

Research Article

Effect of Anode Type and Position on the Cathodic Protection of Carbon Steel in Sea Water

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Abstract

The effects of different parameters and conditions on the impressed current cathodic protection of steel structure in 3% NaCl solution were investigated using both weight loss method and electrochemical polarization technique. The effect of anode type, anode to cathode distance, anode to cathode area ratio, temperature, and time on the effectiveness of cathodic protection was studied and discussed. Graphite and scrap iron of various lengths were used as impressed current anodes. These were placed at different distances from structure (cathode) and different values of protection currents and potentials were applied and effects of time and solution temperature were studied. The results revealed that the scrap iron provides more economical protection than graphite, corrosion rate was decreased as the applied current increased when scrap iron was used. Increasing distance between anode and cathode leads to a decrease in the protection efficiency. The lower the area ratio of cathode to anode, the better the protection against corrosion. Generally, the protection potential shifts to more positive after short time from applying the protection. However, the protection current decreases appreciably with time in a manner depending on anode type and solution temperature which affects both protection potential and protection current.

Keywords: Cathodic protection, Steel structure etc.

1. Introduction

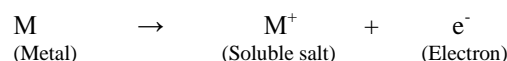
Cathodic protection is more reliable, effective and economic method for protection of a variety of pipelines, tanks, marine structures including ships hulls and submarines against corrosion. Cathodic protection works primarily by depressing the natural corrosion potential of the structure to be protected to a value where it does not corrode (I. Gurrappa, 2005).

Cathodic protection systems are most commonly used to protect steel, water and fuel pipelines and storage tanks; steel pier piles, ships, offshore oil platforms and onshore oil well casings among others. A side effect of improperly performed cathodic protection may, however, be the production of molecular hydrogen, leading to its absorption in the protected metal and subsequent hydrogen embrittlement (C. A. Loto *et al*, 2011).

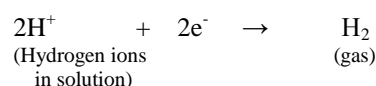
The two mostly used methods of CP are the galvanic or sacrificial anode method; and the impressed current cathodic protection. The impressed current cathodic protection is used for larger structures that galvanic anodes could not economically deliver current to provide complete protection. Impressed Current Cathodic Protection (ICCP) systems use anodes connected to a DC

power source (a cathodic protection rectifier). Anodes for ICCP systems include silicon, cast iron, graphite, mixed metal oxide, platinum and niobium coated wire (C. A. Loto *et al*, 2011).

The Principles of Cathodic Protection metal that has been extracted from its primary ore (metal oxides or other free radicals) has a natural tendency to revert to that state under the action of oxygen and water. This action is called corrosion and the most common example is the rusting of steel. Corrosion is an electro-chemical process that involves the passage of electrical currents on a micro or macro scale. The change from the metallic to the combined form occurs by an anodic reaction:



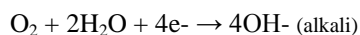
This reaction produces free electrons, which pass within the metal to another site on the metal surface (the cathode), where it is consumed by the cathodic reaction. In acid solutions the cathodic reaction is:



In neutral solutions the cathodic reaction involves the

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consumption of oxygen dissolved in the solution (M, Surkein *et al*, 2010):



Numerous materials can be used as inert anodes, but only few materials satisfy all the parameters required for practical application in view of limitations imposed by electrochemical dissolution rate and/or mechanical durability or both (J.A. Jakobs *et al*, 1981).

Graphite has the advantages of long-life corrosion protection, low maintenance cost and high efficiency. These are generally cylindrical in shape, although other forms are available (Zaki Ahmed, 1981). It has the advantage of being cheap and abundantly available.

Scrap iron is used in impressed current cathodic protection because it is cheap and requires low applied current to give good protection for a period of time. Its consumption rate depends on the medium nature and the prevailing conditions.

Temperature of the medium governs the solubilities of the corrosive species in the fluid, such as oxygen (O₂), carbon dioxide (CO), chlorides, and hydroxides. Temperature increases the rate of almost all the chemical reactions. When the rate determining step is the activation process, the temperature changes have the greatest effect (Henry S.D *et al*, 1999). In open systems, the effect of temperature is complex in that the diffusivity of oxygen increases, but solubility decreases with temperature increases (Henry S.D *et al*, 1999).

The area ratio of the anode to cathode plays a dominant role in cathodic protection. As a given amount of current flows in a galvanic couple, the current density at the anode or cathode controls the rate of corrosion. For a given amount of current, the metal with the smallest area has the largest current density and, hence, is more damaged if corrosion occurs at it. For similar reasons, the current density at a large metal is very small. The rate of corrosion increases with the ratio of cathodic to anodic areas (Zaki Ahmed, 1981).

Konsowa and El-Shazly (Konsowa A.H *et al*, 2002) found that cathodic protection in saline water is controlled by the rate of diffusion of dissolved oxygen towards the walls of the copper tube.

Scantlebury (Scantlebury J.D *et al*, 2006) concluded that in marine environment, mild steel does not corrode under the protection potentials, viz., -780 and -1100 mV.

Sami and Ghalib (Sami, A.A *et al*, 2008) indicated that cathodic protection current density increases with increasing temperature and 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.

Lotto and popoola (Lotto *et al*, 2011) observed that the aluminium anodes proved more effective as sacrificial anode for mild steel in seawater environment. In sulphuric acid environment, the zinc anode gave a more protective performance than aluminium anode. Different sizes of the zinc anode used confirmed that the effective cathodic protection performance of the anode also depends on its

size. The bigger the anode, the more the electrons supplied to protect the cathode and the longer time it takes for replacement (C. A. Loto *et al*, 2011).

The objective of present work is to investigate the effect of anode type, anode to cathode distance, anode to cathode length (or area) ratio, and solution temperature on the impressed current cathodic protection of carbon steel pipe in 3% NaCl solution.

2. Apparatus and procedure

The apparatus (Fig.1) consists of water bath containing sea water (3%NaCl) to obtain different solution temperatures, graphite electrode as anode, carbon steel specimen 15 cm long and 7 mm in diameter as cathode, power supply to apply the required protection potential, digital voltmeter to measure the potential, digital ammeter to measure the current, variable resistance to control the current flow and saturated calomel electrode (SCE) as a reference electrode. Digital balance of high accuracy (4decimal places of gram) to measure the weight loss.

In polarization experiment the solution was prepared containing 3% NaCl, water bath was set at different temperatures (25, 35 and 45 °C). Silicon rubber was used to prevent the leakages in the test section. When the bath reached the required temperature, the specimen was immersed and the electrical circuit was switched on. The power supply was set at 5 V. The specimen was cathodically polarized from a particular potentials (-1.16 to -1.27) to the corrosion potential (where $i_{app.} = 0$) by changing the applied current using rheostat. The current was recorded for step changes in potential. Two minutes were allowed for steady state to be reached after each potential increment. The capillary tube was placed at distance 2mm from the specimen and connected to calomel electrode to measure the specimen potential. Thus polarization curve can be drawn and the limiting current can be obtained. The obtained values of i_L and E_c represents the values for clean surface ($t=0$), i.e., no corrosion products formed, since during the polarization experiment no free corrosion occurs (except at low currents near corrosion potential) because the specimen will be cathodically protected.

In the experiment of the weight loss, the specimen was cleaned with dilute HCl (5%) for 5 seconds immersion time, washed with water with brushing using plastic brush, washed with distilled water. Then it was dried with a piece of cloth, immersed in acetone for 3 minutes, heated in oven at 110 °C for 5 minutes, stored in vacuum desiccator for 5 minutes, and weighted.

Solution of 3%NaCl was prepared using 5 liters of distilled water. The water bath was set at different temperatures (25, 35 and 45 °C) then the graphite electrode and carbon steel specimen were immersed in water bath at different distances (100 and 300 mm). Different lengths of carbon steel specimen were used (75 mm and 150 mm). The tube of saturated calomel electrode (SCE) was placed within 2 mm from the specimen and the calomel electrode was connected with voltmeter. The carbon steel specimen was connected to -ve terminal of power supply as cathode

and graphite electrode to +ve terminal as anode. Power supply was switched on and set at 5 V. The structure (specimen) potential was measured using voltmeter relative to saturated calomel electrode. The current was measured using ammeter. The experiment duration was 3 h ,the specimen was cleaned with dilute HCL(5%) for 2 seconds, washed it with water then with distilled water, dried it with a piece of clothes then was placed in acetone for 3 min, heated it at oven with 110 °C for 5minutes, stored in vacuum desiccator for 8minutes,weighted it in the balance. The experiment was repeated by using scrub iron as anode instead of graphite at different currents. The corrosion rate (CR) was calculated from weight loss:

$$CR = \frac{\text{weight loss(g)}}{\text{area(m}^2\text{)}*\text{time(d)}}$$

The protection percent (pp) was calculated as:

$$PP\% = \frac{CR_0 - CR}{CR_0}$$

Where CR₀ and CR are the corrosion rate in absence and in presence of cathodic protection.

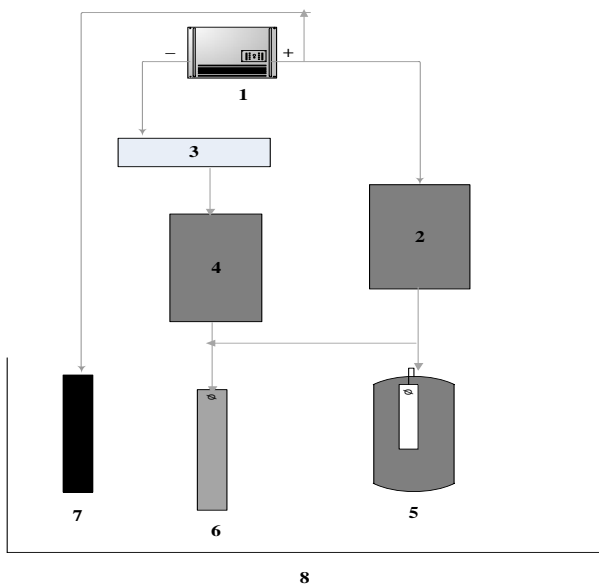


Figure1: Experimental rig: 1-power supply, 2-Voltmeter, 3-Resistance box, 4-Ammeter, 5-Calomel electrode, 6- Carbon steel, 7- graphite, 8-Water bath

3. Results and discussions

3.1. Free corrosion

The free corrosion rate, before applying cathodic protection, was determined by measuring the limiting current density at different conditions. The limiting current density of oxygen reduction (*i_L*) is the most important characteristic of the cathodic region. The limiting current density is determined from the plateau defined in terms of initial and final potentials, i.e., E₁ and E₂ in Fig. 2. *i₁* refers

to the start of the limiting value of oxygen reduction, while *i₂* refers to the start stage of enhanced hydrogen evolution reaction (J.G. Hines, 1983).

The limiting current plateau is not well defined, thus the method given by Gabe and Makanjoula (D.R.Gabe *et al*, 1986) will be adopted to find the limiting current density values, i.e.:

$$i_L = \frac{i_1 + i_2}{2} \tag{1}$$

Where *i₁* and *i₂* are the currents associated with E₁ and E₂ respectively.

The free corrosion potentials (E_c) were also determined from the polarization curves when the applied current becomes zero, i.e., open circuit potential (or free corrosion potential).The cathodic polarization curves were determined experimentally by plotting cathode potential versus current density on semi-log plot for temperatures 25, 35, and 45 °C. Fig. 3 illustrates the polarization curves at various temperatures (25, 35 and 45 °C). It can be noticed that the limiting current was increased as the temperature increased and the limiting current at 25, 35, 45 °C is 37.5, 60, 75 mA respectively. Increasing the temperature will increase the rate of oxygen diffusion to the metal surface, decrease the viscosity of solution which will aid the oxygen diffusion, and increase the solution electrical conductivity. All these factors enhance the corrosion rate. On the other hand, increasing the temperature decreases the oxygen solubility that will restrain the corrosion (S.D. Henry *et al*, 1999).

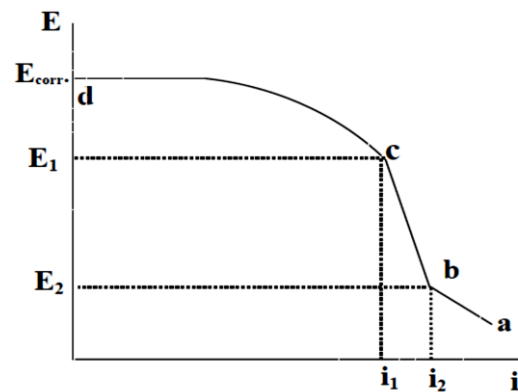


Figure2: Typical polarization curve showing how to determine *i_L*.

The free corrosion rates of carbon steel in sea water at various temperatures were also determined by weight loss method. Table 1 shows the effect of temperature on corrosion rate of carbon steel. It is clear that when the temperature is increased from 25 to 35 °C, the corrosion rate is decreased slightly from 87.59 to 76.01 gmd with further increase in temperature to 45 °C, the corrosion rate is increased to 120.59 gmd. There is no clear behavior with increasing temperature. Several explanations were found to clarify this phenomenon:

When the solution temperature is increased the solution viscosity is decreased with a consequent increase

in O₂ diffusivity according to the Stokes-Einstein equation (Zaki Ahmed, 1981):

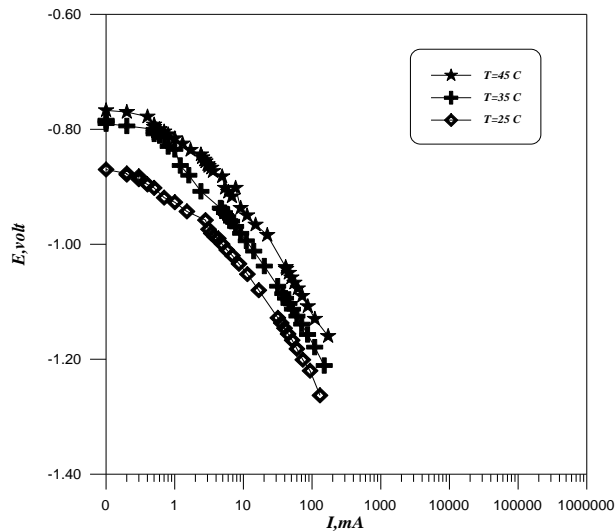


Figure 3: Polarization curve at different temperatures

$$\frac{\mu D}{T} = \text{constant} \quad (2)$$

Where μ : solution viscosity, D :diffusivity, T : solution temperature. As a result of increasing the diffusivity of dissolved O₂, the rate of mass transfer of O₂ dissolved to the cathode surface increases according to Eq. (2) with a consequent increase in the rate of Fe dissolution.

The decrease in solution viscosity with increasing temperature increase the solution conductivity with a consequent increase in the corrosion current and the rate of corrosion. On the other hand, increase of temperature reduces the solubility of dissolved O₂, with a subsequent decrease in the rate of O₂ diffusion to the cathode surface and the rate of corrosion (Konsowa A.H et al, 2002). So, the effect of temperature of the CR is complicated because it affects various parameters.

Table1: Free corrosion rate at different temperatures

C.R.(gmd)	T(°C)
87.59	25
76.01	35
120.5	45

3.2. Impressed current cathodic protection

3.2.1 Effect of distance between anode and cathode

The effect of distance (d) between anode (graphite) and cathode (structure) was studied using different values. These were at $d=100$ mm and 300 mm, in a solution of 3% NaCl at different temperatures of $25, 35$ and 45 °C. The experiment duration was 3 h. The results are shown in Fig. 4. It is evident that the corrosion rate decreases in presence of cathodic protection. It can be noted that when the distance between anode and cathode was decreased, the corrosion rate was also decreased, i.e more protection

is attained. This can be attributed to increasing resistance of electrolyte (R) (Denman W. L, 1956), i.e. decreasing conductivity of electrolyte with increasing distance between anode and cathode, so that increasing cathodic protection current density with increasing resistance of solution. It is to be noted that decreasing the distance three times leads to decrease the corrosion rate considerably depending on the temperature.

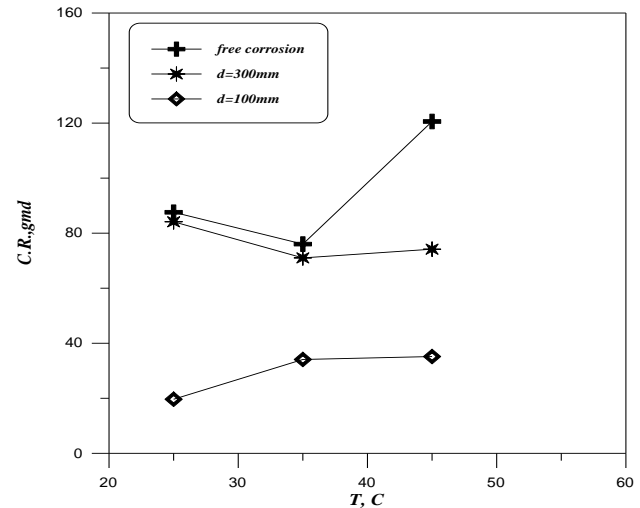


Figure 4: Effect of distance between structure and the anode on the corrosion rate at -0.85V.

Fig. 5 shows the effect of distance between anode and cathode on the protection percent (PP) at different temperatures. The figure reveals that the protection percent increases as the distance decreases because of increasing the conductivity with decreasing distance (Denman W. L, 1956). As short distance, at low temperature (25 °C) the effect of distance on the protection percent is highest, i.e. more protection to the structure is obtained. It can be seen that, the protection percent increase appreciably when decreasing the distance three times. Hence, the closer the distance is the higher the protection.

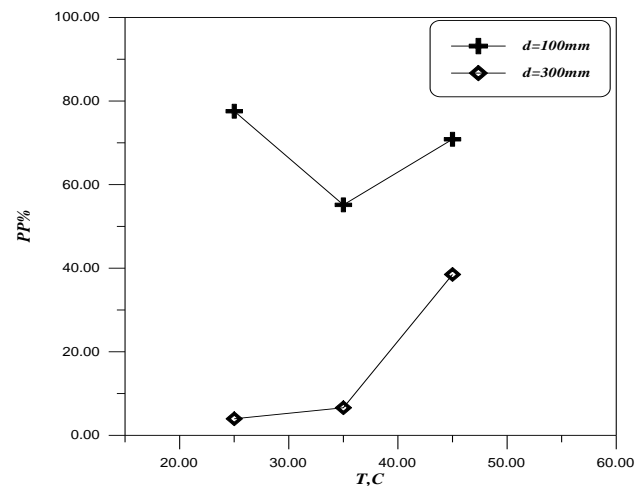


Figure 5: Effect of distance on protection percent at different temperatures.

3.2.2 Effect of time on the protection current and protection potential.

If sufficient direct current is applied, the potential difference between the anode and cathode is eliminated and corrosion would eventually cease to occur.

Figs. 6 and 7 show the change of applied current with time. It is clear that the applied current decreases with time due to the continuous growth of the corrosion product layer which affects the transport of O₂ to metal surface and the activity of the surface and hence the corrosion rate (L.L. Shreir , 1976; B.K. Mahato, 1968).That is in agreement with previous studies (B.K. Mahato, 1968, 1980). The distance between anode and cathode affects the applied current. For both distances and temperatures, the applied current decreases considerably with time. The decrease of applied current with time is due to the fact that despite the applied current present, the corrosion still occur causing formation of corrosion product layer (fouling) which has high electrical resistance leading to prohibit the passage of current through it and hence the current decreases. This findings is in agreement with previous work (Glass et al, 1994).

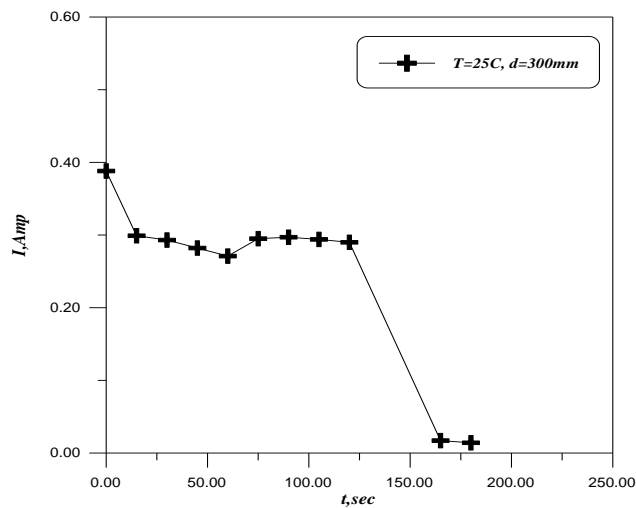


Figure 6: Variation of applied current for temp. 25C and distance 300mm

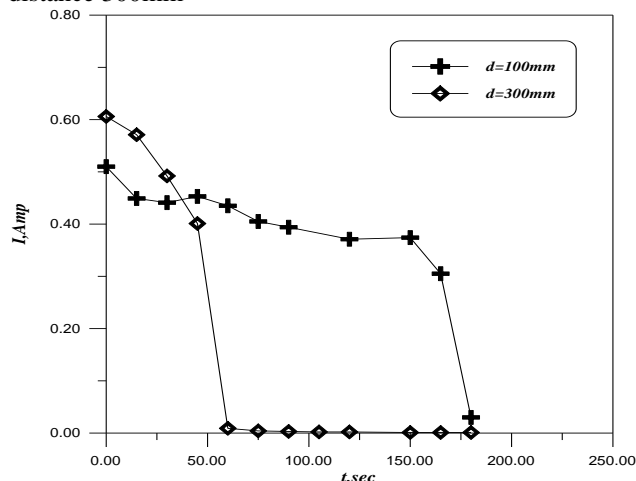


Figure7: Variation of applied current with me for temperature 45 C and distances 100 and 300 mm.

The effect of time on the protection potential is shown in figures 8. It is noticed that the protection potential increases (shift to more positive) with time indicating that the structure is corroding with time due to corrosivity of the solution. After 160 min, the potential becomes -4.5 V (SCE). Therefore, the protection potential must be monitored and reset on the optimum value to control the corrosion. Ion where the oxygen

It is possible to protect steel cathodically at potentials above its initial free corrosion potential in some environments in accordance with currently accepted criteria after an initial conditioning period at a more negative potential. Thus the total cathodic reaction rate on a protected metal surface, which includes that supported by the local corrosion cells, may be reduced below that which occurs on an equivalent unprotected metal surface. (Glass et al, 1994).

The protection potential is influenced by the distance between anode and cathode. At distance 100 mm the protection potential becomes -0.45 V after 180 min while at distance 300 mm the protection potential becomes -0.44 V after 75 min.

Loto and Odumbo (S.A. Eremais, 1973) found unstable trend of Ec with time for mild steel bar in stationary 0.1N NaCl solution.

The potential becomes more positive with the increase of the distance between anode and cathode as shown in figure below.

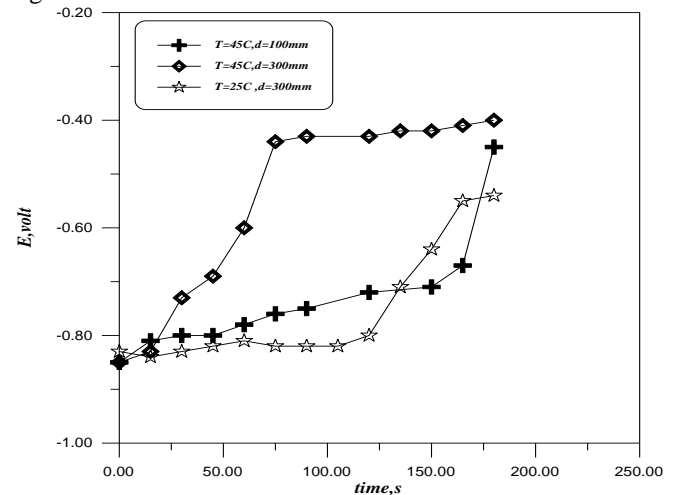


Figure 8: Variation of protection potential with time for temp. 25 and 45 °C with distance 100 and 300 mm

3.3 Effect of cathode to anode length ratio on the cathodic protection

Table 3: Effect of cathode to anode length ratio

C.R.(g/d.m ²)	31.15	34.1	30.697	35.15
Temperature(°C)	35	35	45	45
Length ratio of cathode to anode	1/2	1	1/2	1
Area of cathode(cm ²)	0.165	0.33	0.165	0.33
Length of cathode(cm)	7.5	15	7.5	15

Table 3 lists values of corrosion rate of structure (cathode) when using anode length 150 mm, different lengths of cathode at constant distance between the anode and cathode of 100 mm, -0.85 V potential and different temp.

From table 3 the corrosion rate of the structure is affected by the length of cathode, when the ratio of (cathode to anode) increased from 1/2 to 1 the corrosion rate was increased from 31.15 to 34.1 g/d.m² at 35 °C and 30.697 to 35.15 g/d.m² at 45 °C. This can be attributed to the surface area of the cathode that subjected to the corrosion and hence affect to the amount of electrons will be released to protect the cathode (C. A. Loto et al, 2011) and these results are agreement with lotto and popoola (C. A. Loto et al, 2011).

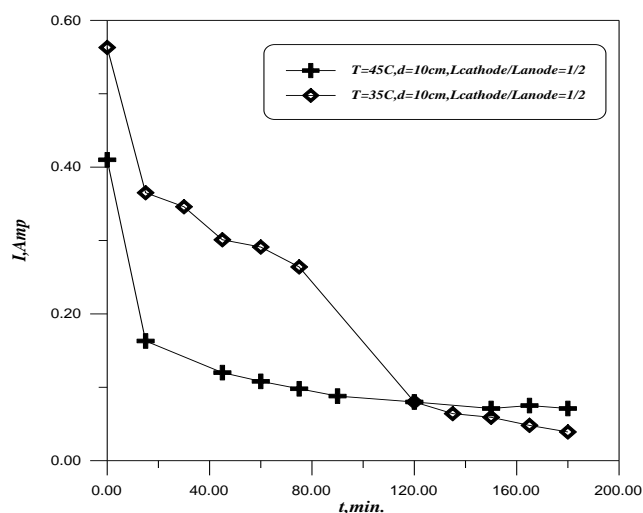


Figure9: Effect of applied current against time at different temperature.

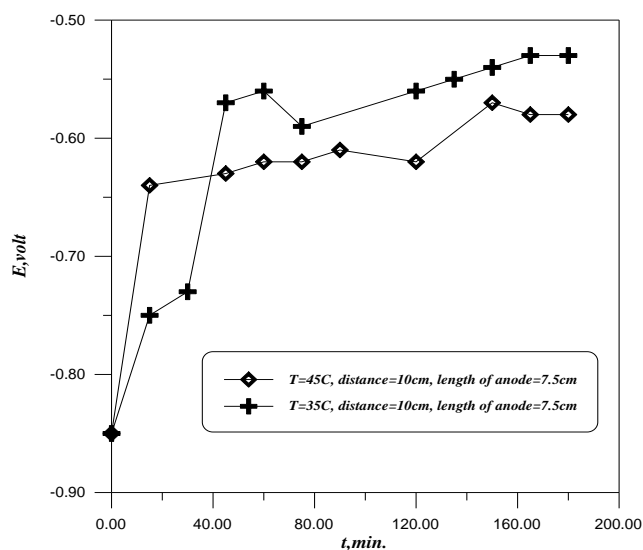


Figure10: Variation of protection potential against time at different temperatures.

Figure 9 shows the variation of applied current with time at ratio of cathode to anode 1/2, distance between anode and cathode 100 mm and different temperature (35 and

45°C), it can be noticed that the applied current is decreased sharply in the first 40,120 min for 45 and 35 °C then decreased slightly with time this can be attributed to the continuous growth of the corrosion product layer which affects the transport of O₂ to metal surface and the activity of the surface and hence the corrosion rate [14,15].

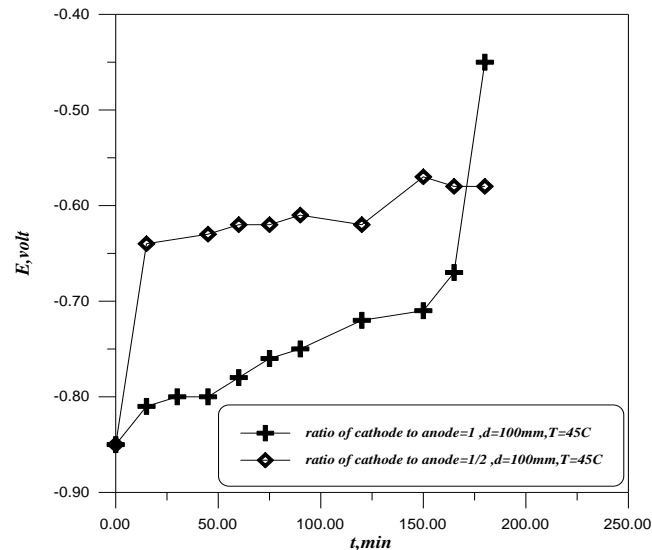


Figure11: Variation of protection potential against time at different ratio of cathode to anode.

Fig.10 and 11 show the effect variation of applied potential with time at ratio of cathode to anode 1/2 and 1, distance between anode and cathode 100 mm and different temperature (35 and 45°C).The protection potential was increased (shift to more positive) with time this indicates that the structure is corroding with time due to corrosivity of the solution. After 200 min the potential becomes -5.5 V (SCE). Therefore, the protection potential must be monitored and reset on the optimum value to control the corrosion.

3.4. Scrap iron as anode electrode

Scrap iron is usually used as an anode in impressed current cathodic protection systems due to its low price.

Graphite is well known material used in anodic protection. It has an electron conductivity of about 200 to 700Ω⁻¹ cm⁻¹, is relatively cheap, and forms gaseous anodic reaction products. The material is, however, mechanically weak and can only be loaded by low current densities for economical material consumption. Material consumption for graphite anodes initially decreases with increased loading and in soil amounts to about 1 to 1.5 kg A⁻¹ a⁻¹ at current densities of 20 Am⁻²

Steel scrap is used as an impressed-current anode. This may be used for temporary protection or for economical reasons. Abandoned steel-lined oil or water wells can be quite suitable.

The effect of type of anode was studied by using both graphite and carbon steel. Different applied currents 0.033, 0.05, 0.5 A were investigated at temperature of 35

°C , and distance between anode and cathode of 100 mm and length of both anode and cathode was 150 mm.

Table 4: comparative protection with scrap iron and graphite

C.R. (gmd)	I(A)	Anode type
54.3	0.033	Scrap iron
32.24	0.05	Scrap iron
64.97	0.5	graphite

Table 4 shows the effect of anode type (scrap iron and graphite). It can be noticed that when scrap iron was used with applied current 0.05A the corrosion rate was 32.24 gmd while for graphite with applied current 0.5A the corrosion rate was 64.97gmd that means scrap iron need current 10% of the current of graphite to protect the structure from corrosion and give the corrosion rate half of the corrosion rate of graphite, this leads to economical benefits.

When scrap iron was used as anode instead of graphite, it was noticed that the corrosion rate was decreased as the applied current increased because corrosion current flows between the local action anodes and cathodes due to the existence of a potential difference between the two. Electrons released in an anodic reaction are consumed in the cathodic reaction. If we supply additional electrons to a metallic structure, more electrons would be available for a cathodic reaction which would cause the rate of cathodic reaction to increase and that of anodic reaction to decrease, which would eventually minimize or eliminate corrosion.

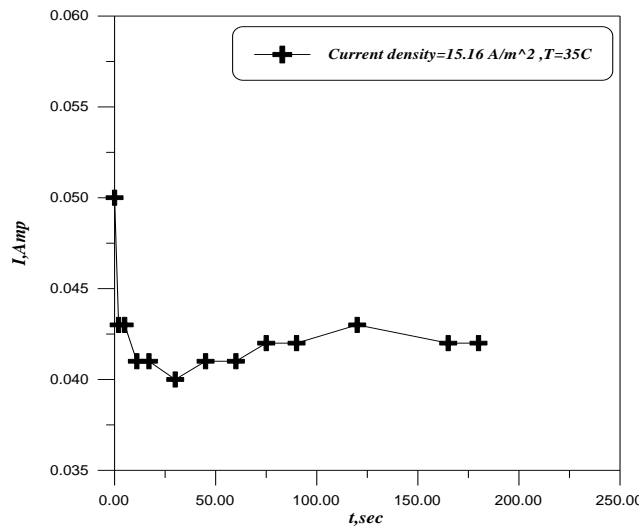


Figure12: Applied protection current against time at 35 °C.

As the cathodic current increases (more transfer of electrons), the cathodic reaction polarizes in the direction of local action anode potential, thus reducing further the potential difference between the anodes and cathodes. Complete cathodic protection is achieved when the

metallic structure becomes cathode (more negative). The severity of corrosion is directly proportional to the magnitude of the difference of potential between the anode and the cathode; hence by eliminating this difference, corrosion may be eliminated.

Fig.12 shows the variation of applied current density (15.16A/m²) with time. It is noticed that the applied current decreases considerably within 30 min from 0.05 to 0.041A then becomes almost constant.

Fig.13 shows the effect of potential with time. The potential at current density 15.16A/m² decreased (shift to more negative) in the first 5min from -0.39 to -0.51 V then varying slightly with time this is due to decreasing oxygen concentration [20].

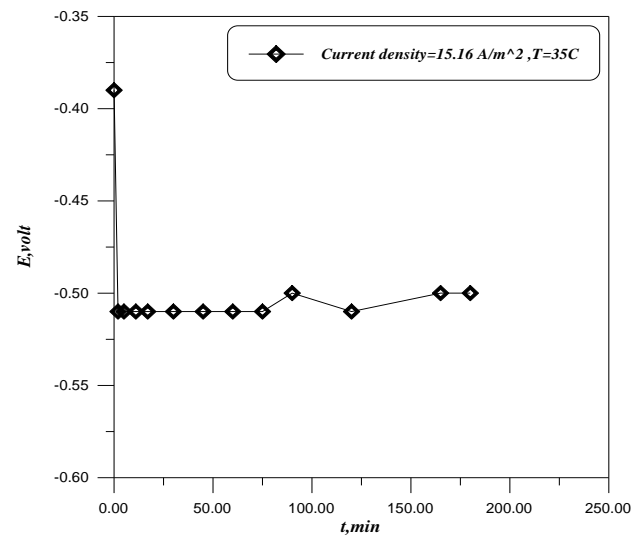


Figure13: Protection potential against time at 35 °C

Conclusions

- 1-Cathodic protection by scrap iron showed more economical protection than graphite. In case of scrap iron, applying 10% of total current required in case of graphite, increase the protection percent twice.
- 2- The protection percent increased from 3.96 to 77.58 gmd as the distance between anode and the structure decreased from 300 to 100 mm at constant temperature for graphite.
- 3- The lower the area ratio of cathode to anode, the higher the protection attained. For the ratio=1/2 the corrosion rate is 31.15gmd while at ratio=1 the corrosion rate is 34.1 gmd at constant temperature.
- 4-Applied protection current decreases significantly with time and protection potential shifts to more positive.
- 5- The behavior of corrosion rate with temperature is unstable in the case of free corrosion and also in the case when the cathodic protection applied.

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Nomenclature

- limiting current density: (A/m^2) i_L
 E_C : corrosion potential (V)
 μ : solution viscosity
 D : diffusivity
 T : solution temperature
 d : distance between anode and cathode (mm)
 I : applied current (A)
 E : applied voltage (V)

Abbreviations

- C.R: Corrosion rate ($g/m^2.d$)
 PP: Protection percent
 SCE: Standard Calomel Electrode