THE INFLUENCE OF TEMPERATURE AND FLOW VELOCITY ON THE CORROSION INHIBITION OF LOW CARBON TUBES IN RECIRCULATING WATER SYSTEM BY A DICOMPONENT INHIBITOR BLEND

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ABSTRACT

The corrosion of low carbon steel tubes, as cylindrical specimens rotated at velocities up to 1250 rpm (124 cm/sec) in water actually taken from a circulating system and containing different concentrations of a dicomponent inhibitor blend (NaNO2 / Na2B4O7) has been studied at temperatures up to 50°c and a test period of 12 hrs. Corrosion was assessed from the change in weight of the cylindrical specimens. Polynomial regression analysis of the corrosion rate in (gm / m2. day) obtained from weight loss of the specimens as function of temperature (x1), flow velocity (x2) and inhibitor blend concentrations (x3), yield the following equation:

$$Y=2.84+1.29X1-0.411X2-1.06X3-0.371X1X2+0.12X1X3-0.129X2X3+0.232X12+0.505X22+0.692X32$$

Where, x1,x2, and x3 are in their coded values. The correlation coefficient of above equation was 0.97, average error =8.32% and the F-value was found to be =11.9. The objective function (Y) in above equation, subjected to the range bounded by the low and high levels of the coded variables (i.e., $-1.732 \leq Xi \leq +1.732$*) for i= 1,2 and 3 as an optimization problem was solved. The optimization method was based on solving three linear equations with the above bounded limits. The optimum conditions were found to be flow velocity = 513rpm(0.5m/s), inhibitor blend concentration = 62.5ppm NaNO2 / 4166ppm Na2B4O7, and the lowest temperature available from cooling tower.*

INTRODUCTION

The presence of water is essential to low temperature corrosion process. However, pure water containing no dissolved substances is only very mildly corrosive to iron. Since iron is anodic to hydrogen in pure water, the iron corrodes to produce H2 gas and Fe(OH) 2, while raises the pH of the water. The attack proceeds until the solubility of Fe(OH)2 is exceeded and the Fe(OH)2 deposits on the metal surface in the form of a film, smothering the corrosion reaction. Water containing impurities or dissolved substances can be corrosive or non-corrosive, depending on the nature of the dissolved substances, i.e., some inorganic chemicals such as chromate and phosphates are dissolved in water to inhibit or reduce corrosion, while other substances such as H2S, CO2 and O2 can increase the corrosivity of the water. In addition to the impurities, which are commonly found in water, temperature and velocity also influence the corrosivity of water. Seldom is a corrosion problem encountered where only one of these contributing factors is present. Generally, the problem is complex because of these various influences and the manner in which they may interact with each other. The removal of low-grade energy from a process is an area of technology, which has steadily developed in the last two centuries. It is concerned with removing heat where there is only a small temperature gradient to the surrounding and distributing the heat into those surroundings, heat transfer plays a major part in this. The process can be classified by the number of intermediate stages involved as follows [1].

a. Single stage process such as air-cooled heat exchangers.
b. Two stage processes such as once through cooling water systems, open recirculating cooling water systems, and closed loop cooling water using an air cooler for the final stage.

In open recirculating cooling water systems there is usually the possibility of a greater range of sources of fouling materials than in other types of cooling system. Possible sources are: raw water, air, corrosion debris from the system and process leaks. The quantity of some of these fouling materials can be minimized by chemical treatment and inhibitors addition. It would be difficult to give a precise definition of an inhibitor, but its effect in most cases is to interpose, a barrier between a metal and an aggressive environment. Desirable characteristics are that the barrier formed should be thin, so that the conductivity is not appreciably affected; that it be reasonably stable to mechanical and thermal stress; and that it can be quickly repaired by the reserve or excess which is in solution [2]. The corrosion behavior of low carbon steel tubes of a heat exchanger in water taken actually from the cooling tower as a main source, under the effect of temperature, flow velocity, and inhibitor blend concentration has been investigated. The optimum operating conditions as a result of using weight loss and central composite rotatable design techniques were found.

EXPERIMENTAL WORK

The inhibitive action of a dicomponent inhibitor blend ($NaNo_2$ / $Na_2B_4O_7$) as an adsorption type inhibitor on the corrosion behavior of carbon steel tubes as cylindrical specimens in water actually taken from a recirculating cooling water system, and under the effect of temperature (30-50)°c, besides flow velocity (250–1250) rpm was investigated using weight loss measurements.

Materials

Electrodes

Cylindrical specimens of low carbon steel of the following chemical composition (%wt) were used throughout the present investigation:

C	Mn	S	Pb	Fe
0.015	0.45	0.05	0.04	balance

Specimens for weight loss tests were 1.9 cm outside diameter, 0.5cm length and 0.1cm thickness.

Solutions

Actual water taken from recirculating cooling water system was used throughout the present experiments as a corrosive solution. The chemical analysis of water used was as follows:

Table (1) chemical analysis of actual Cooling water used

Parameter	Concentration in ppm*
Ca+	187.2
Mg+2	94.08
HCO3-	268.4
CL-	333
pH	8.3
Total Po4-2	7.32
Ortho Po4-2	4.4

* Except of pH

Chemicals

Sodium nitrite ($NaNO_2$) and Borax ($Na_2B_4O_7$) were used in this investigation as a dicomponent inhibitor blend. The specifications of $NaNO_2$ & $Na_2B_4O_7$ used were as follows:

$NaNo_2$ = 99.99%wt $Na_2B_4O_7$ = 99.99%wt
CL$^-$ = 0.04%wt   CL$^-$ = 0.04%wt
So_4^{-2} = 0.06%wt So_4^{-2} = 0.06%wt
Lead = 0.002%wt

Procedure

Cylindrical specimens of (about 1.9cm outside diameter, 0.5cm long and 0.1cm thickness) were used in this investigation. The specimens were first degreased with annular benzene and acetone, then annealed in a vacuum at 600°c for 1 hr, and furnace cooled to room temperature, and kept in a desiccator over silica gel bed until use. Samples were abraded in sequence, under running tap water using emery paper of grade nos.: 220,320,400 and 600 then washed with running tap water followed by distilled water, dried with clean tissue, immersed in acetone and benzene, dried again, kept in a desiccator over silica gel bed until time for using them. The dimensions of each sample were measured with a venire to 2nd decimal of millimeter and accurately weighed to the 4th decimal of gram. For weight loss measurements, the metal samples were completely immersed in 1000cm3 solution of the corrodent contained in one liter round bottom flask fitted with thermometer and rotating vibrationless shaft carrying three specimens in each run. After the test they were cleaned, dried and weighed. Fig. (1) shows a specially designed shaft employed in weight loss measurements.

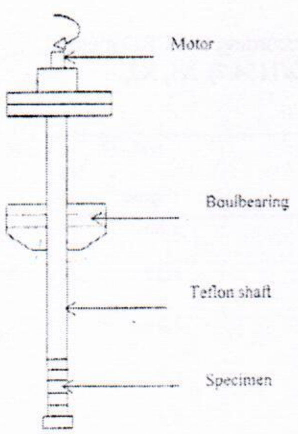

Fig. (1) Shaft specification for weight loss measurement

RESULTS AND DISCUSSION

Experimenting in stationary solutions at different temperatures was the first step in this investigation. Fig. (2) shows the results obtained as average corrosion rates (ACR) versus temperature. When the results were plotted in Arrhenius form, alinear relationship was obtained giving an activation energy equals (1.75) kcal/mole. Such low value of activation energy is indicative and typical of reaction systems controlled by diffusion or mass transfer [3]. Butler [4], in his study of the influence of movement and temperature on the corrosion of mild steel in H2O, within the same range of temperatures as in the present study gave activation energy of (2.35) kcal/mole, which is in good agreement with the present study.

The second phase of the experimentation was performed in order to evaluate the simultaneous effect of temperature and flow velocity on the corrosion process. Fig. (3) shows the relationship between the corrosion rate and flow velocity at different temperatures, after (12)h,s immersion. At (30°c) the amount of corrosion increases steadily with increasing speed of flow up to(1040)rpm and then remains sensibly constant on increasing the speed to(1250)rpm. At (40°c) the initial part of the corrosion / flow speed curve is similar, showing an increase in corrosion with increasing speed up to about (750) rpm, then a pronounced decrease in corrosion rate was observed as the speed flow was increased. The corrosion at higher temperature (50°c) is appreciably higher than that at lower temperature, but with increasing in flow speed at this temperature a non-sensible corrosion was observed indicating that the temperature has little significant influence on the relation between corrosion rate and the flow speed. It can be concluded that the variation of corrosion rates at studied temperature leads to attribute that to the type of corrosion product on the tubes with speed of flow.

Mahato[5] presented fundamental hydrodynamic concepts as applied to corrosion in pipes by many investigators. They indicated that the flow speed of water, degree of turbulence, geometry of pipes and other physical properties have a direct influence on the movement of dissolved oxygen and ions through the fluid, these factors in turn exert effects on the formation of corrosion products, on depolarization and thus on the corrosion reaction itself.

Butler and Ison [6] investigated corrosion of mild steel pipe specimens in flowing water. They found that the corrosivity of water is largely governed by its – scale forming properties and the speed of flow.

In the third phase of experimentation, the experiments were designed according to central composite rotatable design (CCRD) shown in table(2), for three variables respectively [7-9], the temperature, speed of flow, and a dicomponent inhibitor blend concentration ratio of (NaNO2/Na2B4O7). Tests lasted for (12) h`s immersion and the corrosion rates reported were the averages obtained from three specimens with (±10٪max) variation.

A least squares analysis yielded the following equation (correlation coefficient = 0.97):

Y=2.84+1.29X1-0.411X2-1.06X3-0.371X1X2+0.12X1X3-0.129X2X3+0.232X12+0.505X22+0.692X32

Above equation is useful and adequately describe the corrosion behavior of steel tubes within the specified conditions of the variables. The variation of corrosion rate with any of the three independent variables can be easily realized by keeping two at a time constant and for conditions that were not tried experimentally but within the specified limits of the variables as given in figures (4-6). In these figures corrosion rate V's temperature was plotted for given inhibitor blend concentration (i.e., $NaNO_2/Na_2B_4O_7$ = 15/1000, 45/3000, 75/5000 ppm) at different r.p.m values (i.e., 250,461,750,1040, &1250). It is clear that:

Table (2) Inhibited corrosion rates of carbon steel tubes in water planed according to CCRD method, X1=(T-40)/5.77 , X2=(V -750)/288.7 , X3*=(C- 45/3000)/(17.32/1154.7). X1, X2, and X3 are in their coded values.

Run	Coded Variables			Real Variables			(ACR)
No.	X1	X2	X3	X1(T)	X2(V)	X3(C)	gmd
1	+1	−1	+1	46	1039	62.32/4154.7	3.86
2	-1	+1	+1	34	1039	62.32/4154.7	1.37
3	+1	-1	+1	46	461	62.32/4154.7	5.66
4	-1	-1	+1	34	461	62.32/4154.7	1.6
5	+1	+1	-1	46	1039	27.68/1845.3	5.9
6	-1	+1	-1	34	1039	27.68/1845.3	3.8
7	+1	-1	-1	46	461	27.68/1845.3	7.13
8	-1	-1	-1	34	461	27.68/1845.3	3.6
9	$+\sqrt{3}$	0.0	0.0	50	750	45/3000	5.45
10	$-\sqrt{3}$	0.0	0.0	30	750	45/3000	2.04
11	0.0	$+\sqrt{3}$	0.0	40	1250	45/3000	3.78
12	0.0	$-\sqrt{3}$	0.0	40	250	45/3000	5.35
13	0.0	0.0	$+\sqrt{3}$	40	750	75/5000	3.13
14	0.0	0.0	$-\sqrt{3}$	40	750	15/1000	7.12
15	0.0	0.0	0.0	40	750	45/3000	2.98
16	0.0	0.0	0.0	40	750	45/3000	2.84
17	0.0	0.0	0.0	40	750	45/3000	2.70

* Concentration of NaNo2/Na2B4O7 varies from (15/1000)ppm to (75/5000)ppm through out the experiments.

1. Generally at each flow velocity studied, for all inhibitor blend concentration ratios, the corrosion rate increases as the temperature was increased, indicating a pronounced effect of temperature on corrosion rate compared to the other two variables in this case.
2. Generally and at all inhibitor blend concentration ratios, when the temperature is increased the corrosion rate decreases with increasing flow velocity up to 750rpm then began to increase again up to 1250rpm through 1040rpm, indicating the benefit of adding the inhibitor blend ratio to a certain flow velocity within the range of temperature studied.

Figures (7-9) show the relationship between the corrosion rate and inhibitor blend concentration ratios at certain temperature for different flow velocities. These figures show that: The corrosion rate at constant flow velocity for each of the temperature levels mentioned (30,40,&50) decreases with increasing the inhibitor blend ratio until it reaches its minimum value then begins to increase again. Minimum corrosion rate decreases with increasing flow velocity up to 750rpm, then begins to increase with increasing flow velocity except at 50°c it continues decreasing to 1040rpm then increased.

Figures (10-12) represent the relationship between the flow velocity and corrosion rate when the temperature increased from 30 to50°c at constant levels inhibitor blend concentrations of (15/1000,45/3000,75/5000) ppm of $NaNO_2$/ $Na_2B_4O_7$ respectively. These figures show that increasing flow velocity from 250 to 1250rpm at constant temperatures (30,34,40,46,&50) and at different inhibitor blend concentrations of (15/1000, 45/3000, &75/5000 ppm) has a pronounced effect on corrosion rate. So increasing flow velocity at all temperatures and for all inhibitor blend concentration leads to decrease the corrosion rate initially until it reaches a minimum value then it begins to increase again. The results indicate that the corrosion process is not under activation control (i.e., the corrosion process is said to be under activation control if the flow velocity has negligible effect on corrosion rate) this finding or conclusion is in fair agreement with activation energy determined for the corrosion process 1.75Kcal/mole.

The results also indicate that the metal surface area covered by the inhibitor blend added although decreases with increasing the temperatures but generally the inhibitor was enough to reduce the H2 evolution in such away that the following reaction controls the corrosion process to a certain extent:

$$O_2+2H_2O+4e \Rightarrow 4OH^-$$

The relationship given in modeled equation, and the value of this functional form in representing the corrosion system serves as the basis for determining the optimum combination of variable conditions.

Starting with mentioned equation as the objective function and its first derivative for the dependent variable (i.e., corrosion rate) was taken with respect to temperature, flow speed and inhibitor concentration then equating the results to zero at stationary points and solving the three equations to find the optimum values. It was found that: X1 (temperature)= -3.69,X3 (inhibitor conc.)= 1.01, X2 (flow speed)= -0.822 in their coded values. Using the relationships between coded and real values, optimum point was found to be: Temperature = 19°c, Flow velocity = 513rpm,Inhibitor conc. Ratio = 62.5ppm $NaNo_2$/4166 ppm $Na_2B_4O_7$.

Finally its reasonable to conclude that: (1) the corrosion of carbon steel tubes in aerated cooling water will generally be under cathodic control and that the main cathodic depolarizer will be dissolved oxygen. Hence the rate of attack will be controlled by the rate of transport of dissolved oxygen from the bulk of the solution to the corroding surface & its relationship with the temperature and flow velocity. (2) the steps leading to inhibition of corrosion were: (i) the adsorption of inhibitor blend ions at anodic areas. (ii) the reduction of this adsorbed nitrite and borate by hydrogen at adjacent cathodic areas to give a protective oxide layer & reduction products of nitrite & borate.

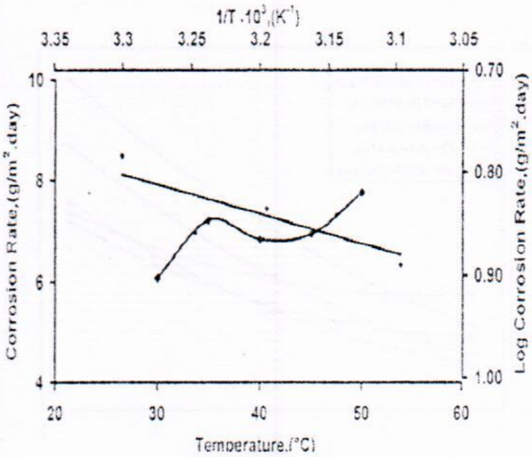

Fig. 2 Corrosion rate by weigh loss of carbon steel tubes in recirculating cooling water as a function of temperature under static conditions

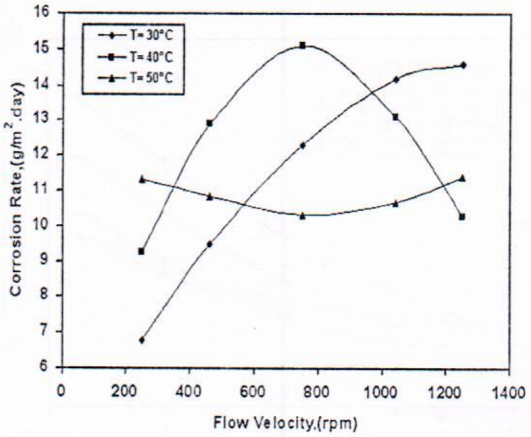

Fig. 3 Corrosion rate by weigh loss of carbon steel tubes in recirculating water as a function of flow velocity at different temperatures

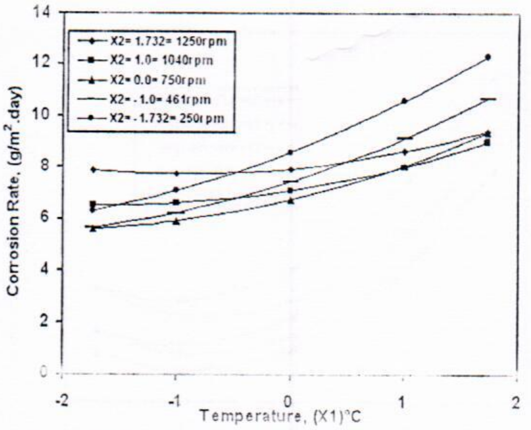

Fig. 4 The relation between the corrosion rate and the temperature at different flow velocities when inhibitor blend concentration leveled (-1.732)=15/1000

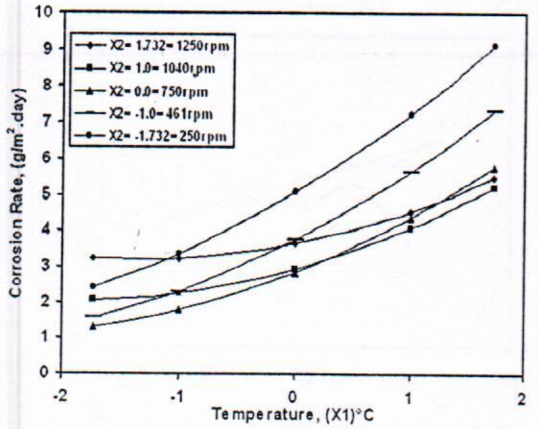

Fig. 5 The relation between the corrosion rate and the temperature at different flow velocities when inhibitor blend concentration leveled (0.0)=45/1000

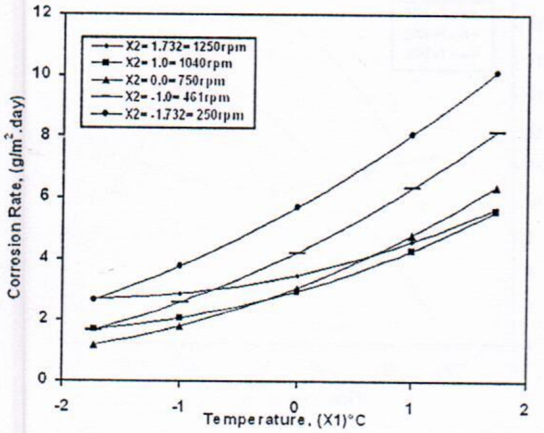

Fig. 6 The relation between the corrosion rate and the temperature at different flow velocities when inhibitor blend concentration leveled (+1.732)=75/1000

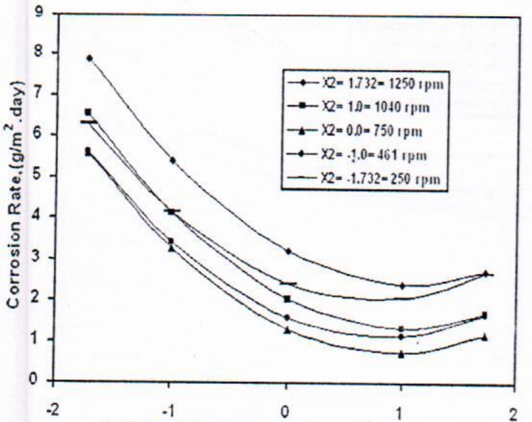

Fig. 7 The relation between the corrosion rate and the temperature at different flow velocities when the temperature leveled (-1.732)=30°C

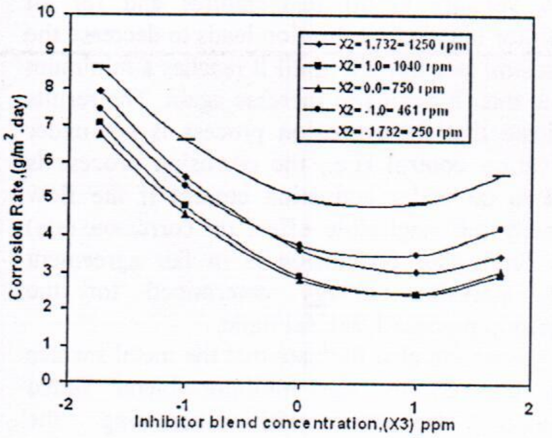

Fig. 8 The relation between the corrosion rate and the temperature at different flow velocities when the temperature leveled (0.0)=40°C

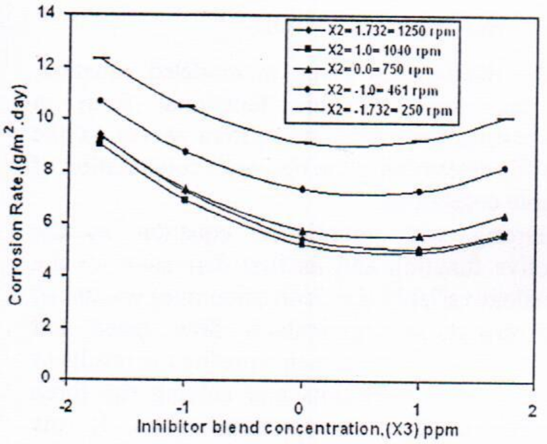

Fig. 9 The relation between the corrosion rate and the temperature at different flow velocities when the temperature leveled (+1.732)=50°C

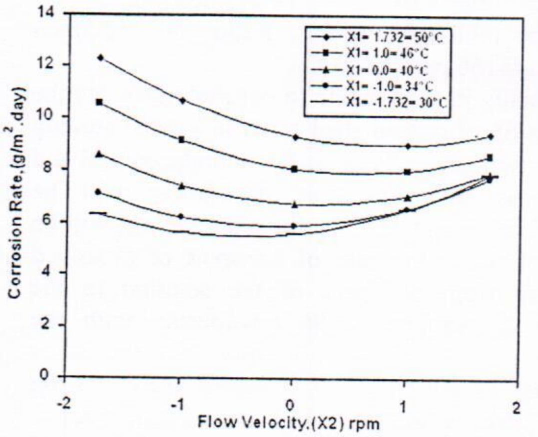

Fig. 10 The relation between the corrosion rate and the flow velocities at different temperatures when inhibitor blend concentration leveled (-1.732)=15/1000

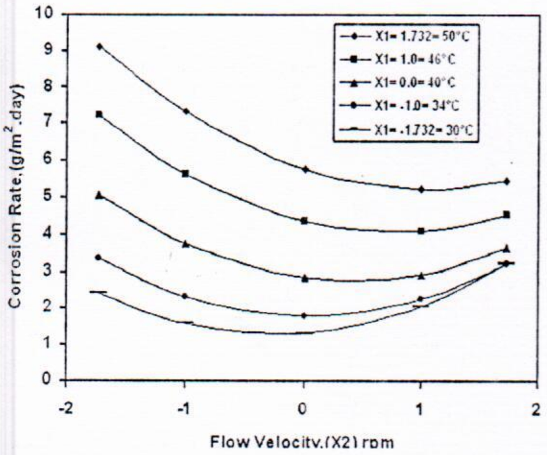

Fig. 11 The relation between the corrosion rate and the flow velocities at different temperatures when inhibitor blend concentration leveled (0.0)=45/1000

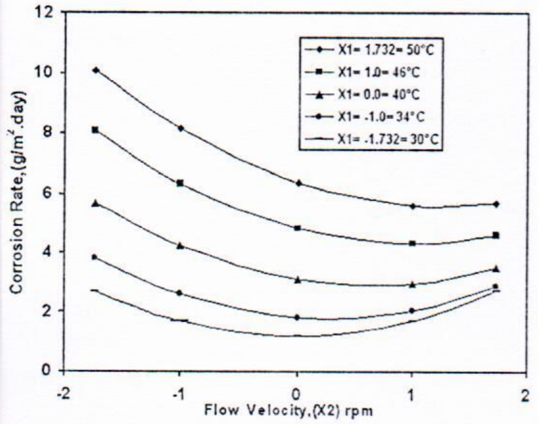

Fig. 12 The relation between the corrosion rate and the flow velocities at different temperatures when inhibitor blend concentration leveled (+1.732)=75/1000

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