

Evaluation of Sodium Chloride and Acidity Effect on Corrosion of Buried Carbon Steel Pipeline in Iraqi Soil

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Abstract

In this work, corrosion parameters were evaluated using potentiodynamic polarization curves. In order to determine corrosion parameters of potential and current density of the interesting metal, carbon steel, environmental conditions of external corrosion of buried carbon steel pipeline in Iraqi soil were prepared in the laboratory using simulated prepared conditions. Solutions of sodium chloride at different concentrations (300, 1100, 1900, 2700, and 3500 ppm) were used. pH of solution were acidic at pH =5, and alkaline at pH = 9. Laboratory conditions were similar to those of Iraqi soil where the pipelines were buried. Temperature was constant at 20 °C. Potentiodynamic polarization curves, of potential vs. log current density, were obtained using M Lab Multi-Channel Potentiostat/Galvanostat. The carbon steel coupon (ASTM A179-84A) was used as the studied metal. The results of this work reveal the behavior of carbon steel in external corrosion conditions under Iraqi soil. The rate of corrosion, of carbon steel, increases with the increase in chloride concentration in solution. As pH changes from acidic to alkaline medium, the rate of corrosion decreases.

Key Words: Corrosion, Carbon steel, Polarization, Potentiodynamic Polarization.

Introduction

Pipelines play an extremely important role throughout the world as means of transporting gases and oils over long distances from their sources to the ultimate consumers [1]. Pipelines are affected by environmental conditions, whether they are buried in soil or sea water or constructed on ground. The major environmental effect on pipelines is corrosion. For buried pipelines, external corrosion, which is

resulted by environmental conditions, is affected by: moist, temperature, pH, salts types and concentrations, type of soil conductivity and resistivity, type of pipeline alloy material and concentration of oxygen in soil.

The parameters which play the major role in external corrosion of pipelines buried in soil are: moist, pH, temperature and salts, especially chlorides.

Cost of pipelines failure, caused by corrosion has taken the attention around the world as a great deal of the problem. In a widely – cited study (NACE corrosion costs study) by the national association of corrosion engineers, NACE, the direct cost of corrosion in the U.S. was estimated to equal \$276 billion in 1998, approximately 3.1 % of Gross Domestic Product (GDP). However, this estimation is incomplete and closer examination of the NACE data indicates that total corrosion costs in the U.S. now exceed \$1 trillion dollars annually.

The indirect cost of corrosion is estimated to be at least equal to the direct cost. In that case, the total cost of corrosion is \$993 billion in March 2013 and estimated to exceed \$1 trillion in June 2013 (based on estimations of GDP) [2].

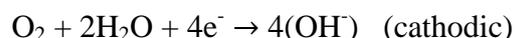
The corrosion process in buried or partly buried pipelines is due to curried flow from anode to cathode through the ground of ionic conductivity and from cathode to anode through metal by electric conductivity [3]. Oxidation process happens at the anode while reduction process happens at the cathode. Iron as a carbon steel has been one of the most extensively studied metals in the environment.

In neutral conditions, oxide or hydroxide, which forms on the metal surface, provides distinctive layers. These layers have significant structure that tends to be determined by anions present in solution [4]. Corrosion kinetics is governed by the reduction of oxygen present in solution. The general reactions that occur are [5]:

- Dissolution of iron as ions at the anode:



- Reduction of oxygen at the cathode, where electrons flow from anode to cathode:



The sum of overall oxidation – reduction reaction would be:



Electrochemical corrosion experiments measure and/ or control potential and current of oxidation/ reduction reactions. Several types of experiments are possible by manipulating and measuring these two variables.

Potentiodynamic polarization technique is generally used to produce a qualitative picture or “fingerprint” of a substance in a given solution. It also detects important 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 [6].

A potentiostat is used for monitoring polarization parameters (potential and current density) [7]. Polarization method, using potentiostat, can show the combined effects of different condition on the polarization parameters. Conditions of which rate of corrosion of carbon steel is measured of different concentrations of chloride as NaCl, different pH and different temperatures levels. Each condition has its characteristic and unique effect on the cathodic and anodic reactions. Therefore, the aim of this work was to evaluate, the effect of corrosion parameters, chloride concentration, pH and constant temperature on the corrosion rate of a well-known, pipeline metal which is the interesting carbon steel.

As the parameters go vary, rate of corrosion was influenced by the three of them at the same time, resulting in a competition between these three parameters, of which one is going to role at particular moment of the reaction.

Experimental Work

Materials

Material used in this work is low carbon steel coupons (ASTM A179-84A) [7].

Table 1, A nominal and the analytical chemical compositions of carbon steel

Chemical Composition, %	A 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 coupon dimensions were 1cm×1cm. Coupons were polished with silicon carbide (SiC). Then, edges and faces of coupons were grinded using UNIPOL–820 grinding/polishing machine. Rotating speed was adjusted in the range of 100 to 400 cycle/second running under tap water. Degreasing was produced, by immersion in acetone after whipping with benzene wet cloth. Afterward each coupon was preserved in the dessicator to prevent moisture.

Chemical Solutions

Solution of pH = 5 and 9 were prepared using HCl and NaOH. Stoke solutions of each HCl and NaOH of 1 M were prepared. Then solutions of 0.01 of each HCl and NaOH solution were prepared from the stoke solutions.

Solution of pH 5 and 9 were prepared from the later, 0.01 M, where the increase in Na⁺ and Cl⁻ were accounted to be negligible [8]. Concentration of chlorides, represented by NaCl, were chosen according to their presence in Iraqi soil after analyzing chloride concentrations in laboratory.

Soil samples were taken from different locations in Iraqi. Concentrations of chlorides in samples were measured using titration with silver nitrate. Potassium chromate was used as an indicator. Results were ranged from 300 to 3500 ppm (in average). pH values of samples were ranged from 5 to 9 (in average). Total Dissolved Solids (TDS) and conductivity were measured for the solution samples using (Reed Yk-22CT conductivity/TDS meter).

Temperature of all solutions was maintained to 20 °C.

Electrochemical Corrosion Tests

Electrochemical polarization experiments were carried out using a potentiostat, M Lab Multi-Channel Potentiostat/Galvanostat.

Graphite carbon rod was used as an auxiliary or counter electrode. All potentials were measured against a saturated calomel electrode. The measurements were carried out in a three electrode cell using a computer assisted potentiostat. A thermo stirrer was used to set the required temperature (20 °C) and to achieve temperature homogenization.

Open Circuit Potential Test

After preparation of cell solution 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 1cm² to obtain the correct value of the free corrosion

potential of the coupon at each measurement.

Corrosion potential value was recorded till it reaches a steady state value. It takes about 30 minutes for the steady state to develop.

Potentiodynamic Polarization Tests

Potentiodynamic tests were carried out after preparation of salt solutions.

These later are chloride concentrations (as NaCl) of 300, 1100, 1900, 2700, and 3500 ppm. Each prepared with pH 5 and 9 where temperature was set at 20⁰ 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.

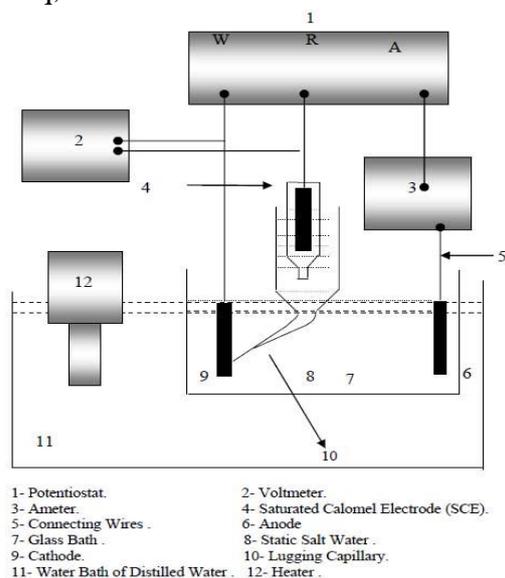


Fig. 1, A simple sketch of polarization circuits

The potentiodynamic polarization cell circuit as shown in figure 1 was set in position to start the potentiodynamic polarization to plot behavior of carbon steel coupon at the studied solutions of different chloride concentration at different pH values where temperature is constant.

By applying the potential from potentiostat and at each setting, the potential applied and the current were recorded using M Lab software of the computerized potentiostat. For more accuracy, time step between each recorded points was set to 500m.sec.

The potentiodynamic polarization curves were 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 (ba, bc respectively), weight loss (gmd) and penetration loss (mmy), curve of potential vs log rate of corrosion were obtained from potentiostat results. The value of cathodic Tafel slope (bc) is neglected in the table due to its large value as a result of almost vertical cathodic curve, mentioning that it is large but not infinite.

Results and Discussion

Potentiodynamic curve plotted between potential and log current density. Each curve shows the behaviour of carbon steel at different conditions of chloride concentration, which represented by NaCl and different pH, acidic and alkaline medium.

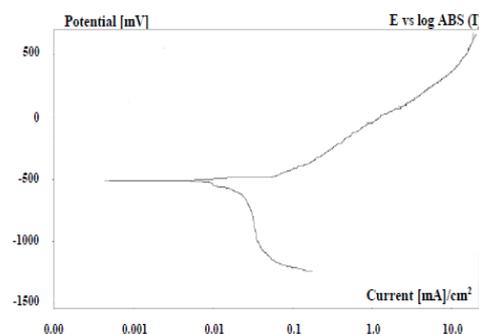


Fig. 2, Potentiodynamic polarization curve of carbon steel in solution of 300 ppm concentration of NaCl and pH= 5 at 20 °C

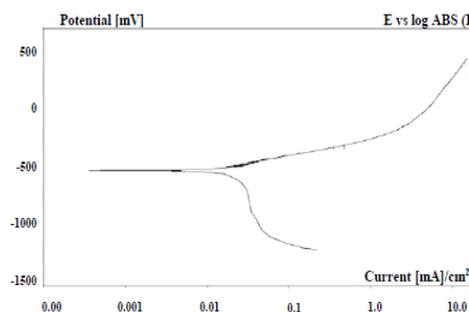


Fig. 3, Potentiodynamic polarization curve of carbon steel in solution of 1100 ppm concentration of NaCl and pH= 5 at 20 °C

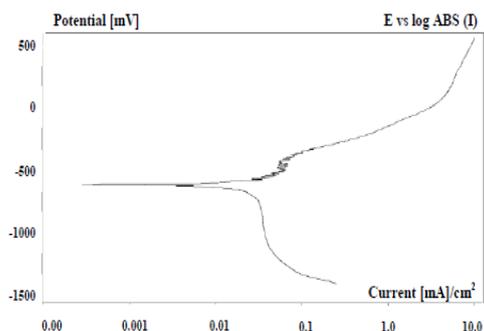


Fig. 4, Potentiodynamic polarization curve of carbon steel in solution of 1900 ppm concentration of NaCl and pH= 5 at 20 °C

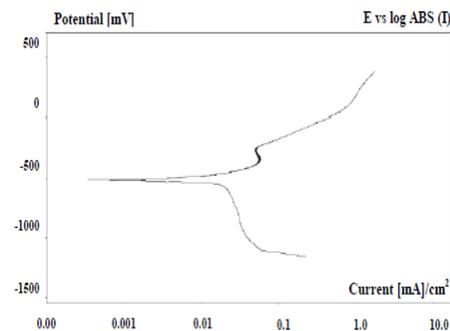


Fig. 8, Potentiodynamic polarization curve of carbon steel in solution of 1100 ppm concentration of NaCl and pH= 9 at 20 °C

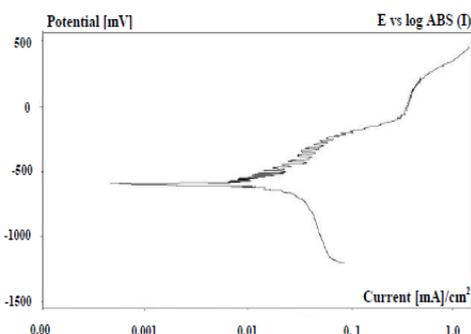


Fig. 5, Potentiodynamic polarization curve of carbon steel in solution of 2700 ppm concentration of NaCl and pH= 5 at 20 °C

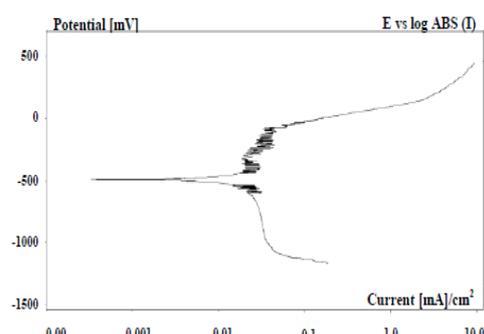


Fig. 9, Potentiodynamic polarization curve of carbon steel in solution of 1900 ppm concentration of NaCl and pH= 9 at 20 °C

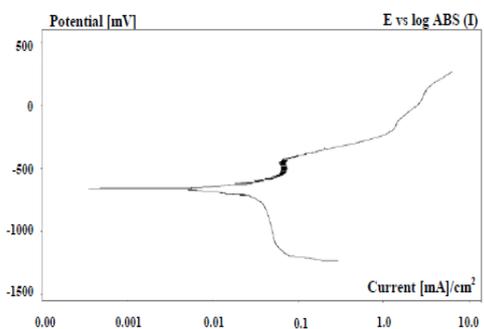


Fig. 6, Potentiodynamic polarization curve of carbon steel in solution of 3500 ppm concentration of NaCl and pH= 5 at 20 °C

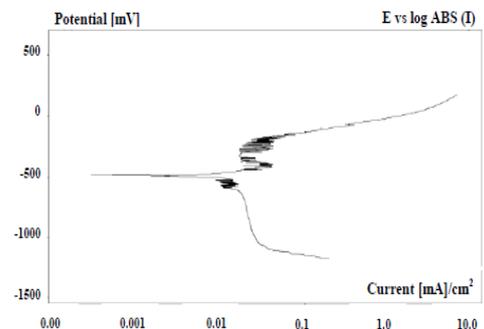


Fig. 10, Potentiodynamic polarization curve of carbon steel in solution of 2700 ppm concentration of NaCl and pH= 9 at 20 °C

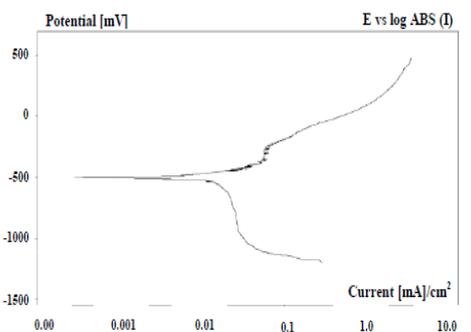


Fig. 7, Potentiodynamic polarization curve of carbon steel in solution of 300 ppm concentration of NaCl and pH= 9 at 20 °C

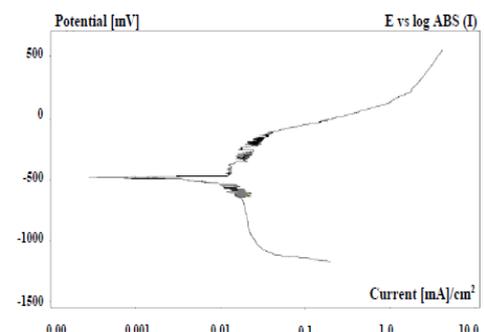


Fig. 11, Potentiodynamic polarization curve of carbon steel in solution of 3500 ppm concentration of NaCl and pH= 9 at 20 °C

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

Since oxygen depolarization controls the rate of corrosion through the sodium chloride concentration range, it is of some interest to understand why the rate increases. 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

Fe(OH)₂ formed at anodes; instead these substances diffuse into the solution and react to form Fe(OH)₂ away from the metal surface. Obviously, any Fe(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 move dissolved oxygen can reach cathodic areas. [9]

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 less negative potentials, the same is noticed in the cases of figures 3 and 8, 4 and 9, 5 and 10, 6 and 11.

Potentiodynamic polarization result of current density and potential of corrosion processes, which were taken places in this work are presented in table 2.

Table 2, Potantiodynamic Polarization Results

pH	Cl- ppm	E _{corr} -mV	I _{corr} mA/cm ²	ba	gmd	mmy	TDS	Conductivity ms
5	300	512	0.0407	266	10.175	219.78	417	0.635
	1100	530	0.0443	190	11.075	239.22	1467	2.29
	1900	607	0.0482	200	12.05	260.28	2573	3.97
	2700	590	0.0513	300	12.83	277.12	3580	5.2
	3500	650	0.0548	250	13.7	295.92	4640	6.63
9	300	498	0.0189	130	4.775	102.06	412	0.618
	1100	517	0.0248	276	6.2	133.92	1473	2.28
	1900	492	0.0305	285	7.625	164.7	2500	3.65
	2700	483	0.0333	279	8.325	179.82	3653	5.43
	3500	477	0.0334	274	8.85	191.16	4700	6.91

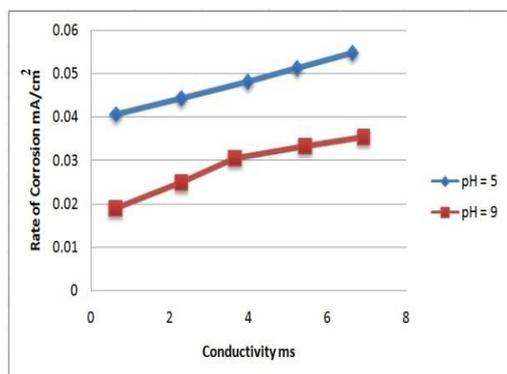


Fig. 12, The relationship between concentration of chloride, as a function of corrosion rate and the conductivity of solution

In figure 12 it's obvious that the increase in chloride concentrations, as a function of increasing rate of corrosion, effects on the conductivity of solution to be increased as the concentration of chloride increases. The way of corrosion rate to increase, when conductivity increases, in acidic medium pH = 5, is more obvious to notice than the way in alkaline medium pH =9.

At the applied anodic potential, ferrous ions are produced at the metal/passive

oxide interface. These are migrated through passive film to the oxide-solution interface and forms ferrous hydroxide.

The applied anodic potential stimulates the migration of the chloride ion preferably to the defect sites of the surface. Sufficient accumulation of Cl^- in these defects leads pitting. With increase of bulk chloride ion concentration, the potential shifts toward more negative value undermining the role of anodic potential [10].

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.

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 [11].

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 [12].

In a broad range of about pH 5 to 9, the corrosion rate can be expressed simply in terms of the amount of OH present (e.g., $\mu\text{m}/\text{y}$ per ml. OH 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.

It is worth mentioning that the corrosion potentials of carbon steel were not dependent on the cation type (Na^+) [13].

Conclusion

The conclusion from the research work which has been presented is as follows:

1. Concentration of chloride ions has the major effect on corrosion rate. When chloride concentration increases, corrosion rate increases.
2. Corrosion rates are increased at acidic medium more than in alkaline medium.
3. Oxygen solubility affects the rate of corrosion at solution of sodium chloride concentrations. The more diluted the solution would be more oxygen can reach cathodic areas, causing more corrosion in the metal surface.

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