Assessing Corrosion Resistance of Powder Form of Geopolymer Concrete

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Abstract: Utilising geopolymer concretes is one of the most promising means of achieving sustainable construction. To expedite the acceptance of the usage of geopolymer concretes in the construction industry, further studies related to reinforcement corrosion are necessary. Among many important aspects of investigation is the carbonation in geopolymer concrete, which is different from that in OPC concrete. In this study, carbonation depths in geopolymer concrete, measured using two different indicators, in an accelerated environment, of a powder form of fly ash/slag based geopolymer concrete are compared. The influence of a set-retarder on the rate of carbonation has also been investigated.

Keywords: Fly ash/slag based geopolymer, carbonation, chloride ion induced corrosion, heat evolution

1. Introduction

Due to the transition towards more environmentally friendly materials for construction, geopolymers have recently received much attention. It is because the production of geopolymers consumes less energy and releases by far less CO_2 emissions than that of Portland cement (1). Geopolymers are produced by a reaction between an aluminosilicate precursors and an alkaline activator. Geopolymer concretes can be designed to possess superior durability properties, compared to concretes made of Portland cement. These properties include high resistance to acid attack, alkali-silica reaction, freeze-thaw, low drying shrinkage and sulphate attack (2–4). Thus, geopolymers can be preferred binder systems to manufacture precast concrete components such as culvert and pipes.

In durability studies of geopolymer concretes, accelerated carbonation test forms an important part of corrosion related investigation. When geopolymers are exposed to different concentrations of CO_2 , different products of carbonation reaction are produced. In the atmosphere where the concentration of CO_2 is low (0.03–0.04%), carbonation in geopolymer leads to the formation of alkali carbonate (5,6). By contrast, if the concentration of CO_2 is higher, the formation of alkali bicarbonate is favoured. It is well known that alkali bicarbonate is a less stable product, or soluble salt, which can make the pore solution pH of geopolymer concrete decrease rapidly. Thus accelerated carbonation test which is used to expedite carbonation rate in order to shorten testing time, appears to underestimate the carbonation resistance of geopolymers (5,6). A concentration of 1% CO_2 in accelerated carbonation test simulates the natural carbonation process well (7) and hence applied in this study.

Another important aspect related to steel corrosion in geopolymer concrete is the chloride threshold values. For OPC concrete, the threshold chloride ion concentration at the steel level is considered as 0.4% by weight of binder (although this may vary between 0.2 to 0.5%). For geopolymer concretes, however, this value can be as high as 1.0% to 1.7% (8), indicating the higher resistance of geopolymer concrete against corrosion initiation. Also, fly ash based geopolymers have a considerably higher chloride threshold when compared with slag based geopolymers (9). These aspects are currently being investigated at University of Technology Sydney.

Applying the already established E_{corr} value (-350 mV) for corrosion initiation in OPC based concrete, to evaluate corrosion initiation of steel in geopolymer and blended geopolymer concretes is not appropriate. At E_{corr} value of -500 mV, there is no corrosion of steel reinforcement in geopolymer concrete was observed (10). This is probably because the composition and pH of pore solutions at the steel-concrete interface of geopolymer concrete and OPC based concrete are different. Thus, it is necessary to establish the threshold values of E_{corr} for geopolymer concrete by appropriate investigation.

The conventional technique of geopolymer production (two-part mix) requires a highly alkali activator in liquid form to dissolve and activate precursors. Handling this highly corrosive liquid at site, in large quantities, is a challenge for the application of geopolymer in construction industry. Hence a dry powder form or one-part mix of geopolymer was introduced to deal with this issue. In this technique, alkali activator in powder form is mixed with precursors and resulting geopolymer binder is a dry mix. This is a safe method of producing geopolymer, because only water is added to activate the dry powder and handling highly alkaline

activator at site is eliminated. Thus, this new type of geopolymer binder can be used similar to that of Portland cement in the field.

A dry powder geopolymer, however, if not retarded, has a fast setting time due to heat released from the dissolution of solid activators, and from the reactions of precursors and activators (11,12). The more calcium dry powder contains, the shorter is the setting time. Although the high calcium content in the mix results in a high early strength development, which is important in precast concrete production. In order to promote more practical applications of geopolymers, use of a set-retarding admixture to prolong its setting time is necessary. Nanoparticles of zinc oxide (13), was found to be very effective in prolonging the setting time of geopolymers made from slag, but showed a negligible impact on geopolymers made from meta-kaolin. This result was obtained by isothermal calorimetry and 'in situ X-ray PDF analysis'. Phosphoric acid (14) found to be significantly delaying the setting time of slag based geopolymers. Sodium phosphate was found to be useful in retarding the setting time of red mud/slag based geopolymers. For high calcium fly ash based geopolymers, sucrose delayed the initial setting time slightly but prolonged the final setting time significantly (15). However, these studies were all carried for two part mixes, and not for one-part mix or dry powder geopolymers. Additionally, the effect of these retarders on other important properties (in precast mortars or concretes) such as workability or compressive strength development has not been well understood. In the present study, the effect of a sodium based retarder on setting time, compressive strength and carbonation rate of dry powder fly ash/slag geopolymer pastes and mortars is investigated. The findings confirm the suitability of this sodium based retarder in improving setting time of dry powder geopolymer, making such a binder more appropriate for precast applications.

2. Materials and Experimental Procedure

2.1 Materials and mix proportions

Two types of dry powder geopolymer G1 and G2 were produced by dry mixing aluminosilicate precursors including low calcium fly ash and ground granulated blast furnace slag with alkali activators in powder form (Table 1).

Table 1. Mix proportions of dry powder form geopolymer G1 and G2

	G1	G2
Low calcium fly ash (%)	50	30
Slag (%)	32	50
Alkali activator powder (%)	16	16

The chemical compositions of fly ash and ground granulated blast furnace slag, determined by X-ray fluorescence analysis, are presented in Table 2.

Oxide compositions wt.%	Fly Ash	Slag
Na ₂ O	0.47	0.32
MgO	1.28	6.84
Al ₂ O ₃	22.29	14.14
SiO ₂	58.15	33.89
P_2O_5	0.77	0.01
SO3	0.15	1.59
K ₂ O	1.39	0.28
CaO	5.39	40.46
TiO ₂	1.03	0.58
V ₂ O ₅	0.02	0.01
Cr ₂ O ₃	<0.01	0.01
Mn ₃ O ₄	0.07	0.21
Fe ₂ O ₃	6.95	0.45
ZrO ₂	0.01	0.02
BaO	0.03	0.05
LOI	1.09	-0.11
Total	99.09	98.74

Table 2. Chemical compositions of precursor

Sand, used to prepare mortar specimens, was Sydney sand and the sand to powder ratio was kept as 2.5 for all mortar specimens.

2.2 Experimental procedure

The G1 and G2 mortars were produced in a Hobart mixer. Water was first added into the mixing bowl and then the dry power was added. The mixing process started at a low speed for 30 seconds, followed by 60 seconds at medium speed. Sand was then introduced and the same mixing sequence was adopted. After casting the 50 mm cube specimens, all the specimens were cured at a temperature of 23°C and at a relative humidity of 90% in a moisture cabinet for 1 day. The specimens were then removed from their moulds and were wrapped in a thin plastic film and placed in an oven at 60°C for 6 hours. The specimens were then taken out, unwrapped and left in air in the laboratory at 23°C until testing.

The compressive strength tests of mortar specimens were performed, as per ASTM C109 /C109M-16a.

For the accelerated carbonation test, 50 mm mortar cubes were placed in a carbonation chamber where CO_2 concentration was maintained at 1% at the age of 28 days. The relative humidity of the carbonation chamber was maintained at 60% and the temperature was 23°C. After 63 days, these specimens were split-opened and carbonation depths were measured by spraying either a Phenolphthalein solution (1%) or an Alizarin Yellow R solution (0.5%).

Different quantities of retarder were added to the mixes, in order to verify the influence of retarder on setting time, compressive strength and depth of carbonation.

3. Results and Discussion

3.1 The influence of retarder on setting time of dry powder geopolymer pastes

Setting times of dry powder geopolymer pastes of G1 and G2, with different amounts of retarder, are shown in Table 3. The increase of retarder content led to increasing setting times. For G1, 1% or 2% retarder is required to give workable initial and final setting times. For G2, however, a minimum of 4% is recommended.

	Percentage Dry powder geopolymer G1		eopolymer G1	Dry powder geopolymer G2	
ratio	of retarder	Initial setting	Final setting time	Initial setting	Final setting time
	(%)	time (minutes)	(minutes)	time (minutes)	(minutes)
0.2	1	80	145		
	2	88	164	14	29
	4	239	-	53	117
	6	> 330	-	181	316
	8			274	-
0.3	1	95	155		
	2	110	269	37	78
	4	218	388	75	203
	6	318	-	218	425

Table 3. Setting time of dry powder G1 and G2 with different contents of retarder

3.2 The influence of retarder on compressive strength development of dry powder geopolymer G1 and G2 mortars

Compressive strength results at the age of 28 days of dry powder geopolymer G1 and G2 mortars, with water/powder ratios 0.3 and 0.4, are illustrated in Figures 1 and 2. Increasing the content of retarder resulted in a reduction of compressive strength of dry powder geopolymer G1 and G2. Further, the optimum retarder content for G1 and G2 was found to be 2% and 4%, respectively.



Figure 1. Compressive strength at the age of 28 days of dry powder geopolymer G1 mortars, prepared with W/P ratios of 0.3 and 0.4



Figure 2. Compressive strength at the age of 28 days of dry powder geopolymer G2 mortars, prepared with W/P ratios of 0.3 and 0.4

3.3 Carbonation depths of geopolymer concretes

Carbonation depths of G1 mortar specimens, measured by the two indicators, are compared and presented in Table 4. Increasing the content of retarder resulted in an increase in carbonation depth.

Table 4. Comparison of carbonation depths, indicated by Phenolphthalein and Alizarin Yellow R, of G1 mortar specimens

Percentage	Carbonation depth indicated by		Carbonation depth indicated by	
of retarder	Phenolphthalein (mm)	Alizarin Yellow R (mm)	Phenolphthalein (mm)	Alizarin Yellow R (mm)
(%)	Water/Powder ratio = 0.3		Water/Powder ratio = 0.4	
2	1.74	2.69	5.14	6.82
4	5.3	5.8	6.3	7.6
6	5.8	7.3	7.8	8.0
10	8.8	9.6	12.3	13.7

The comparison of carbonation depths measured by spraying the two indicators are different. The depth indicated by Alizarin Yellow R is always slightly higher than that indicated by Phenolphthalein. Alizarin Yellow R changes colour from yellow to red when pH is above 10 (at higher pH levels, the colour is red), whereas Phenolphthalein changes from colourless to pink when pH is above 8.5 (at higher pH levels, the colour is pink). Alizarin Yellow R clearly defines the boundary where the pH is changing in geopolymers when compared with Phenolphthalein where the edge is somewhat fuzzy, as shown in Figure 3. From several measurements, it is concluded that Alizarin Yellow R is more suitable for geopolymer concrete to measure carbonation depths. This conclusion is also confirmed by other researchers. A third indicator, suitable for geopolymers in now investigated at UTS.



(a) G1 mortar specimens with 4% retarder with W/P = 0.3

(b) G1 mortar specimens with 4% retarder with W/P = 0.4



(c) G1 mortar specimens with 6% retarder with W/P = 0.3



(d) G1 mortar specimens with 6% retarder with W/P = 0.4

Figure 3. Comparison of carbonation depths, indicated by Phenolphthalein and Alizarin Yellow R, of G1 mortar specimens

4. Conclusions

This study suggests that the a sodium based retarder can be used effectively in dry powder (or one-part mix) geopolymer based on fly ash/slag to control the setting time to desired levels.

Compressive strength reduced considerably and carbonation depth increased with the increase of retarder content. The reason for this result is not entirely. Optimum amount of retarder is 2% for G1 and 4% for G2, in terms of setting time, compressive strength and carbonation resistance.

The comparison of the two indicators used showed that Alizarin Yellow R is more suitable for geopolymer concrete to measure carbonation depths as the boundaries of pH changes is more clearly defined.

5. Acknowledgement

This research is funded through an Australian Research Council Research Hub for Nanoscience Based Construction Materials Manufacturing (IH150100006) with the support of Cement Australia, the Industry Partner.

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