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Early age properties of low-calcium fly ash geopolymer concrete suitable for ambient curing

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Abstract

Geopolymer is a promising alternative binder to Portland cement. It is produced mostly from by-product materials such as fly ash and blast furnace slag; hence recognised as a low-emission alternative binder for concrete. Recent studies have shown that the properties of geopolymers are similar or superior to those of the OPC binder that is traditionally used for concrete. Most of the previous studies employed heat curing for setting and hardening of fly ash geopolymer mixtures. Heat curing process requires special arrangements which is energy-consuming and may not be feasible to apply in cast-in-situ concreting. Therefore, development of geopolymer mixtures suitable for curing at normal temperature will widen its application. This paper presents a study on low calcium fly ash based geopolymer concrete cured in ambient temperature (23°C) without additional heat. Small amount of additives were added with fly ash to accelerate the early-age reaction. Setting times of geopolymer pastes, and workability and compressive strength of geopolymer mortar were studied. The effects of the additives and binder content in the mixtures were determined from experimental results. The results show that inclusion of additives with fly ash significantly enhanced the early age properties. Setting time reduced to reasonable values and compressive strength increased to enable early de-moulding of specimens. Compressive strength increased with the increase of binder content. However, workability results showed an optimum binder content for the fly ash geopolymer blended with the additives. The results suggest that suitable geopolymer mixtures can be designed for ambient curing with low calcium fly ash and the additives as partial replacement.

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1. Introduction

Geopolymer concrete (GPC) is a potential material for structural application as an alternative of ordinary Portland cement (OPC) concrete. It can play a significant role in green concrete technology by eliminating cement and utilizing various by-product materials such as fly ash and blast furnace slag [1]. Studies conducted over the last decades indicated potential benefits of fly ash based geopolymer over OPC concrete [2, 3]. It has been reported that, low calcium fly ash based geopolymer concrete achieved excellent mechanical and durability properties, when cured in high temperature [4, 5, 6].

Geopolymer is an inorganic polymer, which is produced from various alumino-silicate materials reacted by alkaline solutions. The alumino-silicate source materials include by-product materials like fly ash, and blast furnace slag and materials of geological origin such as metakaolin [7]. The general concept of geopolymerisation can be explained with three distinct reactions: (a) destruction-coagulation; (b) coagulation-condensation; and (c) condensation-crystallisation [8, 9].

The polymerisation reaction is dependent on many factors such as the chemical composition of the binder and the alkaline solution, curing condition and water content. Curing temperature has a significant effect on the microstructural and mechanical strength development of geopolymer system. Generally, the polymerisation is accelerated at higher temperature than ambient. Since fly ash based geopolymer paste reacts slowly at low ambient temperature as compared to heat cured samples [10], these mixtures are usually subjected to mild curing temperatures ranging from 30°C to 85°C and high relative humidity of about 95% [11, 12]. Curing time also varied from several hours to several days and requires additional conditioning at ambient temperature.

The amount of calcium content in the fly ash was found to have significant impact on the resulting hardened geopolymer. Calcium oxide is believed to form calcium silicate hydrate (CSH), along with the aluminosilicate geopolymer gel [13, 14, 15]. Notable studies reported on the fly ash geopolymer blended with some additional materials [16]. The amount of internal and external calcium in the fly ash was found to have significant impact on the resulting geopolymer [17]. The suitability of fly ash based geopolymers mixed with silica fume, metakaolin [14] and blast furnace slag [15] has been studied by several researchers. Temuujin et al. [18] showed that, addition of calcium oxide and calcium hydroxide as a replacement of fly ash improved mechanical properties for ambient cured samples and decreased properties for the 70°C cured samples. Fly ash based geopolymer has also been reported to improve by enhancing the reactivity of fly ash; i.e. by increasing the fineness [19]. However, the geopolymerisation process and the resulting products may also be influenced by other factors such as, the type and properties of aluminosilicate sources and composition of alkaline solution [9, 13, 20].

It should be noted that, most of the geopolymer concrete tested so far was either heat cured or steam cured at higher temperature than ambient. While such concrete can be precast easily, it is not always practicable in cast-in-situ applications due to delayed setting and slow strength development in ambient condition. Hence it is necessary to investigate the properties of geopolymer concrete suitable for ambient curing condition. This study aimed to improve the mixtures of low calcium fly ash based geopolymer that can be cured in ambient condition without elevated heat. Fly ash was replaced partially with ground granulated blast furnace slag, OPC and calcium hydroxide to enhance the chemical composition facilitating alkaline reaction. The effect of various additives and total binder content was investigated on the early age properties of geopolymer mortar.

2. Experimental program

2.1. Materials

A low-calcium fly ash (Class F as per ASTM C 618), sourced from a Western Australian power plant, was used as the primary binder material. The additives were commercially available ground granulated blast furnace slag (GGBFS), ordinary Portland cement (OPC) and calcium hydroxide (CH). The chemical compositions of fly ash, GGBFS and OPC are given in Table 1. Calcium hydroxide, also known as slaked lime, was of laboratory reagent grade which contained about 99% pure anhydrous $\text{Ca}(\text{OH})_2$. A combination of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) solutions was used as the alkaline solution. Sodium hydroxide solution was prepared in the laboratory by mixing 97-98% pure NaOH pellets with normal tap water. Sodium silicate solution, collected from a

local producer, has the mass ratio of SiO₂ to Na₂O of 2.64 (SiO₂ = 30.1%, Na₂O = 11.4% and water = 58.5%). Natural sand with nominal maximum size of 1.18 mm was used as fine aggregate for the mortar mixtures.

Table 1. Chemical composition of fly ash, GGBFS and OPC.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	P ₂ O ₅	TiO ₂	Loss on Ignition
Fly ash (%)	53.71	27.20	11.70	1.90	-	0.36	0.54	0.30	0.71	1.62	0.68
GGBFS (%)	29.96	12.25	0.52	45.45	-	0.31	0.38	3.62	0.04	0.46	2.39
OPC (%)	21.10	4.70	2.70	63.60	2.60	0.50	-	2.50	-	-	2.00

2.2. Mixture compositions

Four mixtures were prepared using fly ash and the additives. Table 2 shows the mixture proportions. Mixtures F00 is the control mixture which contained no additive with fly ash and mixtures S10, P08 and C02 contained 10% GGBFS, 8% OPC and 2% CH of total binder (fly ash + additives) respectively. Alkaline liquid was used as 40% of the total binder. The ratio of sodium silicate to sodium hydroxide solutions was constant at 2.5. The concentration of sodium hydroxide was 14 Molar in all the mixtures.

To investigate the effect of binder content on the early age properties, six other mixtures were prepared with varying binder content from 450 kg/m³ to 730 kg/m³. The total alkaline liquid content was kept constant for these mixtures. No extra water or superplasticizer was added to the mixtures.

Setting time of the geopolymer mixtures was tested using the paste samples. The paste mix was prepared with same proportions of the mortars shown in Table 2, but with the fine aggregates excluded.

Table 2. Mixture proportions of geopolymer mortar.

Mix ID	Binder	Quantity (kg/m ³)					Water/ solid	Na ₂ O/SiO ₂
		Sand	Fly ash	Additives	Na ₂ SiO ₃	NaOH		
F00	100% Fly ash	1178	730	0			0.200	0.118
S10	90% Fly ash + 10% GGBFS	1178	657	73			0.200	0.121
P08	92% Fly ash + 8% OPC	1178	671.6	58.4			0.200	0.117
C02	98% Fly ash + 2% Ca(OH) ₂	1178	715.4	14.6			0.200	0.120
P450		450 kg/m ³	1458	405	45		0.301	0.173
P500		500 kg/m ³	1408	450	50		0.277	0.159
P550		550 kg/m ³	1358	495	55		0.256	0.148
P600	90% Fly ash + 10% OPC	600 kg/m ³	1308	540	60	208.6	83.4	0.238
P650		650 kg/m ³	1258	585	65		0.223	0.130
P730		730 kg/m ³	1178	657	73		0.202	0.118

2.3. Casting and curing of samples

The alkaline solution was prepared by mixing the sodium hydroxide and sodium silicate solutions together and left in room temperature to cool down prior to mixing with the solids. Mortars were mixed in a laboratory pan mixer. Saturated surface dry (SSD) sand and the binder solids were mixed thoroughly. Then the alkaline solution was added and mixed properly for another 5-6 minutes. Cube samples (50×50×50 mm³) of mortars were cast for compressive strength tests. The moulds were filled in two layers and compacted manually by using a temping rod.

The moulded samples were then cured in room condition (temperature of 23°C and relative humidity of 70 ± 10%). Once hardened, the specimens were de-moulded after 24 hours of casting except for mixture F00, which were de-moulded at three days of age. The specimens of this mix did not harden for de-moulding at one day due to very slow setting in ambient temperature. After removing from moulds, the samples were left in room environment (23°C and

relative humidity $70 \pm 10\%$) until tested to ensure a consistent environment for all samples rather than different ambient conditions.

2.4. Test methods

The geopolymer mixtures were tested for setting time, workability and compressive strength. Workability of fresh mortar was determined by measuring the flow values in accordance with the method of ASTM C 1437-07 [21]. Compressive strength test of cube specimens ($50 \times 50 \times 50 \text{ mm}^3$) was conducted at a loading rate of 0.33 MPa/s. To determine setting time of geopolymer pastes, a Vicat apparatus was used as per ASTM C 191-08 [22]. The test was conducted in a temperature of 21-23°C.

3. Results and discussions

3.1. Effect of the additives in fly ash geopolymer

The results of the mixtures S10, P08 and C02 designed with GGBFS, OPC and CH respectively show the effects of these additives in the fly ash based geopolymer. The results of these mixtures were compared with those of the control geopolymer mixture (F00) containing fly ash alone as the binder. Figures 1 and 2 show the effects of the additives on the workability, setting time and compressive strength development of geopolymer mixtures.

It can be seen from Fig. 1(a) that the flow of mortar was influenced by the inclusion of additives in the matrix. Though all the mixtures were mixed with the same quantity of alkaline solution, the control geopolymer mixture F00 showed the highest flow value. The flow values decreased noticeably when either 10% GGBFS or 8% OPC was added with fly ash. However, the effect was negligible when 2% CH was added with fly ash.

Fly ash based geopolymer pastes generally take significantly long time to set due to slow rate of chemical reaction at low ambient temperature [5, 10]. At the temperature of 21-23°C, the control geopolymer paste F00 required more than 24 hours to set. When the additives were incorporated in the mixture, setting time of geopolymer pastes reduced significantly to the comparable value of OPC pastes (Fig. 1b). Both initial and final setting time decreased for the mixes blended with an additive. The mixtures having 10% GGBFS and 8% OPC showed the initial setting time of 203 min and 110 min respectively, while mixture having 2% CH achieved initial setting at 607 min. The rate of setting depended on the type of additives and accelerated with the increase of calcium content in the additives as seen in previous studies [23, 24]. This is due to the enhanced reaction of calcium compounds in the binder. The results establish that inclusion of these additives as a part of the binary blended binder is effective to accelerate the setting of fly ash based geopolymer concrete in ambient curing condition.

The compressive strength developments of mortar samples are shown in Fig. 2. It is evident that the geopolymer mixture having fly ash alone as the binder (F00) reacted very slowly to develop strength when cured in ambient condition (23°C). The mixture did not set in one day and showed no substantial strength after three days. When the additives were incorporated in the mixture with unaltered alkaline liquid (40%) and the SS/SH ratio of 2.5, considerable strength was observed at the age of one day (Fig. 2). At age of as early as one day, the mortar mixtures S10, P08 and C02 gained 10.5, 8.0 and 3.6 MPa respectively. Compressive strength of these mixtures exceeded 17 MPa at 3 days, in contrast of the strength of control mixture (F00) which was negligible at the same age. At 28 days, the geopolymer mixtures blended with the additives showed slightly higher compressive strength than that of F00. However strength after 90 days was almost similar for all the mixtures.

Since all the mixtures had same quantity of alkaline liquid and total binder, it is clearly the binder composition that influenced the reaction and the material properties. The quick early strength development of the blended mixtures can be attributed to the reaction of additional calcium bearing compound present in the additives. The improvement of strength is due to the modified binder which constituted reaction products from both alkali-reacted fly ash and the additives.

Thus, the results suggest that fly ash based geopolymer can be modified with additives such as GGBFS, OPC and CH to develop desired early age properties when cured in normal ambient condition. However, the amount of additives governs the rate of setting as well as workability of the mixture.

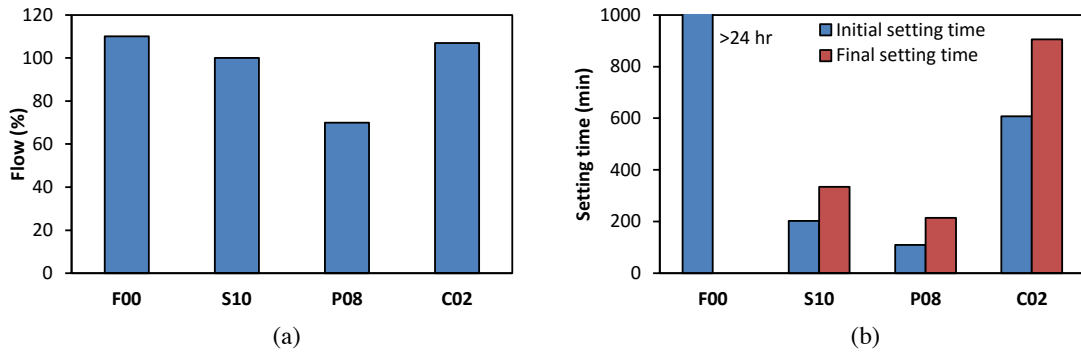


Fig. 1. Effect of different binder on the workability (a) and setting time (b) of geopolymers mixtures.

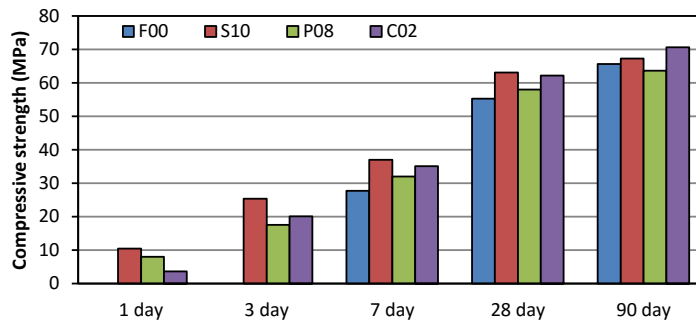


Fig. 2. Effect of different binder on the compressive strength development of geopolymers mixtures.

3.2. Effect of the binder content

Figure 3 shows the results of flow and compressive strength of the mixtures having variable binder content in the range of 450 to 730 kg/m³. Flow values generally increased with the increase of binder content up to 550 kg/m³, after which no significant improvement was seen due to increase of binder (Fig. 3a). A lower value of flow is recorded for having 730 kg/m³ binder than those having lesser binder content. The results indicate that for the given constant amount of alkaline liquid workability is governed by the other ingredients of the mixture. At low binder contents, although the water to solid ratio (*w/s*) increased (Table 2), the relative amount of aggregate (sand) was significantly higher than the binder and caused hindrance to the flow of mortar. On the other hand, at the higher binder contents, the stiffness and viscous nature of paste is believed to resist the flow. Hence, the amount of aggregate and binder need to be adjusted to increase the workability. For the 10% OPC-blended mortar mixes studied, the most flow value (>100%) was obtained when the ratio of total binder to aggregate was between 0.41 to 0.52 and the ratio of alkaline solution to total binder was between 0.45 to 0.53.

The compressive strength development of the mixtures from 3 days to 180 days is shown in Fig. 3(b). It is clear that compressive strength increased proportionately with the increase of binder content in the studied range. Strength at 28 days increased gradually from 26 MPa for 450 kg/m³ to 58 MPa for 730 kg/m³ binder. Strength of the mixtures with less binder content achieved less strength despite having higher Na₂O/SiO₂ ratio. This is due to excess liquid content and inadequate binder materials to bind the increased amount of aggregates in the matrix. Strength increased mostly due to reduced solution to binder ratio which also reduced the water to solid ratio. The results imply that desired compressive strengths of mortar can be achieved by controlling total binder content and reacting with the appropriate amount of alkaline liquid.

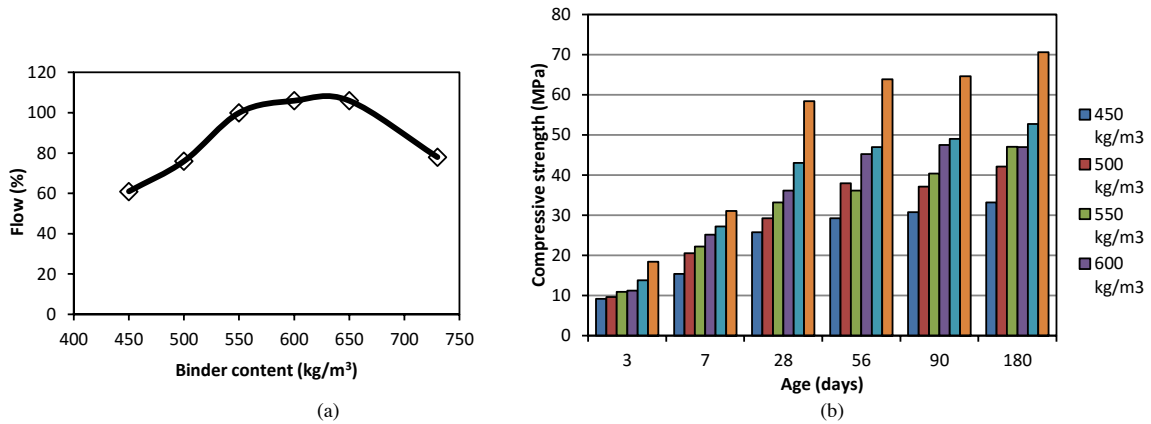


Fig. 3. Effect of variable binder content on the workability (a) and compressive strength (b).

4. Conclusion

Geopolymer mixtures were prepared using low calcium fly ash as the principal binder. Ground blast furnace slag, ordinary Portland cement and calcium hydroxide were used at the rate of 2 to 10% of the total binder in order to enhance the early-age properties when cured at ambient temperature. The effects of the additives and total binder content were investigated on the early age properties such as setting time, workability and compressive strength.

At ambient curing condition (23°C), fly ash geopolymers blended with GGBFS, OPC or CH reduced the setting time to a value comparable to that of OPC. The workability, measured in terms of the flow of mortars, decreased slightly due to the presence of the additives and faster rate of setting. Compressive strength of the mixtures blended with the additives increased noticeably from the age of as early as one day.

Compressive strength increased with the increase of the binder content for fly ash blended with 10% OPC. The 28-day strength increased from 26 MPa to 58 MPa by increasing the binder content from 450 kg/m³ to 730 kg/m³. However, the best flow values of the mortars were observed when binder content was in the range of 550 to 650 kg/m³.

Therefore, the results show that fly ash geopolymers blended with small percentages of GGBFS, OPC or CH can be a suitable binder for low to moderate strength concrete production at ambient curing condition.

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