Analysis of Tafel polarization scans of Magnesium-Steel galvanic couple under different corrosive environments at various temperatures

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ABSTRACT: It is an attributed fact that magnesium, in normal conditions, behaves as active or anodic material and steel as a noble or cathodic material in a galvanic cell. In the current study, various experiments have been conducted to investigate the electrochemical behavior of magnesium and mild steel galvanic couples in tap water and 0.1M NaHCO₃ corrosive environments at different temperatures (40 °C to 80 °C). The potentiodynamic results have confirmed that in tap water, magnesium acts as an anode as it corrodes itself and protects steel surfaces under the influence of galvanic action at selected temperatures. However, magnesium became passive under 0.1M NaHCO₃, making steel anodic, which deteriorates aggressively at higher temperatures in 0.1M NaHCO₃. The polarity reversal phenomenon was also observed in the magnesium-steel couple when exposed to this environment. The microstructural examination has shown that passivation occurred due to the formation of an oxide layer that grew towards the steel side in the galvanic couple as the temperature increased. Thus, the study revealed that the magnesium would be more damaging to steel in a NaHCO₃ environment if utilized in the temperature range of 60 °C to 80 °C.

KEYWORDS: Magnesium-steel galvanic couple; Corrosion; NaHCO₃ environment; Polarity Reversal; Temperature effect

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1. INTRODUCTION

Each metal or alloy has a unique corrosion potential, magnesium has the least electro potential in the galvanic series (Li and Bell, 2004). Magnesium offers a high potential use as a lightweight structural material in transport applications as well as for industrial applications (Göken et al., 2003). In common engineering practices, magnesium is often used as a sacrificial anode to protect ferrous metals structures (Fouladi and Amadeh, 2013).

When magnesium is coupled with steel, it not only corrodes itself but also protects the steel structure (Pathak et al., 2012). The cathodic reaction (oxygen reduction) takes place largely on the steel surface to enhance the pH of the metal, which further facilitates the precipitation of protective carbonate compounds on that surface (Fontana, 2005) and provides cathodic protection by making the steel structure a cathode. The major factor in the corrosion of magnesium is the negative difference effect. The inhibitive function of the anion (e.g. bicarbonate, nitrates, etc.) is related directly to the ability of the anion to adsorb onto the metal surface, hence preventing the dissolution of the metal ion (Thomaz et al., 2010).

Although magnesium is anodic to steel, there are some environments where magnesium acts as the cathode or noble material (Son et al., 2004). The phenomenon where the polarity of the Mg-Fe could reverse is known as polarity reversal (Song et al., 2004). The favorable condition to occur polarity reversal is high temperature along with the presence of oxygen. Magnesium initially, in the galvanic coupled cell, pulls the cell potential to negative values and subsequently rises as the magnesium passivates. The chief anion enhancing the reversal phenomenon is bicarbonate and therefore reversal can occur in saltwater where magnesium sacrificial anodes have an outstanding service record (Dennis et al., 2014). Besides bicarbonates, some other anions that could facilitate the polarity reversal are nitrates, phosphates, and carbonates (Davis et al., 2010). On the other hand, the rise in magnesium potential can be barred by using sulfates, and chlorides including tap water. It is an accepted fact that not only the presence of anions but also the content of iron in an alloy, water pressure, and environmental conditions are also responsible for polarity reversal (Song et al., 2004).

Polarity reversal occurs due to passivation. Passivation refers to the formation of a thin film of corrosion product, which acts as a barrier to further oxidation, known as the passive film on the surface of the metal (Kim and Young, 2013; Eyvaz et al., 2014). The reversal of polarity is generally ascribed to the passivation of Mg, possibly through the formation of a surface layer of oxide or basic magnesium salt. For passivation to occur under open-circuit conditions oxygen must be present but not when Mg is anodically polarized in aqueous media. The presence of chloride and sulfate ions prevents the passivation of Mg. Based on open-circuit potential measurements, it was found that no polarity reversal in the Mg-steel couple occurred in tap water when maintained at constant pH and water composition over the temperature range of 20 to 90 °C. This was thought to be due to the relatively high concentrations of chloride and sulfate present in the water.

A conductive magnesium oxide film has been considered to be an important factor to determine the polarity reversal. A magnesium surface forms an oxide layer and becomes cathodic after being exposed to the carbonate environment, displaying polarity reversal phenomena. Thus, a more general model of magnesium surface giving rise to the passivation would be:

- The maintenance of an adherent protective film on magnesium would strongly polarize local anodic areas.
- Sufficient electronic conductivity in the film
One of the effects of passivation is that magnesium will no longer cathodically protect the steel.

Moreover, the chemical composition and microstructure of a passive film are different from the underlying metal (Montemor et al., 2000; Cardoso et al., 2008; Kim and Young, 2013). The massive difference between a passive layer and an oxide film is that an oxide film is formed at a high temperature with a thickness in the micrometer range. The unique property of passive film is that it heals itself whereas the oxide layer does not (Hoffman et al., 2008).

Therefore, in this research work, the behavior of the steel-magnesium galvanic couple was analyzed in two solutions; Tap water and 0.1M NaHCO₃, at three different temperatures; (i) 40 °C (ii) 60 °C and (iii) 80 °C to study the polarity reversal phenomenon. Since the steel and magnesium are coupled in a variety of engineering applications for providing cathodic protection to steel. Therefore, there must be adequate knowledge of the corrosion behavior of Mg-steel couples under different temperatures and corrosive media. As if polarity reversal occurred in the Mg it will lead to the failure of the steel/structure. Thus, the response of Mg-steel couple under different corrosive media at various temperatures must be determined so that corrective action during the design process can be taken to avoid catastrophic failure. Hence, to replicate the actual service environment and to know the behavior and mechanism of corrosion, the steel and magnesium were coupled during sample preparation. The corrosion behavior of both solutions was studied by using the potentiodynamic polarization method. The results were analyzed by using the Tafel extrapolation method. The corrosion mechanism specifically, the formation of corrosion products at the steel-magnesium interface was elaborated by using optical and electron microscopic techniques.

2. EXPERIMENTAL WORK

For electrochemical testing, Gamry G-750 Potentiostat was used with three electrodes immersed in a selected environment to complete a cell.

- Working Electrode - A sample of magnesium and steel was used (corroding substance).
- Reference Electrode- saturated calomel (SCE), reference electrode with a constant electrochemical potential.
- Counter Electrode – A current-carrying platinum electrode that completes the cell circuit.

Polishing machine to produce a scratch-free mirror-like surface. Two corrosive media i.e. tap water and sodium bicarbonate were selected to study the corrosion behavior of the galvanic couples. In the first phase, tap water was used as a medium for corrosion testing with temperatures of 40 °C, 60 °C, and 80 °C. Secondly, a 0.1M solution of sodium bicarbonate was prepared using deionized water as a corrosive medium, and testing was done at five different temperatures ranging from 40 °C to 80 °C with a difference of 10 °C. The bicarbonate solution used for corrosion analysis was made from distilled and deionized water that had been saturated with a continuous flow of 1 bar of Nitrogen gas. The solution was prepared with analytical grade powder of NaHCO₃ (Sigma-Aldrich) at a concentration of 0.5M and a pH between 8.4 to 8.6. The test temperature was kept constant at room temperature. Compositional analysis of freshly prepared NaHCO₃ solution and the tap water used in the analysis is presented in Table 2.

| Materials | Composition in wt.% |
|-----------|---------------------|
| Fe | C | Mn | Si | P | Mg | Al | Zn |
| Mild Steel | 99.1 | 0.18 | 0.71 | 0.2 | 0.02 | - | - | - |
| Magnesium | - | - | 0.41 | - | 96.87 | 1.77 | 0.92 |

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**Table 1. Compositional analysis of materials used in a galvanic couple**

**Table 2. Composition (mg·L⁻¹) of NaHCO₃ solution and tap water used in corrosion testing**

**Table 2.** Composition (mg·L⁻¹) of NaHCO₃ solution and tap water used in corrosion testing.
The Tafel curves were measured at a scan rate of 1 mV·s\(^{-1}\). The beaker containing corrosive medium was covered with a heating mantle and connected to the omega benchtop controller CSi8D series. Henceforth, the samples were tested at various temperatures (40 °C, 50 °C, 60 °C, 70 °C and 80 °C).

3. RESULTS AND DISCUSSION

The following sections dealt with the results obtained using potentiodynamic analysis of galvanic couples and proceeded with the subsequent sections pertinent to the microstructure evolution of the corroded surfaces.

3.1. Microstructure of as-received samples

As received samples were prepared using standard metallographic techniques as used for working electrodes and analyzed by Olympus image analyzer GX51. Figure 1a represented the microstructure of mild steel consisting of ferrite (light) and pearlite phase (black). Likewise, the microstructure of magnesium in as received condition consisted of a typical bimodal type structure in which grains are ranging from 50 microns to 190 microns as shown in Fig. 1b.

3.2. Potentiodynamic curves of a steel-magnesium galvanic couple in tap water

The results evaluated from the potentiodynamic study of a steel-magnesium galvanic couple exposed to tap water at three different temperatures (40, 60, and 80 °C) are depicted in Fig. 2 (a to c).

From Fig. 2, It was observed that the electrode potential (E\(_{corr}\)) of the steel-magnesium galvanic couple at 40 °C was found to be -1.230 V at a current density (I\(_{corr}\)) of 292 µA while the electrode potential at 60 °C was found to be -1.25 V with the current density of 347.0 µA. Furthermore, the electrode potential at 80 °C was found to be -1.31 V at a current density of 361.0 µA. The change in current density concerning electrode potential near the E\(_{corr}\) region is higher because of activation polarization while this change was decreasing with increasing applied potential due to the concentration polarization phenomenon. Moreover, no passivation was observed at all temperatures.

In the corresponding galvanic cell at 60 and 80 °C, the magnesium was polarized appreciably more than steel and the potential regularly fluctuated. This fluctuation occurs mainly because of the potential increase of electrodes in the electrochemical cell. Principally, throughout all these three experiments the mild steel remains cathodic in the galvanic cell. The magnesium sacrifices itself as a sacrificial anode and hence protecting the steel surface. This happens generally because of the more negative potential of magnesium than that of steel. Therefore, the oxidation reaction takes place only on the magnesium surface whereas the reduction reaction takes place on the steel surface.

In the light of the above-mentioned experiments, there was no polarity reversal phenomenon observed in the potentiodynamic study of the steel-magnesium galvanic couple in tap water at 40 °C, 60 °C, and 80 °C. At all temperatures, the corrosion potential for mild steel was found nobler than magnesium. Thus, when two metals were galvanically coupled and immersed in electrolytic solution the steel was cathodically protected at the expense of an additional corrosion product formed on the surface of magnesium.

3.3. Microstructure of steel-magnesium galvanic couple in tap water

After the removal of electrodes from the electrochemical cell, the image shows that experiment made
at 40 °C, the magnesium surface from the junction was damaged sacrificially by a corrosion attack. The magnesium surface was corroded largely while protecting the steel structure as shown in Fig. 3 (a,b,c). The greater part of the magnesium surface was covered by a thin layer of corrosion product, and widespread pitting occurred. On the other hand, the steel structure remained protected. At temperatures, 60 °C, and 80 °C, the corrosion attack on the magnesium surface was significantly increased and a thick visible corrosion layer consisting of a loosely adherent greyish outer layer formed on the magnesium surface. Additionally, at 80°C, the corrosion became more severe, and widespread pits were developed as seen in Fig. 3c, whereas the steel surface was protected.
3.4. Potentiodynamic curves of a steel-magnesium galvanic couple in 0.1M sodium bicarbonate

The potential-current behavior of mild steel and magnesium galvanic couple electrodes exposed to 0.1 M sodium bicarbonate solution at different temperatures is given in Fig. 4 (a, b, c, d, and e).

At 40 °C, the electrode potential (E_{corr}) of the steel-magnesium galvanic couple was -1.240 V at current density (I_{corr}) 6.970 µA. The electrode potential at this temperature shown in Fig. 5a was related to potential observed at different temperatures in tap water.

At 50 °C, the galvanic couple shows a rapid rise in electrode potential that was stabilized near -1.18 V with a current density of 66.30 mA, suggesting that the passivation begins in the steel-magnesium galvanic couple. Passivation on the magnesium metal
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At this temperature indicated that further oxidation was inhibited. By increasing the temperature of galvanic cell from 60 °C to 80 °C, a huge difference in electrode potentials were observed with the value of -0.52, -0.55 and -0.58 V respectively. The corresponding corrosion current density was found to be 69.90, 76.30, and 84.05 mA at 60°C, 70 °C, and 80 °C respectively. This sudden increase in the electrode potential of the steel-magnesium galvanic couple indicated a passive response of magnesium. A passive thin layer was formed on the surface of magnesium that restricts further oxidation. In this environment, the steel corrodes largely as compared to magnesium also shown in Fig 6. Furthermore, it has been conceived that in the presence of oxygen and under 0.1M sodium bicarbonate, magnesium acted as a cathode at higher temperatures, whereas the steel structure became anodic and corroded. The corrosion rates at various temperatures were calcu-

![Figure 5](image1)

**Figure 5.** Corrosion rates of a steel-magnesium galvanic couple at different temperatures under tap water and NaHCO₃ corrosive environments.

![Figure 6](image2)

**Figure 6.** Microstructure of steel-magnesium galvanic couple exposed to 0.1M sodium bicarbonate: (a) 40 °C, (b) 50 °C, (c) 60 °C, (d) 70 °C and (e) 80 °C.
lated by using the Tafel extrapolation method. The results were displayed in Fig. 5.

In the light of the above-mentioned experiments, there was a polarity reversal phenomenon observed in the potentiodynamic study of steel-magnesium galvanic couple in 0.1M sodium bicarbonate solution at 50 °C, 60 °C 70 °C, and 80 °C. Under the experimental conditions used, magnesium passivated at warm temperatures i.e. 80 °C signified that the steel would deteriorate and became anodic under these conditions.

3.5. Microstructures of a steel-magnesium galvanic couple in 0.1M sodium bicarbonate

Microstructures were captured from the image analyzer (GX51, Olympus) after electrochemical testing of steel-magnesium couples and are shown in Fig. 6 (a to e). Figure 6a shows that in the experiment made at 40 °C, corrosion damage was observed on both steel and magnesium surfaces. However, as the temperature rises the corrosion attack was started from the magnesium-steel junction and covered the large area of steel. The greater part of the steel surface was damaged by corrosion attack, and widespread pitting occurred. On the other hand, the magnesium structure covers by a thin passive layer of carbonates, which stops the magnesium to act as a sacrificial anode. At all the temperatures, it can be seen that a thin layer of corrosion product was developed at 50 °C and grew towards the magnesium side as indicated in Fig. 6f. At warm temperatures, the severity of corrosion increased and steel corroded at a faster rate.

3.6. Scanning electron microscopy

Figure 7 show scanning electron microscopic results of the magnesium electrode. The image in Fig. 7 (a, b), clearly indicates the passivation occur on the magnesium surface when it was galvanically coupled with steel exposed to 0.1M sodium bicarbonate in the presence of oxygen at 70 °C. The passive layer formed on the surface of magnesium reveals that magnesium would no longer act as a sacrificial anode to protect the steel surface. This layer resulted owing to cathode reaction, which took place on magnesium surface and anodic reaction occurred on steel surface as reported by Glass & Ashworth (Glass and Ashworth, 1985).

4. CONCLUSIONS

This research work highlighted the behavior of galvanic couple between magnesium and steel under different temperatures using tap water and 0.1M sodium bicarbonate solution as corrosive media. The main findings of this research work are as follows:

- There was no evidence found of polarity reversal using the potentiodynamic study of...
the magnesium-steel galvanic couple when exposed to tap water at different temperatures.
- Passivation of magnesium surface in the presence of oxygen occurred when exposed to 0.1M sodium bicarbonate solution at higher temperatures. The passive layer formation during passivation of magnesium revealed that magnesium passivated more rapidly at warm temperatures compared to steel. Therefore, the phenomenon of polarity reversal would prevail and the steel structure prematurely failed, if coupled with magnesium and exposed to sodium bicarbonate solution at warm temperatures.
- Corrosion rate increases linearly with the rise in temperature in both environments.
- SEM analysis confirmed the passive behavior of magnesium in bicarbonate solution at a warm temperature. EDX results indicated the formation of oxide-based passive layer formed on the surface.

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