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Durability of Low Calcium Fly Ash Geopolymer Concrete in Chloride Solution

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ABSTRACT

This paper describes a durability study of low calcium fly ash geopolymer concrete under an accelerated wetting drying testing. The main parameters were aggregate content, alkaline/fly ash ratio, ratio of sodium silicate/sodium hydroxide and curing conditions. The accelerated test method was carried out by subjecting the geopolymer concrete to repeated cycles of chloride solution immersion and oven drying. The specimens were immersed in 6.54% chloride solution for 24 hours and were heated at 80^0C for 24 hours. Physical properties such as a change in mass and compressive strength were monitored. The results indicate that the geopolymer concrete has a good resistance on the accelerated wetting drying cycles. The compressive strength of the exposed concrete increased about 16-33% after the wet-dry cycle.

KEYWORDS: accelerated wetting-drying, chloride solutions, fly ash, geopolymer concrete, strength

1 INTRODUCTION

Marine environment is a type of aggressive environment that has detrimental effects to concrete. This environment contains chloride and sulfate ions. Both ions are harmful for concrete because it can corrode the steel reinforcing bars inside of the concrete. The ions also can corrode the concrete itself by attacking calcium compound in the concrete. The marine environment has tidal and splash zones where extreme conditions of wetting drying occurs. The concrete can deteriorate quickly, since the cyclic wetting by seawater and drying by air causes continous moisture movement through concrete pores [7]. When the dry concrete exposed to seawater, the salts are absorbed by concrete until it is saturated under some conditions. Then if the external surface is dry again, the water evaporates from capillary pores, leaving the salts behind. Until certain time, because there is a concentration gradient inside of the concrete, the salts travel further into internal side of the concrete by diffusion. The excess salts inside of the concrete will precipitate out as crystals in the concrete pores. Finally, after the concentration gradient decreases from a peak value, some salts diffuse toward the surface of the concrete. There will be salt crystals appeared on the surface of the concrete.

Fly ash geopolymer concrete has a higher resistance to some aggressive environments than OPC concrete. It can be attributed to its unique gel network and composition that can withstand major causes of degradation. Since it has low calcium content in the mixture, the low calcium fly ash geopolymer concrete only lost its 21% of strength after being exposed to 10% sulfurid acid solution in 28 days [1]. While in the sulfate environment, the geopolymer concrete showed no significant weight loss and change in compressive strength because of ettringite and gypsum formation as in case of the OPC concrete [2]. Previous finding showed that the fly ash geopolymer concrete could resist synthetic seawater [3]. The concrete strength also increased with time and there was no weight loss after being exposed to the synthetic seawater solution. It was also reported that metakaolin geopolymer had a fluctuating flexural strength with time. The porosity of the concrete in the seawater remained low after 270 days of immersion [4]. Slag geopolymer mortar was found has a good resistance to chloride solution [5]. There was no significant change of the compressive and flexural strength of the mortar after 90 days exposure to the chloride solution. Another finding showed that the geopolymer concrete has low chloride ion diffusion coefficient [6]. This fact was also supported by low permeability coefficient of the geopolymer concrete in that research.

The objective of this research is to study the effect of cyclic wetting drying in the chloride solution on the fly ash geopolymer concrete. The resistance of geopolymer concrete to the accelerated wetting drying cycles was measured by change in mass and compressive strength. This method was adopted from Kasai and Nakamura [8] for studying a resistance of mortar to accelerated wetting drying cycle test in salt water.

2 EXPERIMENT

2.1 Materials and Mixtures

Low calcium fly ash from Collie, Western Australia was activated with alkaline solution to form geopolymer matrix. 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

Table 2. Mixture proportion variables of the geopolymer concrete

Mixes	Factor			
	Aggregate content (kg/m^3)	Alkaline/fly ash ratio	Ratio of Sodium Silicate/NaOH	Curing condition
1	1752	0.3	1.5	24h 60^{0}C
2	1752	0.35	2	12h 70^{0}C
3	1752	0.4	2.5	24h 75^{0}C
4	1800	0.3	2	24h 75^{0}C
5	1800	0.35	2.5	24h 60^{0}C
6	1800	0.4	1.5	12h 70^{0}C
7	1848	0.3	2.5	12h 70^{0}C
8	1848	0.35	1.5	24h 75^{0}C
9	1848	0.4	2	24h 60^{0}C
10	1752	0.3	2.5	24h 75^{0}C

The alkaline activators used in this research were sodium hydroxide (NaOH) and sodium silicate (water glass). Sodium hydroxide pearls with concentration of 99% NaOH was diluted with distilled water to produce 14 M solution. The sodium silicate with modulus silicate (Ms) of 2 (Na_2O = 29.4%, SiO_2 = 14.7%, H_2O = 55.9%) was used. A naphthalene based superplasticizer was added to the mixture to improve the workability. Crushed granite coarse aggregate with a maximum size 20 mm and natural sand as a fine aggregate were used in the mixture of the geopolymer concrete.

There were eleven mixes were used in this research. Ten mixes have different compositions that were designed according to Taguchi method [9]. The main variables for all mixes were aggregate content, alkaline/fly ash ratio, sodium silicate/sodium hydroxide ratio and curing methods. Mix 10 was a result from a Taguchi synthesis for all nine previously mixtures. OPC concrete with w/c ratio of 0.50 was used as a control mix. The mixture proportion variables and mix design of the geopolymer concrete used were listed in Tab. 2 and Tab. 3 respectively.

Table 3. Mix design of the geopolymer concrete used in this research

Mix	1	2	3	4	5	6	7	8	9	10	OPC
Fly ash (kg/m^3)	498.5	480	462.9	461.5	444.4	428.6	424.6	408.9	394.3	498.5	-
Aggregates (kg/m^3)	1752	1752	1752	1800	1800	1800	1848	1848	1848	1752	1856
NaOH 14M	59.8	56	52.9	46.2	44.44	68.6	36.4	57.2	52.6	42.7	-
Sodium silicate	89.7	112	132.2	92.3	111.1	102.9	90.9	85.9	105.1	106.8	-
Cement (kg/m^3)	-	-	-	-	-	-	-	-	-	-	355.34
Superplasticizer	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	-
Added water	28.9	26.3	23.9	22.5	20.9	31.3	17.9	26.8	23.9	21.0	177.50
Slump (mm)	260	260	270	245	250	270	140	250	250	240	120
28-day Compressive strength (MPa)	39.93	37.09	49.64	42.51	38.69	28.64	54.89	35.73	29.71	46.55	42.04

2.2 Specimen Preparation and Testing

The specimens were cylinders with diameter of 100 mm and height of 200 mm. Those cylinders were test for compressive strength at 7 and 28 days of age, an accelerated cyclic wetting drying, visual inspection, change in mass and change in compressive strength. Change in compressive strength was calculated according to ASTM C267.

The accelerated wetting drying cycle test was carried out based on a method used by Kasai and Nakamura [8] for investigating a resistance of mortar in synthetic salt water. The test started at the age of 7 days for all concrete specimens. Each concrete specimen was test for 10 cycles (20 days). One cycle consists of wetting the concrete in chloride solution for 24 hours and drying the concrete in the oven at temperature of 80^{0}C for 24 hours (Fig.1). In this test, the specimens were immersed in the chloride solution immediately after the oven drying process. The concentration of the chloride solution was 6.54%. The volume proportion of chloride solution to the specimens was one to four. The solution was replaced after 5 cycles to maintain a chloride concentration.

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 [8]:

$$d_n = \frac{w_{nw} - w_{nd}}{w_{nd}} x100 \quad (1)$$

where:

d_n = weight loss during the drying process at 'n' cycle (percent)

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)

$$w = \frac{w_{nw}}{w_o} x100 \quad (2)$$

where:

w = total weight change (percent)

w_o = weight of speciment at before the accelerated test (kg)

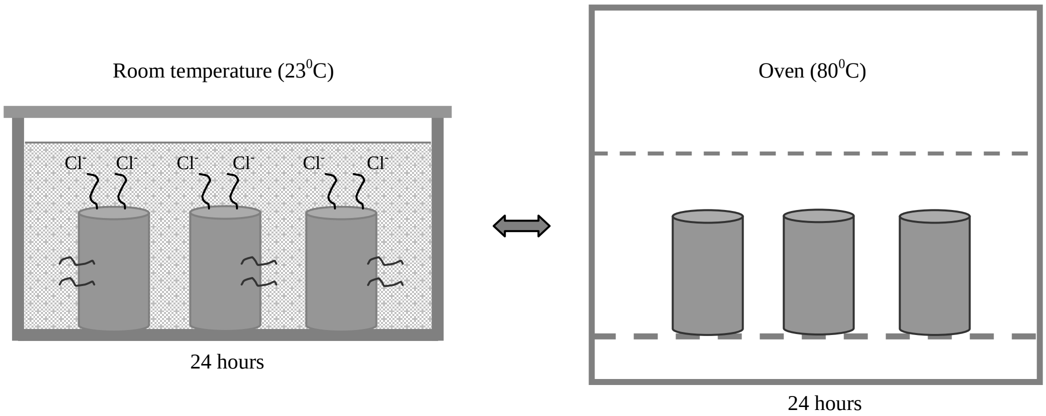

Figure 1. An accelerated wetting and drying cycle.

The compressive strength test was performed on the concrete specimens after exposed to cycles of wetting and drying. Those values were compared with 7-days compressive strength the specimens before exposure to the chloride solution. In addition, a visual inspection was carried out for the specimens to monitor the chloride crystal on the surface of the concrete.

3 RESULTS AND DISCUSSIONS

3.1 An accelerated wetting drying cycle test

The weight loss during the drying process and total weight change of specimens repeatedly subjected to wetting and drying are shown in Fig. 2 through 6. Both values can be used to evaluate a degree of durability of those specimens. Those specimens were classified in one group according to curing methods applied for them. In general, if the total weight loss remained relatively high and total weight change was small then the concrete might be hardly cracked [8]**.** However, when the total weight loss was small, and total weight loss was hardly changed, then the concrete can be had a slight crack.

Fig. 2 showed the weight loss during the drying process and total weight change of geopolymer concrete cured for 24 hours at 60^{0}C. Both values showed a fluctuating trend for all mixes. This can be attributed to fluctuated absorption and evaporation in the geopolymer concrete related to its porosity. Geopolymer cured at 60^{0}C seemed to have higher porosity than the concrete cured at temperature 70^{0}C above. Furthermore, there was a downward trend, showing a decrease in the weight loss during the drying process with time. It seemed that the chloride might have been penetrated into the concrete and was remained in the pores after the drying process.

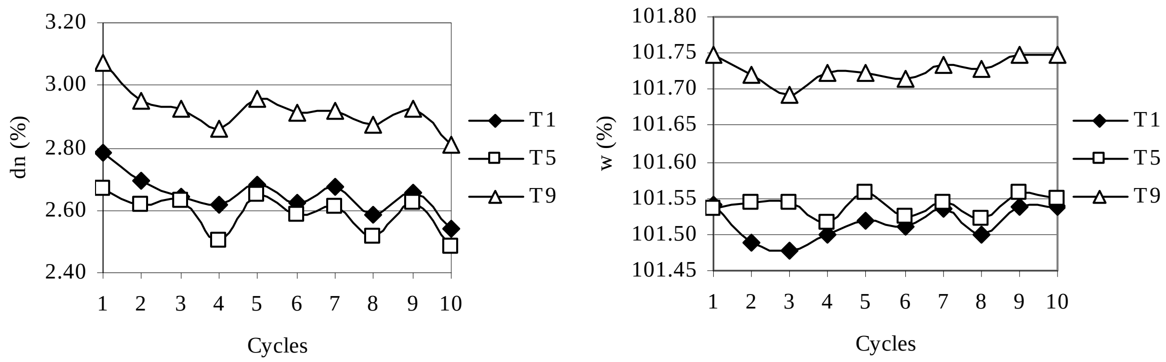

Figure 2. Weight loss during the drying process (dn) and total weight change (w) of specimens with curing method of 24 hours at 60^{0}C.

In general, those mixes cured in a curing method of 12 hours at 70^{0}C showed a constant change in the weight loss during the drying process and total weight change (Fig. 3). Mix T7 had the lowest weight loss and total weight change among the other mixes. Concrete with high strength and low porosity might have contributed to this behaviour. Since the total weight change was constant for mixes T2 and T7, then it can be assumed that the chloride penetration might be small for both mixes. In this research, the number of wetting drying cycle was only 10. This number was probably insufficient to observe the chloride penetration of the concrete for these mixes.

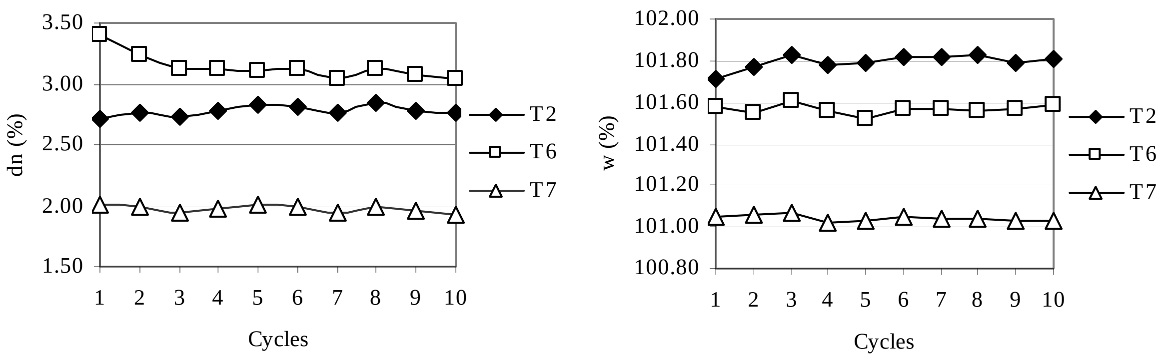

Figure 3. Weight loss during the drying process (dn) and total weight change (w) of specimens with curing method of 12 hours at 70^{0}C.

In Fig. 4 below, the geopolymer concrete mixes cured with a curing method of 24 hours at 75^{0}C showed a small declining trend for all mixes. Mix T4 showed the smallest weight loss during the drying process and among all mixes in this curing method. The total weight change was also lower than other mixes. It can be assumed that the ingress of the chloride might be slower for mix T4 than the other mixes in this group.

In Fig. 5, the OPC concrete was compared to mix T4 and T10. It can be seen that the weight loss during the drying process decreased gradually since the first day of exposure until the last day of test. From this different trend, it can be said that the chloride penetrated into the OPC concrete quite fast. This chloride can reduce the

OPC concrete integrity by attacking the calcium compound and accummulating salts inside the pores. From this figure, mix T10 showed a constant weight loss and the high total weight change.

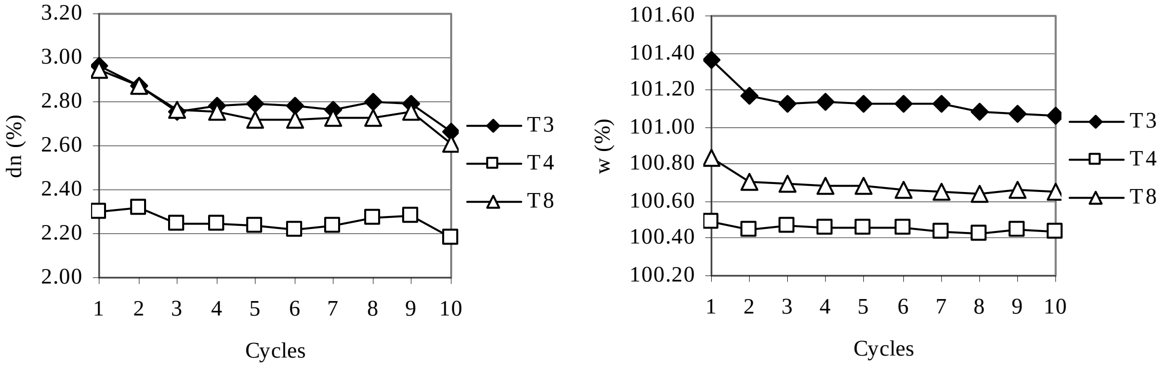

Figure 4. Weight loss during the drying process (dn) and total weight change (w) of specimens with curing regime of 24 hours at 75^{0}C.

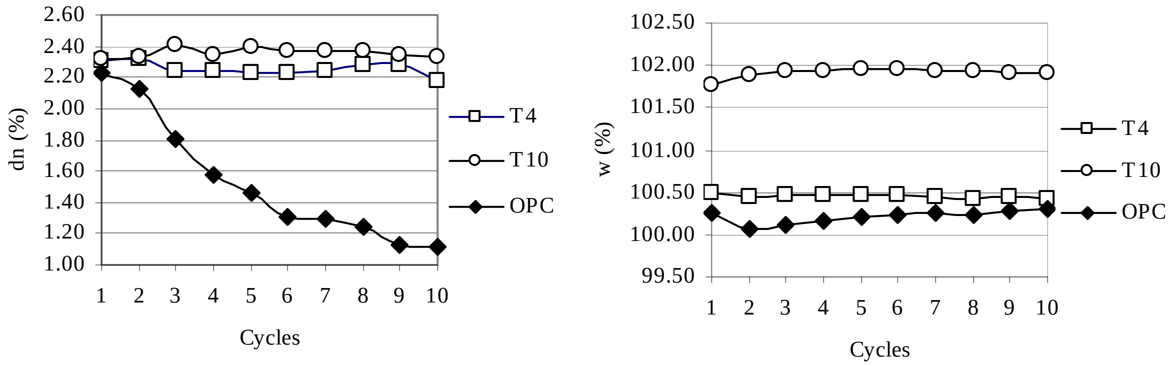

Figure 5. Weight loss during the drying process (dn) and total weight change (w) of specimens.

From all figures above, in general, it can be said that the geopolymer concrete has a different trend of total weight loss during the drying process than the OPC concrete. Although some mixes had a downward trend, but the OPC concrete graph has a steeper gradient than the geopolymer concrete. Most of the geopolymer mixes have a constant change of the weight loss during drying, then it can be assumed that there was a slow chloride ions penetration into the concrete. This was also supported by a constant total weight change for geopolymer concrete. It was also noticed that the number the wetting-drying cycles was not enough to observe the behaviour despite its high chloride content in the solution. In fact, this constant total weight loss change is beneficial for the geopolymer concrete in the marine environment.

3.2 Change in compressive strength

Tab. 4 shows a change in compressive strength and mass of the concrete after exposed to the wetting-drying cycles. There was 16-33% increase in the compressive strength the cycles. Geopolymer concrete is a type of concrete that needs high temperature curing to accelerate the process [10]. It seemed that after drying by oven heating at 80^{0}C, the concrete has undergone further reaction to increase the strength. Although evaporation was occured in this condition, but a high temperature during the drying process might contribute to the increase of strength of the geopolymer concrete. The highest change was observed for mix T1. Mix T1 has the highest fly ash content among all studied mixes, which probably contributed to an increase of strength more than 30%. Mix T3 showed the smallest change in strength. This mix has the highest sodium silicate content compared to other mixes. It has been found that the sodium silicate in the presence of chlorides tend to reduce the geopolymer concrete strength [11]. The same finding was also reported for the geopolymer subjected to ASTM 4842 wet dry cycles [12]. There was no decrease in the compressive strength generally. There was an increase about 11% of strength after 6 cycles. The compressive strength of the OPC concrete increased for 25% after exposed to the wetting drying cycles. The same behaviour was reported for the OPC concrete, since the effect of wetting and drying can accelerate a hydration process in concrete.

Table 4. Compressive strength and mass loss of concrete

Mixes	Compressive strength (MPa)		Change in compressive strength (%)	Mass loss during drying process (%)
	before exposure	after exposure		
T1	39.52	52.62	33.15	2.65
T2	35.31	50.44	29.99	2.78
T3	49.89	59.48	16.12	2.80
T4	40.93	55.48	26.22	2.55
T5	37.55	47.87	21.56	2.59
T6	27.16	38.20	28.90	3.14
T7	52.29	69.81	25.09	1.97
T8	34.53	42.11	18.00	2.76
T9	29.29	37.92	22.76	2.92
T10	46.22	55.46	16.66	2.36
OPC	32.16	45.51	29.39	1.53

3.3 Visual inspection

Fig. 6 and 7 show the geopolymer concrete visual appearance before and after 10 cycles of wetting drying in 6.54% chloride solution and oven at temperature of 80^{0}C. It can be seen that before being exposed to the process, the air-dried geopolymer concrete have smooth surface. The same finding was confirmed from a research based on the ASTM D4842 wet-dry cycles test for the geopolymer [12]. There was no deterioration of the surface such as cracks, fissures and increased of roughness observed for the specimens [12]. Then after 10 times exposure to the wetting drying, concrete surface started to change its original appearance. There were more colour inconsistency, pores, and thin layer of white powder on the surface for all concrete. This white powder was assumed salt crystals. In general, the higher the concrete strength, then the lesser salt appeared on the surface of concrete. Concrete with compressive strength less than 20 MPa (mix T6 and T9) seemed to have more salt crystal on their surfaces than other mixes.

Figure 6. Visual appearance of mix T2, T6, T7 before and after exposure to the wetting drying cycles test (left: before exposure, right: after exposure).

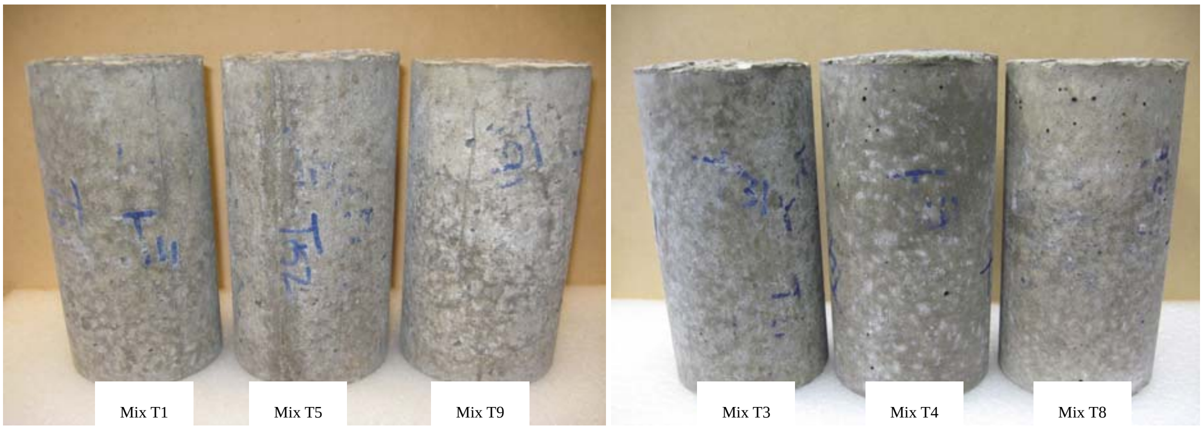

Figure 7. Visual appearance of mix T1, T5, T9, and mix T3, T4, T8 after exposure to the wetting drying cycles test.

4 CONCLUSIONS

Various mixes of geopolymer concrete were tested under the accelerated wetting drying cycles to simulate a marine environment. The conclusions obtained from the above test can be summarised as follows:

(1) The total weight loss during the drying process and total weight change for geopolymer concrete were mostly constant. This means, the chloride might penetrate to the geopolymer concrete slower than the OPC concrete.

(2) The compressive strength concrete changed after exposed to the wetting drying cycles. Concrete with curing method for 12 hours at 70^0C increased its strength more than 25% after the exposure. The drying process might contribute to further reaction and the resulted strength.

(3) Visual appearance of the concrete has changed after exposed to the wetting drying cycles. The surfaces colour changed and there were thin white powder appeared on the concrete surfaces. The lower strength of concrete, then more salt cyrstals appeared on the surface.

It can thus be concluded that geopolymer concrete has a good resistance to chloride solution.

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