THE EFFECT OF TEMPERATURE AND pH ON THE CORROSION RATE OF CARBON STEEL in 1 M NaCl [+]

تأثير درجة الحرارة والحامضية على معدل التاكل الفولاذ الكربوني في ١ مولاري من كلوريد الصوديوم

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ABSTRACT:

An investigation was carried out study the effect of temperature and pH on corrosion rate using carbon steel rotating cylinder electrode in deaerated 1M NaCl solution at pH 3, 6 & 8 and temperatures 25, 50 & 80 C° for one hour. It was found that corrosion behavior of carbon steel was greatly influenced by rotation speed at lower pH whereas at higher pH there was a less effect of rotation speed on the corrosion rate and became constant till reached critical speed .The critical speeds in this study were 4000, 3000 & 2000 rpm at 25, 50 & 80 C° respectively . This was attributed to the fact that at pH3 the corrosion rate was activation-controlled. At pH3 the corrosion rate was increased from (16.347mpy)$_{50c}$□ at static conditions, till reached critical speed, to (88.926mpy)$_{50c}$□ due to the formation of protective hydroxide film on the metal surface which restricts access of H_2O to the surface .Also study the effect of temperature on corrosion rate by derived mathematical model for experimental data.

المستخلص :

تم في هذا البحث دراسة تاثير درجة الحرارة على معدلات التاكل باستخدام قطب اسطواني دوار للفولاذ الكربوني في محلول ١مولاري من كلوريد الصوديوم الخالي من الاوكسجين عند حامضية pH3,6,8 ولدرجات الحرارة ٢٥، ٥٠، ٨٠ م□ ولمدة ساعة.

وجد ان سلوك تأكل الفولاذ الكربوني يتاثر بشدة بسرع التحريك وعند قيم حامضية واطئة لكن هذا التاثير يضعف عند زيادة الحامضية الى ان يصل السرعة الحرجة حيث كانت السرع الحرجة في هذا البحث ٤٠٠٠،٣٠٠٠،٢٠٠٠ دورة بالدقيقة عند درجات حرارة ٢٥،٥٠،٨٠ م□ على التوالي .عند حامضية pH3 وجد ان معدل التأكل يزداد من (16.347mpy) عند درجة حرارة ٥٠ م□ وبدون تحريك الى ان تصل السرعة الحرجة والتي بعدها لايتغير معدل التأكل حيث وصل (88.926mpy)عند سرعة دوران 4000 دورة بالدقيقة ويفسر ذلك بتكوين طبقة الهدروكسيد الواقية على سطح المعدن والتي يحدد او تقيد زيادة الماء على السطح.كذلك تم اشتقاق موديل رياضي يبين تأثير درجة الحرارة على معدل التأكل.

KEYWORDS:Carbon steel rotating cylinder electrode, chloride solution, model.

INTRODUCTION:

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Carbon steel and wide varieties of materials of diverse properties are used in multi stages flash evaporation [1]. At these desalination plant offers numerous corrosion problems due to its process conditions including factors such as temperature and pH, and operation in relatively aggressive environments consisting of deaerated sea water, sea water – air and salt – air aerosols, corrosive gases, slow moving or stagnant liquids or deposit forming liquids [2] . An increase in hydrogen ion concentration will raise the redox potential of the aqueous solution with a consequent increase in rate. On the other hand, an increase in the rate of the cathodic process may cause a decrease in rate when the metal shows an active/passive transition. However, in complex environmental situations these considerations do not always apply, particularly when the metals are subjected to certain conditions of high velocity and temperature [3]. Arrhenius was the developer of an important equation which shows that there is an exponential relationship between rate constant of a chemical reaction and temperature. According to him, Arrhenius gave the equation as:

$$K= A \exp (-Ea\backslash RT)$$

Where:
K = rate constant
R = gas constant (8.314J\mole)
T = temperature in degree Kelvin.
Ea= activation energy (J\mole.K).
A = Modified frequency factor (pre-exponential factor). [4].

In contrast to the influence of velocity, whose primary effect is to increase the corrosion rates of electrode processes that are controlled by the diffusion of reactants, temperature changes have the greatest effect when the rate determining step is the activation process. In general, if diffusion rates are doubled for a certain increase in temperature, activation processes may be increased by 10-100 times, depending on the magnitude of the activation energy. Hydrogen evolution process In de-aerated solutions when this process is under activation control the main effect of increasing the temperature is to increase the exchange current exchange current increased .when the temperature changed from 10 to 75C° and the activation energy was about *59* kJ/mol. Thus the rate of corrosion would be increased by at least 100 times if the anode process was unaffected by the temperature increase, whilst for control by concentration polarization, the diffusion coefficient for hydrogen ions would increase perhaps only twice over the same temperature range. Dissolved oxygen reduction process Corrosion processes governed by this cathode reaction might be expected to be wholly controlled by concentration polarization because of the low solubility of oxygen, especially in concentrated salt solution [5].

As the concentration in the bulk solution increases, corrosion products precipitate in the pits and blocking occurs with a subsequent reduction in dissolution rate. For both film-free and film-forming conditions a decrease in corrosion rate. Many types of corrosive mediums could cause corrosion. These include gases, aqueous solution, hot gases may oxidize a metal and then at high velocity blow off an otherwise protective scale, [6]. Carbon composition ranges for steels. Carbon content in itself has little if any effect on general corrosion resistance of these steels in most cases. Hardness and strength of steels depend largely upon their carbon content and heat treatment. Plain carbon steels exhibit mechanical properties in approximately the following ranges: tensile, 40 to 200,000 lb/in.^{2}, hardness, 100 to 500 Brinell; elongation, 5 to 50%, [7]. Corrosion of carbon steel in seawater is controlled by the availability of oxygen to the metal surface. Thus, under static conditions, carbon steel corrodes at between 100 and

200 mils/year(mpy), reflecting the oxygen level and temperature variations in different locations. As velocity causes a mass flow of oxygen to the surface, corrosion is very dependent on flow rate and can increase by a factor of 100 in moving from static or zero velocity to velocity as high as 40 m\s .that corrosion of carbon steel increases by approximately 50 percent between the winter (average temperature 7C°) and summer (27 to 29C°) months. Although oxygen solubility tends to fall with a rise in temperature, the higher temperature tends to increase reaction rate [8].the cost of metallic corrosion to the total economy must be measured in hundreds of millions of dollars (or euro) per year. Because carbon steel represent the largest. Single class of alloys in use, both in terms of tonnage and total cost, it is easy to understand that the corrosion of carbon steel is a problem of enormous practical importance. This is reason for the existence of entire industries devoted providing protective system for irons and steel [9]. Ismail studied AC impedance on corrosion behavior of carbon steel in deaerated chloride solution was found the effect of velocity on the corrosion behavior of carbon steel, by dc measurements, is pH dependent; while the corrosion rates are greatly influenced by rotation speed at pH 4 but the effect of velocity on the corrosion rate decreases as pH increases [10].

EXPERIMENTAL WORK:

1- Materials

- Carbon steel.
- Sodium chloride 1M, WECO West German.
- Distilled water.

2- Equipments

- Sensitive balance with three digits sensitivity, (type: BBB-600,England,0.0001).
- Electrical heater, Vulcan^{TM}, A-130, Ney.
- Stirrer, AC-DC motor.
- Thermometer, Nabertherm, Germany.
- Close container, 1000ml.

Experimental setup:

Commercial grade carbon steel was used for the tests, with chemical composition as shown in Table 1. Cylindrical Specimens were machined from carbon steel rod, 1.5 cm long and 1 cm in diameter with a central hole in order to fit it on the stainless steel shaft which rotates the specimen, as shown in figure 1. Above the specimen, the shaft was fixed in long Teflon cylinder and below the specimen Teflon cap was screwed on to hold the specimen tightly. The diameter of the specimen was exactly the same as that of the upper shaft or lower. Thus the specimen became a part of the long cylinder exposing to the test solution. The samples were rotated using (BARNANT) equipment model (NO.700) which enables the rotation speed to be varied from 50 to 10,000 rpm. Rotating cylinder electrode was machined and grinded and polished sequentially with silicon carbide paper of grades 600 – grit then washed, and dried up. After taking the initial weight and dimension, carbon steel electrode was immersed in close container (1000ml) volume with de-aerated 1M NaCl solution. The pH of solution was adjusted to different ranges value from pH3 to pH8 by adding dilute HCL and NaOH solutions. To scavenge the dissolved oxygen, Na_2SO_3 was added to maintain the deaerated conditions [3]. Test solution was heated to 25, 50 & 80 C°. For 1 hour, the weights were taken recorded .The process was repeated for 7 speeds, mainly 0, 500, 1000, 2000, 3000,

4000 & 5000 rpm, almost empirical studies were used this range of speed rotation, for each temperature as shown in tables (2-4).
Corrosion rates were calculated according to the following correlation. [3]

$$\text{CORROSION RATE (mpy)} = \frac{534\,W}{ADt}$$

Where:
W: weight loss (mg)
D: density of coupon material (g/cm^3)
A: area (inch^2)
t: time of exposure (hr)

Table 1: composition of carbon steel elements

STEEL	**% COMPOSITION OF ELEMENTS**									
	C	**Si**	**Mn**	**P**	**S**	**Ti**	**Ni**	**Mo**	**Cu**	**Fe**
Carbon Steel	0.12	1.21	1.29	0.01	0.022	0.069	0.37	-	0.061	96.827

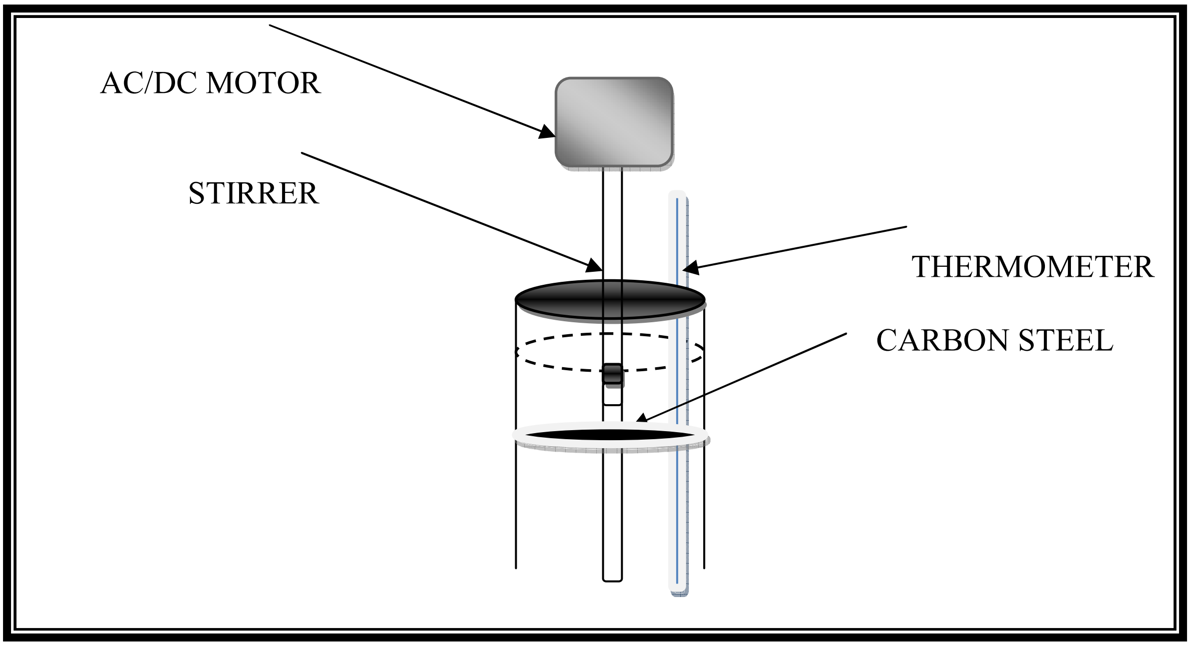

Figure 1: A schematic diagram of the experimental setup

RESULTS & DISCUSSIONS:

Temperature accelerates all the processes involved in corrosion. One would expect that the corrosion rate steadily increases with temperature. Since the corrosion rate was raised due to the oxygen diffusion on the metal surface, therefore, at low pH protective films do not occur. The situation changes markedly when solubility of salt was exceeded, typically at high pH. In that case, increased temperature accelerates rapidly the kinetics of precipitation and protective film formation, decreasing the corrosion rate. The peak in the corrosion rate was usually seen between 50 and 80 ^{0}C depending on water chemistry and dynamic condition [10].
The corrosion rate was constant between about pH8 and pH6. As solution was made more acid, the corrosion rate raised sharply at pH3.This system may be considered one where the

corrosion rate was determined by maximum rate at which oxygen can diffuse to the surfaces, by the limiting diffusion for oxygen. In the range pH8 and pH6, the carbon surface was covered by insoluble corrosion products Increasing the hydrogen ion content does not affect the limiting oxygen diffusion rate. As the solution was made more acid, the corrosion product film dissolves removing one of the barriers to oxygen diffusion Thus, the oxygen limiting diffusion increases giving rise to a rapid increase in the corrosion rate.

At lower pH, the corrosion rate was activation –controlled also, the H^+ was consumed by this reaction on carbon steel surface.

$$2H^+ + 2e \rightarrow H_2$$

The higher temperature tends to increase reaction rate, the corrosion rate of carbon steel increases by approximately11 times between (50-25) C° at pH3wheares the increasing was less than 1.5 times between (80-50) C°.

The results in figure 2 indicates that the corrosion rate was increased with increasing rotation speed become in dependent at very high speed, the effect may be nil or increase slowly till a critical speed was reached, which means that the reduction reaction becomes activation-controlled at each temperature.

The results at 25 C° show that the corrosion rate of carbon steel increased from 2.445 mpy at static conditions to 11.491 mpy at speed of 4000 rpm. With increasing in speed greater than 4000 rpm, the corrosion rates don't change.

Similar behavior at 50C° & 80C° ,the results indicate that the corrosion rate of carbon steel increased from 16.347 & 22.734 mpy at static conditions to 88.926 & 94.013 mpy at speeds of 4000 & 3000rpm ,respectively .the critical speed in this study were 4000, 3000 & 2000 rpm at 25, 50 & 80C□ respectively.

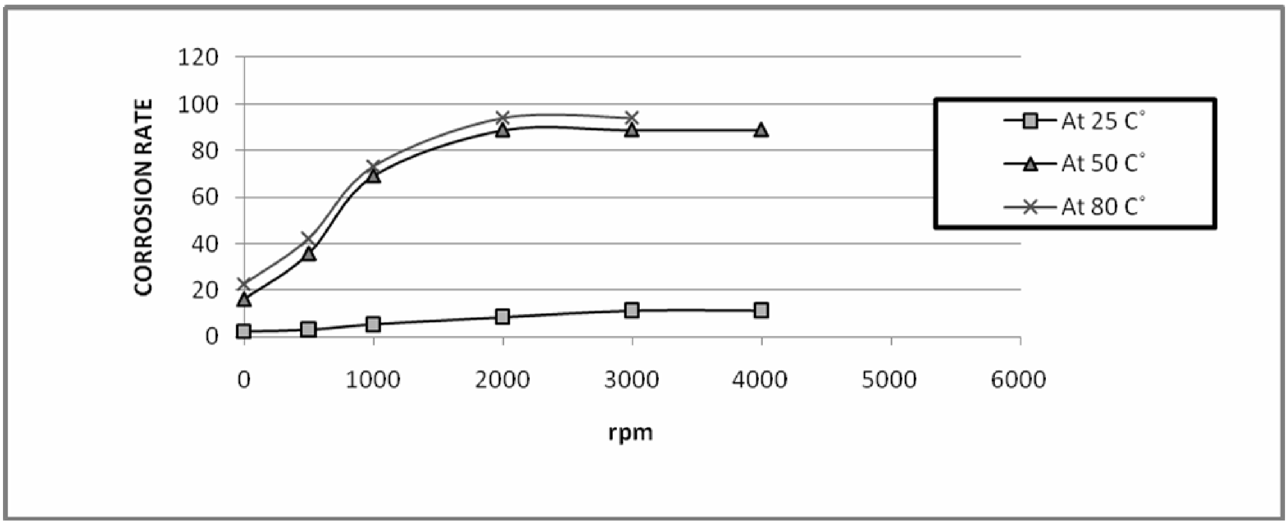

Figure 2: corrosion rates of carbon steel in deaerated 1 M NaCl at 25, 50 &80 C and pH3 at different rotation speeds under static conditions.

Very little general corrosion occurs at 6 & 8 pHs. In this range, hydrogen ions much lower on carbon steel surface and corrosion rate was concentration – controlled under static conditions at 25C° and with increasing the temperatures at different rotation speed the corrosion rate was activation- controlled, also the water was decomposed directly to hydrogen by:

$$H_2O + 2e \rightarrow H_2 + 2OH^-$$

The results at pH6 & pH8 in figures (3, 4) show that the effect of rotation speed of solution on corrosion rate was less pronounced. It shows that protective film was formed on the steel surface.

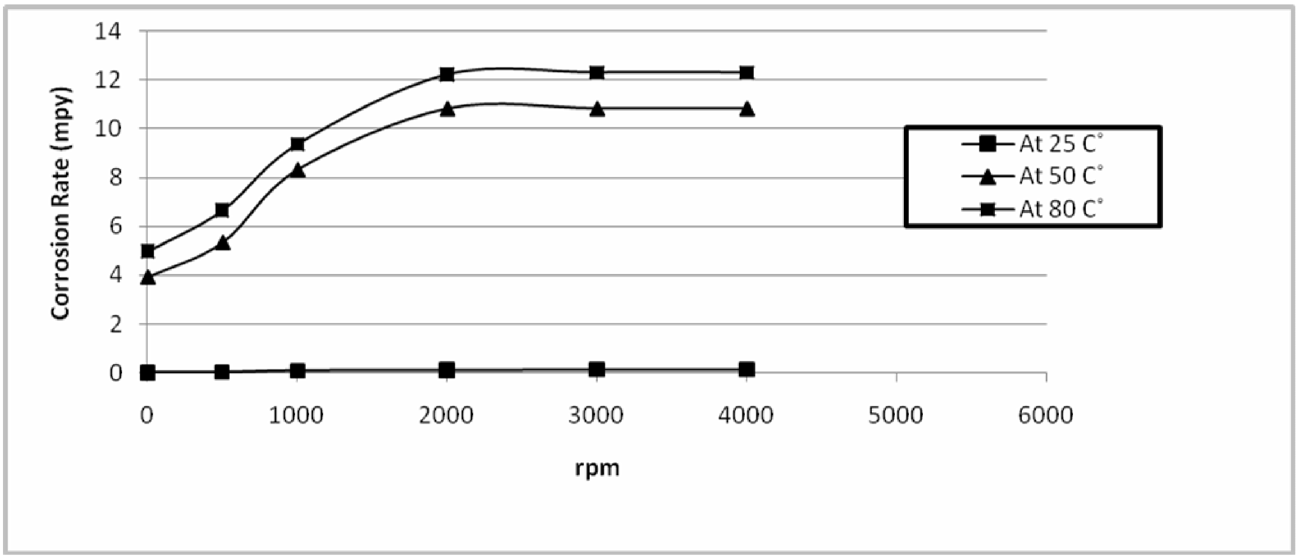

Figure 3: corrosion rates of carbon steel in deaerated 1 M NaCl at 25, 50 &80 C at pH6 at different rotation speeds and static conditions.

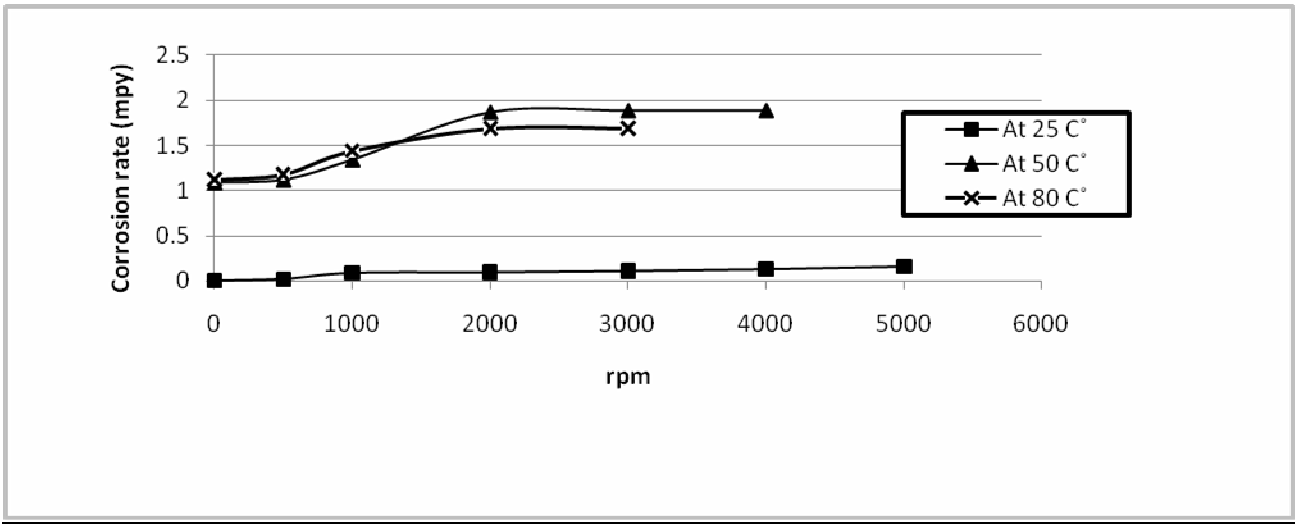

Figure 4: corrosion rates of carbon steel in deaerated 1 M NaCl at 25, 50 &80 C at pH8 at different rotation speeds and static conditions.

Mathematical models:

In order to study the effect of temperature on the corrosion rate of carbon steel in 1M NaCl solution at pH3, 6 & 8 under static conditions by derived mathematical models for experimental data, the Arrhenius equation was used:

$$\mathbf{CR=A\ exp^{(-Ea\backslash RT)}} \quad \text{------------------------------}(1)$$

Where:
CR: corrosion rate of carbon steel (mpy).
E_a: Activation energy (J\mole).
R: gas constant (8.314 J\mole.k).
T: temperature (k).
Taking **ln** of both side of equation 1

$$ln\ CR= lnA - E_a\backslash RT \quad \text{---------------------------------}(2)$$

Assuming that at temperature T_1, the corrosion rate of carbon steel is CR_1 and at another temperature, T_3 the corrosion rate changes to CR_3 (where $T_3>T_1$) then equation 2 can be expressed as follow:

$$ln\ CR_1= lnA - E_a\backslash RT_1 \quad \text{--}(3)$$
$$ln\ CR_3= lnA - E_a\backslash R\ _3 \quad \text{------------------------------}(4)$$
$$Ea = R\left[\frac{lnCR1-lnCR3}{\frac{1}{T3}-\frac{1}{T1}}\right] \quad \text{-------------------------------}(5)$$

The Value of Ea (average) calculate from equation 5, submit this value in equation 2 to obtain lnA.

Ea & lnA were recorded in the following:

pH	**Ea(average)(J\mole)**	**lnA**
3	39695	16.894
6	106817	38.691
8	112688	39.268

Actual values of activation energy for each case of carbon steel corrosion with different temperatures, 298, 323 & 353K and pH3, 6 & 8 under static conditions were calculated by equation 2 as shown in table5, results were revealed the activation energy values of the reaction increased with increase values pH. However rising of the temperature acts in the reverse direction increasing the activation energy of the reaction at pH_3, molecules have enough energy to react at higher temperature; therefore the activation energy decreases with increasing temperature. At pH6, 8 the reaction was needed to maximum to energy for molecules to react.

The various mathematical models were shown in equations 6, 7 & 8.

At pH3 $\quad ln\ CR=16.894 - 39695\backslash RT$ ------------------------------
(6)

At pH6 $\ln CR=38.691 - 106817\backslash RT$ -------------------------------- (7)

At pH8 $\ln CR=39.268 - 112688\backslash RT$ --------------------------------- (8)

The temperature has a significant effect of corrosion rate on carbon steel as described in figures 6, 7 & 8; the model also indicates the similar relationship of temperature and corrosion rate. In general, corrosion rates rise as the temperature increases .if the other parameters were held constant.

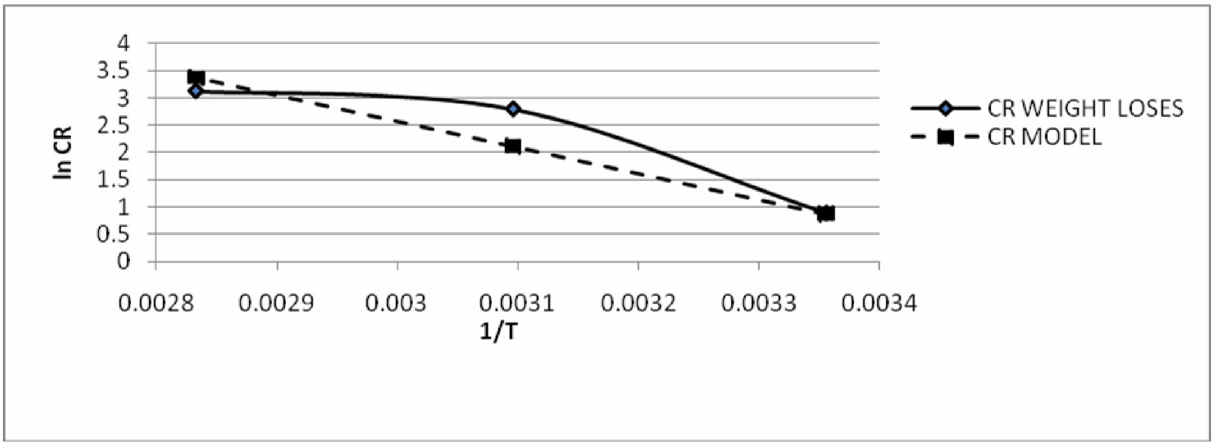

FIGURE 6: Comparison between weight loses and mathematical model method at pH 3

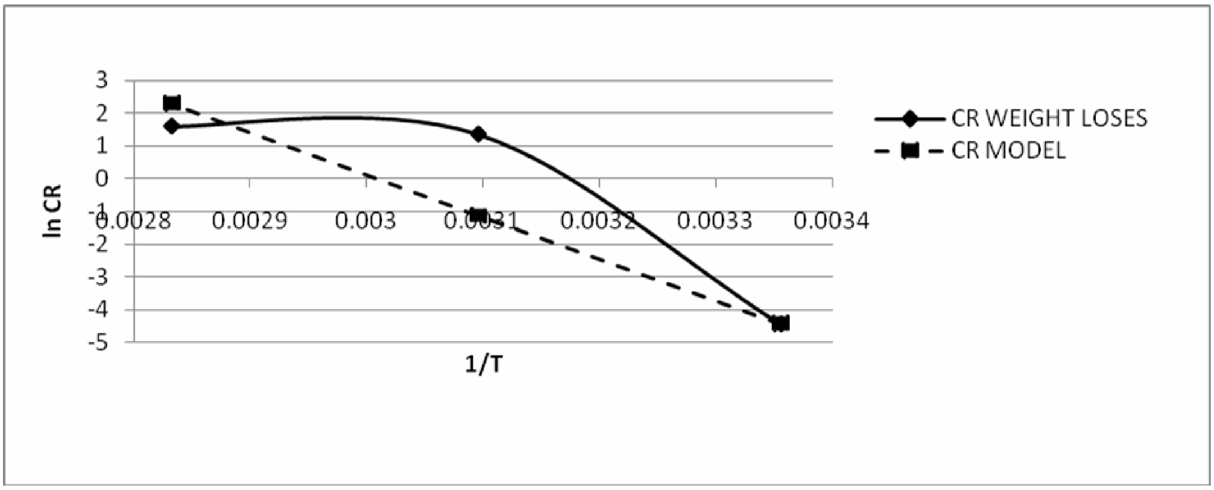

FIGURE 7: Comparison between weight loses and mathematical model method at pH 6

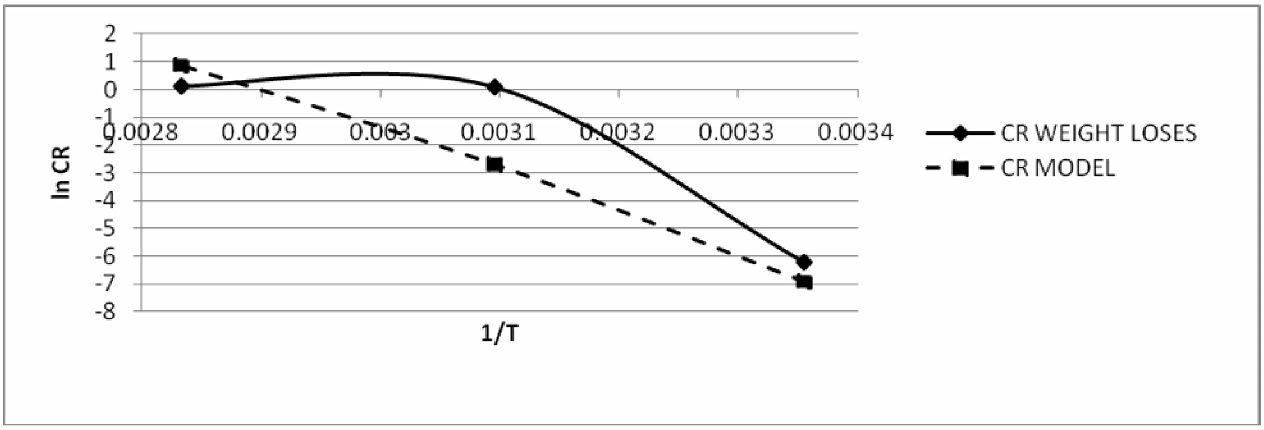

FIGURE 8: Comparison between weight loses and mathematical model method at pH 8

As seen from the table 6, the comparison of corrosion rate by weight loss and mathematical model methods. The observed corrosion rate values from the experimental data were in a good agreement with that predicated by the mathematical equation except the corrosion rate by weight loss was less than mathematical model by 1.9 times at pH3 and temperature 323k. The adjusted corrosion Rates were stilled about 1.2 and 1.9 times higher than that from weight loss at the temperature 353k and pH3, 6, respectively .In spite of the weight loss method can be readily determined and corrosion rate easily calculated otherwise it was not delicate therefore; mathematical models have solved important problems and hold the promise of solving major outstanding problems.

CONCLUSION:

1. The change in the rotation speed influence the corrosion behavior of carbon steel .However, as rotation speed was increased from 500 rpm to 4000 rpm, the corrosion rate was remained constant at 11.491 mpy at 25C° for pH3. Corrosion rate became in depended at very high speed, which means that the reduction reaction became activation -controlled.
2. The effect of rotation speed on corrosion rate was more pronounced at lower pH, whereas at higher pH the effect of rotation speed on corrosion rate was less pronounced.
3. With increasing temperatures from 25C° to 80C°, the corrosion rates increase from $(2.445\text{mpy})_{pH3}$ to $(22.734\text{mpy})_{pH3}$ under static conditions.

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TABLE 2: corrosion rates of carbon steel in deaerated 1M NaCl at 25, 50 & 80 C° and pH 3 at different rotation speeds under static conditions

RPM C.R.(mpy)	0	500	1000	2000	3000	4000	5000
At 25 C°	2.445	3.178	5.519	8.621	11.443	11.491	11.491
At 50 C°	16.347	35.921	69.211	88.881	88.921	88.926	
At 80 C°	22.734	42.321	73.198	94.011	94.013		

TABLE 3: Corrosion rates of carbon steel in deaerated 1M NaCl at 25, 50 & 80 C° at pH 6 at different rotation speeds and static conditions

RPM C.R.(mpy)	0	500	1000	2000	3000	4000	5000
At 25 C°	0.012	0.024	0.098	0.109	0.131	0.132	
At 50 C°	3.913	5.339	8.321	10.828	10.833	10.834	
At 80 C°	4.988	6.676	9.381	12.229	12.311	12.312	

TABLE 4: Corrosion rates of carbon steel in deaerated 1M NaCl at 25, 50 & 80 C° at pH 8 at different rotation speeds and static conditions

RPM C.R.(mpy)	0	500	1000	2000	3000	4000	5000
At 25 C°	0.002	0.021	0.089	0.096	0.11	0.13	0.16
At 50 C°	1.088	1.121	1.343	1.871	1.888	1.889	
At 80 C°	1.122	1.181	1.441	1.691	1.694		

Table 5: Actual values of activation energy for corrosion rate at 298, 323 &353 k and PH3,6,8

pH	**Temperature(k)**	**$CR_{(weight\ loss)}$ (mpy)**	**E_a (J\mole)**
3	298	2.445	39641.152
3	323	16.347	35463.682
3	353	22.734	35218.00
6	298	0.012	106817.664
6	323	3.913	107565.395
6	353	4.988	108835.577
8	298	0.002	112686.5
8	323	1.088	105224.659
8	353	1.122	114907.537

Table 6: The comparison of corrosion rate by weight loss and mathematical model methods.

pH	**Temperature(k)**	**$CR_{(weight\ loss)}$ (mpy)**	**$CR_{(model)}$ (mpy)**
3	298	2.445	2.391
3	323	16.347	8.264
3	353	22.734	29.028
6	298	0.012	0.012
6	323	3.913	0.33
6	353	4.988	9.922
8	298	0.002	0.001
8	323	1.088	0.0675
8	353	1.122	2.39