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Short Communication

Influence of Fe^{3+} Diffusion on the Rate of Corrosion of Carbon Steel Imbedded in Porous Media in Acidic Solutions

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In this work, rates of corrosion of a steel disc placed underneath a porous bed of inert particles in acidified $FeCl_3$ solution were measured. Variables studied were particle size (from 10 to 85 mesh), bed height (from 0.5 to 5 cm) and $FeCl_3$ (depolarizer) concentration (from 0.1 to 1 M). The rate of corrosion was found to decreases by an amount ranging from 9 to 84 compared to the case without deposit. The rate of corrosion was found to increase with increasing particle size (d) and $FeCl_3$ concentration, while increasing bed height (x) was found to decrease the rate of corrosion. The rate constant of the partially diffusion-controlled of steel (k) was correlated to bed height and particle diameter. Implication of the present results for the corrosion of underground structures such as pipelines, storage tanks, cables, etc. by acid rain and industrial waste solutions was highlighted. The importance of the present work for minimizing under-deposit corrosion in storage tanks and pipelines handling slurries was pointed out. The relevance of the present study to corrosion of underground steel pipelines buried in the river bed and sea bed was noted.

Keywords: Diffusion-controlled corrosion; Underdeposit corrosion; Storage tank corrosion; Slurries pipeline corrosion; Porous materials; Contacts

1. INTRODUCTION

Many industries such as chemical, metallurgical, oil, wastewater treatment involve handling slurries in steel equipment such as pipelines and storage tanks, typical examples include transportation and storage of pulp slurry, pulverized coal and minerals, wastewater containing suspended matter, crude oil (a mixture of oil, water and sand). During transportation of these slurries in steel pipeline at low flowrates formation of a porous layer of deposit on the lower part of the pipeline takes place (Fig. 1).

Also, sedimentation takes place during the storage of slurries in steel storage tanks (Fig.1). The presence of a porous layer of deposit on the steel surface affects its rate of corrosion via controlling the diffusion of dissolved oxygen depolarizer to the cathodic sites of the corrosion cells [1,2].

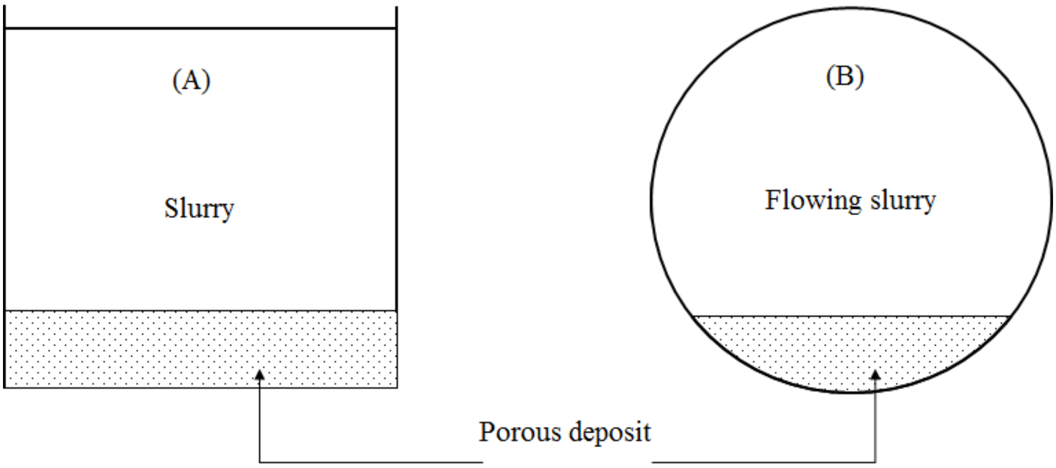

Figure 1. Steel surface lying below a layer of porous sludge (A: storage tank containing solution with a porous deposit at the bottom; B: cross-section of a pipeline carrying flowing slurry with a porous deposit at its bottom)

The aim of the present is to study the effect of different variables on the diffusion-controlled corrosion of a horizontal steel surface placed under a bed of inert particles. Although it is expected that the rate of steel corrosion will decrease in porous media, the present study seeks to determine the extent to which the rate of corrosion decreases and the relative effects of particle size and bed height on the decrease in the rate of corrosion. To this end an accelerated test, namely the corrosion of steel on acidified $FeCl_3$ was chosteel sen to conduct the present study in view of the diffusion controlled nature of steel corrosion in acidified ferric salts [3] which simulates natural corrosion where the rate is controlled by the diffusion of dissolved O_2 to the cathode sites of the corrosion cells in the pH range 4 – 10. The present accelerated technique obviates the long time needed in case of natural corrosion with dissolved O_2 as a depolarizer. The low rate of steel corrosion with dissolved O_2 as a depolarizer arises from the low solubility of O_2 in aqueous solutions and its low diffusivity [4]. Although some work has been done on the effect of moving particles (slurries) on metal damage [5-7], little has been done on the corrosion behavior of steel tanks and pipelines containing solid sediments at their bottom.

Previous studies on steel corrosion under porous media [8,9] focused on atmospheric corrosion where the rate of corrosion is determined by the diffusion of O_2 and moisture through the porous media to the steel surface.

The present study is relevant to the corrosion of underground steel structures (pipelines, fuel tanks, piles, etc) by acid rain which may flood the soil. Soils containing Cl^- ions are more susceptible owing to the high ability of theses ions to destroy protective oxide film [1,2].

2. EXPERIMENTAL TECHNIQUE

The apparatus used (Fig. 2) consisted of a 250 cm^3 glass beaker, a weighed carbon steel disc (0.15% C) of 7 cm diameter, with its bottom isolated with epoxy resin, was placed at the bottom of the beaker. A bed of inert ceramic particles was placed above the steel disc. Bed height ranged from 0.5 to 5 cm while particle size ranged from 10 to 85 mesh. 200 cm^3 of acidified $FeCl_3$ were placed above the bed. Corrosion was allowed to take place for 1 hour after which the steel disc was washed, dried, and reweighed.

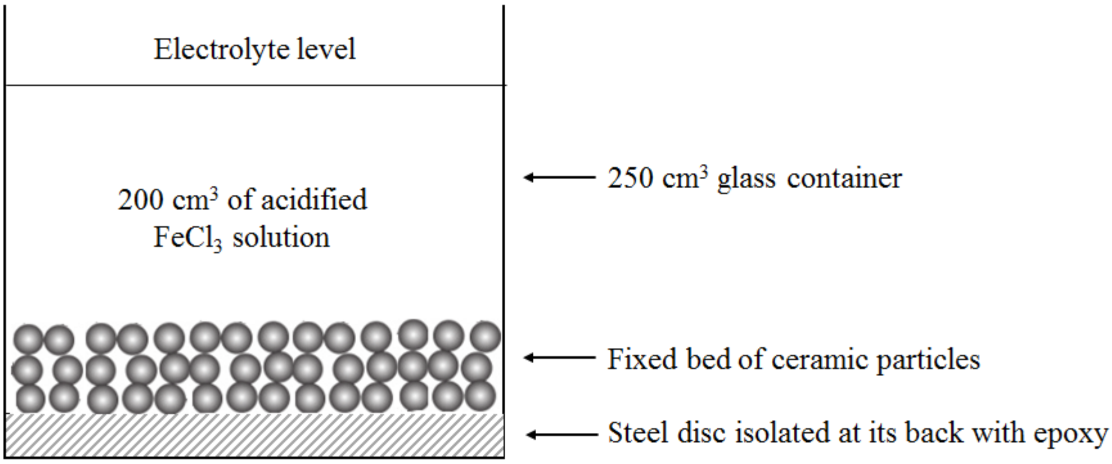

Figure 2. Experimental apparatus

The average rate of corrosion was calculated from the formula:

$$\text{Rate of corrosion} = \frac{\text{loss in weight}}{\text{disc area} \times \text{time}} \tag{1}$$

All experiments were carried out at 22 ± 1˚C. For each run, a fresh $FeCl_3$ solution was used. $FeCl_3$ ranged in concentration from 0.1 to 1 M dissolved in 0.1 N HCl. Before each run the steel disc was polished with emery paper, pickled in 5% HCl for 10 minutes to remove iron oxide films then washed and dried.

3. RESULTS AND DISCUSSION

Steel corrosion in aqueous solution takes place through the formation of a multitude of microscopic cells formed between the less noble iron and the more noble cementite (Fe_3C) grains according to the following reactions [1,2]

Cell: Fe/electrolyte/Fe_3C

Fe (anode)

$$Fe \rightarrow Fe^{2+} + 2e \tag{2}$$

Fe_3C (cathode)

$$\frac{1}{2}O_2 + H^+ + 2e \rightarrow H_2O \tag{3}$$

In the pH range 4 – 10 steel corrosion is controlled by the rate of dissolved O_2 diffusion to the cathodic sites [1,2]. Assuming there is no oxide film on steel the rate of steel corrosion R in mol/cm^2·s is given by the equation [10]

$$R = \frac{2\,C_{O_2}}{\frac{1}{k_o} + \frac{1}{k}} \qquad (4)$$

where k is the mass transfer coefficient of O_2 diffusion to the steel surface, k_o is the rate constant of O_2 reduction at the cathodic sites and C_{O_2} is the saturation solubility of O_2 depolarizer in water. Since the rate of O_2 reduction is fast [1,2] compared to the diffusion step, equation (4) reduces to

$$R = 2\,k\,C_{O_2} \qquad (5)$$

$$k = \frac{D}{\delta} \qquad (6)$$

where D is the diffusivity of the depolarizer (dissolved O_2 in natural corrosion and $FeCl_3$ in the present work), δ is the diffusion layer thickness at the corroding steel surface.

In the present case the cathodic reaction

$$Fe^{3+} + e \rightarrow Fe^{2+} \qquad (7)$$

replaces O_2 reduction (equation 3) at the cathodic sites.

Figs. 3 and 4 show the effect of bed height (x) on the rate of steel corrosion at different $FeCl_3$ concentration and particle diameter (d_p), respectively. The rate of steel corrosion in $FeCl_3$ solution decreases with decreasing bed particle, this may be attributed to: (i) fine particles tend to mask the steel surface and act like a surface coating which protects the steel surface against corrosion. (ii) the decrease in $FeCl_3$ diffusivity in the porous bed as a result of the tortuous path followed by the decrease in the diffusion of $FeCl_3$ through the porous media [11], the effect of tortuosity on the effective diffusivity, Ď, is given by [11,12]

$$\check{D} = \frac{D\mathcal{E}}{\sigma} \qquad (8)$$

where Ď is the diffusivity of $FeCl_3$ in the porous media; D is the diffusivity of $FeCl_3$ outside the bed in the solution; Ɛ is the bed porosity and σ is an empirical constant called the tortuosity factor, its value ranges from 1.44 to 6.25 [11,12].

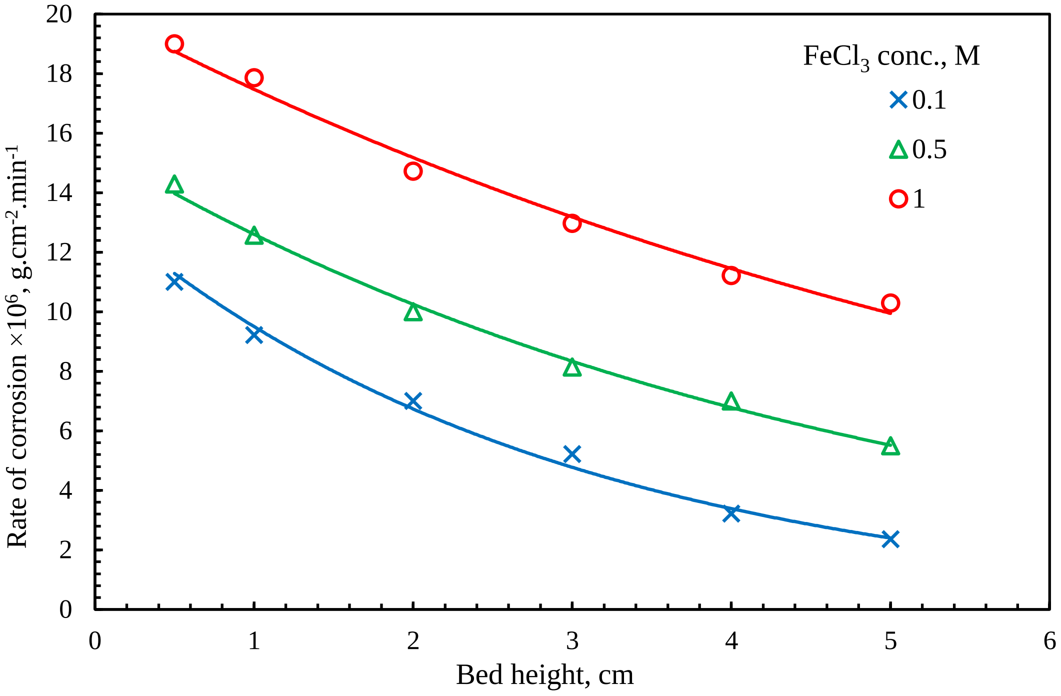

Figure 3. Effect of bed height on the rate of steel corrosion at different $FeCl_3$ concentrations.

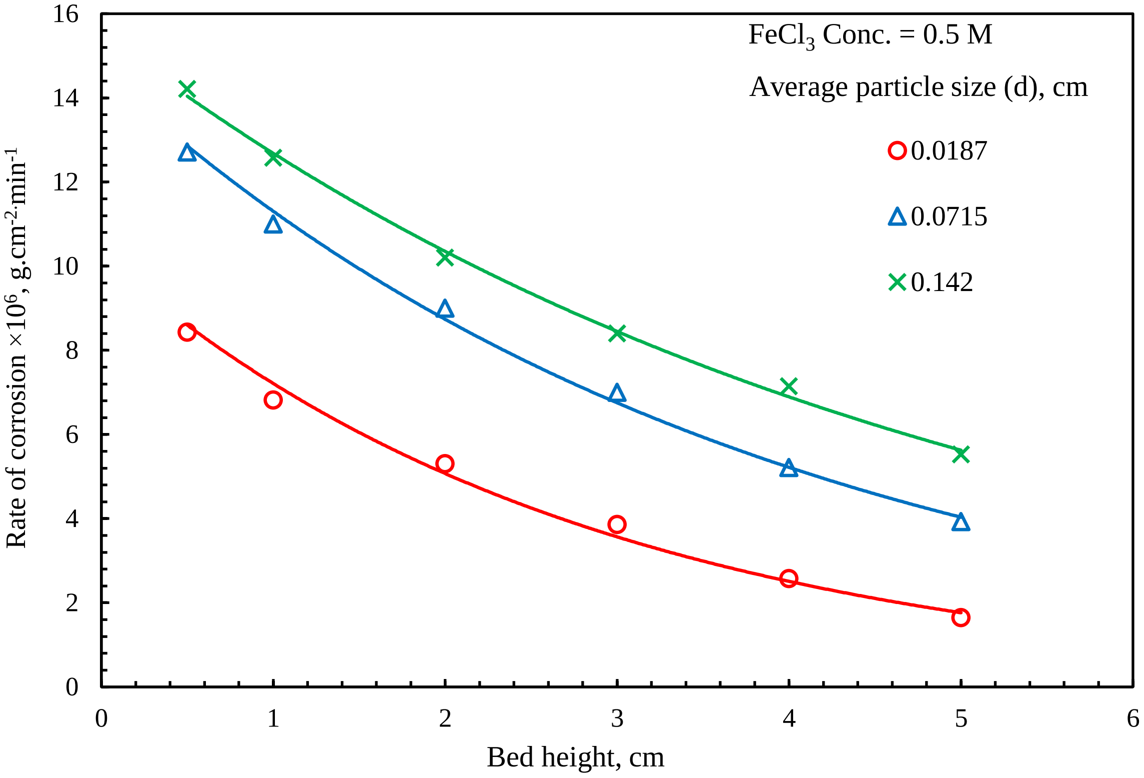

Figure 4. Effect of bed height on the rate of steel corrosion at different particle sizes.

In an attempt to quantify the present data the rate constant of the corrosion process was calculated from the equation

$$R = K\,C \tag{9}$$

where R is the rate of corrosion, mol/cm^2.s, C is the depolarizer concentration in the bulk of the solution, and K is the rate constant which depends on the bed height (x) and particle size (dp).

K was found to decrease with increasing bed height according to the equation

$$K = a\,x^{-0.404} \qquad (10)$$

Also, it was found that, for a given set of conditions K increases with increasing particle size according to the equation

$$K = a_1\,d^{0.404} \qquad (11)$$

Combining equations (10) and (11) gives:

$$K = a_2\,x^{-0.404}\,d^{0.404} \qquad (12)$$

Where a, a_1, a_2 are constants, the value of the constant a_2 ranges from 1×10^{-5} to 6×10^{-5} (Fig. 4) depending on the $FeCl_3$ concentration, this can be attributed to the following effects:

(i) The physical properties of the solution especially the depolarizer diffusivity D of $FeCl_3$ depend on $FeCl_3$ concentration [12,13], as the concentration of $FeCl_3$ increases its diffusivity tends to decrease owing to the increase in the solution viscosity and interionic attraction [12,13].

Fig. 5 shows that the values of K for $FeCl_3$ concentrations 1 and 0.5 M are close and are much lower than K for $FeCl_3$ concentration of 0.1 M, it seems that as $FeCl_3$ concentration decreases below 0.1 M during corrosion, H_2 evolution from the acidic solution becomes possible along with Fe^{3+} reduction at the cathodic sites of the corrosion cells as indicated by the schematic polarization curve shown in Fig. 6 [1,2, 14] in which $i_{Fe^{3+}}$ is the current due to Fe^{3+} reduction and i_{H_2} is the current due to H^+ reduction. H_2 bubbles induce microconvection at the corroding surface during their growth, detachment, and rise through the porous bed with a consequent decrease in the diffusion layer thickness δ and a corresponding increase in the mass transfer coefficient of $FeCl_3$ transfer to the corroding surface [15].

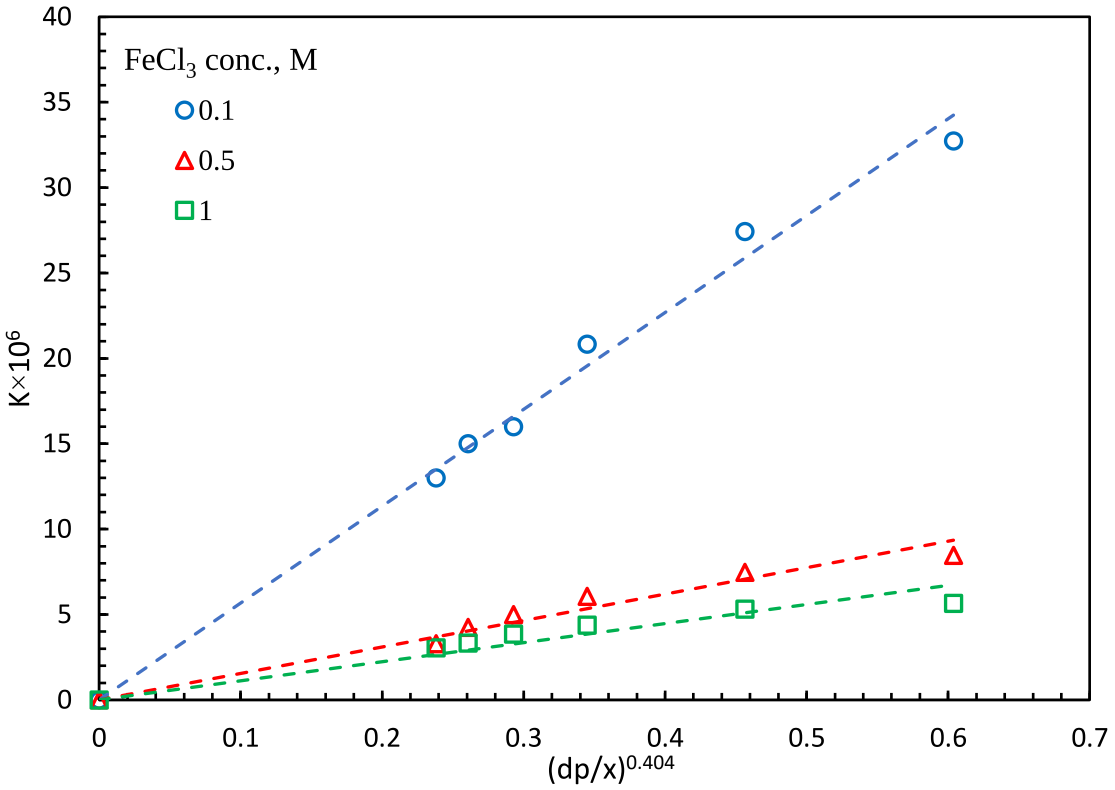

Figure 5. Effect of the combined bed height and particle size on the corrosion rate constant

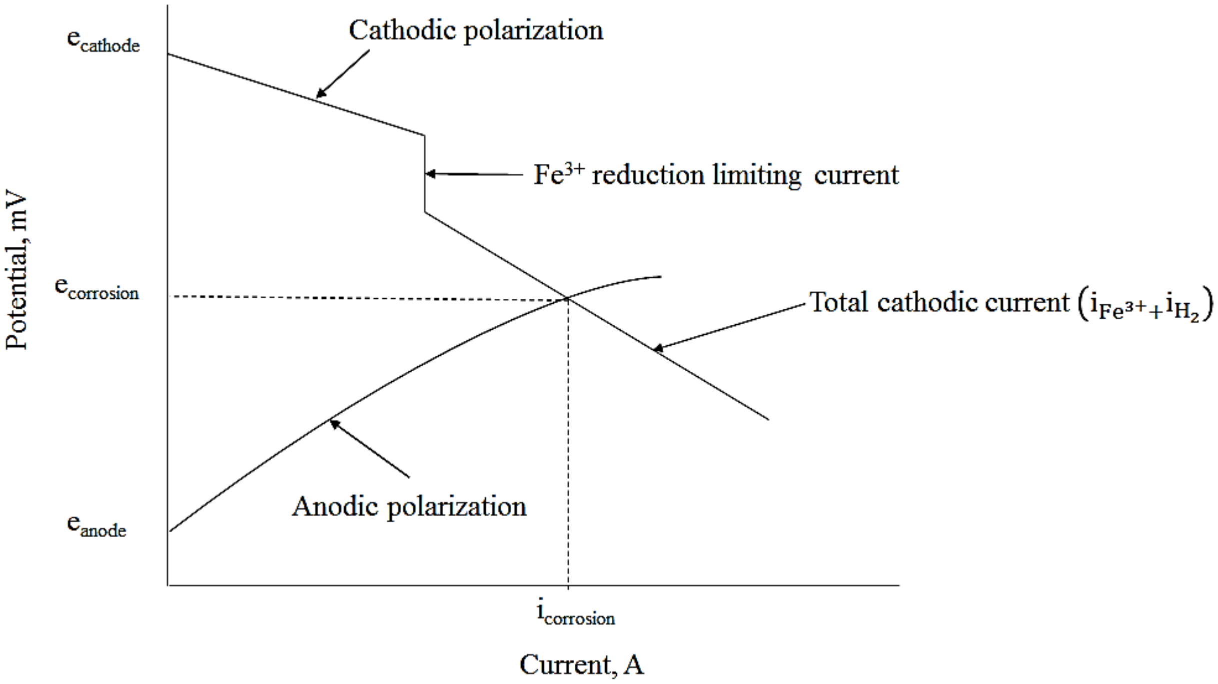

Figure 6. Schematic Evans corrosion diagram showing the contribution of $FeCl_3$ with H^+ as a cathodic depolarizer in the corrosion of steel in acidified $FeCl_3$

Table 1. Effect of bed height on the % decrease in the rate of steel corrosion at different particle size ($FeCl_3$ concentration = 0.5 M)

Bed height, cm	% decrease in the rate of corrosion at different particle size d_p		
	d_p = 0.0187 cm	d_p = 0.0715 cm	d_p = 0.142 cm
0.5	18	13	9
1	33	25	19
2	48	38	34
3	62	52	46
4	75	64	54
5	84	73	64

Table 1 shows that the rate of steel corrosion under-deposit decreases by an amount ranging from 9 to 84 % depending on bed height and particle size. This result gives some credit to porous deposits which are usually accused of initiating corrosion through the formation of differential aeration cells on metal surfaces [1,2].

4. CONCLUSION

The present results have shown that the presence of a porous layer of deposit on a steel surface decreases the rate of steel corrosion via hindering the rate of depolarizer diffusion to the metal surface. Under the present conditions, the rate of corrosion of steel under-deposit decreases by an amount ranging from 9 to 84 % depending on bed height and particle size compared to the case without a porous deposit.

Although the presence of porous deposits on metallic surfaces is objectionable in view of their ability to initiate differential aeration cells, the present retarding effect should not be ignored in dealing with corrosion under deposits which may be formed in equipment such as pipelines and storage tanks. The relevance of the present results to corrosion of steel pipelines buried in the sea bed, river bed, and soils flooded with acid rain should be considered in managing corrosion of these structures.

An important implication of the present results is that in case of protecting the buried steel structure by cathodic protection (C.P), the load on cathodic protection would be alleviated by the protective effect of the porous media i.e the operating costs of cathodic protection would decrease due to the decrease in Zn consumption in case of sacrificial C.P and the current magnitude in case of impressed current C.P.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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