

Cathodic Protection of Copper Pipes Carrying Saline Water in the Presence of Aerobic Bacteria

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Abstract

Rates of zinc consumption during cathodic protection of a copper pipeline carrying saline water were measured by the loss in weight technique. The study of sacrificial anode cathodic protection of short copper tube using zinc strip extended axially in the pipe revealed that : (i) The increase of zinc consumption with time of exposure (1-3 h's) at different flow rates (turbulent flow) (300-600 l/hr) while the temperature, solution concentration and the pH were fixed at 20°C, 3.5%wt NaCl, and pH=8 respectively in absence and presence of bacteria. (ii) Increase of zinc consumption with flow rates (300-600 l/hr) at different temperatures (10-40°C) while solution concentration and time of exposure were fixed at 3.5 %wt NaCl and 3hr's respectively, in absence and presence of bacteria. (iii) Increase of zinc consumption with flow rates (300-600l/hr) at different solution concentrations (1-3.5 %wt NaCl) while the time of exposure and temperature were fixed at 3h's and 30°C respectively in absence and presence of bacteria. Generally the Zn consumption during cathodic protection ranges from (2.424- 26.741 g/m²) and (5.352-27.296g/m²) in absence and presence of bacteria respectively.

Key Words: Sacrificial anode, Cathodic protection, Seawater, *Pseudomonas fluorescens*, microbiological corrosion.

Introduction

Microbiological corrosion is the deterioration of materials caused directly or indirectly by bacteria, algae, moulds or fungi; singly or in combination. Microbiological corrosion refers to corrosion and ensuing loss of metal caused by biological organisms. Microbiological influenced corrosion (MIC) can occur in any aqueous environments, and because of the omnipresent nature of microbes in fluid systems, MIC is a commonly occurring phenomenon. MIC is a common problem in industrial processes due to the presence of microbes, adequate nutrients and corrosive byproducts [1]. Biological organisms fall under two groups based on the type of corrosion they engender: (a) Anaerobic corrosion (b) aerobic corrosion. Sulfate reducing bacteria (SRB) from the genera desulfovibrio are a typical example of anaerobic MIC. Aerobic sulfur oxidizing bacteria of the type thiobacillus can create an environment of up to 10 percent sulfuric acid, thereby encouraging rapid corrosion [2].

The mechanisms potentially involved in MIC are summarized as:

1-Cathodic depolarization associated with anaerobic growth, whereby the cathodic rate limiting step is accelerated by micro-biological action.

2-Formation of occluded surface cells, whereby microorganisms form "patchy" surface colonies. Sticky polymers attract and aggregate biological and non-biological species to produce crevices and concentration cells, the basis for accelerated attack.

3-Fixing of anodic reaction sites, whereby microbiological surface colonies lead to the formation of corrosion pits, driven by microbial activity and associated with the location of these colonies.

4- Underdeposit acid attack, whereby corrosive attack is accelerated by acidic final products of the MIC.

5-Depassivation of metal surfaces and induction of corrosion

6- Attack of metal by a process in which microbes and the metal cooperate to sustain the corrosion reaction.

7- Attack due to a combination of bacteria.

8- Removal of corrosion inhibitors (oxidation of nitrite or amines). [3, 2].

Pseudomonas Fluorescens

Pseudomonas is a gram-negative, aerobic, rod-shaped bacterium with unipolar motility [4]. These bacteria are common inhabitants of soil and water [5]. Maximum activity at pH (7.5-8.5) no activity at pH 6 and below [6]. *Pseudomonas* bacteria is now being found in heating and chilled water systems. Until the last couple of years bacteria in these types of systems were of little concern and not often investigated. Now a bacteria known as *pseudomonas* has started to appear in main water supplies, where it has no significant health concerns, but can have a major effect on the water systems in commercial buildings. *Pseudomonas* is a biofilm or slime-producing bacteria and left to proliferate can cause severe corrosion and blockages within pipework. This particularly affects modern buildings with the small-bore pipework and small orifices associated with control valves [7]. The biofilm can reduce the water flow and provide a habitat for other corrosion inducing bacteria that will lead to pitting and leaking pipework. The net result of *pseudomonas* in heating and chilled water systems is a decrease in their efficiency and to increase down time and costs from occurrence of leaks. The presence of *Pseudomonas Fluorescens* in artificial tap water affects the composition of the oxide layer and the susceptibility to pitting corrosion of copper and 70/30 brass. In the sterile conditions the mass loss is lower in brass than in copper while the presence of bacteria enhances the attack in brass. Bigger and deeper pits can be seen in the presence of microorganisms [8]. The adhesive properties of the bacterium *Pseudomonas Fluorescens* to stainless steel were found to be highly dependent on surface shear stress and the time and concentration of cells used in the incubation procedure. Maximum levels of adhesion occurred in zones of lowest surface shear stress [9].

Apparatus and procedure:

The apparatus shown in figure(1) was used to study the variables: flow rate (300-600 l/h) and time (1-3h) at fixed NaCl concentration (3.5wt%) and temperature (20°C); flow rate (300-600 l/h) and temperature (10-40°C) at fixed NaCl concentration (3.5wt%) and time (3h); and, flow rate (300-600 l/h) and NaCl concentration (1-3.5wt%) at fixed temperature (30°C) and time (3h) in absence and presence of bacteria. After the container vessel was filled with saline water pH (8) the NaCl concentration and temperature were adjusted to the desired values. Before each run, the zinc strip used as sacrificial anode was weighed and then fixed at the inlet of the copper tube by rubber stopper and was electrically connected by an insulated copper wire to the copper tube outlet. The zinc strip is extending along the copper tube to ensure uniform current and potential distribution along the tube wall. The saline water was pumped from the vessel through the rotameter to measure the desired flow rate (i.e. the saline water is circulated between the vessel and copper tube for desired time). After each run the zinc strip was rinsed in distilled water and brushed with emery paper to remove the corrosion products, dried with clean tissue then immersed in Chloroxenol, dried again, and then re-weighed to determine the weight loss. The copper tube was also rinsed and dried with clean tissue before the next run. After each run the vessel was emptied from the solution, washed with distilled water and then filled with a new prepared solution for new run.

In the presence of bacteria the bacterial cells were grown in nutrient broth for 6 hours at 32 °C in a rotary shaker (120 rpm) then the absorbance of this broth was set to an 600 A° of Optical Density (O.D) 0.15 (243x10⁷ Bacteria/cm³). [8]. After the container vessel was filled with nutrient broth containing bacteria(pH (8)), the NaCl concentration and temperature were adjusted to the desired values. The inoculated broth was pumped from the vessel through the rotameter to measure the desired flow rate, then through the copper tube and returned back to the vessel (i.e. the inoculated broth is circulated between the vessel and copper tube for desired time).

After each run the vessel is emptied from the solution and washed using recirculating hot water loop (greater than 90°C) to kill bacteria, then filled with a new prepared solution for new run.

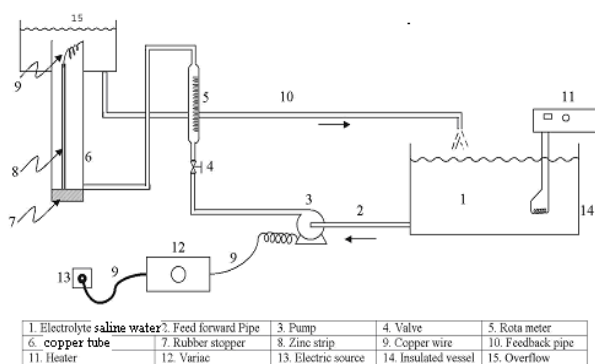


Fig.1: Schematic diagram of apparatus used in sacrificial anode test system

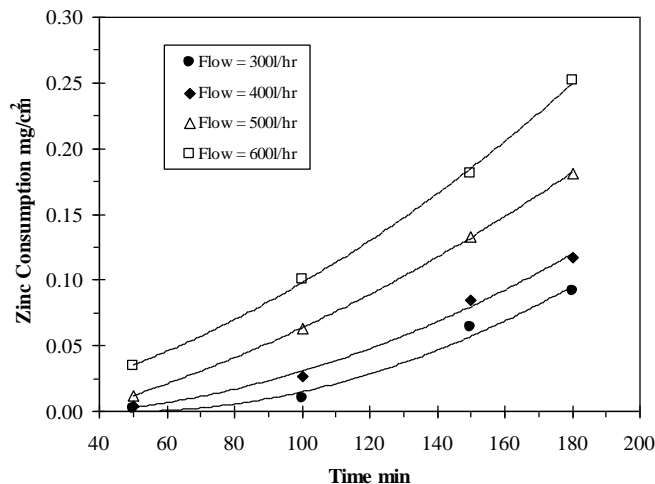


Fig.2: Zinc Consumption with Time for Different Flow Rates (Temperature 20 °C, NaCl 3.5% and pH=8) in absence of bacteria

Preparation of Bacterial inoculum

Pure culture of *Pseudomonas fluorescens* that were used in the experiments have been taken from the Department of Biotechnology. They were previously isolated from soil. *Pseudomonas fluorescens* activated on nutrient agar at 32 °C overnight. Cells were harvested from cultures then inoculated into nutrient broth containing 0.5% peptic digest of animal tissue, 0.15% Beef extract, 0.15% yeast extract and 0.5% sodium chloride dissolved in distilled water (pH 8) and incubated at 32 °C with rotary shaker (120 rpm) for 6 hours [8,10].

Results and Discussion

1- Time effect

Figures 2 and 3 show the rate of zinc consumption (dissolution), increases with increasing time at various flow rates and constant temperature (20°C), NaCl concentration (3.5%)wt and pH = 8 in absence and presence of bacteria respectively. This can be attributed to the relative movement between the corrosive fluid and the metal surface *i.e., erosion corrosion. It is important to mention here that in the presence of *Pseudomonas fluorescens* the rate of zinc consumption increases because the aerobic bacteria (*Pseudomonas fluorescens*) accelerate anodic and cathodic reactions. The anodic oxidation was enhanced by the localized acidity at the anodic sites due to the excretion of organic/inorganic acids by microorganisms [11]. Increasing the time of exposure, the amount of organic and inorganic acids increases.

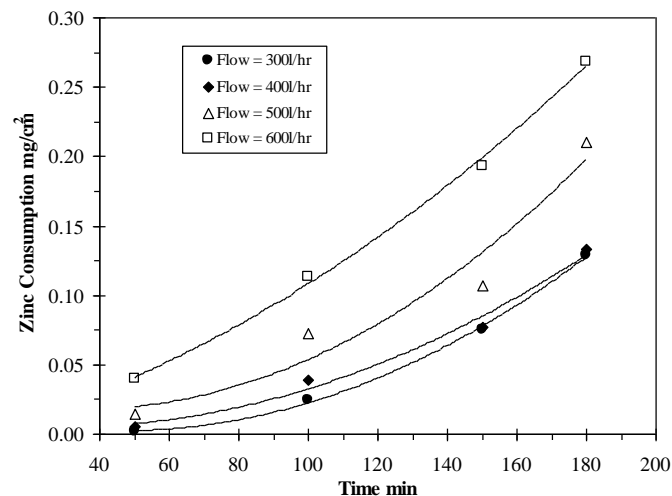


Fig.3: Zinc Consumption with Time in the Presence of *Pseudomonas fluorescens* for Different Flow Rates (Temperature 20 °C, NaCl 3.5% and pH=8)

2-Temperature effect

Figures 4 and 5 show the effect of temperature on the rate of zinc dissolution at different flow rates and constant NaCl concentration (3.5%) wt and time of exposure (3 h) in absence and presence of bacteria respectively. The increase in the rate of zinc dissolution with increasing saline water temperature (particularly from 10 to 40 °C) may be explained in terms of the following effects:

1. Increasing saline water temperature leads to decrease saline water viscosity with a consequent increase in oxygen diffusivity according to Stokes-Einstein equation [12 and 13]:

$$\frac{\mu D}{T} = \text{constant} \quad 1$$

Where μ is the saline water 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 [13]:

$$J = k_d C_{O_2} = \frac{D}{\delta_d} C_{O_2} \quad 2$$

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

2. The decrease in saline water viscosity with increasing temperature improves the saline water conductivity with a consequent increase in corrosion current and the rate of corrosion [14].
3. On the other hand, increase of temperature reduces 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 and 2 are predominating .

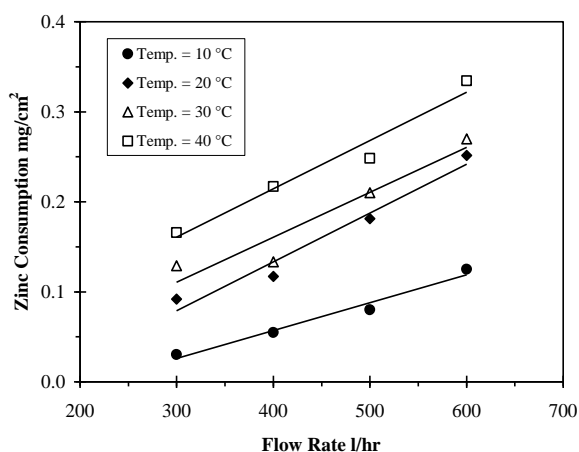


Fig.4: Zinc Consumption with different Flow Rates at Different Temperatures (NaCl Concentration 3.5% wt, and Time 3 hr) in absence of bacteria.

In the presences of *pseudomonas fluorescens* the corrosion rate increases with increasing temperature until it reaches the optimum temperature ,after that the increase in temperature will decrease the bacterial effect. The maximum activity of *pseudomonas fluorescens* at temperature (25-30°C) [5]. For slime producing bacteria Feron (1995) has, however, shown that an active slime layer will build up at 30°C, but not at 40°C. These results indicate that maximum temperature may vary somewhat depending on where on earth you are located.

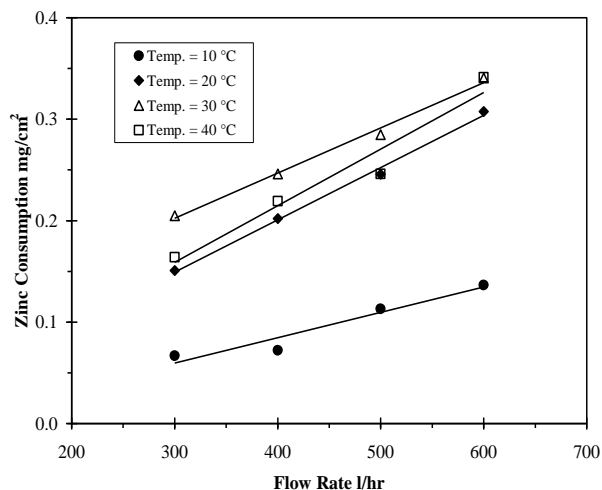


Fig. 5: Zinc Consumption with Flow Rate in the Presence of *pseudomonas fluorescens* at Different Temperatures (NaCl Concentration 3.5% wt, and Time 3 hr)

3-Salt effect

Figure 6 and 7 show the effect of salt concentration on the zinc dissolution at different flow rates and fixed time of exposure, 3h. and temperature of 30°C in absence and presence of bacteria respectively. It can be seen from figure 6 that the dissolution rate of zinc at any flow rate increases with increasing solution concentration. The initial increase in the rate of Zn dissolution with increasing solution concentration may be attributed to the increase in solution conductivity which gives rise to increasing the corrosion current and the rate of Zn corrosion. The high rates of Zn dissolution observed at 3.5%NaCl concentration associated with high solution flow rates, may be ascribed to the increase in solution conductivity [13]. At 3.5% wt NaCl concentration, maximum corrosion of carbon steel occurs due to maximum conductivity of solution and maximum O₂ solubility in the solution [15]. Kuntia et al [16] mentioned that changing the medium composition by the addition of sodium chloride (0.5% w/v) resulted in a faster decrease in the cell surface hydrophobicity. The formation, growth and reformation after detachment of the membrane-attached biofilm were also slower in the presence of sodium chloride, confirming the cell growth studies.

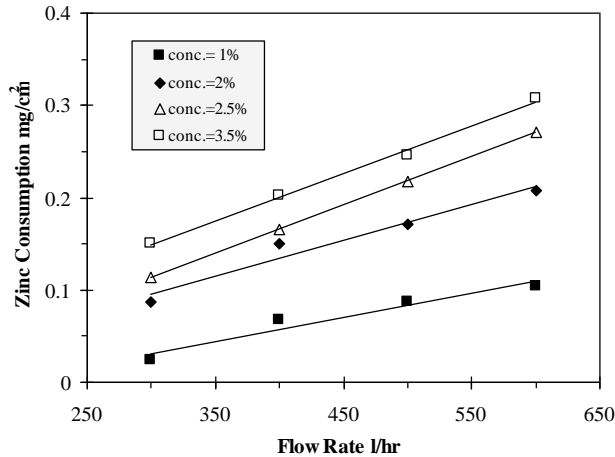


Fig. 6: Zinc Consumption with solution flow rates at fixed time of exposure, 3hr's, different solution concentrations and fixed temperature(30°C), in absence of bacteria.

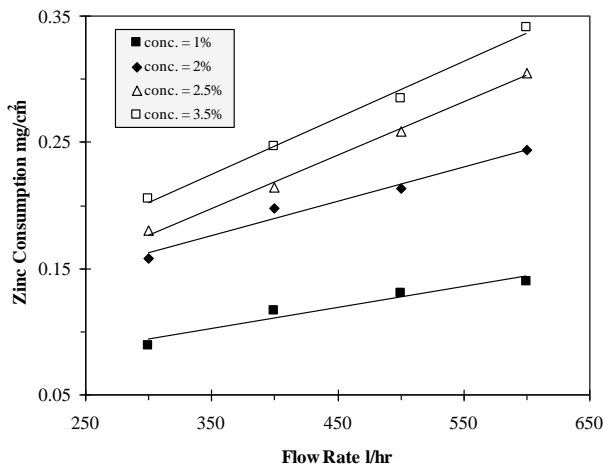


Fig. 7: Zinc Consumption with solution flow rates at fixed time of exposure, 3hr's, different solution concentration and fixed temperature (30°C), in the Presence of *Pseudomonas fluorescens*

4-Flow rate effect

Figures 2, through 7 shows the effect of solution flow rate on the zinc dissolution with time, different temperatures and NaCl concentrations, respectively. It can be seen from figures 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[17], consequently, increases the rate of oxygen diffusion[18]. The flow rate of saline water may also cause erosion which is combined with electrochemical attack.

In the presence of *Pseudomonas fluorescens* the effect of flow rate is important in bacterial corrosion process because it not only affects the transfer of species to the metal surface but also influences the overall bacterial adhesion process and the transfer of nutrients to the metal surface [19]. Stagnant fluid offers the lowest mass transfer rates because convective mass transfer does not exist without fluid flow. However, cell adhesion and biofilm formation may benefit from the absence of shear. At the other end, a fast moving fluid generates turbulence that provides enhanced mass transfer, but the accompanying high shear stress may prove to be harmful to the cells and may lead to the prevention of cell adhesion and thus biofilm formation. A sufficiently high shear stress may even detach an established biofilm [20]. Mild fluid flow offers the most favorable environment for cell adhesion and sessile growth and it likely yields the highest MIC corrosion rate [21].

5- Effect of cell concentration

The absorbance of the test solution was set to an A°600 of 0.5, 0.15 and 0.05 O.D (optical density) by using visible spectrophotometer. The strips were weighed and immersed in nutrient broth inoculated with bacterial suspensions of O.D 0.5,0.15 and 0.05 respectively and then incubated overnight at 32 ° C in a rotary shaker (120 rpm). Then the corrosion rate was determined by weighing the zinc strips after incubation. The strip which inoculated with bacterial suspensions of O.D 0.15 gave the higher corrosion as shown in Fig.8. It was reported in biofouling studies that biofilm thickness increased with a higher nutrient concentration when fluid shear held constant, biofilms act like a mass transfer barrier. Nutrients, metabolites and corrosion products are transported across the biofilms, so increase the biofilm thickness increase the corrosion rate [21, 22]. Figure 8 shows the effect of cell concentration on corrosion rate.

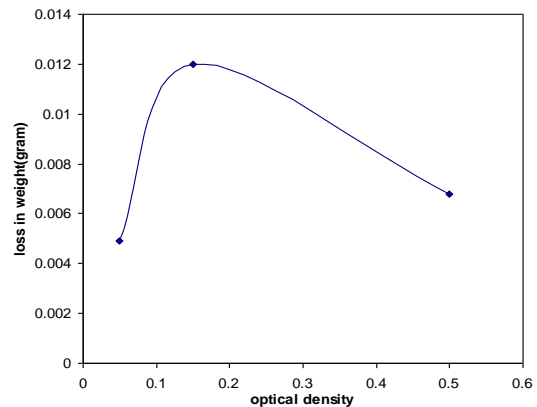


Fig. 8: Effect of Cell Concentration of *Pseudomonas fluorescens* on Corrosion

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