Variable Conditions Effect On Polarization Parameters Of Impressed Current Cathodic Protection Of Low Carbon Steel Pipes

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Abstract

Cathodic protection is an effective electrochemical technique for preventing corrosion of metallic structures. It has widespread applications on various structures, suffering serious problems of corrosion in the environments.

The main problem with this protection method is to determine the parameters (current density and potential). The previous works in this area used classical statistical methods to determine these parameters.

In order to determine the cathodic protection potential, it is important to deal with the electrochemical studies of open circuit potential (OCP) and polarization investigations of low carbon steel used in pipeline application in 3.5 % NaCl solution at temperature range(30- 50°C).These studies define the corrosion potential and also help one to understand the corrosion behavior of the used metal (low carbon steel). This system was used to investigate the influence of various conditions on the minimum cathodic protection current that would provide a full cathodic protection for steel tube immersed in sea water. The variable conditions studied are concentration of (0.01 – 3.5) % NaCl , temperature (30- 50°C), distance between pipe (cathode) and graphite electrode (anode) of (10 – 20) cm and pH solution of (5.0 – 9.0) using a selected range of these conditions, the experimental results for the minimum cathodic protection current were obtained and recorded.

The electrochemical results show that cathodic protection current density increases with increasing temperature and concentration. The current density also slightly increases with increase distance between cathode and anode.

The effective sequence of these parameters on cathodic current density is as follows:
Temperature > concentration > pH solution > cathode – anode distance .

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1- **Introduction**

Corrosion is an electrochemical reaction based on universal laws of nature. All metallic structures corrode, steel, for example is a man made substance produced from iron oxide. The energy added in the refining process is unstable given a suitable environment; steel will release this energy and return to its natural state of iron ore [1]. The cost of corrosion has been estimated at $300 billion per year in the United States. The corrosion-related cost to the transmission pipeline industry is approximately $5.4 to $8.6 billion annually. This can be divided into the cost of failures, capital, and operations and maintenance (O&M) at 10,38, and 52 percent, respectively[2]. Cathodic protection is an electrochemical technique for preventing corrosion of a metal exposed to an electrolyte .The process involves application of DC electrical current to the metal surface from an external source .The external source can be either a commercial power source or through connection to sacrificial metals such as magnesium or aluminum [3,4,5].

Cathodic protection (CP) is perhaps the most important of all approaches to corrosion control. By means of an externally applied electric current , corrosion is reduced virtually to zero, and a metal surface can be maintained in a corrosion environment without deterioration for an indefinite time [6].

Galvanic cathodic protection uses anodes which have a natural potential more reactive than that of the structure being protected. For steel structures, magnesium and zinc have proven

practical for buried applications, while aluminum and zinc are used to protect marine structures. It is also possible to use an external power source to impress current on a relatively inert material such as cast iron, graphite or mixed metal oxide anodes; this method is called impressed current cathodic protection [1].

The difference between the two methods is that the galvanic system relies on the difference in potential between the anode and the pipe, and the impressed current system uses an external power source to drive the electrical cell [7]. The two mentioned methods require the identification of the polarization parameters (current density and potential). The methods used for the identification of the polarization parameters of cathodic protection systems are the statistical method.

2- **Experimental Work**
2.1 Material

The material used in this work is low carbon steel pipe (ASTM A179-84a) type as X60 of (3) cm out side diameter and (2) cm in side diameter. Analysis of these specimens was carried out using (spectrometer DV.4) in Nasser Company. Table (1) shows the nominal and the analytical chemical compositions of the carbon steel pipe.

2.2 Solution

The solution was prepared experimentally in different concentrations of (0.01 %, 0.1 %, 1 %, 2 % & 3.5 %) by adding different weights of (0.1, 1, 10, 20&35) gm sodium chloride NaCl to 1 litter of distilled water. The NaCl purity = 99.55 %, supplied by BDH Ltd. was used in the experiment.

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2.3 Experimental Procedure
2.3.1 Specimen Preparation

The specimens were cut out in dimensions of (1.5) cm length and (3) cm out side diameter for polarization test , and (10) cm length and (3) cm out side diameter for impressed current cathodic protection procedure . The specimens were annealed at 300°C and derotor type furnace to release stresses [9]. After cutting, specimens were a braded in sequence on 180,220,320,500,800 and 1000 grades of emery papers under running tap water on a hand grider. Before each experiment run , the specimen was immersed in 3% HCl for 30 minutes , type annular hydrochloric acid of concentration 35% supplied by BDH chemicals Ltd. , then washed with distilled water to clean it , dried with paper tissue followed by immersing in annular Ethanol for 2 minutes , type $C_2 H_4$ OH of concentration = 99% supplied BDH chemicals Ltd. , then dried and immersed in annular Acetone for 2 minutes , type $C_3 H_6$ OH of concentration = 99% supplied BDH chemicals Ltd. and finally left to dry for 1 hour at $60^°C$ in the electrical furnace. Weighting of the specimens was carried out using a digital balance.

2.3.2 Open Circuit Potential Test

After the supplying of (3.5 %) NaCl solution to the cell, the free corrosion potential was measured with respect to Saturated Calomel Electrode (SCE) with time using the digital ammeter. E_{corr} value was recorded, till it reaches a steady state value. This steady state value is reached after 180 min and it can be considered the actual E_{corr} in this environment.

2.3.3 Polarization Investigation Test

Polarization was carried out using potentiostatic after the electrolyte was prepared to obtain 3.5 (wt) % NaCl then the glass bath was put in water bath with a thermo stirrer used to control the temperature of the solution to set the required temperature and after

achieving the temperature homogenization, the working electrode tube was a 1.5 cm length and 3 cm outside diameter and an electrical connector was connected to the pipe. The potentiostatic circuit as shown in figure 1 was set to position to start the potentiostatic technique to plot the behavior of specimen (CS) at the studying temperature of 3.5%NaCl solution.

By applying the potential from potentiostat and at each setting, the potential applied and the current were recorded using the voltmeter and ammeter respectively after (1min) between each setting in order to reach a steady state value of the polarization process. The potentiostatic polarization curves were recorded by a constant sweep rate of 10 mV/min.

When the run ended by putting off the potentiostat, glass bath (salt bath) emptied from the used electrolyte and washed by distilled water to make sure that there was no electrolyte left in the system. The above procedure was repeated exactly for other conditions of temperature and at constant 3.5% NaCl solution.

2.3.4 Impressed Current Cathodic Protection (ICCP) Test

The tube specimen was cut with dimensions 10cm length and 3cm outside diameter and these specimens were used for all impressed current cathodic protection procedures. The electrolyte was stirred by using mechanical stirrer to obtain a homogenous solution and then using the heater controller in the bath to set the solution at the required temperature and after achieving the temperature homogenization, the experiments were started.

Before starting each run, the cross sectional area of one end of the specimens closed using a rubber stopper then covered by thermal silicon to ensure that no water enter the inner tube

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surface, and the other end isolated using plastic tube. The electrical connection (connection point) then fixed into plastic stand and passed through the above plastic tube. An auxiliary electrode entered the electrolyte at 5cm from solution surface level then the electrical circuit (ICCPS) was connected as shown in Figure 2.

After switching on the electrical circuit and supplying the E_{corr} of (-850 mV vs. SCE) from potentiostat the impressed current was recorded at intervals of 1 min over a period of 20 min by using the digital ammeter. The experiments were ended when the (icp) reached the steady state value giving the best value of impressed current cathodic protection.

In order to obtain the effects of the studied parameters on (ICCPS) like temperature, distance between cathode and anode, electrolyte concentration and PH, the above procedures were repeated for each run, but this was done after the glass bath was emptied from the used solution and washed by distilled water to ensure that no salt was left in the glass bath.

3- Results and Discussion
3.1 Effect of Conditions
3.1.1 Temperature
In this section, the effects of temperature on corrosion potential, limiting current density and cathodic protection current density are discussed.
3.1.1.1 Open Circuit Potential Curves
Figure (3) shows the variations in the open circuit potential (OCP) of low carbon steel specimens with time at temperature range of 30 – 50 °C during their immersion time in 3.5% NaCl solution with a fixed distance between cathode and anode of 10 cm. The potential was measured every 5 minutes for all the time of the test. This Figure indicates that the corrosion potentials increase in the negative direction with an increase in temperature from 30 to 50 °C. All these curves are

started at a relatively different potential range within -540 to -600 mV relative to temperature increase from 30 to 50 °C. The steady state potentials for these Figures are increased in the negative direction from -620 to -700 mV relative to temperature increase from 30 to 50 °C .The steady state potentials are achieved after 130,120 100,70 and 100 minutes respectively. The reduction in the established time for the steady state potential is related to temperature increase. This can be explained due to the chloride ions mobility increases with increase in temperature[10]

In general, the potential for low carbon steel is changed with temperature from an initial high negative value to more negative value within 130-70 minutes in which steady state potential values are established for all curves.

3.1.1.2 Polarization Curves
The polarization curves of low carbon steel in the temperature range of 30 - 50°C at 3.5% NaCl solution and 10 cm distance between cathode and anode are shown in Figure (4).This Figure is typical polarization curves for low carbon steel which show two regions ;cathodic and anodic regions. The cathodic region is displaced to the potential axis due to an increase in solution temperature from 30 to 50 °C.

The corrosion potential from these polarization curves are increased in the negative direction with increase in temperature from 30-50°C. The corrosion potentials obtained from open circuit Figure (3) and polarization curves Figure (4) are tabulated in Table 2.These values are very close to each others and the slight differences are due to resistance polarization of the solution. Pipelines operation shows that the temperature varies between seasons or the climatic changes. The temperature can modify the interaction between steel electrode and the electrolyte. In the studied temperature range of 30-50°C ,the corrosion current density increases

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with increasing temperature and the steel corrosion potential moves towards the negative values when the temperature increases in the studied solutions. The polarization curves present parallel Tafel straight lines indicating that the oxygen reduction reaction to steel surface is always done according to concentration mechanism in all the temperature range from 30-50 °C .This conclusion agreas with the work of foroutis[11].In general, an increase in temperature of corroding system increases the rate of chemical reaction, decreases the solubility of gases in solution changes the solubility of some of the reaction product [7] .

3.1.1.3 Limiting Current Density

A series of experiments were carried out at various controlled cathodic currents with recording the corresponding potentials. The purpose of carrying out these experiments was to find effect of the temperature on the uniformity of the limiting current. The results of the polarization curve as given in Figure (5) shows that the limiting current density (minimum cathodic protection current density) increases with increasing temperature and NaCl concentrations. This is due to a combination of factors first the common effect of temperature on the reaction kinetics themselves and the higher diffusion rate of many corrosion by-products at increased temperatures. This can be attributed to the relaxation of electrons mobility, so that limiting current density increases with decreased environment resistivity[10]. The limiting current density (i_L) is the most important characteristic of the cathodic region under diffusion control by oxygen reduction reaction. It allows determining the minimum cathodic protection current density [10].

3.1.1.4 Cathodic Protection Current Density

Experiments were carried out at constant protection potential of (-

850 mV) with recorded current densities at different temperatures and concentrations for different distances (D) between cathode and anode. These variables are shown in Figure (6). Cathodic protection current density increases as temperature and NaCl concentration increase .This can be attributed to the relaxation of the electrons (given by the anodic reaction) mobility, so that conductivity will increase due to decrease in environment resistivity[10].

Figure (6) shows that the higher value of cathodic protection current density is observed at higher NaCl concentration at the same temperature and fixed distance of 10 cm. This can be explained as a result of increasing chloride ions mobility with increase in temperature and conductivity in sea water [12].

3.1.2 Concentration

Figure (7) shows the effect of the solutions concentration on cathodic protection current density at various operating conditions of temperature and distance between cathode and anode. The cathodic protection current density is increased when the solution temperature increases at various NaCl concentrations and at fixed distance of 10 cm.

The bulk oxygen concentration in the electrolyte decreases with increasing NaCl concentration. An increase in solution temperature from 30 to 50 ◦C, cathodic protection current density is increased and this also increases with increase in NaCl concentrations. This is due to the fact that chloride ions mobility increases with increase in temperature which will increase solution conductivity.

This induces an increase in the cathodic protection current density. The cathodic protection current can be reduced with decrease in NaCl solution concentration. Therefore, the applied current needed to protect the

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pipe increases in the marine application than any other environments.

3.1.3 Distance Between Cathode and Anode

Figure (8) illustrates the relationship between cathodic protection current density (i_{cp}) and distance between cathode and anode. It can be observed that cathodic protection current density increases slightly with distance at lower concentration and higher value is observed at high concentration of 3.5% NaCl. Greater distance between cathode and anode shows higher current density values. The higher current density needed is due to the electrolyte resistance increase [12], also the increase in distance between cathode and anode will cause best distribution of cathodic protection current density, then the whole pipe surface will receive a uniform cathodic protection current density [13].

The conductivity of electrolyte decreases with increasing distance between cathode and anode (D), so that cathodic protection current density increases with an increase in solution resistance [14].

3.1.4 pH Solution

Figure (9) indicates the relation between cathodic protection current density and pH in the temperature range of 30-50°C at fixed distance between cathode and anode of 10 cm. The current density increases with increase in pH and temperature. The effect of temperature is clearly higher than that of pH. The current density increases with increase in pH and distance between cathode and anode. All these curves are started at a relatively different current density range within 22 to 36 µA at pH value of 5.0 relative to temperature increase from 30 to 50 °C while this difference becomes higher when current density range is within 37 to 53 µA at pH 9.0 and temperature increases from 30 to 50°C. The cathodic protection current density is a function of pH and temperature. In neutral pH, oxygen reduction reaction and diffusion speed are favorable in reaction with increase in temperature and cause a reduction in solubility. In acidic pH, corrosion speed grows in an exponential form with the temperature because of the over tension reduction of hydrogen release.

The temperature effect is more active than distance effect on cathodic protection current density. The sequence effect on cathodic protection current density is:

Temperature > concentration > pH solution > distance between cathode and anode.

The arrangements of the four parameters studied are shown in Table 3 with the response of minimum cathodic protection current density i_{cp} ($\mu A/cm^2$) accomplished by the experimental work.

4- Conclusions

The conclusion from the research work that has been presented in last paper is as flows:

1. Cathodic protection current density and limiting current density increase with increasing temperatures.
2. Cathodic protection current density increases with increasing distance between cathode and anode.
3. The sequence effects of temperature, concentration, distance between anode and cathode and pH solution on cathodic protection current density is as follows:

Temperature > concentration > pH solution > distance between anode and cathode.

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Table (1) A nominal[15] and the analytical chemical compositions of carbon steel pipe

chemical composition	C %	Mn %	P %	S %	Cr %	Ni %	Mo %	V %	Cu %	Fe %
A nominal	0.199	1.95	0.016	0.018	0.015	0.007	0.008	0.004	0.024	Rem.
Analytical	0.191	1.95	0.014	0.015	0.015	0.003	0.008	0.003	0.028	Rem.

Table (2) Corrosion potential at different solution temperatures

T(°C)	30	35	40	45	50
$E_{corr.}$(mV) from polarization Curve	-620	-640	-660	-680	-698
$E_{corr.}$(mV) from $E_{corr.}$ Vs. Time	-618	-648	-667	-681	-694

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Table (3) The conditions for the calculation of i_{cp} at E_{cp}(-850 mV).

No.	C(%)	T(°c)	D(cm)	pH	i_{cp} ($\mu A/cm^2$)
1	3.5	30	10	9.0	26.648
2	2	30	20	8.5	24.840
3	1	30	15	7.0	24.091
4	0.1	30	10	6.5	24.222
5	0.01	30	10	5.0	23.553
6	0.01	30	20	5.0	23.919
7	3.5	35	15	9.0	33.129
8	2	35	20	8.5	32.726
9	1	35	10	7.0	30.761
10	0.1	35	20	6.5	29.918
11	0.01	35	15	5.0	29.228
12	0.1	35	10	7.0	29.001
13	3.5	40	20	9.0	40.787
14	2	40	15	8.5	39.267
15	1	40	10	7.0	38.825
16	0.1	40	15	6.5	37.511
17	0.01	40	10	5.0	36.922
18	1	40	20	7.0	39.115
19	3.5	45	10	9.0	45.949
20	2	45	20	8.5	44.713
21	1	45	15	7.0	43.883
22	0.1	45	20	6.5	43.125
23	0.01	45	15	5.0	42.000
24	2	45	10	8.5	44.018
25	3.5	50	10	9.0	52.641
26	2	50	15	8.5	51.405
27	1	50	10	7.0	50.912
28	0.1	50	15	6.5	49.416
29	0.01	50	20	5.0	48.026
30	3.5	50	20	9.0	53.157

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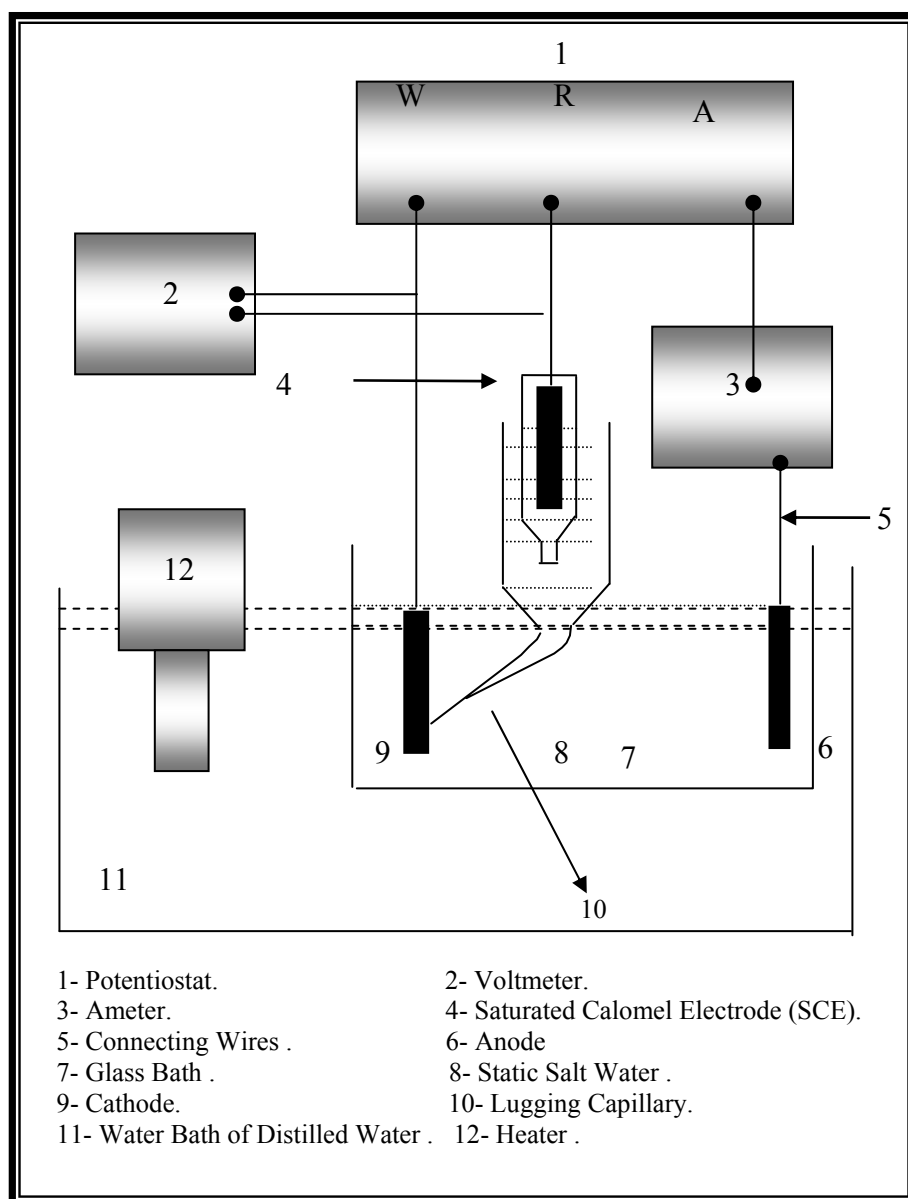** Nasser State Company For Mechanical Industries

Figure (1) A simple sketch of polarization circuits.

The figure contains the following legend:

1- Potentiostat.
3- Ameter.
5- Connecting Wires .
7- Glass Bath .
9- Cathode.
11- Water Bath of Distilled Water .

2- Voltmeter.
4- Saturated Calomel Electrode (SCE).
6- Anode
8- Static Salt Water .
10- Lugging Capillary.
12- Heater .

1- Potentiostat.
3- Ameter.
5-Stands.
7- Cathode.
9- Saturated Calomel Electrode (SCE) .
11- Heater .

2- Voltmeter.
4- Connecting Wires.
6- Pipe Plastic.
8- Lugging Capillary.
10- Anode .
12- Water Bath of Distilled water.
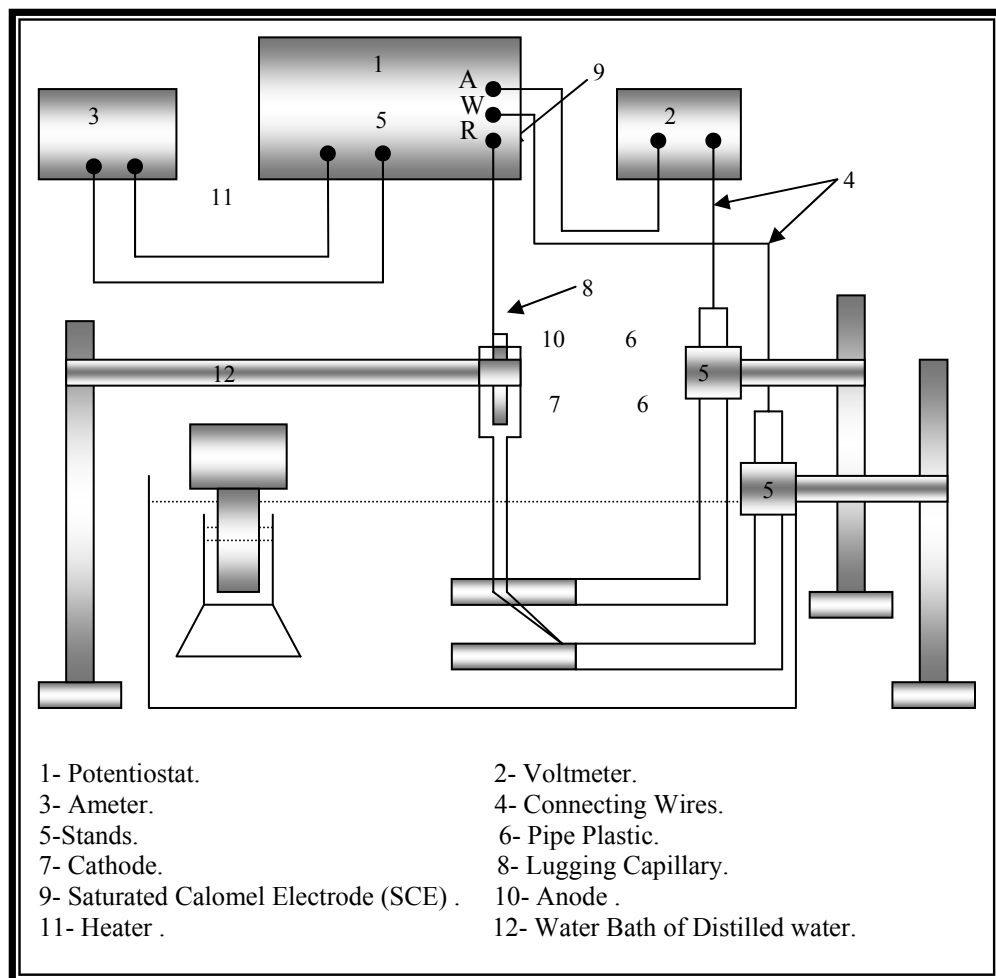
Figure (2) A simple sketch showing the laboratory plane design of cathodic protection (ICCPS).

Figure (3) potential vs. Time curves for carbon steel.
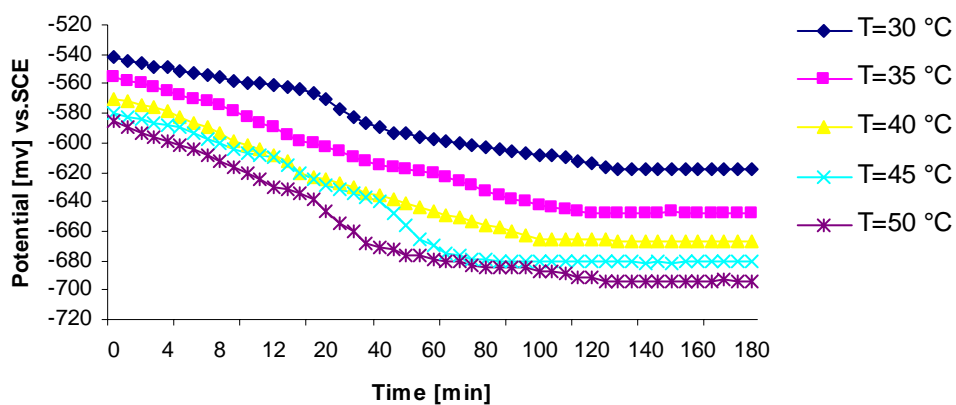
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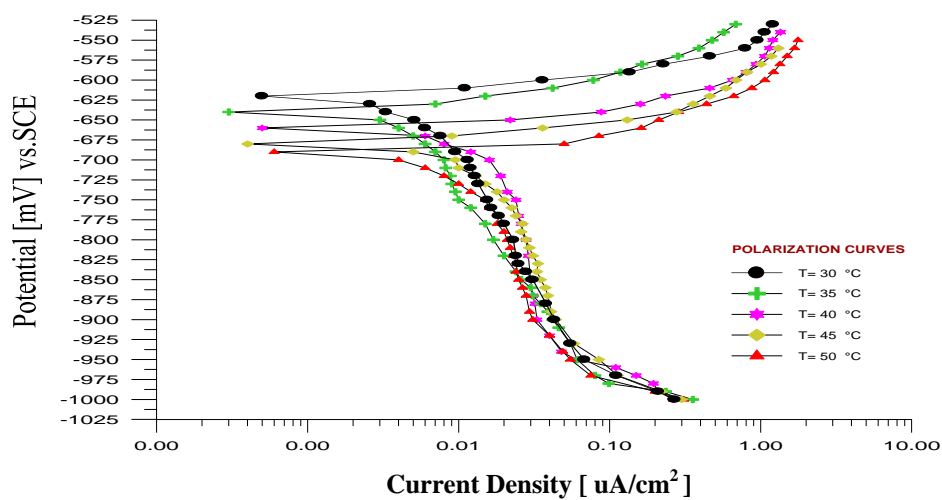
Figure (4) Polarization curves for carbon steel.

$$i_L = 1.225*T+28.25$$
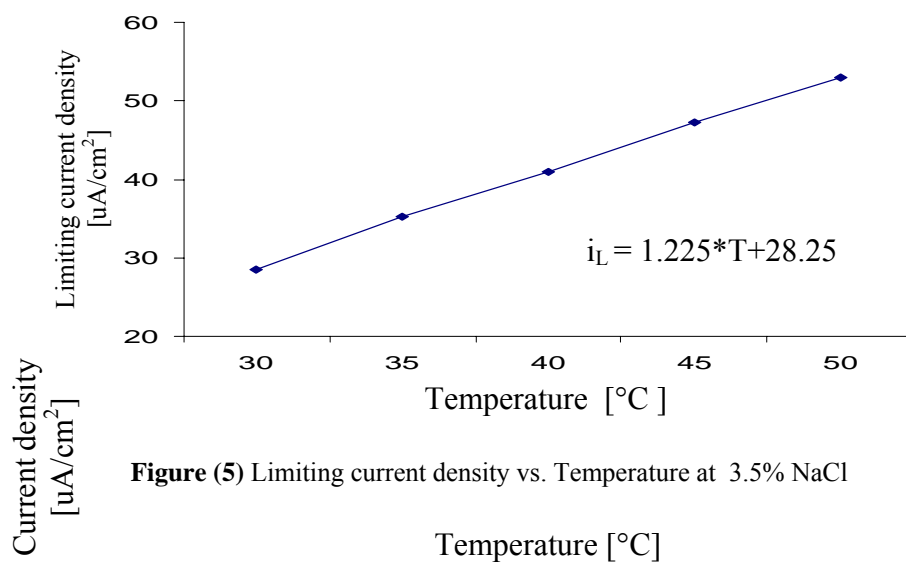
Figure (5) Limiting current density vs. Temperature at 3.5% NaCl
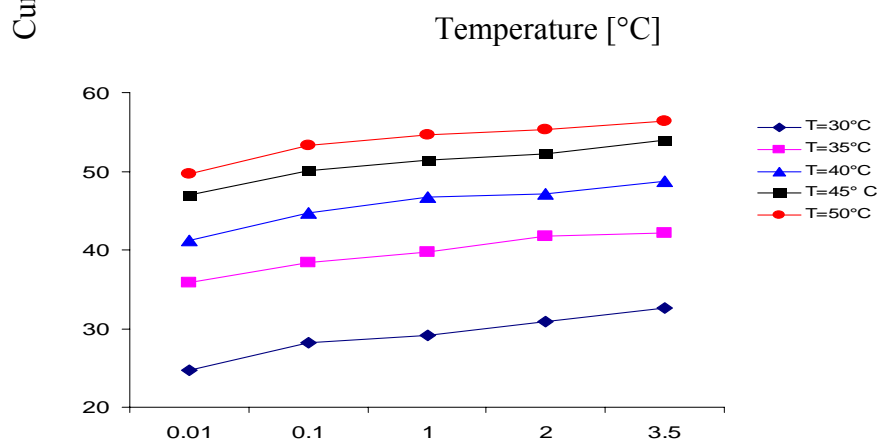
Figure (7) Current density vs. concentration D=10 cm and-850mV.

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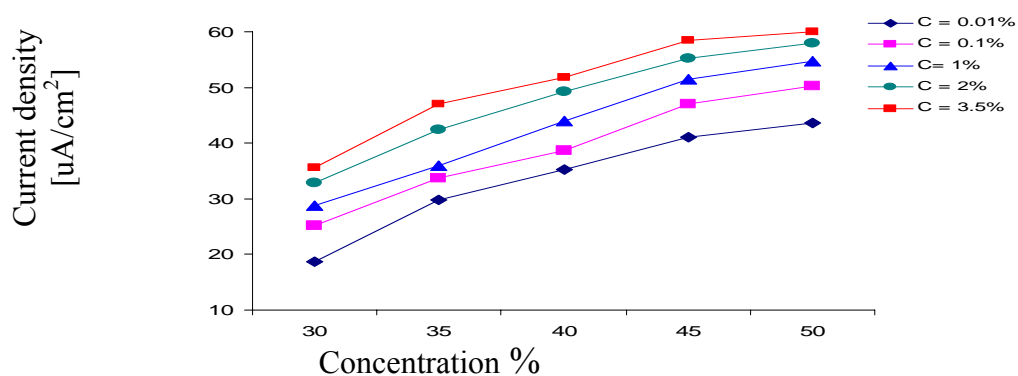** Nasser State Company For Mechanical Industries

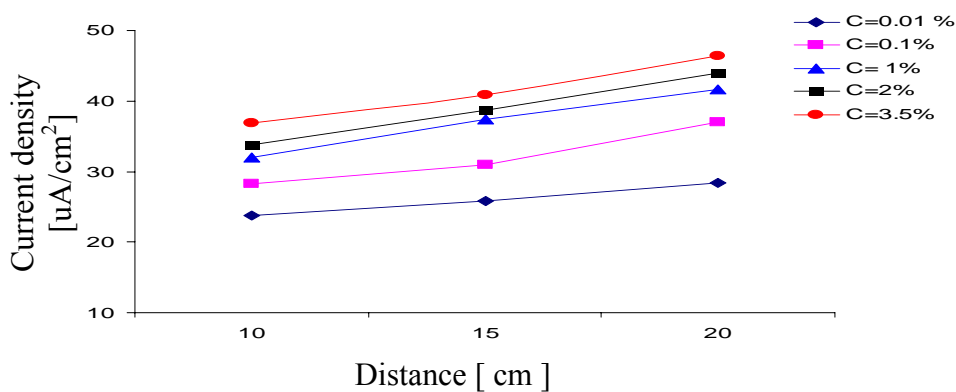**Figure (6)** Current density vs. Temperature at D=10 cm and -850mV.

Figure (8) Current density vs. distance between cathode and anode at T=30°C and -850mV.
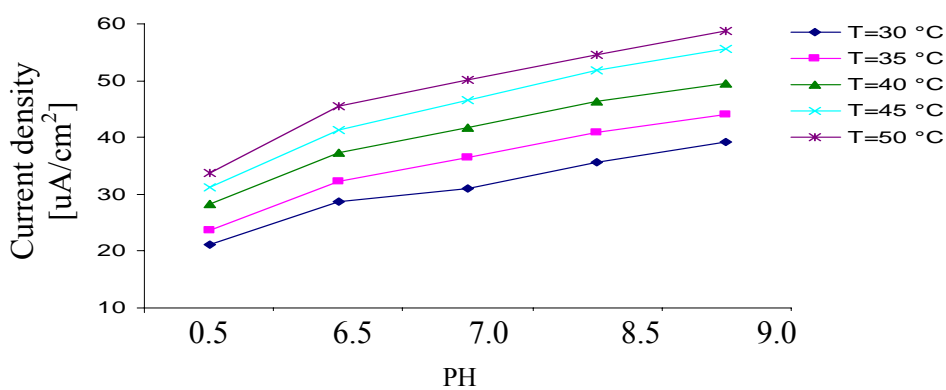

Figure (9) Current density vs. PH at distance between cathode and anode = 10 cm and -850mV.

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