SACRIFICIAL ANODE CATHODIC PROTECTION OF LOW CARBON STEEL IN SEA WATER

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ABSTRACT

Cathodic protection is a corrosion-prevention technique which uses the electrochemical properties of metals to insure that the structure to be protected becomes the cathode of an electrolytic cell.

Laboratory evaluation was conducted on zinc electrode as anode material that used for sacrificial anode cathodic protection (SACP)of carbon steel.

Rate of zinc consumption during cathodic protection of carbon steel pipeline carrying seawater (4 % w/v NaCl solution) were measured by the loss in weight technique. Variables studied were seawater temperature (0-45^o C), flow rate (5-900 lit/h), pH (2-12) and duration time (1-4 h). It was found that the rate of zinc consumption increases with increasing seawater temperature, flow rate and duration time and decreases with pH increase. Under the mentioned operating conditions, the rate of zinc consumption during cathodic protection of steel ranged from 5.65×10^{-3} to 98.9×10^{-3} g/cm^2.day.

For the system under investigation, the cell responsible for cathodic protection is Zn/NaCl/Fe.

INTRODUCTION

Corrosion is an electrochemical process in which a current leaves a structure at the anode site, passes through an electrolyte and reenters the structure at the cathode site. Current flows because of a potential difference between the anode and cathode that is the anode potential is more negative than the cathode potential, and the difference is the driving force for the corrosion current. The total system-anode, cathode, electrolyte and metallic connection between anode and cathode is termed a corrosion cell (Shrier(1), 1976 and Halford, 1985).

Corrosion control is a process in which humans are very much in control of materials and environments can regulate the rate of corrosion, keeping it within acceptable or at least predictable limits for life of the structure (Trethewey and Chamberlain, 1996).

There are many methods for corrosion control as illustrated some of them (Bosich, 1970 and Schweitzer, 1987),(cathodic protection, anodic protection ,protective coating such as paint ,corrosion-resistant metals and alloys ,addition of inhibitors , very pure metals, ….etc).

The selecting method depends on many factors such as cost,efficiency, availability, contamination of environment with corroding metal, …etc.

Cathodic protection is unique amongst all the methods of corrosion control in that if required it is able to stop corrosion completely, but it remains within the choice of the operator to accept a lesser, but quantifiable, level of protection. Manifestly, it is an important and versatile technique. In principle, cathodic protection can be applied to all the so-called engineering metals.

In practice, it is most commonly used to protect ferrous materials and predominantly carbon steel. It is possible to apply cathodic protection in most aqueous corrosive environments, although its use is largely restricted to natural near-neutral environments (soils, sands and waters, each with air access). Thus, although the general principles outlined here apply to virtually all metals in aqueous environments, it is appropriate that the emphasis, and the illustrations, relate to steel in aerated natural environments (Shrier, (2), 1994 and Almardy, 1999).

Cathodic protection involves the application of a direct current (DC) from an anode through the electrolyte to the surface to be protected. This is often through of as "overcoming" the corrosion currents that exist on the structure. There is no flow of electrical currents (electrons) through the electrolyte but flow of ionic current. Cathodic protection eliminates the potential differences between the anodes and cathodes on the corroding surface. A potential difference is then created between the cathodic protection anode and the structure such that the cathodic protection anode is of a more negative potential than any point on the structure surface. Thus, the structure becomes the cathode of a new corrosion cell. The cathodic protection anode is allowed to corrode; the structure, being the cathode, does not corrode (Brown and Root, 2003 and Jezmar, 2003).

There are two proved methods of applying cathodic protection: sacrificial anode (galvanic) and impressed current. Each method depends upon a number of economic and technical considerations and as certain advantages. For every structure, there is a special cathodic protection system dependent on the environment of the structure (Scully, 1975).

Current distribution in cathodic protection system is dependent on several factors, the most important of which are driving potential, anode and cathode geometry, spacing between anode and cathode and the conductivity of the aqueous environment which is favorable toward good distribution of current (Shrier (2), 1994)

Structures commonly protected are the exterior surfaces of pipelines, ships' hulls, jetties, foundation piling, steel sheet-piling and offshore platforms. Cathodic protection is also used on the interior surfaces of water-storage tanks and water-circulating systems. However, since an external anode will seldom spread the protection for a distance of more than two or three pipe-diameters, the method is not suitable for the protection of small-bore pipework. Cathodic protection has also been applied to steel embedded in concrete, to copper-based alloys in water systems and exceptionally to lead-sheathed cables and to aluminum alloys, where cathodic potentials have to be very carefully controlled (Halford, 1985 and Davies, 2001).

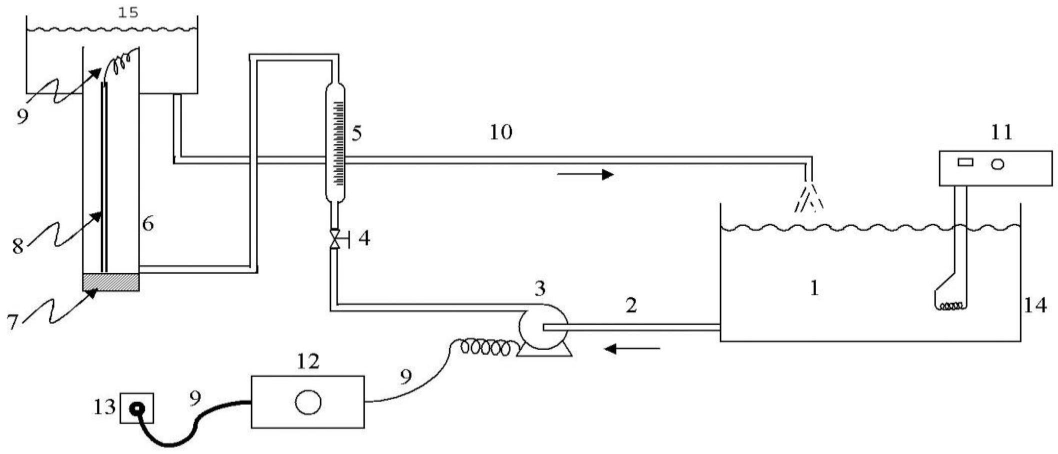
The present work considered the sacrificial anode cathodic protection. The effect of temperature (0-45^{o} C), flow rate (5-900 lit/h), pH (2-12) and time (1-4 h) on the rate of zinc consumption during cathodic protection of steel tube exposed to seawater (4 %w/v $NaCl$ in distilled water). The rate of zinc consumption was determined by the loss in weight technique.

EXPERIMENTAL WORK

The apparatus shown in figure (1) was used to study the variables, temperature (0-45^{o} C), flow rate (5-900 lit/h), pH (2-12) and time (1-4 h) in the sacrificial anode cathodic protection system.

The container vessel was filled with seawater (4% (w/v) $NaCl$), then adjusting the pH and temperature to the desired values. Before each run, the zinc strip was weighted and fixed at the inlet of the steel tube by rubber stopper and was electrically connected by an insulated copper wire to the steel tube outlet as shown in figure (1).The zinc strip is extending along the steel tube to ensure uniform current and potential distribution along the tube wall.

The seawater was pumped from the vessel by the pump through the rotameter to measure the desired flow rate, then the seawater inter from the below the steel tube and out from upper the steel tube to return to the vessel again (i.e. the seawater is circulated between the vessel and steel tube for desired time).After each run the zinc strip was rinsed in distilled water and brush to remove the corrosion products, dried with clean tissue then immersed in the benzene and acetone, dried again, and then re-weighted to determine the weight loss. The steel tube is also rinsed and dried by the same way above in order to re-use another time. After each run the vessel is emptied from the solution and washed with distilled water, then filled with a new prepared solution for new run.



1. Electrolyte (seawater)	2. Feed forward Pipe	3. Pump	4. Valve	5. Rota meter
6. Tube steel	7. Rubber stopper	8. Zinc strip	9. Copper wire	10. Feedback pipe
11. Heater or chiller	12. Variac	13. Electric source	14. Insulated vessel	15. Overflow

Fig. 1, Schematic diagram of apparatus used in sacrificial anode test system

RESULTS AND DISCUSSION

Time effect

Figures 2,3 and 4 show the rate of zinc consumption (dissolution), as an instead of corrosion rate of steel, with time at different temperatures, different flow rates and different pH, respectively. Where the rate of zinc dissolution increases with increasing time and this is normal case. But this increasing is not equally with time, where the dissolution rate in the first hour is more than second hour and so on. The reasons of that are attributed to continuous growth of the corrosion products layer with time, which affects the transport of oxygen to the metal surface and the activity of the surface and hence the corrosion rate. Also, the cathodic reactions will result an increase in pH with time either by the removal of hydrogen ions ($2H^+ + 2e \rightarrow H_2 \uparrow$) or by the generation of hydroxyl ions ($2H_2O + 2e \rightarrow H_2 \uparrow + 2OH^-$ and $O_2 + 2H_2O + 4e \rightarrow 4OH^-$) both reasons are reduced the corrosion rate of steel and hence the dissolution rate of zinc.

Temperature effect

Figures 2, 5 and 6 show the effect of temperature on the rate of zinc dissolution with time with different flow rates and with different pH's, respectively. The increase in the rate of zinc dissolution with increasing seawater temperature (particularly from 15 to 30^o C) may be explained in terms of the following effects:

1. A temperature increase usually increases the reaction rate which is the corrosion rate and according to the Freundlich equation (Shrier (2), 1976):

$$\mathit{Corrosion}\,\mathrm{rate} = \mathrm{k}\,\mathrm{C}_{\mathrm{O_2}}^{\mathrm{n}} \tag{1}$$

Where k is rate constant of reaction, C_{O2} (concentration of oxygen) and n is order of reaction. The rate constant (k) varying with temperature according to Arrhenius equation (Shrier (2), 1976):

$$k = k_o e^{-E/RT} \tag{2}$$

Where k_o is constant, E is activation energy, R is universal gas constant and T is temperature. Then from this formula ($k = k_o e^{-E/RT}$) indicates that the k is increased with increasing temperature and then the corrosion rate which is leads to increasing the rate of zinc dissolutions.

2. Increasing seawater temperature leads to decreasing seawater viscosity with a consequent increase in oxygen diffusivity according to stokes-Einstein equation (Cussler, 1984 and Konsowa and El-Shazly, 2002):

$$\frac{\mu D}{T} = \mathrm{constant} \tag{3}$$

Where μ is the seawater viscosity and D is the diffusivity of the dissolved oxygen. As a result of increasing the diffusivity of dissolved oxygen, the rate of mass transfer of dissolved oxygen to the cathode surface increases according to the following equation (Konsowa and El-Shazly, 2002):

$$J = k_d C_{O_2} = \frac{D}{\delta_d} C_{O_2} \tag{4}$$

With a consequence increase in the rate of zinc dissolution. Where k_d is mass transfer coefficient and J is mole flux of oxygen.

3. The decreases in seawater viscosity with increasing temperature improve the seawater conductivity with a consequent increase in corrosion current and the rate of corrosion.
4. On the other hand, increase of temperature reduce the solubility of dissolved oxygen with a subsequent decrease in the rate of oxygen diffusion to the cathode surface and the rate of corrosion.

It seems that within the present range of temperature effects 1, 2 and 3 are predominating.

Flow rate effect

Figures 3, 5 and 7 show the effect of solution flow rate on the zinc dissolution with time, with different temperatures and with different pH's, respectively. It can be seen from figures 3, 5 and 7 that the dissolution rate of zinc increases with increasing the flow rate. This may be attributed to the decrease in the thickness of hydrodynamic boundary layer and diffusion layer across which dissolved oxygen diffuses to the tube wall of steel with consequent increase in the rate of oxygen diffusion which is given by equation 4. Then the surface film resistance almost vanishes, oxygen depolarization, the products of corrosion and protective film are continuously swept away and continuous corrosion occurs. The flow rate of seawater may also caused erosion which combined with electrochemical attack.

pH effect

Figures 4, 6 and 7 show the effect of pH on dissolution of zinc with time, with different temperatures and with different flow rates, respectively. It can be seen from these figures that the rate of zinc dissolution increases with decreasing of pH (particularly at range of pH 5 to 2). Within the range of about 5 to 12 the corrosion rate of steel and hence dissolution rate of zinc is slightly dependent of the pH, where it depends almost on how rapidly oxygen to the metal surface. Although it was expected that at very high of pH value (12), the dissolution rate of zinc is much reducing because the steel becomes increasingly passive in present of alkalies and dissolved oxygen, but the nature of electrolyte (seawater) prevent that where chloride ions depassivate iron even at high pH. Within the acidic region (pH<5) the ferrous oxide film (resulting from corrosion) is dissolved, the surface pH falls and steel is more direct contact with environment. The increased rate of reaction (corrosion) is then the sum of both an appreciable rate of hydrogen evolution and oxygen depolarization.

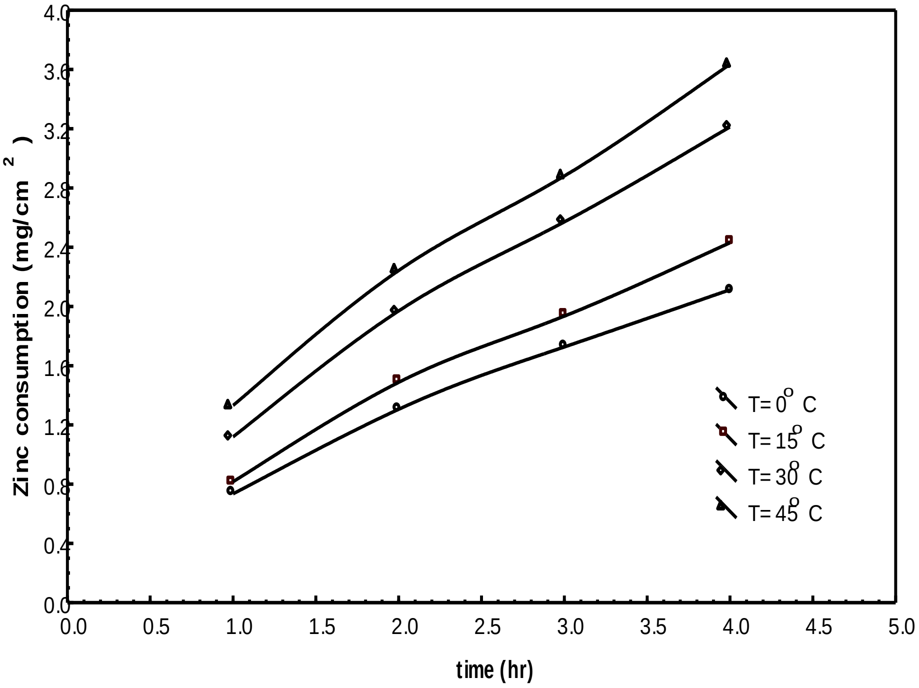


Fig. 2, Zinc consumption with time for different temperatures at flow rate=600 lit/h and pH=8

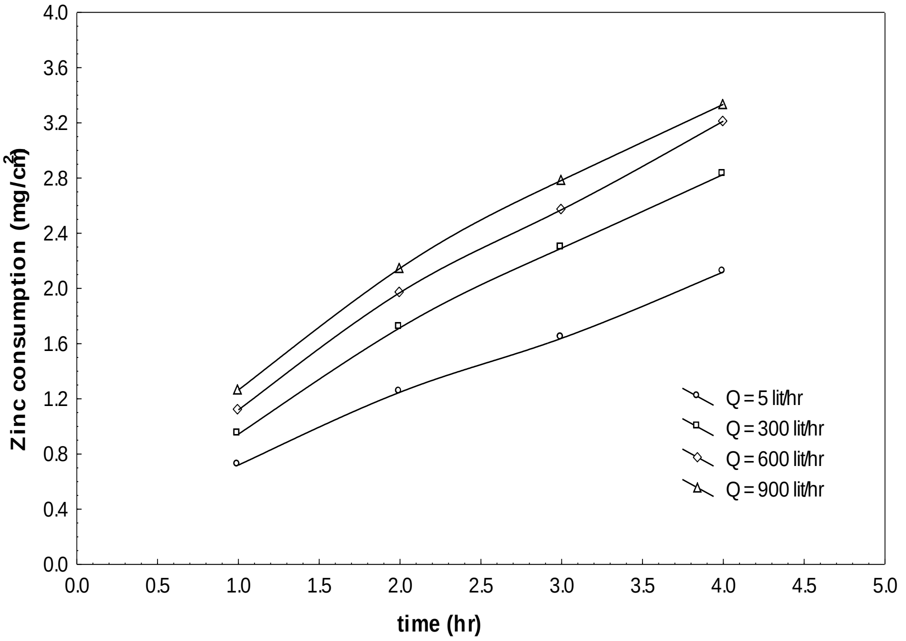


Fig. 3, Zinc consumption with time for different flow rate at temperature=30^o C and pH=8

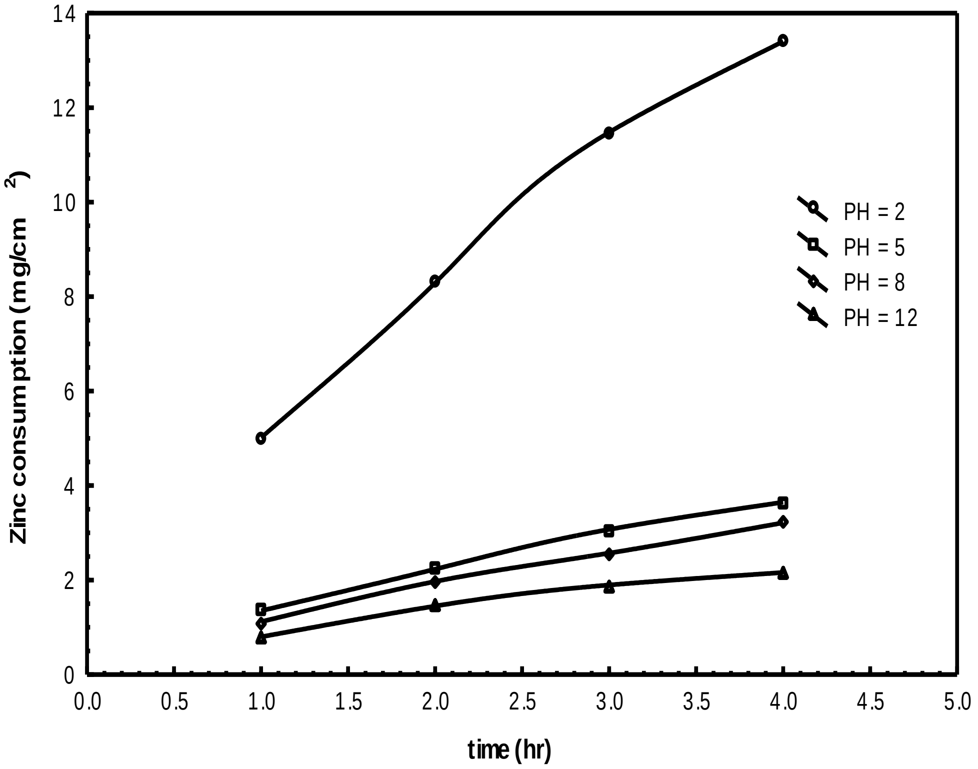


Fig. 4, Zinc consumption with time for different pH's at temperature 30^o C and flow rate=600 lit/h

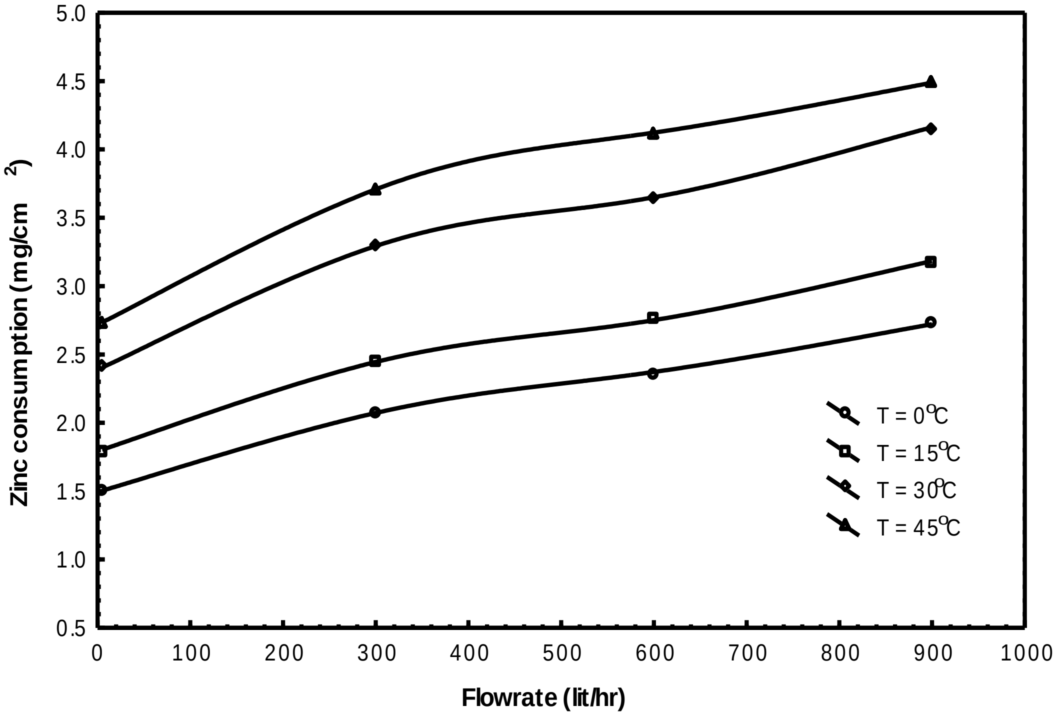


Fig. 5, Zinc consumption with flow rate for different temperatures at time=4 h and pH=5

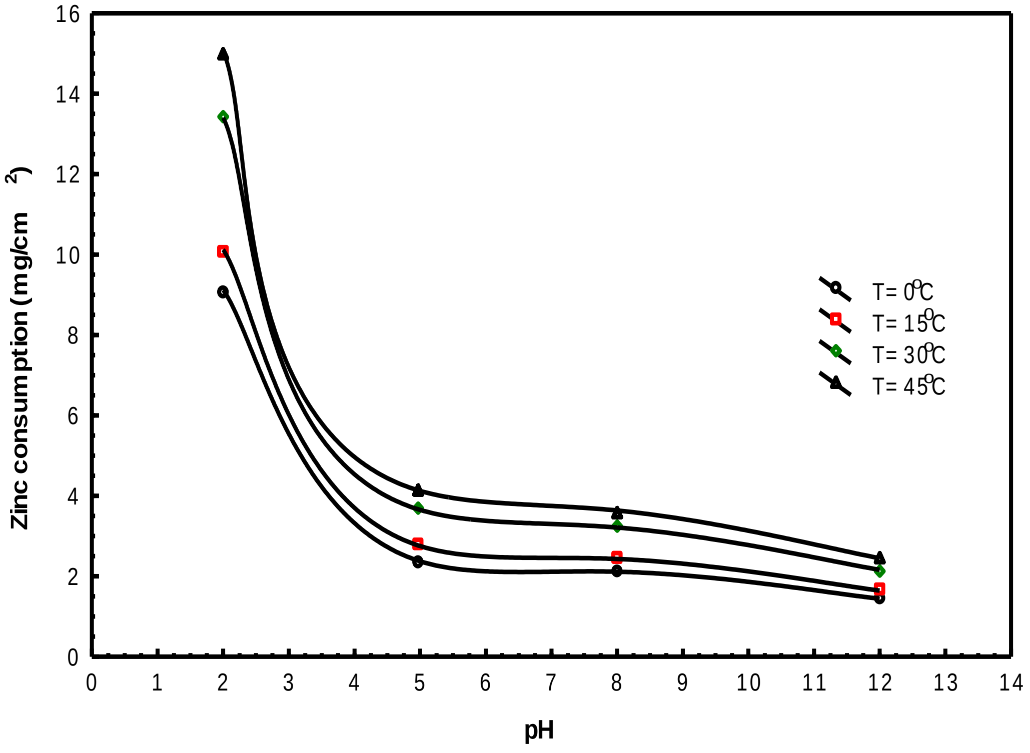


Fig. 6, Zinc consumption with pH for different temperatures at time=4 h and flow rate=600 lit/h

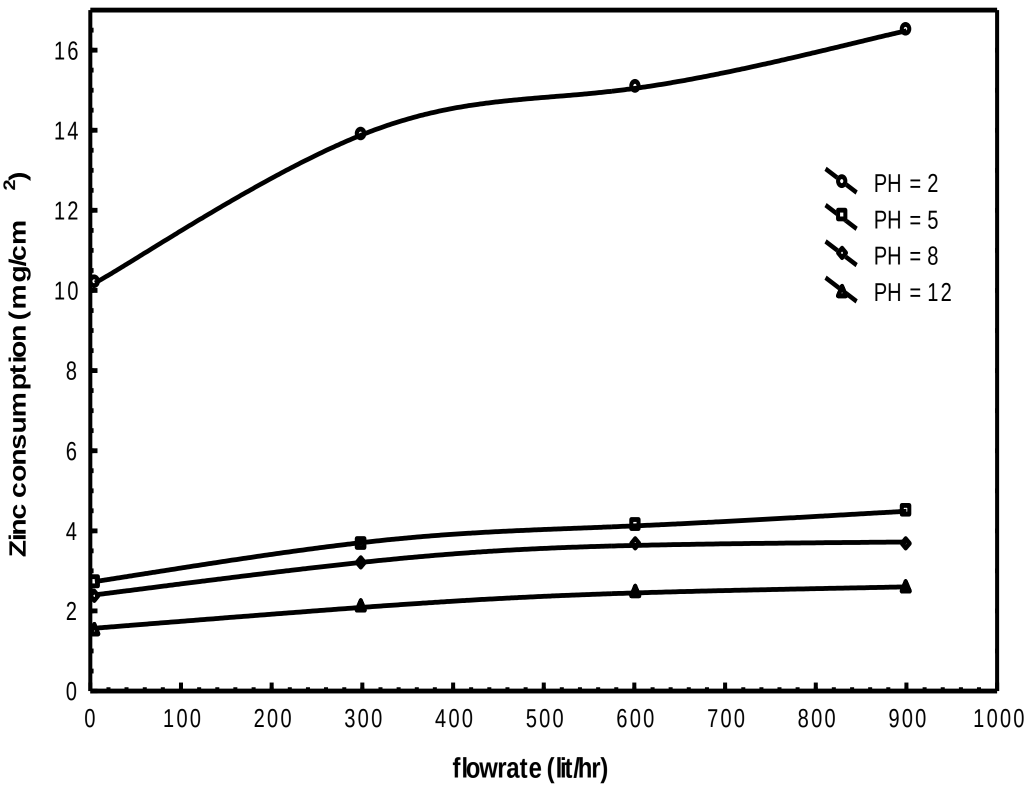


Fig. 7, Zinc consumption with flow rate for different pH's at time=4 h and temperature=45^o C

CONCLUSION

From the results obtained in the present work the following conclusion can be drawn: The study of sacrificial anode cathodic protection of short steel tube using zinc strip extended axially in the pipe revealed that under the present range of conditions of temperature, flow rate, pH of seawater and protection time, the rate of zinc consumption increases with increasing temperature, flow rate and time and with decreasing of pH. Zinc consumption during first hour is greater than during second hour and so on. The zinc consumption with very low pH is very high and the cathodic protection becomes unreliable.

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