Effects of different pH of 3.5% NaCl solution on steel under zero charge corrosion protection technique

Rajaselan Wardan1, Shaiful Rizam Shamsudin2, Thivyasai Sampasivam2, Mohd Fitri Mohamad Wahid2 and Mohd Subhi Din Yati3

1Center of Excellence Geopolymer Geopolymer and Green Technology, Faculty of Chemical Engineering Technology, University Malaysia Perlis, Arau, 02600 Perlis
2Faculty of Mechanical Engineering Technology, University Malaysia Perlis, Arau, 02600 Perlis
3Maritime Technology Division (BTM), Science & Technology Research Institute for Defence (STRIDE), Ministry of Defence, Malaysia

Abstract. The study is carried out to understand the new corrosion protection technique, non-polarization concept, using current/voltage pulses to achieve a potential of zero charges ($E_{pz}$) of the metal-solution interface. As a result, a cost-saving and ecological method has been proposed as a new anti-corrosion method. In the methodology, U-bend samples are immersed in a 3.5% NaCl solution with different pH values. The readings prove the occurrence of electrochemical reaction, absence of charges, and the effect of $E_{pz}$. An examination on the ZCCP on low-carbon steel in 3.5% NaCl solution was analyze for 120 hours days. This study is carried out to understand the concept of corrosion behaviour and a new corrosion protection technique which applies non-polarization concept. A U-bend mild steel is used to corrosion effect in various pH values under zero charge protection. Samples were then immersed in 3.5% NaCl solution with different pH values. Electrochemical behaviour of steel sample in 3.5% NaCl solution was analysed by means of Tafel extrapolation. It was found that $E_{corr}$ and $i_{corr}$ recorded dissimilar readings at different pH values. As $E_{corr}$ rises, $i_{corr}$ drops from pH 6 to pH 9, hence corrosion rate also decreases from pH 6 to pH 9. Zero charge corrosion protection (ZCCP) technique is used to study the efficiency of corrosion protection method in different pH values. Readings of alternating current ($I_{ac}$) and direct voltage ($V_{dc}$) are recorded throughout the ZCCP experiment. These readings prove the occurrence of electrochemical reaction, absence of charges and the effect of $E_{pz}$.

1 Introduction

Mild steel is one of the most commonly used steels in marine industries due to its good mechanical behaviour. Mild steel is iron’s primary composition, carbon content below

1Corresponding author: rajelan9143@gmail.com
0.30%, and other alloy elements such as silicon and manganese [1]. The challenge faced due to the usage of mild steel is its low corrosion resistance [2]. The concept of mild steel corrosion in the marine environment can be understood by the electrochemical reaction of iron and water. First is the anodic reaction, where a metal atom is ionized and passed into the solution leaving its electrons. Then, the cathodic reaction involves reducing free electrons with chemical species such as oxygen (O₂) and water (H₂O) [3]. The speed at which the anodic reaction proceeds is directly related to the rate of corrosion. Determination of corrosion rate is essential to analyze corrosion behaviour. One of the significant factors is seawater’s pH value, which is influenced by the surrounding atmosphere, thus difficult to control. Failure analysis on corrosion must be done to find its cause and preventative actions [4].

Corrosion occurs due to potential differences in the corrosion cell, which is the difference between cathodic reaction half-cell potential and anodic reaction partial potential. Therefore, the potential of metal should be altered by either cathodic protection or anodic protection. Both methods are well known to solve marine corrosion, but a new approach has been proposed in order to save cost and ensure a longer service life of steel [5].

A new technique has been developed that uses the concept of non-polarization, and high surface tension to prevent deterioration of the metal, namely zero charge corrosion protection (ZCCP) is studied. In the ZCCP technique, metal is protected from corrosion due to the formation of an electrical resistance layer, which indicates that no charges lead to oxidation and reduction [6]. The purpose of this study is to determine the potential of zero charges, E_{pzc}, on U-shaped mild steel immersed in 3.5% NaCl solution with different pH values.

2 Experimental Procedure

Carbon steel samples were obtained from a source of steel. The sample’s chemical composition was determined using optical emission spectrometry (OES) (Q8, Magellan, Bruker). The samples were polished to eliminate the oxide and rust associated layer, which resulted in a clean and shiny surface. Following that, the steel sample was bent into U shapes per ASTM G 30. Next, the rectangular strip sample was twisted 180 degrees around a 6 cm radius. A 1 cm² region was covered with black tape before the application of the coating. Following that, the coated samples were dried for a whole day. Before further testing, the black tapes on the samples were removed, revealing a 1 cm² portion of the metal to be studied.

![Coated U-bend mild steel sample with 1 cm² of the exposed area.](image)

The electrolyte is prepared by dissolving 35 grams of sodium chloride (NaCl) into 1000ml of distilled water. First, the pH value of the NaCl solution is determined by using a pH meter (pH 211, Microprocessor pH meter, HANNA instruments, Italy). Next, NaCl solution is
added with either hydrochloric acid (HCl) or sodium hydroxide-based solution (NaOH) to provide the required pH. Tafel extrapolation was carried out using a potentiostat/ galvanostat (Gill AC, ACM instruments, UK). A custom-made power supply designed for ZCCP experiments is connected to a steel sample. An oscilloscope is used to measure the waveform pulse frequencies generated by the power supply. The experiment was performed by immersing the steel sample in 3.5% NaCl solution for 120 hours at room temperature. The mild steel immersed in NaCl solution of desired pH value. The ZCCP was carried out in NaCl solution with a pH value of 6 to 9. One unit of steel sample was also immersed without any corrosion protection as a reference and designed as open circuit potential (E_{ocp}). Voltage and current reading for both AC and DC were obtained from the multimeter (MT-1820, Proskit). The observation was done for 120 hours consecutively.

3 Results and discussion

The carbon steel utilized as the sample in this study complies with AISI 1016 (Table 1). Accordingly, the steel sample exhibits thermodynamically unstable in an aqueous environment and is more susceptible to corrosion. It is known that, in the presence of salt water, the sample surface reacts, resulting in the formation of oxyhydroxides iron (FeOOH) [7], which is reddish in color.

Table 1. Chemical composition of the mild steel sample.

| Element      | Sample   | AISI 1016   |
|--------------|----------|-------------|
| Ferrous, F   | 98.55    | 98.13-99.58 |
| Manganese, Mn| 0.78     | 0.60-0.90   |
| Carbon, C    | 0.13     | 0.12-0.18   |
| Sulfur, S    | 0.038    | ≤ 0.050     |
| Phosphorous, P| 0.02    | ≤ 0.040     |

Figure 2 depicts the subsequent test results, i.e., the electrochemical behaviour of AISI 1016 type steel. The test was carried out using the Tafel plot with variable pH of 3.5% NaCl solution. From the Tafel plots shown, the values obtained are B_a, B_c, E_{corr}, and i_{corr}. After obtaining i_{corr} from the Tafel extrapolation based on Faraday’s law, it can be used to calculate corrosion rate according to Eq. (1). Finally, the penetration rate equation can be applied [9].

\[
\text{CR} = k \cdot i_{\text{corr}} (\text{EW}/\rho \cdot A) \tag{1}
\]

where \( k \) is 0.00327, known as constant defining corrosion rate, \( \text{EW} \) is the equivalent weight, \( \rho \) is the density, and \( A \) is the exposed surface area. The equivalent weight of mild steel is 28.25 g, and the density of mild steel is 7.85 g/cm^2. The exposed area can be neglected as the value is 1 cm^2, not changing the calculation. The corrosion rate was estimated using the data and Eq. (1) above, and the results are shown in the last column of Table 2. The corrosion rate is defined as the speed at which metal corrodes.
Fig 2. Tafel plots of mild steel samples in a 3.5% NaCl solution of different pH.

| pH   | $E_{\text{corr}}$ (mV vs SCE) | $\beta_a$ (mV/decade) | $\beta_c$ (mV/decade) | $I_{\text{corr}}$ (uA/cm²) | Corrosion rate ($x10^{-2}$ mm/year) |
|------|-------------------------------|------------------------|------------------------|-----------------------------|--------------------------------------|
| 6    | -584.52                       | 446.26                 | -721.29                | 1.6115                      | 1.896                                |
| 7    | -566.03                       | 515.01                 | -600.13                | 1.5141                      | 1.782                                |
| 8    | -546.31                       | 395.50                 | -475.45                | 1.4740                      | 1.735                                |
| 9    | -518.02                       | 549.45                 | -534.60                | 1.3871                      | 1.632                                |

Table 2 shows that the decrease in corrosion rate occurs when the pH is increased. Corrosion rate drops from pH 6 to pH 9. In other words, corrosion occurs rapidly in acidic solutions compared to alkaline solutions. According to the corrosion rate equation given above, it is noticeable that corrosion current density, $I_{\text{corr}}$ plays a crucial role in determining corrosion rate. Both $E_{\text{corr}}$ and $I_{\text{corr}}$ are related to corrosion rates. More negative $E_{\text{corr}}$ indicates that the metal has a higher corrosion tendency, and this statement is only applicable for the natural corrosion behaviour of metal. On the other hand, less negative $E_{\text{corr}}$ indicates more excellent stability, so it is more resistant to corrosion as its passivation is better. Less negative $E_{\text{corr}}$ results in lower $I_{\text{corr}}$. As $I_{\text{corr}}$ is proportional to corrosion rate, lower $I_{\text{corr}}$ values can delay the corrosion rate. Corrosion current density, $I_{\text{corr}}$ is the same as oxidation current [10]. When a metal is less prone to oxidation, it is said to have more excellent corrosion resistance. In this experiment, it has been observed that pH 9, an alkaline solution, has the least negative $E_{\text{corr}}$ value and minimum $I_{\text{corr}}$ value, thus resulting in a lower corrosion rate. A lower corrosion rate indicates better corrosion protection [11]. However, pH 6, an acidic solution, resulted in the most negative $E_{\text{corr}}$, maximum $I_{\text{corr}}$, and the highest corrosion rate. In conclusion, it can be summarized that corrosion attacks metal faster in acidic solutions compared to alkaline solutions.

In Fig. 3, pH 9 has a minimum average IAC of 0.38 μA/cm², whereas pH 7 has a maximum average IAC of 0.67 μA/cm². As the standard deviation value for pH 6 is the lowest, pH 6 has the least error. Concise IAC data for pH 6 is the main reason for its low error compared to the other, with a greater range of data. A greater range of data results in more error, and pH 7 is observed to have the highest error. In alkaline media, the steel develops the so-called ‘passive layer’ that maintains the metal in passive state for decades unless aggressive substances reach the reinforcement [12]. Based on the average of IAC, pH 9 has the least corrosion attack as its...
current consumption is lower than other pH values. However, its error is slightly higher than pH 6. IAC proved that alkaline solution is less prone to corrosion.

![Fig 3. Average alternating current density (IAC) of the circuit system for different 3.5% NaCl solution pH.](image)

According to Fig 4, pH 9 has the more negative V_{DC} reading of -677.28 mV vs SCE, whereas pH 8 has a V_{DC} of -630.28 mV vs SCE, which is the less negative V_{DC}. For the errors encountered, pH 9 has the slightest error as its standard deviation value is the lowest compared to the others. As pH 9 gives a more negative V_{DC}, it can be confirmed that it had maintained a lower value than E_{corr}. This can be proved that mild steel in pH 9, NaCl solution has been well protected from corrosion by E_{pzc}.

![Fig 4. Average steel potential (V_{DC}) for in different 3.5% NaCl solution pH.](image)

Summarily, based on IAC, and V_{DC} readings obtained through ZCCP, it can be concluded that the most optimum pH value used for ZCCP is pH 9. This is proved by the least IAC consumption, more stable V_{AC}, and more negative value of VDC. All of these leads to a successful E_{pzc} that protected the exposed area of mild steel for 120 hours from corrosion. Moreover, pH 9 has the minimum error throughout ZCCP. However, the other mild steels immersed in 3.5% NaCl solution of pH 6, 7, and 8 also been protected by E_{pzc}, but pH 9 showed better results than them. Therefore, mild steel immersed in a 3.5% NaCl solution of pH 9, the most alkaline solution, is the most optimum for ZCCP.

### 4 Conclusion

A new corrosion prevention technique is studied in this project called zero charge corrosion protection (ZCCP). The concept of non-polarization is applied in ZCCP to remove charges at the metal-solution interface, preventing an electrochemical reaction. ZCCP is studied by
monitoring alternating current (I_{AC}), and metal potential (V_{DC}). Based on this experiment, an alkaline solution is less susceptible to corrosion compared to an acidic solution. The pH value of 9 gave a less negative E_{corr}, lowest i_{corr}, thus has a minimum corrosion rate of 1.632 x 10^{-2} mm/year. On the other hand, pH 6 has the most negative E_{corr}, highest i_{corr}, thus has a maximum corrosion rate of 1.896 x 10^{-2} mm/year. From pH 6 to pH 9, i_{corr} drops as E_{corr} rises, resulting in a lower corrosion rate. After studying the electrochemical concept by corrosion behaviour of mild steel, a corrosion protection method has been carried out. Based on all the readings obtained, it is proved that pH 9 is the most optimum due to its minimum I_{AC} consumption of 0.38 μA/cm², stable V_{AC} with an average of ±0.68 mV, a more negative metal potential, or E_{pzc} of -677.28 mV vs SCE. The alkaline solution is more corrosion resistant as it is less prone to stress corrosion cracking (SCC). Thus it is more effective during ZCCP.

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