

Corrosion Behavior of Buried Carbon Steel Pipeline In Iraqi Soil in Different Sodium Chloride Concentrations

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ABSTRACT : In this work, external corrosion behavior of oil pipeline was evaluated using potentiodynamic polarization curves. The corroding metal was carbon steel. To estimate corrosion by potential and current density of carbon steel, different concentrations of sodium chloride were chosen and prepared in the laboratory to simulate external condition of buried carbon steel pipeline in Iraqi soil. NaCl concentration in Iraqi soil was tested by taking samples from different areas, from north to south of Iraq. pH of soil samples were ranged from acidic to basic. Temperature of prepared solutions was constant at 35^o C which Iraq environment is hot most of the year. Carbon steel coupon of (ASTM A179-84A) type was used as the studied metal. Potentiodynamic polarization curves, of potential vs. log current density, were obtained using M Lab Multi-Channel Potentiostat/Galvanostat. The results revealed the behavior of carbon steel in different chloride concentrations, pH, and relatively high temperature. The rate of corrosion increases with the increase in chloride concentration, and decreases with acidity decrease. Triple relationship between these parameters was studied.

KEYWORDS -Corrosion, Carbon steel, Potentiodynamic Polarization, Chloride.

Date of Submission: 25-05-2018

Date of acceptance: 09-06-2018

I INTRODUCTION

Pipelines play a critical role worldwide as means of transporting fuels of gas and oil over long distances from the sources to the end consumers. Pipelines are subjected to environment change, whether they are extended under the sea or underground or constructed on the ground. Corrosion has the major impact on pipelines. This impact on buried pipelines called external corrosion and it is a combine effect of moist, temperature, pH, salts types and concentrations, type of soil conductivity and resistivity, type of pipeline alloy material and concentration of oxygen in soil. Most important of them are moist, pH, temperature and salts, especially chlorides.

The reason behind extensive studies of corrosion is the cost of pipelines failure; it is a threat to the oil and gas industries. This threat comes mostly in three forms: financially, waste of resources, and danger of accidents. In addition to this threat, expensive cost and time spending in replacing, repairing, and maintaining the corroded parts still being a big deal of issue to the oil and gas companies [1-6].

Iraqi soil corrosively represented by the effect of chloride concentrations and acidity as well as temperature on buried pipeline. It was not studied specifically especially on carbon steel. And that is the aim of this work and our further work, to provide database to the oil and gas companies of the government to evaluate the problem indeed.

With little fanfare, a significant milestone in the effect of corrosion on the global economy will occur when database of corrosion is presented to the world to get attention to this enormous and continual problem that puts not only pipelines in danger but any industry uses carbon steel or any kind of iron alloys such as bridges, skyscrapers, tunnels and defense industries. The National Association of Corrosion Engineers, NACE, reported in its 2016 NACE International Impact Report: International Measures of Prevention, Application, and Economics of Corrosion Technologies Study, that the global cost of corrosion is estimated to be 2.5 trillion US\$, which is equivalent to 3.4% of the global Gross Domestic Product (GDP) in 2013 [7].

Pipelines are subjected to corrosion due to its metallurgy. They are commonly based on carbon steel. Carbon gives the steel good mechanical properties and is also relatively cost effective. But the problem still standing of corrosion and its damage [8]. Corrosion that occurs in buried or partially buried carbon steel

pipelines is caused by curried current flow from anode to cathode through the ground of ionic conductivity and from cathode to anode through metal by electric conductivity [9].

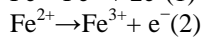
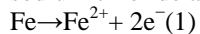
Corrosion is a result of two reactions: Oxidation reaction which happens at the anode and reduction reaction happens at the cathode. Carbon steel has been one of the most extensively studied metal worldwide due to its importance as a metal used in almost every industry in the world.

In neutral solution, oxide ion or hydroxide ion, which composes right at the metal surface, forms characteristic layers. Significant structure formed by these layers, could be determined by anions present in solution [10]. Monitoring the behavior of carbon steel corrosion in acidic and alkaline medium is applied in this work using potentiodynamic polarization technique. This technique measures potential and current of oxidation/reduction reactions. In result, corrosion rates are obtained and evaluated.

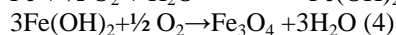
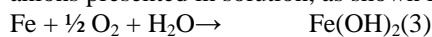
Potentiodynamic polarization technique is generally used to obtain a qualitative picture or “fingerprint” of a molecule or an ion in a given solution. It also reveals specific information such as:

1. The potential region over which the specimen remains passive.
2. The corrosion rate in the passive region.
3. The ability of the material to spontaneously passivate in the particular medium [11].

In previous work [12-14], results show that carbon steel as iron metal corrodes when immersed in solutions of sodium chloride and dissolute into ferrous and ferric cations as follows:



On the other hand, oxide layers are being developed and cumulated on the surface of iron. These layers would slow down the corrosion for some while and sort of protect the surface from being further attacked by chloride anions presented in solution, as shown in the following reactions [12, 14]:



It has also been recorded [15] that iron and carbon steel could produce up to nine different oxide phases on the metal surface. Most of these iron oxides dissolve under the attack of chloride anions and the increased applied potential in the positive direction during the electrochemical polarization process [12-14, 16-17].

The object of this paper, is to investigate the corrosion effect of chloride ion on carbon steel of oil pipeline in Iraqi soil simulating conditions of salt and acidic and basic medium, as concentrations are shown in the experimental work. Methodology used is Potentiodynamic polarization technique.

II EXPERIMENTAL WORK

2.1 Preparation of Material

The metal used in this work is low carbon steel coupons (ASTM A179-84A) [18].

Table (1) Nominal and analytical chemical compositions of carbon steel

Chemical Composition	Nominal	Analytical
C %	0.199	0.191
Mn %	1.95	1.95
P %	0.016	0.014
S %	0.018	0.015
Cr %	0.015	0.015
Ni %	0.007	0.003
Mo %	0.008	0.008
V %	0.004	0.003
Cu %	0.024	0.028
Fe %	Rem.	Rem.

Chemical composition is shown in Table (1). Flat coupons were used with dimensions of (1cm×1cm). Coupons surfaces were polished with silicon carbide (SiC) paper (Electro Coated Waterproof Abrasive Paper, High Degree of Brightness 6M1 HORSE AA240 grit size). After that, the faces and edges of coupons were grinded using UNIPOL-820 grinding / polishing machine, equipped with grinding disk and water supply. Rotation speed was adapted as the following speeds: 100, 150, 200, 250, 300, 350, 400 cycle/sec running under tap water. Then, silicon carbide round disk was used, initially with 400 grade and thereafter with 1200 grade. Degreasing was produced, after polishing processes, by immersing the coupons into acetone after whipping them with benzene wet cloth. Final step of preparation each coupon, was to preserve them in a dessicator to prevent moisture contact.

2.2 Preparation of Solutions

Solutions of pH = 5 and pH = 9 were prepared using HCl and NaOH. Stock solutions of HCl and NaOH of 1 M were prepared. After that solutions of 0.01 M of each HCl and NaOH were prepared from the stock solutions. Solutions of pH = 5 and pH = 9 were prepared from the later, where the increase in Cl^- and Na^+ from the acid and base were accounted to be negligible [19]. Concentrations of chloride salt, represented by NaCl, were chosen according to their presence in Iraqi soil.

Soil samples were taken from different locations in Iraqi nearby pipelines. Concentrations of chlorides in samples were measured using titration with silver nitrate. Potassium chromate was used as an indicator. Results were ranged from 300ppm to 3500ppm (in average). pH of samples were ranged from acidic to alkaline. In this work we focused on pH = 5 and pH = 9. Temperature of all solutions was maintained at 35°C .

2.3 Polarization Investigation Test

Electrochemical polarization experiments were carried out using a potentiostat, M Lab Multi-Channel Potentiostat/Galvanostat. The auxiliary or counter electrode was graphite carbon rod. In all experiments, potentials were measured against a saturated calomel electrode. The measurements were carried out in a three electrode cell type using a computer assisted with potentiostat. A thermo stirrer was used to maintain the required temperature (35°C) and to achieve temperature homogenization in solution.

2.4 Open Circuit Potential Test

After preparation of cell solutions and electrodes, the free corrosion potential was measured with respect to saturated calomel (SCE) with time using digital ammeter. The exposure area of the working electrode (carbon steel coupon) must be (1cm^2) only to obtain the correct value of free corrosion potential of the coupon at each measurement. Corrosion potential value was recorded till it reached a steady state value. It takes about 30 minutes for the steady state to develop.

2.5 Potentiodynamic Polarization Tests

Potentiodynamic tests were carried out after preparation of salt solutions of chloride (as NaCl) with concentrations of 300ppm, 1100ppm, 1900ppm, 2700ppm, 3500ppm. Each prepared with pH = 5 and pH = 9 where temperature was set at 35°C . These solution parameters were based on the tests of Iraqi soil which were taken from different places in Iraq, from the north to the south in depth of 2-3 meters underground.

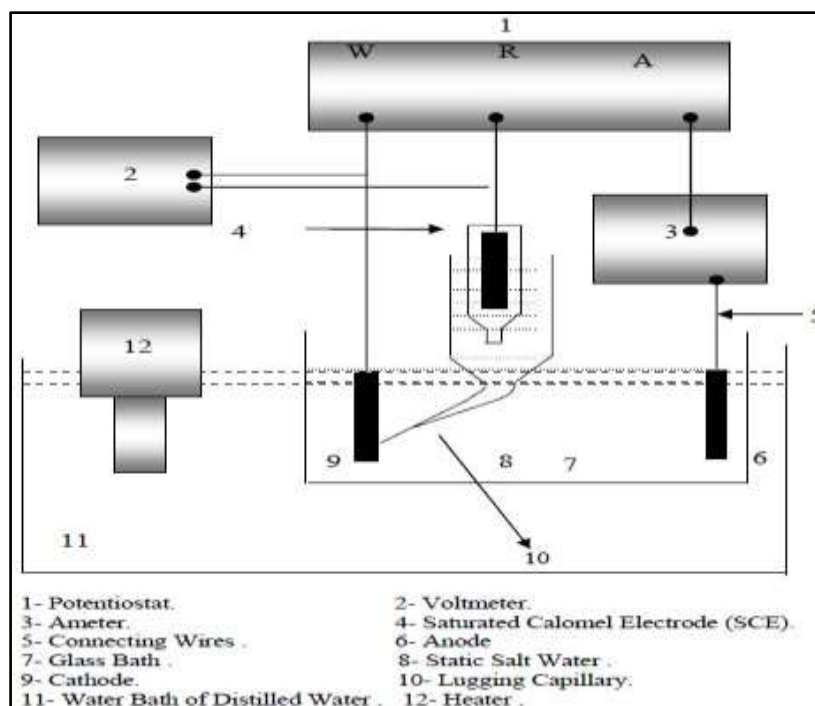


Figure (1) Polarization cell circuit.

The potentiodynamic polarization cell circuit as shown in Figure (1) was set up in position to start the potentiodynamic polarization tests in order to plot curves of the behavior of carbon steel at the studied solutions of different chloride concentration at pH = 5 and pH = 9 where temperature is constant.

The potential applied from the Potentiostat and the current were recorded using M Lab software of the computerized Potentiostat. For precise test, time step between each recorded points was set to 500m.sec in the software. The potentiodynamic polarization curves were obtained and recorded by a constant sweep rate of 2.0 mV/sec. M Lab Multi-Channel Potentiostat/Galvanostat gives automatic results of corrosion (i_{corr}), anodic and cathodic slopes (b_a , b_c respectively), weight loss (gmd) and penetration loss (mmy), curve of potential vs log rate of corrosion were obtained.

III RESULTS AND DISCUSSION

3.1 Results

Potentiodynamic curves were plotted between potential and the log of current density. Each curve shows the behavior of carbon steel at different conditions of chloride concentration, which represented by NaCl at pH = 5 and pH = 9 and temperature higher than room temperature, at 35°C

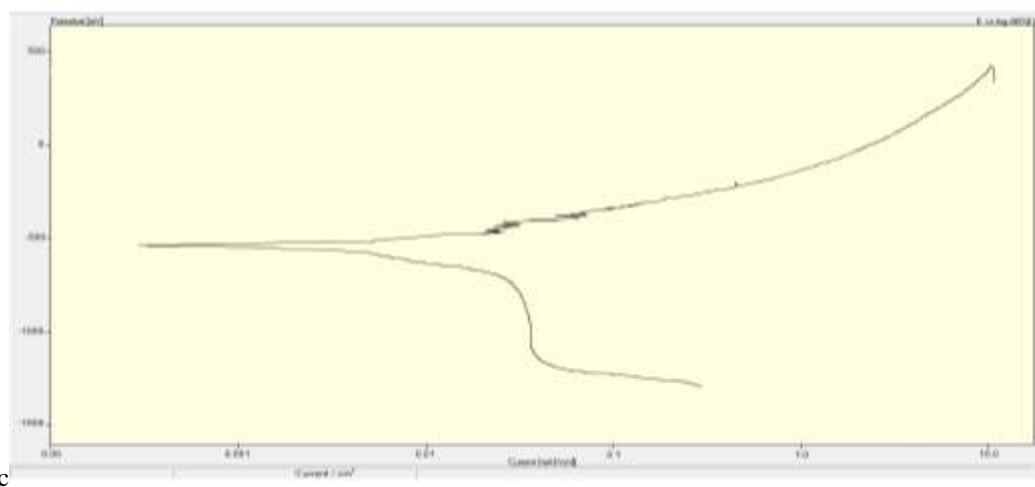


Figure (2) Potentiodynamic polarization curve of carbon steel in solution of (300) ppm concentration of NaCl and pH= (5) at 35°C

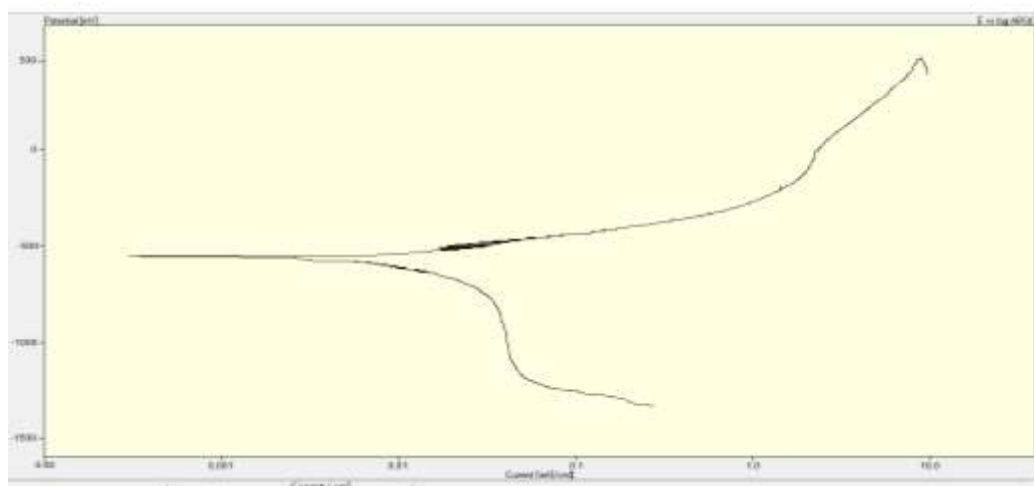


Figure (3) Potentiodynamic polarization curve of carbon steel in solution of (1100) ppm concentration of NaCl and pH= (5) at 35°C

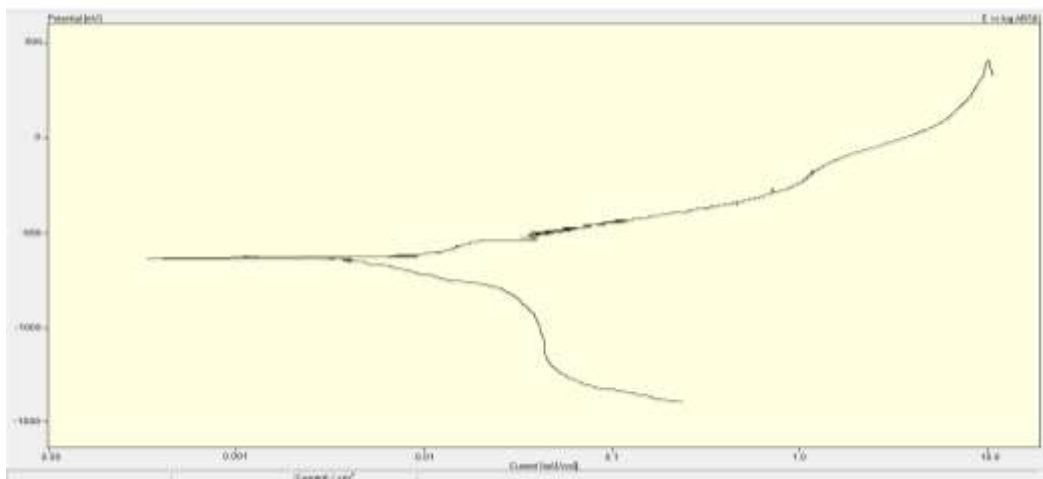


Figure (4) Potentiodynamic polarization curve of carbon steel in solution of(1900) ppm concentration of NaCl and pH= (5) at 35⁰C

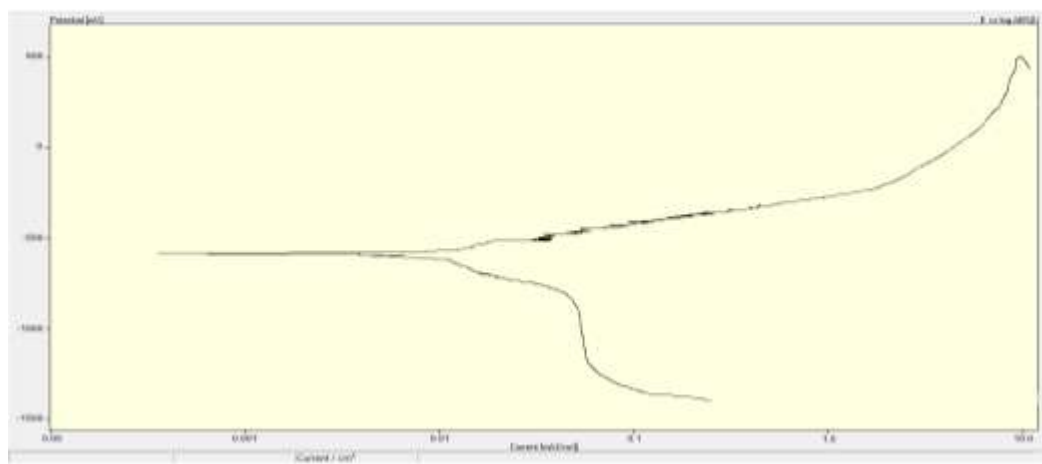


Figure (5) Potentiodynamic polarization curve of carbon steel in solution of(2700) ppm concentration of NaCl and pH= (5) at 35⁰C

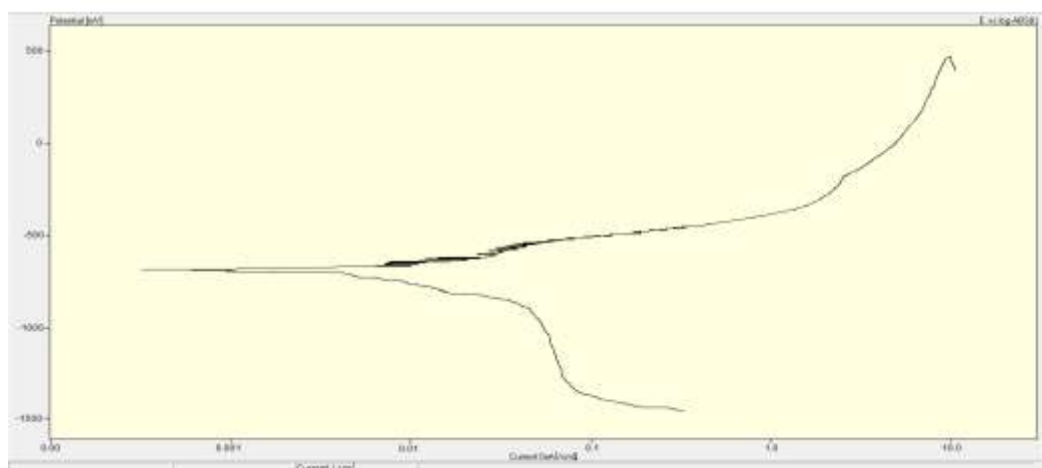


Figure (6) Potentiodynamic polarization curve of carbon steel in solution of(3500) ppm concentration of NaCl and pH= (5) at 35⁰C

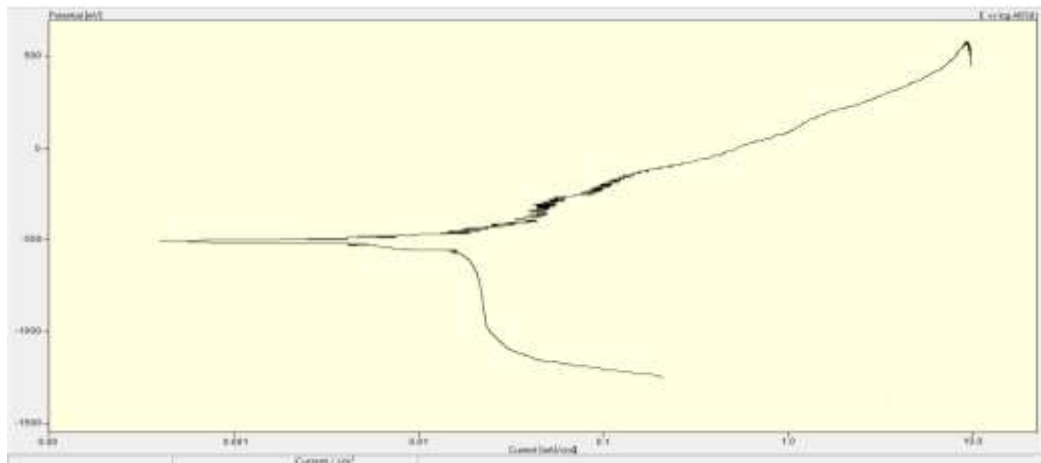


Figure (7) Potentiodynamic polarization curve of carbon steel in solution of (300) ppm concentration of NaCl and pH= (9) at 35⁰C

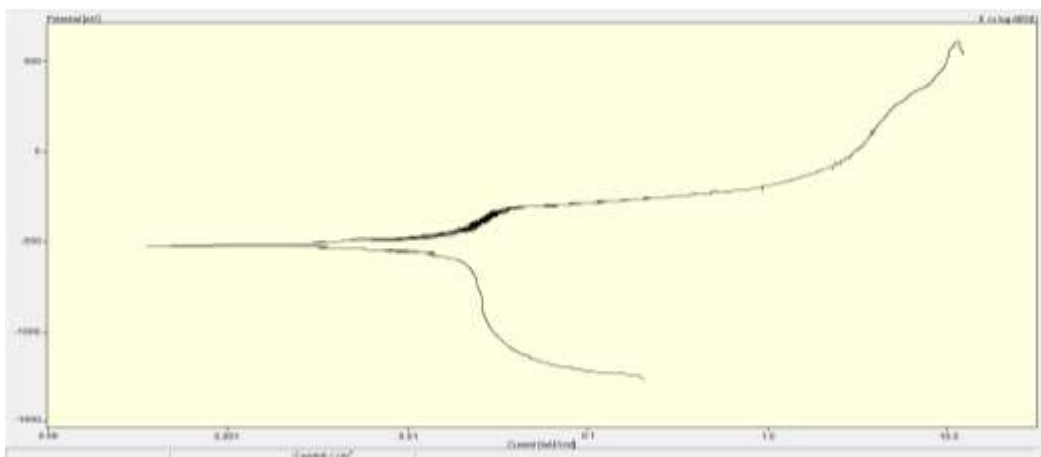


Figure (8) Potentiodynamic polarization curve of carbon steel in solution of (1100) ppm concentration of NaCl and pH= (9) at 35⁰C

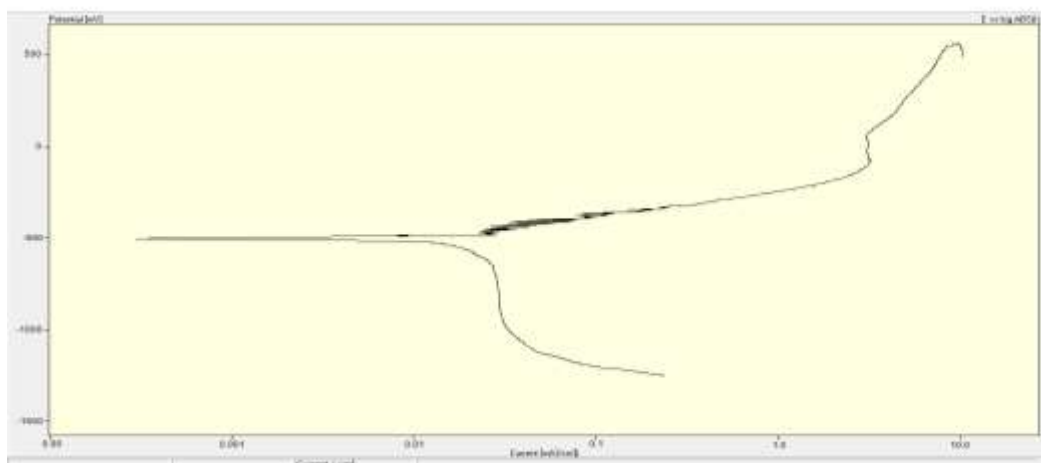


Figure (9) Potentiodynamic polarization curve of carbon steel in solution of (1900) ppm concentration of NaCl and pH= (9) at 35⁰C

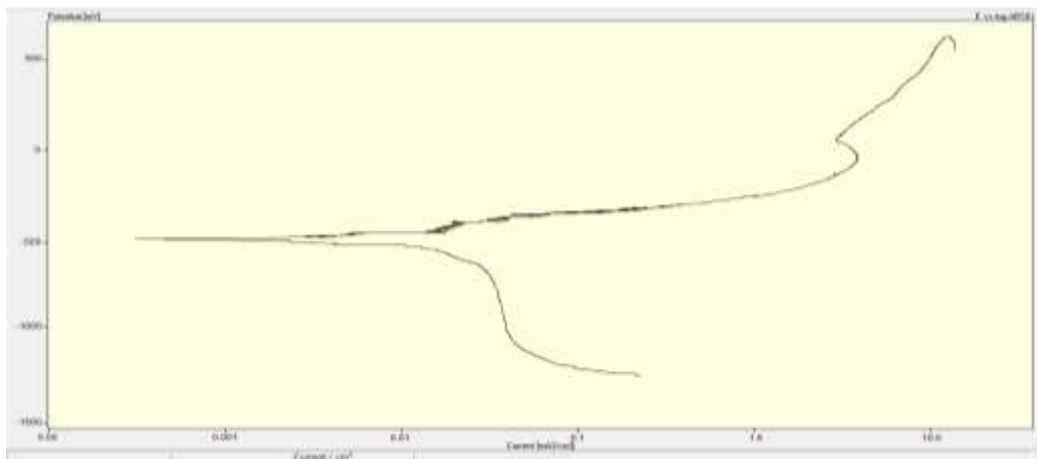


Figure (10) Potentiodynamic polarization curve of carbon steel in solution of (2700) ppm concentration of NaCl and pH= (9) at 35⁰C

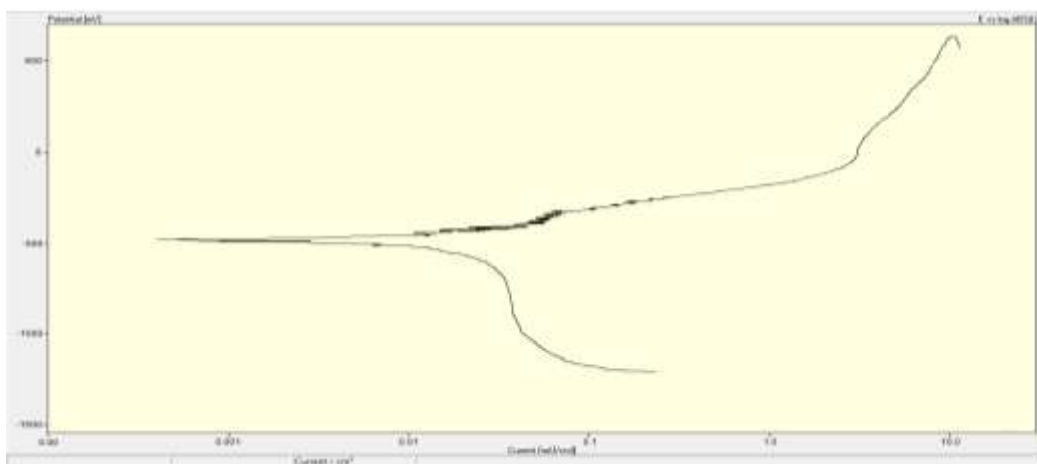


Figure (11) Potentiodynamic polarization curve of carbon steel in solution of (3500) ppm concentration of NaCl and pH= (9) at 35⁰C

From Figures (2, 3, 4, 5, 6), it is shown that the corrosion is heading towards the negative potential while chloride ion concentration increases in solution. The same is shown in case of Figures (7, 8, 9,10, 11).

Comparing Figure(2) with Figure (7), it is shown that with pH change from acidic to alkaline medium, the corrosion rate decreases and corrosion is heading towards more positively potentials, the same is noticed in the cases of Figures (3&8), (4&9), (5&10), (6&11).

Table (2) Potantiodynamic Polarization Results

pH	[Cl ⁻] ppm	E_{corr} -mV	i_{corr} mA/cm ²	b_a	Gmd	mmy
5	300	532	0.0502	240	12.55	271.08
	1100	550	0.0525	200	13.125	283.5
	1900	628	0.0541	210	13.525	292.14
	2700	620	0.0627	250	15.675	338.58
	3500	676	0.0650	255	16.25	351.0
9	300	503	0.0297	260	7.425	160.38
	1100	524	0.0351	150	8.775	189.58
	1900	499	0.0407	90	10.175	219.78
	2700	486	0.0497	80	12.425	268.38
	3500	479	0.0514	85	12.85	277.56

Potentiodynamic polarization result of current density and potential of corrosion processes, which were taken places in this work are presented in Table (2). M Lab Potentiostat also gives information about E_{corr} , I_{corr} , b_a , b_c , i_{corr} , and m_{py} .

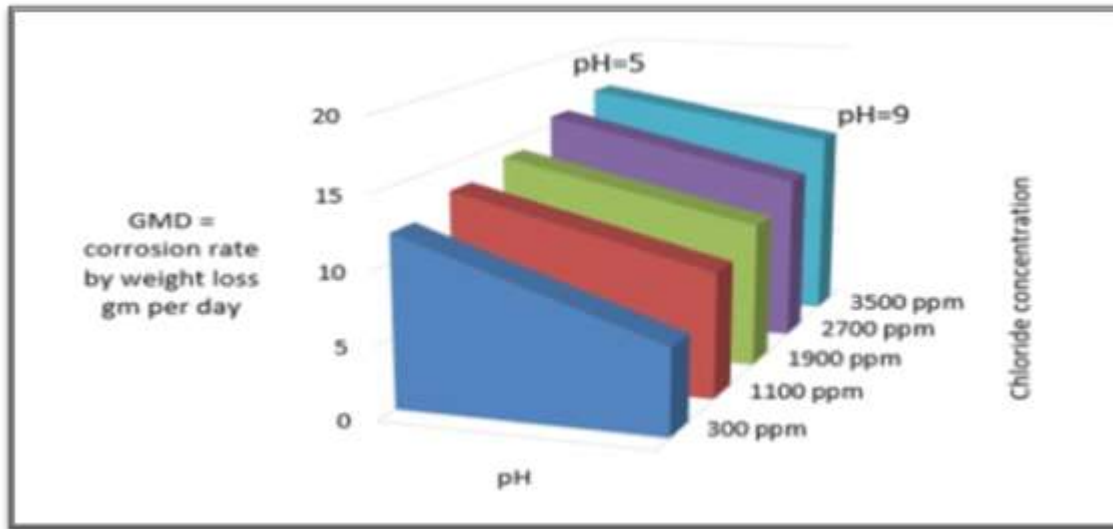


Figure (12) Comparison of corrosion rate (gmd) for each chloride concentration in each pH, pH=5 & pH=9

In Figure (12) it is shown that the increase in chloride ions in solution pushes the corrosion process towards more weight loss measured by gm per day (gmd). This happens for each solution of pH = 5 and pH =9. The way that corrosion rate increases in each pH set is the same, that is by increase of chloride. But for each chloride concentration, acidic medium promotes corrosion rate more than alkaline medium

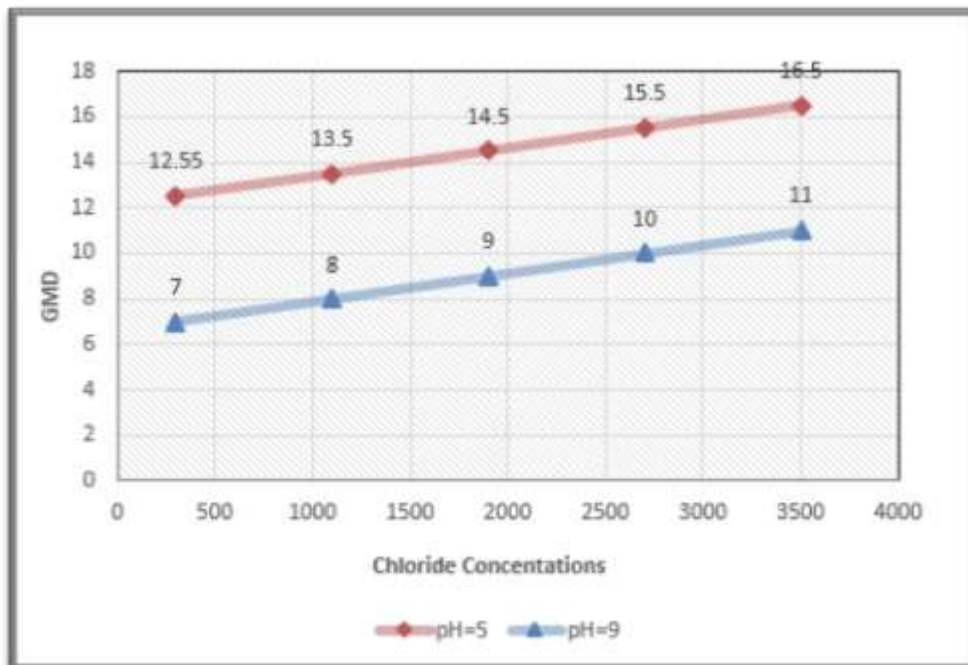


Figure (13) Comparison of corrosion rate (gmd) for each pH in five different chloride concentrations

Linear relationship appeared when corrosion rate of carbon steel (of its weight loss) drawn against chloride concentration in a certain pH of solution, Figure (13).

3.2 Discussion

1. Passive film:

From equation (1, 2) at the applied anodic potential ferrous ions are formed by oxidation reaction at the metal/passive oxide interface. Then ferrous ions migrate through the passive film to the oxide-solution interface and forms ferrous hydroxide equation (3, 4). After that, chloride ions are stimulated by applied anodic potential to migrate preferably to the defected sites of metal surface. Adequate accumulation of Cl^- in these defected sites leads to damage the metal surface. This damage called pitting. As bulk of chloride ion concentration increases, the potential shifts down toward more negative value undermining the role of anodic potential [20]. Thus, either applied anodic potential or increased concentration of chloride ion is necessary to increase corrosion process. It is convenient to state that the breakdown of passive film is the start of corrosion process, and the cause of pitting corrosion in carbon steel.

2. Oxygen role:

Since oxygen depolarization controls the rate of corrosion through the sodium chloride concentration range, it is of some interest to understand why the rate first increases, reaching a maximum at about 3% NaCl (sea water concentration) and then decreases.

3. Rust barrier:

The rise of corrosion rate appears to be related to a change in protective nature of the diffusion barrier rust film that forms on corroding iron. In distilled water having low conductivity, anodes and cathodes must be located relatively near each other.

In sodium chloride solutions, on the other hand, the conductivity is greater, hence additional anodes and cathodes can operate much farther removed one from the other. At such cathodes, NaOH does not react immediately with $\text{Fe}(\text{OH})_2$ formed at anodes; instead these substance diffuse into the solution and react to form $\text{Fe}(\text{OH})_2$ away from the metal surface. Obviously, any $\text{Fe}(\text{OH})_2$ so formed does not provide a protective barrier layer on the metal surface. Hence iron corrodes more rapidly in dilute sodium chloride because more dissolved oxygen can reach cathodic areas [21].

4. The increase in Cl^- ion concentration generally enhances the passivation current density which is a criterion of anodic dissolution of the metal in passive state. These findings could be attributed to weakness and thinning of the passive film as a result of adsorption of Cl^- ions on the oxide surface. The adsorbed Cl^- ions tend to enhance the dissolution of the oxide film. After the incubation time, when a certain critical potential is reached, the passive current density begins to rise suddenly, indicating passivity breakdown and initiation of pitting attack [22].

5. In pH range from 5 to 10, corrosion current quickly decreases; in such stable region, the oxygen diffusion rate through the passive film was likely to be lower than the corrosion reaction rate [23]. In a broad range of about pH 5 to 9, the corrosion rate can be expressed simply in terms of the amount of DO present (e.g., $\mu\text{m}/\text{y}$ per ml. DO per liter of water). At about pH 4.5, acid corrosion is initiated, overwhelming the oxygen control. At about pH 9.5 and above, deposition of insoluble ferric hydroxide tends to stifle the corrosion attack.

6. It is worth mentioning that the corrosion potentials of carbon steel were not dependent on the cation type (Na^+) [24].

IV CONCLUSION

This work shed lights on the behavior of carbon steel in an environment simulated to Iraqi soil of different chloride concentrations in acidic and alkaline medium and relatively high temperature, and here are conclusions of this behavior recorded by potentiostat:

1. External factors of environmental conditions of the soil influence the potentiodynamic polarization curves and push them towards positive or negative directions.
2. Chloride ions have the utmost effect on corrosion rate. The increase in chloride ion concentration, raise up the corrosion rate.
3. Acidic medium promotes corrosion (and corrosion rate) more than alkaline medium.

Highlights:

3. For each polarization curve, carbon steel makes its own path through the process of corrosion starting by concentration corrosion at the beginning of the curve until it reaches activation corrosion area. Each point in the curve represents the act of carbon steel.

- Oxygen solubility influences directly the rate of corrosion at solution contain chloride ions. The more diluted the solution would be, more of oxygen can reach cathodic areas, causing more corrosion to the metal surface.
- The corrosion current, that exemplifies the corrosion rate, increases steadily, for low carbon steel, as the chloride concentration increases in solution. That could be shown from Table (2),

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M.Sc. Dalia Mohammed Almonderi." Corrosion Behavior of Buried Carbon Steel Pipeline In Iraqi Soil in Different Sodium Chloride Concentrations."American Journal Of Engineering Research (AJER), Vol. 7, No. 6, 2018, PP.99-108.