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Study the Corrosion Behavior of Carbon Steel in Presence of CO_2 Gas in Oil Pipe Lines

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Abstract

The current work is the study of corrosion behaveior of carbon steel, in naturally aerated (3.5%wt NaCl) solution. A rotating cylinder electrode (RCE) system was used to produce conditions of turbulent flow, polarization experiments were conducted at various temperature and various rotating speed at each temperature.Similar experiments were carried out using CO_2 gas at (32 ml/sec) flow rate.Corresponding experiments by weight loss were carried out in (3.5%wt NaCl) solution with Kerosene + 10% V salt solution and Gas oil + 10% V salt solution at 328k and (0, 400) r.p.m .Similar experiments were carried out in kerosene + 10% V salt solution at (298, 308 and 318)K and rotating speed (0) r.p.m at each temperature.Other experiments were carried out in pure kerosene at temperature (298 and 318)K and speed (0) r.p.m. All experiments were carried out with and with out CO_2 gas .The results indicate that the corrosion rate of carbon steel is increasing70% with CO_2 gas.

Keywords: Oil , Polarization , Pipe Lines , Carbon Steel ,Rotating cylinder.

Paper History:-

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Introduction

The corrosion is alwayes one of the main problems in petroleum refineries and in petrochemical plants .Billions of dollars are lost every years because of corrosion. Since 1940 the main problems in the oil industry was the corrosion of carbon steel with CO_2 (1). Presently, the problem of corrosion has increased due to use CO_2 injection technique that enhanced of the oil recovery by exploiting the deep natural gas reservoirs , which contains carbon dioxide. And this type of corrosion is continues to cause a great concern for the petroleum industry, especially in oil transport steps(2,3,4). The presence of carbon dioxide, various salt (Na^+,K^+,Ca^{+2},SOH^-,Cl^-,etc) ,organic acid and free water can cause extreme corrosion problems in oil and gas pipe lines. There are many factors that cause internal corrosion of wells and pipe lines such as temperature, carbon dioxide and H_2S content, water wetting, velocity of flow , oil or water wetting,composition and surface condition of the carbon steel. A small change in one of these parameters can change the corrosion rate considerably. At higher temperature , the rate of corrosion can be easily reduced in presence of carbon dioxide under conditions that when corrosion product, (iron carbonate) a precipitate on the carbon steel surface and form a dense and protective corrosion product film (5).

The main chemical reactions of carbon dioxide dissolution and formation of carbonic acid was shown in equations (1) and (2) (6,7),

$$CO_{2(g)} \longrightarrow CO_{2(aq)} \qquad (1)$$

$$CO_2 + H_2O \longrightarrow H_2CO_3 \quad (2)$$

Then dissociate the carbonic acid to bicarbonate which also dissociates into carbonate as shown in equation (3) and (4),

$$H_2CO_3 \longrightarrow H^+ + HCO_3^- \quad (3)$$

$$HCO_3^- \longrightarrow H^+ + CO_3^{-2} \quad (4)$$

The reactions of electro-chemical at the steel surface include the anodic dissolution of iron as shown in equation (5)

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad (5)$$

The reaction of proton reduction as in equation (6) and the direct reduction of carbonic acid as in equation (7) they are represent the cathodic reaction.

$$2H^+ + 2e^- \longrightarrow H_2 \quad (6)$$

$$2H_2CO_3 + 2e^- \longrightarrow H_2 + 2HCO_3^- \quad (7)$$

the direct reduction for bicarbonate ion has been recommended occurs more easily at high pH(8) .

The overall reaction is:

$$Fe + CO_2 + H_2O \longrightarrow FeCO_3 + H_2 \quad (8)$$

The increasing in the reaction rate of hydrogen evolution has cause the increase in the iron corrosion rate in aqueous solutions at presence of CO_2. The hydrogen evolution rate cannot exceed the transport rate of H+ ions to the surface from the bulk solution in strong acids that completely dissociated. The limiting current of mass transfer controlled was small in solutions with a $pH > 4$ and occur a higher rate for the hydrogen evolution at presence of H_2CO_3 (1,9). Many researches assumed that the net cathodic current is the sum of the currents for the two reactions and the two reactions are independent (10,11) At $pH > 5$ and very low partial pressures of CO_2 gas are important to occur the hydrogen evolution from the direct reduction of water at lower potentials.

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \quad (9)$$

That in CO_2 solutions at higher pH the direct reduction of the bicarbonate ion becomes important:

$$2HCO_3^- + 2e^- \longrightarrow H_2 + 2CO_3^{-2} \quad (10)$$

because of the increasing in concentrations of bicarbonate with increasing pH (12,13).

The coal of this investigation is to study the behavior of corrosion for carbon steel in presence of CO_2 gas in oil pipeline under different conditions of temperatures and flow rate in (3.5wt%NaCl)solution and kerosene and gas oil immersion. Rotating cylinder electrode (RCE),was employed in the present work in which the corrosion test was carried out under turbulent flow condition,at five controlled rotating speeds of(0,100,200,300 and 400)r.p.m at different temperatures (298,308,318 and 328)K.Two methods used to measure corrosion rate were, electrochemical method and immersion test method.The experiments were carried out with and without CO_2 gas.

Experimental work:

➢ Materials

Materials used in this work is low carbon steel the composition is given in table (1) . The chemical analysis was performed by state company for Inspection and Engineering Rehabilitation(S.I.E.R).The specimen was cylinder of 16mm i.d., 28 mm o.d.and 20 mm hight with surface area of 17.6 cm^2 .

Table (1): Spectrographic composition of carbon steel

Sample	C%	Co%	Mn%	Si%	Ni%	S%	Cr%	Al%	P%	Mo%	Cu%	V%	W%	Fe%
Specimen used	**0.051**	**0.012**	**0.653**	**0.287**	**0.115**	**0.011**	**0.146**	**0.031**	**0.002**	**0.028**	**0.132**	**0.0005**	**0.017**	**Bal.**
Bolt Standard L.C.S	**0.001**	**0.001**	**0.386**	**0.148**	**0.022**	**0.016**	**0.006**	**0.003**	**0.018**	**0.002**	**0.001**	**0.005**	**0.018**	**Bal.**

Prior to every experiment, the carbon steel electrode surface was abraded on successive grades of silicon carbidefrom (100 ,120 ,400 ,600 ,800,1000) grit under running tap water. It was then washed with running tap water followed with distilled water , rinsed with acetone and dried with clean tissue paper , it was then kept in a desiccator over a silica gel. Figures (1) and (2) show the surface of low carbon steel as polished and after Etching respectively, it's shown clean and smooth.

Fig. (1)The surface of low carbon steel.

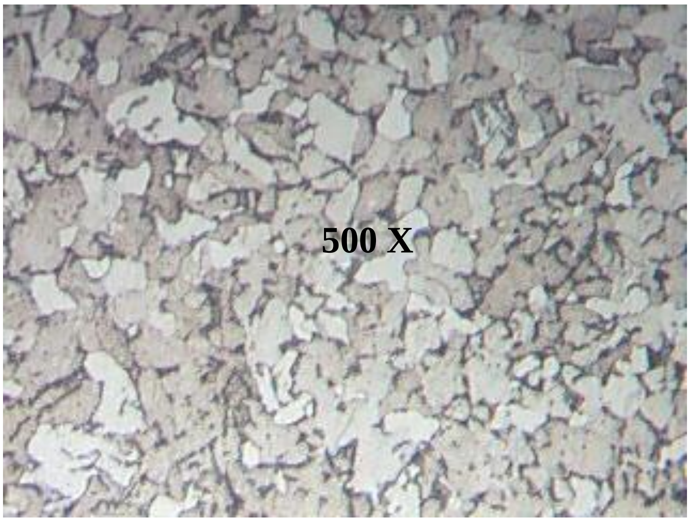


Fig. (2) The surface of carbon steel after Etching

• Chemical Solutions

Distilled water, analar NaCl to prepare 3.5wt% solution. The electrolyte pH was measured before each test by using digital pH meter (HANNA instruments -H 19811-5 pH/C0/Ec/TDS) meter, which was calibrated using buffer solution of pH 4 and 9. The initiall electrolyte pH was 5, and the finl electrolyte pH was 3.8. Kerosene and gas oil samples were availabled commercially from (oil marketing companies) operating in (Daura refinery). The density of each kerosene and gas oil was measured using density bottle, they are about 0.802 and 0.844 gm/cm^3 respectively.

• Testing Procedure

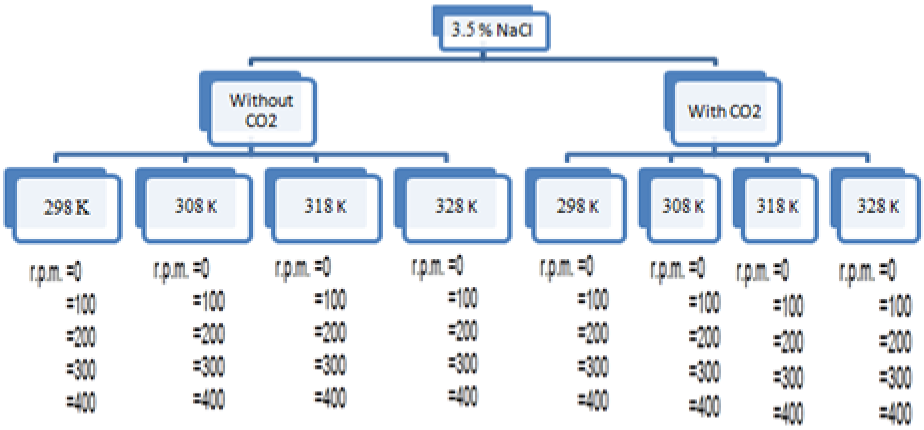
The experimental work is divided into two parts, the first was achieved using polarization techinque to determine the corrosion rate of carbon steel in 3.5 weight percent of NaCl solution at temperatures (298,308, 318 and 328) K and (0,100,200,300 and 400)rpm. All above experiment were repeated in presence of CO_2 gas at a rate of 32ml/sec. A schematic representation of the polarization test shown in figure(3).

The second part was immersion test using weight loss method at the following conditions:

1) Kerosene +10%V salt solution at (298,308 and 318)K and rotation speed (0) at a temperature of 328K and (0, 400) rpm rotation speed.

2) Gas oil +10%V salt solution at 328K and (0,400)rpm.

3) Pure kerosene at (298 and 318)K and o rpm



Kerosene and gasoil were provided from Daura refinery and all above experiment were carried out with and without CO_2 gas as shown in figure (4).

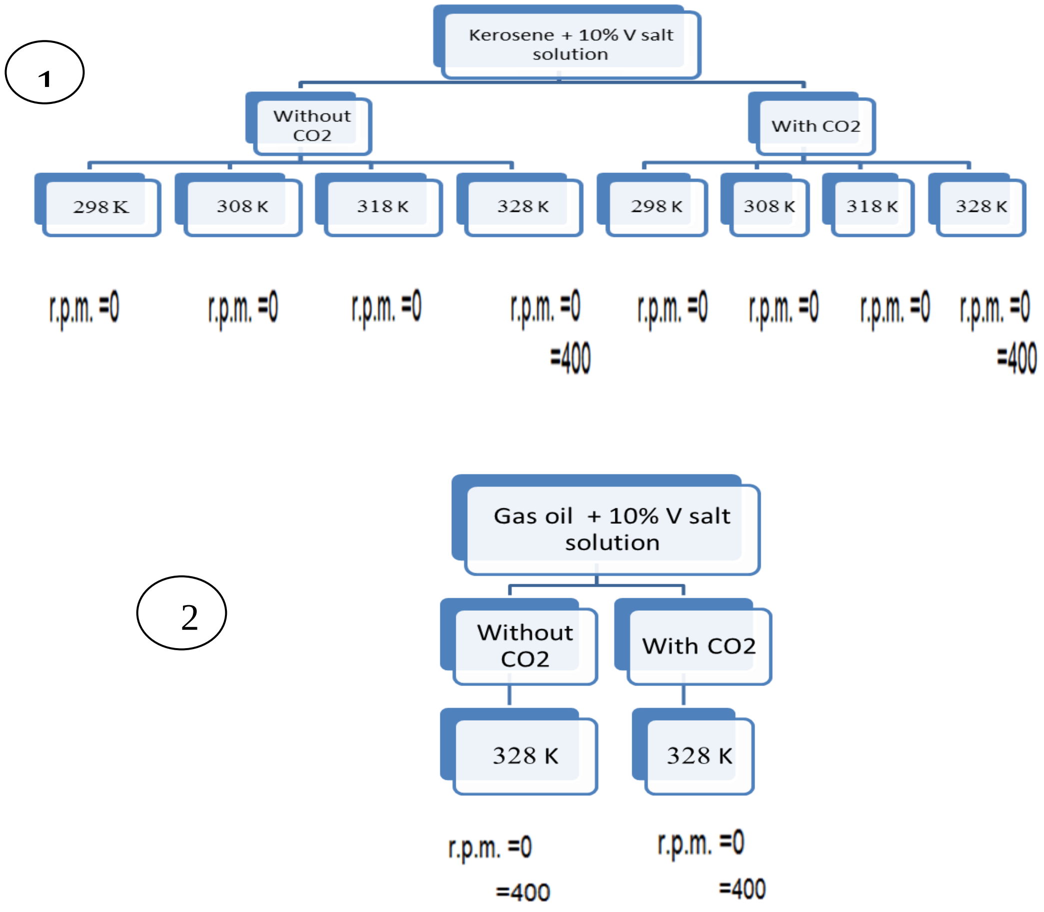


Fig (3) Schematic Representation for Polarization Tests Experiments

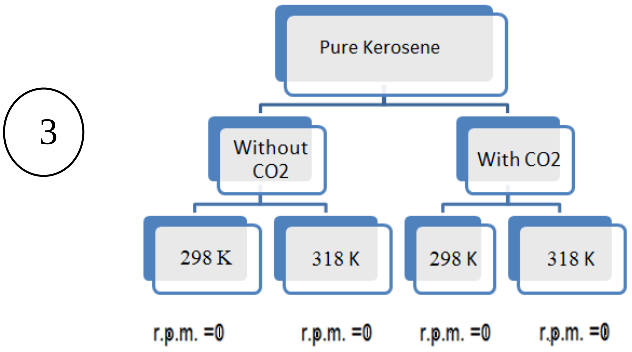


Fig. 4 Schematic Representation for Immersion test.

After surface preparation of the sample, the weight of carbon steel specimen was recorded then immersed in the prepared solution at the preset temperature and rotating speed. After 4hr exposure the specimen was cleaned with distilled water then with aceton and dried with a clean tissue and kept in a desiccator over a silica gel for one hour before weighing.

- **Electro-chemical corrosion tests**

The polarization cell was filled with 2 liter of the required test solution , and then placed inside a constant temperature water bath supplied with thermostat to keep the temperature constant at about (±1 °C) the preset temperature . After that, the water bath was raised up using a car jack, until the RCE was introduced into the solution.A capillary connection to the reference electrode (saturated calomel electrod, SCE) was used with its tip acting as the luggin prob.The tip was adjusted to within (1-2)mm from the specimen surface. The SCE was used throughout the whole programme. Potentials were measured with reference to this electode.The working , counter (graphite) and reference electrode were connected to a potentiostat (WenkingLT.87), The carbon steel electrode was electrochemically polarized to (-1.000V) the RCE was set in motion at the required r.p.m by manually adjusting the speed controller . The potential was kept at (-1.000V) for (15min.) then a complete electrochemical polarization was carried out and scanned potentiostatically in the noble (positive) direction with scan rate of $20*10^{-3}$V/min until (-0.3V) potential. The current and voltage were checked and read from two digital millimeters MT8045 . The reported results are the average values of duplicated experimental runs obtained with satisfactory reproducibility

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Fig. (5)The Apparatus

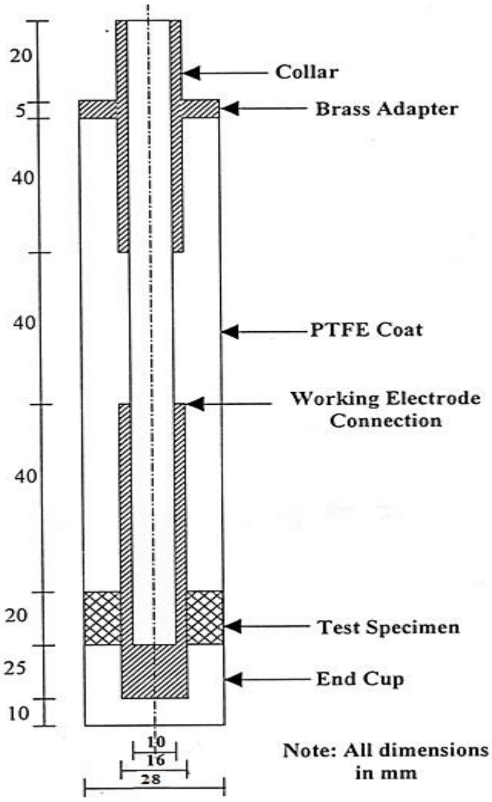

Fig.(7)Rotating cylinder electrode

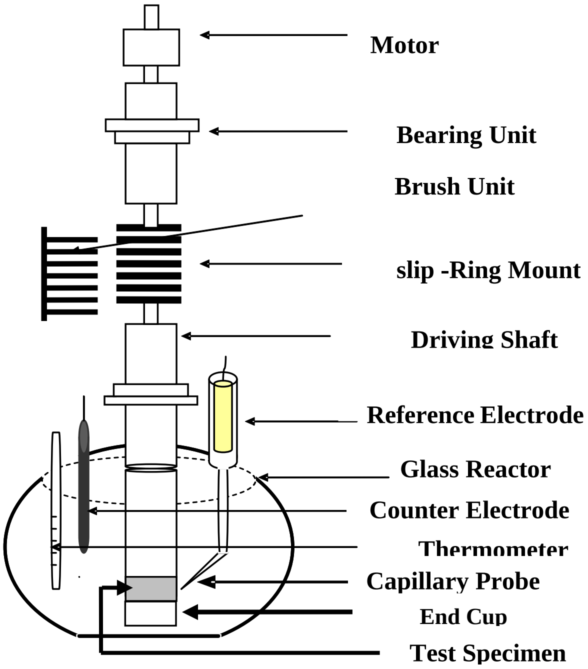

Fig. (6)The Rotating cylinder electrode assembly in polarization cell.

Results and discussion

Two different techniques were used in this study. Firstly polarization technique from negative potential in a cathodic region -1V till -0.3V in anodic region with and without CO_2 using 3.5weight percent from sodium chloride solution to calculate the corrosion rate in mils penetration per year (mpy) using the following formula:

$$mpy = 0.13\, i_{corr} \frac{at\ wt}{\rho\ \ n}$$

Where :
i_{corr} = current density in µA/cm^2,
αt wt = atomic weight of specimen g/gmol
ρ = density of specimen in g/cm^3
n = electron loss. 2

Figs . 8 -15 show the polarization diagram of carbon steel in different temperatures and rotation speed without and with CO_2 .Tables 2 and 3 show the corrosion current density of carbon steel without and with CO_2 respectively .

Secondly immersion test for kerosene and gas oil with 10% V salt solution with and without CO_2 using weight loss, the most convenient way of expressing corrosion rates is mils penetration per year (mpy) and is calculated by using the following formula(9):

$$mpy = \frac{k\Delta w}{\rho A\, t}$$

where: w=weight loss in gm,
ρ=density of specimen in g/cm^3,
K=Constant factor is 3.45*10^{-6},
A=area of specimen in cm^2,
t=time in hours.

Tables 4 and 5 show the rate of corrosion for carbon steel in kerosen and gas oil without and with CO_2 gas respectively .

1) Effect of temperature on corrosion current density:

Figures (8-11) show the polarization digram of carbon steel in 3.5wt%NaCl solution while figures (12-15) show them with the presence of CO_2 gas.The corrosion current density increase with increasing temperature at constant rotation speed. Increasing temperature almost increase the rate of all chemical reactions according to Arrhenius equation. Also it inhence the diffusion of oxygen in the solution due to increase molecular diffusion coefficient, in spite of decreasing the solubility of oxygen. Finally increasing temperature cause decrease of the compactness of the corrosion product which in turn decreases the resistance to corrosion (14). Figure (16) shows the corrosion rate behaviour verses temperature without CO_2 gas. Moreover the current density of corrosion within of CO_2 gas was more than that obtained without CO_2 gas at the same conditions. Figure (17) shows the rate of corrosion for carbon steel in 3.5 wt% sodium chloride solutio with CO_2 gas. This is because the existance of carbonic acid which leads to increase the cathodic reactions equations (2–4) which it must be in equilibrium with the oxidation rate, i.e., the anodic reaction

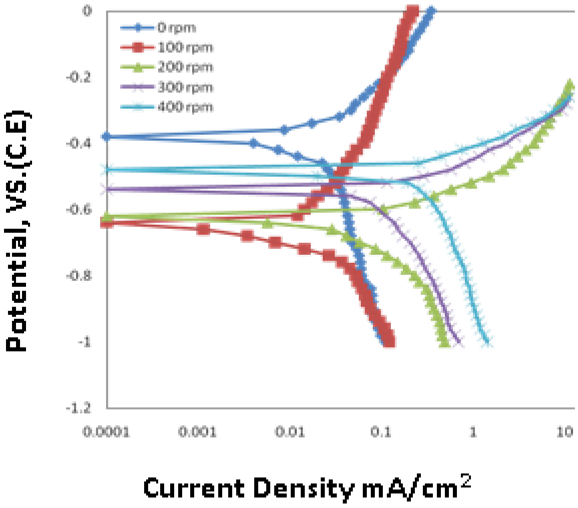

Fig. 8 Potentiostatic polarization curves in 3.5wt%NaCl solution, without CO_2, Temp.= 298 K.

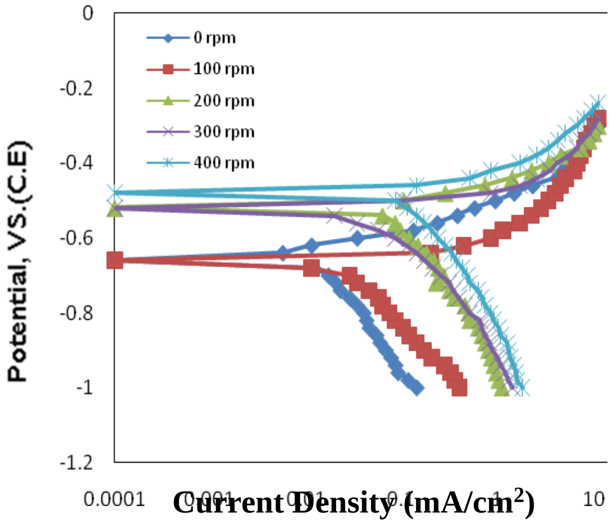

Fig. 9 Potentiostatic polarization curves in 3.5wt% NaCl solution, without CO_2, Temp.= 308 K.

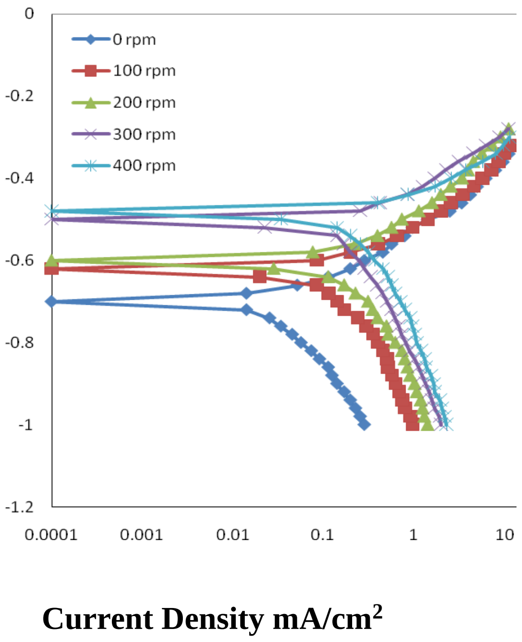

Fig. 10 Potentiostatic polarization curves in 3.5wt% NaCl solution, without CO_2, Temp. 318 K.

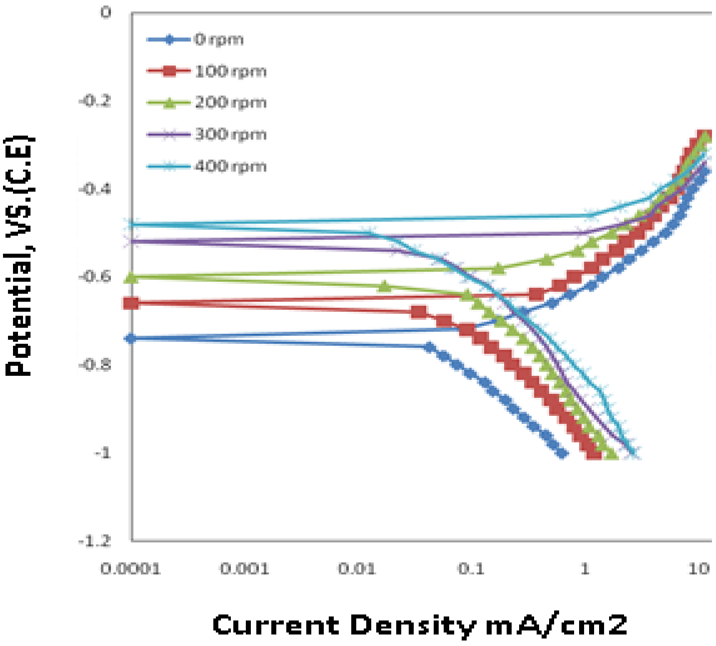

Fig. 11 Potentiostatic polarization curves in 3.5wt% NaCl solution, without CO_2, Temp.= 328 K

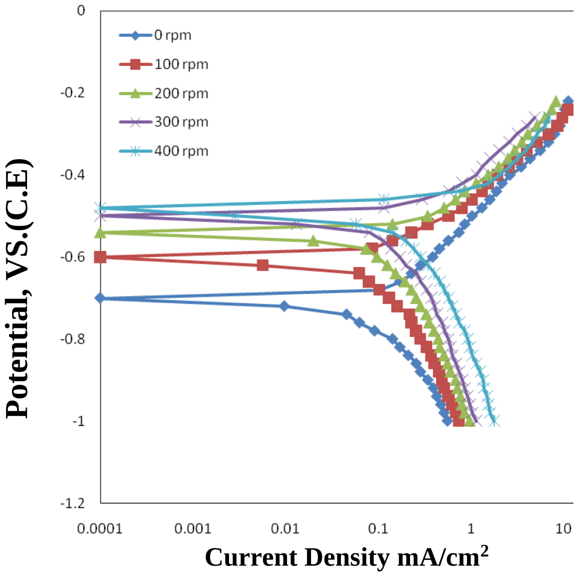

Fig. 12 Potentiostatic polarization curves in 3.5wt% NaCl solution, with CO_2, Temp.= 298 K.

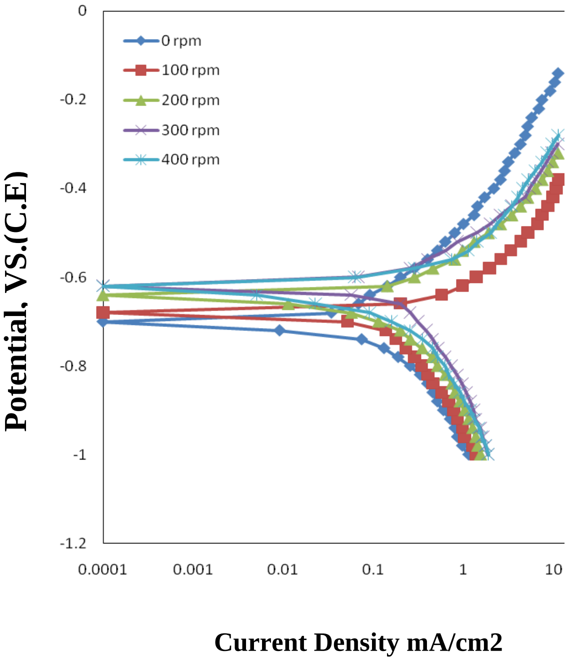

Fig. 13 Potentiostatic polarization curves in 3.5wt% NaCl solution, with CO_2, Temp.= 308 K.

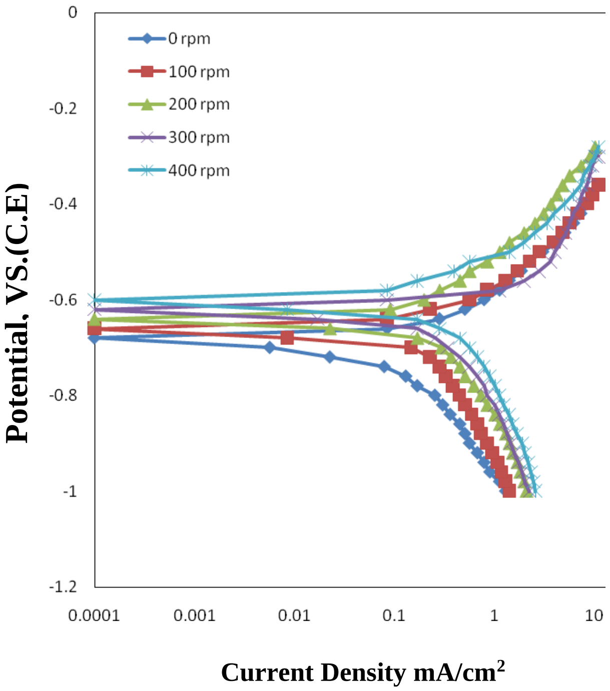

Fig. 14 Potentiostatic polarization curves in 3.5wt% NaCl solution, with CO_2, Temp.= 318 K.

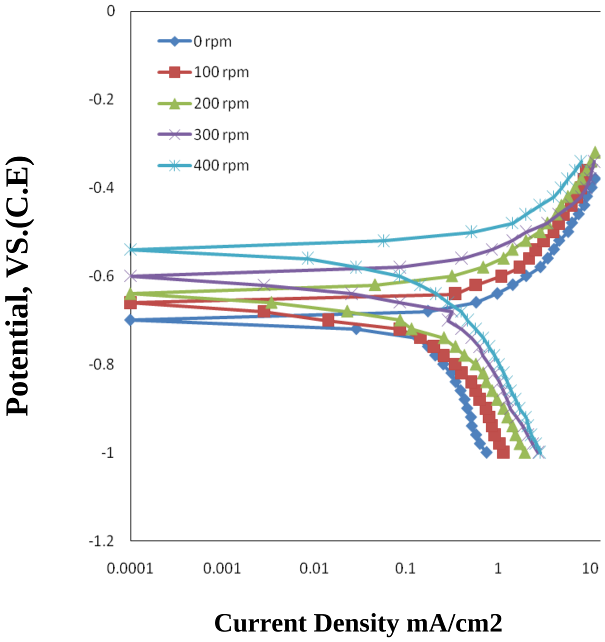

Fig. 15 Potentiostatic polarization curves in 3.5wt% NaCl solution, with CO_2, Temp.= 328 K.

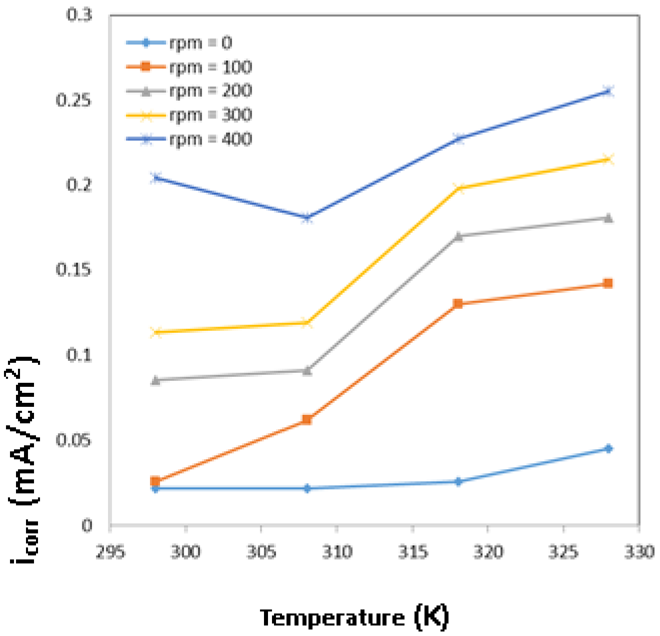

Fig 16 Variation of corrosion current density vs temperature for constant (r.p.m) without CO_2

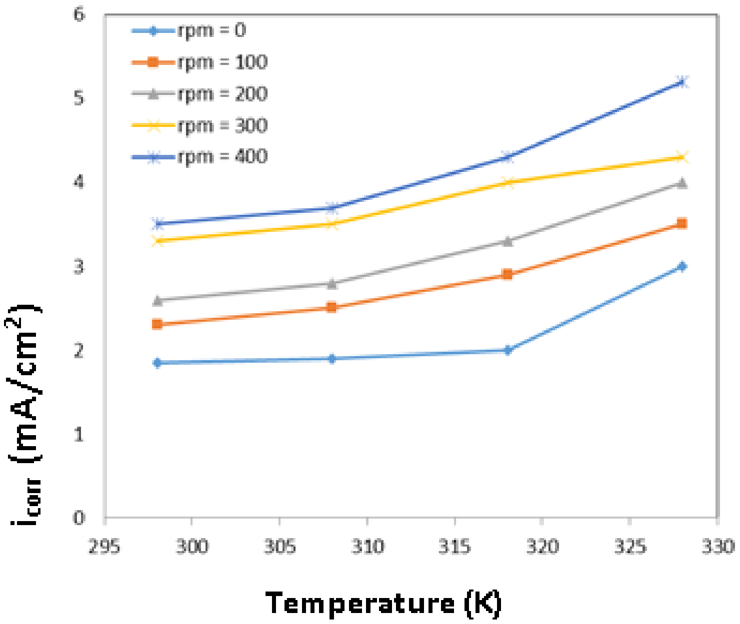

Fig 17 Variation of corrosion current density vs temperature for constant r.p.m with CO_2

2)The effect of velocity on the corrosion current density:

From figures (18 and 19) it is clear that increasing rotation speed leads to increase the corrosion current density without and with CO_2 gas respectively at constant temperature.Increasing velocity enhance turbulence which in turn increase the transport rate of oxygen close to the metal surface, and act to erode the formed film so higher mass transfer rate introduced (15).

Moreover the corrosion current density of carbon steel with CO_2 gas are higher than that obtained without CO_2 gas. This is also due to carbonic acid formation that increased the attack on carbon steel by increasing the hydrogen diffusion to the metal surface and the diffusion of metal ions from the metal surface to the bulk of solution(16). The current density of corrosion at different temperatures and flow rates are given in Tables (2 and 3).

Table (2): The Corrosion current density mA/cm^2 without CO_2 gas.

r.p.m	**Temperature, K**			
	298	308	318	328
0	0.0215	0.022	0.026	0.045
100	0.026	0.062	0.130	0.142
200	0.085	0.091	0.170	0.181
300	0.113	0.119	0.198	0.215
400	0.204	0.218	0.227	0.255

Table (3): The Corrosion current density mA/cm^{2}with CO_2 gas.

r.p.m	**Temperature, K**			
	298	**308**	**318**	**328**
0	1.85	1.9	2	3
100	2.3	2.5	2.9	3.5
200	2.6	2.8	3.3	4
300	3.3	3.5	4	4.3
400	3.5	3.7	4.3	5.2

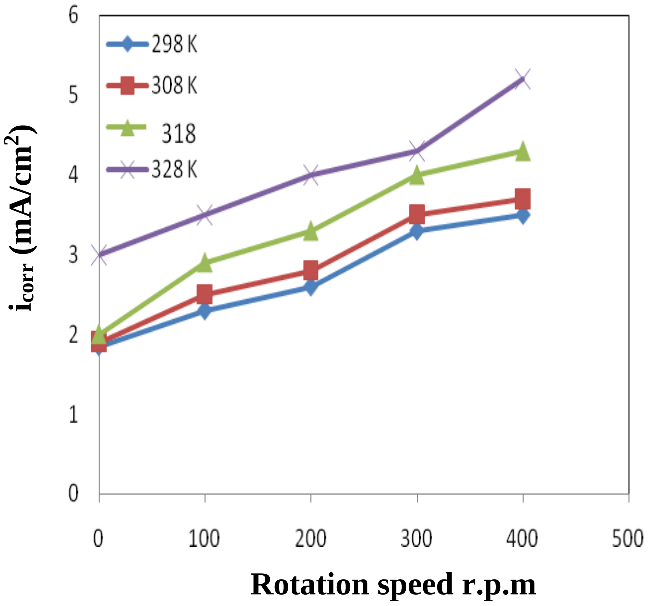

Fig. 19 Variation of corrosion current density vs rotation speed for constant temperature, with CO_2

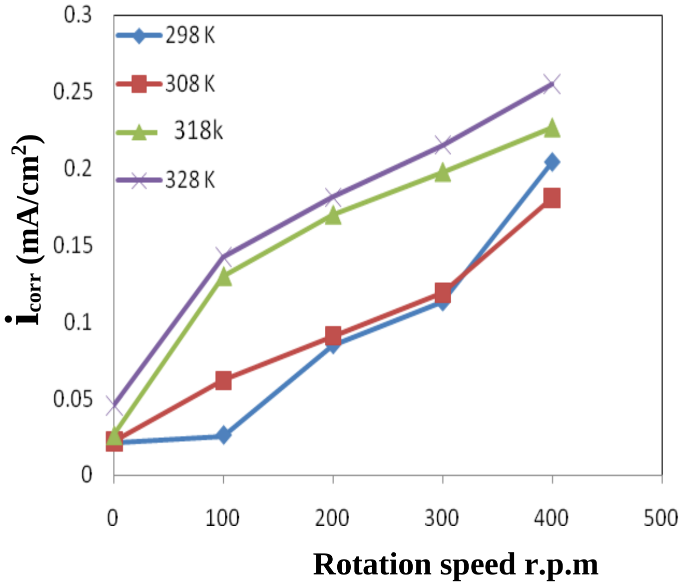

Fig. 18 Variation of corrosion current density vs rotation speed for constant temperature, without CO_2

Immersion Tests:

Tables (4 and 5) show the corrosion rate of kerosene and gasoil with 10%V salt solution without and with CO_2 gas at constant temperature and 0,400 rpm rotation speed. Corrosion rate increases with increasing rotation speed at constant temperature. It appears that the corrosion rate of gas oil higher than that of kerosene, this may be attributed to that gas oil contains more sulfur compound than that in kerosene. It contains10000 ppm H_2S ,higher percent of margabtian and water according to the labrotary test of Al Doura refinery.

Table (4): Corrosion rate of carbon steel for both kerosene and gas oil in 10%V NaCl solution at 298 K without CO_2 gas .

r.p.m	Kerosene mpy	Gas oil mpy
0	12.4809	16.374
400	20.043	33.39

Table (5): Corrosion rate of carbon steel for both kerosene and gas oil in 10%V NaCl solution at 298 K with CO_2.

r.p.m	Kerosene mpy	Gas oil mpy
0	28.7062	32.567
400	38.43	48.87

Table 5 shows that the corrosion rate in the presence of CO_2 gas are more than that obtained without CO_2 . This is also because the formation of carbonic acid from the hydration for CO_2 gas ,which in turn dissociates to give H^+ and HCO^-_3 .And also HCO^-_3 dissociates to give H^+ and carbonat. According to equations (1 - 4) .

Table (6): Corrosion rate of carbon steel for kerosene in 10V% NaCl at r.p.m = 0

Temperature K	Without CO_2 mpy	With CO_2 Mpy
298	7.4885	13.1050
308	9.3607	21.8417
318	11.2328	26.2100
328	12.4809	28.7062

Table 6 indicates that the corrosion rate with CO_2 are higher than that without $CO_2$with increasing temperature due to formation of carbonic acid.

Table (7) : Corrosion rat of carbon steel for 4hr in pure kerosene at static condition r.p.m = 0

Temperature	Without CO_2 mpy	With CO_2 Mpy
298	1.2480	1.8721
318	2.49619	3.12024

Table 7 indicates that the corrosion rate higher with CO_2 than that without CO_2. The corrosion rate of pure kerosene is much lower than that obtained in kerosene contain 10V% NaCl solution.

Microscopic observations :

Figure 20 shows the surface of carbon steel after polarization in 3.5wt%NaCl solution, it's found that the pitting occurs on the surface but these pittings are not deep and small in size.

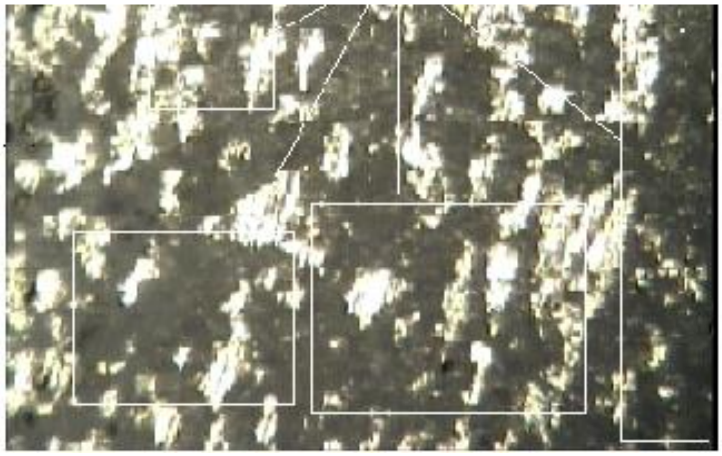

Fig. 20 Corrosion on surface of carbon steel in3.5wt% NaCl without CO_2 at 328 K and 400 r.p.m.

Figure 21 shows the pitting formation on the carbon steel in salt solution containingCO_2 gas , the dark zones represent appearance of deep pits in the surface, these pits are initiated and grow until they cover most of surface with increasing potentials.

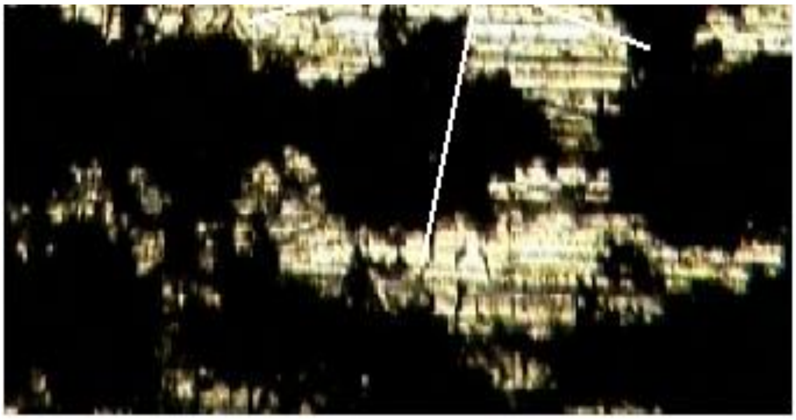

Fig. 21 Corrosion on surface of carbon steel in 3.5wt% NaCl with CO_2 at 328 K and 400 r.p.m.

Figure 22 shows the pitting formation on carbon steel in gasoil +10V% salt solution containing CO_2.It's found that the pits in big size and large number compared with the pits in figure 23, that’s mean the kerosene do not attack the surface of carbon steel aggressively like gasoil with CO_2.

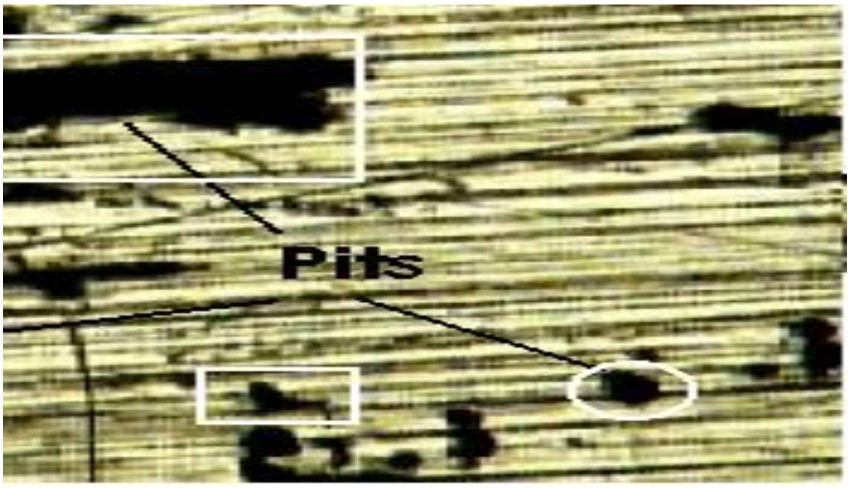

Fig. 22 Corrosion on surface of carbon steel in gas oil + 10%V NaCl with CO_2 at 328 K and 400 r.p.m.

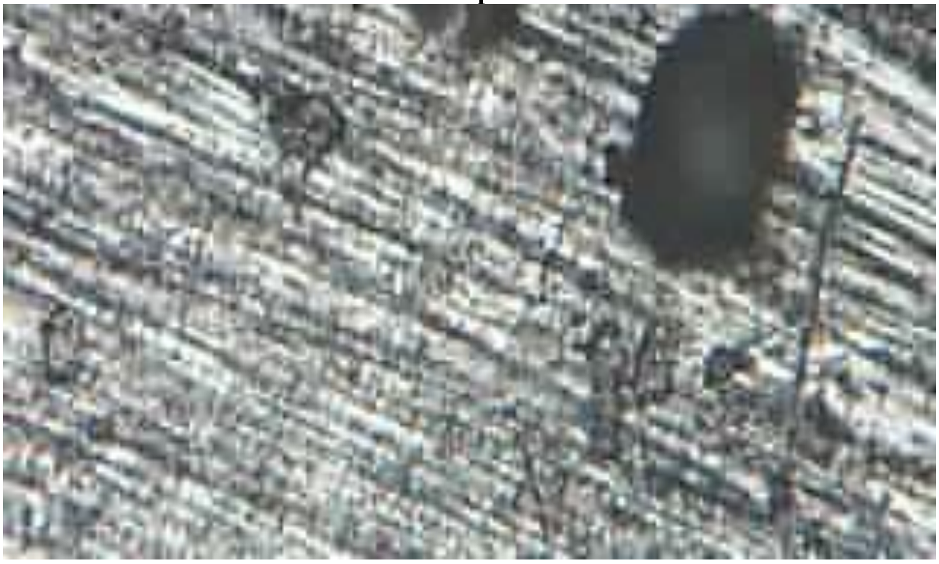

Fig. 23 Corrosion on surface of carbon steel in kerosene + 10% V NaCl with CO_2 at 328 K and 400 r.p.m.

Figures 24 shows the pitting formation on the surface for carbon steel. The observed pits are clearly not deep with small size in large numbers compared with the other specimens.

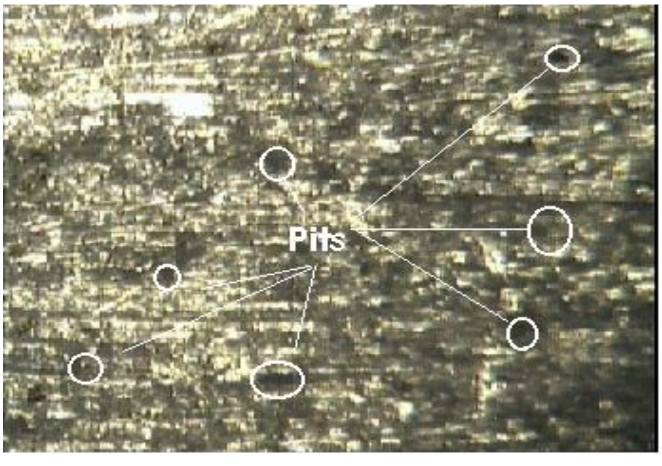

Fig. 24 Corrosion on surface of carbon steel in kerosene pure at 318 K and 0 r.p.m

Conclusion:

From the present study, the following conclusions are drawn:

1.The corrosion rate is higher with the presence of CO_2 gas than that with out CO_2 gas.

2.The corrosion rate in general increases with increasing flow rate and temperature.

3.If the concentration of the carbonate in the solution is not saturated, the Iron carbonate film formed appears to be a loose film.The dependent of temperature and flow rate are the important conditions.

4.The corrosion potential shifted to more noble values with increasing the flow rate and shifted to more negative with increasing the temperature.

5.The corrosion potentials and corrosion rates were found to be under mixed control of the anodic and cathodic processes. The corrosion rates increased with increasing temperature according to Arrhenius equation. The flow rate had significant effect on the corrosion potentials.

6.The present investigation has featured the corrosive nature of some samples of kerosen and gas oil ; and it appears that corrosion of carbon steel metal surface which in contact with these liquids is increased more significantly as the temperature is raised.

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Table : Sample Definition

6	**Definition**	**Unit**
I	Current Density	mA/cm^2
i_{corr}	Corrosion Current Density	mA/cm^2
n	Number of Electrons	
R	Gas Constant 8.314	J/(gmole) . K
O . d	Outer diameter of Cylinder Specimen	Cm
i . d	Inner diameter of Cylinder Specimen	Cm
T	Temperature	K

Subscripts

A	Anodic
C	*Cathodic*
Corr.	Corrosion

Abbreviations

ppm	Parts Per Million
RCE	Rotating Cylinder Electrode
RPM(r.p.m)	Rotation Per Minute
S.C.E	Saturated Calomel Electrode
S.H.E	Saturated Hydrogen Electrode
Mpy	Mils per year
S .I .E.R	State Inspection Engineering Rehabilitation