Effect on Current Density on Zero Charge Corrosion Protection of Pure Mg in 3.5% NaCl Solution

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Abstract. The cathodic protection uses two-electrode polarization, which requires large currents and substantial voltages. Efforts are being made to identify possibilities for improvements by developing zero-charge corrosion protection techniques. Studies were performed to determine the zero-charge potential effect by analyzing corrosion signs on reactive metal samples such as pure Mg. Mg samples were fed by current/voltage pulses for 120 hours, with specified pulse parameters and varied Ecorr offsets, ranging from +2 to -218 mV. The volumetric hydrogen gas collection technique is used to determine the hydrogen evolution rate. Surface observation is carried out by stereomicroscope to determine the presence of corrosion signs on the sample surface. Overall, all current densities and hydrogen evolution rates had very low readings on the studied Ecorr offset parameters. Mg samples fed with pulses at -1800 and -1900 mV vs SCE revealed zero charge potential effects since their surface was clean and showed no indications of corrosion even after being exposed to the corrosive solution for 120 hours. Thus, corrosion protection is successfully done and meets the E_{pzc} condition.

1 Introduction

The cathodic protection (CP) method uses the polarization of two electrodes (anode and cathode) as a concept. As indicated in the potential-pH (E-pH) Pourbaix diagram, the metal to be protected is polarized to a cathode by donating excess electrons (or negative charges) until its potential is dropped to the immune zone. This process makes the CP method require...
a substantial driving voltage and high current for its implementation. The protected potential of steel materials is known to range between -850 to -1100 mV vs Copper/Copper Sulfate (Cu/CuSO₄). Baboian & Treseder [1] have outlined that the current density requirement for bare steel in stagnant seawater is between 20 to 30 μA/cm², depending on the temperature. Several efforts are being made to explore ways to improve the CP approach to make it the best corrosion prevention technique available.

Zero charge corrosion protection, or ZCCP, is one of the approaches that has been tested. It uses the zero-charge potential (E_{pzc}) introduced by the previous electrochemistry researchers around 1930 to 1960s. The E_{pzc} comes from the electrochemistry term and denotes a metal that has no charge [2]. In the Pourbaix diagram, E_{pzc} is located in the corrosion region [3]. Therefore, the metal in the E_{pzc} closed-circuit system has no or minimal current flow. E_{pzc} is a characteristic value of the electrode potential at which a clean surface of the metal will not acquire any electrical charge when it comes into contact with an electrolyte or water-based solution. The lack of charges on the metal-solution interface prevents the dipole moment of water molecules from adsorbing to the metal.

In this study, the pure Mg was fed with current/voltage pulses for 120 hours in a 3.5% sodium chloride (NaCl) solution. The pulse feeding was carried at a slightly negative than E_{corr}, and significantly positive compared to the immune potential line of approximately -2967 mV vs SCE to maintain its potential in the corrosion region. The effect of pulse cathodically polarized the metal surface from E_{corr} to E_{pzc} on the potential of the metal and the charges on the metal surface. The study was conducted to determine the E_{pzc} effect by analyzing a corrosion indicator on reactive metal samples such as pure Mg using the pulse feeding technique.

2 Methodology

Mg samples were cut into rectangles measuring 2.2 x 2.2 cm. The rectangular sample surface was ground to 600 grits, washed in alcohol before rinsing with distilled water. The samples were washed and dried before being placed in a corrosion cell, then filled with 1 liter of 3.5% NaCl solution. Custom-built pulse generators feed electric current/voltage pulses to the studied corrosion protection system at a slightly negative than steady-state potential (or corrosion potential, E_{corr}). An oscilloscope (GDS-1102A, GW Instek, Taiwan) was also used to monitor and measure the characteristics of the pulse waveform signal. The volumetric hydrogen gas collecting approach was used to measure hydrogen evolution (HER) as carried out by Salleh et al. [5]. A funnel is placed over the Mg sample to collect all the H₂ gas to enter the burette. Bubbles containing H₂ gas then slowly accumulate at the top of the burette by pushing down the NaCl solution to measure the volume of H₂ gas collected.

Once the materials, apparatus, and everything are ready, Mg is allowed to be immersed in the 3.5% NaCl solution at an open circuit until the potential reaches a steady-state or E_{corr} condition. It usually takes around 6 to 7 hours. The Mg potential is tuned to be somewhat lower than the (E_{corr}), where this tuning is then utilized as the experimental E_{corr} offset parameters. The pulse generator was tuned to a 90% duty cycle, 2.5 V amplitude, and 100 Hz frequency, using a voltmeter and an ammeter to measure the current/voltage pulse feeding. All of the tests were carried out for 120 hours at a temperature of 25°C. Upon completing the pulse feeding experiment, the Mg sample was cleaned with a specific cleaning solution per ASTM G1-03. Finally, a stereomicroscope (SZX16, Olympus) was used to visually analyze the Mg samples' surface morphology to observe for signs of corrosion.
3 Results & Discussion

Table 1 depicts the results of a current/voltage pulse feeding experiment performed on Mg sample that exposed in a corrosive (3.5% NaCl) solution. The study revealed that the $E_{corr}$-offset is tuned to $+2$ mV (-1680 mV vs SCE), which is slightly positive than $E_{corr}$-1682.1 mV vs SCE. In this case, the Mg to be protected is fed with positive charges at $2.54 \pm 0.62 \mu A/cm^2$ electrical currents. Regardless of the slight differences of the $E_{corr}$-offset, the positive charges flow into the Mg sample and accumulate on the surface. As a result, the Mg sample is no longer protected because the accumulation of positive charges on the surface causes the attraction of nearby opposite charges resulting in a potential difference at the interface.

| $E_{corr}$- Offset (mV) | Metal Potential (mV vs SCE) | Current Density (µA/cm$^2$) |
|------------------------|-----------------------------|-------------------------------|
| +2                     | -1680                       | $2.54 \pm 0.62$              |
| -18                    | -1700                       | $-0.06 \pm 0.16$             |
| -48                    | -1730                       | $-0.97 \pm 0.41$             |
| -78                    | -1760                       | $-1.82 \pm 0.52$             |
| -118                   | -1800                       | $-4.38 \pm 0.93$             |
| -218                   | -1900                       | $-6.86 \pm 1.07$             |

The rest reading shows the metal potential has gradually recorded an increment of current density as an $E_{corr}$-offset that is increasingly negative. In the beginning, the electric current was $-0.06 \mu A/cm^2$ at a metal potential of -1700 mV vs SCE. Then, the metal potential increasing toward a more negative, an electric current feeding also increases, e.g., at -1730 and -1760 mV vs SCE. According to this potential, the current density recorded is $-0.97$ and $-1.82 \mu A/cm^2$, respectively. After that, the electric current continuously increases as the metal potential is set to -1800 and -1900 mV vs SCE. At these potentials, the current density readings are about $-4.38$ and $-6.86 \mu A/cm^2$, respectively. Although the increment in electric current appears high on paper, compared to the ICCP current requirement for steel in stagnant seawater (which ranges from 20 to 30 $\mu A/cm^2$) [1], the experimental reading is much lower. Additionally, the testing sample is a reactive metal. Thus, at this level, the current consumption recorded in the experiment is tremendously small.

It should be noted that when an $E_{corr}$-offset is established, metal potential stability is not always excellent in the beginning. Furthermore, the current density has a high noise level, which could be related to Mg's strong surface reactivity, resulting in a complex rate of charge transfer, ion exchange, etc. The surface of Mg seems to have air bubbles that are believed to be $H_2$ gas. Sometimes, the $H_2$ gas is constantly attached to the sample surface throughout the experiment. Therefore, to determine the effect of $H_2$ formation on the sample surface, the analysis was extended by analyzing (HER) of the Mg metal sample after 120 hours fed with current/voltage pulses.

$H_2$ evolution measurement tests were conducted throughout the current/voltage pulses experiment, and their result is shown in Fig. 1. It shows the volume of $H_2$ gas accumulated in the burette for every metal potential setting parameter. According to the result, the pulse voltage of -1680 mV vs SCE has a high volume of $H_2$ which is 1.28 ml/cm$^2$ followed by 0.89 ml/cm$^2$ at metal potential -1700 mV vs SCE. The volume of $H_2$ accumulated at both of these potentials indicates that the HER on Mg metal also occurs at the anodic reaction. Although -1680 mV vs SCE and -1700 mV vs SCE are slightly positive and negative than $E_{corr}$, respectively, it is assumed to be in anodic reaction because the values have only a minimal difference from $E_{corr}$. It is undeniable that the HER that occurs on this Mg is quite different from that of other metals because $H_2$ evolution also occurs during an anodic reaction [6]. The
dissolution of Mg supports the growth of cathodic hydrogen on its surface during anodic polarization. The rate of HER that increases with the polarization of this anodic reaction are called the negative difference effect (NDE). The statements by Yang et al., 2016 [7] agreed that the increment in the positive potential during anodic polarization would also increase the active cathode site, whereas this cathodic site acts as the primary mechanism that generates the evolution of H2. In addition, similar to that noted by Yuwono et al., 2019 [6], MgH species also undergo oxidation during anode polarization resulting in H2 evolution and dissolution of Mg.

Fig. 1. Histogram of Hydrogen Volume vs Metal Potential of Mg Sample under Studied Pulse Feeding

The lowest HER was recorded at -1730 mV vs SCE with an accumulated H2 volume of 0.35 ml/cm2, followed by -1760 mV vs SCE of 0.43 ml/cm2. The sample Mg is stable in this potential range, with the charge at the metal-electrolyte interface expected to be around the zero-charge potential, E_{pzc}. Furthermore, the pulses at the higher negative metal potentials of -1800 and -1900 mV vs SCE cause an increase in the HER on the surface of the Mg metal as a result of water reduction (2H2O + 2e^- → H2 + 2OH^-) during a cathodic reaction in an aqueous environment. It collected H2 volumes of 0.66 and 0.97 ml/cm2, respectively. Nonetheless, it can be regarded as a low and arguably steady potential that is believed has been reached to E_{pzc}. The fact that the potential Mg has achieved E_{pzc} within -1800 to -1900 mV vs SCE is confirmed by the surface morphological appearance of the Mg surface (Fig. 2).

Firstly, let look at the surface morphology of the Mg sample fed by current/ voltage pulses at E_{corr. offset} +2 mV shown in Fig. 2(a). At -1680 mV vs SCE metal potential, pitting may be seen on Mg surfaces in several spots. This confirms the previous statement that the Mg surface is fed with positive charges when pulsed slightly with positive E_{corr. offset}. The Mg metal atoms on the surface cannot be prevented from being oxidized by donating electrons and converting them to Mg ions (Mg → Mg^{2+} + e^-). Mg is corroded because it is not adequately protected. As a result, the pulses set at a +2 mV E_{corr. offset} fail to prevent Mg metal corrosion. At an E_{corr. offset} of -18 mV, Mg experienced a slight corrosion effect on the edges near the sharp corner side of the sample (Fig. 2b). In areas like this, the propensity of the corrosion reaction is inherently high. At other surface areas, it also exhibits the effects of spots and patches that are relatively dark compared to the surface background color, which indicates an oxidation reaction taking place there. This finding demonstrates that the pulse feeding setting of -1700 mV vs SCE and an electric current density of 0.06 mA/cm2 is insufficient to fully protecting the Mg sample.
Pitting corrosion issues seem to be avoided in Mg samples when exposed to potentials in the range -1730 to -1900 mV vs SCE (Fig. 2c - 2f). However, there are noticeable stain patterns on the surface, especially in Fig. 2 (c), which results from a moderate reaction effect with NaCl solution. This staining pattern is reduced on the polarized surface at a potential of -1760 mV vs SCE (Fig. 2d). It is increasingly disappearing at more negative potentials up to -1800 mV vs SCE (Fig. 2e). Finally, the staining pattern on the metal surface could no longer be observed on the Mg sample surface that fed at a potential of -1900 mV vs SCE and current density of -6.86 µA/cm² (Fig. 2f). It can be said that the corrosion reaction did not occur within the experimental period of 5 days at a potential of -1900 mV vs SCE (E_{corr. offset} = -218 mV). As a result, providing pulses at this metal potential is an excellent way to protect Mg samples using this technique. It shows that the metal surface is clean, and no evidence of Mg reaction in NaCl solution. The Mg has been established it did not acquire an electrical charge when it came into contact with the electrolyte. As a result, there is no charge transfer or electrochemical reaction at the metal-solution interface since no charges adsorption occurs.
Fig. 2. Surface morphological image of Mg samples that fed by current/voltage electric current at (a) -1680, (b) -1700, (c) 1730, (d) -1760, (e) -1800, and (f) -1900 mV vs SCE uses a square wave signal. The test is performed for 120 hours.

In summary, the optimum polarization in this current/voltage pulse supply experiment is between -1800 to -1900 mV vs SCE. Even though Mg at this potential consumed the most electric current as compared to the other parameters, the current density was observed less than 20 – 30 µA/cm² (current density required for the cathodic protection of steel in stagnant saltwater). In contrast, HER was not considered too high because H₂ formation was only seen in the early stages of the experiment. Furthermore, surface morphological characteristics support the selection of current/voltage pulse feed at -1800 to -1900 mV vs SCE potential.
polarization. It appears that at the potential of -1800 to -1900 mV vs SCE, the Mg got a clean surface that believes it does not acquire any charge, preventing an electrode-electrolyte surface interaction. Such a characteristic meets the requirements of the metal that is on the \( E_{pzc} \).

Experimentally, when the pulse generator is turned off to zero volts, the potential signal changes towards the positive direction, producing a positive charge. Then when the pulse generator is turned on, the potential signal heads in a negative direction, producing negative charges. It should be bear in mind that most of the \( E_{corr} \) offset of the pulse generator are set at negative polarization (except \( E_{corr} \) offset = +2 mV, please refer to Table 1); therefore, the current/voltage pulses in a negative direction to the corrosion protection system is intended to eliminate the excessive positive charges, \( \delta^+ \), and preventing electron donation by Mg atoms. On the other hand, pulses in the positive direction to zero potentials activate the positive charges to be eliminated by the opposite charges around. Therefore, the positive charge formed during the pulses is mutually neutralized by the negative charges due to the negative \( E_{corr} \) offset polarization.

4 Conclusion

The current/voltage pulse feeding method successfully protects reactive metals such as Mg in corrosive 3.5% NaCl solutions. In this method, corrosion protection is successfully done on the metal potential of -1800 to -1900 mV vs SCE and meets the \( E_{pzc} \) condition.

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