The efficiency of Zero Charge Corrosion Protection on pure Mg by Planned Interval Test

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Abstract. The concept of zero charge potential (E_pzc) is manipulated to eliminates the effect of the electric double layer in order to mitigate the corrosion reactions through the zero-charge corrosion protection (ZCCP) method. The efficiency of the ZCCP method was examined by planned intervals test on pure Mg metal in 3.5% NaCl solution. The test results showed that the tendency of both liquid corrosiveness and metal corrodirbility are decreased from -1562.7mm/yr (Eocp) to -98.2mm/yr (Epzc). ZCCP technique was succeeded by corrosion protection efficiency of pure Mg which was recorded between 93 to 96% in 3.5% NaCl solution.

1 Introduction

A novel new technique in controlling and preventing corrosion of a metal by bringing the potential to a value known as zero-charge potential or potential of zero charges, E_pzc [1]. At E_pzc, the excessive charges on the metal surface are neutralized to zero charges. This condition works to turn-off the effect of the electric double layer, thus, weakening the charge adsorption force due to the electrostatic attraction of the electrode-electrolyte interface. This process is further hindered the charge transfer on the metal-solution interface, thus, prevent the corrosion reaction of the metal in aqueous solution.

The application of E_pzc concept is manipulated through a method called zero charge corrosion protection (ZCCP). ZCCP technique requires a power supply that potentiostatical capability of giving a negative current or voltage pulsed, hence bringing the potential of a metal to a net-potential value whereby no charges on the metal surface. This can be achieved by cyclic charging-discharging the metal surface between corrosion (E_corr) and polarized potential (E_impressed) repeatedly. The pulse charging-discharging of the metal to be protected can be restricted to a maximum of ±2 mV at about E_pzc. Since the E_corr is known, the corrosion current (i_corr) of metal also known, hence E_pzc can be determined by the application of pulse current/voltage equivalent to i_corr to the metal surface. This novel method of corrosion protection at E_pzc does not use the conventional concept of polarization of two electrodes (anodes & cathodes), it only needs a single electrode or metal to be protected.

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Epzc can be applied to metal in various corroding environments such as acidic, neutral, and alkaline medium, static, and dynamic flow as well as any climate-changing environments [3].

The planned interval test (PIT) is a good technique for assessing the effect of time on metal corrosion and corrosion (solution) environment. Normal immersion methods can generally only measure normal corrosion rates during the exposure period in corrosive environments. However, this PIT can measure the variation of corrosion rates, both uniform and local corrosion with time throughout the test period. Measurement of corrosion rate through PIT is a study involving the formation or breakdown of protective film on metal surfaces during the test period. Variations in corrosion rates can also occur as a result of changes in the concentration of corrosion agents in an environment or solution medium.

The PIT procedure involves exposure of a metal sample for at least three periods. The exposure period selected is for initial, prolonged, and short periods of exposure after the long exposure period. Differences in corrosion rates between these three periods help to assess (i) differences in corrosion rates for short- and long-term exposure, and (ii) differences in corrosion rates for the same period at the beginning and end of the test period.

Magnesium (Mg) is a highly reactive metal and is easy to corrode when exposed to aqueous environments, especially in 3.5% NaCl solution. The reaction between the Mg surface with a 3.5% NaCl solution left a corrosion-resistant effect [4]. Mg alloys are often used as a sacrificial anode in underground environments due to their high reactivity properties. The reason for using pure Mg is because Mg is more reactive than steel. Therefore, if a corrosion protection method is effective at Mg, then it certainly works for steel [5]. The Mg reactivity factor and the precision of the weighing apparatus (± 0.5 mg) caused the measurement of weight loss to be detected within a short immersion period compared to the use of steel that took longer to detect weight loss [6]. The objective of the study is to measure the efficiency of corrosion protection with the zero charge techniques on pure Mg metal through a planned interval test.

2 Methodology

Pure Mg (99.8%) in the form of a solid rod was lathed to 3.3 cm in diameter. It was then cut into 2 cm high. The planned interval test (PIT) is performed per ASTM G31 without corrosion protection under open circuit potential (E_ocp) condition. All of these Mg samples were weighed by analytical balance (AL204, Mettler Toledo) to obtain the initial sample weight (W_i). Glass container containing 3.5% NaCl solution was prepared. Four Mg samples were used in this PIT, one for each interval. The planned interval test (PIT) was performed to assess the effect of immersion time and changes in the corrosive environment on metal corrosion. This test is to prove that corrosion protection at zero charge capacity, E_pzc, occurs on metal exposed to a corrosive solution. For comparison, immersion tests on pure Mg samples were performed on the open-circuit potential, E_ocp, and at zero charge potential, E_pzc. For this purpose, a pure Mg sample is used as a metal to be protected. Mg is known to be a more reactive metal than Fe where Mg reacts actively when exposed to 3.5% NaCl solution. The samples were inserted in different containers and each container was labeled with A_1, A_2, and A_{1+1}, which were marks to represent their respective immersion intervals. The immersion time interval is shown in the schematic diagram of Fig. 1.
Fig. 1. Schematic diagram of the immersion time interval in the PIT.

After immersion for 5 days, sample in A₁ container was taken-out, for sample A₂ after 20 days of immersion it was removed and replaced by another sample and marked as B in the same container. Sample B was immersed in the same period as A₁ for 5 days. Finally, A₉+₁ samples were released after immersion for 25 days. This PIT step was repeated on the Mg sample subjected to the ZCCP method system.

ZCCP was applied by using a customized power supply capable of supplying current/voltage pulses to steel samples. The ammeter with USB connection was connected in series in the circuit to measure electrical current consumption for both techniques at 1 reading/hour interval. All corrosion protection tests were performed at room temperature with 1-ATM pressure.

Once the immersion period of PIT was completed, all samples were rinsed with distilled water. The samples were then soaked in 1000 ml of a solution containing 200 g of chromium trioxide (CrO₃), 10 g of argentum nitrate (AgNO₃), and 20 g of barium nitrate (Ba(NO₃)₂) to remove oxide and residue of chloride as suggested by ASTM G1. The cleaning was done for 5 minutes to ensure that all oxides were completely cleaned. The samples were weighed again to obtain the final weight (Wₕ). Weight loss (W) is calculated according to Eq. 1;

\[ W = W₁ - Wₕ \]  

while corrosion rates are calculated from Eq. 2;

\[ \text{Corrosion rate} = \frac{K \times W}{A \times T \times D} \]

where K is a constant \( (8.76 \times 10^4) \), T is an immersion time (units of hours) with a precision of up to 0.01 hours, A is a surface area exposed in cm² units with a precision of up to 0.01 cm², W is a weight loss in gram (g) units with precision up to 1 mg and D is density in g/cm³ units. Immersion time intervals with symbol A₂ are obtained by subtracting the weight loss obtained by A₉+₁ with the total weight loss A₁. The relationship between electrolyte corrosion and metal corrosion as a function of weight loss was analyzed and compared based on Table 1. The surface condition was then analyzed by stereomicroscope (SZX16, Olympus).
Table 1. Guidelines for corrosion analysis in planned interval test

| Corrosion Factors | Observation of weight changes during immersion test | Criteria |
|-------------------|-----------------------------------------------------|----------|
| Liquid corrosiveness | Unchanged | $A_1 = B$ |
|                    | Decreased  | $B < A_1$ |
|                    | Increased  | $A_1 < B$ |
| Metal corrodibility | Unchanged | $A_2 = B$ |
|                    | Decreased  | $A_2 < B$ |
|                    | Increased  | $B < A_2$ |

3 Results and discussion

The results of these planned interval tests are shown in Tables 2 and 3. According to Table 2, the most significant weight loss occurred in the sample immersed under $E_{\text{ocp}}$. This indicates that the corrosion process occurs on Mg that immersed in a 3.5% NaCl solution without any protection procedure. On the other hand, the pure Mg metal immersed under $E_{\text{pz}}$ only recorded a very small decreased in weight loss, which actually due to non-protective procedure for 3 days to achieve stable and steady-state conditions before $E_{\text{pz}}$ pulse charged-discharged are performed. Mg samples in which immersed under $E_{\text{pz}}$ were found to have significantly lower corrosion rates than $E_{\text{ocp}}$. The ZCP technique under $E_{\text{pz}}$ recorded the efficiency of corrosion protection as much as 93% to 96%. This percentage of efficiency is believed to increase further if it is practiced on steel.

Table 2: Weight loss and corrosion rate of Mg sample in $E_{\text{ocp}}$ & $E_{\text{pz}}$

| Sample Marker | Immersion Period (Day) | Weight Loss ($\pm$ 0.5 mg) | Corrosion rate (mm/year) | Corrosion Protection Efficiency at $E_{\text{pz}}$ (%) |
|---------------|------------------------|-----------------------------|--------------------------|---------------------------------------------|
| $A_1$         | 5                      | 1896.1                      | 19.28                    | 1.21                                        | 93.7                                       |
| $A_2$         | 20                     | 3105.5                      | 7.90                     | 0.32                                        | 96.0                                       |
| $A_{1+1}$     | 25                     | 3458.3                      | 7.03                     | 0.25                                        | 96.3                                       |
| B             | 5                      | 333.4                       | 3.39                     | 1.26                                        | 93.9                                       |
| $A_2$         | 5                      | 352.8                       | 3.59                     | 0.00                                        | 99.2                                       |

The data obtained from Table 3 are found to be $B < A_1$ for both $E_{\text{ocp}}$ and $E_{\text{pz}}$. This suggests that there is a clear reduction of liquid corrosiveness for both $E_{\text{ocp}}$ & $E_{\text{pz}}$. The lower liquid corrosiveness over the immersion time is due to the depletion of Mg ion ($Mg^{2+}$) concentration in NaCl solution. Additionally, the corrosion rate for immersion at $E_{\text{pz}}$ was 16 times lower than that of $E_{\text{ocp}}$. In contrast, the metal corrodibility under $E_{\text{pz}}$ shows a significantly reduced from -1562.7mm/yr to -98.2mm/yr. This is believed because of the absence of an electric double layer which resulting in no charge transfer on the metal-electrolyte interface.
Although Mg is a reactive metal that is susceptible to oxidation reactions, however, a long-term immersion causes Mg surfaces to be less stimulated with the formation of positively charged Mg ions. By comparing the data between B and A2, the Mg metal corrodiability is increased in the Eocp system (B < A2), while the immersion in the Epzc, showed the decreasing of metal corrodiability (B > A2) (Table 3). The increasing in metal corrodiability in the Eocp system is a natural process as the presences of Mg ions (Mg²⁺) the presence of Mg ions (Mg²⁺) in the electrode-electrolyte interface creates an electric double layer that constantly promotes a charge transfer between the Mg surface and NaCl solution, resulting in corrosion reaction to occur. Thus, at Eocp, corrosion does occur due to charge transfer, meanwhile, the metal corrodiability under Epzc was significantly reduced. It is believed caused by the absence of an electric double layer which resulting in no charge transfer on the metal-electrolyte interface [7].

Table 3: Corrosion analysis and findings through PIT

| Parameter | Eocp    | Epzc  |
|-----------|---------|-------|
| B - A₁    | -1562.7 | -98.2 |
| B - A₂    | -19.4   | 17.5  |

| Criteria   | Description                                               |
|------------|-----------------------------------------------------------|
| A₁ > B < A₂| The tendency of corrosion due to liquid corrosiveness is decreased, whereas metal corrodiability is increased. |
| A₁ ≥ B > A₂| The tendency for liquid corrosiveness is decreased whereas the metal corrodiability is decreased. |

The morphology of the immersion effect on the Mg samples surface is shown by the stereomicroscope images in Fig. 2 and 3. From the top views, it is noted that Mg immersed in 3.5% NaCl solution under Eocp, for 20 and 25 days suffered severe corrosion (Fig 2). The masking profile measured by volume shows A₁ and A₁+1 samples losing 1.15 and 1.28 g/cm³, respectively. The increase of Mg volume loss due to corrosion reaction from day 20 to day 25 shows that Mg is a highly reactive metal in 3.5% NaCl solution. However, Mg soaked under Eocp showed no corrosion effect (Fig 3 for the same period. It is also observed that there are still machining marks on the sample surface. These findings suggest that corrosion protection at Epzc, has been proven to be a successful method for Mg oxidation mitigation.

Fig. 2. Stereoscopic images of the Mg surface of the Mg under Eocp exposed in 3.5% NaCl solution for (a) 20 and (b) 25 days.
4 Conclusion

The efficiency of ZCCP at $E_{pzc}$ for pure Mg metal in 3.5% NaCl solution is in the range of 93 to 96%. The protection efficiency of ZCCP is higher than 93% for iron-based metal or steel. The morphology of the immersion effect on the Mg immersed in 3.5% NaCl solution under $E_{ocp}$ suffered severe corrosion while Mg soaked under $E_{ep}$ showed no corrosion effect for the same period.

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