Research Article

Corrosion Inhibition of Passivated AISI – 1020 Steel in 3.5 % NaCL Solution Using Organic Inhibitors

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ABSTRACT

It is well know that recirculating open cooling water system at metal/ water surface contact appear frequent corrosion products, like scales, foaling and material losses which are have great effect on cooling process.

Passivation helps to maintain clean heat transfer surface by inhibiting oxides scales through creating outer passive layer.

After definite time breakdown due to mechanical or chemical actions will take place.

Therefore, it is necessary to add other organic compounds to treat the places pf collapse of previous protective layer formed by reaction of passivator with carbon steel.

Corrosion inhibitor is a chemical compound that, when added to corrosive medium decreases the corrosion rate of a material with medium. Corrosion inhibitors are common used in industry.

Organic inhibitors Phosphonobutane-1,2,4-tricarboxylic acid (PBTC) - $\mathbf{C_7H_{11}O_9P}$ and Amine - $\mathbf{C_{35}H_{38}Cl_2N_8O_4}$ will be used.

The study of corrosion inhibition for passivated carbon steel pipe line in recirculation open cooling water system was the aim of this present work. Maximum efficiency of inhibitors was determined and surface morphology were investigated using optical, scanning microscopy, phase analysis of the formed protective layer was examed by XRD and EDX.

Corrosion in running water with and without inhibitors at 2 m^3/hr flow rate was investigated using corrosion coupon rack.

In running flow test, the corrosion rate of passivated carbon steel decreases from about 18 mpy to about 3 mpy after adding 200 ppm PBTC and 2.5 mpy after adding 150 ppm amine respectively in 3.5% NaCL solution at 25^0C and 6.5-7.5 PH, while In potentiodynamic polarization technique (stagnant), the corrosion rate of passivated carbon steel decreases from 7 mpy to 1.2 mpy after adding 200 ppm PBTC and 1 mpy after adding 150 ppm amine respectively in 3.5% NaCL solution at 25^0C and 6.5-7.5 PH.

Key words: Corrosion, AISI – 1020 steel, passivation, passive layer, organic passivator, organic Inhibitors, polarization curves.

1. Introduction

Open recirculating cooling water systems or wet cooling towers are the most widely used designs in industry [1].

The open system uses the same water over and over again. Its most visible feature is the large, outdoor cooling tower that uses evaporation to release heat from the cooling water [2-3].

This system consists of three main pieces of equipment: the recirculating water pump(s), the heat exchanger(s), and the cooling tower which are normally connecting with each other by AISI-1020 carbon steel pipe line [4].

Corrosion of open water cooling system causes two basic problems. The first and most obvious is the failure of equipment with the resultant cost of replacement and plant downtime. The second is decreased plant efficiency due to loss of heat transfer-the result of heat exchanger fouling caused by the accumulation of corrosion products [5].

One of corrosion prevention methods is passivation, "passivation" means to make something chemically passive. Active surfaces react readily while passive surfaces are resistant to reactions, including corrosion reactions According to ASTM A 967 specification [6].

The effectiveness of passive oxide layers depends on the type of elements involved. Not all oxide layers are protective: If the oxide is porous enough for oxygen to get through, then no seal will be formed, and the metal beneath will continue to corrode [7-8-9].

Passivation process behavior of carbon steel in presence of Ethylenediaminetetraacetic acid (EDTA) was studies by P.S. Joshi they observed that protective magnetite thin film was formed on the steel surface [10].

The passive oxide film of carbon steel in saturated calcium hydroxide solution was investigated by P. Ghods, O.B. Isgor ,J.R.Brown.They found that the thickness of the oxide films was approximately 4 nm [11].

Passivation of Carbon Steel by Sodium Borosilicate in Simulated Recirculating Cooling Water was clarified by Jun Cui, Wenjio, Donghaiyuan[12].

Passivation of carbon steel in neutral aqueous solution by dicarboxylic acid was investigated by G. Chan- Rosado and M.A.Pech – Canul they discovered that the passive layer consisted of inner oxide region and outer hydroxylated region [13].

To be effective, passive film must provide a barrier. An effective passive film must resist breakdown. Sometimes the breakdown is localized to small areas, the localized anode reactions can lead to localized corrosion [14].

Breakdown of the passive film can occur by chemical factors and \ or mechanical factors, one of the major species in water that causes chemical breakdown of passive films is the chloride ion. Mechanical breakdown can also occur due to stress or abrasive wear, such as if the water velocity is too high.

Due to passive film ability for breakdown second line defense (inhibitors) should be used to avoid huge corrosion rate take place at the cooling system.

The present work was aimed at investigating the corrosion inhibition for passivated carbon steel [17] by Phosphonobutane-1,2,4-tricarboxylic acid (PBTC) - $C_7H_{11}O_9P$ and Amine - $C_{35}H_{38}Cl_2N_8O_4$ in 3.5% NaCL solution using electrochemical measurements as well as corrosion coupon rack testing (running flow)

Surface morphology will be investigated using optical, scanning microscopy and phase analysis of the formed protective layer will be examined by XRD and EDX.

2. Experimental

2.1 Materials and specimen Preparations

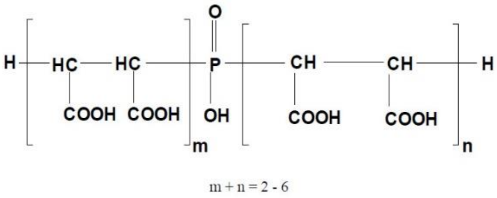
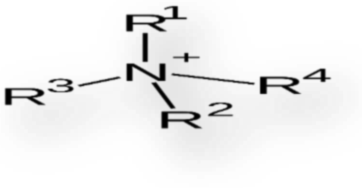
Cold rolled – AISI-1020 low carbon steel passivated by using 200 ppm organic phosphate Phosphinosuccinic oligomer **$C_{15}H_{14}O_4P$** component (PSO) has been used in this study [15]. Table 1 and 2 summaries the chemical composition and mechanical proprieties of the steel under investigation.

Table (1): Chemical composition of AISI-1020

Element	C	Si	Mn	Cr	P	S	Fe
wt.%	0.20	0.25	0.50	0.059	0.012	0.017	balance

Inhibitors were used is Phosphonobutane-1,2,4-tricarboxylic acid (PBTC) - $C_7H_{11}O_9P$ and Amine - $C_{35}H_{38}Cl_2N_8O_4$ which have the following chemical formula and structure which have been tested in 3.5% NaCL solution.

Table (2): Chemical formula and structure inhibitors.

Inhibitor	Chemical formula	Structure
Phosphonobutane-1,2,4-tricarboxylic acid (PBTC) Inhibitor (1)	$C_7H_{11}O_9P$	
Amine Inhibitor (2)	$C_{35}H_{38}C_{l2}N_8O_4$	

2.2 Specimen Preparations and Characterization

For testing and calculating the inhibitors efficiencies and corrosion rate at different concentrations of inhibitors, specimens of (20x20x2mm) were utilized, which were abraded with different sizes of emery papers and polished with polishing clothes and 0.3-micron alumina solution was used to polishing then rinsed and air-dried. To ensure that the specimens were free of dust, oil, and extraneous materials, they were washed with ethanol in an ultrasonic bath and then cooled mounted. The test solutions were prepared by adding, 200 ppm from PSO [17] and different concentrations of PBTC and amine to a 3.5% NaCL solution. passivation film and second layer defense of the passivated-steel where characterized by X-ray diffraction (XRD) patterns were recorded by a Siemens D5000 powder diffract meter equipped with Cu-Ka radiation (Siemens D5000, Germany). Scanning electron microscopy compiled with an energy dispersive spectrometer (SEM-EDS, Jeol JSM-6360LA, Japan) was used to investigate the microstructure of the passivated and inhibited steel. Salt spray tester was also used for five days.

2.3 Corrosion Rate Measurement

Potentiodynamic polarization technique was used to study the corrosion behavior of passivated AISI 1020 carbon steel in 3.5% NaCL solution with and without inhibitors. Potentiodynamic polarization experiments were carried out using Versastat3 (Potentiostat /Galvanostat Model, Germany). All potentials were measured concerning the SCE. All electrochemical experiments were conducted using a conventional three-electrode 250 ml cell assembly, with the counter electrode made of platinum and saturated calomel electrode (SCE) as a reference electrode. A copper wire, 3 mm diameter, was mounted to the rear side of the samples as an electrical connection. The exposed surface of the specimen was flat with a cross-section area of 4 cm^2.

The potentiodynamic current / potential curves were recorded by changing the electrode potential automatically from -2500 to +2500 mV with a scan rate of 1 mV.S-1 and the corresponding current was recorded.

Running flow corrosion testing was carried out using corrosion coupon rack as described in **ASTM D 2688-05**

Which is simulated to the conditions applied in industry used for calculation of erosion-corrosion. Specimens were tested for one day in running flow of 3.5% NaCL (Pressure = 3 bar, Flow rate 2 m^3/h, RPM = 2000)

A specimen is cleaned, weighed, attached to a rope and put in the pipe.

The specimen is left in the device for 3 days, then we take it out from the device, clean it from corrosion products, and weighed it again. Corrosion rate have been calculated. Then the process repeats again for many specimens with different values of inhibitors and calculate the corrosion rate for all specimens to determine the effect of each inhibitor. Corrosion rate was calculated in running flow method by the following equation in previous research [15].

3. Results and discussion

The corrosion rate (CR) is decreased with the addition of passivator. The corrosion rate is decreased to its lowest level when 200 ppm of PSO was used as mentioned in previous work [15].

Figure 1 shows the polarization curves from passivated AISI 1020 carbon steel in 3.5 % NaCL solution with different concentrations of (PBTC) at 25^0C with 6.5-7.5.

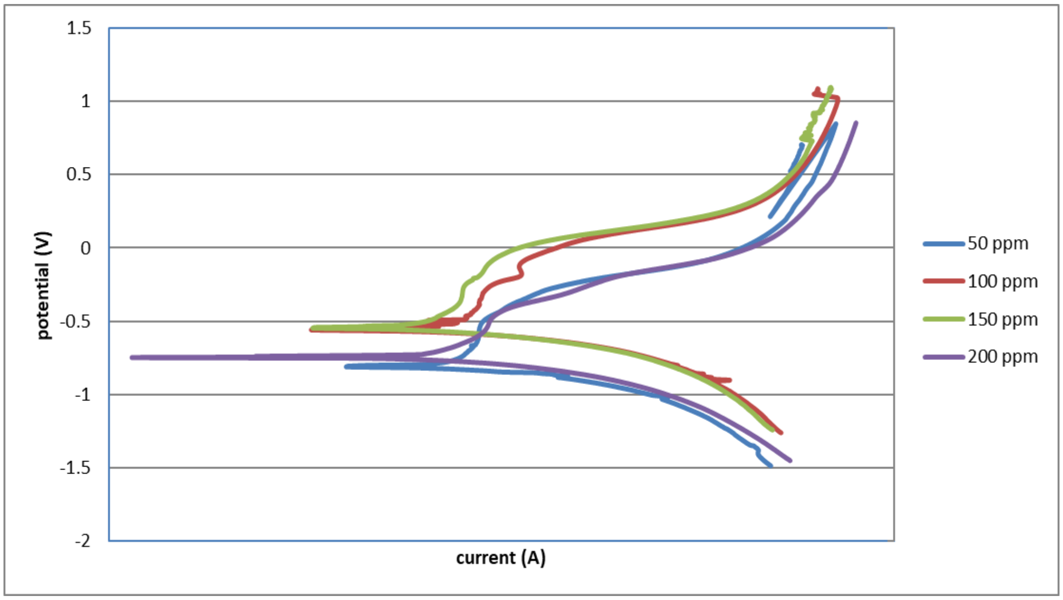


Figure 1 polarization curves for passivated AISI 1020 carbon steel in 3.5 % NaCL solution at 25^0C and 6.5–7.5 PH with different concentration of (PBTC).

Figure 2 shows the effect of concentration of (PBTC) and efficiency % on the corrosion rate of passivated AISI 1020 carbon steel in 3.5% NaCL solution at 25^0C and 6.5-7.5 PH using potentiodynamic method. The addition of PBTC leads to react with not passivated areas and reacts as second line defens. Then it decreases the corrosion rate from 7 mpy to 1 mpy at 200 ppm.

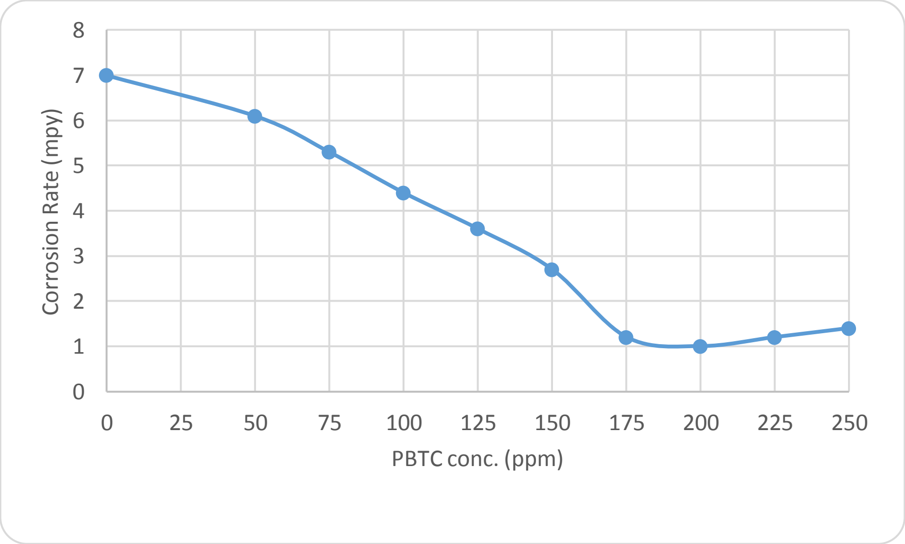


Figure 2 (a) Effect of PBTC concentration on the corrosion rate of passivated AISI 1020 carbon steel in 3.5% NaCL solution using potentiodynamic polarization technique at 25^0C and 6.5-7.5 PH.

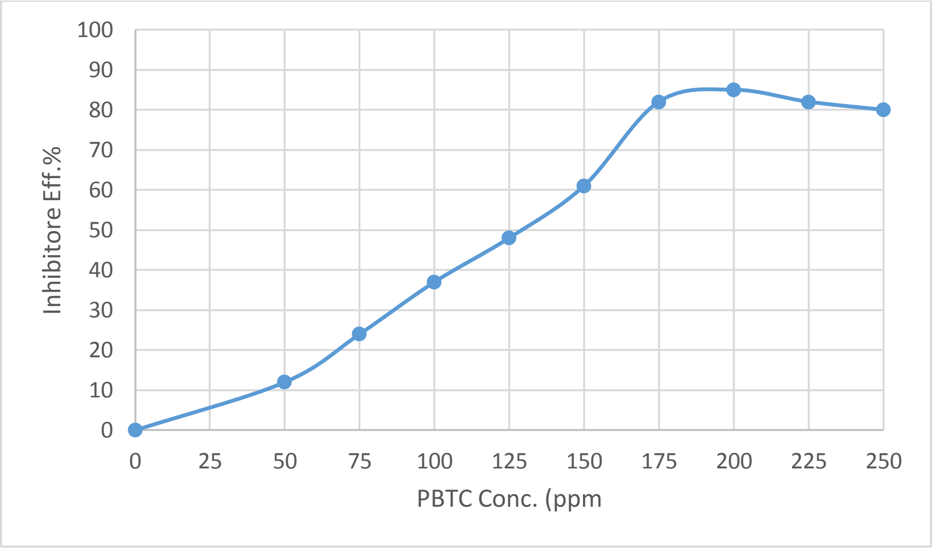


Figure 2 (b) Effect of PBTC concentration efficiency % on the corrosion rate of passivated AISI 1020 carbon steel in 3.5% NaCL solution using potentiodynamic polarization technique at 25^0C and 6.5-7.5 PH.

Figure 3 shows the effect of concentration of PBTC and efficiency % on the corrosion rate of passivated AISI 1020 carbon steel in 3.5% NaCL solution at 25^0C and 6.5-7.5 PH using running flow method. The addition of PBTC leads to react with to react with not passivated areas as a second line defens. Then it decrease the corrosion rate from 18 mpy to 2.5 mpy at 200 ppm.

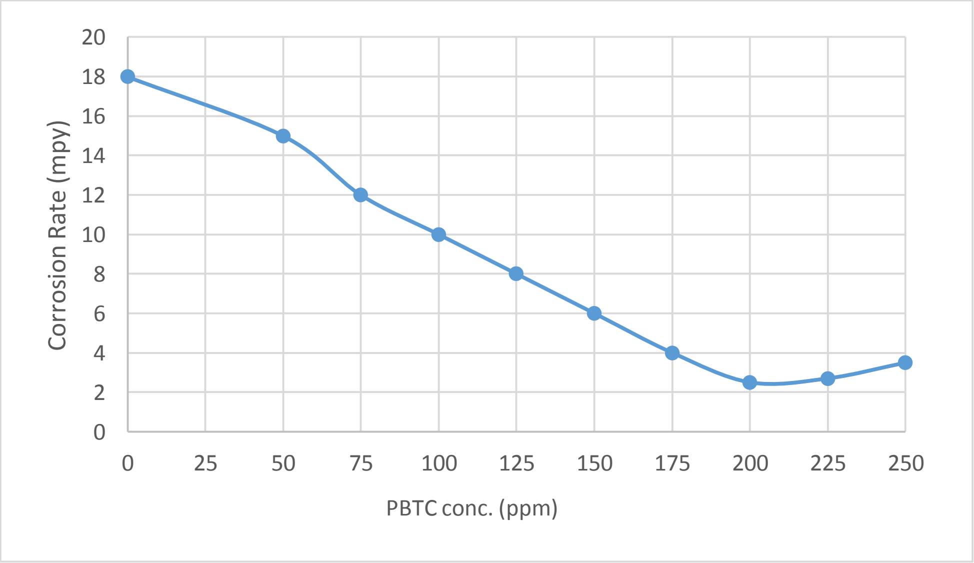


Figure 3 (a) Effect of PBTC concentration on the corrosion rate of passivatedAISI 1020 carbon steel in 3.5% NaCL solution using running flow technique at 25^0C and 6.5-7.5 PH

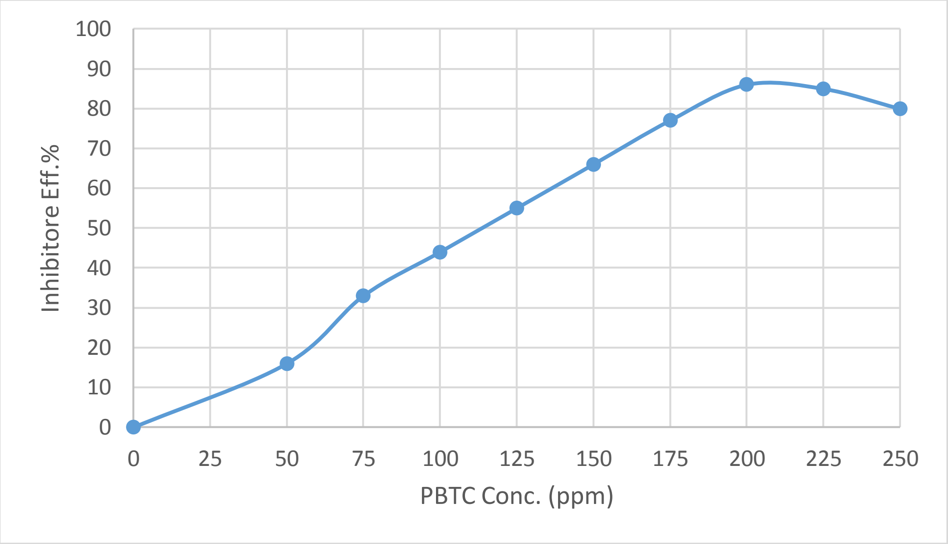


Figure 3 (b) Effect of PBTC concentration efficiency % on the corrosion rate of passivated AISI 1020 carbon steel in 3.5% NaCL solution using running flow technique at 25^0C and 6.5-7.5 PH

The corrosion rate (CR) is decreased with the addition of inhibitor (1). The corrosion rate is decreased to its lowest level when 200 ppm of PBTC was used.

Figure 4 shows the polarization curves from passivated AISI 1020 carbon steel in 3.5 % NaCL solution with different concentrations of amine at 25^0C with 6.5-7.5.

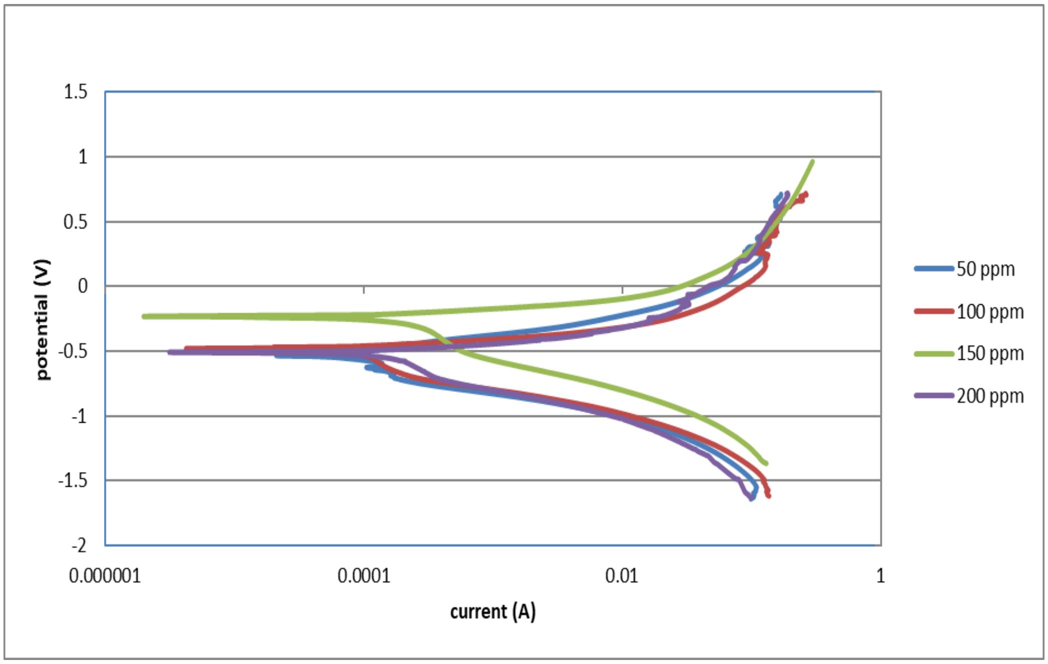


Figure 4 polarization curves for passivated AISI 1020 carbon steel in 3.5 % NaCL solution at 25^0C and 6.5–7.5 PH with different concentration of amine.

Figure 5 shows the effect of concentration of amine and efficiency % on the corrosion rate of passivated AISI 1020 carbon steel in 3.5% NaCL solution at 25^0C and 6.5-7.5 PH using potentiodynamic method . The addition of amine leads to protect from corrosion and decrease the corrosion rate from 7 mpy to 1.2 mpy at 150 ppm.

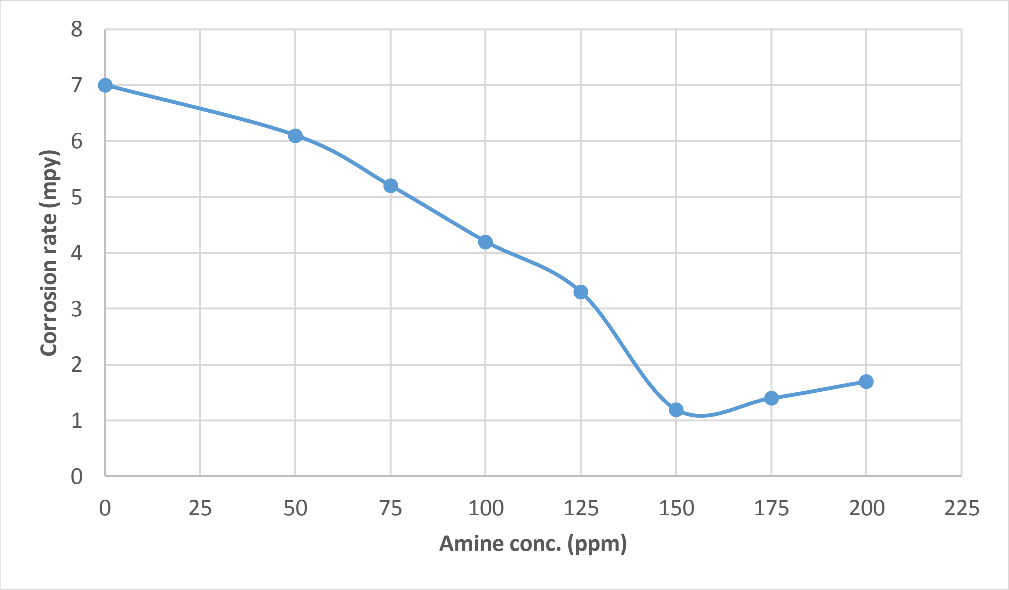


Figure 5 (a) Effect of Amine concentration on the corrosion rate of passivated AISI 1020 carbon steel in 3.5% NaCL solution using potentiodynamic polarization technique at 25^0C and 6.5-7.5 PH.

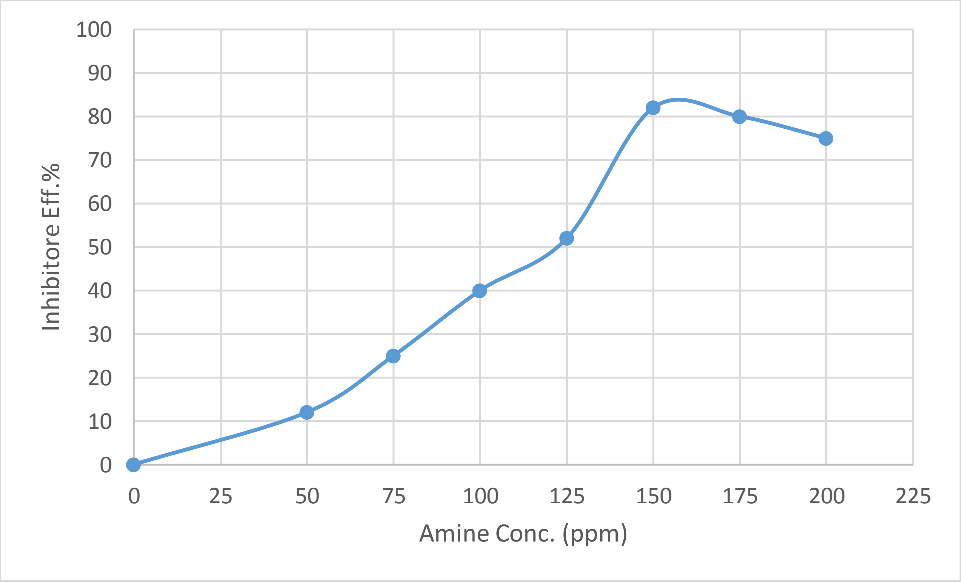


Figure 5 (b) Effect of Amine concentration efficiency % on the corrosion rate of passivated AISI 1020 carbon steel in 3.5% NaCL solution using potentiodynamic polarization technique at 25^0C and 6.5-7.5 PH.

Figure 6 shows the effect of concentration of amine and efficiency % on the corrosion rate of passivated AISI 1020 carbon steel in 3.5% NaCL solution at 25^{0}C and 6.5-7.5 PH using running flow method. The addition of amine leads to protect from corrosion and decrease the corrosion rate from. 18 mpy to 3 mpy at 150 ppm.

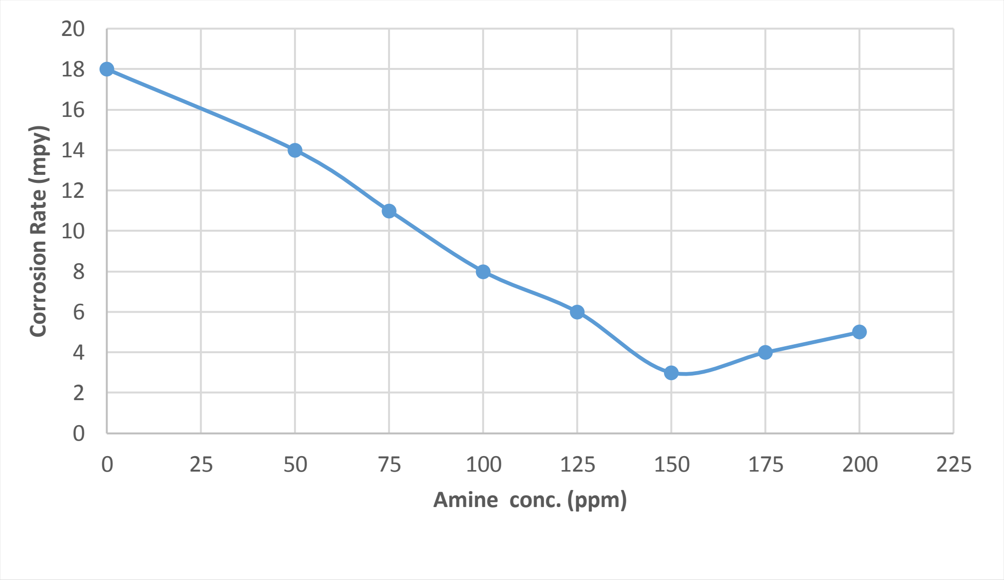


Figure 6 (a) Effect of amine concentration on the corrosion rate of passivated AISI 1020 carbon steel in 3.5% NaCL solution using running flow technique at 25^{0}C and 6.5-7.5 PH.

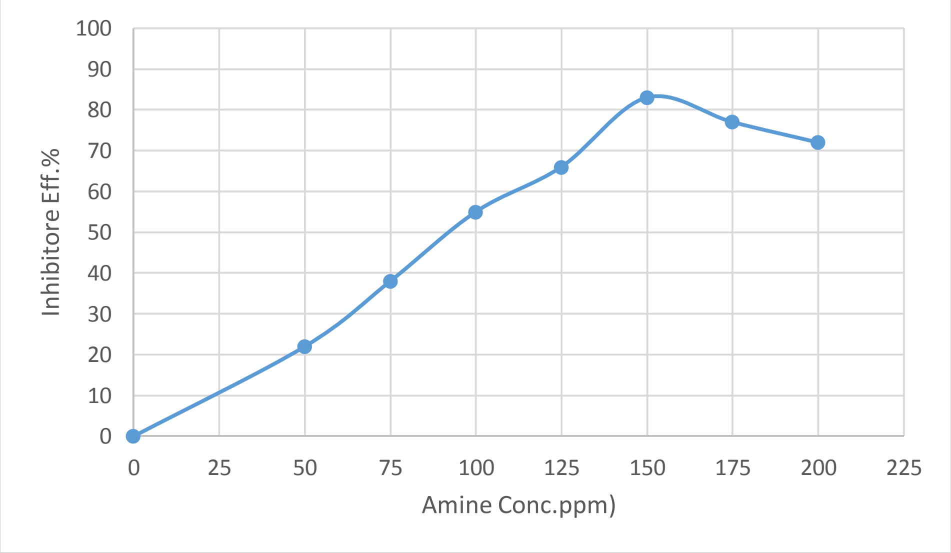


Figure 6 (b) Effect of amine concentration efficiency % on the corrosion rate of passivated AISI 1020 carbon steel in 3.5% NaCL solution using running flow technique at 25^{0}C and 6.5-7.5 PH.

The corrosion rate (CR) is decreased with the addition of inhibitor (2). The corrosion rate is decreased to its lowest level when 150 ppm of amine was used.

Figure 7 shows relations between corrosion rates with different chemicals concentration in both potentiodynamic and running flow techniques, it is found that corrosion rate in running flow technique is around twice and half in potentiodynamic technique.

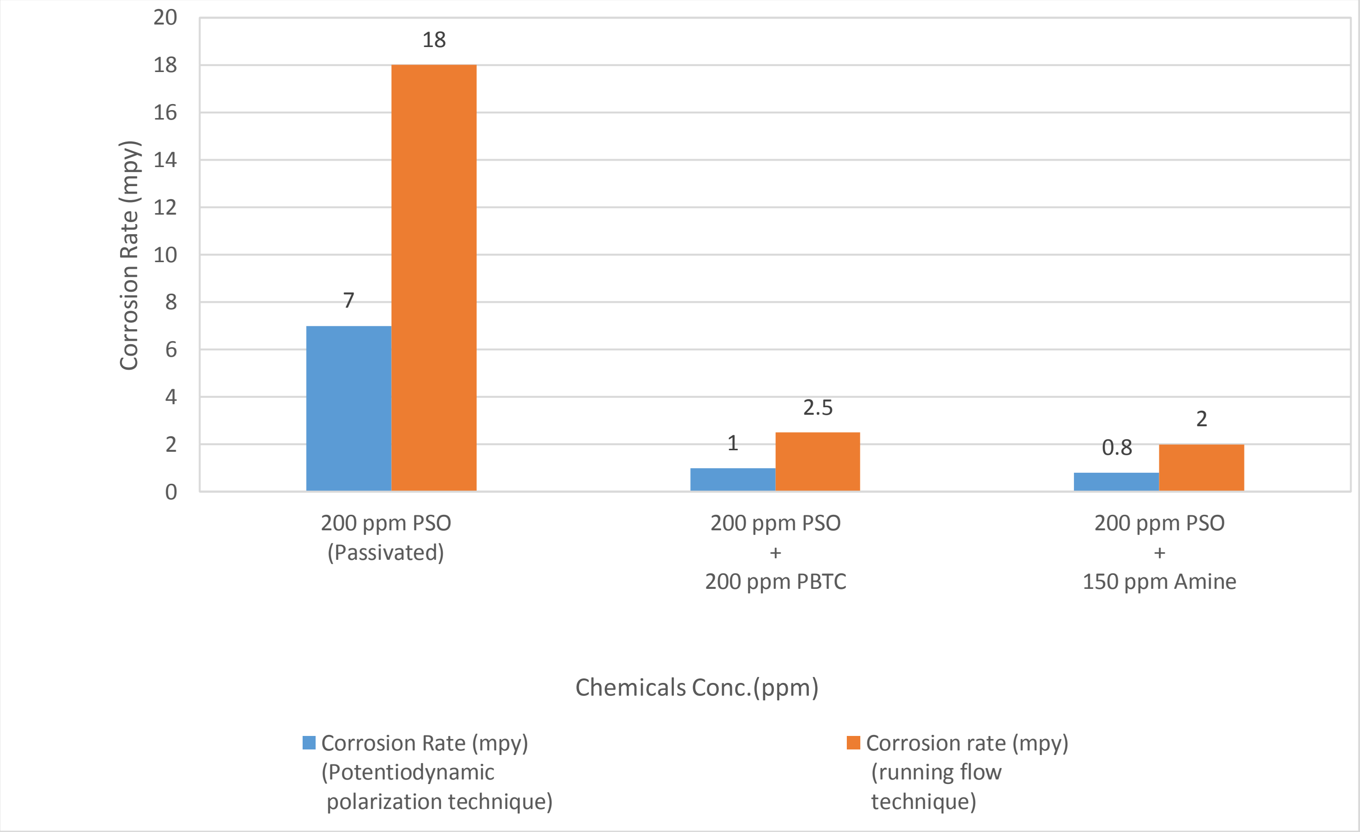
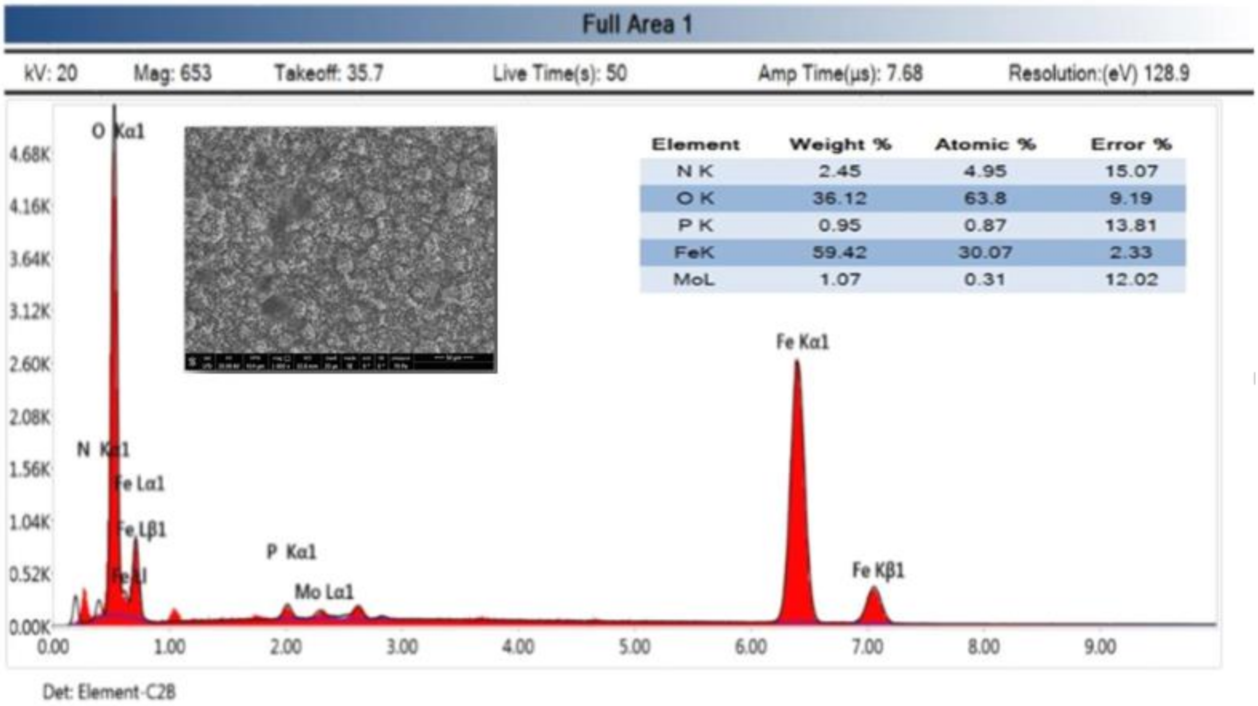


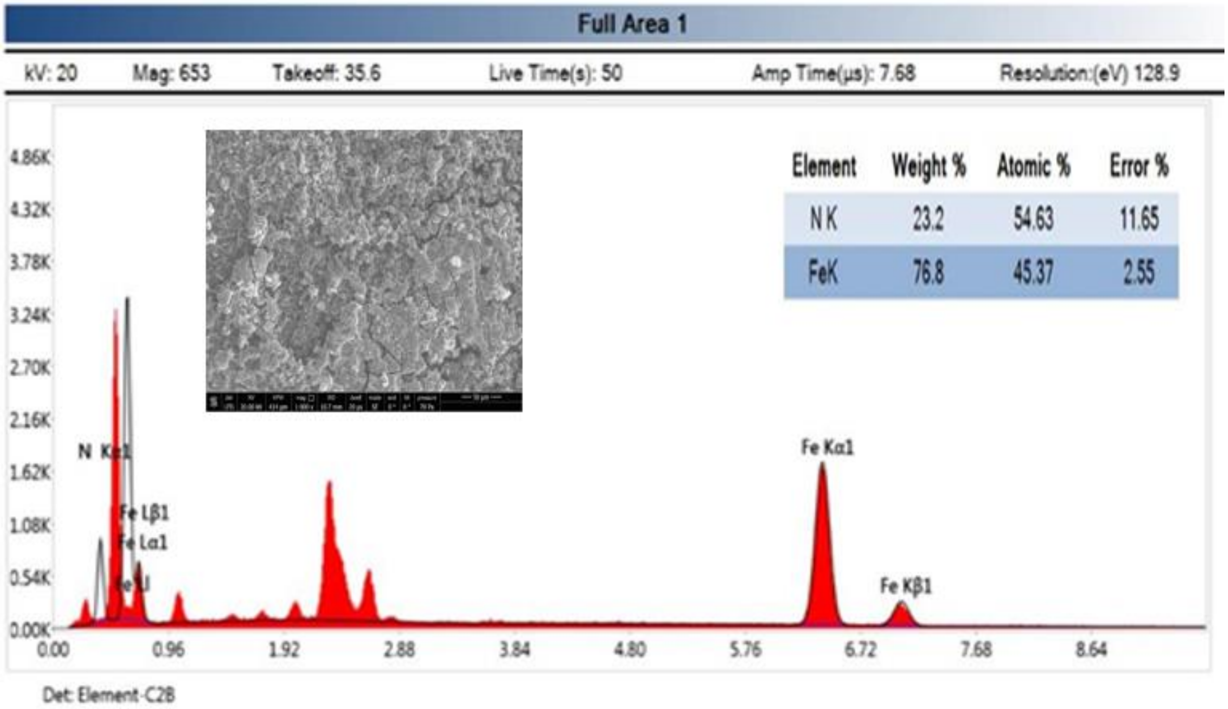
Figure 7 Relation between corrosion rate at different chemicals concentration during potentiodynamic and running flow techniquesat 25^{0}C and 6.5-7.5 PH.

Figure 8 shows Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Analysis (EDX) results for different passivated AISI 1020 carbon steel in 3.5% NaCL solution samples with (a) 200 ppm passivatore + 200 ppm PBTC ,(b) 200 ppm passivatore + 150 ppm amine, using potentiodynamic polarization technique at 25^{0}C and 6.5-7.5 PH.



Element	Weight %	Atomic %	Error %
N K	2.45	4.95	15.07
O K	36.12	63.8	9.19
P K	0.95	0.87	13.81
FeK	59.42	30.07	2.33
MoL	1.07	0.31	12.02

Figure 8 (a) SME & EDX for of passivated AISI 1020 carbon steel in 3.5% NaCL solution with 200 ppm PBTC using potentiodynamic polarization technique at 25^{0}C and 6.5-7.5 PH.



Element	Weight %	Atomic %	Error %
N K	23.2	54.63	11.65
FeK	76.8	45.37	2.55

Figure 8 (b) SME & EDX for of passivated AISI 1020 carbon steel in 3.5% NaCL solution with 150 ppm amine using potentiodynamic polarization technique at 25^{0}C and 6.5-7.5 PH.

Figure 9 shows X-ray Diffraction Analysis (XRD) results for different passivated AISI 1020 carbon steel in 3.5% NaCL solution samples with (a) 200 ppm passivatore + 200 ppm PBTC ,(b) 200 ppm passivatore + 150 ppm amine, using potentiodynamic polarization technique at 25^0C and 6.5-7.5 PH.

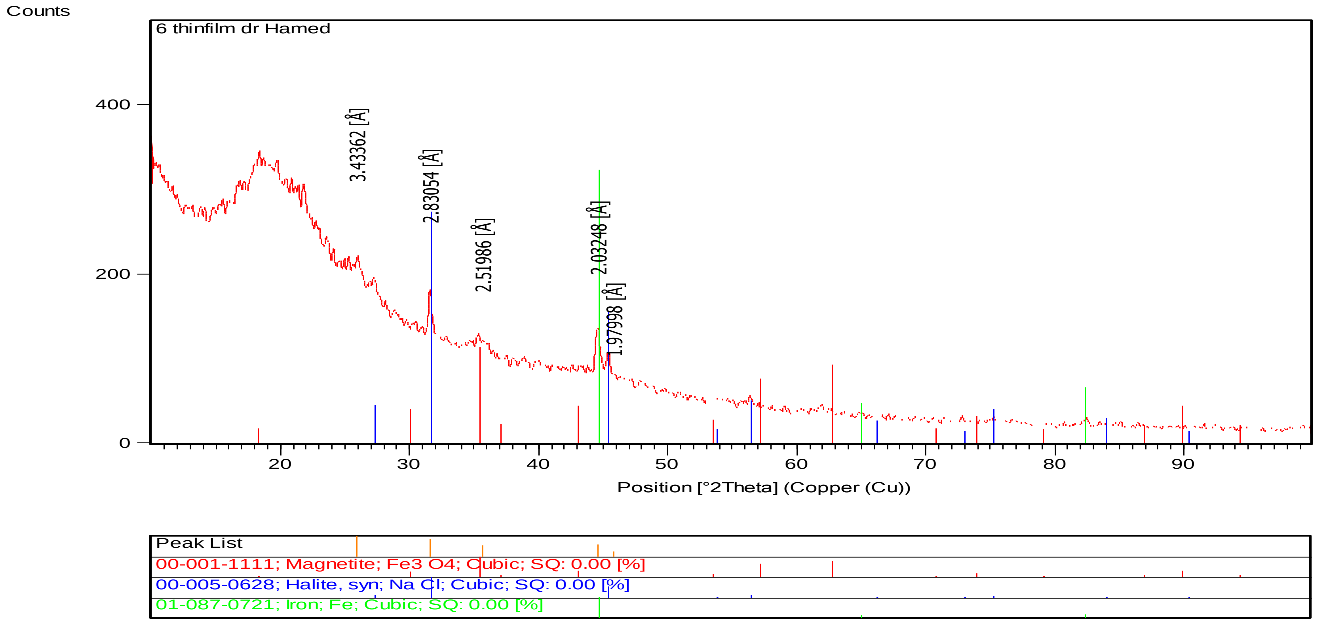


Figure 9 (a) XRD for of passivated AISI 1020 carbon steel in 3.5% NaCL solution with 200 ppm PBTC using potentiodynamic polarization technique at 25^0C and 6.5-7.5 PH.

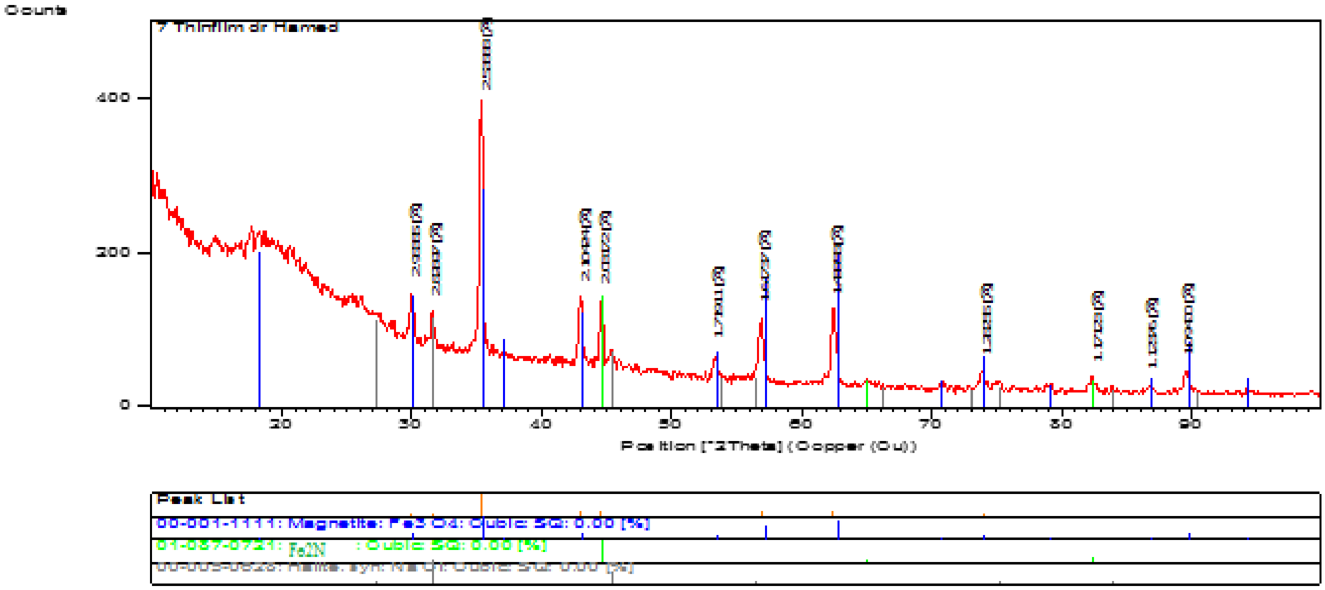


Figure 9 (b) XRD for of passivated AISI 1020 carbon steel in 3.5% NaCL solution with 150 ppm amine using potentiodynamic polarization technique at 25^0C and 6.5-7.5 PH.

It is clear that the passive layer was magnetite Fe_3O_4 and iron nitride has been appear on sample surface in after using amine as inhibitor .The corrosion products caused by immersion in the test solution are represented by the compounds, as seen in figure 9. On the metal surface, a layer from iron oxide and iron nitride are formed. The layer represent the protective film formed due to the interaction of iron with passivator and inhibitors molecules. As evidenced by the corresponding peaks, the intensity is much higher on the metal surface. Additionally, the narrow peaks in the obtained XRD patterns suggested that the produced films were crystallized, resulting in a higher level of protection.

Salt spray test was carried out by (Alpha +) Salt spray testing equipment with the following test conditions time = 2 days, chamber temperature = 35oC, PH = 6.5 to 7.2 and 5% sodium chloride aqueous solution.one day in mentioned equipment simulate one year in normal condition and it is shows high performance for created passive layer for the sample after one day in second day the passive layer draw back and corrosion rate increase but after used mixture of 200 ppm passivator + 150 ppm amine with another sample passive layer hold even after five days as shows in figure 10.

Figure 10 (a) Macrograph (10x) of passivated steel sample before salt spray test.

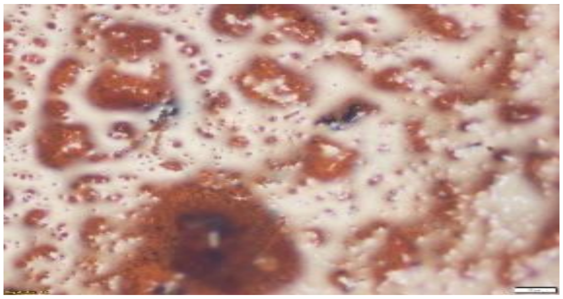


Figure 10 (b) Macrograph (10x) of passivated steel sample after 1 day

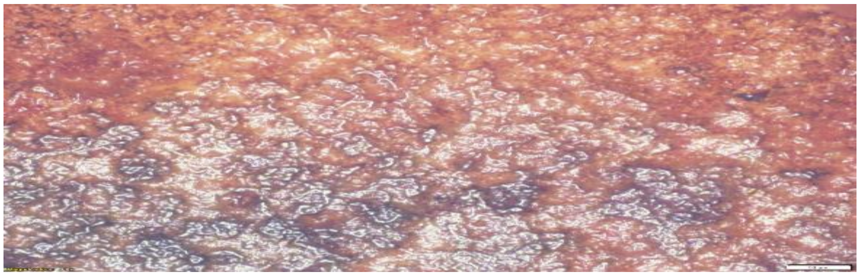


Figure 10 (c) Macrograph (10x) of passivated steel sample using 150 ppm amine after 5 day

4. Conclusion

- The results from running flow test and potentiodynamic polarization technique show that 200 ppm passivator is the best value for protection the water-cooling piping system but corrosion rate increased after about one year due to Passive layer draw back.
- In potentiodynamic polarization technique (stagnant), the corrosion rate of passivated carbon steel decreases from about 7 mpy to about 1.2 mpy after adding 200 ppm PBTC and 1 mpy after adding 150 ppm amine in 3.5% NaCL solution.
- In running flow test, the corrosion rate of passivated carbon steel decreases from about 18 mpy to 3 mpy after adding 200 ppm PBTC and 2.5 after adding 150 ppm amine in 3.5% NaCL solution.
- The results from running flow test and potentiodynamic polarization technique show that the corrosion rate values using running flow test is to be about twice the corrosion rate values using potentiodynamic polarization technique.
- Results of XRD, showed that Magnetite (Fe_3O_4) & iron nitride, which is the protective layers, are formed on the surface.
- Salt spray test results also show that the best protection to carbon steel in water cooling piping systems can be achieved by adding a mixture of 200 ppm passivator and 150 ppm PBTC.

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