PROPERTIES OF FLY ASH BASED GEOPOLYMER FOR CURING AT AMBIENT TEMPERATURE

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ABSTACT

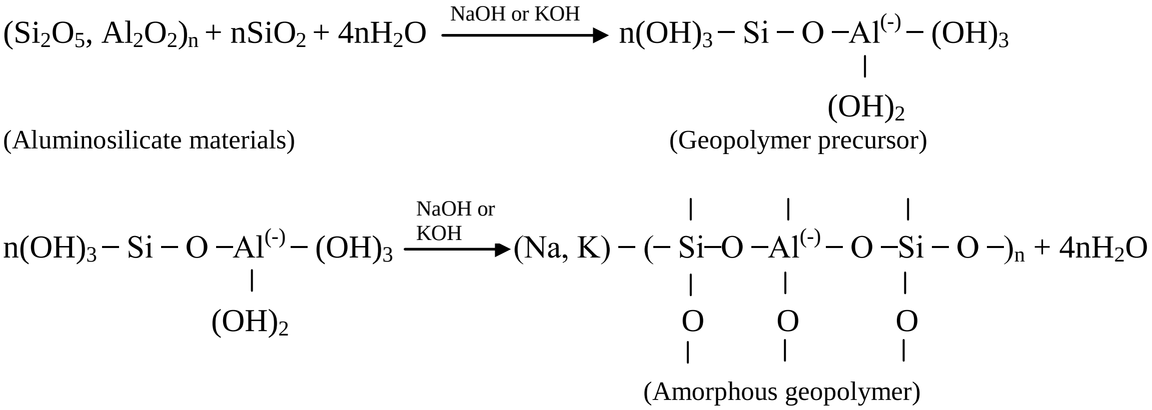
Geopolymer concrete is a promising material with regard to precast construction for the ease of parametric and curing control. Most of the studies available in the literature used heat curing to demonstrate the properties of geopolymer mixture. This study aimed to achieve fly ash-based geopolymer suitable for ambient curing condition and eliminate energy consuming heat curing process. Class F fly ash was used as the base material which was reacted by sodium hydroxide and sodium silicate solutions. Ground granulated blast furnace slag (GGBFS) and calcium hydroxide (CH) was added in different proportions to the mixture. Setting times of geopolymer pastes and compressive strength after curing at 20-23^{o}C were investigated. Results were compared with a control geopolymer mixture designed with fly ash alone as the binder. Inclusion of additives helped achieve setting time and compressive strength comparable to those of ordinary Portland cement (OPC). Setting time and compressive strength of geopolymers varied with the variation of alkaline activator to fly ash ratio. Generally, fly ash blended with slag or calcium hydroxide influenced the properties of geopolymer concrete cured at ambient temperature.

Keywords: Ambient Curing**,** Fly Ash, Geopolymer, Setting Time, Slag.

INTRODUCTION

Geopolymer is an inorganic polymer, which is gaining interest gradually in concrete technology due to its potential benefit over ordinary Portland cement concrete. The increasing demand of environment-friendly materials in construction compelled to find low energy consuming and low CO_2 emitting alternative binders by utilizing industrial by-product materials. In this respect, geopolymer binder can be a sustainable and economical building material as it is produced from industrial by-products such as fly ash replacing 100% of cement in concrete[1].

Geopolymer is produced as a result of activating various aluminosilicate materials with strong alkaline solution such as sodium hydroxide, potassium hydroxide, sodium silicate or potassium silicate. The source materials may include by-product materials like fly ash, metakaolin, blast furnace slag etc and materials of geological origin[2]. In the alkaline environment, aluminosilicate materials dissolve in the solution to form free SiO_4 and AlO_4 tetrahedral units. With the progress of the reaction, water is gradually removed, and the SiO_4 and AlO_4 tetrahedral units are linked together through the sharing of all oxygen atoms between two tetrahedral units to yield polymeric precursors[2]. Continuous linking of these precursors eventually forms amorphous geopolymer. The final products of geopolymerization are characterized by many factors regarding chemical composition of the source materials and alkaline activators[3, 4, 5]. The following reactions show a schematic of geopolymer material formation[2, 6].



$$(Si_2O_5, Al_2O_2)_n + nSiO_2 + 4nH_2O \xrightarrow{\text{NaOH or KOH}} n(OH)_3 - Si - O - \underset{\underset{(OH)_2}{|}}{Al^{(-)}} - (OH)_3$$

(Aluminosilicate materials) (Geopolymer precursor)

$$n(OH)_3 - Si - O - \underset{\underset{(OH)_2}{|}}{Al^{(-)}} - (OH)_3 \xrightarrow[\text{KOH}]{\text{NaOH or}} (Na, K) - (- \overset{|}{\underset{\underset{|}{\overset{|}{O}}}{Si}} - O - \overset{|}{\underset{\underset{|}{\overset{|}{O}}}{Al^{(-)}}} - O - \overset{|}{\underset{\underset{|}{\overset{|}{O}}}{Si}} - O -)_n + 4nH_2O$$

(Amorphous geopolymer)

Geopolymer binders exhibit similar or superior engineering properties compared to cement. Low-calcium fly ash (Class F) has been investigated as a suitable material for geopolymer for its wide availability, pertinent silica and alumina composition and less water demand. Fly ash based geopolymer concrete have shown good mechanical and durability properties both in short term and long term tests[7].

The polymerization process is dependent on curing temperature to a great extent. Generally, the polymerization is accelerated at higher temperature than ambient. Heat cured fly ash based geopolymer samples achieve higher strength in the early days as compared to those cured in ambient temperature[8]. Some researchers tried to enhance the reactivity of fly ash in alkaline environment by increasing the fineness of fly ash[9] and by adding some calcium containing materials. The amount of calcium oxide in the fly ash was found to have significant impact on the resulting hardened geopolymer. Calcium oxide is believed to take part in forming additional binding product such as calcium silicate hydrate (CSH), along with the aluminosilicate geopolymer gel[5, 10]. With the increase of calcium oxide content, compressive strength increases and setting time decreases[3]. However, the geopolymerization process and the resulting products may also be influenced by the type and properties of calcium sources and activating alkaline solution[5]. Recently, the suitability of fly ash based geopolymers mixed with silica fume, metakaolin[11] and blast furnace slag[12] has been studied by several researchers. However, most of the findings were reported for samples cured in temperature higher than ambient for variable lengths of time.

This study aimed to produce geopolymer mixtures suitable for ambient curing condition. Ground granulated blast furnace slag and calcium hydroxide were added with low calcium fly ash to study the setting time and the compressive strength properties of geopolymer mortar.

EXPERIMENTAL PROGRAM

MATERIALS

Locally available materials were used to produce geopolymer mortar. The primary binder fly ash (Class F as per ASTM C 618[13]) was obtained from a Western Australian power plant. Commercially available ground granulated blast furnace slag (GGBFS) and general laboratory reagent grade calcium hydroxide (CH) were used as additives with fly ash. The chemical compositions of fly ash and GGBFS are shown in Table 1. A mixture of sodium hydroxide and sodium silicate solutions was used as the activator solution. Sodium hydroxide solution was prepared in the laboratory by mixing 97-98% pure pellets of NaOH with tap water. Sodium silicate solution was collected from a local producer. It has the ratio of SiO_2 to Na_2O by mass of 2.69 (SiO_2 = 30.7%, Na_2O = 11.4% and water = 57.9%). Natural sand with nominal maximum size of 1.18 mm (0.0465 inch) was used as fine aggregate. Physical properties and size distribution of aggregates are presented in Table 2.

Table 1: Chemical composition of fly ash and GGBFS.

Sample	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**SO_3**	**P_2O_5**	**TiO_2**	**LOI[a]**
Fly ash (%)	50.00	28.25	13.50	1.79	0.89	0.32	0.46	0.38	0.98	1.54	0.64
GGBFS (%)	32.46	14.30	0.61	43.10	3.94	0.24	0.33	4.58	0.02	0.55	0.09

[a] Loss on ignition

Table 2: Properties of fine aggregate.

Properties	**Result**						
Sieve analysis	Sieve, mm (mesh no.)	4.75 (4)	2.36 (8)	1.18 (16)	0.60 (30)	0.30 (50)	0.15 (100)
	Percent passing	100.0	100.0	99.7	77.2	24.2	2.7
Fineness modulus	1.96						
Specific gravity (SSD)	2.62						
Absorption (%)	0.99						
Unit weight, kg/m^3 (lb/yd^3)	1687 (2844)						

Table 3: Mixture proportions of geopolymer mortar.

Mix no.	**Quantity (kg/m^3)**[*]						**Molar ratio**			**w/s**[d]
	Sand	**Fly ash**	**Slag**	**CH**[a]	**SS**[b]	**SH**[c]	**Na_2O/ SiO_2**	**H_2O/ Na_2O**	**Si/Al**	
GM1 (A40 S00 R2.5)	1178	730	0	0	208.6	83.4	0.118	11.73	1.765	0.2
GM2 (A40 S10 R2.5)	1178	657	73	0	208.6	83.4	0.121	11.75	1.802	0.2
GM3 (A40 S20 R2.5)	1178	584	146	0	208.6	83.4	0.125	11.76	1.842	0.2
GM4 (A40 C2 R2.5)	1178	715.4	0	14.6	208.6	83.4	0.120	11.98	1.771	0.2
GM5 (A40 C3 R2.5)	1178	708.1	0	21.9	208.6	83.4	0.121	12.10	1.773	0.2
GM6 (A35 C2 R2.5)	1214.5	715.4	0	14.6	182.5	73.0	0.108	11.93	1.737	0.178

[*] 1 kg/m^3 = 1.686 lb/yd^3; [a] Calcium hydroxide; [b] Sodium silicate solution; [c] Sodium hydroxide solution; [d] Water to solid ratio.

MIXTURE PROPORTIONS

The geopolymer mortar mixtures were proportioned with constant total binder content while the percentage of slag and CH varied in different mixtures. The mixture proportions are presented in Table 3. The proportions of ingredients were designed assuming the final unit weight of dry mortar as 2200 kg/m^3 (3710 lb/yd^3). The total binder content constitutes one-third of the total mixture. Mixture GM1 was the control mixture designed with only fly ash as the binder. Mixture GM2 and GM3 were designed by replacing 10% and 20% of fly ash with GGBFS respectively. Mixture GM4 and GM5 were designed by replacing 2% and 3% of fly ash with CH respectively. All the mixtures were proportioned with the alkaline activator to total binder ratio of 0.4, except mix GM6 which had a ratio of 0.35. No extra water or superplasticizer was added to the mixtures. Other variables of the mixtures remained constant as follows: the ratio of sodium silicate to sodium hydroxide solution was 2.5 and the concentration of sodium hydroxide solution was 14 Molar for every mixture. To Prepare 14 Molar sodium hydroxide solution, 0.56 kg (1.23 lb) of NaOH pellet was mixed in water for one liter of the solution.

The geopolymers were labeled with their variable constituents in the mixture, as shown in the parenthesis in the first column of Table 3 and in all subsequent graphs. The symbols indicate as follows: alkaline activator solution (A), slag (S), calcium hydroxide (C) and the ratio of sodium silicate to sodium hydroxide solution (R). For example, A40 S10 R2.5 represents a geopolymer mixture having alkaline activator solution (A) as 40% of total binder, slag (S) as 10% of total binder and the ratio of sodium silicate to sodium hydroxide solutions (R) as 2.5.

Geopolymer pastes were prepared to determine setting time of the corresponding mixtures. The mixture proportions of these pastes are similar to those of the mortar mixtures but with the fine aggregates excluded.

MIXING AND CURING

The alkaline activator solution was prepared about 30 minutes before actual mixing to enhance reactivity of the solution. The sodium hydroxide solution and sodium silicate solution of desired quantity were mixed together in the laboratory and left in the room temperature. Mortars were mixed manually in a laboratory pan. Saturated surface dry (SSD) sand and the binders (fly ash and slag or CH) were dry mixed thoroughly before adding the activator solution. Premixed alkaline activator solution was then added gradually and mixing was continued for another 4 to 6 minutes until a consistent mixture was obtained. Cube samples (50×50×50 mm^3) were cast with geopolymer mortar mixture in two layers. The moulds were then stored in a controlled temperature of 20-23^oC without covering the exposed surface. 24 hours after casting, samples were de-molded and cured in air at 20-23^oC and relative humidity 65±5% until tested to ensure a consistent environment for all samples rather than a variable ambient condition. The control geopolymer mixture was de-molded 3 days after casting, as it was too soft to remove from mold after 24 hours due to its slow setting time in ambient temperature.

TESTING OF SPECIMENS

Flow of fresh geopolymer mortars were measured in accordance with ASTM C1437-07[14]. Compressive strength test was conducted at 3, 7 and 28 days. Cube specimens (50×50×50 mm^3) were tested at a loading rate of 0.33 MPa/s.

To determine setting time of geopolymer pastes, ASTM C 191-08[15] standard was followed. The test was conducted in a temperature of 21-23^oC. The paste was prepared by mixing the binders and the alkaline solutions manually in a bowl and cast into the conical mould of Vicat apparatus. Penetration of Vicat needle (1.00 ± 0.05 mm in diameter) in the paste was measured at regular intervals. Initial setting time was measured by plotting the graph of penetration against time and interpolating the time for 25 mm penetration. The final setting time of the paste was also recorded when the needle left negligible mark on the surface of the paste.

RESULTS AND DISCUSSION

A total of six mixtures were designed to study the effect of slag and calcium hydroxide additives on the compressive strength and setting time of fly ash based geopolymer mortar at ambient temperature. The results of the control mixture GM1 were compared with those of the mixtures having slag (GM2 and GM3) and CH (GM4 and GM5). Mix GM6 was compared with the mix GM4 to determine the effect of the amount of alkaline activator in the mixture.

PROPERTIES OF FRESH GEOPOLYMER MORTAR

The geopolymer mortars prepared in this study contained no extra water other than that in the alkaline solution and the moisture in the saturated surface-dry sand. The combined alkaline solution had a high content of sodium silicate which is a viscous liquid. When the solution is mixed with sand and fly ash, it forms a sticky paste for mixtures with relatively low liquid to solids ratio. It may stick to the mixer bowl and make it difficult to produce a uniform mix. Hence, mixing of the ingredients was done manually to obtain a uniform mixture. The final mixture was highly cohesive in nature. Fig. 1 shows a mortar mixture immediately after mixing. It slowly flowed towards gravity and showed a

Fig. 1 Fresh geopolymer mortar mixture immediately after mixing.

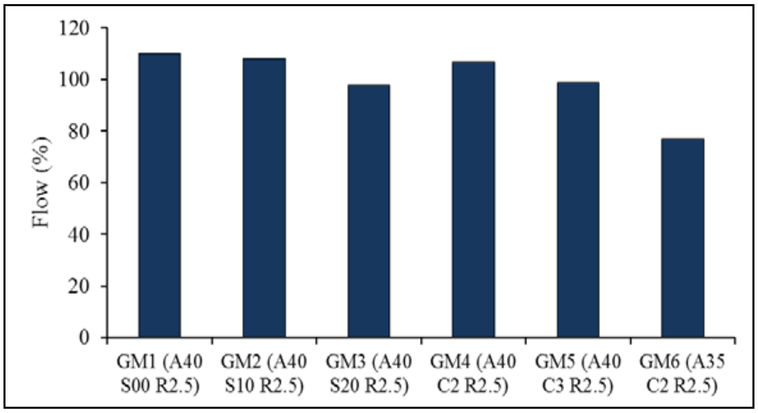


Fig. 2 Flow measurement results of different mortar mixtures.

viscous property. However these properties varied with the inclusion of slag and with the variation of the alkaline liquid content. Fig. 2 shows the results of the flow test of the mixtures. The flow ability of the mixture usually decreased with the increase of slag (GM2 and GM3). This can be attributed to the increase of inter-particle sliding resistance due to incorporation of slag. Flow also decreased with the addition of CH (GM4 and GM5) and with the decrease of alkaline liquid in the mixture (GM6). To improve workability, extra water or superplasticizer can be added; however this is likely to affect the mechanical properties of the hardened mortar.

SETTING TIME OF GEOPOLYMER PASTES

Fly ash based geopolymers generally have much longer setting time at ambient temperature as compared to ordinary Portland cement paste. This is because of its slow rate of chemical reaction at low temperature. In this study, the setting time tests were carried out in a controlled temperature of 21-23°C and relative humidity 65±5%. Fig. 3 depicts the variation of setting time of different pastes. The control mixture GM1 which was designed with only fly ash as the binder did not reach initial setting even in 24 hours. Setting time of geopolymer pastes decreased significantly when slag and CH were used in the mix together with fly ash as a part of the total binder. Both initial and final setting time decreased with the increase of slag or CH content. Mixtures GM2 and GM3 having 10% and 20% slag of total binder respectively achieved initial setting time of 290 minutes and 94 minutes, respectively. These values are comparable to those usually obtained for ordinary Portland cement pastes. Accelerated rate of setting was also observed in the mixtures incorporating slag (GM2 and GM3), as the difference between the initial and final setting time reduced with the increase of slag content in the paste. Thus, the results show that slag as a part of fly ash binder is an effective additive to accelerate setting time of geopolymer concrete cured in ambient temperature.

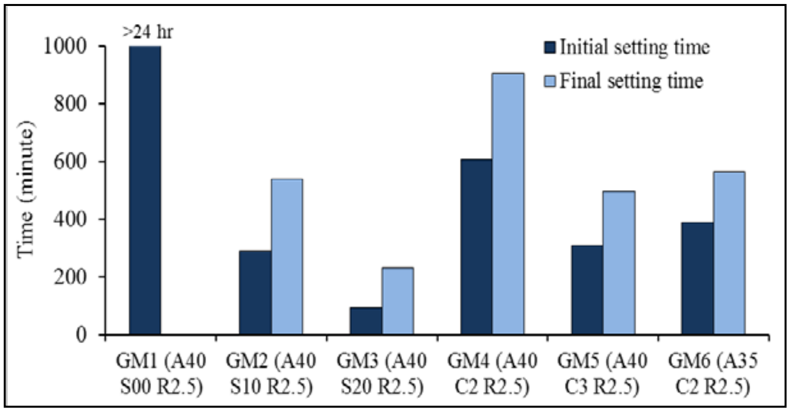


Fig. 3 Comparison of the setting times of different geopolymer pastes.

The presence of CH also improved the setting time of fly ash based geopolymer paste. Mixtures designed with 2% and 3% CH (GM4 and GM5, respectively) achieved enhanced rate of setting when compared to the control mix GM1. Mixture GM5 had only 1% more CH than mixture GM4 but had an initial setting time 50% less than that of mixture GM4. Hence, the quantity of CH as an additive in the fly-ash based geopolymer has a remarkable impact on setting time of the mixture when other variables remain constant.

Setting time was also influenced by the alkaline activator solution to binder ratio. As shown in Fig. 3 mixture GM4, having 5% more alkaline liquid than mixture GM6, required more time for initial as well as final setting. This is due to higher water to solid ratio (w/s) of mixture GM4 for increased alkaline solution in the mixture. Higher water content caused deceleration of the condensation process of geopolymerization.

COMPRESSIVE STRENGTH OF GEOPOLYMER MORTAR

Compressive strength test of ambient air cured (21-23^{o}C and relative humidity 65±5%) geopolymer mortars were conducted up to 28 days. Fig. 4 shows the variation of 28-day compressive strength of the mixtures. Strength development was compared for the mixtures containing slag and CH with the control mixture GM1 in Fig. 5 and Fig. 6 respectively. The results shown in the following figures are the mean value of three specimens tested at the test age.

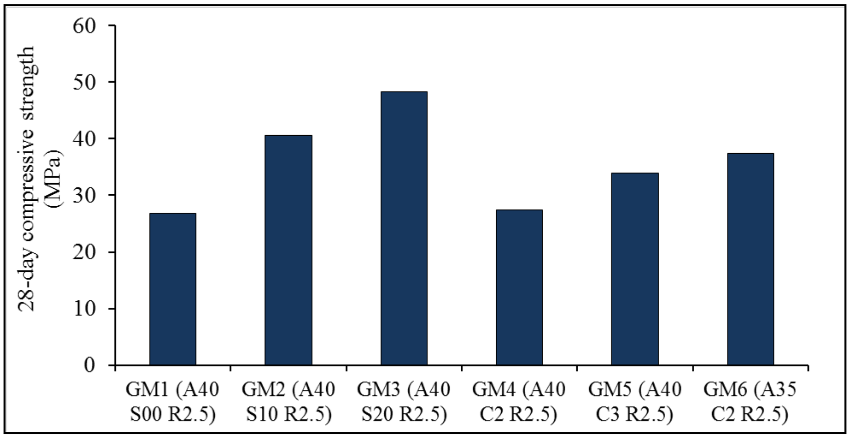


Fig. 4 Variation of 28-day compressive strength of different geopolymer mortars. (1 MPa = 0.145 ksi)

The control geoploymer mixture with fly ash alone as the binder (mixture GM1) generally reacts slowly in ambient temperature (20-23^{o}C) which leads to very low compressive strength in early age. Although the strength development can be accelerated by heat curing, the present study focused on the strength development in ambient temperature. Hence the strength measurement was started from 3 days. When GGBFS was used up to 20% of total binder in the mixture (GM2 and GM3) with constant alkaline activator, the strength increased significantly. Higher strength was achieved from the early age of 3 days with the increase of slag content in the mixtures (Fig. 5). At 28 days, mixtures GM2 and GM3 achieved 1.5 and 1.8 times higher strength as compared to the strength of control geopolymer mixture GM1, for adding 10% and 20% GGBFS, respectively. The enhancement of strength of fly ash and slag blended geopolymer can be attributed to the generation of aluminosilicate hydrate (A–S–H) and calcium silicate hydrate (C–S–H) gels which are the reaction products from both alkali activated fly ash and slag[16]. The higher Si/Al ratio of slag incorporated mixtures may also contribute to fast condensation and strength development.

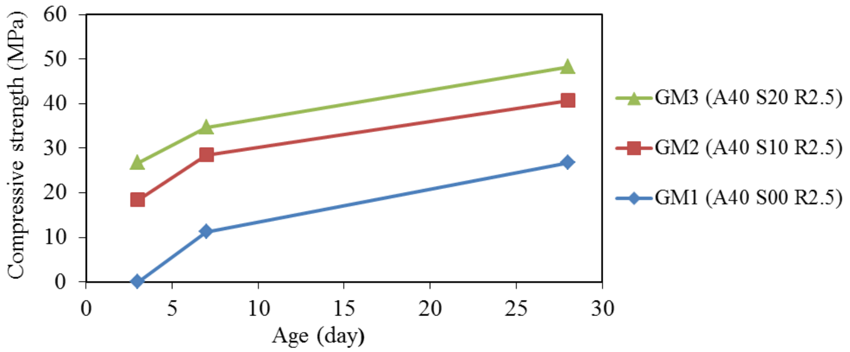


Fig. 5 Development of compressive strength of the geopolymer mortars having different percentage of GGBFS. (1 MPa = 0.145 ksi)

Incorporation of CH in small quantities also contributed to increase the strength of geopolymer mortars. From Fig. 6 it is clear that, additional CH in the mixture improved the early-age strength significantly at 3 and 7 days. At 28 days, mixture GM4 - with 2% CH, reached a strength similar to that of control concrete, GM1, and mixture GM5 - with 3% CH, achieved 26% higher strength than the control concrete (GM1). Being insoluble, the additional CH could precipitate early in the paste matrix which augments the setting rate and strength development. The coexistence of both aluminosilicate and C–S–H phases in the CH included pastes at room temperature was also found to contribute to the strength[17].

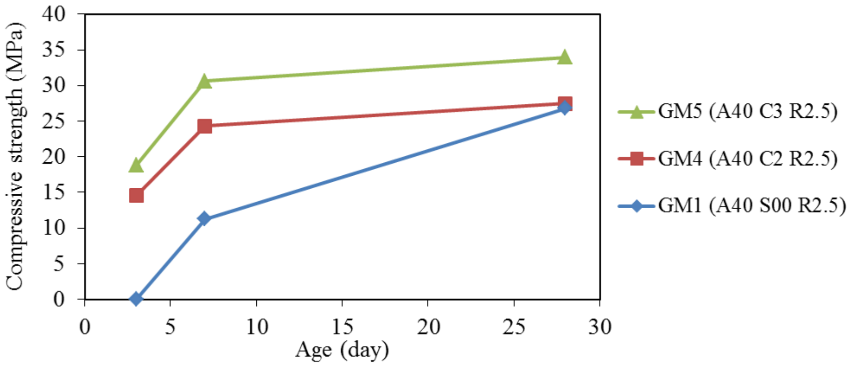


Fig. 6 Development of compressive strength of the geopolymer mortars having different percentage of calcium hydroxide. (1 MPa = 0.145 ksi)

The ratio of alkaline activator to total binder in the mixture also influences the compressive strength. Comparing the results of mixtures GM4 and GM6 it can be seen that, the mixture GM6 having alkaline activator to total binder ratio of 0.35 achieved higher strength than GM4 having 0.4 (Fig. 7). Both of these mixtures had similar quantity of CH (2%) and constant sodium silicate to sodium hydroxide ratio. The mixtures GM4, though had higher Si/Al ratio, was also associated with higher w/s ratio than mixtures

GM6. Hence, the quantity of water present in the mix influenced the strength development at ambient temperature. This is similar to the effect of water-cement ratio in OPC concrete; however, further investigation is required to establish the trend.

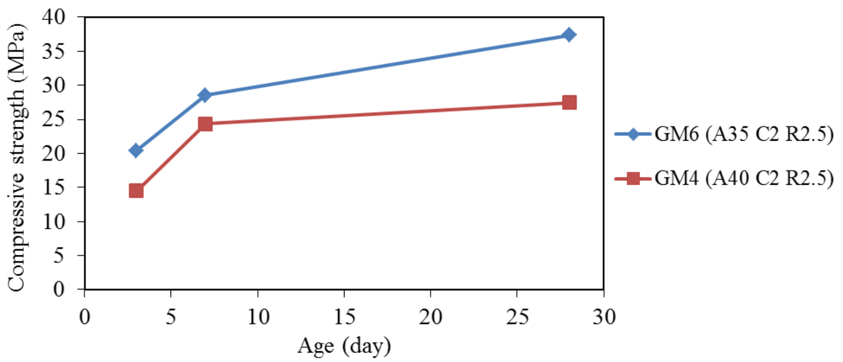


Fig. 7 Effect of alkaline activator to total binder ratio. (1 MPa = 0.145 ksi)

CONCLUSION

Six geopolymer mixtures were designed with fly ash as the primary binder. Slag and calcium hydroxide (CH) were added to the mixtures to enhance reactivity of fly ash based geopolymer in ambient temperature. Setting time and compressive strength of geopolymers were compared for the variation of slag and CH content with a control mixture. The results can be summarised as follows:

- Geopolymer mixture, when mixed without any extra water and superplasticizer, is very cohesive and sticky in nature. Addition of slag increases the cohesiveness further and decrease the workability.
- When compared to control geopolymer mixture, the mixtures having slag and CH have achieved quicker setting time which is comparable to that of OPC. The rate of setting increased with the increase of slag up to 20% and CH up to 3% of total binder.
- Adding slag up to 20% of the total binder achieved compressive strength up to 48 MPa (6.96 ksi) at 28 days. When CH was added up to 3% the strength reached up to 34 MPa (4.93 ksi). However the strength can be enhanced further by adjusting alkaline activator content, as higher strength was achieved with 35% alkaline activator of the total binder as compared to that with 40%.

Finally, geopolymer modified with GGBFS or CH could be a suitable material for low to moderate strength precast concrete production at ambient curing condition, as it eliminates the necessity of heat curing. For high early strength requirements, heat curing can be applied for a limited period. However additional research is required to establish mixture proportions suitable for precast concrete cured at low ambient temperatures.

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REFERENCES

1. Juenger, M. C. G., Winnefeld, F., Provis, J. L., and Ideker, J. H., “Advances in alternative cementitious binders,” *Cement and Concrete Research*, V. 41, No. 12, 2010, pp. 1232-1243.
2. Davidovits, J., *Geopolymer Chemistry and Application*. 2nd edn, Institut Géopolymère, Saint-Quentin, France, 2008.
3. Diaz, E. I., Allouche, E. N., and Eklund, S., “Factors affecting the suitability of fly ash as source material for geopolymers,” *Fuel*, V. 89, 2010, pp. 992–996.
4. Duxson, P., Ferna´ndez-Jime´nez, A., Provis, J. L., Lukey, G. C., Palomo, A., and van Deventer, J. S. J., “Geopolymer technology: the current state of the art,” *Journal of Materials Science,* V. 42, No. 9, 2007, pp. 2917–2933.
5. Yip, C. K., Lukey, G. C., Provis, J. L., and van Deventer, J. S. J., “Effect of calcium silicate sources on geopolymerization,” *Cement and Concrete Research,* V. 38, 2008, pp. 554–564.
6.van Jaarsveld, J. G. S., van Deventer, J. S. J., and Lorenzen, L., “The potential use of geopolymeric materials to immobilize toxic metals: Part I. Theory and application”, *Mineral Engineering*, V. 10 (7), 1997, pp. 659-669.
7. Wallah, S. E., and Rangan, B. V., *Low-calcium fly ash-based geopolymer concrete: long-term properties.* Research Report GC 2, Faculty of Engineering, Curtin University of Technology, Perth, Australia, 2006.
8. Vijai, K., Kumutha, R., and Vishnuram, B. G., “Effect of types of curing on strength of geopolymer concrete,” *International Journal of the Physical Sciences,* V. 5, No. 9, 2010, pp. 1419-1423.
9. Somna, K., Jaturapitakkul, C., Kajitvichyanukul, P., and Chindaprasirt, P., “NaOH-activated ground fly ash geopolymer cured at ambient temperature”, *Fuel*, V. 90, No. 6, 2011, pp. 2118-2124.
10. Granizo, M. L., Alonso, S., Blanco-Varela, M. T., and Palomo, A., “Alkaline activation of metakaolin: effect of calcium hydroxide in the products of reaction,” *Journal of American Ceramic Soceity*, V. 85, 2002, pp. 225–231.
11. Wu, H. C., and Sun, P., “Effect of mixture compositions on workability and strength of fly ash-based inorganic polymer mortar,” *ACI Materials Journal,* V. 107, No. 6, 2010, pp. 554-561.
12. Guerrieri, M., and Sanjayan, J. G., “Behavior of combined fly ash⁄slag-based geopolymers when exposed to high temperatures,” *Fire and Materials,* V. 34, 2010, pp. 163–175.
13. ASTM C 618, *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete,* ASTM International, West Conshohocken, PA, 2008.
14. ASTM C 1437-07, *Standard test methods for flow of hydraulic cement mortar,* ASTM International, West Conshohocken, PA, 2008.

15. ASTM C 191-08, *Standard test methods for time of setting of hydraulic cement by Vicat Needle*, ASTM International, West Conshohocken, PA, 2008.
16. Kumar, S., Kumar, R., and Mehrotra, S. P., “Influence of granulated blast furnace slag on the reaction, structure and properties of fly ash based geopolymer”, *Journal of Materials Science*, V. 45, 2010, pp. 607–615.
17. Dombrowski, K., Buchwald, A., and Weil, M., “The influence of calcium content on the structure and thermal performance of fly ash based geopolymers”, *Journal of Materials Science*, V. 42, 2007, pp. 3033–3043.