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Corrosion of Low Calcium Fly Ash Geopolymer Concrete: a Preliminary Study

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ABSTRACT

A study of the durability of geopolymer concrete is a step forward in ensuring this material's technical viability. Geopolymer concrete from low calcium fly ash was reported to have a good resistance in aggressive environments, such as acid and sulfate. This research presents a preliminary study of the corrosion resistance of low calcium fly ash geopolymer concrete. The resistance of geopolymer concrete against damage caused by corrosion of steel reinforcement has been investigated using an accelerated impressed voltage setup in 4% sodium chloride solution. The chloride resistance, water absorption and sorptivity of the concrete were also determined. An SEM investigation of geopolymer microstructure was also presented. The results of the test indicated that the geopolymer concrete has a good resistance to corrosion in a chloride solution environment.

KEYWORDS: accelerated testing, chloride solution, corrosion resistance, geopolymer concrete

1 INTRODUCTION

Corrosion of reinforcing steel bars is a significant issue for in the durability of reinforced concrete structures. Corrosion is detrimental to the service life of the structures, in particular in aggressive marine environments. Chloride in seawater penetrates to the concrete and initiates the corrosion of the steel bars. Some environmental factors, like temperature, chloride concentration and the characteristics of concrete pore structures, can increase the corrosion rate of the reinforced concrete structures [1]. It is also important to control the chloride content of raw materials and produce low permeability concrete to reduce the chloride penetration into the concrete in a marine environment.

Fly ash geopolymer concrete is an alternative material for construction through the activation of 100% fly ash and chemical solutions. This concrete has a different composition and microstructure to OPC concrete. Geopolymer concrete has good strength properties and is reported durable in sulfuric acid and sulfate environments. Some earlier works confirmed the steel corrosion resistance of the geopolymer concrete. A study using a half-cell potential measurement [2] showed that the geopolymer concrete has a better resistance to steel bar corrosion than the OPC concrete. It was also found that the higher the compressive strength of the concrete, then the better its corrosion resistance. It has been reported that the probability of steel bar corrosion for geopolymer concrete tended to decrease with time [3]. However, this still depends on the variability of mixtures, since a mix with high fly ash content showed particular behaviour. Fly ash geopolymer mortar was also reported as being as effective as OPC concrete in passivating steel reinforcement [4]. It was found that the corrosion resistance of geopolymer mortar activated with waterglass and NaOH was better than other mixes. Furthermore, geopolymer concrete made from class C fly ash and reinforced with five engineering metals (steel, copper, stainless steel, aluminium and zinc) can reduce the metal's risks of corrosion [5]. This was because the high alkaline geopolymer matrix can control corrosion of steel reinforcing bars.

This paper presents a preliminary study on evaluating the corrosion resistance of the fly ash geopolymer concrete and the OPC concrete in chloride solutions using an accelerated corrosion setup. Some tests were also carried out to support the findings, namely water absorption, sorptivity and static chloride resistance testing of the geopolymer concrete. The microstructure of concrete was also observed using a Scanning Electron Microscope.

2 EXPERIMENT

2.1 Materials and Mixtures

Two types of concrete were cast in this research. The control mix was OPC concrete using type I Portland Cement. The geopolymer concrete was manufactured using low calcium fly ash from Collie Power Station, Western Australia. The chemical composition of the fly ash is given in Tab. 1.

Table 1. Chemical composition of fly ash (XRF analysis)

Elements	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	Na_2O	P_2O_5	SO_3	LOI
% by mass	50.3	26.3	13.6	2.27	0.55	1.44	0.36	1.58	0.32	0.54

The alkaline activators used were a combination of NaOH and sodium silicate (Na_2SiO_3). Sodium hydroxide (99% technical grade NaOH) in form of small pearls was diluted with distilled water to obtain 14M solution. Sodium silicate, with a SiO_2 and Na_2O ratio of 2.0, was used as a major component of the alkaline activator in this experiment. To improve the workability of the geopolymer mix, a naphthalene-based superplasticizer in a dosage of 1.5% was included in the mixture. Aggregates used in this research were crushed granite aggregate and a local sand dune fine aggregate. Sodium chloride (99% NaCl) was used as an electrolyte in this research.

The mixture proportions of both the OPC and geopolymer concrete are shown in Tab. 2.

Table 2. Mixture proportions of concrete

Mix	Quantity (kg/m^3)							
	Cement	Fly ash	NaOH (14M)	Na_2SiO_3	Aggregate		Water	Superplasticizer
					Coarse	Fine		
Geopolymer	-	408	41	103	1201	647	19	6.1
OPC concrete	377	-	-	-	1209	642	188	-

2.2 Specimen Preparation and Testing

The specimens for both concrete consisted of cylinders (100 x 200 mm) and lollipop cylinders (100 x 200 mm) with steel reinforcing bars (diameter 16 mm and 350 mm length). The reinforcing bars used were new bars supply that specially ordered for this experiment. For a lollipop sample, a steel bar was embedded into the concrete cylinder to a depth of 30 mm from the bottom surface. A special cap was used to hold the bar in its place during the casting and curing processes. Fig.1 is a diagram of a lollipop sample.

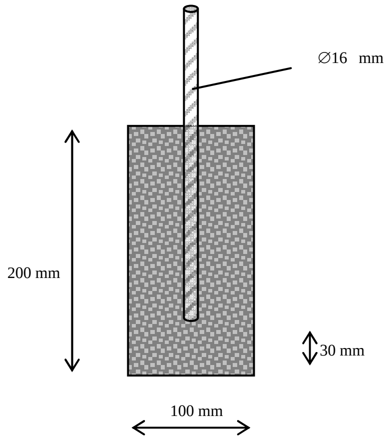

Figure 1. Schematic diagram of the lollipop sample.

Both concretes were cured in a steam-curing chamber for 24 hours at a temperature of 60^{0}C. Then the specimens were left for air curing in the curing room at a temperature of 23-25^{0}C until testing days. These experiments were conducted on three replicates, except for the corrosion test. The average of the three results is reported in this paper. These samples were tested for compressive strength at 7, 28, 56, 91 and 365 days of age. Water absorption and sorptivity were carried out based on the ASTM C642 and GHD methods, respectively. Changes in mass and compressive strength tests were performed for both types of concrete in a 4% sodium chloride solution according to ASTM C267. The specimens for SEM were cut from the concrete. They were air dried, vacuumed and coated with carbon before being ready for placing under the microscope.

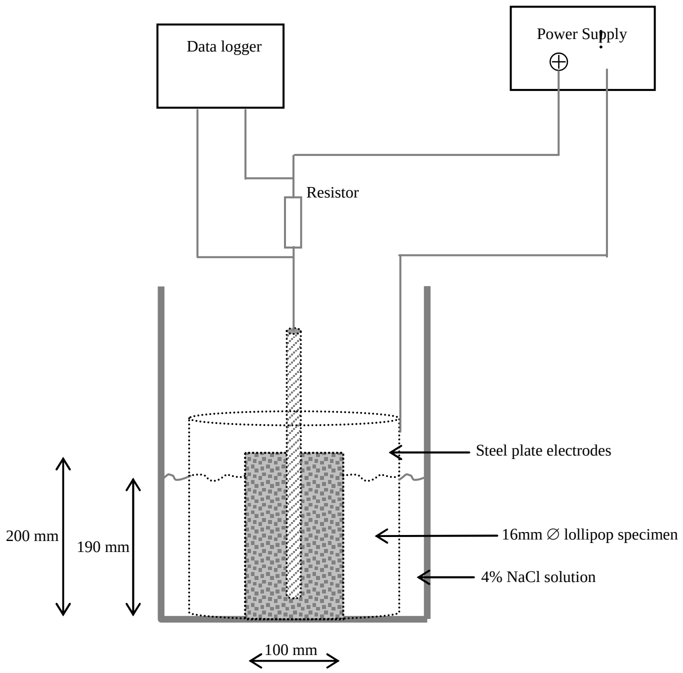

Figure 2. Schematic of the setup for accelerated corrosion test [7].

Fig. 2 shows an accelerated set up that has been used to obtain the corrosion initiation time and the time until the cracking of the concrete. The corrosion set up was adopted from this previous study [6]. Two samples placed in an individual container were tested for each run. The sample was immersed in 4% salt (NaCl) solution and an anodic potential of 30 Volts was used to initiate the corrosion process. The corrosion test setup was located in a curing room with a constant temperature of 22-24^{0}C. A data logger was used to store the current variation readings of the specimens for 5-minutes increments. The concrete specimens were tested at 90 and 365 days of age. The specimens were monitored daily to check the corrosion process of the steel reinforcement bars.

3 RESULTS AND DISCUSSIONS

3.1 Compressive strength

The strength development of both geopolymer and OPC concrete were investigated in this study. It can be seen there was no significant change to the geopolymer strength from 14 to 56 days of age. However, a gradual increase in the strength was observed at 91 to 365 days of age (Fig. 3). Conversely, the OPC concrete showed a gradual increase in the strength up to 91 days of age, but then there was no change in the strength of the OPC concrete right through to 365 days of age.

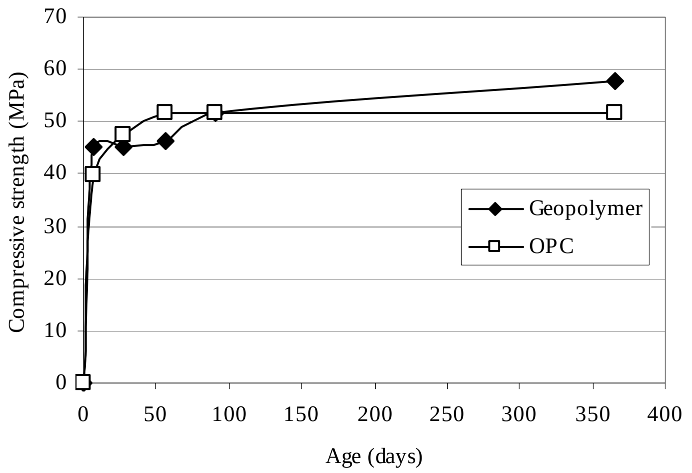

Figure 3. Strength development of the concrete.

3.2 Water Absorption, VPV and Sorptivity

An investigation on water absorption, VPV and sorptivity was carried out to measure the water penetrability properties of the geopolymer and OPC concretes. Fig. 4 shows the immersed and boiled water absorption values for both concretes. The former was to determine the open porosity (Ai) and the latter was to measure the closed porosity (Ab). As can be seen from Fig. 4, the OPC concrete was more porous than the geopolymer concrete under the same curing condition for this investigation. The OPC concrete was steam-cured in this research. This condition can produce high porosity concrete, because high temperatures can shorten the hydration process but produce concrete with coarse microstructure [7]. It was found that the geopolymer concrete has lower water absorption values compared to the OPC concrete. Previous findings [8], [9] were also confirmed the same trend. After 28 days of age, the water absorption tends to increase for both concretes and then decreased after 365 days. This can be attributed to a decrease of VPV values and an increase in the density of the geopolymer concrete (Fig. 5 and 6). On the other hand, the OPC concrete showed a different density trend.

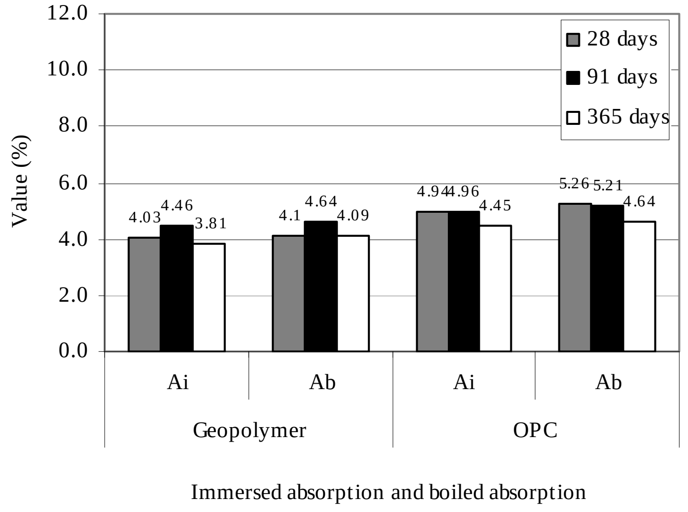

Figure 4. Water absorption values for geopolymer and OPC concrete.

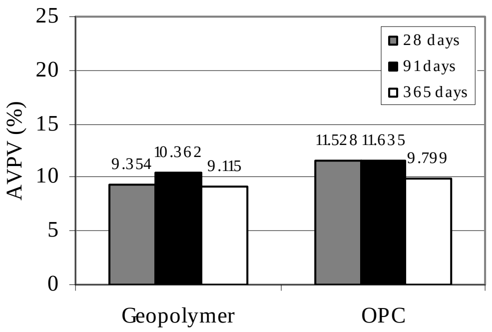

Figure 5. AVPV values.

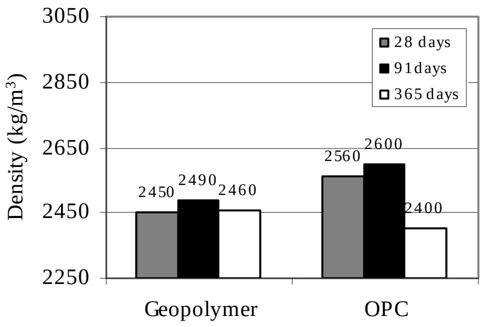

Figure 6. Density values.

Table 3. Sorptivity values for OPC and geopolymer concrete

Mix	Age (days)	Sorptivity ($mm/min^{0.5}$)	R^2 Values
OPC	28	0.2080	0.9971
	365	0.1711	0.9980
Geopolymer	28	0.1252	0.9877
	365	0.0892	0.9921

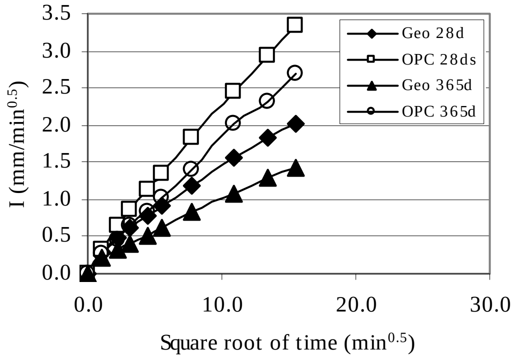

Figure 7. Sorptivity graphs for both concrete.

A sorptivity investigation was carried out to examine the rate of water absorption into the concrete over time. Tab. 3 and Fig 7. showed the sorptivity values and plotted graphs of time versus sorptivity for the geopolymer and OPC concretes. The geopolymer concrete showed lower sorption than the OPC concrete as the water absorption. This positive characteristic is important in that it indicates the ability of the concrete surface to reduce the aggressive ions to penetrate into the concrete.

3.3 Corrosion Resistance

3.3.1 Visual Inspection

As can be seen in Fig. 8, the OPC concrete showed a significant amount of corrosion product of the upper surface on the specimen. The first rust was spotted on the surface after 30 hours and was followed by cracking of the concrete. It was also a change in the appearance of the geopolymer concrete at 1000 hours after the concrete was placed in the set up (Fig. 9). There was only a small amount of rust that appeared on the upper surface, with no cracking observed on the side surface of the concrete.

Figure 8. Appearance of OPC concrete specimen (left: before test started, right: after crack).

There was wetting of the upper part of the specimens above the solution level in the experimental set up. There was no wetting observed for the OPC concrete specimens until they cracked. The geopolymer concrete showed a sign of wetting on the concrete surface 15 days after the experiment was started. This probably attributed to the low water penetrability properties and slow moisture movement in the geopolymer concrete.

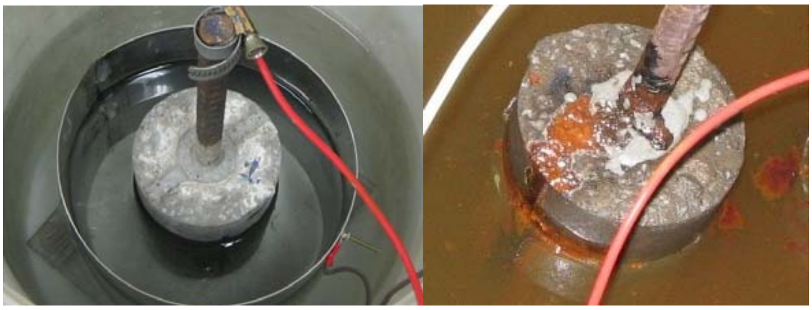

Figure 9. Appearance of geopolymer concrete specimen (left: before test started, right: after first rust observed).

3.3.2 Corrosion Test

Two different cases were investigated in this part of the study, namely time of corrosion initiation and time required to crack the specimens. Corrosion initiation is the time when rust appears on the upper surface of the concrete. The time required to crack the specimens can be defined as when a sudden rise in the current reading occurs. In this study, both the geopolymer and OPC concrete were investigated. The corrosion current versus time relation for both concrete initially was assumed to have a steady low rate of increase in the current over time. It can be seen that the OPC concrete cracked after 30 hours (Fig. 10). The time of corrosion initiation with the time required to crack was relatively short for this concrete. Rust stains appeared on the upper surface of the concrete, and suddenly after that, the concrete cracked. The current reading increased gradually showing a high penetration of chloride ions into the concrete until the test was terminated.

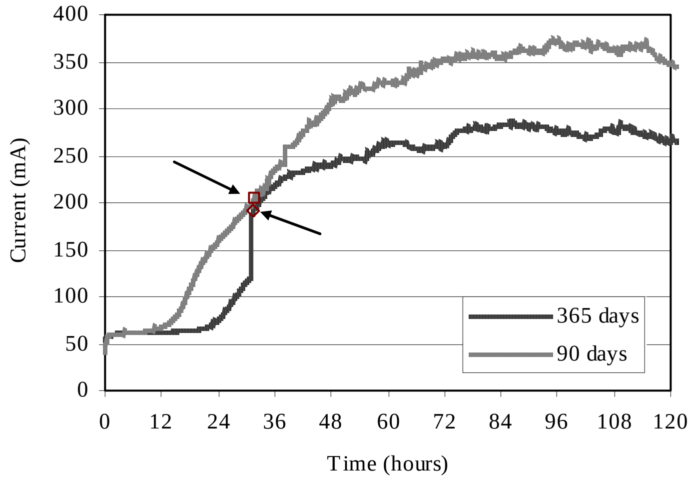

Figure 10. Typical curve of corrosion current with time for the OPC concrete.

On the other hand, the geopolymer specimens showed different behavior. There was a fluctuation in the corrosion current intensity. This fluctuation was not observed for the OPC concrete specimens before the specimens cracked. The time of corrosion initiation was longer than the OPC concrete (Fig. 11). Besides, there was no gradual increase in the current reading when the first rust stain was spotted. The current reading was very low until the specimens crack. The time to crack was reached after 40 days after the first current reading. When the specimen cracked, there was a sudden increase in the current reading. It was interesting to note that the geopolymer concrete cracked after 1100 hours since the first rust stain was observed on the upper surface of the concrete. This means geopolymer concrete offers better protection to steel reinforcement against corrosion. The same finding was reported for geopolymer slag tested with an electrochemical method in chloride solutions [10]. The geopolymer slag mortar showed a protective action towards the steel reinforcing bars corrosion in the chloride environment. There was a tendency of the combination of high alkalinity and dissolve silicates of the geopolymer matrix to stabilize the passive film on steel bars if the matrix remains adequately alkaline [5].

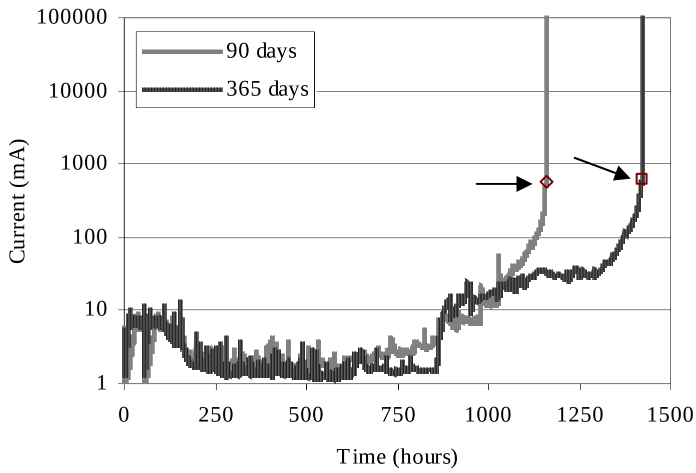

Figure 11. Typical curve of corrosion current with time for the geopolymer concrete.

Tab 4. shows the average time required to crack for the OPC and geopolymer concrete. The information reported below lists the time when the crack was spotted. The applied voltage seemed too high to apply the definition of time to crack above for the OPC concrete. There was no sudden rise for the OPC concrete when the specimens cracked, so the information quoted was gathered from the visual inspections from time to time. It was also found that there was a small difference in the time to crack for the OPC concrete specimens aged 90 and 365 days. It seems that the low density of the OPC concrete at 365 days of age is a reason for this behavior. In contrast, the geopolymer concrete showed a longer time required to crack of the specimens at all test ages than for the OPC concrete. This trend of a sudden rise of current was spotted when the geopolymer concrete specimens cracked. The time to crack was longer for the geopolymer specimens tested after 365 days. This was probably because of an increase in the concrete density over time for the geopolymer specimens.

Table 4. Average time required to crack (hours) for the OPC and geopolymer concrete at different test ages

Type of concrete	Time to crack (hours)	
	Test age (days)	
	90	365
OPC	31.9	31.5
Geopolymer	1157.2	1421.7

It was interesting to notice that there was a connection between the time required to crack with the tensile strength of both concretes. Various researchers have reported that the geopolymer concrete has a higher tensile strength than the OPC concrete [11, 12]. The geopolymer concrete was found to have no special interfaces, which constitute a weak point in the material prone to cracking or other types of failure as in the OPC concrete. The interfaces between the geopolymer matrix and aggregates have the same compact and dense microstructure as found in the bulk of the material [13]. Furthermore, when the concrete has a high tensile strength, it will not crack easily because of internal forces from the corrosion product. This explains the interesting behaviour of the geopolymer concrete in this research.

3.4 Microstructure

Fig. 12 shows SEM micrographs of the geopolymer concrete before and after the corrosion test. Both samples were taken from the geopolymer concrete at 90 days of age.

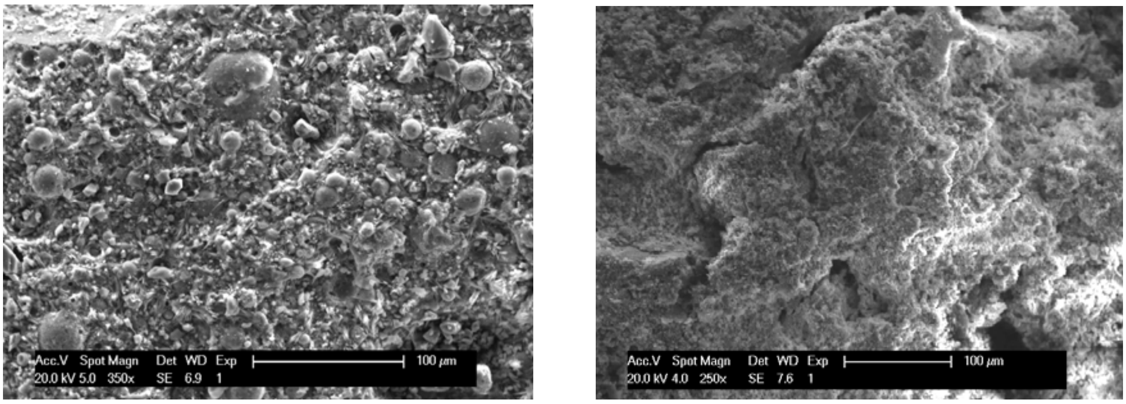

Figure 12. SEM micrographs of the geopolymer concrete
(left: before corrosion test, right: after corrosion test).

Before exposure to the corrosion test in the chloride solution, the microstructure of geopolymer concrete was a typical aluminosilicate material. It had no uniform surface with some unreacted sphere of fly ashes. However, after the corrosion process on the specimens, there was no sign of the unreacted fly ashes. The microstructure of the geopolymer concrete was totally changed with rough and eroded surfaces of the constituents of activated fly ash. There were new products observed in the concrete, since the samples were shining under the microscope.

3.5 Chloride Resistance

A change in mass test was carried out to study the chloride resistance of geopolymer concrete. This static test showed that there was no significant change in mass for both concretes after 91 days immersed in the chloride solution. As can be seen from Fig.13, the OPC concrete showed a higher percentage of relative mass change than the geopolymer concrete.

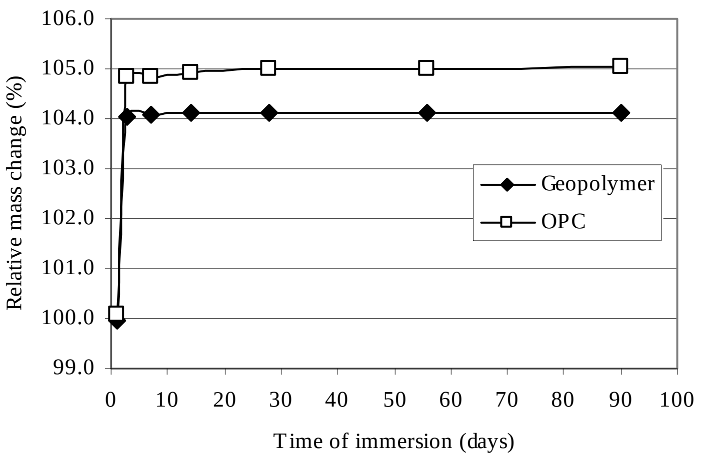

Figure 13. Relative mass change with time in 4% chloride solution for OPC and geopolymer concrete.

Tab. 5 shows the change in compressive strength for both concretes after the sodium chloride immersion. There was a smaller change in the compressive strength of the OPC concrete than for geopolymer concrete after exposure to the chloride solution. It was found that metakaolin geopolymer concrete immersed in ASTM seawater showed the lowest flexural strength among other types of concrete after 270 days exposed in the medium [14]. It was also reported that chloride salts have no beneficial effect for the geopolymer, because chloride can deteriorate it by attacking the geopolymer gel network [15]. Despite these findings above, the change in compressive strength was minor and the geopolymer concrete can still resist the 4% chloride solution exposure.

Table 5. The change in compressive strength of OPC and geopolymer concrete

Type of concrete	Compressive strength (MPa)		Change in compressive strength (%)
	before exposure	after exposure	
OPC	51.60	48.69	0.056
Geopolymer	57.83	51.04	0.117

4 CONCLUSIONS

A preliminary study on the corrosion resistance of fly ash geopolymer concrete was carried out with an accelerated corrosion test set up. Some tests, such as water absorption, sorptivity, and chloride solution resistance, were used to support the findings. The major results obtained in this study are as follows:

(1) The water absorption, AVPV and sorptivity of the geopolymer concrete were lower than the OPC concrete for all test ages.

(2) The geopolymer concrete specimens had a longer time before corrosion initiation and time required to crack of the specimens than the OPC concrete. The geopolymer concrete cracked after 1100 hours exposure to the accelerated corrosion test.

(3) The microstructure study showed that the geopolymer concrete has rough and eroded surfaces after the corrosion test.

(4) There was a slightly higher percentage of compressive strength change for the geopolymer concrete than for the OPC concrete after 91 days immersion in 4% chloride solution.

Thus, it can be concluded that geopolymer concrete has a good resistance to corrosion, particularly in a marine environment.

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