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Study of the Rate of Zinc Consumption During Sacrificial Cathodic Protection of the Bottom of Crude Oil Storage Tanks

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Abstract

The bottom of crude oil storage tank suffers from severe corrosion as a result of the presence of an aqueous layer containing electrolytes $MgCl_2$, NaCl, $CaCl_2$ and H_2S beside porous deposits of sand and clay. Sacrificial cathodic protection using Zn anodes can be used to protect the tank bottom from corrosion. To contribute to the economic assessment of sacrificial cathodic protection the rate of Zn consumption under different condition was studied during cathodic protection in the present work. Variables studied were NaCl concentration, porosity of the porous bed overlying the tank bottom, height of the porous bed and the area ratio between Zn and the steel bottom. It was found that the rate of Zn consumption increases with increasing NaCl concentration and increasing porous bed height but decreases with increasing bed porosity. Increasing cathode/anode area ratio was found to increase the rate of Zn consumption.

Keywords: Crude storage tank; Cathodic protection; Zinc scarifying; Different aeration

Introduction

Steel equipment used in petroleum industry such as pipelines storage tanks heat exchangers distillation towers, etc. suffer from severe corrosion owing to the presence of same water containing electrolytes such as NaCl, $CaCl_2$ and $MgCl_2$ in crude oil [1-9]. The rate of corrosion of steel in crude oil is accelerated by the presence of H_2S in the crude [10]. The present work deals with the problem of steel crude oil storage tank corrosion. Although corrosion and protection of the outer surface of the storage tank has received a great attention, little has been done on the internal corrosion of crude oil storage tanks. The most studying vulnerable area to corrosion in crude oil storage tank is the bottom of the tank where an aqueous layer of electrolyte resides at the bottom, besides an insoluble porous sludge (e.g., sand and clay) settles on the tank bottom leading to corrosion by differential aeration cells [11,12].

Materials and Methods

Steel disk of 5 cm diameter isolated from the bottom by epoxy, Worked Zinc disks of different diameters (Zn diameter/Steel diameter) are of (0.1-0.15-0.2-0.25-0.3-0.35-0.4-0.45-0.5-0.55), broken ceramic rock size was adjusted using mortar then separate by Taylor sieves into four kinds have porosities (0.2-0.25-0.3-0.4), then washed by distilled water then dried in a furnace. Sodium chloride solution was prepared in different concentrations of (1-5)%, and weight loss method has been used in this experiment.

Procedures

Ceramic particles of selected velocity (e.g., 20) was prepared and placed with required height over the galvanic cell in the saline solution with desired concentration. The galvanic cell is composed of zinc and steel. Both electrodes are precleaned using emery paper, distilled water then ethanol before each run. The system (Galvanic cell in saline solution coated with ceramic bed) is left for 8 hours. The zinc disk is cleaned with distilled water followed by ethanol and weighted. The loss in weight for zinc disk is thus calculated (loss in weight=weight before test-weight after test) by turn Rate of Zn consumption=loss in weight of Zn disc/(area × time). The previous steps were repeated for different area ratio, saline solution concentration, bed height and porosity (Figure 1).

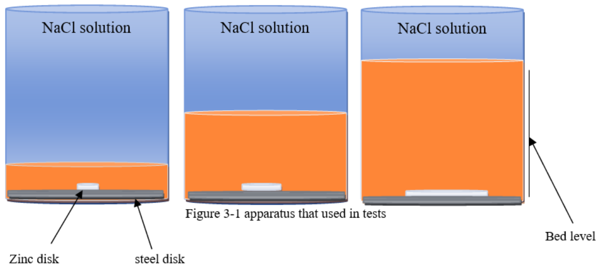

Figure 1: Apparatus used in test.

Results and Discussion

To explain the present results, it would be useful to discuss first the galvanic cells responsible for crude oil tank bottom corrosion and the reactions involved in these cells. Under the conditions existing at the tank bottom the following cells are likely to set up. Since steel contains a certain amount of carbon in the form of insoluble cementite (Fe_3C) which is more noble than Fe the following cell is formed in the presence of electrolytes [13].

(1) Fe/electrolyte/Fe_3C (cementite)

Whose reactions are

Anode: $Fe \rightarrow Fe^{++} + 2e$

Cathode: $\frac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^-$ (pH 4-10)

or $2H^+ + 2e \rightarrow H_2$ (pH<4)

The second type of corrosion cells arises as a result of the presence of porous deposits on the steel bottom where dissolved O_2 concentration is less than at areas without porous deposits; this situation leads to the formation of the cell.

(2) Differential aeration cell (under deposit corrosion)

Fe (O_2 poor area)/electrolyte/(O_2 rich area) Fe

Whose reactions are: Anode: (O_2 poor area under the deposit): $Fe \rightarrow Fe^{++} + 2e$

Cathode :(deposits free area): $\frac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^-$

Figure 2 shows the effect of NaCl concentration on the rate of Zn consumption at different bed porosities, the data show that the rate of Zn consumption increases with increasing NaCl concentration and decreasing bed porosity. The increase in the rate of Zn consumption with increasing NaCl concentration may be attributed to the decrease in cell reactance and the consequent increase in the potential difference between Zn and steel (driving force) which increase the cell current and the rate of Zn dissolution in the cell: Zn/electrolyte/Fe, whose reactions are:

Zn anode (-Ve): $Zn \rightarrow Zn^{++} + 2e$

Fe cathode (+Ve): $\frac{1}{2} O_2 + H2O + 2e \rightarrow 2OH^-$ (pH 4-10)

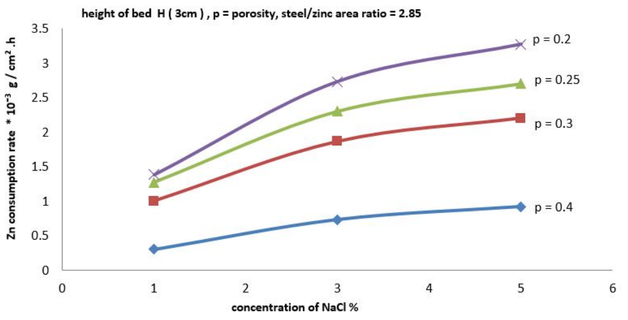

Figure 2: Effect of NaCl concentration on zinc consumption at different porosity at steel/zinc ratio of 2.85 and bed height 3 cm.

The increase in the rate of Zn consumption with decreasing bed porosity may be explained as follows. With increasing bed porosity dissolved O_2 diffuses through the bed where it is reduced at the steel cathode as shown above, in the meantime dissolved Zn ions diffuses away of the Zn anode through the highly porous bed. As the bed porosity decreases diffusion of dissolved O_2 and Zn^{++} ions through the bed becomes difficult. Accordingly, $ZnCl_2$ accumulate at the anode surface where it undergoes hydrolysis to produce acidic solution according to the equation,

$ZnCl_2 + 2H_2O \rightarrow Zn(OH)_2 + 2HCl$

The decrease in pH at the cell Zn/Fe changes the cathodic reaction from dissolved O2 reduction to H_2 evolution reaction [14].

$2H^+ + 2e \rightarrow H_2$

H_2 evolution reaction is faster than the O_2 reduction reaction, because it is not diffusion controlled as O_2 reduction [14]. Accordingly, H_2 evolution reaction increases the rate of Zn dissolution by an amount higher than that where the cathode reaction is O_2 reduction [14].

Figure 3 shows the effect of Steel/Zinc area ratio on the rate of Zn consumption at different bed porosities, in all case the rate of Zn consumption increases with increasing the cathode/anode area ratio.

This may be explained by the fact that by increasing cathode (Fe) area the amount of dissolved O_2 reduced at the cathode increase with a corresponding increase in the limiting current (corrosion current), accordingly the corrosion current density at the anode increases with a consequent increase in the rate of Zn dissolution. This finding is consistent with the results of previous studies on the role of cathode/anode area ratio in the rate of galvanic corrosion [15-18].

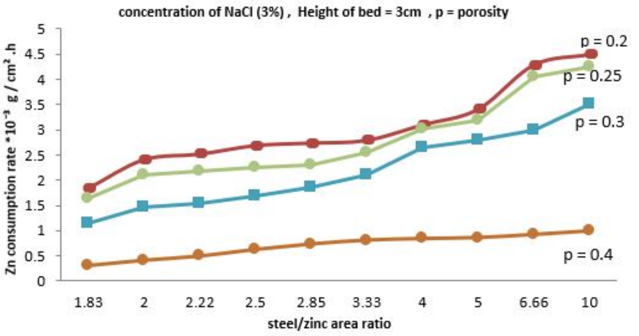

Figure 3: Effect of steel/zinc area ratio on zinc consumption at different porosity and fixed bed high of 3 cm.

Figure 4 shows the effect of bed porosity on the rate of Zn consumption at different bed heights , the data show that the rate of Zn consumption increases with decreasing bed porosity as maintained and explained earlier, the larger the bed height the higher the rate of Zn consumption.

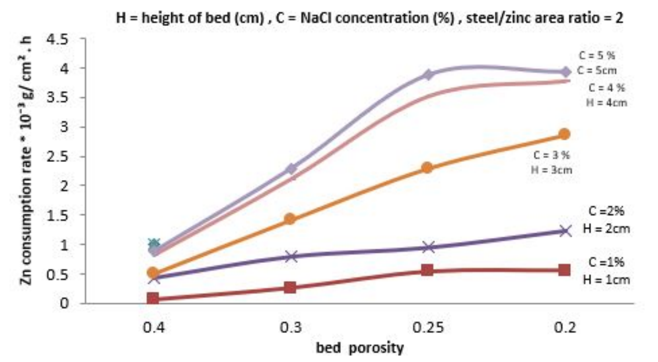

Figure 4: Effect of bed porosity on zinc consumption at different bed height, steel/zinc ratio=2.

Figure 5 shows the effect of bed height on the rate of Zn consumption, the rate of Zn consumption increases with increasing bed height, this can be explained by an agreement similar to that used in case of the effect of bed porosity i.e., increasing bed height hinders the diffusion of dissolved O_2 from the aqueous solution to the cathode surface and delays the diffusion of $ZnCl_2$ from the anode surface to the aqueous solution above the bed. As a result of $ZnCl_2$ hydrolysis at the Zn/Fe couple, the cathode reaction changes from dissolved O_2 reduction to H_2 evolution which intensifies the rate of Zn consumption in view of the fact that H_2 evolution reaction is much faster than dissolved O_2 reduction [14,19].

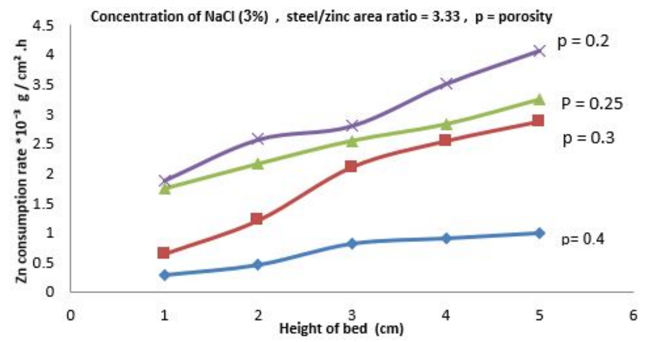

Figure 5: Effect of bed height on rate of zinc consumption at different porosity and steel/zinc ratio of 3.33 and salt concentration 3%.

Dissolved O_2 reduction is slowed by the diffusion of dissolved O_2 to the cathode surface while H_2 evolution in not hindered by diffusion of H^+ to the cathode surface [20,21].

Conclusions

- Generally, zinc consumption rate increases with increasing NaCl concentration solution.
- Increasing bed height and/or decreasing the bed porosity leads to zinc consumption rate increases, because they hinder the diffusion of dissolved the O_2 from the solution above the bed to cathodic sites and changes the cathodic reaction from O_2 reduction to H_2 evolution.
- Steel/zinc (cathode/anode) area ratio increases the rate of Zn consumption increasing.
- Sacrificial cathodic protection of the bottom of steel crude oil storage tank is a promising process.

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