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PROPERTIES OF FLY ASH GEOPOLYMER CONCRETE IN SEAWATER ENVIRONMENT

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ABSTRACT

This paper presents properties of fly ash geopolymer concrete subjected to continuous immersion in 3.5% NaCl solution and accelerated wetting drying at 80^oC and 24-hour cycle in NaCl solution. Three geopolymer mixtures and a control mix with target strength of higher than 55 MPa were evaluated. Change in compressive strength, effective porosity, and weight were observed. There was no significant decrease in strength for both geopolymer and OPC after exposed to the continuous immersion and cyclic wetting drying. Continuous immersion for 365 days changed the effective porosity of the geopolymer concrete. The effect of a change in porosity could be seen from a marginal weight change of the geopolymer concrete. The geopolymer concrete was found to perform better under cyclic exposure than the OPC concrete judging from the compressive strength, porosity and weight change were considered.

Keywords: fly ash, geopolymer, porosity, seawater, wetting-drying

1. INTRODUCTION

Concrete may endure many different types of attacks when fully immersed in seawater or under wetting-drying cycles for an extended time. Seawater normally has 3.5% dissolved salts comprising magnesium sulphate and sodium chloride. Sulphate ions cause a common attack on cement paste by promoting chemical reactions that result in expansion, cracking and spalling. Although the exact mechanism remains unclear, a reaction between the sodium sulphate (Na₂SO₄) with portlandite (CH), monosulphate and unreacted C₃A, forms gypsum (CSH) and ettringite (C₆AS₃H₃₂) (Bassouni and Nehdi, 2009). It was found that softening, erosion and loss of concrete constituents in continuous immersion is more dominant than expansion due to the ettringite formation. This unfavorable condition could lead to concrete pores (Liu, 1991). The wetting-drying process is related to immobilization chloride with moisture through the concrete pores under cyclic action (Neville, 1995). Surface degradation in the presence of salts and a temperature difference in continuous immersion and wetting-drying exposure of seawater environments increases the concrete porosity and affect the overall durability.

Fly ash geopolymer concrete is a new type of concrete that has good engineering properties that were comparable or even higher than the OPC concrete. The geopolymer was claimed to be durable in some aggressive environments such sulfate and fire (Bakharev, 2005; Kong et al. 2007). This is mainly due to the reaction product or aluminosilicates and low calcium content in the geopolymer. High calcium cement is considered more prone to the aggressive ions attack. The geopolymer concrete could resist synthetic seawater without strength degradation and significant weight loss (Fernandez-Jimenez et al. 2007). The porosity of the concrete in the seawater remained low after 270 days of immersion (Palomo et al. 1999). The fly ash geopolymer concrete has low chloride ion diffusion coefficient due to low permeability coefficient (Adam et al. 2009).

This research is to study the effect of cyclic wetting-drying on the fly ash geopolymer concrete. The change in compressive strength, change in effective porosity and change in weight for specimens undergoing continuous immersion and cyclic wetting drying in the chloride solution are presented.

2. MATERIALS AND METHOD

2.1 Materials

Fly ash class F (ASTM C618) from Collie power station, Western Australia was used as the source material for geopolymer concrete. An Ordinary Portland Cement Type I (AS 2350) was used as control concrete. The chemical composition of fly ash and cement are presented in Table 1. The coarse and fine aggregates used were in saturated dry conditions.

Oxides	SiO ₂	Al_2O_3	CaO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	P_2O_5	SO_3	LOI	Chloride
Fly ash	50.50	26.57	2.13	13.77	0.77	1.54	0.45	1.00	0.41	0.60	-
Cement	21.10	4.70	63.80	2.80	-	2.00	0.50	-	2.50	2.10	0.01

Table 1: Chemical composition of fly ash and cement (%)

A combination of sodium hydroxide (NaOH) and sodium silicate (water glass) was used as alkaline solution. Sodium hydroxide pearls were diluted in distilled water to produce sodium hydroxide solution with 14M concentrations. The sodium silicate with a specific gravity of 1.52 and a modulus silicate ratio (*Ms*) of 2 (where $Ms = SiO_2/Na_2O$, $Na_2O = 14.7\%$, $SiO_2 = 29.4\%$) was provided in the alkaline activators preparation. A naphthalene sulphonate polymer-based superplasticizer was included to improve workability in the mixture.

2.2 Mixture proportions

The optimum mixture proportion in Table 2 was designed using Taguchi method. The full methodology and optimization process is explain in detail elsewhere (Olivia and Nikraz, 2009). This method was using a combination various factors and levels to produce mixtures with desirable properties for concrete in a seawater environment. An adjustment of extra water was added to achieve the target strength of approximately 55 MPa.

	Unit weight (kg/m ³)									
Mixtures	Fly ash	Cement	Total	NaOH	Sodium	SP	Water			
WIIAtures	TTy ash	Cement	aggregate	14M	Silicate	51	vv ater			
OPC	-	422.3	1788.3	-	-	-	190			
T4	461.5	-	1800.0	46.2	92.3	6.9	18.6			
Τ7	424.6	-	1848.0	36.4	90.9	6.4	17.9			
T10	498.5	-	1752.0	42.7	106.7	7.5	18.8			

Table 2: Optimum mixture proportions

SP: Superplasticizer

2.3 Casting and curing of specimens

The specimens were cast in the 100x200mm cylinders for compressive strength and change in mass, and 100x50mm for AVPV and effective porosity tests. Both the geopolymer and the OPC concrete specimens were cured with different method. The geopolymer specimens were steam cured with three different curing regimes, i.e. 12h-70°C, 24h-60°C, and 24h-75°C were adopted from various authors (van Jaarsveld et al. 2002, Hardjito et al. 2004, Shindunata et al. 2006). After removal from the moulds, the geopolymer specimens were left air cured in the curing room with temperature of 23-25°C. The OPC specimens were placed in the water pond for 28 days before testing.

2.4 Test Methods

Upon reaching the target strength, the specimens were immersed in 3.5% sodium chloride solution. The solution was replaced once a month to maintain the salinity. The specimens were subjected to two different exposure regimes, i.e. continuous immersion and wetting-drying cycles. The seawater resistance was taken by measuring the change in compressive strength and change in mass (ASTM C267), and change in effective porosity (ASTM C462). The compressive strength change was measured at 28, 91 and 365 days. The weight change were taken on 1, 7, 14, 21, 28, 42, 56, 84, 112, 140, 168, 196, 224, 252, 280, 380, 336, 364 days.

The accelerated wetting-drying cycles was carried out according to Kasai & Nakamura (1980) for investigating a resistance of mortar in synthetic salt water. A cycle was comprised of exposure to 3.5% sodium chloride at room temperature for 24 hours and drying at 80°C for 24 hours. At 28, 91 and 200 days or 14, 45 and 100 cycles, the change in compressive strength, change in mass and change in effective porosity were carried out. Only mix T4 and OPC concrete were exposed to the cycles. The concrete was weighed after each wetting or drying to obtain a weight loss during the drying process and a total weight change. The weight loss during the drying process and total weight change can be calculated as follows:

$$d_n = \frac{w_{nw} - w_{nd}}{w_{nd}} x 100$$
 (4)

where d_n = weight loss during the drying process at 'n' cycle (%), w_{nw} = weight of specimen at the end of immersion of 'n' cycle (kg), w_{nd} = weight of specimen at the end of drying of 'n' cycle (kg).

4. RESULTS AND DISCUSSION

4.1 Change in compressive strength

In Figure 2(a) the OPC and T10 cured at continuous immersion showed an approximate strength loss of 4-6% at 365 days. In reverse, the continuous immersion has also increased compressive strength of T4 and T7 by 6% at 365 days. The strength losses in the OPC was marginal and this could be due to leaching of portlandite or Ca(OH)₂. When the chloride diffuses into the OPC, the hydroxide ions leach out to maintain the electro neutrality of paste, which results in the portlandite solubility, and a decrease of concrete strength (Delagrave et al. 1994; Gegout et al. 1992). An increase of strength was observed for T4. Crystallization of aluminosilicates for mixtures with high alkali content could be the reason (Fernandez-Jimenez, et al. 2007). Leaching of alkalis that alter the integrity of aluminosilicates network might contribute to a decrease of strength in T10. This confirms the effect of alkalis leaching of geopolymer from a previous study (Llyod et al. 2010). Mix T7 that high in aggregate amount, showed a slow increase of strength with concrete age older than 91 days. The small amount of alkali and silica content could be the reason. This is certainly positive for geopolymer applied in chloride environment.

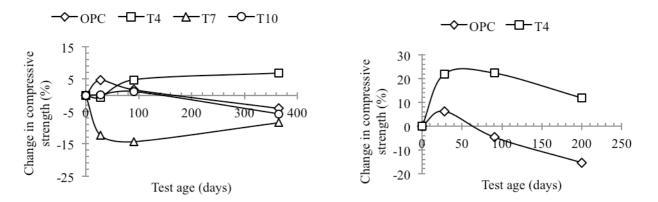


Figure 2: Change in compressive strength subjected to continuous immersion (a) and wetting-drying cycles (b).

Generally the compressive strength increased and began to decrease at the end of the wetting-drying cycles in Figure 2(b). There was a 15% decrease of strength of OPC concrete at 100 cycles or 200 days. In contrast, compressive strength of the geopolymer increased to 22% at 28 days before eventually decreasing to 11% at 200 days. In fact, a decrease of strength was more dominant for the OPC, because of the extreme temperature difference. It seems the physical attack of temperature difference had a significant impact to the OPC, compared to the increase of hydration rate during the cycles. On the other hand, the cyclic exposure was adversely affecting the geopolymer concrete strength. The geopolymer is known as a ceramic material that performs well under high temperature heating (Kong et al. 2007). The repetitive exposure to the high temperature during drying cycles slightly increased the geopolymer strength because of a faster crystallization process. A decrease of

strength was observed at 100 cycles showing a faster rate of degradation on the concrete paste than the crystal formation. Since there was no significant change in compressive strength in the fly ash geopolymer subjected to wetting-drying cycles could be beneficial for applications in tidal and splash zones.

4.2 Change in effective porosity

There was a reverse trend for T7 with a decrease of porosity in Figure 3(a). This could be due because of a porosity improvement and a very low rate of alkalis leaching in the paste. It can be seen that the alkalis leaching in the mixes with high aluminosilicates content such as T10 and T4 change the porosity of fly ash geopolymer concrete during continuous immersion. Further investigation is needed to observe the porosity change could affect the integrity of geopolymer structures in full immersion zones in the long term.

The most significant result is a decrease of the OPC porosity by 96% after 365 days subjected to wetting/drying cycles (Figure 3(b)). This might be attributable to an accelerated hydration that reduced the concrete porosity and the damaging effect from repetitive wetting-drying cycles. It confirms similar behavior from a previous study of wetting-drying in sulphate attack medium (Sahmaran, 2007). On the other hand, there was no significant change in geopolymer porosity, such as in the OPC concrete. Due to low calcium content in the geopolymer paste, there was no replenishment of the pores due from continuous hydration, except the alumina silicates crystallization. The crystallization seemed to be affecting the mechanical strength more than the porosity under wetting-drying cycles.

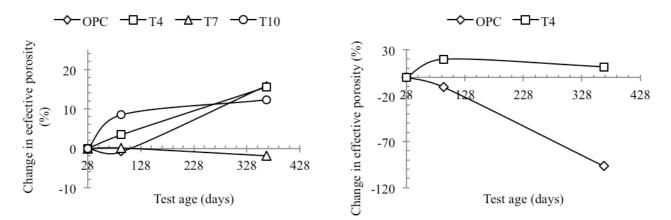


Figure 3: Change in effective porosity subjected to continuous immersion (a) and wetting-drying cycles (b).

4.3 Change in weight

Figure 4 displays the weight changes of concrete subjected to continuous immersion in NaCl 3.5%. The geopolymer concrete performed a steady weight change, although it started with a considerable high value of 1%. There was a steady trend of weight change for all geopolymer concrete. Mix T4

has low weight change percentages compared to T7 and T10, indicating no sign of chloride accumulation in the specimens. All mixtures showed a constant change in weight with time, revealing that a marginal microstructure alteration occurred in the specimens.

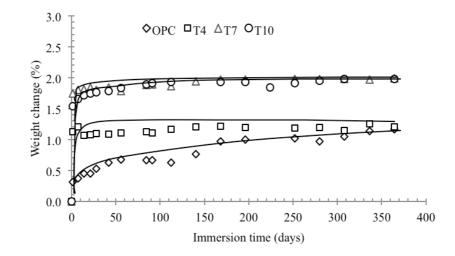


Figure 4: Weight changes of concrete subjected to continuous immersion.

In contrast, the OPC concrete showed a gradual increase in the percentage of weight change with time. This might be due to the chloride crystal accumulation into the concrete pores that could increases the final concrete mass. Since there is no chloride accumulation in the geopolymer concrete paste this could be related to the high change of porosity.

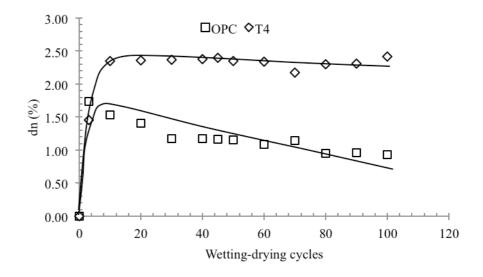


Figure 5: Weight losses during the drying process of concrete subjected to wetting-drying cycles.

Figure 5 displays the weight losses for both geopolymer and OPC concrete subjected to the wetting-drying cycles. There was a substantial initial weight loss of 2.4% for the geopolymer

concrete up to 60 cycles before it decreased slightly at 100 cycles. On the other hand, there was a high initial weight loss for the OPC before it went down gradually by 0.5% at 100 cycles. The elevated weight loss of the fly ash geopolymer can be attributed to the high pores interconnectivity that allows rapid chloride ion movements from the outer to inner side of concrete. Moreover, constant values indicated no sign of repetitive chlorides crystallization formed in the fly ash geopolymer pores. Chlorides crystallization in the pores was more noticeable on the OPC concrete as there was a gradual reduction of weight percentage over time.

4. CONCLUSIONS

Seawater resistance of fly ash geopolymer and OPC concrete were investigated under different exposure conditions. The following conclusions can be drawn from the study:

- a. As expected, the OPC concrete was prone to degradation in a seawater environment. The cyclic exposure to seawater increased the rate of degradation of OPC concrete. While the geopolymer concrete showed no significant change in strength and degradation following continuous immersion and the wetting-drying cycles. The high resistance of geopolymer concrete due to high temperature after being exposed to wetting-drying cycles was due to faster crystallization.
- b. The alkalis leaching in the mixes with high aluminosilicates content could change the porosity of fly ash geopolymer concrete during continuous immersion. However, there is no significant change on the low calcium fly ash porosity under the wetting-drying cycles since no replenishment of the pores such in OPC with the continuous hydration.
- c. Fly ash geopolymer showed a marginal weight change after being exposed to continuous immersion and wetting-drying cycles. On the other hand, chloride crystallization in the OPC pores was noticeable due to a gradual reduction of weight percentage over time.

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