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The Influence of Micro Algae on Corrosion of Steel in Fly Ash Geopolymer Concrete: A Preliminary Study

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Abstract. Chloride is not the only main cause of corrosion of reinforced concrete structures in seawater environment. Microorganisms, such as bacteria and microalgae, in the seawater can induce microbiologically influenced corrosion (MIC) that leads to degradation of the concrete structures by formation of biofilm on the metallic surface. In this preliminary study, the impact of microalgae on the corrosion of steel reinforced bars in fly ash geopolymer concrete was studied. Corrosion potential, algae cells number, and pH measurement were carried out for fly ash geopolymer concrete and a control mix (Ordinary Portland Cement) samples. The results indicate that the corrosion potential of fly ash geopolymer concrete was influenced by the cathodic reaction during photosynthesis activities. The geopolymer concrete in algae-inoculated medium was found to be more tolerant to algal growth than the control mix (OPC concrete). There was a positive correlation between algae cell densities and the potential reading of the geopolymer.

Introduction

Seawater is a complex medium that not only contains chloride, but also various microorganisms that can initiate and enhance the localized corrosion process of metallic materials. The type of corrosion causes by microorganisms such as bacteria and algae is known as microbiologically influenced corrosion (MIC). Sulfate Reducing Bacteria (SRB) that can deteriorate concrete in sewer pipes by producing hydrogen sulfide with very low pH performed the most common MIC [1, 2]. While microalgae induced corrosion on welds joints or the structures in a massive North Sea oil drilling platforms [3]. Algae are authotropic and photosynthetic organism that needs light and oxygen to grow. The algae photosynthetic process has a role on corrosion by changing pH and oxygen production [4, 5]. Their participation in biocorrosion is linked to biofouling process and formation of biofilm, which is responsible for biodeterioration process or corrosion.

Fly ash geopolymer concrete is a new type of binder from activation of fly ash and chemical solutions. Many investigations have focused on the strength and durability [6, 7] than the corrosion resistance steel reinforcement bar in fly ash geopolymer. It was found that geopolymer concrete can passivate the steel bar and reduce the susceptibility to corrosion as effectively as the Portland cement concrete even in a chloride-containing environment [8, 9]. The studies were carried out in artificial environments without the presence of any microorganisms. Hence, the actual effect of MIC on steel reinforcement in geopolymer paste was still unknown. The present study was designed to investigate the influence of microalgae on the corrosion potential of steel reinforcing bars embedded in fly ash geopolymer concrete. The influence of concrete properties such as pH in the presence of algae and cell densities were also determined.

Material and Method

Fly ash geopolymer concrete specimens were prepared by mixing fly ash with alkaline solutions and aggregates. The binder was cured in a steam-curing chamber for 24 hours at 75^{O}C and this method was adopted from Sindhunata *et al.* [10]. Mix T10 was used in this experiment and details of the mixture optimization process was explained in the previous publication [11]. Ordinary Portland Cement (OPC) concrete, as a control mix was cast with a w/c ratio of 0.45 to achieve the target compressive strength of 55 MPa. The fresh mixes were cast in 50x100mm cylinders with mild carbon steel rods of 10mm diameter and 150mm length embedded centrally in the sample. The final composition and some properties of the concrete are presented in Table 1.

Table 1. Mixture proportions and some properties of concrete.

Mix type	Geopolymer (GP)	OPC
Fly ash [kg/m^3]	498.5	-
Cement [kg/m^3]	-	422.5
Aggregates [kg/m^3]	1752.0	1788.3
NaOH 14M [kg/m^3]	42.7	-
Sodium silicate [kg/m^3]	106.7	-
Superplasticizer [kg/m^3]	7.5	-
Water [kg/m^3]	18.8	190
Slump [mm]	250	90
Compressive strength [MPa]		
28 days	60.03	56.22
91 days	63.29	65.15
Tensile strength [MPa]		
28 days	3.37	3.97
91 days	4.29	4.25

The microalga used was *Pleurochrysis carterae* Braarud et Fagerland (CCMP647) obtained from the Centre for Culture of Marine Phytoplankton, Biglow Laboratory, Marine, USA. *Pleurochrysis carterae* was maintained in a modified f/2 medium. The algae were cultured in the modified f/2 medium and showed best growth at pH 8.0. Due to photosynthetic CO_2 uptake, *P. carterae* increases the pH to 8.1-9.9 in the daylight and the pH decreases to pH 8.1 in the dark [12].

The electrochemical chamber test was a 1 L circular Teflon tube. The bioreactor has fitted with a transparent acrylic lid to allow light penetration and oxygen exchange. The bioreactor was chemically sterilized using sodium hypochlorite. A fluorescent lamp provided 60 ± 8 μmol photons.m^{-2}.s^{-1} and a light/dark cycles of 12 hours light: 12 hours dark. The bioreactor was continuously mixed using a mechanical stirrer. The operating volume of solution was 800 ± 20 ml. Algae were freshly inoculated for each test with an initial cell density of approximately 1.4 ± 0.3x10^{5}cells/ml^{-1}. Each test was carried out for approximately 14 days. A reference electrode, Ag/AgCl with KCl solution (equals to SCE), was used to measure the free corrosion potential of a steel bar in the chamber. Measurement of corrosion potential with time in all media was conducted two times. Data was collected with a data logger controlled with a computer. The potential measurement was taken at increments of 10 minutes. The pH was measured every hour for 8 hours a day, three times a week. Cell density measurement was carried out using a Neubaeuer haemocytometer. Cell number was counted twice a day, three times a week. Fig. 1 shows a schematic diagram of the experimental apparatus.

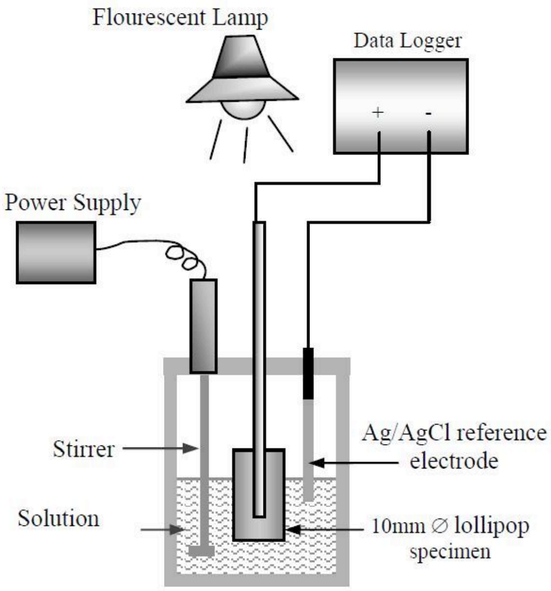

Fig. 1 Schematic diagram of the experimental apparatus for the MIC test.

Results

Fig. 2 shows the corrosion potential of geopolymer and OPC concrete samples exposed to the algae and f/2 medium without algae. The corrosion potential of the OPC concrete in algae inoculated medium was generally steady at -55mV, although there were oscillations of corrosion potential with increasing exposure time. The same trend was not occurred for the geopolymer concrete, since there was a gradual decrease of the potential reading heading to negative potential before it plunged to -270mV at day 12. Gradually, the corrosion potential started to shift in a positive direction. There was a drift of potential to -250 mV and then leveled off to a steady value fo geopolymer concrete in f/2 medium. In contrast, no periodic oscillation was detected for samples in the f/2 medium.

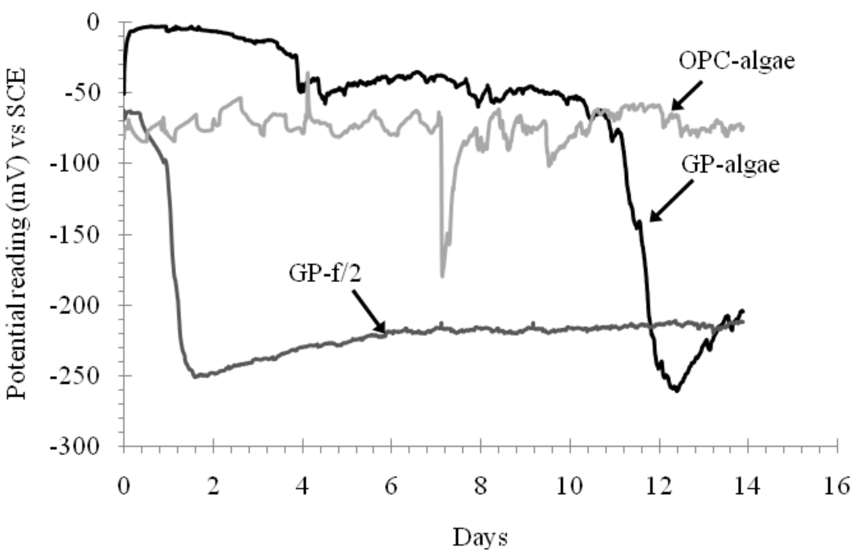

Fig. 2 Variation of potential with time for geopolymer (GP) and OPC concrete in the biotic (algae+f/2 medium) and abiotic (f/2 medium) testing environments.

The results showed that the presence of microorganisms could influence the electrochemical behavior of steel reinforcement bars in both type of concrete. Some oscillations of the corrosion potential were observed for specimens in the algae inoculated medium. The oscillations can be due to the photosynthesis activity of algae, which produce and consume oxygen during light and dark cycles. This pattern could change the oxygen content in the steel surface. In the previous research, the photosynthetic and respiratory activities were believed to produce differential aeration cells that can create varying oxygen partial pressures to facilitate corrosion [5].

Fig. 3 indicated that the alkalinity of OPC concrete increased the pH of algae-inoculated medium by 2 units. The geopolymer concrete increased the pH by 0.5 units after dropping by 0.5 units on day 2. The mean pH of the algae medium with the OPC concrete was 10.2, while the mean pH of the algae medium with the geopolymer concrete was 8.5.

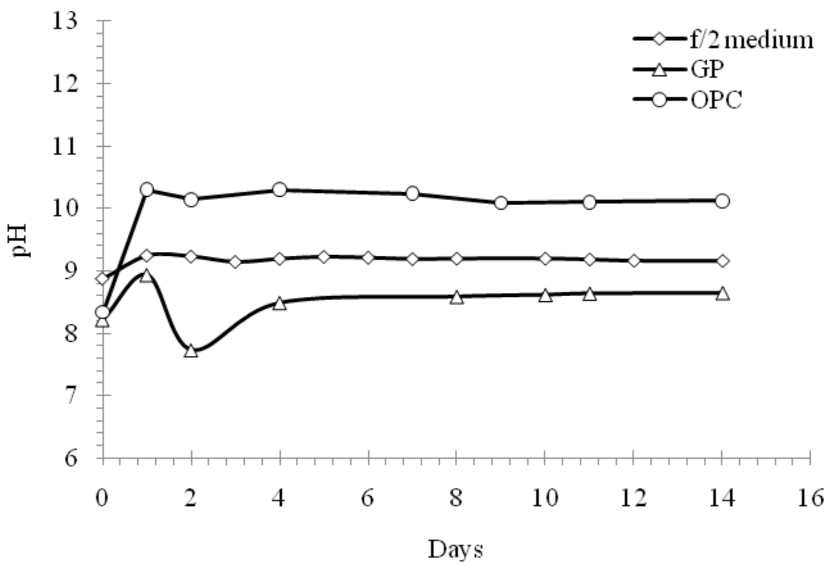

Fig. 3 Variation of pH with time of the geopolymer (GP) and OPC concrete.

The high alkalinity from the OPC concrete serves as an ideal chemical barrier to reduce the corrosion possibility. There was no change of potential that showing a risk of corrosion of steel reinforcement bar. However, the pH might be too far from ideal condition for algae to grow, since there was a reduction of cell densities at day 7 as can be seen in Fig. 4.

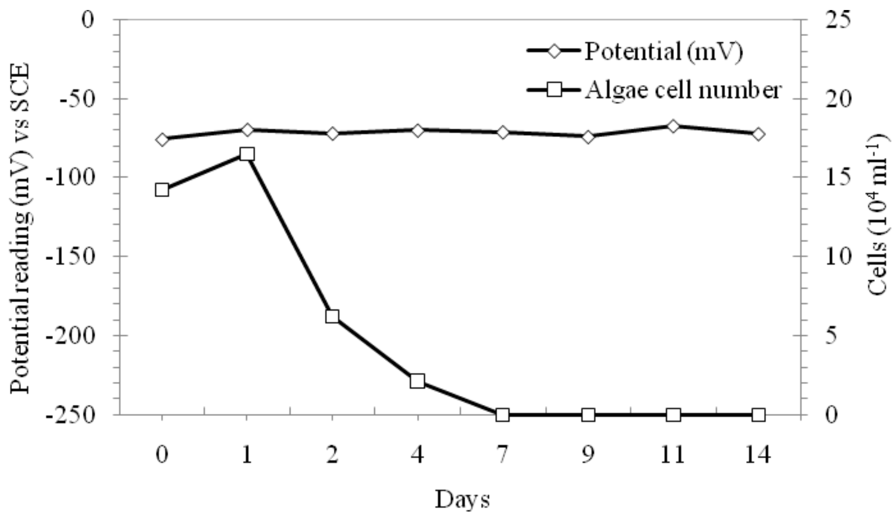

Fig. 4 Potential vs cell densities at particular time for the OPC concrete.

This figure revealed that there was no change in the corrosion potential with increasing time corresponding to the cell densities of the algae culture. In fact, there was no correlation between the algae density with the potential reading at any time for the steel reinforcement in the OPC samples.

On the other hand, the geopolymer concrete in algae inoculated medium has a pH of less than 9.0. Although this condition was ineffective to prevent corrosion in the long term, the resulting pH has a positive influence on algae growth in the medium, as can be seen in Fig. 5. The ideal pH for growing microorganisms such as bacteria and algae is 7-8 [13]. Since the geopolymer concrete could provide a pH lower than the OPC system, a slow algae growth was performed until day 14. In a study of algae attachment using slag and fly ash geopolymer mortars in freshwater and brackish water environments [14], it was observed that the porous paste, relatively low pH and high carbonation levels contributed to high attachment of algae into the geopolymer paste.

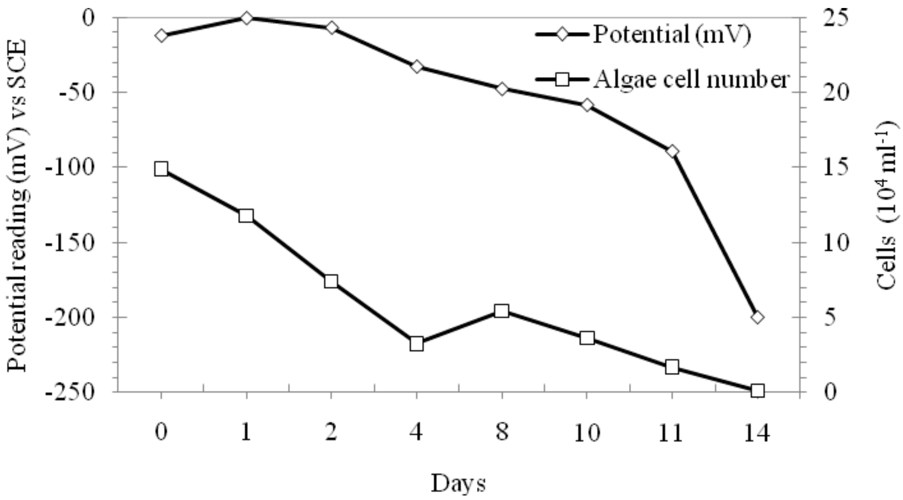

Fig. 5 Potential vs cell densities at particular time for the geopolymer concrete.

While cell densities indicated no sign of significant contribution to the electrochemical effect for the OPC sample in the *P. carterae* culture, it was a different trend for the geopolymer concrete. Cell densities had a positive correlation with corrosion potential of steel reinforcement bar in geopolymer concrete. This means more algae in the system; there will be more photosynthesis activities to produce oxygen that could increase cathodic reaction and pH of the environment. This could shift the corrosion potential into more positive direction and reduce the corrosion risk [15, 16]. Although the effect of cell densities was marginal in this research due to slow algae growth, this finding certainly can be a new insight to use algae as bio remedial agent to increase the steel reinforcement resistance in concrete in the seawater environment.

The result from this paper was still a preliminary observation on the influence of microorganisms such as micro algae on corrosion resistance performance of geopolymer concrete. It is obvious that a different nature of the concrete paste has influenced the algae activity steel reinforcement corrosion resistance. Further research is needed to investigate the corrosion resistance of geopolymer paste induced by MIC to make it more viable in application.

Conclusions

The photosynthesis by micro algae affected the electrochemical corrosion of fly ash geopolymer concrete. There was a light/dark cycle that responsible to produce oscillations in the corrosion potential. It was found that the impact of chlorides as in the f/2 abiotic medium could be more enhancing in terms of inducing corrosion as shown by more active potentials attained in such media. While there is no correlation observed between the number of algal cells and potential change pattern for OPC concrete, cell densities had a positive correlation with the potential reading for the geopolymer concrete, because the electrochemical potential decreased as the cell densities decreased with time.

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