

EXPERIMENTAL EVALUATION OF THE DURABILITY OF FLY ASH-BASED GEOPOLYMER CONCRETE IN THE MARINE ENVIRONMENT

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ABSTRACT

The construction industry is increasingly turning to the use of environmentally friendly materials in order to meet the sustainable aspect required by modern infrastructures. Consequently, for the last two decades, the expansion of this concept, and the increasing global warming have raised concerns on the extensive use of Portland cement due to the high amount of carbon dioxide gas associated with its production. The development of Geopolymer Concretes (GPC) offers promising signs for a change in the way of producing concrete. However, to seriously consider geopolymer binders as an alternative to ordinary Portland cement, the durability of this new material should be evaluated in any comparative analysis. The main purpose of this study was to evaluate the durability characteristics of low calcium fly ash-based geopolymer concretes subjected to the marine environment, compared to ordinary Portland cement concrete with similar exposure. To achieve this goal, 8 Molar Geopolymer, 14 Molar Geopolymer and Ordinary Portland Cement Concrete (OPC) mixes were prepared and tested for exposure in seawater. The test results indicate that the GPC shows excellent resistance to chloride attack, with longer time to corrosion cracking, compared to ordinary Portland cement concrete.

Keywords: Geopolymer concrete, corrosion, durability.

1. INTRODUCTION

Geopolymer fly ash-based concrete, concrete made up of fly ash, sand, coarse aggregate, and an alkaline solution of sodium hydroxide and sodium silicate, can play a significant role in its environmental control of greenhouse effects. The reduction in the carbon dioxide emission from cement production can contribute significantly to the turning down of the global thermostat.

Concrete exposed to marine environment is subjected to several types of aggressive agents: mechanical agents, such as waves and tides, and erosion due to the effects of the waves; chemical attacks due to the action of chlorides present in seawater and sulfates, and climatic agents due to the variations of temperature. Within this context, the deterioration of concrete structures might be the result of the action of aggressive waters, such as sea water, or the corrosion of steel reinforcement in the case of reinforced concrete. Additionally, it should be noted that durability of concrete, independent of its intrinsic characteristics, is variable according to the type of exposure

in the marine environment and the degree of immersion. Concrete in contact with seawater is subjected to various chemical reactions involving sulfates, chlorides, and magnesium ions where several mechanisms, specifically crystallization of expansive salts, precipitation of insoluble composites, ionic attacks etc, are taking place. Permeability is the major factor for determining the long-term durability of concrete in the marine environment. The more dense the concrete, the more it will be difficult for destructive agents to penetrate and flow through its pores.

In the making of geopolymer concrete, the mix is a one hundred percent by-product (fly ash,), i.e. the Portland cement is completely replaced by the geopolymer paste. Current studies on geopolymer concrete are mainly focused on geopolymer technology to make fly ash-based geopolymer concrete and the determination of its properties. However, no specific publications are available concerning the durability of geopolymer concrete in the marine environment. This paper describes an accelerated durability testing program, based on accelerated corrosion of reinforced concrete prisms, to investigate the durability performance of geopolymer fly ash-based concretes, subjected to natural seawater exposure.

2. OBJECTIVE

The main objective was to evaluate the durability of low calcium fly ash-based geopolymer concrete, compared to OPC, by means of accelerated corrosion testing of the reinforcing steel.

3. EXPERIMENTAL PROGRAM

3.1 MATERIALS

3.1.1 AGGREGATES The same types of coarse and fine aggregates were used for both the control mix concrete and the geopolymer concretes (ASTM C125). The fine aggregate was natural river sand provided by Rinker/Cemex. The coarse aggregate used was 3/8" pearock.

3.1.2 FLY ASH For this project low-calcium dry fly ash (ASTM Class F) from a power station was used in accordance with ASTM C618 Class F, and the ACI Committee 226 report. This fly ash was obtained from Rinker/Cemex Corporation.

3.1.3 ALKALINE LIQUID Combinations of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) were employed to achieve the activation of the fly ash material. As suggested by Wallah and Rangan (2006), this alkaline solution was prepared twenty-four hours prior to use. Two different concentrations of sodium hydroxide were used namely 8 M and 14 M. The making of these solutions, with the required concentration, followed the work of Hardjito and Rangan (2005).

3.1.4 ORDINARY PORTLAND CEMENT ASTM Type I Portland cement was used for the manufacture of the control mix concrete.

3.1.5 SUPERPLASTICIZER The workability of the fresh concrete was improved with the use of ADVA 120 super plasticizer in liquid form, which was added to the mix.

3.2 MIX PROPORTIONS Two Geopolymer Concrete (GPC) mixes were used, which were designated as Mix 1 and Mix 2. The procedure for the mix proportions was based on ASTM Class F fly ash and the work of Wallah and Rangan (2006). The proportions of these mixes, per cubic foot of concrete, are given in Table 1. Similar to OPC concrete, coarse and fine aggregates occupied about 75 to 80% of the mass in the composition of the low-calcium fly ash-based concrete, and the remaining represented the chemical components of the mixtures. In the design of the mixes, the parameter "water-to-geopolymer solids ratio" by mass was considered. For the alkaline activators, the parameters chosen for the mix constituents included a ratio of sodium silicate solution-to-sodium

hydroxide solution, by mass, of 2.5, a molarity of sodium hydroxide (NaOH) solution in the range of 8M and 14M, and a ratio of activator solution-to-fly ash, by mass, of 0.3. The control mix concrete was made with (OPC).

3.3 SPECIMEN PREPARATION For the experimental program seventy-eight specimens were used, including 4"φ x8" OPC and geopolymer concrete cylinders, and 6"x6"x21" beams, centrally reinforced with 1/2"φ. The specimen description is shown in Table 2.

Table 1: Mix Proportions of Geopolymer Concrete for Curing in Oven

MATERIALS		WEIGHT (LB/FT ³)	
		Mix 1	Mix 2
Coarse Aggregate	1/2 in	17	17
	3/8 in	23	23
	1/4 in	40	40
Fine Sand		34	34
Fly Ash		25	25
Sodium Silicate Solution		6.42	6.42
Sodium Hydroxide Solution		2.55 (8 M)	2.55 (14 M)
Super Plasticizer		0.374	0.374
Extra water		None	1.4

Table 2: Number and Type of Specimens

CONCRETE TYPE	MIX TYPE	CONCENTRATION	SPECIMEN TYPE		TOTAL
			Control Cylinders (4"φ x 8")	Beam (6"x6"x21") singly reinforced with 1/2"φ rebar	
OPC	Control	-	12	6	18
Low-Calcium Fly Ash	Mix 1	8 M	24	6	30
	Mix 2	14 M	24	6	30
	Total		60	18	78

3.4 CURING AND EXPOSURE CONDITIONS After their casting, the specimens were allowed to set for four days for the cylinders, and five days for the beams. Then, the specimens were removed from the molds and heat cured in oven at 60°C for 24 hours. After that, the specimens were cured in room temperature until they reached the 28th-day of age.

3.5 TEST PROCEDURE The beam specimens were partially immersed into a seawater solution at room temperature after 28 days of curing for 21 days. The prewetting allows to keep the initial D.C. to a manageable low value. Then, the exposed steel bars were connected to the positive terminal of a constant 30 volt D.C. power supply, to make the steel bars act as anodes. This high voltage was used to accelerate the corrosion and shorten the test period. The negative terminal of the DC power source was connected to a stainless steel mesh placed near the beams in the solution, and sat on a stainless steel plate placed beneath the beams. The stainless steel plate and the mesh were used as the cathode, and isolated from the beams. Moreover, the steel mesh was cleaned periodically to prevent the deposition of calcium, on the surface (see Figs. 1 and 2). Each time the current intensity showed a sudden rise indicated the cracking of the beam by corrosion. So, in order to determine the time

at which the specimen cracked (referred to as corrosion time), the intensity of the electric current was recorded at different time intervals. The beams were visually inspected daily for cracks while the current flow was continuously monitored using an ammeter and a Fluke 87 multimeter. Following Sahmaran et al., the weight of the steel bar was measured, and recorded for weight loss measurement before the accelerated corrosion test was started.

3.6 ACCELERATED REINFORCEMENT CORROSION An accelerated laboratory electrochemical method for corrosion was used, first developed by the Nordtest method (1989), followed by the Florida Department of Transportation (2000), and Sahmaran et al. (2008) In order to accelerate the corrosion process, chemical attack was simulated by immersion of the test specimens in saline solution; whereas, a constant potential was used to induce different degrees of corrosion into the reinforcement, embedded in the geopolymer and OPC concrete beams. The schematic of the experimental setup of the electrochemical system used is shown in Fig. 1.

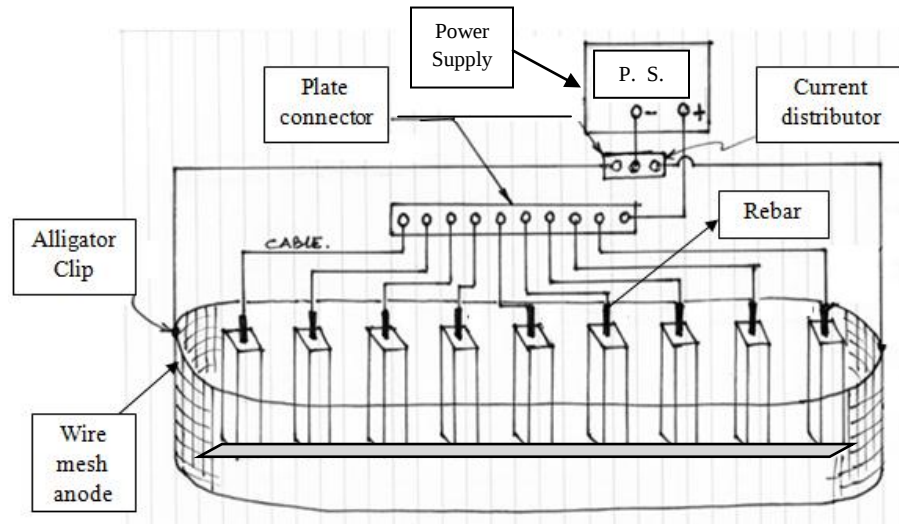


Figure 1: Schematic of the accelerated corrosion test setup

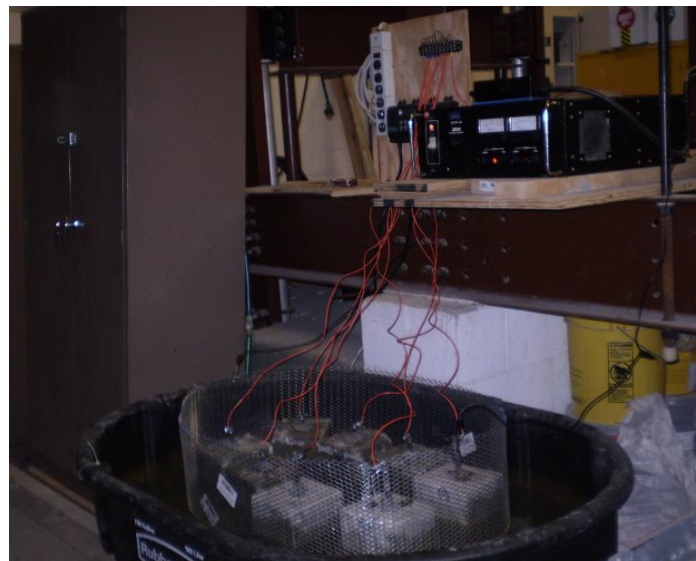


Figure 2: Accelerated corrosion-monitoring test setup in the Lab

4. RESULTS AND DISCUSSION

4.1 COMPRESSIVE STRENGTH The compressive strength of the different types of concrete was measured for 4"φx8" cylinders. The beams were tested at 7 days and 28 days of age after casting, and heat curing in oven at 60°C for 24 hours in the case of the geopolymer mixes, and cured in ambient condition for the normal weight concrete. A minimum of three compression cylinders were utilized for this test. The average compressive strengths for the GPCs were 4,310 (8M) and 8,160 (14M) psi at 7-days; 5,800 and 8,737 psi at 28-days. For the OPC, the strengths were 3,200 and 4,800 at 7 and 28-days respectively (145 psi = 1 Mpa). The plane failure surfaces of the geopolymer cylinders through the aggregates showed by the geopolymer cylinders after the compression test imply that the binder formed in the making of the specimens was strong enough to prevent failures through the interfaces between the aggregates and paste. In addition, most of the cylinders tested did not go to complete destruction after failure, which is a proof once again of the toughness of the geopolymer paste.

4.2 SPLITTING TENSILE STRENGTH Splitting tests were performed on 4"φx8" concrete cylinders in order to determine the tensile strength properties of OPC and GPC beams. In accordance with the ASTM C496 standard practice, three cylinders were tested at seven days and twenty-eight days after casting. The results demonstrated that the indirect tensile strength of the 8M and 14M low calcium fly ash-based geopolymer concretes exceed the recommended values given in ASTM standard (10 to 15% of compressive strength), for control mixes. The splitting strengths measured were higher than those calculated. Moreover, the beams demonstrated an even split through their axial plane. It should also be noted that the splitting of the GPC cylinders generated very little fragmentation, which implied the existence of tough and cohesive bonds between the aggregates. The results were consistent with the higher compressive strengths found for the GPC mixes, compared with the control mix.

4.3 CORROSION CURRENT AND CRACKING BEHAVIOR During the corrosion process, the electrical potential applied to the reinforcing bars attracts negatively charged chloride ions from the salt solution into the concrete, and toward the positively charged steel bars. As the chloride ions reach the steel/concrete interface above the threshold concentration, the steel surface begins to corrode, Sahmaran et al. The crack development, due to corrosion at the rebar, leads to increased salt water access to the steel surface, creating a direct current path between the reinforcement and the electrodes in solution. Any sudden increase in the current flow indicated a reduction in electrical resistance. The variation of current with time in steel reinforced GPC and OPC concrete beams is shown in Figs. 3 and 4. The beams were time-monitored to determine when the reinforcement corrosion started, by observing any sudden increase in current and by visual cracking on the beams. As seen from Fig. 3, the trends for the corrosion current/time for the 8M and 14M geopolymer beams were similar, decreased for approximately 80 hours, and remained quasi-constant for the rest of the duration of the test. The current in the OPC beams decreased for about 15 hours, then started to increase Fig. 4.

The results in Figs. 3 and 4 show a distinct difference in performance between the GPC and the OPC concrete beams. The average current in the 8M GPC beams, for 24 hours, decreased from 71 mA to 18 mA, from 91 mA to 24 mA, in the 14M GPC, and then remained nearly steady. The OPC beams recorded a decrease from 772 to 689 mA, for 12 hours, and then the current started to increase from 689 to 758 mA for the next twelve hours. The initial decreases were due to filling of the pores by salt and other deposits in the salt water. Obviously, the geopolymer mixes demonstrate better resistance against chloride penetration than the Portland cement mix, since not only were the initial current readings recorded for the GPC beams were much lower than the OPC beams, but also their recorded currents never showed significant increase. When chloride solution reached the steel/concrete interface, a current path is created along with a decrease in electrical resistivity of the beam. Therefore, the significant differences in current recorded at this stage depict a better electrical resistivity of the GPC.

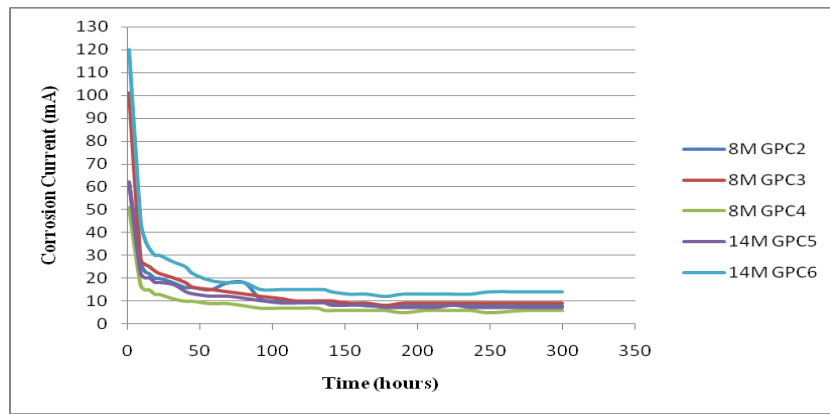


Figure 3: Variation of current with time in GPC

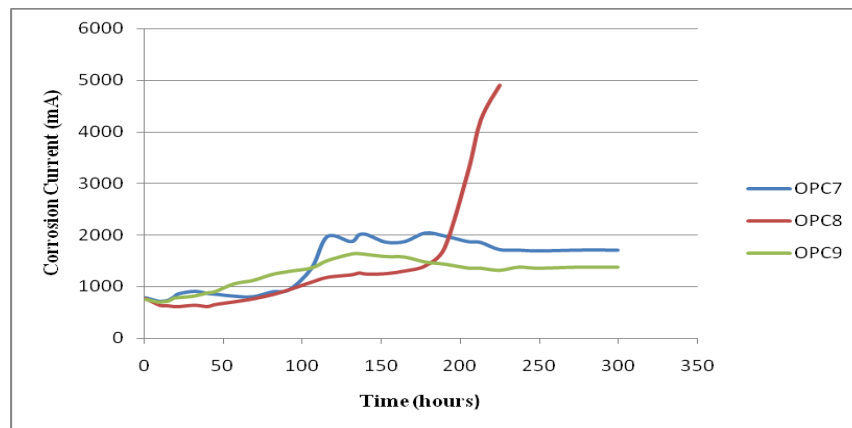


Figure 4: Variation of current with time in OPC

As seen in Figs. 4 and 5, the OPC beams already started to show current increase, and rusted products on the top of the beams, after 40 hours of testing. On the other hand, the current in the GPCs continued to decrease, and the beams showed no sign of chloride attack for the same period. The brown rust stains seen on the top of the beams (Fig. 5) were the first visual evidence of corrosion in the embedded steel (OPC). It may be noted that early age exposure performance of concrete is an important factor in offshore construction, since concrete structures in severe marine environments should be able to resist attacks from aggressive agents for the durations of the construction projects.



Figure 5: beams after 40 hours of accelerated corrosion testing
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It took about 60 hours for the OPC beams to crack, as shown in Fig. 6, where after a decrease in current for a period of time, a sudden increase was recorded, which coincided with the cracking at the bottom of the OPC beams. Corrosion products floating on the surface of the chloride solution were also observed. For the two types of geopolymer concrete, the recorded currents continued to decrease, while visual inspection showed no sign of corrosion attack. As the experiment was continued, visible cracks were observed on the top of the OPC beams, after 100 hours. The cracking was associated with a total current rise in the power supply ammeter, where the recorded intensity increased from 2.5A to 4.5A. Fig. 4 shows the sudden current increase specifically in OPC-8 and OPC-9 beams. It can be seen in Fig. 6 that the cracks propagated along the reinforcing bar, and the crack width was about 0.009 in. (0.25 mm) on OPC-7 beam, and 0.020 in. (0.5 mm) on OPC-8, which represented a failure state.

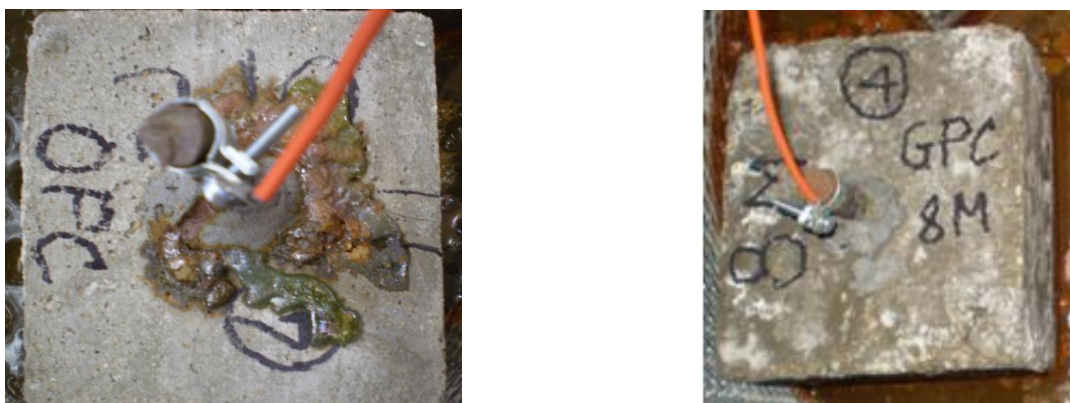


Figure 6: Typical crack and rust stains on OPC and GPC top view during accelerated corrosion testing

In contrast to the OPC beams, no cracks were noticed in the GPC beams (Fig. 6). According to ACI 318-95, a concrete material is in failure state when crack widths on its surface reach 0.012 in (0.3 mm). Within this context, failure of all OPC beams occurred past 100 hours, since cracks greater than 0.012 in. (0.3 mm) were observed by visual inspection. Dramatic increases in current reading were recorded, where particularly the OPC-8 beam jumped from 1.74A after 190 hours to 4.9A after 220 hours, and the total intensity from 5 A to 8 A. The crack width variation on OPC-8 was from 0.02 in. to larger than 0.06 in. (1.50 mm). For the geopolymer beams, visual inspection of the beams and the corrosion current trend (Fig. 3) showed that both 8M GPC and 14M GPC appeared to be “healthy” for the same time interval; still no noticeable cracks were observed on their surface, and the recorded current stood steady. Obviously, the results demonstrate that the GPC concrete beams have a superior durability performance than the OPC beams in severe marine environment. As suggested by Gjorv (2009), the rate of corrosion reduced over time due to clogging up of the cracks by both corrosion products and other reaction products. Fig. 7 shows that the longitudinal crack openings, which formed on the faces on these beams, were obstructed by these products. Consequently, the recorded current in OPC-7 and OPC-9 started to slowly decrease and behave in steady manner (Fig. 4).

The accelerated corrosion test was stopped at 300 hours, and the beams were removed from the tank for visual inspection and mechanical testing. Figs. 7 and 8 show the physical appearance of the different beams shortly after accelerated durability testing. The failure limit for crack width in a concrete structure is specified as 0.012 in. (0.3 mm) by the ACI Building code, 2008. The maximum longitudinal crack widths on the surface of the OPC beams, illustrated in Figs. 7 and 8, were 0.19 in. (5 mm).



Figure 7: Physical appearance of OPC and GPC beams after accelerated durability testing



Figure 8: Top view of OPC beams shortly after accelerated durability testing (300 hrs)

4.4 MASS LOSS MEASUREMENTS It is well known that the most accurate method to determine the degree of corrosion in embedded steel is the mass loss measurement. Therefore, in order to determine the mass loss of the corroded reinforcing steel, the beams were completely broken to retrieve the entire rebar. Samples of GPC and OPC broken beams, with the embedded steel, are shown in Fig. 9.



Figure 9: Broken OPC and GPC beams

Following the ASTM standard, it was necessary to remove all corrosion products from the steel reinforcement before weighing. Therefore, deionized water was used as stripping solution to clean the rebar, and metal brush was also used to remove any remaining corrosion products. After that, the retrieved rebars were weighed to be compared with their initial weight. The steel bars after removal are presented in Fig. 10, which shows severe corrosion damage of the OPC beams, while the rebars from the GPC beams were “healthy”, with almost no corrosion effects on their surfaces.

The initial mass, the final mass, and the percentage of mass losses of reinforcing bars from GPC and OPC beams are shown in Table 3. The percentage mass losses in the ordinary Portland cement beams (OPC 7, 8 and 9), after accelerated corrosion testing, were respectively 51%, 71.2% and 58%. For the two types of geopolymer beams, there was no mass loss of reinforcing bars, after the 300 hours of corrosion testing.



Figure 1: Retrieved rebars after accelerated corrosion testing

Table 3: Percentage Mass losses of Reinforcing Bars after Accelerated Corrosion Exposure

Specimen Type	Initial Mass (g)	Final Mass (g)	Mass Loss (%)
OPC-7	590	290	51
OPC-8	590	170	71.2
OPC-9	590	250	58
GPC-2	530	530	0
GPC-3	520	520	0
GPC-4	540	540	0
GPC-5	530	530	0
GPC-6	540	540	0

Therefore, the better corrosion resistance exhibited by the geopolymer concretes in the marine environment, compared to the ordinary Portland cement concrete, is evidence of their compactness, and the consequent resistance to chloride penetration. The low permeability of the GPC beams delayed the depassivation of the reinforcing steel surface. The main reason that the OPC beams showed such high mass losses may be due to the wide longitudinal cracks observed on the beams (Figs. 7 and 8), which allowed chloride ions to penetrate more quickly into the concrete and accelerate the rate of corrosion.

4.5 RESIDUAL FLEXURAL LOAD At the end of the accelerated corrosion testing, the beams were removed from the chloride solution tank, and flexural load tested under three-point bending to determine their residual ultimate flexural loads. The flexural testing was performed according to ASTM C 78 – 09. For the OPC beams, with longitudinal cracks, the bending loads were applied on the face where the cracks were located. According to Sahmaran et al., this setup provides a more realistic evaluation of the residual flexural load capacity of the corroded beams. The average flexural strengths for 8 M and 14 M were 708 and 757 psi; the average flexural strength for the OPC was 305 psi (145 psi = 1 Mpa). Obviously, the GPC beams exhibited higher flexural strengths, compared to the OPC beams.

5. CONCLUSIONS

The primary focus of this investigation has been to experimentally evaluate the durability of fly ash-based geopolymer concrete in the marine environment, compared to ordinary Portland cement concrete (OPC). The key outcome expected is the better corrosion-resistant performance of GPC. Therefore, by analyzing and comparing the behavior and properties of both types of concrete, it was observed that the geopolymerization product of low calcium fly ash-based concrete is more homogeneous and well-bonded to the aggregate, than ordinary Portland cement concrete. Consequently, better crack resistance and long-term durability are obtained with GPC concrete.

The effects of age on the strengths of the geopolymer mixtures are different from those of the OPC. It was found that the GPC concretes, actually, possess high early compressive strength, where strengths in the range of 4,310 psi and 8,160 psi were obtained at 7 days, and 5,800 psi and 8,737 psi at 28 days, for 8 M and 14 M GPC. For the OPC, the values were 3,200 psi at 7 days and 4,800 psi at 28 days (145 psi = 1 MPa). These results show variations of 15% and 7% for GPC, respectively, which showed that strengths were acquired more quickly with geopolymer concretes. In the case of OPC concrete, the variation was 33% from 7 to 28 days.

The electrical resistivity and permeability of the low calcium fly ash-based GPC were not significantly affected by the severe marine environment in view of reduced cracking.

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