Preliminary study of zero charge corrosion protection on steel plate embedded in geopolymer paste

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Abstract. Steel reinforced concrete usually protected against corrosion by passivation of the steel arising from the high alkalinity of the pore solution within the geopolymer concrete. The ingress of chlorides to the steel or concrete interface or carbonation of the concrete reducing the alkalinity of the pore solution at the steel or concrete interface. This will cause loss of durability in reinforced concrete. The corrosion behavior of steel embedded in geopolymer paste was studied by open circuit potential, $E_{\text{ocp}}$ and potential zero charge method $E_{\text{pzc}}$ under 3.5% NaCl solution exposure. The $E_{\text{corr}}$ (-660 mV vs SCE) more negative than $E_{\text{pzc}}$ value (-630 mV vs SCE). It shows the steel plate have an excessive negative charges. It is noted that the zero charge corrosion protection (ZCCP) method successfully prevents the steel surface suffering from corrosion. Therefore, it is strongly believed that metal under $E_{\text{pzc}}$ is not in contact with H+ and OH‾ ionic charges due to the absence of electrical charge as well as electrostatic attraction on metal surface.

1 Introduction

The major durability issues faced by infrastructure components are corrosion of steel in reinforced concrete structures, and it also influences the lifespan of the structure. Nowadays, the prevention of corrosion prevention methods still in progress, such as one of the efforts being made is the development of components of materials such as geopolymers to replace, OPC.

The durability of concrete is important role in infrastructure, it depends on the interactions of the material with the environment. The application of geopolymers could enhance the corrosion protection by reducing the corrosion rate of steel in the concrete [1, 2]. The alkalinity environment of geopolymers which is pH of 12 to 13 will protect the steel reinforced on steel surface or passivation [3].

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According to ACI 222, the passive film does not actually stop corrosion, it reduces the corrosion rate to an insignificant level which is 0.1 µm per year and without the passive film,
the steel would corrode at rates at least 1,000 times higher [4]. The destruction of the passivating layer occurs when the alkalinity of the concrete is reduced or when the chloride concentration in concrete is increased to a certain level [5].

Therefore, the steel reinforced exposed to the active environments such as sea bridge and costal area can corrode, it is because the sea water and it contains high chlorides which reduce the alkalinity of concrete and due to outside moisture in coastal area [6]. If the porous concrete is permeable the sea water in the form of moisture will enters in to the concrete form the porous surface.

Geopolymer binders have a nano-porous pore system, which are the reduction of ionic diffusion and low permeability. It is due to the steel rebar embedded Geopolymer concrete is low water absorption when less of porosity [7]. Previous researcher, have stated that the water absorption of fly ash geopolymer is less than that of OPC paste [8, 9]. Table 1 gives the results of water absorption tests for fly ash geopolymer and OPC paste.

| Table 1. Water absorption of fly ash geopolymer and OPC paste. |
|---------------------------------------------------------------|
| Days | Water absorption% geopolymer paste | Water absorption %, OPC paste |
|------|-----------------------------------|-------------------------------|
| 7    | 16                                | 24                            |
| 14   | 12.4                              | 20                            |
| 28   | 9.3                               | 12                            |
| 90   | 7.2                               | 10                            |

The result shows, a percentage of the water absorption geopolymer paste is smaller than OPC paste with long period which is at 90 days has different percentage of water absorption for both sample was 2.8%. Geopolymer paste has concluded the decrease of pore size or water absorption with long time [8].

The less of water absorption still affect the corrosion resistance, which are the low pH of sample, iron atoms lose electrons and move into the surrounding concrete as ferrous ions. Anodic reaction is represented as $2\text{Fe} \rightarrow 2\text{Fe}^{2+} + 4\text{e}$. [5]. The metal surface charge is a positive charge. Meanwhile, at the high pH, a thin oxide layer forms on the steel and prevents metal atoms from dissolving. The reaction at the cathode is called a water reduction reaction $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^{-} \rightarrow 4\text{OH}^{-}$ [5]. The surface charge is negative charge and to maintain electrical neutrality. The ferrous ions migrate through the concrete pore water to these cathodic sites and combine to form iron hydroxides.

The corrosion protection of steel reinforced has been introduced by many researchers, but most of technique provide or donate electrons from anode to cathode such as cathodic protection and impressed current corrosion protection (ICCP). However, it is known that the metal will corrode and break down after a certain period of time.

Thus, this process makes corrosion protection very important in extending the lifespan of the metal from damage. The corrosion can be controlled and prevented by bringing the potential of the metal to a zero charge level. It is plays major role in eliminating of electric double-layer, ionic adsorption and neutralization of organic molecules on the electrode [10].

Syazwan et. al. has concluded that the pH variations with the presence of Cl- ions affect the $E_{pzc}$ value. The high of pH value shows that the small value of $E_{pzc}$ and steadily stable of current when a passive layer exist [11]. From the previous study, the value of open circuit potential and zero charge potential for mild steel, the Table 1 shows that, the value of $E_{corr}$ is more than $E_{pzc}$, it is due to the acidic solution and low pH.

| Table 2. The value of $E_{corr}$ and $E_{pzc}$ (mV vs SCE) for mild steel using EIS method. |
|-------------------------------------------------------------------|
| Solution              | $E_{corr}$ | $E_{pzc}$ | References                  |
| 1.0MHCI + 0.5M H$_2$SO$_4$ | -427       | -483      | Mallaiya et al. [12]. |
2 Methodology

The geopolymer paste raw materials are fly ash class F, sodium hydroxide (NaOH) and sodium silicate (Na₂SiO₃) solution [12]. AISI 1016 steel plate used as reinforcement and embedded in geopolymer paste. The dirt and rust was removed and cleaned according to ASTM G1-03(2017) [16]. Sodium hydroxide (NaOH) solution with optimum molarity 12 M was prepared by dissolving of its flake into 1 litre of distilled water. A combination of sodium silicate (Na₂SiO₃) and NaOH solution (ratio was 2.5:1) as an alkaline activator for geopolymerisation prior to mixed with fly ash, where are solid/liquid ratio was 2:1. Then, the mixture was placed in a mold with dimension of 50 x 50 x 50mm. A retort stand was used to clamp the steel. It is because the paste was still in liquid form and steel cannot stand on its own as graphical illustration of sample preparation shown in Figure 1. The samples kept in the molds until its became hardened and after 24 hours, the samples were taken out from the molds and cured at 60°C in the oven for 24 hours.

Fig. 1. Sample preparation.

The corrosion behaviour of steel embedded geopolymer was measured by open circuit potential, $E_{ocp}$ using a high-impedance voltmeter based on saturated calomel electrode (SCE) [17]. Potential of zero charge, $E_{pzc}$, is measured by specific method in closed circuit using pulsed power supply at 100Hz of frequencies. The potential of the steel plate in geopolymer paste is measured by using the similar voltmeter and reference electrode as $E_{corr}$.

3 Results and Discussion

Fig. 2 shows that the first 6 days, the corrosion potential $E_{ocp}$ of steel embedded geopolymer paste is drop sharply due to initial formation of passive layer in contact with 3.5 wt% of NaCl solution. After days 13, $E_{corr}$ is decrease uniformly until days 28. It is because the growth of passive layer is slowly stable. After days 17, $E_{corr}$ reach the steady state potential at -613 mV vs SCE. This potential is assumed as $E_{corr}$, of steel embedded geopolymer in NaCl solution.
Fig. 2. Potential, E (volt vs SCE) against Time (Days).

On the other hand, $E_{pzc}$ curves show a smoothly exponential reduction. The steel embedded geopolymer under zero charge corrosion protection (ZCCP) recorded -630 mV vs SCE. This -630mV vs SCE is stated as zero charge potential ($E_{pzc}$) is achieved just when the steady state curve achieved and the AC voltage recorded as $V_{dc} = 0$ mV by voltmeter. This zero charges potentials, 0 mV, means that there is limited or no charges different on steel surface. In this condition, the electrode- electrolyte interface is no longer absorbed any negative or positive charges to the metal surface, hence prevents any charges transfer within the interface as reported by Shaiful [18]. The zero charge of the metal-solution interface is the elimination of electric double layer where it weakens the over-potential energy to react among negative and positive charges at the metal-solution interface. The absence of this reaction energy resulted in the slowdown of the charges reaction which would eventually eliminated the effects of corrosion.

IUPAC defines the potential difference with respect to the potential of zero charge, $E_{pzc}$ [19]:

$$E_{pzc} = E_{corr} - E_{σ=0}$$

where, $E_{pzc}$ is the electrode potential difference with respect to the point of zero charge, $E_{corr}$ that the potential of the same electrode against a defined reference electrode and $E_{σ=0}$ is the potential of the same electrode when the surface charge is zero, where are in the absence of specific adsorption other than that of the solvent.

According to Figure 2, $E_{pzc}$ are found to be more positive as compared to steady state potential, $E_{corr}$ (-660mV vs SCE). This situation is very different from previous findings in acid electrolytes (see Table 2). In acidic aqueous, it contains the positive charges (H+) that favor the metal surface to have excessive positive charges. However, in this experiments, the aqueous solution with a pH of ~12 have the negative charges (OH‾) that dominates the solution which are believed to be due to alkaline medium in a geopolymer paste. This condition causes the metal surface to be also surrounded by excessive negative charges. When the ZCCCP method was applied to the metal embedded in the geopolymer paste, it was found that, $E_{pzc} > E_{corr}$. This means that the power supply supplies positive charge pulses to remove a negative charge on the metal surface. This process occurs until the metal surface loses all electrical charges. The removal of electrical charges at the electrode- electrolyte interface (as a capacitor discharging) leads the desorption of ionic charges which causes the
metal surface no longer suffers a corrosion reaction due to the absence of a charge transfers. It is strongly believed that metal under $E_{pzc}$ is not in contact with H$^+$ and OH$^-$ ionic charges due to the absence of electrical charge as well as electrostatic attraction on metal surface.

4 Conclusion

The corrosion can be protected by bringing the potential of the steel embedded geopolymer to a potential of zero charge. The corrosion potential $E_{corr}$ (-660 mV vs SCE) is more negative than $E_{pzc}$ (-630 mV vs SCE). It is shows the steel embedded in geopolymer paste in 3.5% NaCl solution have an excessive negative charge. In $E_{pzc}$, the steel surface does not suffer from corrosion reaction as it is not in contact to H$^+$ and OH$^-$ based molecules due to the absence of electrical charge as well as electrostatic attraction.

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