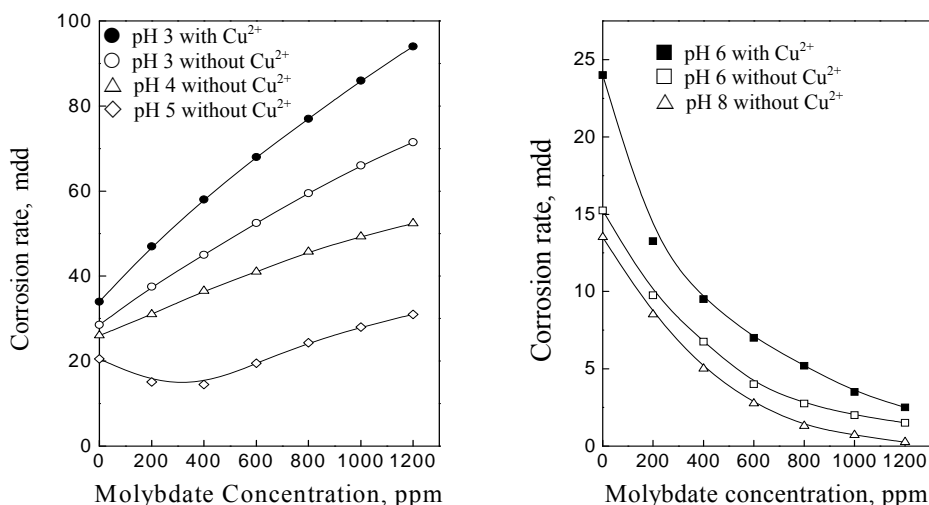
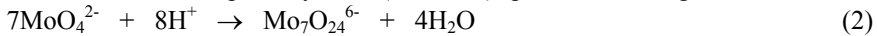


Fig. 3. Effect of molybdate concentration on corrosion rate of mild steel with or without cupric ions in 500 ppm chloride ions at different pH media.

Fig. 2 show that cupric ions in chloride medium greatly increase the corrosion of mild steel. Cupric ions are adsorbed, reduced and deposited on the steel surface. The deposited/adsorbed copper acts as a cathode where accelerated reduction of dissolved oxygen and H^+ takes place. This enhances iron dissolution reaction on the anodic area which accelerates corrosion. The increase of the cupric ions concentration in the bulk solution increases the cathodic areas and sites on the metal surface. As corrosion reaction is mainly cathodically controlled, this results in an increase of corrosion rate with the increase of Cu^{2+} concentration in Cl^- medium.

Fig. 3 shows the effect of molybdate concentration on the corrosion behavior of mild steel at different pH values. The corrosion rate is increased steadily with increasing molybdate concentration in acidic solution (pH 3, 4, and 5) both in the presence and absence of cupric ions in 500 ppm chloride media. At these pH values, mild steel shows higher corrosion rate in the presence of cupric ions. These results indicate that molybdate is a corrosion accelerator for mild steel in acidic media, although surface oxide can exist

up to pH 4 [2]. It is known [14-16] that polymerization of molybdate species starts below pH 6 with the formation of heptamolybdate ($\text{Mo}_7\text{O}_{24}^{6-}$) species according to the reaction:



and is completed at pH 4.5. Below this pH level, formation of octamolybdate ($\text{Mo}_8\text{O}_{26}^{4-}$) species begins according to the reaction:



and is completed at pH 1.5. Therefore, the accelerated corrosion of mild steel in the acidic pH range is caused by these heptamolybdate and octamolybdate species possibly due to the formation of soluble complexes with iron ions.

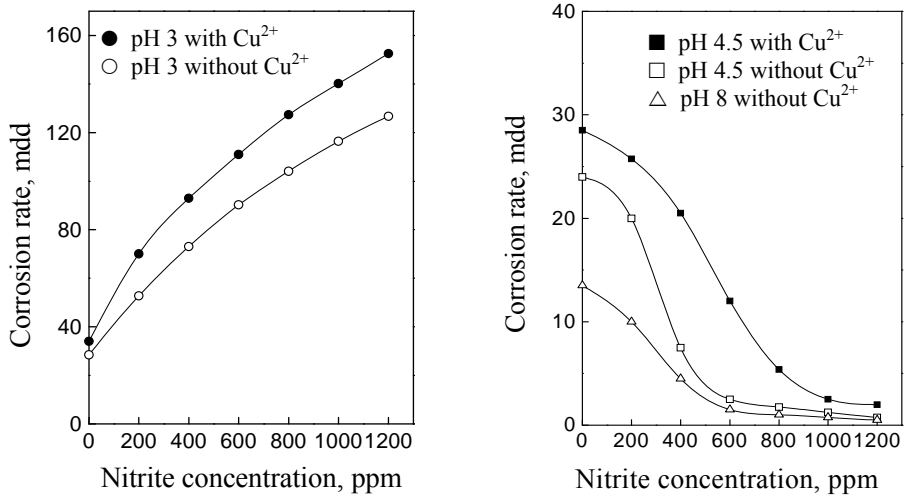


Fig. 4. Effect of nitrite concentration on corrosion rate of mild steel with or without cupric ions in 500 ppm chloride ions at different pH media.

On the other hand, the corrosion rate of mild steel is decreased with the increase of molybdate concentration in near neutral and alkaline solution both in the presence and absence of cupric ions. This indicates that molybdate acts as a corrosion inhibitor for mild steel in near neutral and alkaline solution (at pH 6 and above). In alkaline solution molybdate produced more pronounced corrosion inhibition than in near neutral solution. The stability of the surface iron oxide increases with the increase of pH, hence, the improved corrosion inhibition at high pH values is due to the improved stability of the surface oxide layer. The corrosion inhibition effect of the molybdate is due to its adsorption on the surface in competition with negatively charged aggressive chloride ions by hydrogen bonding between the oxygen atom of the molybdate and hydroxyl hydrogen atom of the hydrous oxide layer on the surface. This makes surface negatively charged

and prevent corrosion from the aggressive Cl^- attack [17, 18]. It has been observed in the present investigation that the inhibition efficiency of mild steel corrosion by molybdate increases with the increase of pH. At higher pH ($\text{pH} > 8$), the stability of the surface oxide is also increased as more oxide forms on the surface. Such a covered oxide surface protecting the metal surface from the chloride ions attack by the adsorbed molybdate can have better corrosion resistance. Thus, the presence of an oxide layer is essential for the corrosion inhibition action of molybdate.

It is shown in Fig. 4 that the corrosion rate of mild steel increases with the increase of nitrite concentration at pH 3 with or without cupric ions. This indicates that nitrite is also a corrosion accelerator like molybdate at this pH. However, decreased corrosion rate with increase of nitrite concentration is observed at pH 4.5 and 8 with or without cupric ions. As reported elsewhere [7, 19], the corrosion inhibition of mild steel by nitrite is mainly due to its oxidizing property. The ferrous ions produced on the surface by corrosion are converted to insoluble and stable hydrous ferric oxide and inhibits corrosion in the oxide stability region (above pH 4). At pH 3 oxide layer cannot exist on the surface and nitrite increases corrosion by enhancing anodic iron dissolution.

Fig. 5 shows the corrosion inhibition behavior of molybdate in the presence of 250 ppm nitrite ion in chloride medium. In alkaline medium (pH 8), the corrosion rate of mild steel is decreased rapidly with the increase of molybdate concentration. Only 250 ppm molybdate is required to reduce the rate to as low as 1.0 mdd. This rate is lower than that for the case of molybdate alone indicating that molybdate and nitrite ions together act as a synergistic corrosion inhibitor for mild steel in the alkaline medium.

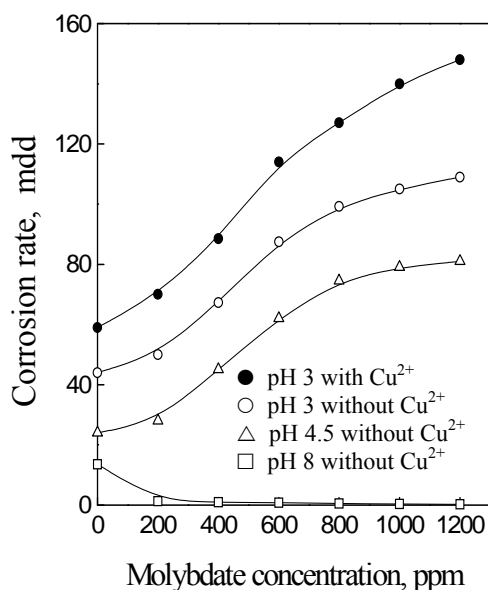


Fig. 5. Effect of molybdate concentration on corrosion rate of mild steel in presence of 250 ppm nitrite ions and 500 ppm chloride ions at different pH media.

The effect of nitrite concentration on the corrosion behavior of mild steel in the presence of molybdate is shown in Fig. 6. At pH 3, the corrosion rate increases with the increase of nitrite concentration first and then rapidly decreases with the further increase of concentration. The inhibitive effect at high concentration is due to the formation of ferric octamolybdate on the surface. On the other hand, at other higher pH, the corrosion rate of mild steel decreases rapidly with the increase of nitrite concentration and 200 ppm nitrite reduced the rate to 1.0 mdd (at pH 8). This is a significant low corrosion rate and indicates the synergistic corrosion inhibition effect of molybdate and nitrite.

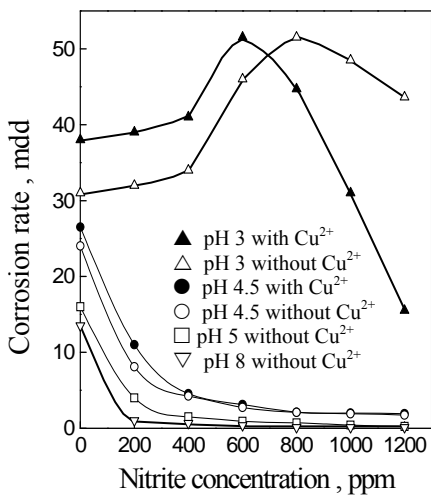


Fig. 6. Effect of nitrite concentration on corrosion rate of mild steel in presence of 125 ppm molybdate ions and 500 ppm chloride ions at different pH media.

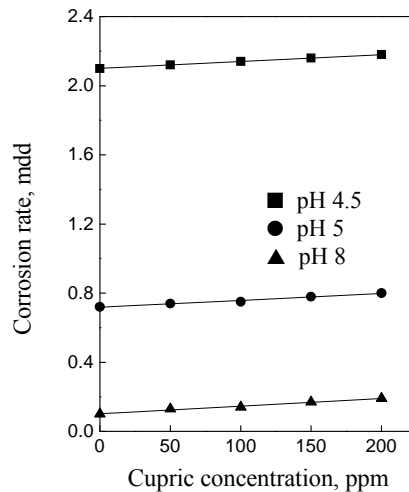


Fig. 7. Effect of cupric ions concentration on corrosion rate of mild steel in 500 ppm chloride ions at different pH media containing 125 ppm molybdate and 800 ppm nitrite mixture.

The effect of cupric ion concentration on the corrosion rate of mild steel in 500 ppm chloride medium containing 125 ppm molybdate and 800 ppm nitrite mixture at different pH values is shown in Fig. 7. The corrosion rate of mild steel is almost independent on cupric ions concentration at pH 4.5, 5 and 8 respectively. These results indicates that cupric ions has no effect on the corrosion behavior of mild steel due to the presence of 125 ppm molybdate and 800 ppm nitrite mixture as a synergistic inhibitor which block the iron surface by forming ferric octamolybdate species on iron surface.

Fig. 8 shows the effect of pH on the corrosion rate of mild steel in 500 ppm chloride medium containing 125 ppm molybdate and 800 ppm nitrite. The corrosion rate decreases

sharply with the increase of pH. High corrosion rate at pH 3 is due to the formation of soluble ferrous and ferric ions. However, higher corrosion rate in the presence of Cu^{2+} ions is due to accelerated cathodic reaction on the surface with Cu deposition.

In the near neutral and alkaline region, a combined action of molybdate and nitrite inhibitor produces much improved corrosion inhibition of mild steel than either of them alone. Nitrite maintains a good oxide layer on the surface and repairs any damage by allowing the formation of ferric oxide, especially at defect sites where corrosion takes place. Adsorbed molybdate makes the outer layer negatively charged and protects the surface from the attack of aggressive anions by repelling them. Thus, molybdate and nitrite together become a synergistic corrosion inhibitor for mild steel in near neutral and alkaline solutions.

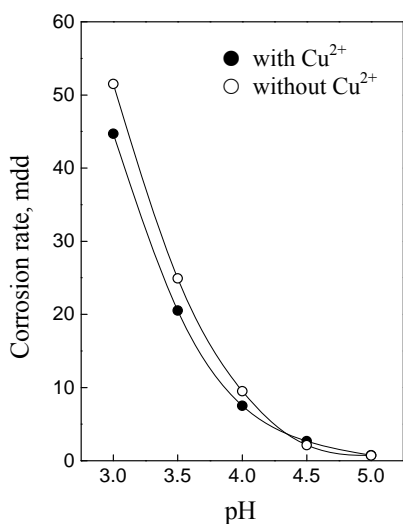


Fig. 8. Effect of pH on corrosion rate of mild steel in 500 ppm chloride medium containing 125 ppm molybdate and 800 ppm nitrite mixture.

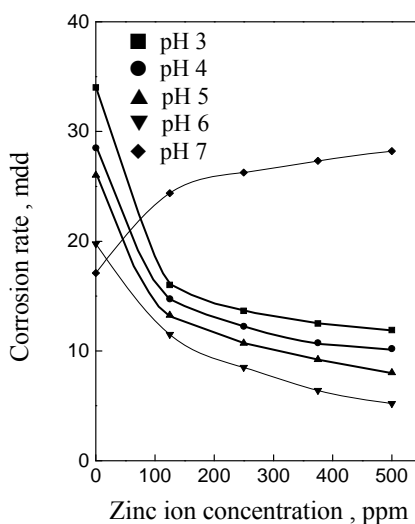


Fig. 9. Effect of zinc ions concentration on corrosion rate of mild steel in presence of 500 ppm chloride ions and 50 ppm cupric ions at different pH.

Fig. 9 shows the effect of zinc ions on the corrosion rate of mild steel in 500 ppm chloride and 50 ppm cupric ions at different pH media. The corrosion rate of mild steel decreases at pH 3, 4, 5 and 6 but increases at pH 7 with the increase of zinc ions concentration in the solution. It is known [20, 21] that zinc ions is a cathodic inhibitor for iron and steel below pH 6, and the main cathodic reactions [22] in the acidic region are:



and



Thus corrosion inhibition by zinc ions is due to its adsorption on the cathodic [21] reaction sites, and thereby blocking the reaction path of iron dissolution. However, at pH 7 and above zinc ions cannot exist due to the precipitation of zinc ions as ZnO or Zn(OH)₂. Therefore, corrosion reaction continues unhindered.

4. Conclusions

The following conclusions can be drawn from this investigation:

- (1) Molybdate is a corrosion inhibitor for mild steel in presence and absence of cupric ion at pH 6 and above. Below pH 6, molybdate accelerates corrosion due to the polymerization of molybdate to the hepta- or octamolybdate species that form soluble complexes with iron ions.
- (2) Nitrite can act as a corrosion inhibitor at pH ≥ 4.5 when a hydrous oxide layer can exist on the surface. However, nitrate ions can also accelerate corrosion at \leq pH 3 due to the dissolution of hydrous oxide layer.
- (3) Molybdate and nitrite together act as a synergistic corrosion inhibitor for mild steel in near neutral and alkaline solutions containing chloride and cupric ions. The combined inhibiting action results from the maintenance of the surface oxide by nitrite and protection of the surface oxide from aggressive anion attack by the adsorbed molybdate.
- (4) Zinc ion inhibits mild steel corrosion in low acidic and near neutral media containing chloride and cupric ions. However, it cannot inhibit mild steel corrosion in neutral and alkaline solution.

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