



Study the Possibility of using Sodium Molybdate as an Environmentally-Friendly Corrosion Inhibiter for Water Heating/Cooling System of Mellitah Plant – Libya

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ABSTRACT

The cooling water system is one of the most critical systems in the oil industry; it requires precise management to operate the system in the right way. Open recirculation cooling water systems continuously reuse the water that go through the heat transfer equipment. This use needs in especially cases treatments to minimise the corrosion of processes metals. Therefore, the aim of this work was to study the inhibition of corrosion of carbon steel in cooling water system solution by using sodium molybdate (Na_2MoO_4). The corrosion behaviour of carbon steel in presence of inhibitor ions were studied by carrying out experiments under different sets of conditions. The conditions were as pH of the test media : 6 (moderately acidic), 7 (neutral) and 8, 10 (alkaline) and different temperature: 25°C, 38 C and 55°C; stirring condition (1200 rpm) ; 2 hrs immersion time. However, inhibited solutions were prepared in makeup water of cooling water by using different concentration of molybdate (5 ppm , 10 ppm and 15 ppm). The electrochemical studies were based on Linear Polarization Resistance method (LPR). The corrosion rate values showed that the systems maintained low value and good passivity at $\text{pH} \geq 7$. However, the maximum corrosion rate was obtained at 5 ppm of sodium molybdate and $\text{pH} = 6$. Also, the obtained results lead that the corresponding inhibition efficiency increases by increasing of inhibitor concentration and also by addition of molybdate ions.

Key words: cooling water, sodium molybdate, pH, temperature, corrosion rate, inhibition efficiency

Introduction

Corrosion control is the application of engineering principle and procedures to minimize corrosion to an acceptable level by the most economical method. It is rarely practical or economical to eliminate corrosion completely and in practice, one or more of the following methods would be applied. However, there are several methods for protection against corrosion which are derived from electrochemical principle. Corrosion can be controlled by coating, Inhibitors, material selection and cathodic protection[1].

Corrosion Inhibitors are substances which can lower the corrosion attack even when they are applied in very low concentration. The mechanism behind decrease in corrosion is that the inhibitor chemically or physically adsorbs onto the metallic surface and forms a protective layer and thereby minimizes corrosion attack by blocking aggressive ions from meeting the metallic surface or slowing down the kinetics of either the cathodic or anodic reaction, or both. In most cases corrosion inhibitors are not pure substances, they are mixtures or by-products. Commercial inhibitors contain active ingredients as corrosion inhibitors along with surfactants, biocides and emulsifiers. Certain examples of inorganic corrosion inhibitors are molybdates, nitrates, phosphates and silicates [2,3].

Molybdates are widely used as a component in inhibitor formulations. It acts as a good synergistic co-inhibitor with zinc, silicates, phosphates and phosphonates. Sodium molybdate, like chromate is a versatile inhibitor that protects ferrous and non- ferrous metals over wide range of operating conditions. The agent is classified as anodic inhibitor, but its use requires the presence of oxygen or other oxidizing agents in solution. Furthermore, although it is an inorganic material, molybdate's low toxicity to fish and other aquatic life. For steel, the concentration of sodium molybdate must be exceeding the critical level [4].

Since molybdate inhibits only in the presence of air, oxygen was judged to be the primary passivator with the adsorbed molybdate acting in film repair to maintain the passive oxide film. Moreover, the mechanism of inhibition by molybdate is thought to be a process of ion exchange, followed by the formation of an insoluble film reported to be ferric molybdate (FeMoO_4). The adsorption produces a layer that resists the corrosive effects to other anions, particularly chlorides and sulfates. The effectiveness of protection against metal surface corrosion depends on the construction of the protective layer [5].

This work mainly focuses on the investigation of Sodium Molybdate (Na_2MoO_4) as an environmentally friendly corrosion inhibitor to prevent internal corrosion in a water heating / cooling system of Mellitah Plant. Also the interaction of sodium molybdate (Na_2MoO_4) with the surface of carbon steel under different experimental conditions such as; different sodium molybdate concentrations (Na_2MoO_4), pH and temperature are studied. The inhibition efficiency of the corrosion inhibition process is calculated under these conditions.

2. Experimental work

This section elaborately describes the materials, solutions, experimental methodology and the research techniques that are used for the experiments done for this work.

2.1 Electrochemical Corrosion Rate Method Liner Polarization Resistance (LPR)

Electrochemical technology, commonly referred to as linear polarization resistance, is one of the most common corrosion monitoring methods that allow corrosion rates to be measured directly, in real time. The response time and data quality of this technology makes it clearly superior, where applicable, to all other forms of corrosion monitoring [6]. The linear polarization method is based on the equations below, which were developed by Stern and Geary from earlier work by Wagner and Traud. This technique works by taking a linear section of the polarization curve near (± 10 mV) the corrosion potential of the metal and makes it possible to find the ratio existing between the ($\Delta E = E - E_{\text{corr}}$) and the applied current ΔI for polarization of typically less than 10 mV as shown in figure 1.

Therefore

$$R_p = \Delta E / \Delta I$$

Where

R_p = polarization resistance and the corrosion theory shows that for an activation controlled system.

$$I_{\text{corr}} = \beta / R_p$$

Where β is a constant for the metal / environment combination.

This is called the Stern – Geary relationship.

$$\Delta E / \Delta I = R_p = \frac{b_a \times b_c}{2.3 \times I_{\text{corr}} \times (b_a + b_c)}$$

Where

R_p is a polarization resistance

I_{corr} is the corrosion current

b_a and b_c are Tafel constants for anodic and cathodic processes.

Corrosion rate calculations were performed for each concentration. Corrosion rate was calculated according to the Stern-Geary equation, which was used to calculate corrosion rates (β is 25 mv) and then converted to mm/year using Faraday's law as shown in equation below:

$$\text{CR (mm/year)} = \frac{31.5 \times 10^7 Z I_{\text{corr}}}{\rho n F}$$

where

CR = Corrosion rate (mm/year)

I_{corr} = Corrosion current density, A/cm²

P = Density of iron, g/cm³

F = Faraday's constant, 96500 C/mole

Z = Atomic weight, gm/mol

n = Number of exchanged electron.

In this work, linear polarization resistance (LPR) measurements were performed using the CorratereAquaMate™ portable instrument [6].

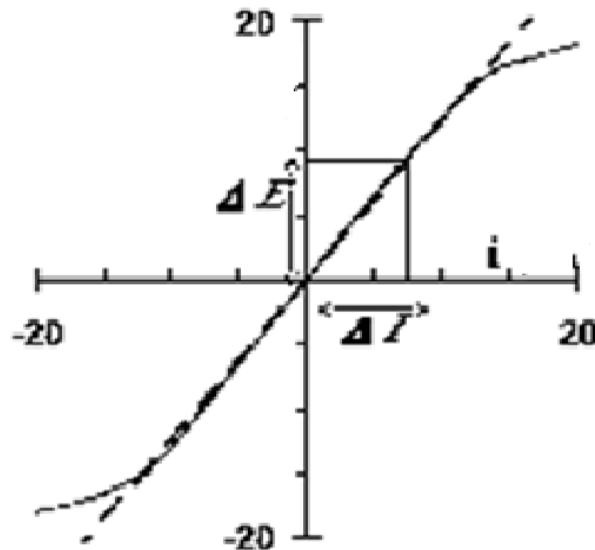


Figure 1 Typical Linear Polarization Resistance (LPR) Curve [7]

2.2 Apparatus and Material

2.2.1 Two Element Probe



Figure 2: Two Element Probe

2.2.2 CORRATER Linear Polarization Resistance Corrosion Rate Monitoring

The CORRATER family is the most advanced electrochemical field instrumentation available for measuring corrosion rate and pitting tendency. Through patented solution resistance compensation (SRC). The operating range beyond traditional two and three-electrode Linear Polarization Resistance (LPR) methods .



Figure 3 The CorratereAquaMate™ Portable Instrument

2.2.3 Reference Electrode

The role of the reference electrode (RE) is to provide a fixed potential which does not vary during the experiments. The reference electrode was saturated calomel (SCE), which was cleaned before each experiment to avoid inhibitor contamination



Figure 4 Reference Electrode

2.2.4 Test Electrode Carbon Steel

Carbon steel is a steel with carbon content up to 2.1% by weight. The definition of carbon steel from the American Iron and Steel Institute (AISI) states as shown in

figure 5.

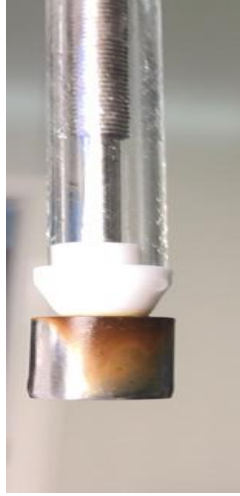


Figure 5 Test Electrode Carbon Steel

2.2.5 Voltammeter

Voltammetry is a category of electro analytical methods used in analytical chemistry and various industrial processes.



Figure 6 Voltammeter

2.2.6 pH Meter

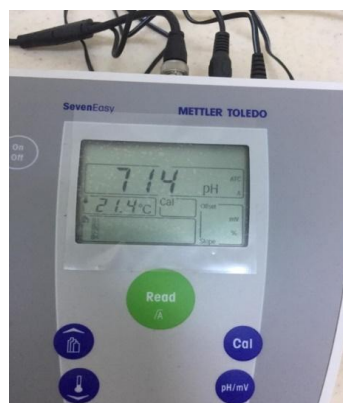


Figure 7 pH Meter

2.2.8 Experimental Cell

A standard one litre electrochemical cell was used for this work. The cell designed with five holes to hold the working electrode, reference electrode, pH meter and two element probe. The experiments were carried out in one litre of makeup water solution which collected from cooling water (Mellitahplant). Schematic illustration of the experimental cell is shown in figure 8.

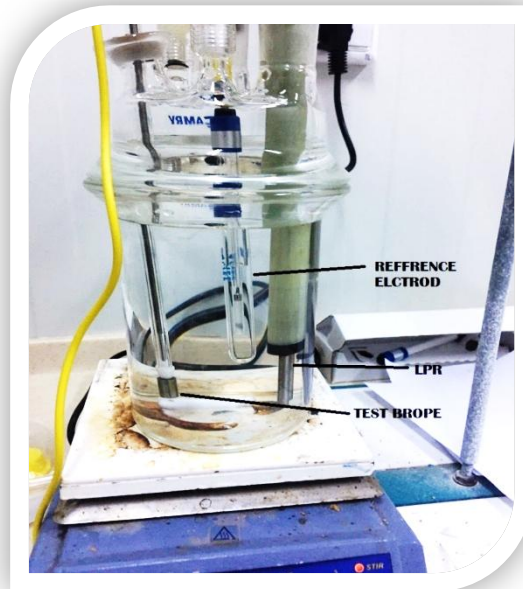


Figure 8 Image of Electrochemical Experiment Set-up

2.3 Solution Preparation

In the beginning, the idea of the test was to know the efficiency of the chemical addition that were added into the water or the corrosive and aggressive environment that helps to oxidize and form deposits on the surface of the metal and what causes the corrosion of the metal. Hence the idea of this test, which was to prepare three concentrations of sodium molybdate in a one-liter flask. Hence 5ppm, 10ppm, 15ppm and provide different conditions and know the behavior of this slowdown in terms of a change in the specifications of makeup water coming out of the tank. In the table shown below, there is a complete analysis of make-up water.

Table 1 Cooling Water Analysis

	Unit	
PH		7-10
Conductivity	Us/cm	4-7
Chloride	Ppm	9-15
TSS	Ppm	2-10
Calcium	Ppm	15-20
Magnesium	Ppm	6-10
Sodium	Ppm	30-70
Bicarbonate	Ppm	30-40

The water specifications in terms of pH, temperature were changed, and measured the rate of corrosion. The solution has a capacity of one liter with injection three different concentration to same solution to find optimum protect efficiency to the surface metal.

2.4 Experimental Details

The corrosion of carbon steel was investigated in different environments (different pHs and temperature) that commonly existed on the surface of carbon steel in blank cooling water system. During the whole experimental process, the pH value and temperature of solution were monitored all the time to make sure that they still maintained a constant level. All experiments were carried out in the stirring condition by using magnetic stirrer (1200 rpm). At the end of the experiments, specimens were taken out from the solutions and examined the formation of any visual rust on their surface.

Specimens used in the electrochemical measurements were machined from carbon steel

rod and was polished with different emery papers up to 800 grades, washed thoroughly with deionised water, degreased with acetone and dried in streaming air. All test solutions were prepared with makeup cooling water. The base electrolyte was 10 ppm NaCl naturally aerated. Standard buffers for pH meter calibration were used. Where necessary the pH of each test solution was adjusted to desired pH by addition of small quantities of 1M

NaOH or 1M HCl test solution.

Inhibited solutions were prepared in water by using different concentration of molybdate (5ppm , 10ppm and 15ppm).However, the first set of experiments were done using 0.0 ppm concentration of molybdate at pH 8 makeup water and at 25 C°(control measurements in the absence of inhibitor). The measurements were also done at temperatures ranging from 25C° to 55C° and pH range of pH 6 until pH 10. All these measurements were done in the absence and presence of inhibitor in the solution.

Record the corrosion rate (mpy) by using CORRATER instrument and potential by using voltameter every 10 minutes. Collection of data will be until steady state condition is reached and this takes approximately 100 minutes "the value of the corrosion rate remains low and almost constant". The experimental measurements repeated several times, all of these repeated measurements were close to each other in both graphical shape and the parameter values.

3. Results and Dissection

This section is dedicated to the discussion of experimental results done using electrochemical procedures LPR to establish the possibility of using corrosion inhibitor of sodium molybdate for water heating/cooling system.

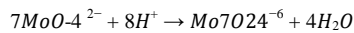
3.1 Influence of Change pHs

The operating pH value affects the solubility of almost all the salts that responsible for many problems of cooling water system. In particular the tendency of calcium to form deposits of carbonate is dependent upon pH value.

The effect of pH on the corrosion of carbon steel was studied in the absence and presence of 5 ppm , 10 ppm , 15 ppm concentration of inhibitor $[\text{Na}_2\text{MoO}_4]$ in the makeup water of cooling water at 25C°. The pH of water was adjusted to pH6, pH7, pH8, and pH 10.

Figure9 to figure13 represented the effect of solution pH with different concentration of molybdate inhibitor $[\text{Na}_2\text{MoO}_4]$ on the corrosion rate (mpy) of carbon steel. The variation of corrosion rates with time showed a significant rise in the corrosion rate with the decrease in pHs. It can be seen that there was only a small decrease in corrosion rate where pH =6 specially at low concentration of corrosion inhibitor, for example at pH = 6, the initial corrosion rate of around 1.55mpy was observed for the carbon steel exposed to blank solution (without inhibitor) for ten minutes, then adding corrosion inhibitor (5ppm, 10 ppm, 15 ppm)this value of corrosion rate decreased during the next mints until low values were observed and reached a minimum value of corrosion rate about (1.41mpy, 1.22mpy, 0.97mpy)respectively and then these values started to go up again.

However, the highest corrosion rate was obtained at pH=6 for the all concentrations of corrosion inhibitor. This seems possibly due to, at low pH≤ 6 there are few H^+ ions in the solution the pre formed oxide film of carbon steel dissolves in acidic solutions, rather than depositing on the metal surface to form a protective barrier film . In the absence of the protective oxide film, the metal surface is in direct contact with the acid solution, and the corrosion reaction proceeds at a greater rate than it does at higher pH values and examination of the electrode surface after polarization experiments showed visible pits as showed in figure 14. Also, MoO_4^{2-} react with hydrogen ions in acidic solutions to form heptamolybdate ($\text{Mo}_7\text{O}_{24}^{6-}$). This form of anions, $\text{Mo}_7\text{O}_{24}^{6-}$ formed are not as effective in the inhibition of carbon steel as MoO_4^{2-} [8].



On the other hand, the corrosion rate values showed that the systems maintained low value and good passivity at pH7, pH 8 and pH 10. It can conclude that molybdate acts as a corrosion inhibitor for carbon steel in neutral and alkaline solution (at pH 7 and above) as showed in figure 13.

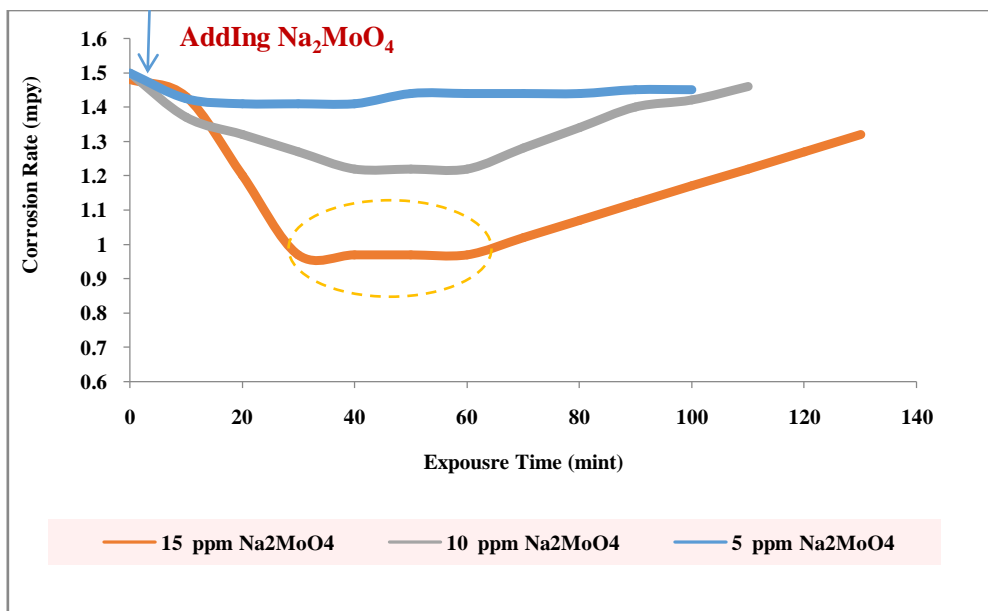


Figure 9 Corrosion Rate (mpy) Vs Time for Carbon Steel in Aerated Stirring Solution and Different Inhibitor Blend at pH 6 and 25°C

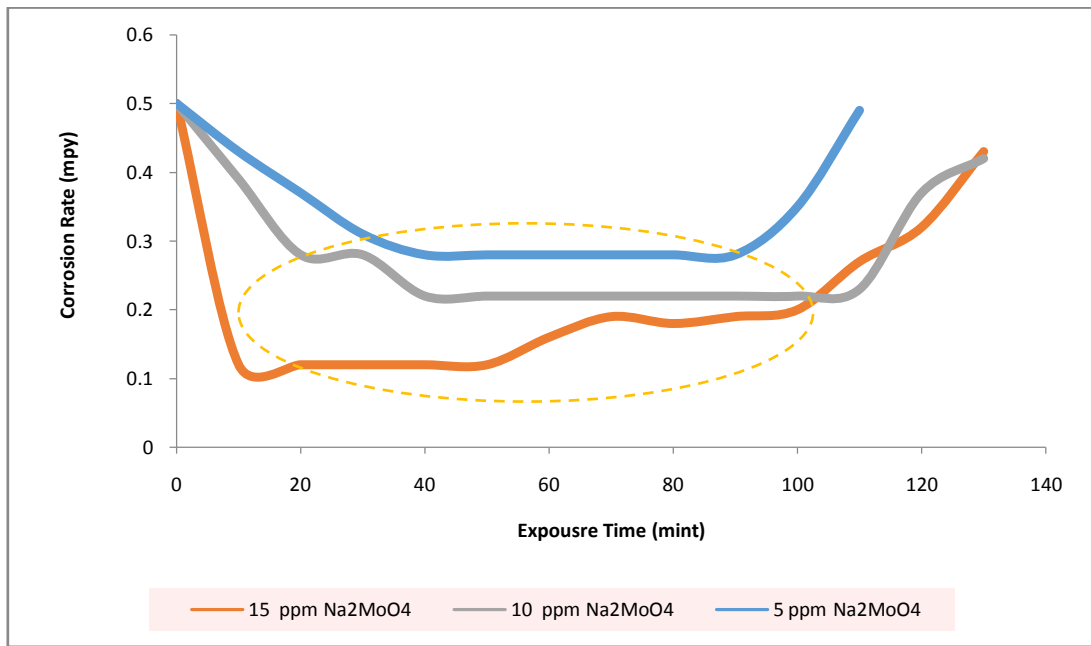


Figure 10 Corrosion Rate (mpy) Vs Time for Carbon Steel in Aerated Stirring Solution and Different Inhibitor Blend at pH 7 and 25°C

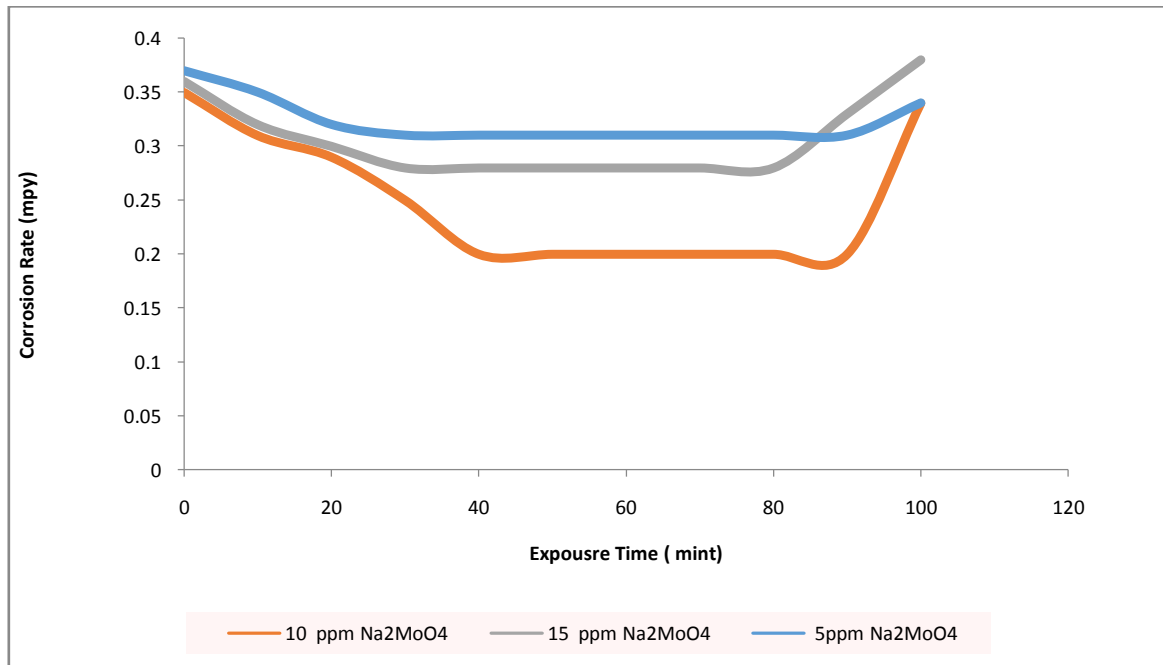


Figure 11 Corrosion Rate (mpy) Vs Time for Carbon Steel in Aerated Stirring Solution and Different Inhibitor Blend at pH 8 and 25°C

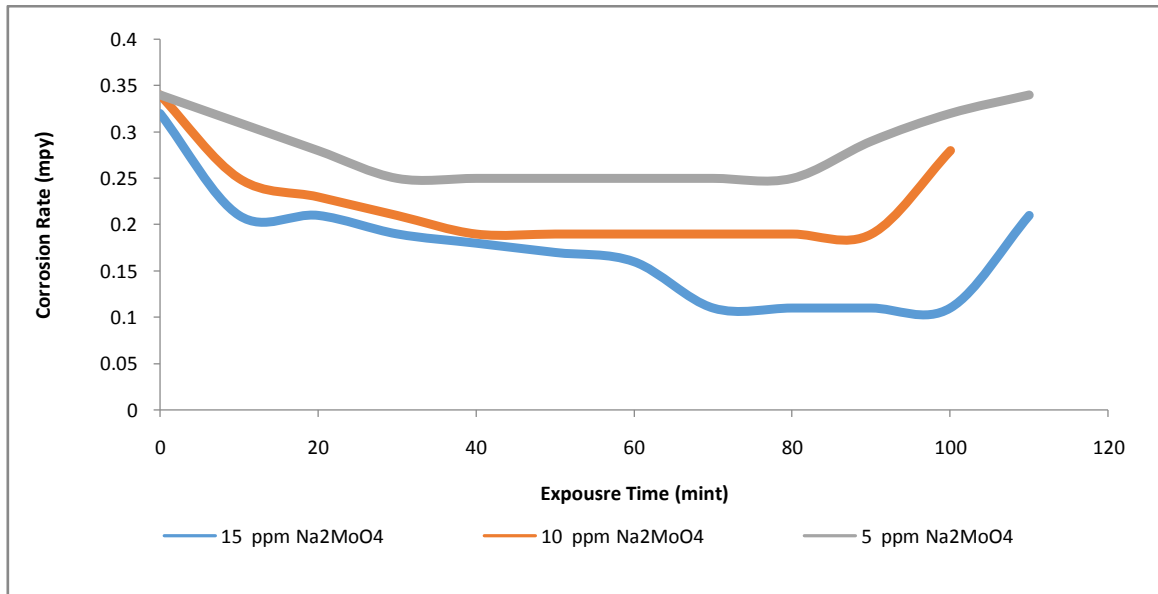


Figure 12 Corrosion Rate (mpy) Vs Time for Carbon Steel in Aerated Stirring Solution and Different Inhibitor Blend at pH 10 and 25°C

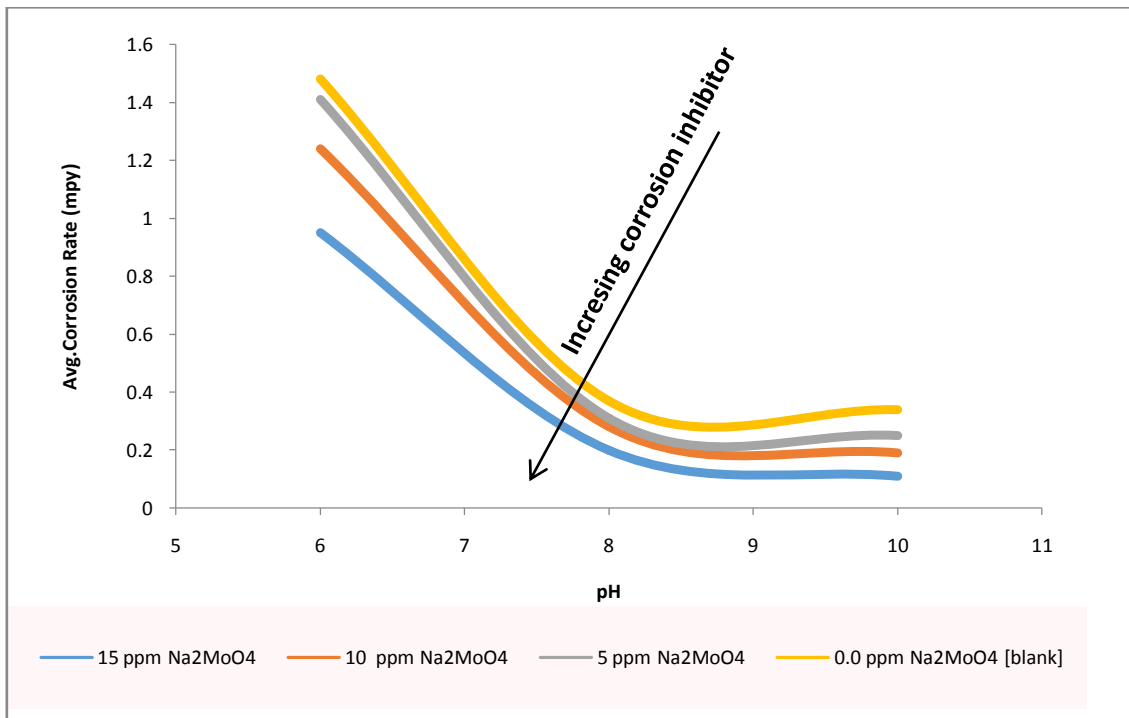


Figure 13 Average Corrosion Rate As A Function of pH For Different Concentration of Corrosion Inhibitor at 25°C.



Figure 14 Examination of the Electrode Surface After Experiments at pH6 [Visible Pits]

Figure15 to figure18 represented the percentage of corrosion protection efficiency with varying concentrations of molybdate at pHs 6, 8 and 10. The percentage of corrosion protection efficiency (PE%) was calculated using the relationship:

$$PE\% = [(CRB - CRI) / CRB] \times 100 .$$

Where:

CRB: corrosion rate in blank solutions.

CRI: corrosion rate in presence of inhibitor Ions.

The results showed that there was an increase in the corrosion inhibition efficiency obtained when the concentration of corrosion inhibitor $[Na_2MoO_4]$ increases for example at pH 10 and 15 ppm molybdate, the inhibition efficiency increases about 2.5 times compared to that caused by 5 ppm at the same conditions. This is an interesting trend for an efficiency vs concentration plot. The results also showed that the highest inhibition efficiency of 80% could be obtained by the 15 ppm molybdate at pH 7. But when the pH of cooling water is decreased to 6, the inhibition efficiency is reduced to 35% at the same concentration of Na_2MoO_4 . However, molybdate ions form a complex with iron as the basis of its film. So, these inhibitor ions acted as a corrosion inhibitor at pH 7 and above in cooling water, and aggravated corrosion at or below pH 6.

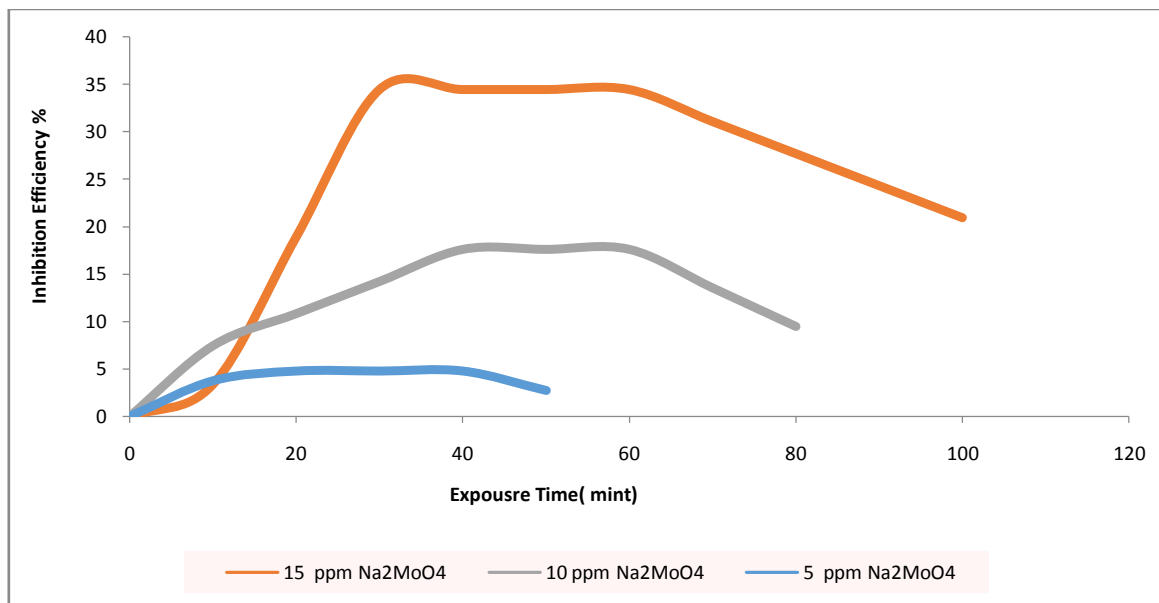


Figure 15 Inhibition Efficiency (%) of Different Inhibitors Concentration at pH 6.

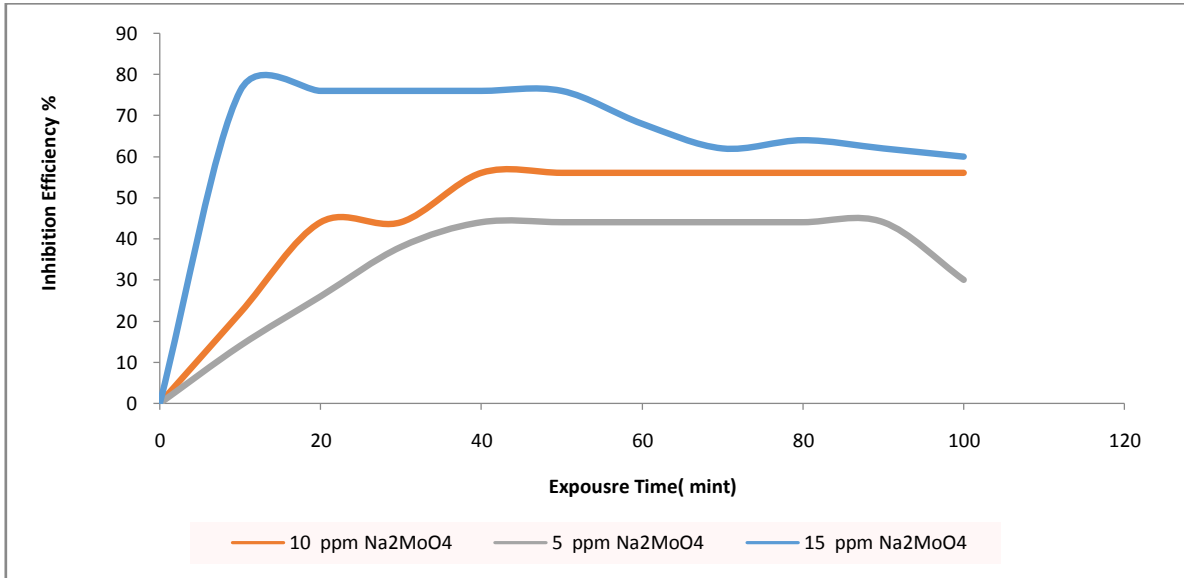


Figure16 Inhibition Efficiency (%) of Different Inhibitors Concentration at pH 7.

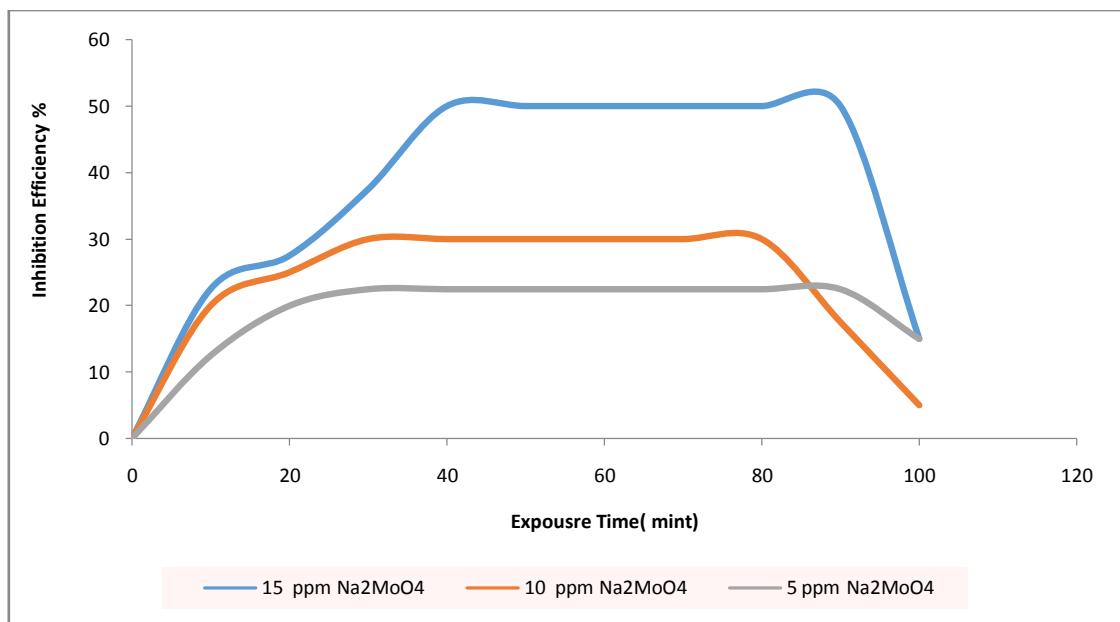


Figure 17 Inhibition Efficiency(%) of Different Inhibitors Concentration at pH 8.

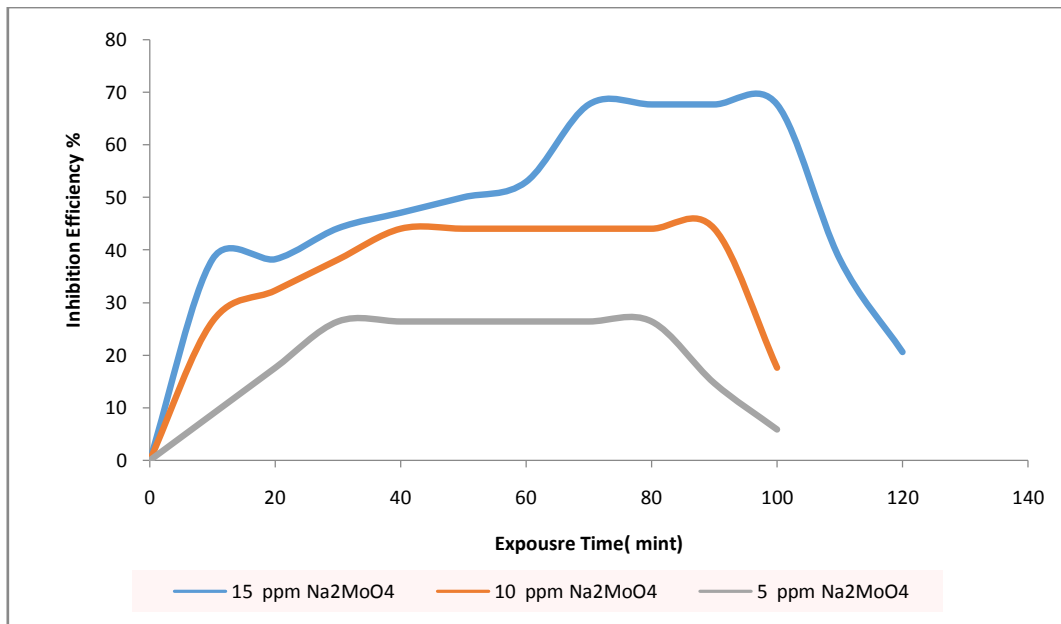


Figure 18 Inhibition Efficiency (%) of Different Inhibitors Concentration at pH 10.

4.2 Effect of Temperature

The effect of temperature on the inhibited solution-metal reaction is highly complex, because many changes occur on the metal surface such as rapid etching, in acidic solution, desorption of inhibitor and the inhibitor itself may undergo decomposition and/or molecular rearrangement [9].

To evaluate the effect of temperature on the performance of corrosion inhibition. Experiments were carried at varying temperatures (25°C, 38°C and 55°C) in the absence and presence of corrosion inhibitor at 5 ppm and 10 ppm concentration at pH 8, makeup water of cooling water.

corrosion rate values, figures 19 to 21 were obtained from the linear polarization resistance, experiments carried out for carbon steel immersed in different concentrations of corrosion inhibitor [Na₂MoO₄] (5 ppm, 10 ppm) and different temperatures of 25°C, 38°C and 55°C during about 2 hrs of immersion time. From these figures, an initial corrosion rate of around 1.45, 0.98 and 0.4 mpy was observed for the carbon steel exposed to 55°C, 38°C and 25°C respectively, and this value decreased during the next minutes until low values were observed. However, it can be observed that with an increase in temperature, the corrosion rate increases. However, the effect of temperature was not so significant up to 38°C when 5 and 10 ppm Na₂MoO₄ was present, but above this temperature the corrosion rate increased slightly especially at low concentration of Na₂MoO₄ as shown in figure 21.

This is expected given that the protection of the carbon steel surface by Na₂MoO₄ inhibitor depends on the surface coverage by Na₂MoO₄ and orientation of Na₂MoO₄ molecules on the surface. With an increase in temperature, it appears that the surface coverage by Na₂MoO₄ decreased at low concentration of inhibitor, which then resulted in an increase in corrosion rate [10]. In addition, to decrease of oxygen solubility at high temperature, desorption of molybdate ions at the higher temperature may be the other reason for the increase in the corrosion rate, since the surface metal becomes less covered. On the other hand, continuation of passivation in room temperature, which increased still further, indicates increasingly effective passivation [10].

Furthermore, at room temperature and low concentration of inhibitors Na₂MoO₄ (5 ppm) the corrosion product is gelatinous and adherent but at about 55°C the film becomes granular and non-adherent. A maximum corrosion rate is reached at about 55°C. Nevertheless, even at high temperature (55°C) the protection of the surface is relatively high, indicating a better performance of Na₂MoO₄ at higher concentration (10 ppm) as shown in figure 21. Also the results showed that for the highest concentration of Na₂MoO₄, the corrosion rate decreases about 3 times compared to a solution without inhibitor. This result reveals the capability of sodium molybdate to act as a corrosion protective layer on carbon steel surface with high concentration of inhibitor.

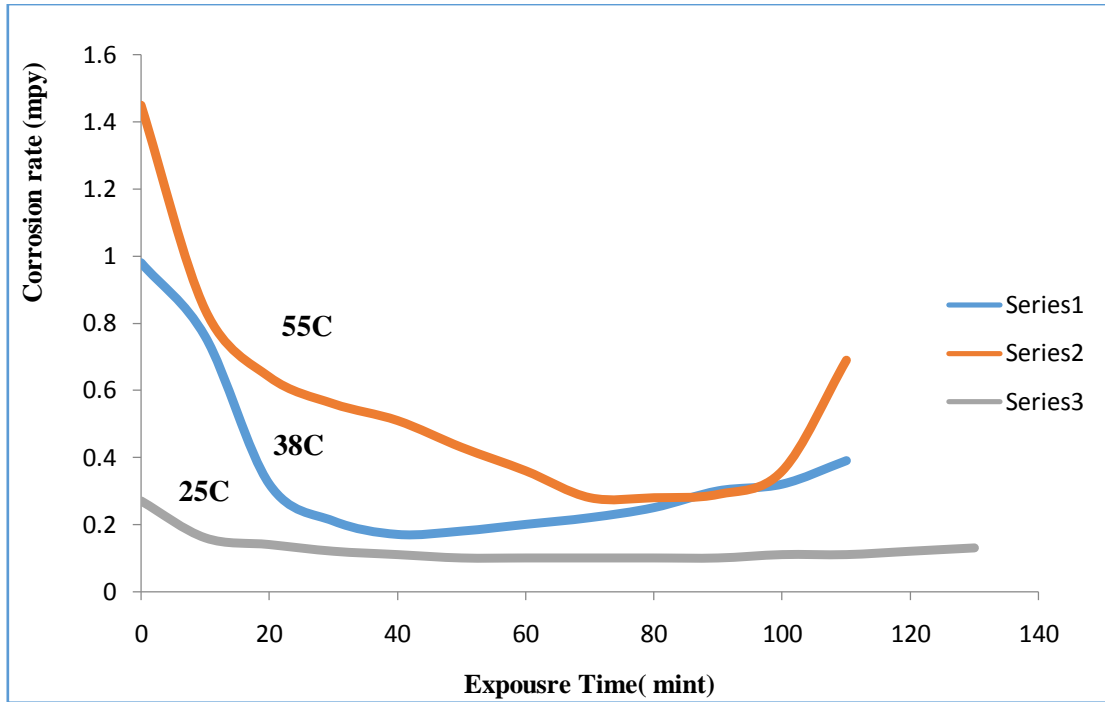


Figure 19 Corrosion Rate (mpy) Vs Time for Carbon Steel in Aerated Stirring Solution and Different Temperatures, pH 8 and Corrosion Inhibitor Na_2MoO_4 (10ppm)

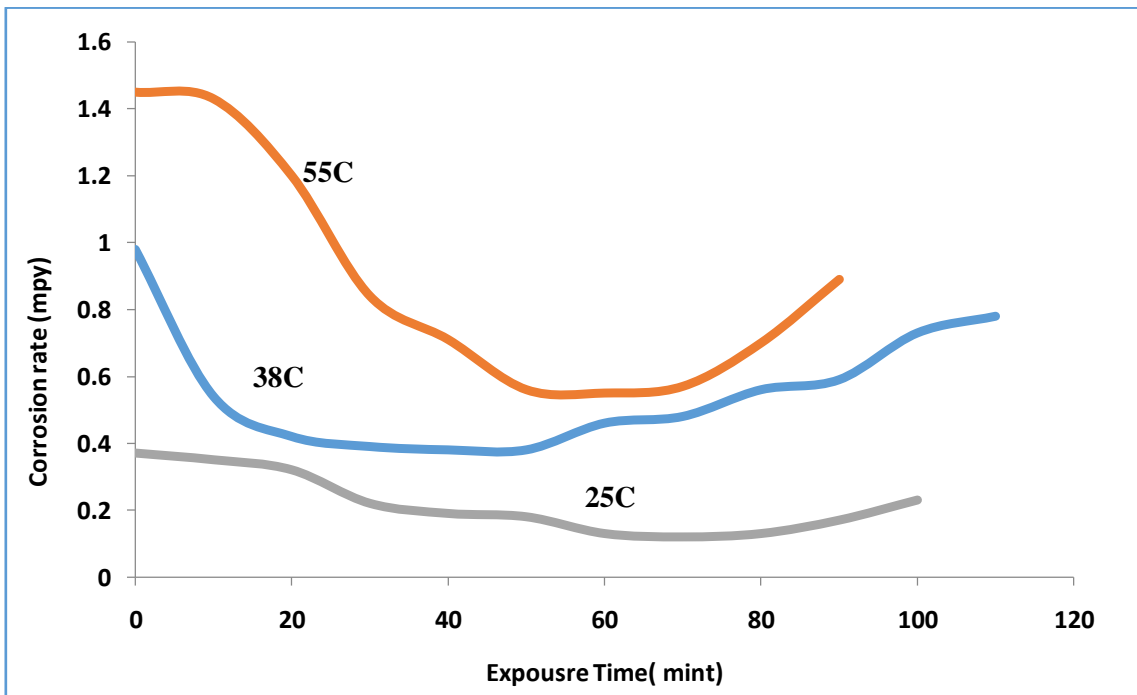


Figure 20 Corrosion Rate (mpy) Vs Time for Carbon Steel in Aerated Stirring Solution and Different Temperatures, PH 8 and Corrosion Inhibitor Na_2MoO_4 (5ppm)

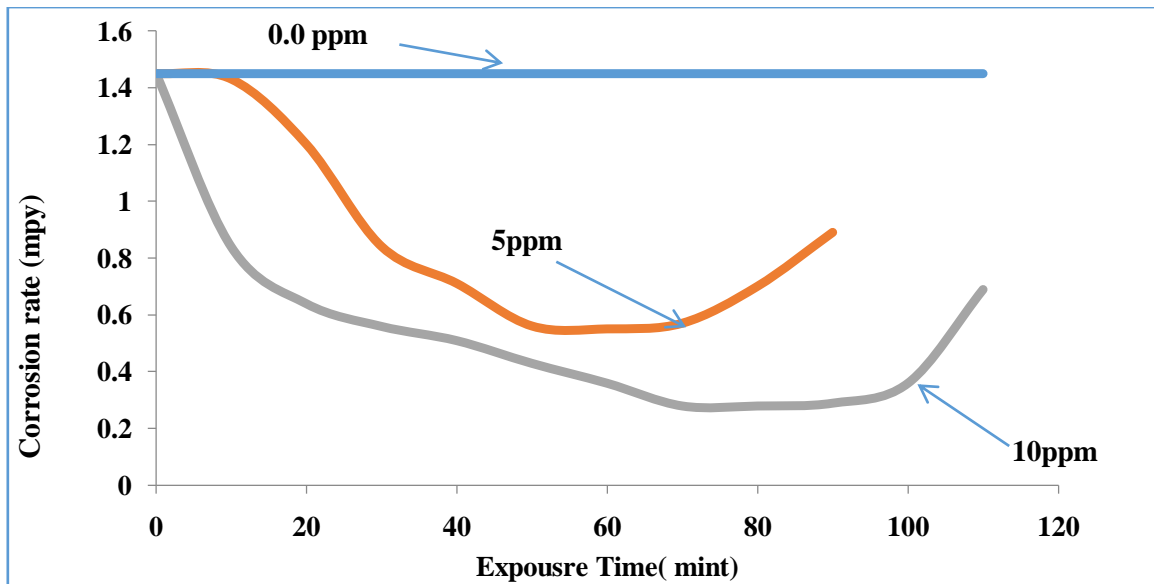


Figure 21 Corrosion Rate (mpy) Vs Time for Carbon Steel in Aerated Stirring Solution and Different Corrosion Inhibitor Na_2MoO_4 and Temperature 55°C and pH 8

Figure 22 showed the corrosion inhibition efficiency obtained from equation above values on the Na_2MoO_4 concentration at 55°C and pH8. As it clearly shown in figure 22 the corrosion inhibitor of Na_2MoO_4 concentration an increase, the corrosion inhibition efficiency increases with immersing time until reaching 60% at 5 ppm concentration of Na_2MoO_4 . With further increase in Na_2MoO_4 concentration (10ppm), the corresponding inhibition efficiency increases to 80%, and it then remains relatively constant for 20 minutes. However, the maximum efficiency obtained was 80% at concentration 10 ppm of Na_2MoO_4 .

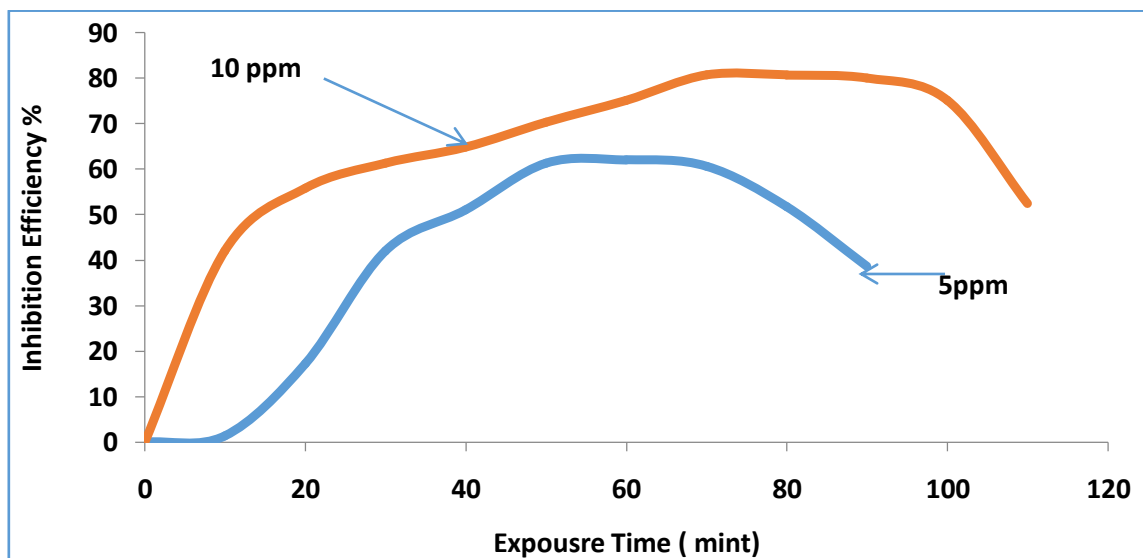


Figure 22 Inhibition Efficiency (%) of Different Inhibitors Concentration at Temperature 55°C and pH 8.

5. Conclusions

The possibility of using Sodium Molybdate (Na_2MoO_4) as corrosion inhibitor for cooling water system of Mellitah Plant was investigated using Linear Polarization Resistance (LPR) and following conclusions were drawn:

- ✓ The addition of molybdate showed a reducing the corrosion rate of carbon steel
- ✓ Molybdate acts as a corrosion inhibitor for carbon steel in neutral and alkaline solution (at pH 7 and above) and was not good effective in low pH values.
- ✓ Sodium Molybdate showed high inhibition efficiency in the pH range between pH 7 to pH 10.
- ✓ The inhibition efficiency of inhibitor blend increased to the maximum value of 80% at 15 ppm molybdate in pH 7 and decreased to 5% at 5

ppm molybdate in pH6 and room temperature.

- ✓ Sodium Molybdate gave 80% corrosion inhibition efficiency when applied at 10 ppm concentration and temperature range of 55C, implying it is applicable for high temperature applications.

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