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THE EFFECT OF EFFLORESCENCE ON THE MECHANICAL PROPERTIES OF FLY ASH-BASED GEOPOLYMER BINDERS

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ABSTRACT

In this study, six typical geopolymer binders were synthesised using three different fly ashes (from Gladstone, Callide and Millmerran power stations) and two different activators (NaOH and $Na_2O \cdot 1.5SiO_2$). The curing of the binders was performed at room temperature (20±5 ℃) for 24 hours followed by sealed curing at 75 ℃ for 12 hours and then 7 days of ageing at ambient conditions. When the geopolymer binder specimens were put in contact with water at the bottom, efflorescence took place very quickly (within 3 hours) on NaOH-activated specimens. The effect of efflorescence on the compressive strength and modulus was studied by comparing specimens under dry, water contact and water immersion conditions for 28 days. The results showed that in general the dry samples achieved highest compressive strength while the water immersed samples exhibited the lowest strength. The NaOH-activated specimens under water contact conditions suffered intense efflorescence due to porous structure and exhibited lower strengths than those under leaching conditions. The compression modulus was tested to be proportional to the compressive strength. Both water contact and immersion seemed to be negative for the strength development. This issue should be considered when geopolymer products are applied under humid conditions.

KEYWORDS

Alkali-activated cement, geopolymer, fly ash, efflorescence, durability.

INTRODUCTION

Geopolymer is a new material currently being regarded as an alternative binder to Ordinary Portland cement. It is synthesized by alkali activation of aluminosilicate materials at, or slightly above, room temperature conditions. The alkaline activators are usually alkali metal hydroxide solutions (NaOH, KOH) with or without silicate solutions ($Na_2O \cdot nSiO_2$, $K_2O \cdot nSiO_2$). The aluminosilicates can be calcined clay (such as metakaolin) and alumina- and silica-rich industrial wastes (such as fly ash and slag) (Zhang et al. 2014a). The potential environmental advantages of geopolymer in the reduction of CO_2 emissions compared to Portland cement and the valuable utilization of waste materials as feedstock have been reported (Duxson et al. 2007; McLellan et al. 2011). However, in real engineering

world, the application of geopolymer is still rare because of both technical and cost issues. Despite the prudence of engineering industry in applying building materials, there is a lack of long term investigations and application cases that can prove the durability of such a new material. Efflorescence of geopolymer is one of the durability issues (Zhang et al. 20114b). In Portland cement concrete, efflorescence involves the reaction of soluble calcium with water and CO_2 to form carbonate deposits, and is generally considered harmless except for surface discolouration. However, because geopolymers contain much higher soluble alkali metal concentrations than Portland cement, efflorescence could be a significant issue when their products are exposed to humid air or partially in contact with water.

Many literatures have reported the effects of the reactivity of raw materials, alkali metal type and reaction conditions on the intensity of efflorescence of geopolymers (Temuujin and van Riessen 2009; Szklorzová and Bílek 2008; Škvára et al. 2008). However, there is very limited information about the consequent influences of efflorescence on properties of geopolymers. Škvára et al. (2012) reported that geopolymer mortars immersed in water exhibited lower compressive strength than those exposed to ambient air. The reason is attributed to sodium leaching, a mechanism of diffusion of alkali cations into leachant. However, they did not compare the compressive strengths of samples after efflorescence and those under ambient condition, although efflorescence product was observed in their study. Our previous study (Zhang et al. 20114b) has shown that both NaOH- and sodium silicate-activated geopolymers possess the potential of efflorescence when they contact with water. From the perspective of durability, it is important to understand the consequent influences of efflorescence on both mechanical and chemical properties of geopolymer. The aim of this study is to examine the effects of efflorescence on the strength development and reaction products of geopolymers.

MATERIALS AND METHODS

Materials

Three fly ashes, denoted as A, B and C, were obtained from Gladstone, Millmerran and Callide power stations in Queensland, Australia. The elemental composition of the three fly ashes were determined by X-ray fluorescence (XRF, Thermo Scientific), with results shown in Table 1. Their SO_3, moisture contents and loss on ignition (LOI) are all less than 1%. The particle sizes of the three fly ashes were determined using a leaser particle analyzer (Malvern Mastersizer 2000) with wet particle dispersion technique. The volumes of the particles >45 μm in the three samples are all less than 25%. According to AS3582.1 (1998) the three fly ashes used in this study can be classified as fine grade.

Table 1. Composition of fly ashes as determined by XRF. LOI is loss on ignition at 1000 ℃.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	SO_3	TiO_2	LOI
A	47.5	27.3	14.3	4.2	1.5	0.5	0.7	0.9	0.3	1.5	0.5
B	53.3	32.5	3.1	6.9	0.9	0.6	0.3	0.1	0.3	1.6	0.5
C	54.4	32.1	7.5	1.1	0.8	0.2	0.1	0.1	<0.1	2.1	0.8

Two activators used for geopolymer synthesis were NaOH solution and sodium silicate solution. The NaOH solution was prepared by dissolving NaOH pellets (99% purity, Formosa Plastics Corporation, Taiwan) in distilled water to a concentration of 12 mol/L. The sodium silicate solution was prepared by mixing NaOH and distilled water with D-Grade™ liquid sodium silicate (Na_2O=14.7 wt.%, SiO_2=29.4 wt.%, PQ Australia Pty. Ltd.) to a modulus (SiO_2/Na_2O molar ratio) of 1.5 and a concentration of 35%. The two activators were allowed to equilibrate to room temperature prior to use.

Geopolymer Synthesis and Testing

Geopolymer pastes were synthesized by adding an activator to a fly ash in a cement mortar mixing bowl. Due to the different particle properties, the fly ashes B and C required some additional water to achieve a similar workability as fly ash A. Table 2 lists the mix proportions of the six mixtures. The fresh pastes were poured into Ø23 mm × 24 mm polyvinyl chloride tubular moulds, sealed with

polypropylene wrap and subjected to humid curing at 20 ℃ for 24 h, followed by oven curing at 75 ℃ for 12 h and then allowed to cool down in the oven to 20 ℃ and stored for 7 days. The specimens were then demoulded and aged for 28 days at (1) ambient conditions, (2) contacting with water at bottom and (3) immersed in water. These three specific conditions simulated the service of geopolymer in air, water contact and water immersion conditions, respectively.

Table 2. Mix proportions of geopolymer mixtures

	Mixture	Fly ash /g	NaOH solution /g	Sodium silicate /g	Water /g
GPA	NaOH	600	180	-	-
	$Na_2O \cdot 1.5SiO_2$	600	-	162	-
GPB	NaOH	600	180	-	60
	$Na_2O \cdot 1.5SiO_2$	600	-	162	74
GPC	NaOH	600	180	-	36
	$Na_2O \cdot 1.5SiO_2$	600	-	162	54

The appearance changes of the geopolymers under the efflorescence conditions were recorded using a digital camera. The compressive strength of geopolymer was tested using an MTS universal mechanical testing machine. The loading speed was 0.5 mm/min. Before testing, the top surfaces of the cylindrical specimens were sanded to flat and parallel. Compressive strengths are reported as mean among 5 replicate specimens. The fractured samples were selected, milled and dried at 105 ℃ for 24 hours for XRD analysis. The XRD data were collected using an ARL 9900 Series X-ray workstation (Thermo Scientific) with Co K_α radiation, operated at 40 kV and 40 mA, with a step size of 0.02 ° and count time of 4 s/step from 8 to 80 ° 2θ. The compression modulus of geopolymers was calculated based on the strain and stress curves by linear regression of a part of the curves, usually between 30 to 70% of stress, where a best regression was obtained. Average values of 4 to 5 samples of each mixture are reported.

RESULTS AND DISCUSSIONS

Compressive Strength Development

Figure 1 shows the compressive strength development of geopolymers under different curing conditions. In general, sodium silicate-activated geopolymers exhibit higher strengths than those activated by the NaOH solution. It is due to the more compact microstructure of the former as sodium silicate provides some binding function in addition to its activation nature. This has been clearly shown in the previous microstructure analysis of metakaolin-based geopolymers that activated with NaOH and sodium silicate solutions at the same quantity of alkali concentration (Zhang et al. 2013). The strength varies depending on the source of fly ash and probably partially due to the additional water usage. Geopolymers synthesized from fly ashes A, particularly those by the sodium silicate solution, exhibited much higher compressive strengths than those from fly ashes B and C.

At ambient conditions, the compressive strengths of all of the tested geopolymers increase by 20 to 35% after 28 days. When the samples are put in contact with water at their bottoms (around 1 mm height in water) to allow efflorescence occur, their strengths increase very slightly. The NaOH-activated samples GPB and GPC even exhibit lower compressive strengths after 28 days compared to their demoulded samples. The samples immersed in water for 28 days are still able to achieve some increase in strength, except for GPA-NaOH and GPC-NaOH, although lower than air cured specimens. It means that the leaching of sodium and hydroxide cations from the binders or pore solution in binders has some effects on compressive strength development. This study did not test the compressive strength of geopolymers at early stage of water contact, for example, after 3 to 7 days in contact with water at bottom. The strength could be higher compared to the demoulded samples at early stage, as the efflorescence products fill in the pores of geopolymers (Zhang et al. 2014b); however, from a long term of view, it is evident that efflorescence has negative effects on the compressive strength development of geopolymers.

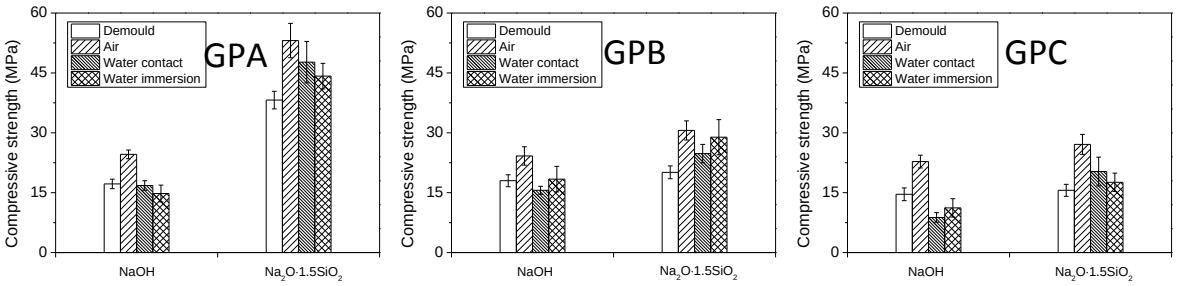

Figure 1. Compressive strength of demoulded geopolymers followed by 28 days of curing under air, water contact and water immersion conditions

The sodium silicate-activated binders GPA and GPC show lower strength after water immersion than water contact conditions. This does not mean that leaching is more harmful on the strength development of geopolymers than efflorescence. The leaching of sodium and hydroxide cations affects the late activation in geopolymer, which contributes less strength improvement. The sodium silicate-activated geopolymer GPB shows a lower compressive strength than the leached sample. It should be noted that GPB specimens were prepared with more additional water than the other two groups, which means that the porosity of the hardened binder could be higher. The higher porosity leads to more efflorescence products formed in the pores, maybe leading to higher inner stress. A foamed geopolymer can reveal this situation better (Zhang et al. 2014b). It could be the same reason for the NaOH-activated geopolymers GPB and GPC, both of which show lower strengths under the water contact conditions than under the leaching conditions. Table 3 shows the compression modulus of geopolymers. It can be seen that the negative effect of efflorescence on the modulus of geopolymers is more significant than that of leaching, particularly for those NaOH-activated samples. This issue should be considered in designing and engineering of large size geopolymer structures.

Table 3. Compression modulus of geopolymer under different conditions (unit: GPa)

Geopolymer		Ambient air	Water contact	Water immersion
GPA	NaOH	2.0 ±0.2	1.3 ±0.2	1.6 ±0.2
	$Na_2O \cdot 1.5SiO_2$	2.4 ±0.3	2.4 ±0.2	2.5 ±0.3
GPB	NaOH	1.6 ±0.3	1.1 ±0.1	1.2 ±0.2
	$Na_2O \cdot 1.5SiO_2$	1.8 ±0.1	1.7 ±0.2	2.0 ±0.3
GPC	NaOH	1.7 ±0.2	0.9 ±0.2	0.9 ±0.1
	$Na_2O \cdot 1.5SiO_2$	1.7 ±0.1	1.5 ±0.1	1.2 ±0.2

Changes of Appearance of Geopolymers

Figure 2 to 4 show visible changes of appearance of the geopolymers under water contact conditions.

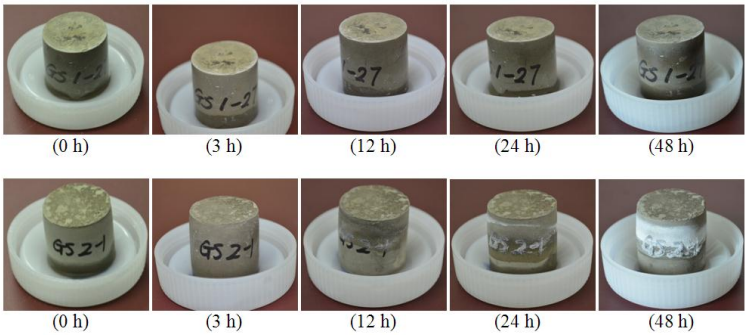

Figure 2. Changes of apparences of geopolymers GPA-$Na_2O \cdot 1.5SiO_2$ (GS1) and GPA-NaOH (GS2) under water contact conditions

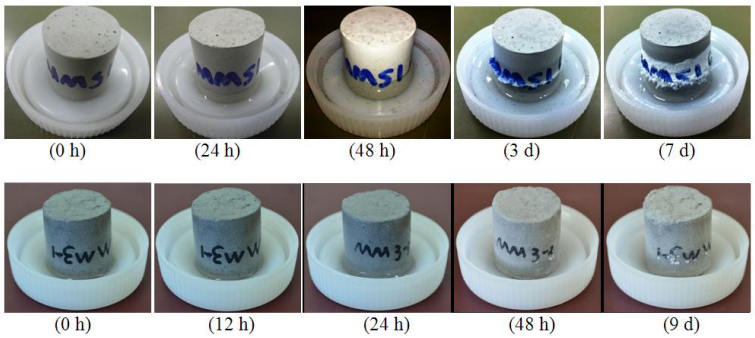

Figure 3. Changes of appearances of geopolymers GPB-$Na_2O \cdot 1.5SiO_2$ (MMS) and GPB-NaOH (MM3) under water contact conditions

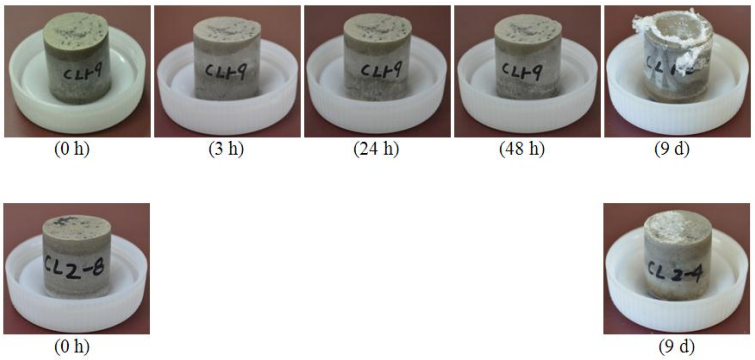

Figure 4. Changes of appearances of geopolymers GPC-$Na_2O \cdot 1.5SiO_2$ (CL1) and GPC-NaOH (CL2) under water contact conditions

White efflorescence products appear on the NaOH-activated specimens rapidly. Specimens derived from the three fly ashes that activated sodium silicate solution do not show visible efflorescence products in 48 h; however, the specimen GPB-$Na_2O \cdot 1.5SiO_2$ (MMS) shows efflorescence after 3 days. After 7 days a clear skin off at the efflorescence zone on MMS is observed. This shows that efflorescence affect the integrity of geopolymer, at least on the surface.

XRD Analysis

Figure 5 shows the XRD analysis of hardened geopolymers that synthesized from fly ash A.

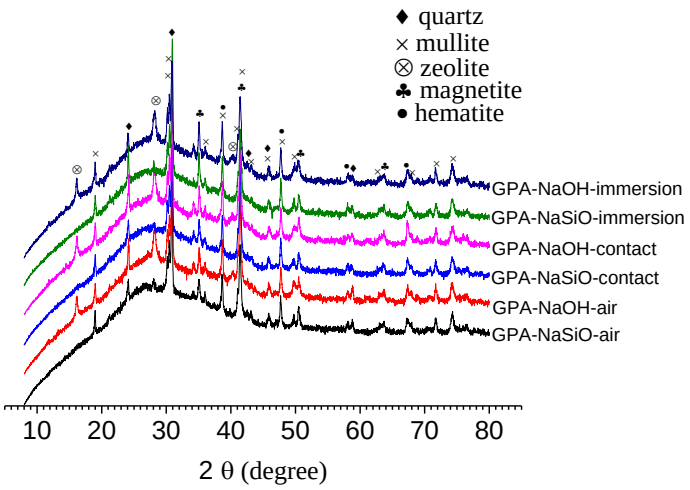

Figure 5. XRD patterns of geopolymers by different curing conditions

The patterns of either the binder activated by sodium silicate or the binder activated by NaOH solution do not show notable differences among the three curing conditions. It means that efflorescence and leaching have little influences on the mineral structure of the formed products. This result is in agreement with the previous research (Škvára et al. 2012), which has shown that the bond environments of Si and Al in framework did not change after leaching of sodium. It seems that the mechanical effect of efflorescence, rather than phase changing, accounts for the strength loss of NaOH-activated specimens and the slower strength development of sodium silicate-activated specimens under the efflorescence conditions than those under the ambient curing conditions.

CONCLUSIONS

Several very important findings, which have not been widely raised into consideration as significant issues in the academic and industrial sections, are reported in this study reports. They include: (1) efflorescence can take place rapidly when geopolymers are exposed to humid conditions, may be within 3 hours for some samples activated by alkali hydroxide solution; (2) efflorescence has negative effects on the compressive strength development and the compression modulus of geopolymers due to the mechanical influence to binder; and (3) from long term of view, the effects of efflorescence due to the contact of water could be worse than that of leaching, which the sample is fully immersed in water, particularly on the stability and integrity of geopolymer structures.

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