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A Study on Corrosion Behavior of Reinforcement Bar Embedded in Geopolymer Paste by Open Circuit Potential

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Abstract: Corrosion is an undesirable effect which could lead to the loss of billions of dollars in construction industry all over the world. Generally, Ordinary Portland Cement (OPC) is used as construction materials. Fly ash based geopolymer may replace the OPC because it is more environmental friendly. In this paper the study on corrosion behavior of reinforcement bar has been conducted in several geopolymer environments such as geopolymer paste without curing process, geopolymer paste which undergoes curing process, soaked in tap water by using the open circuit potential (OCP) method. The OCP of reinforcement bar was recorded with time. The reinforcement steel bar in cured geopolymer has showed more positive potential values compared with samples without curing process. However, for sample soaked in tap water, the potential value fluctuated. From the Pourbaix diagram, all the potential values were located in passivity region. The oxide formed the passive layer to protect the reinforcement bar from corrosion.

Key words: Corrosion, geopolymer, open circuit potential, reinforcement bar.

INTRODUCTION

Corrosion means the deterioration or degradation of a metal when it is exposed to corrosive agents such as salts, acids, bases and liquid chemicals. Water and moisture in the presence of oxygen are the corrosive agent. The processes involved in corrosion are electrochemical in nature. An electrochemical nature of corrosion involves two half-cell reactions; an oxidation reaction at the anode and a reduction reaction at the cathode.

The state of corrosion may be interpreted using a Pourbaix Diagram or E_H-pH diagram as Figure 1. The combination of potential and pH in a Pourbaix diagram may be used to indicate the three regions such as immunity, passivity and corrosion, that is the thermodynamic tendencies of corrosion.

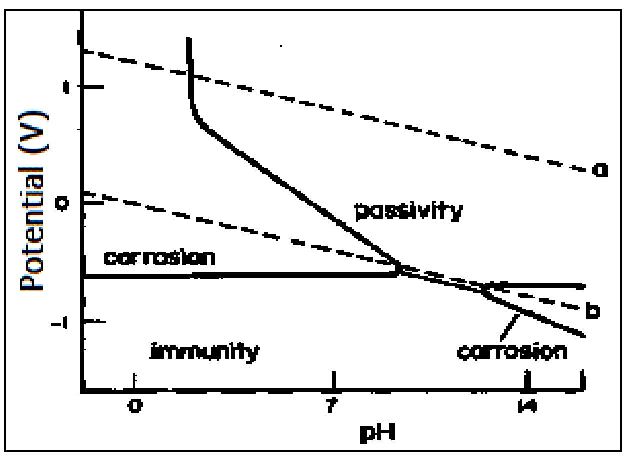

Fig. 1: Pourbaix diagram of iron at 25˚C (Jerome Kruger, 2001).

Open Circuit Potential (OCP) is a method of measuring potential of a metal when current is not flowing. The OCP values were measured by using digital multimeter in units of volts. The thermodynamic tendencies for the metal to corrode will be interpreted using the Pourbaix diagram.

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2. Experimental Methodology:
2.1 Sample Preparation:
2.1.1 Reinforcement Bar:

A low carbon steel or mild steel was used as reinforcement bar embedded in a geopolymer paste. The carbon content in the carbon steel is between 0.05%-0.29%. This carbon steel was chosen because it is readily available and cheap, which make it suitable for use in construction industries. Besides that, the carbon steel has strong strength, has high resistance to heat and can be recycled. The Table 1 below shows the composition analysis of the carbon steel that was used in this study. The composition was determined by an Arc Spark Spectrometer. The reinforcement bars were lathe prior to use to remove all the contaminants, and cleaned following the ASTM G1-03 (ASTM G1-03, 2011).

Table 1: Composition analysis of carbon steel.

Elements	Weight %	Elements	Weight %	Elements	Weight %
Fe	98.09	Al	0.020	Nb	0.0023
Mn	0.554	P	0.016	Ti	0.0013
Cu	0.443	Mo	0.014	Sb	0.0010
C	0.269	O	0.013	Zr	0.0010
Si	0.265	S	0.012	V	0.00080
Cr	0.123	Co	0.012	Ca	0.00060
Ni	0.096	W	0.0097	B	0.00052
Sn	0.043	N	0.0083	Total	100

2.1.2 Geopolymer Paste:

During the sample preparation of the geopolymer paste the following steps were followed. An alkaline activator was prepared 24 hrs prior to use with the ratio of the mixture of $Na_2SiO_3/NaOH$ is 2.5. The ratio is very important in order to obtain a homogeneous solution. The alkaline activator was later mixed with the fly ash for about 30 minutes. Fly ash was used as a source material in this study. It was obtained from Coal Power Plant, Ipoh, Perak. The reason for choosing fly ash is because it can reduce the release of carbon dioxide to the atmosphere, concrete permeability and mitigates against corrosion of reinforcement, alkali silica reaction, chemical and sulfate attack. It is highly pozzolanic material and contains almost 70% of pozzolanic compounds (silica oxide, alumina oxide and iron oxide) (Boral Fly Ash, 2002).

Then, the mixtures were placed in a 50 mm x 50 mm x 50 mm moulds. The samples in these moulds were compacted 25 times using rods in three layers of equal weight. After that, the reinforcement bar was embedded in the geopolymer paste. A retort stand was used to clamp the reinforcement bar because the paste was still in liquid form and the reinforcement bar cannot stand on its own. The samples were kept in the moulds until it becomes hardened. After 24 hrs, all the samples were taken out from the moulds. The samples requiring curing where cured at 60˚C in the oven for 24 hrs while the other samples remained at ambient temperature (Rangan, 2008; Swanepoel and Strydom, 2002).

2.1.3 Reference Electrode:

A 10 mm graphite was obtained from a pencil and burned to make a porous membrane. The graphite was burned until the color turned black which means the carbon covering the graphite was totally burned. Then, the graphite was inserted into the end of the pipette, before the silicon sealant was used to cover the whole graphite's surface. This is to prevent leakage from occurring. The end part of the pipette was heated to make it slightly bend and easier to touch down on the concrete (ASTM C876-09, 2009).

Afterwards, a saturated copper sulfate solution was prepared. The copper sulfate salt was continuously added to the distilled water until the salts becomes supersaturated (Nurdee, 2012). Then, the copper sulfate solution was poured to the pipette and ensuring no bubbles entrapped in the solution. The pipette was closed and the copper wire was inserted into the pipette for voltage measurement. Table 2 shows an ASTM criterion for corrosion of steel in concrete for different standard reference electrodes. The results should be in the range more than -200 mV so that it is in the lowest corrosion risk condition.

Table 2: ASTM criteria for corrosion of steel in concrete for different standard reference electrodes (John P. Broomfield, 2007).

Copper/copper sulfate	Silver/silver chloride/ 1.0M KCl	Standard hydrogen electrode	Calomel	Corrosion condition
>-200 mV	>-100 mV	+120 mV	>-80 mV	Low (10% risk of corrosion)
-200 to -350 mV	-100 mV to -250 mV	+120 mV to -30 mV	-80 mV to -230 mV	Intermediate corrosion risk
<-350 mV	<-250 mV	<-30 mV	<-230 mV	High (>90% risk of corrosion)
<-500 mV	<-400 mV	<-180 mV	< -380 mV	Severe corrosion

2.2 Open Circuit Potential (OCP) Measurement:

In an open circuit potential (OCP) no current or potential is being applied to the cell. The potential of the working electrode in the cell is relative to the reference electrode. In this experiment, the OCP test set up is shown in Figure 2. The Sanwa digital multimeter CD 771 was used to measure the potential difference between the steel in the concrete and the metal in the reference electrode. The positive side was connected to the reinforcement bar embedded in the geopolymer paste while the negative side was connected to the copper-copper sulfate reference electrode.

A sponge was used as an electrical junction device to provide a low electrical resistance liquid bridge between the surface of the concrete and the copper-copper sulfate reference electrode. The readings were taken accordingly with the time set. Investigations were conducted in several geopolymer environments such as geopolymer paste without curing process, geopolymer paste which undergo curing process and cured geopolymer paste soaked in tap water. This experiment has been done for 7 days by using the open circuit potential method except the cured geopolymer paste soaked in tap water has been done for 140 days. The readings were taken at the same time every day until day 7 and day 140. Afterward, the reinforcement bars which undergo curing and without curing processes were cut to small size to had X-Ray Diffraction (XRD) testing.

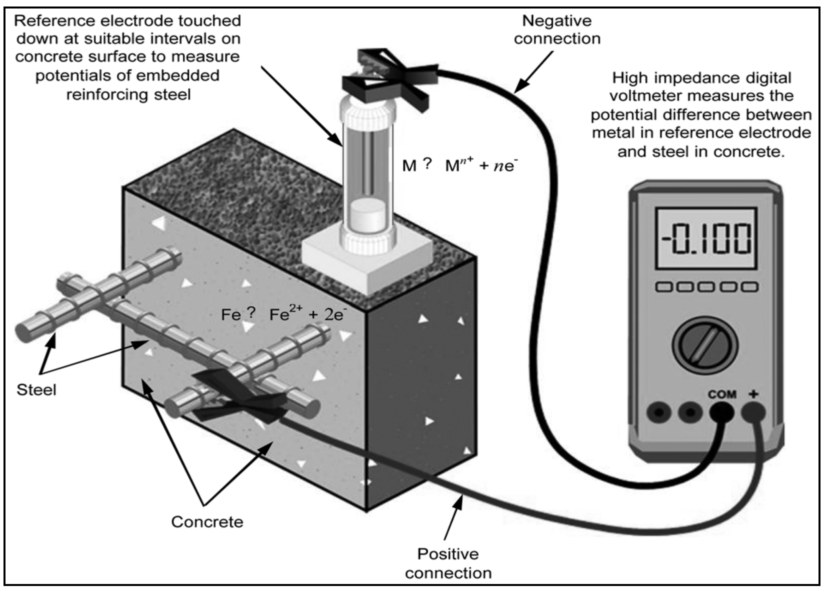

Fig. 2: Reference Electrode Circuitry (ASTM C876-09, 2009).

RESULTS AND DISCUSSION

Figure 3 shows a graph of potential in units of volts against time (day) of reinforcement bar embedded in geopolymer paste. From the graph, the samples which undergo curing process have higher potential values compared to the samples without curing process. This is because when the sample undergoes curing process, the sample becomes denser and more crystalline. When it becomes hard, the durability and workability would be improved. The potential values also becomes more positive because when the samples undergo curing process, the paste changes from liquid to solid at a faster rate when compared with the samples without curing process. Hence, the potential value started at a more positive value than sample without curing.

The potential values for samples curing 1 and curing 2 were 0.311V and 0.299V respectively at the beginning. Then, the values increases to 0.362V and 0.360V respectively. The potential value of sample curing 1remained same 0.362V until day 4 while the potential value of sample curing 2 slightly fluctuated between 0.350V, 0.363V and 0.368V until day 4. The potential value for curing 1 raised to 0.368V on day 5 though the curing 2 slightly decreased to 0.366V. The curing 2 sample was remained same on day 6 until it reduced to 0.348V at day 7 while the curing 1 sample reduced to 0.360V and 0.355V at day 6 and 7 respectively.

However, when samples with curing process and without curing process are compared it was observed that it shown the potential values for all samples were nearly same except for the first three days. The potential values of sample without curing 1 started with 0.232V before it rapidly increases to 0.356V for day 1. After that, it slightly reduced to 0.342V and 0.341V for day 2 and day 3 respectively. Then, it fluctuated between 0.355V, 0.364V, 0.362V and 0.366V for day 4 until day 7.

Difference with the sample without curing 2, it increased uniformly until day 5 (0.278V, 0.280V, 0.294V, 0.345V, 0.369V and 0.372V), then it decreases to 0.366V on day 6 and increased again on day 7 to 0.371V. Although, some differences were observed, but the potential values still in the passivity region, which protects the reinforcement bar from corrosion by the passive layer that was formed in this region.

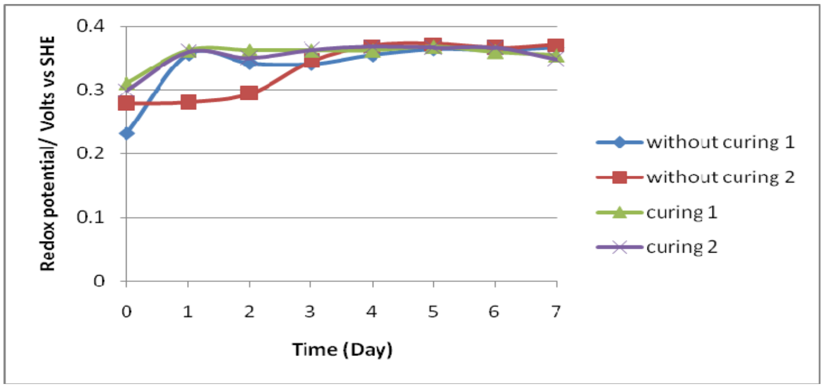

Fig. 3: Graph of redox potential (volts) against time (day) for open circuit potential of reinforcement bar embedded in geopolymer paste at ambient temperature.

Besides, if the potential values of all samples in this study were converted to volts versus $Cu/CuSO_4$, the potential values would be more than -100 mV. Referring to the ASTM C 876-09 it shows there is only 10% risk of corrosion will occur to the reinforcement bar if the potential value more than -200 mV by using $Cu/CuSO_4$ reference electrode.

Figure 4 shows the graph of potential (units of volts versus SHE) against time (day) for reinforcement bar embedded in broken geopolymer paste. From the graph, the maximum potential value is 0.208V and the minimum potential value is -0.120V. The pH value for this geopolymer paste was observed by using the pH paper. The pH value for this paste is 12 as the concrete was always is alkaline in nature. According to Davidovits, he stated that the pH of geopolymer paste should be in the range of 11.5 to 12.5 depending on the formulations (Joseph Davidovits, 2005).

Thus, when referring the Pourbaix diagram for pH 12 with the maximum and minimum value of redox potential, the results were located at passivity region. In this region, the iron reacts to form protective oxide films. The Fe_2O_3 is the stable phase in which this oxide acts as a protective film or passive layer in this region. It would be expected to provide some protection against corrosion. The use of the fly ash based geopolymer had good corrosion performance and it could protect the reinforcement bar in the concrete from corrosion.

The XRD testing was used to analyze the passive layer which was formed from the reaction between the steel and oxygen when exposed to air. Figure 5, the Iron Oxide Hydroxide (FeOOH) was found in two different reinforcement bars. On dehydroxylation mechanism either in the dry state or in the solution, the final product of FeOOH is hematite (Fe_2O_3) (Cornell and Schwertmann, 2003). Dehydroxylation means the loss of water molecules of structural hydroxyl ions during heating.

As mentioned above, the results were located at passivity region, Fe_2O_3. However, the FeOOH exists in the XRD results not the Fe_2O_3. It is because the first experiment was done only for 7 days while the dehydroxylation process might be taking a long time to transform to the final product, Fe_2O_3. When both samples which undergo curing process and without curing process are compared, the intensity for sample with curing process is higher than the sample without curing process. The higher the intensity, the sample is more crystalline. The change in intensity also occurred at 45˚ which the iron (Fe) peak is lower in sample which undergoes curing process than the sample without curing process. It might be when the sample was cured at 60˚C, the Fe in the reinforcement bar is changed to FeOOH. Thus, the FeOOH is higher and the Fe is lower in the curing sample.

Currently, the corrosion performance of embedded steel rebar in fly ash geopolymer also was studied by many researchers. One of the researches is about corrosion performance of embedded steel in fly ash geopolymer concrete by using impressed voltage method. Olivia et. al concluded that after making comparison with OPC concrete, fly ash geopolymer concrete take a long time to fail and had good corrosion performance. It is because the OPC specimen cracked after 2.5 days while by geopolymer concrete T7 and T10 cracked after 8.7 and 9.2 days respectively. The corrosion activity of steel rebar in geopolymer concrete also is lower than OPC concrete and steel rebar in OPC concrete have high current readings and shorter time to failure (Olivia and Nikraz, 2011).

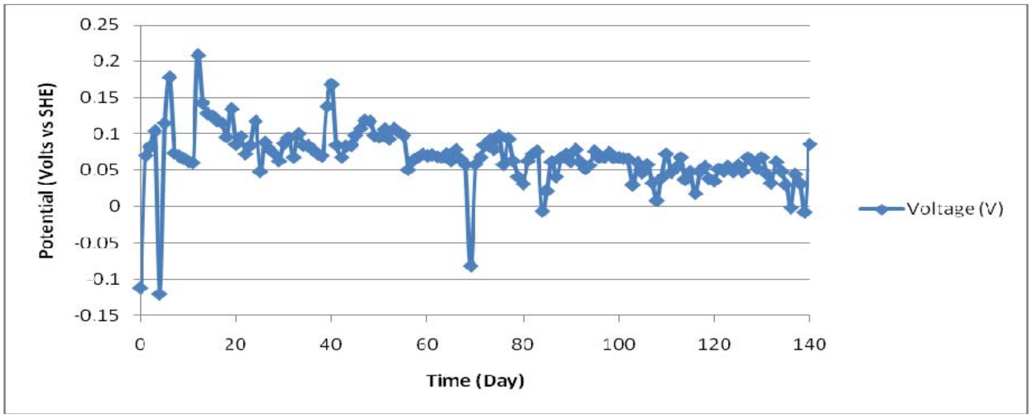

Fig. 4: Graph of potential (volts) against time (day) for open circuit potential of reinforcement bar embedded in broken geopolymer paste at ambient temperature.

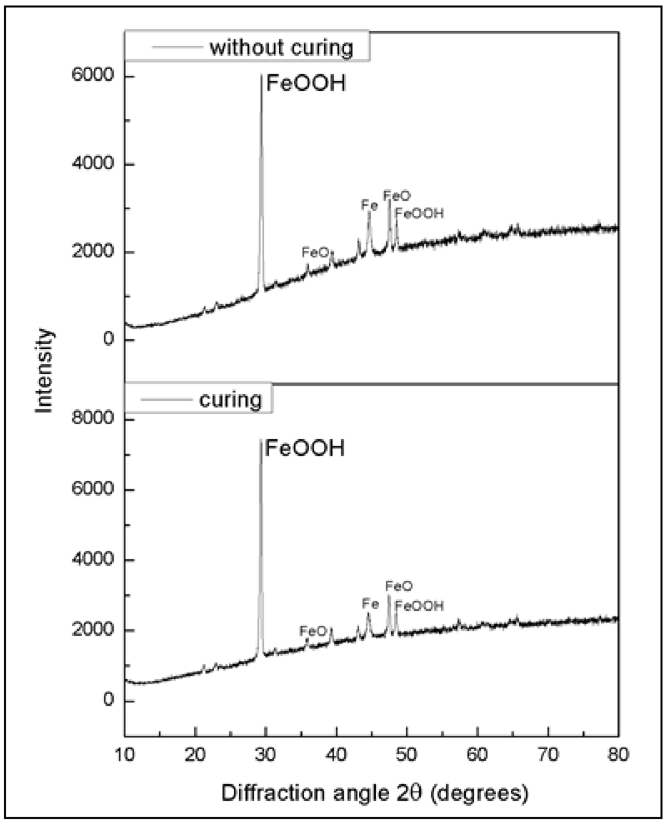

Fig. 5: X-Ray diffraction of samples which undergo curing and without curing process.

Conclusion:

Based on this study, the following conclusions were drawn. The samples which undergo curing process had more positive potential values than samples without curing process because the curing process had made the paste becomes harden in a short time. From Pourbaix diagram, all the samples of geopolymer paste were in passivity region which mean the passive layer was formed to protect the reinforcement bar from corrosion.

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