Effect of Pulse Frequencies on Low Carbon Steel in 3.5 wt% NaCl Solution under Zero Charge Corrosion Protection

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Abstract. Zero charge corrosion protection (ZCCP) is an alternative to the existing cathodic protection methods. It applies a current/voltage pulse with a certain particular frequency to attain a potential of zero charge (E_{pzc}) on the electrode-electrolyte interface. A study on the pulse frequencies of ZCCP system on low-carbon steel in 3.5 % NaCl Na solution was carried out for 14 days. The pulse frequencies are varied from 4, 20, 50 and 100 Hz. The ability of these frequencies in protecting samples is determined by means of corrosion rate based on weight loss analysis and surface morphology. Experimental observations indicate that low carbon steel corrosion protection is strongly influenced by changes in pulse frequency. Corrosion rates were found to gradually decrease as pulse frequency increased from 4, 20 to 50 Hz, nevertheless at higher frequencies (100 Hz), corrosion protection was observed to be less effective where the corrosion rate dramatically grew up. The surface morphology of the steel surface is smooth and protected at a pulse frequency of 50 Hz. This indicates that the current/voltage pulse of ZCCP system only requires 50 Hz which is equivalent to a standard AC power frequency applied in most countries including Malaysia.

1 Introduction

Carbon steel is utilized as a significant construction material because of its low generation cost and extraordinary mechanical properties required to be utilized as strengthening bar [1]. However, the challenge is that it has low corrosion resistance especially in seawater environment. A high integrity of corrosion protection is required as it is utilized in numerous destructive conditions, for example, chemical production, marine, and contaminated condition. Corrosion product shaped on the steel surface called rust involves different oxides. Among these oxide, ferrous hydroxide, Fe(OH)₂ can be shaped in impartial to fundamental condition, while geothite a-FeOOH and lepidocrocite cFeOOH are the significant constituents in medium to high acidic condition [2]. Moreover, in marine condition, a.k.a.

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ganeite, b-FeOOH is present in alpha and gamma variations. Magnetite, Fe₃O₄ and hematite, a-Fe₂O₃ are additionally seen as present in normal just as in faster corrosion state [3].

During corrosion, metals will in general proselyte to all the more thermodynamically stable mixes, for example, oxides, hydroxides, salts, or carbonates. Corrosion is a leading cause of premature failure in metallic structures [4-5].

The zero-charge corrosion protection (ZCCP) is a promising technique to control metal structures harm brought about by oxidation response because of atmosphere changes, ecological variables, and operational conditions. Potential of zero charge (Eₚzc) is an estimation of the electrode potential for any metal at which a spotless surface of the metal would not procure any electrical charge when it comes into contact with an electrolyte [6-7]. At Eₚzc, a metal surface is not in contact with a fluid arrangement because of the non-appearance of electrical charge and no electrostatic appeal [8]. ZCCP exploit the frequency of current/voltage pulse waves to the metal that needs to be protected. The frequency of a current is the number of repetitions of one complete cycle of the waveform per second and it is measured in hertz (Hz). The waveform describes the shape of one cycle of the voltage or current. Current can be generated as an alternating current (AC), where the direction of the current flow alternates around zero with positive and negative direction. Most of the countries use 50/60 Hz as the utility frequency because power been supplied is more stable and efficient. Moreover, higher frequency than 50/60 Hz causes some distribution losses [9]. This indicates that frequency change can impart serious effect on the corrosion protection.

The purpose of this study is to investigate the effect of different frequencies of pulse current/voltage of ZCCP system on low carbon steel in 3.5 wt% NaCl solution.

2 Research methodology

The samples of carbon steel was ground and analyzed by optical emission spectrometry, OES (Q8, Magellan, Bruker) for the chemical composition content. The samples were polished to remove the upper oxide layers, rust and corrosion deposits to get a smooth and shiny surface. It was then coated with polymer-based paint. An area of 1 cm² was exposed for experimental purposes. The shape and size of the sample are shown in Fig. 1.

![Fig. 1. Shape and size of the sample exposed area.](image)

The painted steel samples were weighted by using analytical balance (GR-200, A&D Weighing) to record the sample weight before the immersion test loss. A custom-made power
supply designed for ZCCP experiments is connected to a steel sample. 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 14 days at room temperature (25 °C). The ZCCP system was set at different frequencies from 4, 20, 50 and 100 Hz. After immersion testing, exposed steel surface was cleaned by 2 % nital solution and rinsed with the distilled water. Samples were then weighted again to determine their weight loss. The corrosion rates were determined by using Equation (1) [10]

\[
\text{Corrosion rate} = \frac{87.6 \Delta w}{\rho At}
\]  

where \( A \) is the exposed surface area (cm\(^2\)), \( t \) is the exposure immersion time, \( \rho \) is the density of the sample (g/cm\(^3\)) and \( w \) is the weight loss (g).

One unit of steel sample was also immersed without any corrosion protection, which is used as a reference and designated as open circuit potential (\( E_{ocp} \)). The surface morphology was then observed using stereomicroscope (SZX16, Olympus) to visualize the presence of corrosion attack on the steel samples. The purpose of this study is to investigate the effect of different frequencies of pulse current /voltage of ZCCP system on low carbon steel in 3.5 wt\% NaCl solution.

### 3 Results and discussion

The carbon steel used in this study is in compliance with AISI 1016 (Table 1). Thus, it is a thermodynamically unstable material in aqueous environment, which tends to corrode, moreover in the presence of saltwater to give a product of oxyhydroxides of iron, reddish color, FeOOH. [11].

| Element      | Sample | AISI 1016 |
|--------------|--------|-----------|
| Iron, Fe     | 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  | \( \leq 0.050 \) |
| Phosphorous, P| 0.020  | \( \leq 0.040 \) |

Fig. 2 shows the corrosion rate versus immersion time for different pulse frequencies of ZCCP system. The corrosion rate of \( E_{ocp} \) shows the highest value 3.018 \( \mu \)m/year. It is the actual thermodynamically stable potential of AISI 1016 steel in 3.5 % NaCl solution under experimental condition. A high corrosion rates in \( E_{ocp} \) samples are indeed expected. It is noted that in literature, the \( E_{ocp} \) value of mild steel is within the range of 60 - 70 \( \mu \)m/year [12].
In ZCCP system, lower pulse frequency (4 Hz) recorded 0.528 μm/year and it was gradually decrease to 0.359 μm/year at 20 Hz frequency. The lowest corrosion rate, 0.122 μm/year was obtained at 50 Hz, while at 100 Hz frequency, the corrosion rate was dramatically increase to 0.445 μm/year. The changes in the corrosion rate is due to the pulse frequency factor. In this case, frequency is a function of the pulse energy [13]. Frequency plays an important role in pushing the flow of electrons out of the metal center into the steel “skin” layer. This mechanism is called “skin effect”. This skin effect reduces the ability of a metal to act as an electrical conductor. The amount and energy of electrons in the skin’s effect prevent the conversion of Fe atoms to Fe$^{2+}$ ions. Taking into account the characteristics of charges on the electrode-electrolyte interface, the effect of the skin is equivalent to the metal character at the zero charge potential, $E_{pzc}$. At the low frequencies, 4 Hz, the pushing energy of the electrons in the metal center is insufficient to develop a skin effect. Therefore, a corrosion reaction occurs at high rates. The corrosion rate decreases as the frequency of the pulse energies to form a skin effect gradually reaching the maximum effect to 50 Hz where all the Fe atoms exchange to Fe$^{2+}$ ions are inhibited. Coincidently, this 50 Hz frequency is the same as the alternating current in the household electrical outlets in most countries including Malaysia [14]. It is possible that 60 Hz frequency can be studied where it could have an effect that is almost identical to the corrosion rate at 50 Hz. However, at high frequencies (more than 50 or 60 Hz) the current/voltage pulse produces high energy. The flow of the electrons in the metal center is pushed out beyond the metal skin or surface. This mechanism causes the metal surface to have an excessive negative charge. This in turn causes the metal with excess negative charge to react with the ionic charges of opposite polarity.

The results have been strengthened by the evidence of the surface morphology shown at Fig. 3 as the 4 Hz has the worst corrosion attack as the surface represented by crater-like morphology. Flat but rough and uneven surface was produced at 20 Hz. At the 50 Hz, smooth and much even surface was produced indicating the samples were well protected. Meanwhile, sample of 100 Hz shows identically morphology as the lower frequency. However, smaller craters were produced.

![Graph showing corrosion rate vs frequencies](image Url)

**Fig. 2.** Corrosion rate of different frequency of zero charge corrosion protection.
Fig. 3. Surface morphology of immersed samples, (a) 4 Hz, (b) 20 Hz, (c) 50 Hz and (d) 100 Hz.

Low frequencies of pulse current/voltage (e.g. 4 Hz) were insufficient to restrain the adsorption of the excessive negative charges from oxygen water dipole. It also failed to prevent the conversion of Fe atoms to Fe$^{2+}$ ionic charges. Therefore, at low frequencies, the ZCCP mechanism is unable to act as a carbon steel corrosion protection. However, this corrosion protection capability gradually increases as the frequency were amplified from 20 Hz to 50 Hz. With the removal of the charges at the interface until the magnitude of the charge reaches zero, the charge transfer does not occur and no corrosion response occurs. At zero charge, the double-layer no longer exists at the metal-solution interface. To protect against corrosion, this zero-charge situation must be maintained to prevent the charge transfer. This shows that at this frequency range, ionic charges are depleted or removed from the surface of the samples and it is sufficient enough to maintain the zero-charges layer and promote the capability of ZCCP towards corrosion protection. But at 100 Hz, the current become overload than the current needed. At the higher pulse frequency, the charging and discharging processes vigorously applied to the ZCCP system, resulting the changes of water molecule orientation to be more energetic and faster. It provides sufficient energy to reinduced the adsorption and charges transfer at the electrode-electrolyte interface [15]. On the metal side, it also made the surface loses the capability to produce a metastable protective layer to hinder further corrosion reaction to occur.

4 Conclusion

The effect of corrosion on low carbon steel was significantly influenced by different pulse-current frequency of current/voltage in the ZCCP system. Corrosion rate at $E_{ocp}$ indicates the highest value, 3.018 $\mu$m/year and 50 Hz the lowest value, 0.122 $\mu$m/year. Increasing the
frequency from 0 to 50 Hz showed changes in both corrosion rate and the surface morphology. At high frequency of 100 Hz, it has high corrosion rate compared to 20 to 50 Hz, and the surface are rougher, with small crater like surface. 50 Hz has much smooth and flat surface demonstrate the sample was well protected by ZCCP technique. Therefore, the ZCCP for the carbon steel (AISI 1016) in 3.5 % NaCl solution only required 50 Hz, which was equivalent to the standard AC power frequency applied in most countries.

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