

## Corrosion Inhibition of Carbon Steel in Chloride and Sulfate Solutions

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### ABSTRACT

Corrosion is a major problem in industry and in infrastructure; a huge sum of expenditure every year is spent on preventing, retarding, and repairing its damages. This work studies the engineering of an inhibitor for carbon steel metal used in the cooling systems containing high concentration of chloride and sulfate ions. For this purpose, the synergy between the dichromate, molybdate and nitrite inhibitors is examined and optimized to the best results. Moreover, care was taken that the proposed inhibitor is compliant with the environmental laws and regulations.

**Keywords** - Corrosion inhibitor, Passivation, Steel, Molybdate, Nitrite, Dichromate.

### I. INTRODUCTION

Corrosion is a worldwide known problem. The serious consequences of the corrosion process is not represented in the loss of the material, but the loss of reliability and efficiency: process shutdown and failure, product contamination and loss, and personals fatality. Most studies and researches have attacked this problem from two different fronts; either the development of new materials and alloys that are more immune and resistant to corrosion, or the continuous arrest or retardation of the corrosion process itself. The second approach embrace many different techniques, such as surface coating of metals, cathodic and anodic protection, and the use of corrosion inhibitors. In industry, it is not unusual to apply one or more of these methods depending on the importance and economics.

Cooling water systems are found in a lot of important industries such as oil refineries, petrochemicals and energy plants. In cooling water systems, many factors will have an impact on the rate of the corrosion process, such as the high temperature, the fluid turbulence and the quality of water. Thus, they have to be included in the design and operation of the corrosion protection scheme. Previous researches agreed that most cooling water will usually have at maximum 300 ppm  $\text{Cl}^-$  ion [1]. Chloride ions can cause pitting or general corrosion. However, most cooling water systems have also high concentrations of  $\text{SO}_4^{2-}$  ion, which restrain the adsorption of  $\text{Cl}^-$  ions on the passive film [2], and increases the pitting potential which impede the pitting corrosion [3, 4]. Usually, in cooling systems, the protection against corrosion will include the addition of inhibitors to the solution that will passivate the metal or form a persistent protective

film on the surface of the metal. Of these compounds, the dichromate, nitrite, molybdate and orthophosphate have proven their successfulness. The dichromate ion is an excellent corrosion inhibitor, particularly from a cost prospective [5, 6]. However, the hexavalent chromium is also known to be a very noxious compound. It affects the respiratory system, the gastrointestinal tract, the liver, the kidney and the immune system. Also it is a known human carcinogen [7-9]. Thus, local environmental laws limit its discharge in wastewater to 0.5 ppm [10]. This has caused the decrease of the use of dichromate salts significantly. Nitrite is an oxidizing agent with corrosion inhibitive properties. It has been used for improving the corrosion inhibition efficiency of molybdate [11, 12]. However, though nitrite ion has no environmental limit, but it can be easily oxidized to the nitrate form which has a limit of 50 ppm [10]. Molybdate can be a very effective inhibitor, especially when combined with other chemicals. Its main drawbacks are its high cost and its inefficiency in the absence of oxygen due to its weak oxidizing power [13].

This work studies the design of a corrosion inhibition mixture based on the combination of dichromate, nitrite and molybdate salts. The mixture should demonstrate a high corrosion inhibition for water cooling systems while not exceeding the limits established by the environmental laws.

### II. EXPERIMENTAL WORK

The process was simulated by rotating a steel coupon in a synthetic solution containing 0.01 M NaCl (equivalent to 335 ppm  $\text{Cl}^-$ ), 0.02 M  $(\text{NH}_4)_2\text{SO}_4$  (equivalent to 1920 ppm  $\text{SO}_4^{2-}$ ) [14]. The speed was fixed at 1000 rpm and the time at two hours. The

corrosion rate was determined by the weight loss technique using a 0.0001 g accuracy balance. The steel coupons composition was as follows: C= 0.042%, Si= 0.034%, Mn= 0.161%, P= 0.007%, S= 0.003%, Cr= 0.015%, Ni= 0.01%, Cu= 0.024%, and the balance iron. The radius of the coupons used was 70 mm, and the thickness was 3 mm. Before each run, both sides of the coupons were abraded with decreasing number waterproof silicon carbide paper then washed with tap water followed by distilled water, and the solution pH was adjusted to 5. The corrosion rate is determined in (g/m<sup>2</sup>d) according to:

$$CR(g/m^2d) = \frac{\text{weight loss}(g) \cdot 12}{\text{Surface Area}(m^2)} \quad (1)$$

The inhibition efficiency was calculated accordingly:

$$\text{Inhibition Efficiency, \%} = \frac{CR_{\text{uninhibited}} - CR_{\text{inhibited}}}{CR_{\text{uninhibited}}} \quad (2)$$

In order to find the best combination of ions, the experimental work was divided into four consecutive parts: the start of each part depends on the final results of its precedent.

The first part is the study of the stability of the protective passivation layer formed on the steel using the different ions. The coupon was submerged in a 1% sodium salt solution of the inhibitor and heated at 80 OC for 15 minutes to insure the formation and thermal stability of the passive layer. These tested ions were: dichromate, nitrite, molybdate, mixtures of dichromate and nitrite in the ratio of 4 to 1, and mixture of dichromate and permanganate in the ratio of 4 to 1. The coupons were then immersed in the test solution with no inhibitors and rotated for 2 hours at 1000 rpm.

In the second part, the interaction among the three corrosion inhibitor ions is studied. Therefore, the coupons were immersed in the passivating solution for 15 minutes. Table 1 shows the different concentrations of the salts used. After the 15 minutes, the corrosive species were added to the solution and coupons were rotated at 1000 rpm for 2 hours. The interaction between the different species is studied using the factorial design technique [15]. This is an experimental strategy which allows the different factors to be varied together, instead of one at a time, to determine the best combination of ions and the extent of their interaction. The Minitab statistical software was used to design and interpret the results of this part.

TABLE I  
 CONCENTRATION OF PASSIVATING SPECIES

Inhibitor	level; ppm		
Sodium molybdate	150	250	
Sodium dichromate	1	3	
Sodium nitrite	50	250	350

The third part is dedicated to study the effect of the change of the concentration of each ion on the corrosion inhibition of the carbon steel. Starting from the best combination of ions previously determined at the second part, the one-factor-at-a-time approach was used to locate any other possible alternative combinations.

And in the last part, the effect of the change of the conditions and environment of the test (concentration of corrosive species, rotation speed, and pH of solution) on the performance of the chosen combination is addressed.

### III. RESULTS AND DISCUSSIONS

The results of the four different parts are presented and discussed as follows:

#### III.1. Passivation of Steel

The test was conducted as described in the experimental part. The results in figure 1 shows the following points:

- The dichromate ion formed the most passive layer, with corrosion inhibition of about 85%.
- Nitrite ion developed the weakest passive layer, and even increased the corrosion rate by 10% more than the control sample. The oxidation of the nitrite to the corrosive nitrate in the test solution is a possible cause.
- The addition of either nitrite or permanganate to the dichromate resulted in decreasing the passivation power of the dichromate. The inhibition was only 42, and 70 % respectively, instead of the 85% accomplished by the dichromate solely.

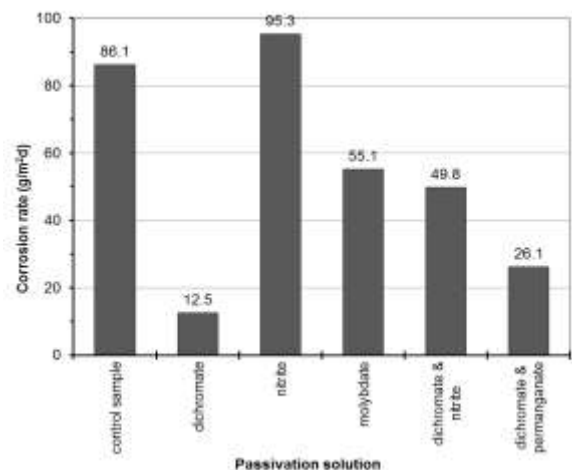


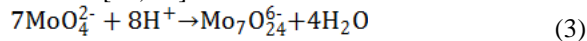
Fig. 1 Corrosion rate of different passivating solutions for carbon steel.

#### III.2. Ions interaction study

The results of this part are shown in figures 2 and 3. Figure 2 shows that, in general, increasing the concentration of each salt when present solely in the solution results in decreasing the corrosion rate.

However, the study of the interaction of these ions, presented in figure 3, shows that:

- While the rate of corrosion decreased with the increase of the concentration of sodium nitrite at 150 ppm sodium molybdate, the opposite was found at the 250 ppm of sodium molybdate. This may be ascribed to the oxidation of nitrite to the nitrate with a subsequent decrease of the pH which favors the polymerization of the molybdate to the heptamolybdate (Mo<sub>7</sub>O<sub>24</sub>)<sup>6-</sup> according to the reaction [16, 17]:



The resultant heptamolybdate ions are known to form soluble complexes with iron ions and hence increases the rate of corrosion [18].

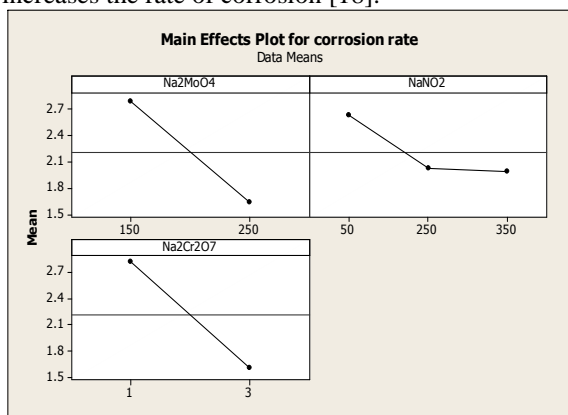


Fig. 2 The individual effect of each component (sodium molybdate, sodium nitrite and sodium dichromate).

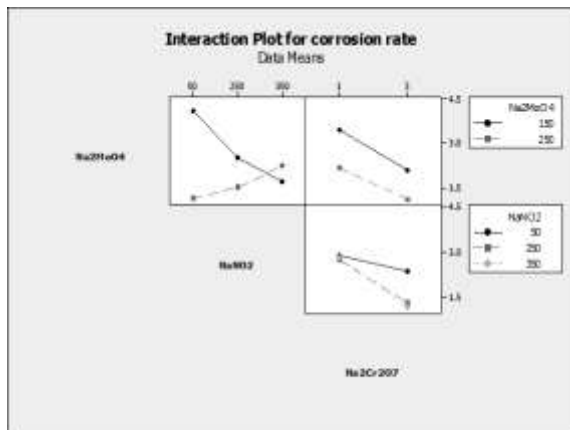


Fig. 3 The interaction effects of components (sodium molybdate, sodium nitrite and sodium dichromate).

- Increasing the concentration of sodium dichromate resulted in a decrease of corrosion rate. Nevertheless, this decrease was comparatively low in the case of the presence of 50 ppm of sodium nitrite.

However, since as discussed previously that most environmental laws limit the concentration of the dichromate ion to below 1 ppm, thus the best combination was fixed at the 1 ppm sodium

dichromate, while the sodium molybdate and sodium nitrite were found to be best at 250 and 50 ppm respectively.

### III.3. Concentration study

#### III.3.1. Effect of Nitrite

The optimum sodium nitrite concentration is 100 ppm (66.7 ppm of nitrite) as shown in figure 4. Increasing the sodium nitrite concentration beyond the 50 ppm decreased the corrosion rate by 50 % owing to the formation of insoluble and stable hydrous ferric oxide FeOOH layer which inhibits further corrosion [13, 19]. Moreover, at concentration higher than 100 ppm of sodium nitrite, the corrosion rate increases again due to the formation of the aggressive nitrate ion [20]. Nevertheless, some environmental laws [10] limits the concentration of the nitrate to 50 ppm, which can forbid the use of the 100 ppm concentration of the sodium nitrite. However, in case of closed systems, this concentration can be allowed to reach the up to 100 ppm.

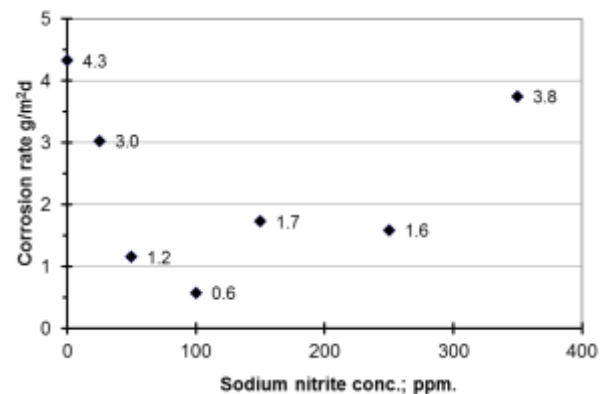


Fig. 4 Effect of sodium nitrite conc. on the corrosion inhibition of steel.

#### III.3.2. Effect of Molybdate

Figure 5 shows that the optimum sodium molybdate concentration is 250 ppm (equivalent to 194 ppm molybdate). This is slightly lower than the 300 ppm previously reported by Ali et al [21]. This is a result of the adsorption of the molybdate ions on the steel surface which renders the surface negatively charged and protected [22, 23]. It is noted that increasing the molybdate ion beyond this concentration will result on the increase of the rate of corrosion. This is a result of the polymerization reaction of the molybdate to the heptamolybdate (Mo<sub>7</sub>O<sub>24</sub>)<sup>6-</sup> ion which forms soluble complexes with iron ions as shown previously in (3).

#### III.3.3. Effect of Dichromate

As previously discussed, According to the results shown in figure 6, concentration of sodium dichromate as low as 1 ppm (0.4 ppm hexavalent chromium) is effective in inhibiting the corrosion and

does not violate local environmental law. Thus, the optimum concentration recommended by this part is 250 ppm sodium molybdate, 50 ppm sodium nitrite, and 1 ppm sodium dichromate, which did not differ from the concentration deduced in the second part.

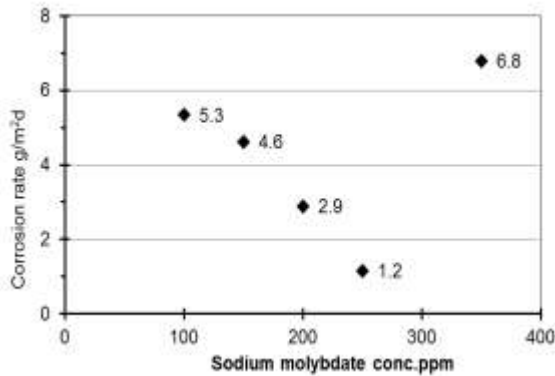


Fig. 5 Effect of sodium molybdate conc. on the corrosion inhibition of steel.

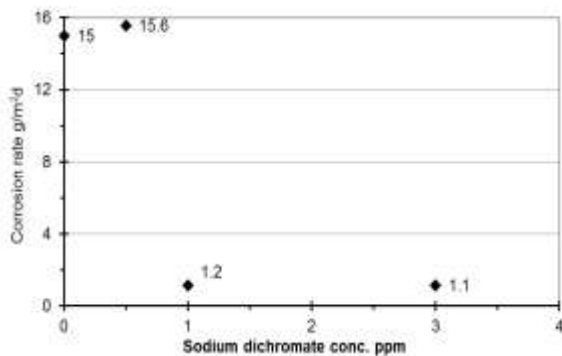


Fig. 6 Effect of sodium dichromate conc. on the corrosion inhibition of steel.

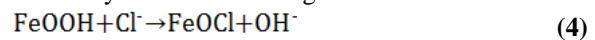
#### III.4. Effect of environmental parameters

In this part, the experimental parameter were changed to study of the performance of the inhibitor in different environments. It is seen from figure 7 that as the sodium chloride concentration increases, the corrosion rate first decreases by 66 %, and then starts to increase again: the sodium chloride does not only increase the corrosion rate and attacks the protective passive layer, but, on the other hand, decreases the concentration of oxygen in the solution. This is the reason for the change of the corrosion rate behavior with the increase of the sodium chloride concentration. This indicate that the designated combination is even able to withstand hand concentration of chloride ion.

As expected, the corrosion rate increases with the increase of the concentration of the sulfate ions in the test solution (fig. 8): The corrosion rate increased by 200% for just an increase of 25% in concentration. This outcome indicate that the combination is very sensitive to the sulfate ion concentration and care must be taken to limit its presence. Furthermore, either the increase or decrease of the rotation speed

and turbulence resulted in increase of the corrosion rate (fig. 9). The turbulence is expected to increase the diffusion of the attacking or passivating ions as well as the oxygen to the surface of the metal. Moreover, the shear velocity of the fluid is expected to affect the stability of the oxide layer. The interaction and competition between these repercussions is considered responsible for this adverse behaviour of the circulation rate.

Regarding the effect of the pH of the solution, it is seen in figure 10 that at higher pH, the corrosion is nearly almost nonexistent. However, at lower pH, the rate of corrosion increases extensively. This is because oxide layer cannot exist on the steel surface below pH 4, and iron oxide layer is converted to the ferric oxychloride according to:



which is highly soluble, and thus the iron surface is left bare and is attacked according to: [1, 21]:



Moreover, at this low pH, molybdate tends to form the heptamolybdate according to (3) and more iron is allowed to dissolve in the solution.

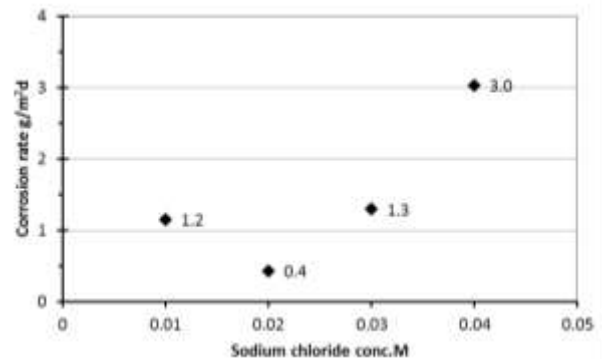


Fig. 7 Effect of Sodium chloride concentration on the corrosion rate of steel in the presence of the selected corrosion inhibitor.

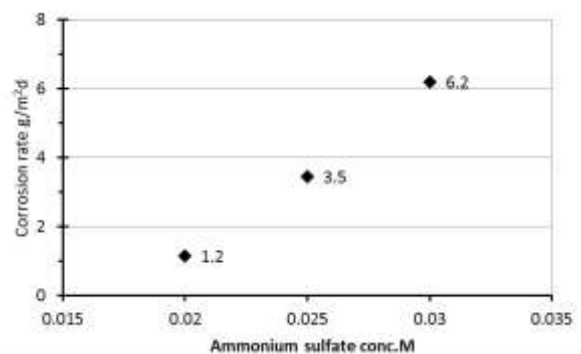


Fig. 8 Effect of Ammonium sulfate concentration on the corrosion rate of steel in the presence of the selected corrosion inhibitor.

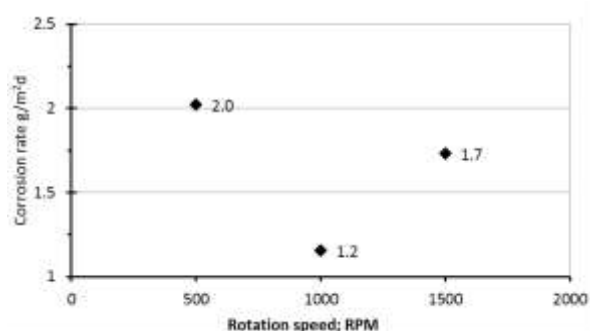


Fig. 9 Effect of coupon rotation speed on the corrosion rate of steel in the presence of the selected corrosion inhibitor.

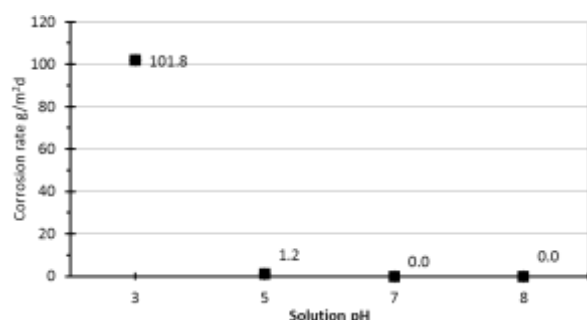


Fig. 10 Effect of solution pH on the corrosion rate of steel in the presence of the selected corrosion inhibitor.

#### IV. CONCLUSIONS

The pursuit of a combination between known corrosion inhibitors for a better performance in industrial water cooling systems with high concentrations of chloride and sulfate ions has revealed that a corrosion inhibitor of sodium dichromate, molybdate and nitrite in the concentration of 1, 250 and 50 ppm respectively, has shown to be an effective corrosion inhibitor. The corrosion inhibition reached 98.6% in the case of solution of sodium chloride and ammonium sulfate solution of 0.01 and 0.02 M respectively. This inhibition is very sensitive to the increase of the sulfate ion or the decrease of the pH, and to a lesser extent to the change in the turbulence of the flow or the chloride ion concentration.

#### References

- [1.] Karim, S., et al., Effect of nitrate ion on corrosion inhibition of mild steel in simulated cooling water. Chem. Eng. Res. Bull. Chemical Engineering Research Bulletin, 2010. 14(2): p. 87.
- [2.] El-Naggar, M.M., Effects of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> anions on the anodic behavior of carbon steel in deaerated 0.50M NaHCO<sub>3</sub> solutions. APPLIED SURFACE SCIENCE, 2006. 252(18): p. 6179-6194.

- [3.] Deyab, M.A. and S.T. Keera, Cyclic voltammetric studies of carbon steel corrosion in chloride-formation water solution and effect of some inorganic salts. EJPE Egyptian Journal of Petroleum, 2012. 21(1): p. 31-36.
- [4.] Singh, V.B. and M. Ray, Effect of H<sub>2</sub>SO<sub>4</sub> addition on the corrosion behaviour of AISI 304 austenitic stainless steel in methanol-HCl solution. International Journal of Electrochemical Science, 2007. 2: p. 329-340.
- [5.] Popov, B.N., Chapter 14 - Corrosion Inhibitors, in Corrosion Engineering, B.N. Popov, Editor. 2015, Elsevier: Amsterdam. p. 581-597.
- [6.] Sayin, K. and D. Karakaş, Quantum chemical studies on the some inorganic corrosion inhibitors. Corrosion Science, 2013. 77: p. 37-45.
- [7.] 7  
<http://pubchem.ncbi.nlm.nih.gov/compound/25408#section=Top>. 7/1/2016].
- [8.] [http://www.who.int/water\\_sanitation\\_health/dwq/chemicals/chromium.pdf](http://www.who.int/water_sanitation_health/dwq/chemicals/chromium.pdf). [cited 2016.
- [9.] <http://www3.epa.gov/airtoxics/hlthef/chromium.html>. [cited 2015.
- [10.] Egyptian Environmental Law Number 4 of 1994.
- [11.] Mustafa, C.M. and S.M. Shahinoor Islam Dulal, Corrosion behaviour of mild steel in moderately alkaline to acidic simulated cooling water containing molybdate and nitrite. BRITISH CORROSION JOURNAL, 1997. 32(2): p. 133-137.
- [12.] Kim, K.T., et al., Corrosion Inhibiting Mechanism of Nitrite Ion on the Passivation of Carbon Steel and Ductile Cast Iron for Nuclear Power Plants. Advances in Materials Science and Engineering, 2015. 2015: p. 16.
- [13.] Pryor, M.J. and M. Cohen, The Inhibition of the Corrosion of Iron by Some Anodic Inhibitors. Journal of The Electrochemical Society, 1953. 100(5): p. 203-215.
- [14.] Abd El Haleem, S.M., S. Abd El Wanees, and A. Bahgat, Environmental factors affecting the corrosion behaviour of reinforcing steel. V. Role of chloride and sulphate ions in the corrosion of reinforcing steel in saturated Ca(OH)<sub>2</sub> solutions. Corrosion Science, 2013. 75: p. 1-15.
- [15.] Montgomery, D.C., Design and Analysis of Experiments. 2006: John Wiley & Sons.
- [16.] Vukasovich, M.S. and J.P.G. Farr, Molybdate in corrosion inhibition—A review. Polyhedron Polyhedron, 1986. 5(1-2): p. 551-559.

- [17.] Wilcox, G., D. Gabe, and M. Warwick, The role of molybdates in corrosion prevention. *Corros. Rev.*, 1986. 6: p. 328-365.
- [18.] Ali, M.R., C.M. Mustafa, and M. Habib, Effect of Molybdate, Nitrite and Zinc Ions on the Corrosion Inhibition of Mild Steel in Aqueous Chloride Media Containing Cupric Ions. 2008, 2008. 1(1): p. 10.
- [19.] Joseph, G. and R. Perret, Inhibitor action on the corrosion of iron in salt-water solution. *Corrosion Science*, 1967. 7(9): p. 553-562.
- [20.] Roberge, P.R., *Handbook of corrosion engineering*. 2000, New York: McGraw-Hill.
- [21.] Ali, M.R., C.M. Mustafa, and M. Habib, Effect of Molybdate, Nitrite and Zinc Ions on the Corrosion Inhibition of Mild Steel in Aqueous Chloride Media Containing Cupric Ions. *Jnl.Sci.Res. Journal of Scientific Research*, 2008. 1(1): p. 82-91.
- [22.] Bentley, A.J., et al., Molybdates in aqueous corrosion inhibitionIII. Effects of molybdate in the anodic filming of steel. *Polyhedron*, 1986. 5(1-2): p. 547-550.
- [23.] Sakashita, M. and N. Sato, The effect of molybdate anion on the ion-selectivity of hydrous ferric oxide films in chloride solutions. *Corrosion Science*, 1977. 17(6): p. 473-486.