Determination of Protective Potential in the Zero Charge Corrosion Protection System

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Abstract. Zero charge corrosion protection, ZCCP, is a new invention in the field of corrosion protection. It applies alternating current, AC, mode while the protective potential to ensure that the metal exposed in the corrosive environment still does not exist in any of the previous works of literature. The study was conducted by the voltage scanning within corrosion potential, Ecorr, and polarized potential, E impressed, using potentiostat. It was carried out by examining the behavior of the current flow in the circuit. The experimental results found that the protective potential for maximum protection in the ZCCP system is 0 mV. By keeping the AC metal potential at 0 mV, the surface will not acquire any charges, hence the corrosion reaction will be inhibited.

1 Introduction

When a piece of metal is exposed in an electrolyte, such as salted or acidic solution, an electrochemical corrosion reaction occurs where the electron conductor (metal electrode) meets the ion conductor (electrolyte) at the electrode-electrolyte interface. Metal in aqueous solutions creates a potential difference due to the adsorption of water molecules on an electrode. Generally, water molecules are seen to be electrically neutral, nevertheless, the water molecule has dipoles moment that described as bipolar molecules that have an excessive positive (Hδ+) and negative charges sides (O 2δ–). These polarity differences create a high gradient potential across the metal-solution interface result in a layer of an electric field known as an electric double-layer [1].

The presence of an electric double-layer is due to the separation of the opposite charges in between both metal and solution phases in contact [2]. A potential difference caused by the electric double layer results in the adsorption of ionic charges to metal surfaces then finally brought corrosion reaction. In electrochemistry study, the potential difference between metal and reference electrodes commonly called a half-cell electrode. It is referred to as corrosion potential (Ecorr), open circuit potential (Emcp), or native potential (Enat). If the electric double-layer can be neutralized, both excessive positive and negative charges on the metal surfaces are eliminated and finally making the metal surface maintained at the potential

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of zero charges. The term of zero charge potential ($E_{pzc}$) is a characteristic value of the electrode potential for any metal at which a clean surface of the metal will not acquire any electrical charge when it comes into contact with an electrolyte [3]. The surface of zero charges occurs when the positive and negative charges on the surface have been neutralized by giving a negative and positive direct current to the metal. In the previous study, it is known that the $E_{pzc}$ is slightly negative than $E_{corr}$ [4].

The application of $E_{pzc}$ concept is manipulated through a method called zero charge corrosion protection (ZCCP). ZCCP technique requires a power supply that capable of giving current/ voltage pulses. When pulses input signals are applied, the current/ voltage must be measured in alternating current (AC) mode. Therefore, in this technique, the protective potential should be measured in different concepts, which is something opposite to the cathodic protection system (CP). It is well known that the protective potential of the CP system for steel in the corrosive environment must be within -850 to -1100 mV vs Cu/CuSO4 [5]. Conversely, to find out a suitable protective voltage in AC mode, a study should be done to determine the presence of electric charges on the metal surface to keep the metal-solution interface at zero charges (or $E_{pzc}$).

In this study, a potentiostat is manipulated as a power supply to control the net potential of the metal at $E_{pzc}$. The excessive charges on metal surface is measured based on the current density profile that can be detected by the supersensitive current sensor embedded in the potentiostat. Here, the potentiostat was set in the cyclic mode for micro-voltage scan within $E_{corr}$ and polarized potential ($E_{impressed}$) repeatedly.

2 Methodology

The steel samples were cut into 1.5 cm diameter and 0.4 cm thickness. It was ground by silicon carbide paper up to 600 grit, washed by alcohol, and rinsed by distilled water. The cleaned and dry samples was locked into a flat sample holder and inserted into a corrosion cell. 1 liter of 3.5% NaCl solution was filled into the corrosion cell. Steel sample and saturated calomel reference electrode (SCE) were then connected to the potentiostat (Gill AC, ACM Instruments). The steel samples were initially soaked within 5 days to ensure that $E_{corr}$ is properly in a steady-state condition. The micro-voltage scan was performed at a rate 1 mV/ minute. The micro-voltage scan magnitude ranges (r - s) were ±1 to ±5 mV offset to $E_{corr}$ toward an impressed potential ($E_{impressed}$). The experiment was repeated to the smaller micro-voltage down to ±0.125 mV. The micro-voltage scanning profile is displayed in Fig. 1. All experiments were performed in a Faraday cage and the temperature was controlled at 25°C.

![Fig. 1. The micro-voltage scanning profile around, $E_{pzc}$. (m, is the magnitude, r and s are the maximum and minimum voltage distance respectively).](image)

- Potential (mV)
- Time (min)
- $E_{corr}$
- $E_{pzc}$
- $E_{impressed}$
The micro-voltage scan setup preventing all oxidation & reduction reactions to avoid a reproduction of excessive positive and negative charges on the metal surface. The current density data from the micro-voltage scanning within $E_{pzc}$ to $E_{impressed}$ were analyzed and displayed as a plot of current density against time. To make it easier observation, these data were also converted into a histogram form displaying average current density vs magnitude of micro-voltage scanning.

3 Results and discussion

The voltage scanning test to determine the protective voltage in the ZCCP system was performed by measuring the current density profile (Fig. 2). The current density was recorded 1 reading/s for 24 hours. The reading was taken out as soon as the steady-state $E_{corr}$ achieved within 5 days of immersion period.

Fig. 2. (a) Plot and (b) histogram for micro-voltage scan from ±1 mV to ±5 mV magnitudes.
Fig. 2(a) shows a plot of current density vs time at the magnitude range i.e. ±1 to ±5 mV within $E_{\text{corr}}$ & $E_{\text{impressed}}$ as the position $E_{\text{pzc}}$ is believed to be within these potentials [4]. There is a wild movement pattern of current flow. The behavior of the electrical current is observed to form an unstable pattern. All current density is still lower as compared to the current requirement for cathodic protection in stagnant seawater (20 to 30 $\mu A/cm^2$) [5]. To make it clear, the average current density is displayed in histogram form (Fig. 2b). The scanned magnitudes, especially for ±5 mV and a part of ±4 mV are found to be pulsating beyond the zero lines of electric current. The negative electric charges were shifted the positive charge region. This means that there are charges transfer at the metal-solution interface, hence promotes the adsorption/desorption of ionic charge species in the metal-solution interface. Consequently, the metal potential at ±4 and ±5 mV were failed to bring down the metal potential to zero charges line which is automatically failed to act as protective potential in the AC mode of the ZCCP system.

The current densities that do not exceed the zero line occur at ±1 to ±3 mV magnitude of voltage scanned ranges. At this stage, the magnitude of the voltage scan at ±1 mV is considered to be a relatively good tolerance to referred to as the protective potential, while the minimum tolerance in the ZCCP system is about ±3 mV AC. However, the trustworthiness of these three voltage magnitudes is still questionable. It is observed that the flow of electric currents generally tends to be in the region of the negative charges. Although oxidation of metals does not occur in the negative region, the flow of current below the zero line causes the possibility that the metal surface tends to acquire a negative charge. In the long run, these negative charges can potentially accumulate, absorb, and cover the metal surface which eventually makes it possible to enter the immune region as described in the E-pH Pourbaix diagram. This process would make the metal back to the cathode protection system. What is bad about this CP system is that, if the electricity supply is cut off, then the metal reaction rate will soar rapidly, whereas in the ZCCP system, if the metal surface is in a stable state of $E_{\text{pzc}}$ in the long period, the corrosion reaction does not occur or takes a long time to suffer failure [4].

To prevent the metal from being covered by the excessive negative charges, a voltage scanning is performed on a smaller magnitude scale. A few similar voltage scan step at ±0.125 to ±1 mV (Fig. 3). Fig. 3(a) shows all voltage magnitude ranges were observed that the current density output does not exceed the zero line. It seems like the current flow, mainly for ± 0.5 and ± 1 mV, moves quite wildly. On the other hand, the scanning at ± 0.125, and ± 0.25 mV scanned magnitude show a very stable situation at the zero lines. Fig. 3 (b) confirms that scans on a scale of magnitude ±1 mV (or less) make the current flow direction would never exceed the zero line position. This indicates that, to ensure that corrosion does not occur on metals which exposed to corrosive environments, protective potential in AC mode or ZCCP systems should reach ±1 mV or below. However, the best protective potential for the ZCCP system can reach a value of 0 mV is confirmed to be more convincing. It is noted that the excessive positive charge on the metal surface is a sign of corrosion reaction. When sufficient electron (or negative current) supplied to the metal just necessary to neutralize the positive charges on the metal surface, the metal will be eventually in a situation that having no charge on the metal surface. Therefore, the water molecules will be no longer can be adsorbed on the metal surface due to the absence of charges. In terms of an electrical double layer model, this is the lowest capacitance value being measured. In the absence of adsorbed water molecules, a sort of higher electrical resistance layer is created between the metal and the solution at the metal-solution interface. In the AC mode of the ZCCP system, 0 mV is the best protection potential where metals and solutions are believed not to be in contact with each other.
Fig. 3. (a) Plot and (b) histogram for micro-voltage scan from ±0.125 to ±5 mV magnitudes.

4 Conclusion

A corrosion protection method by applying AC mode has been invented and named as zero charge corrosion protection, ZCCP. Micro-voltage scanning has been performed on the steel samples in a corrosive environment shows that the maximum protective potential is at 0 mV. If metal potential could be maintained at 0 mV, its surface will not acquire any charge, hence the corrosion reaction will be inhibited completely.

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References

1. Y. L. Wu, D. P. Zhang, G. Y. Cai, X. X. Zhang, Z. H. Dong. Corr. Eng. Sci. & Tech. 1-13 (2020)
2. A. Groß, S. Sakong. Curr Opin Electrochem. 14. 1-6 (2019)
3. F. El-Hajjaji, M. E. Belghiti, B. Hammouti, S. Jodeh, O. Hamed, H. Lgaz, R. Salghi. Port. Electrochim. Acta, 36. 197-212 (2018)
4. S. R. Shamsudin. PhD Thesis. Universia Malaysia Perlis (2016)
5. R. Baboian, R. Treseder. NACE Corrosion Engineer's Reference Book. 3 (2002).