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Evaluation of Corrosion Inhibitor Blend Efficiency in Recirculation Cooling Water of Al-Doura Refinery

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Abstract

The corrosion behavior of carbon steel in circulating cooling water (C.T.) of Al Doura Refinery and performance of sodium nitrite (SN) and sodium hexametaphosphate (SHMP) inhibitor blend for inhibition of such corrosion process have been investigated at different temperatures, i.e., 303, 313, 323 K.

Weight loss experiment, under isothermal conditions, together with polarization method were carried out at 303, 313, and 323K using C.T., and make up with SN:SHMP (500:100) solutions. The results proved that the inhibition efficiency of the corrosion inhibitor used in this work is better than that obtained by the corrosion inhibitor used in C.T. of Al Doura Refinery and less effected by the change in temperature.

Keywords: Corrosion inhibitors, circulating cooling tower, Polarization, Corrosion.

Introduction

Water an excellent transporter of heat and quite inexpensive, it is also an excellent polar solvent which will dissolve about all known materials. Given this fact the chemistry of all cooling water treatment programs must be dealing with corrosion, which is basically an electrochemical oxidation process results in destruction of the metals from which most cooling systems are constructed.

Uncontrolled corrosion is often responsible for equipment failure and the plugging of cooling water passage from deposition of corrosion products [1].

More effects, often not linked to corrosion, are loss of production speed and decreased energy efficiency from deposition of corrosion products on heat transfer surfaces where the deposit acts as an insulator to decrease thermal conductivity [1]. Natural water is frequently used in cooling systems. If absolutely pure water was used in cooling system none of the problems would exist. Unfortunately waters containing dissolved and suspended solids, dissolved and suspended organic matters, and dissolved gasses [2] .Finally the open recalculating system, with longer holding times at higher temperatures in the presence of higher dissolved solids concentration produces more severe corrosion scaling and microbiological growth [2]. These problems can occur jointly, reducing the thermal efficiency of the circuit with significant economic repercussion [3]. The rate of corrosion can also be reduced by using corrosion inhibitors. These corrosion inhibitors are chemical compounds that reduce the corrosion rate of metals existing in actively corrosive environmental [4].

Most successful cooling water treatment programs utilize several chemical corrosion inhibitors blended into one product to take advantage of a synergetic effect where the net reduction in corrosion from using the mixture is greater than that obtained from individual components. Because of this substantial increase in effectiveness, almost all successful cooling water programs is as used several corrosion inhibitors blended together .

The exact corrosion inhibitor chemistry to be used must be determined by the water treatment program supplier following an evaluation of makeup water chemistry, system construction materials, and operating conditions [5]. Many corrosion inhibitors have been used in cooling water systems in order to reduce or eliminate these problems. Particularly; fatty amines associated with phosphonocarboxylic acid salts, hydroxyethane diphasphonic acid (HEDP) and hydroxyphosphonoacetic acid (HPA) were the standard corrosion inhibitors [6,7].

Other authors used other corrosion inhibitors such as triazole and its derivatives associated with cetyl trimethyl ammonium bromide (CTAB) or with isothiazolone in order to kill micro-organisms [8] [9].

Most of inorganic inhibitors are toxic e.g., chromate, mercuride nitrite, arsenate etc. [10]. As an environmentally acceptable and effective corrosion inhibitor for zinc, galvanized steel, and other metals, molybdate ion has been widely investigated in a variety of corrosive media [11,12]. Many other researches [13] have concentrate on the synergetic effect between molybdate ions and other organic and inorganic compounds for corrosion reduction in cooling water system.

Different operational parameters such as cooling water pH, corrosion inhibitor concentration of the other ions present in water may have a considerable influence on molybdate inhibition efficiency in cooling water [14].

Open recalculating cooling water system (ORCS) is one of the most vital units of a petroleum refinery. The most common problems affecting the performance of this system are corrosion, scale formation and befouling, which directly have an impact on the productivity. A substantial quantity of utility water of petroleum refinery is used in cooling system [15].

The treatment philosophy of open recirculating cooling system (ORCS) of petroleum refinery takes an important role on its productivity and profitability. It is necessary to control scaling, fouling, under deposit, and microbiological problem simultaneously. Although a large number of investigations have been performed with various chemicals individually, their synergic study in a blend is an interesting problem to inhibit scaling, fouling, under deposit and microbiological problem at the same time.

This work aimed to study the behavior of carbon steel in recirculating cooling water of Al- Doura Refinery and performance of multi component corrosion inhibitor (Sodium Nitrite (SN) and Sodium Hexameta Phosphate(SHMP)) on the corrosion rate of carbon steel at different temperature (303, 313, and 323K).

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Experimental Work

The experiments involved two main measurements, immersion tests and polarization measurements. They were carried out to estimate the corrosion rate of carbon steel in makeup, recalculating cooling water and make up with inhibitor solutions. The solutions used in the experiments were obtained from Al Doura Refinery while the corrosion inhibitors (Sodium Nitrate (SH) BHD 99.5%, and Hexameta Phosphate (SHMP) BHD 99%) were added in the laboratory; the specifications of solutions are shown in Table (1). All experiments were performed at three different temperatures i.e., 303, 313, and 323K. .

Table (1) Analysis of C.T. Makeup with SN/SHMP Solution [17]

	C.T.	MAKEUP	MAKEUP WITH SN/SHMP
M-alkalinity	240ppm	144ppm	**144ppm**
pH	8.45	7.5	**7.18**
Cl^-	380ppm	188ppm	**188ppm**
Conductivity	1830µ/cm	1060µ/cm	**1060µ/cm**
T.D.S.	1190ppm	700ppm	**700ppm**
Turbidity	9.9NTU	0.93NTU	**0.93NTU**
Cl_2	0.1	0.7	**0.7**
(CaH)	**420ppm**	**220ppm**	**220pmm**

Surface Preparation

Test space mines were annealed at 873K for one hour and then cooled to room temperature. These were abraded on successive grade of silicon carbide paper ranging from 120 through to 1000 grit under running tap water to avoid heating due to friction. It was then washed with distilled water, rinsed with acetone and dried with clean tissue paper. It was the kept in desiccators over silica gel [18].

Immersion Test

Test coupons 50mm x 25mm x 1.5mm were prepared from low carbon steel sheet grade ASTM 1018. Glass containers (500ml volume each) were used and placed inside a constant temperature water bath (Memmre) supplied with a thermostat to keep the temperature constant within 313.1K.

The specimens were weighed using electronic balance (Mettler AE200) and then suspended inside the solution by a glass hook. After 48 hr the specimens were raised from the solutions, immersed for a moment in 20% HCL solutions [17], washed and brushed under running tap water (using smooth brush) in order to remove all the corrosion product from the metal surface. The specimens were washed again with tap water followed with distilled water, rinsed with acetone, dried with clean tissue paper and kept in desiccators for 1hr before being weighed again. The specimens were then immersed in a fresh solution for another 48 hr and the same procedures were repeated. A total of five immersions were made for each specimen. Weight loss (Δ w) with time was drawn and the slope of straight line was calculated ($\Delta w/t$).The chemical composition of the specimens wt% is shown in Table (2).

Table (2) Composition of Carbon Steel Coupon (wt %) [19]

C	MN	SI	NI	S	CR	FE
0.13	0.371	0.044	0.031	0.0171	0.0033	balance

Electrochemical Polarization

The specimens were cut and turned down to cylindrical shape (30mm diameter x 20mm height) from 100mm diameter rod of a carbon steel having total purity of Fe= 99.4%. The chemical composite of the specimens wt% are shown in Table (3). Each experiment involved electrochemical polarization of carbon steel electrode from -0.9V to + 0.2V by mean of 20×10^{-3}V steps at 60s intervals. The polarization cell was placed inside a constant temperature water bath supplied with a thermostate. The luggin probe was kept at a distance of 1-2mm from the surface of the electrode.

The working counter (graphite) and reference (SCE) electrodes were connected to a potentiostate (wenking LT.87). The potential was kept at -0.9V for 5 min then a complete electrochemical polarization was carried out from -0.9V to +0.2V. Potentials and currents were checked and read off a digital multi meter (B 1031siemens).

Table (3) Composition of Carbon Steel Cylinder (wt%) [19]

C	Mn	Si	Ni	S	Cr	Fe
0.1611	0.367	0.043	0.0225	0.0162	0.0033	balance

Result and Discussion

Immersion Test

The most desirable way of expressing corrosion rates in mils per year (mpy) and is calculating by using the following formula [17]:

$$\text{mpy} = \frac{\Delta wk}{t\,\rho A} \qquad \text{..............................} (1)$$

Where:

Δw : weight loss in (g).

t: time of exposure in hours.

A: area in cm^2.

ρ: density in gm/cm^3.

k: constant = $3.45x10^6$

The weight loss values were plotted versus time for studied temperatures in Figs. (1-3). These figures show clearly that weight loss increases with time for the three solutions in all temperatures. Moreover they show that the weight loss values of makeup solution are the largest than those of the makeup with corrosion inhibitor solution.

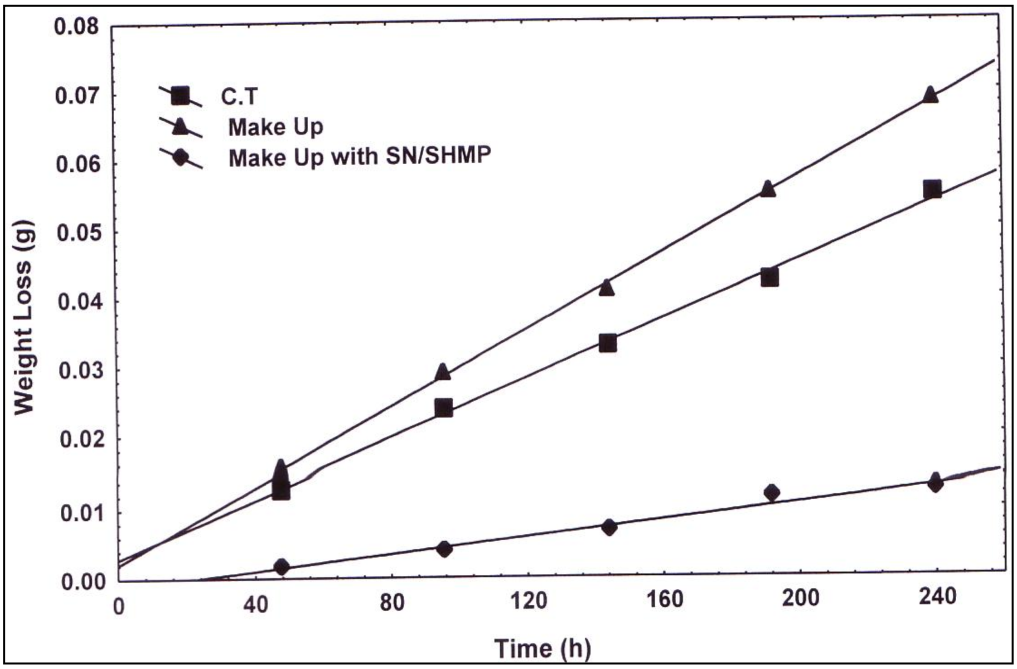

Fig. (1) Weight Loss of Carbon Steel Coupon vs. Time at 303K

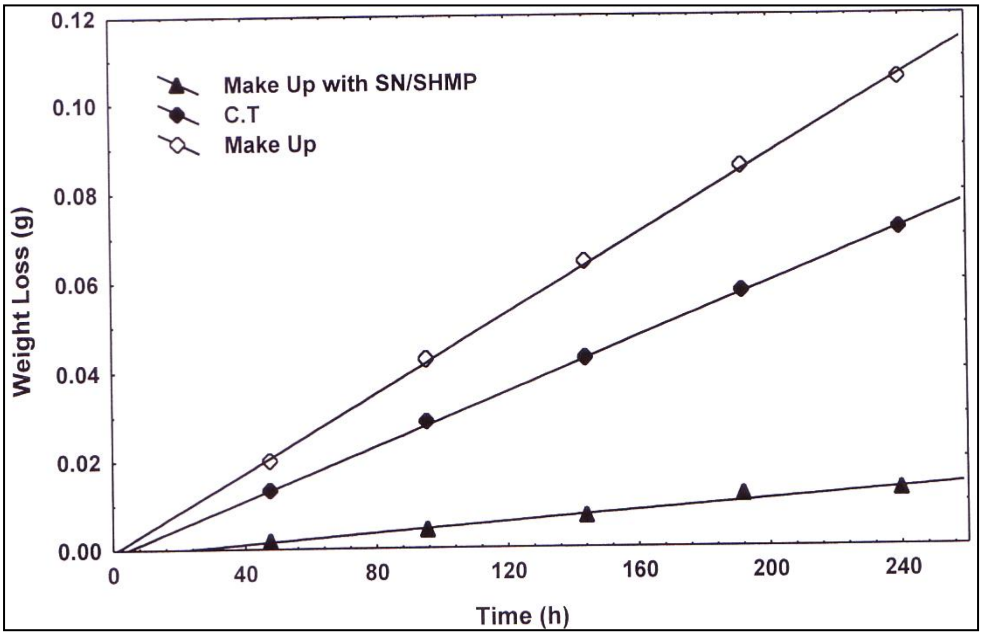

Fig. (2) Weight Loss of Carbon Steel Coupon vs. Time at 313K

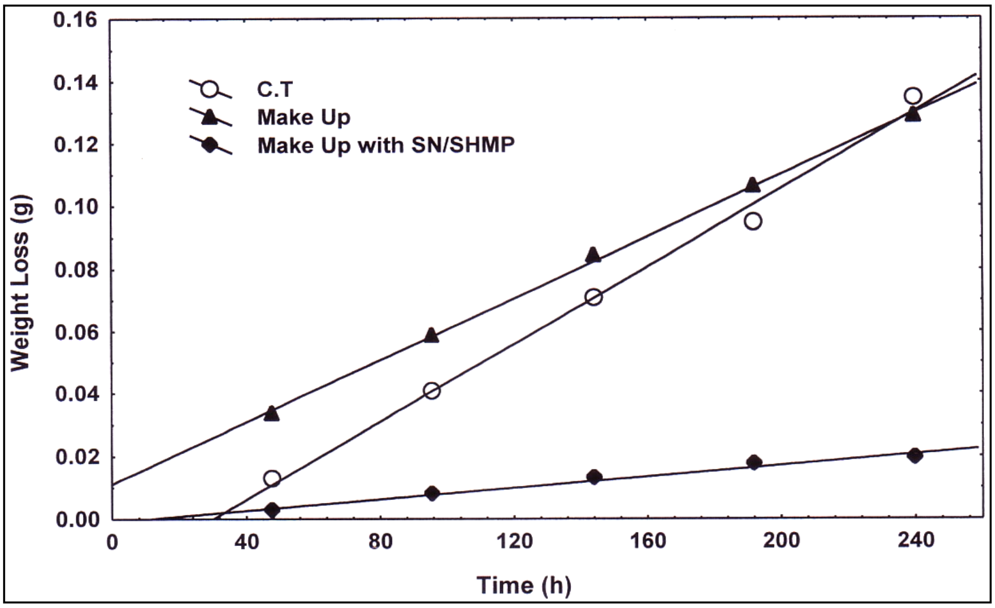

Fig. (3) Weight Loss of Carbon Steel Coupon vs. Time at 323K

Figs. (4-6) show the weight loss for C.T. makeup and makeup with corrosion inhibitor solution respectively at various temperatures. Fig. (4-5) show that the weight loss increase linearly with time at 303, 313, and 323 K. This indicate that the weight loss increase systematically for all temperature in C.T. and makeup solutions.

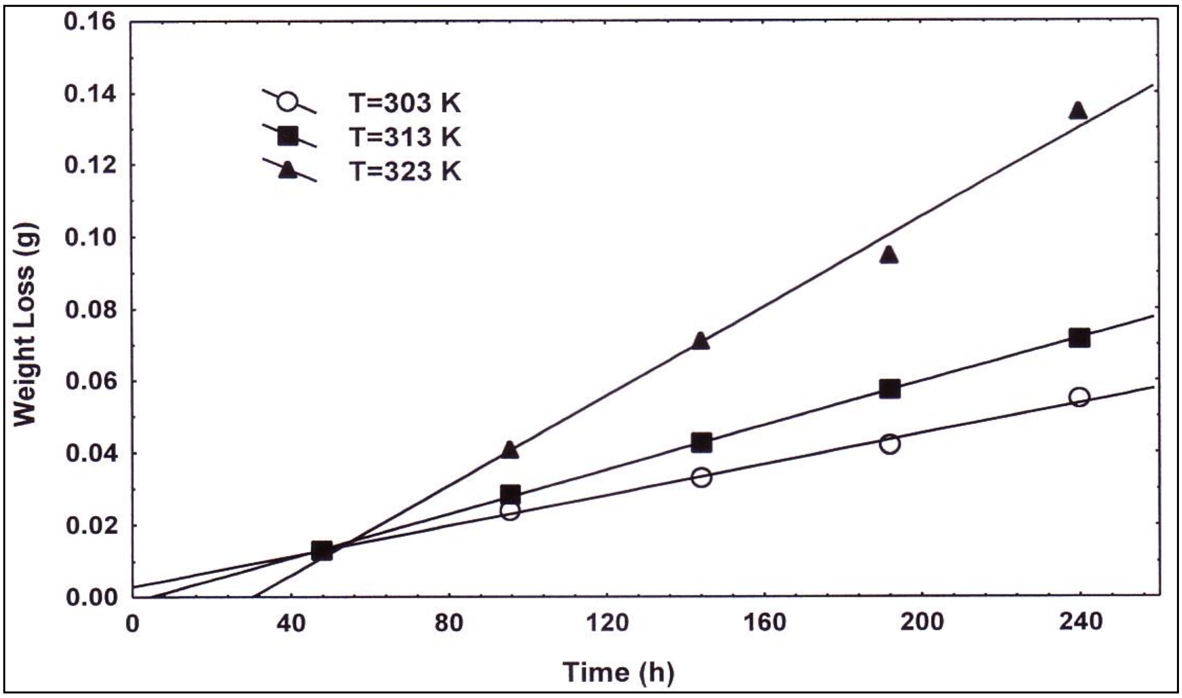

Fig. (4) Weight Loss vs. Time of C.T. Solution

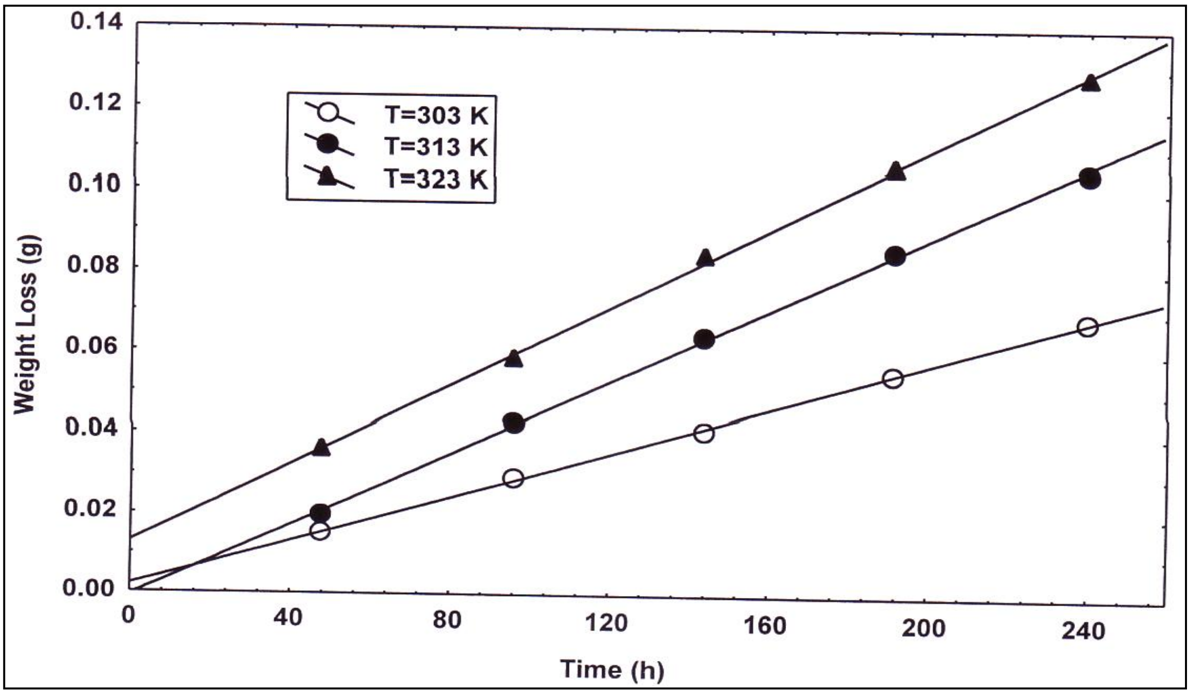

Fig. (5) Weight Loss vs. Time of Makeup Solution

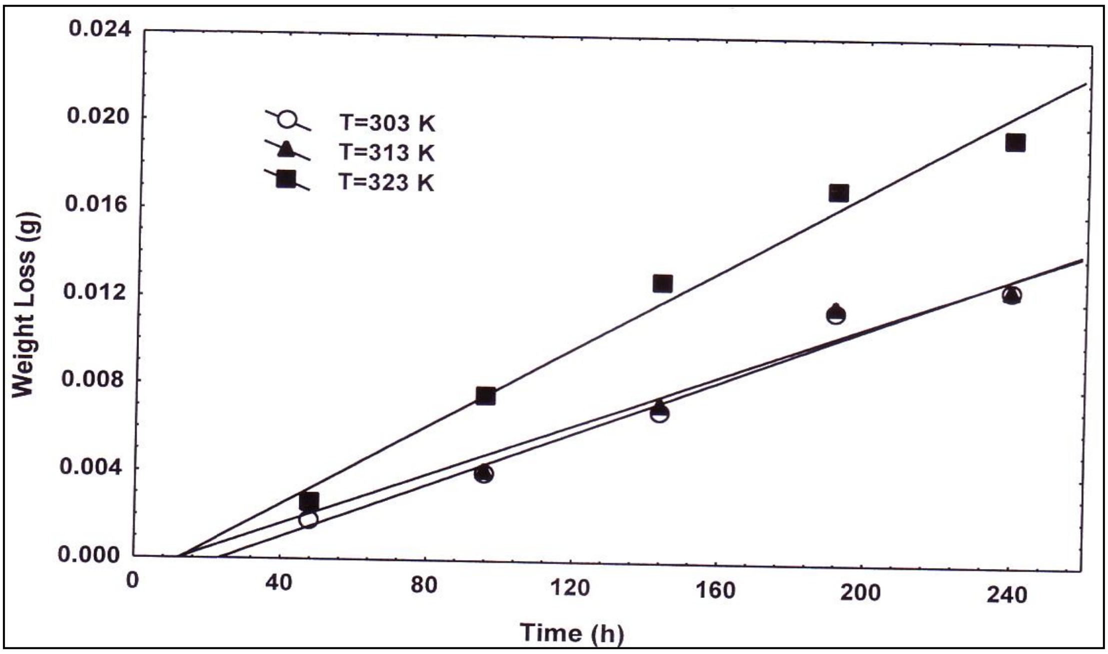

Fig. (6) Weight Loss vs. Time of Makeup with SN/SHMP Solution.

Fig. (6) shows that the weight loss for makeup with inhibitor solution at 303 and 313K are almost equal, while it increase, largely at 323K. From fig. (7) and Table (4), it can be concluded that the corrosion rate increase, with increasing temperature for C.T. and makeup solutions and this was expected since the corrosion rate increases with increasing the temperature for many chemical reactions. Moreover the inhibition effect at 323K has no significant, this can be attributed to that the corrosion inhibitor used in Al Doura Refinery was designed to work below 318K as this is the higher temperature reached by recirculation cooling water.

Table (4) and fig. (7) are given information that the corrosion inhibitor used in this research was very effective because the corrosion rate was remained constant at 303 and 313K and it was much less than that obtained for the other two solutions. At 323K the corrosion rate increase slightly but still less than that obtained for other two solutions.

Table (4) Corrosion Rate of the Three Solutions at Different Temperatures

TK	MPY		
	C.T.	Makeup	Makeup with SN/SHMP
303	4.09	4.85	1.22
313	7.04	7.71	1.22
323	10.51	10.23	1.60

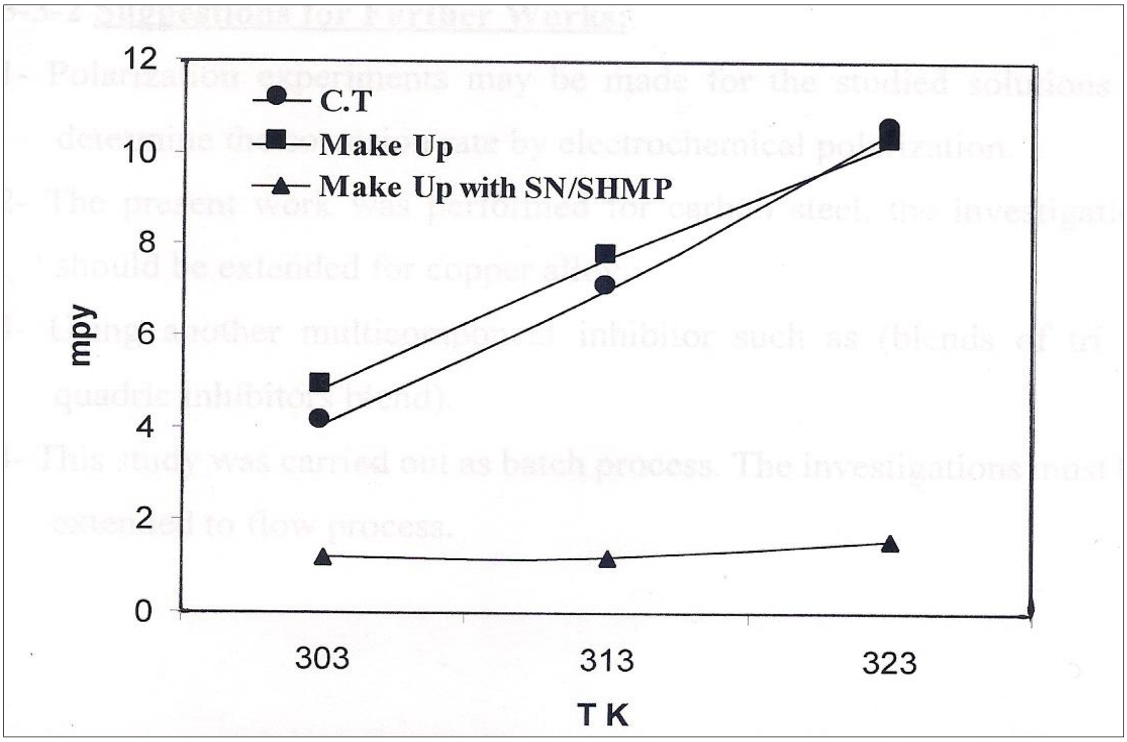

Fig. (7) Corrosion Rate vs. Temperature K

Electrostatic Polarization

The polarization curves illustrated in fig. (8-10) show the limiting current density of cathodic reaction, i.e. the oxygen reduction reaction. Table (5) shows the value of limiting current density for C.T., makeup and makeup with corrosion inhibitor solutions for various temperatures. In general, the limiting current densities, i.e., corrosion current density, in inhibited solutions are lower than those under identical temperatures in an uninhibited solution (makeup). Moreover the values obtained in makeup with corrosion inhibitor are lower than that for C.T., this gave an indicator that the corrosion inhibitors used in this research are more efficient than these.

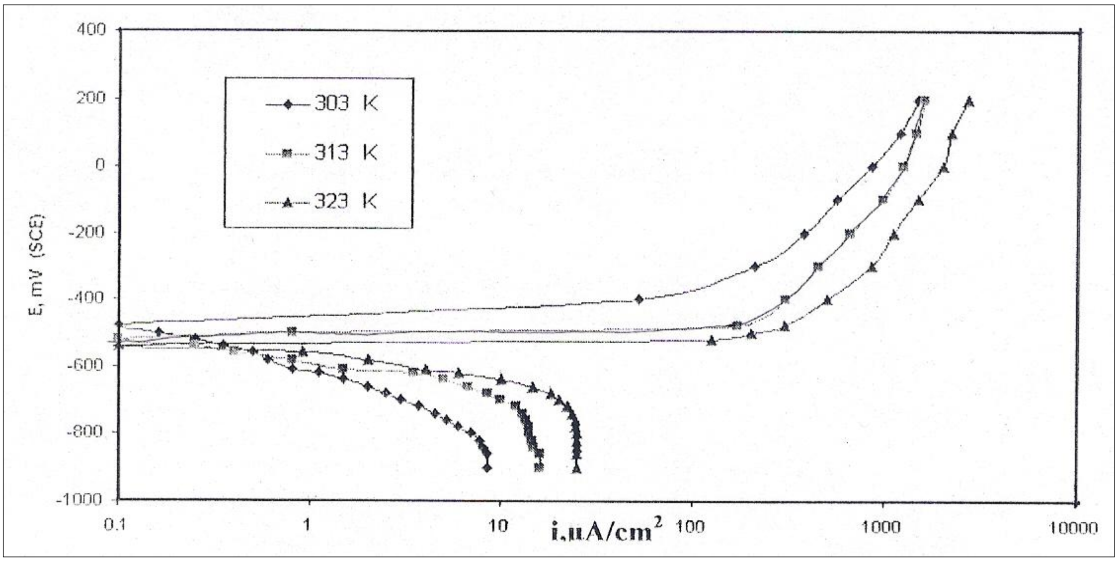

Fig. (8) Polarization Curves of Carbon Steel in Makeup Solutions.

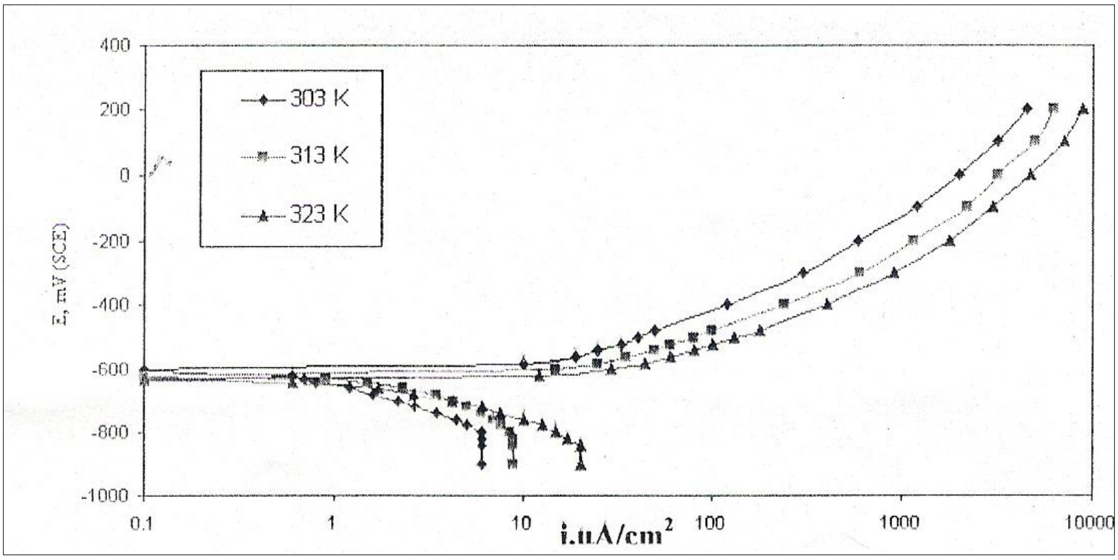

Fig (9) Polarization Curves of Carbon Steel in C.T. Solutions.

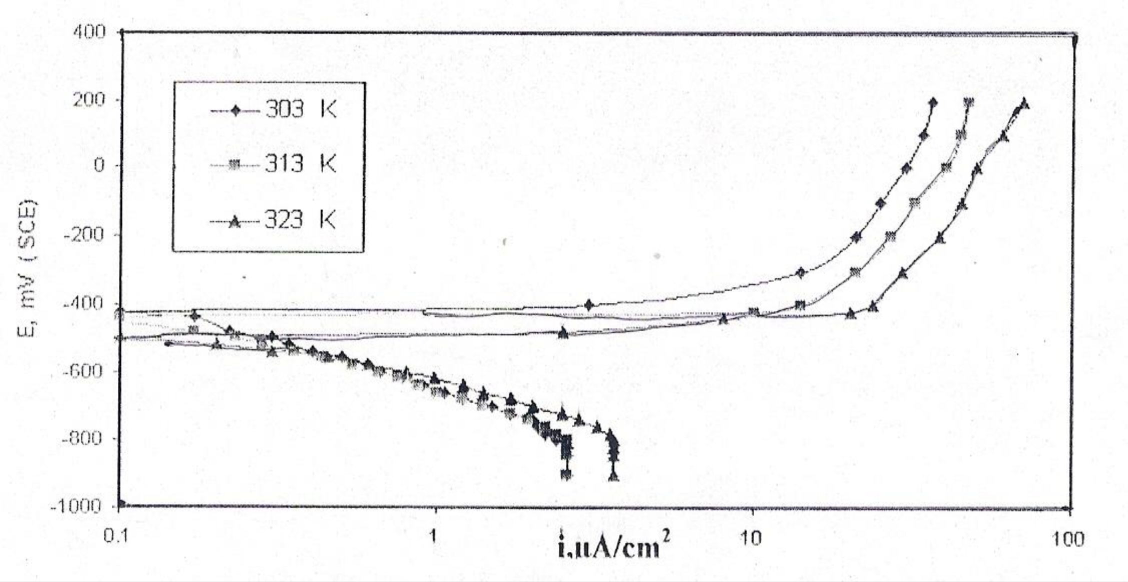

Fig. (10) Polarization Curves of Carbon Steel in Inhibited Solutions

Table (5) the Limiting Current Density (Corrosion Current Density) μA/cm^2

TEMP.K	C.T.	MAKEUP	MAKEUP + INHIBITOR
303	6	8.6	2.6
313	9	16	2.6
323	**20**	**25**	**3.6**

The correction potential values for the three solutions at various temperatures listed in Table (6) indicated that the corrosion potential was shifted to more negative values with increasing temperature. This can be attributed to the effect of high temperature in simulating the anodic kinetics than the cathodic kinetics as schematically shown in fig. (11).

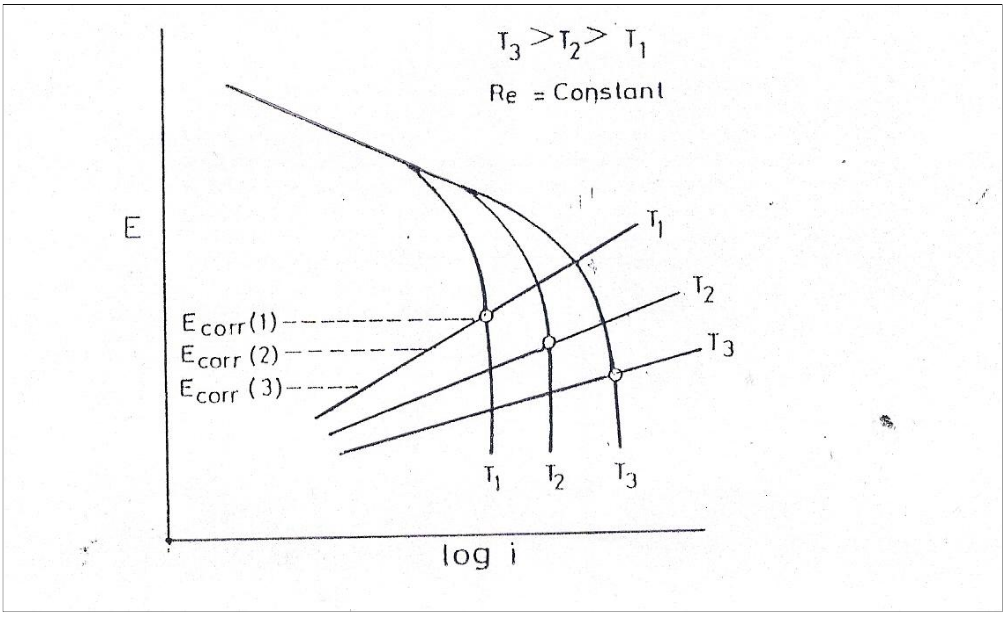

Fig. (11) Schematic Representation of the Effect of Temperature on the Corrosion Potential in the Presence of Oxygen at a Constant Flow Rate [20].

Table (6) the Corrosion Potential, V_{vs} (SCE)

TEMP. K	C.T.	MAKEUP	MAKEUP + INHIBITOR
303	-600	-480	-420
313	-620	-520	-440
323	**-630**	**-540**	**-500**

The corrosion potential values of C.T. are more negative than that of makeup solution, this indicates that the corrosion inhibitor used in Al Doura Refinery acts as cathodic inhibitor. While the corrosion inhibitor used in this work acts as mixed corrosion inhibitors, it shifts the corrosion potential to slightly more noble direction. The inhibitive effect in this region is due to both sodium nitrite (as anodic inhibitor) [21], and sodium hexametaphosphate (as cathodic inhibitor) [21] in the corrosion inhibitor blend, i.e., a mixed inhibition action.

The inhibition efficiencies C.T. and makeup with SN/SHMP at different temperatures are calculated from the equation:

$$\textbf{eff}\ \% = \frac{\text{Corr.Rate (uninhibit)} - \text{Corr.Rate (inhibit)}}{\text{Corr.Rrate (uninhibit)}} \qquad \ldots\ldots\ldots\ldots.(2)$$

The results of inhibition efficiency for the two solutions at different temperatures are shown in Table (7) for immersion test and Table (8) for polarization test.

Table (7) Inhibition Efficiency for the Two Solutions at Difference Temperatures (Immersion Test)

TK	EFFICIENCY%	
	C.T.	Makeup + Inhibitor
303	16	75
313	9	84
323	-3	84

Table (8) Inhibition Efficiency for the Two Solutions at Difference Temperatures (Polarization Test)

TK	Efficiency%	
	C.T.	Makeup + Inhibitor
303	30	70
313	43	83
323	20	85.3

Conclusion

The present work has been mainly aimed to investigate the inhibition of carbon steel corrosion in recycling cooling water of Al Doura Refinery using a formulated corrosion inhibitor blend ,i.e., SN/SHMP = 500: 100 under isothermal conditions. The results indicate that the great effect of increasing temperatures on the corrosion behavior of carbon steel in inhibited and uninhibited solution.

The inhibition efficiency of the mixed corrosion inhibitors used in this research i.e., SN/SHMP, was much higher than that obtained by the corrosion inhibitor used by Al Doura Refinery which is organic phosphate (imported materials from Nalco Company).The efficiency of the corrosion inhibitor is unaffected by the change in temperature, while the efficiency of the corrosion inhibitor used in the Refinery became less at 323K.

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