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ScienceDirect
Cement & Concrete Composites 29 (2007) 224–229
Cement & Concrete Composites
www.elsevier.com/locate/cemconcomp

Workability and strength of coarse high calcium fly ash geopolymer

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Received 10 February 2006; received in revised form 1 August 2006; accepted 11 November 2006
Available online 27 December 2006

Abstract

In this paper, the basic properties viz., workability and strength of geopolymer mortar made from coarse lignite high calcium fly ash were investigated. The geopolymer was activated with sodium hydroxide (NaOH), sodium silicate and heat. The results revealed that the workable flow of geopolymer mortar was in the range of 110 ± 5%–135 ± 5% and was dependent on the ratio by mass of sodium silicate to NaOH and the concentration of NaOH. The obtained compressive strength was in the range of 10–65 MPa. The optimum sodium silicate to NaOH ratio to produce high strength geopolymer was 0.67–1.0. The concentration variation of NaOH between 10 M and 20 M was found to have a small effect on the strength. The geopolymer samples with high strength were obtained with the following practices: the delay time after moulding and before subjecting the sample to heat was 1 h and the optimum curing temperature in the oven was 75 °C with the curing duration of not less than two days.

Keywords: Geopolymer; High calcium fly ash; Lignite; Workability; Strength

1. Introduction

Manufacturing of Portland cement is an energy intensive process and releases a large amount of green house gas to the atmosphere. It has been reported that 13 500 million ton is produced from this process worldwide, which accounts for about 7% of the green house gas produced annually [1]. Efforts have, therefore, been made to promote the use of pozzolans to replace part of Portland cement. Recently, another form of cementitious materials using silicon and aluminum activated in a high alkali solution was developed [2]. This material is usually based on fly ash as a source material and is termed geopolymer or alkali-activated fly ash cement [3–7]. The mortar and concrete made from this geopolymer possess similar strength and appearance to those from ordinary Portland cement. It is also well known that geopolymers possess excellent mechanical properties, fire resistance and acid resistance [8,9].

The work on this geopolymer so far has been based on the normally used type-F low calcium fly ash [2–6]. It is known that high calcium fly ash contains a reasonable amount of silica and alumina. This high calcium fly ash could also be suitable for use as a base material for making geopolymer.

The annual output of lignite fly ash from Mae Moh power station in the north of Thailand is around 3 million tons. This fly ash contains a high percentage of calcium and is being used quite extensively for construction in Thailand. The knowledge of the use of high calcium lignite fly ash in producing geopolymer would be beneficial to the understanding and to the future applications of this material.

2. Materials and experimental details

2.1. Materials

Lignite fly ash (FA) from Mae Moh power station in the north of Thailand, sodium hydroxide (NaOH) of three

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0958-9465/$ - see front matter
doi:10.1016/j.cemconcomp.2006.11.002

concentrations viz., 10, 15 and 20 M, and sodium silicate with 15.32% Na_2O, 32.87% SiO_2 and 51.81% water were used. Local river sand with specific gravity of 2.65 in saturated surface dry condition was used for making mortar. Chemical compositions and loss on ignition (LOI) of the fly ash is given in Table 1. This lot of fly ash from the Mae Moh power station contains a reasonably large amount of calcium oxide and is rather coarse. The fly ash has mean particle size of 65 μm, Blaine fineness of 2100 cm^2/g and percentage retain on sieve #325 of 50%. Type F melamine formaldehyde superplasticizer (SP) as per ASTM C494/C494M [10] with solid content of 50% was also used to control the workability for some mixes.

2.2. Details of tests

2.2.1. Mix design and mixing of mortar

All geopolymer mortars were made with sand to fly ash ratio of 2.75. The NaOH of three concentrations viz., 10, 15 and 20 M and the sodium silicate to NaOH ratios by mass of 0.67, 1.00, 1.50, and 3.00 were used. In order to obtain the workable geopolymer mortar, a minimum base water content of 5% by mass of the geopolymer paste (fly ash, NaOH, sodium silicate and base water) was used for all mixes. For example, a typical 10 M NaOH and 1.00 sodium silicate to NaOH ratio mix consisted of 503 kg fly ash, 1382 kg sand, 127.5 kg NaOH, 127.5 kg sodium silicate and 40 kg base water. The mixing was done in an air conditioned room at approximately 25 °C. The mixing procedure started with mixing of NaOH solution, base water and fly ash for 5 min in a pan mixer. Sand was then added and mixed for 5 min. This was followed by the addition of sodium silicate solution and extra water or superplasticizer (in case the workability was not obtained) followed by a final mixing of another 5 min. Right after the mixing, the flow of the fresh geopolymer mortar was determined in accordance with ASTM C124 [11].

2.2.2. Compaction and strength test

After the determination of the flow, the fresh mortar was placed in the 50 × 50 × 50 mm cube mould. The specimens were compacted with two-layer placing and tamping as described in the ASTM C109 [12]. This was followed by an additional vibration of 10 s using a vibrating table. The specimens and moulds were then wrapped with vinyl sheet to prevent moisture loss. The specimens were then put in the oven after a predetermined delay time. After curing at an elevated temperature, the specimens were put in the laboratory to cool down and demoulded the next day and kept at in the 25–28 °C room until the testing age. The compressive strength tests were performed at the age of seven days in accordance with ASTM C109. The reported strengths are the average of three tests.

2.3. Test series

A number of procedures were designed to test the influence of the variables on the workability and the strength of geopolymer mortar. The variables include workability, method of curing, concentration and dosage of NaOH and sodium silicate and the effect of extra water and SP on strength.

2.3.1. Workability

In this series, the workability of geopolymer mortars with the lowest concentration of NaOH of 10 M were first determined to find out the flow characteristics of the geopolymer mortars. The minimum flow of 110 ± 5% was considered desirable as the mortar was workable and easily placed into the mould. This was achieved with mixes with sodium silicate to NaOH ratios of 0.67, 1.00 and 1.50 with the flow of 135 ± 5, 125 ± 5 and 110 ± 5%, respectively. For the sodium silicate to NaOH ratio of 3.00, extra water or SP was needed to obtain the flow of 110 ± 5% as shown in Table 2. The flows of 135 ± 5, 125 ± 5, 110 ± 5 and 110 ± 5% were therefore considered as 'basic flows' for the mixes with sodium silicate to NaOH ratios of 0.67, 1.00, 1.50, and 3.00, respectively. In order to observe the flow characteristics of the geopolymer mortar, similar flow patterns of 135 ± 5, 125 ± 5, 110 ± 5 and 110 ± 5% were therefore used for the 15 M and 20 M NaOH mixes. Additional water or SP was used to obtain mixes with similar flow as shown in Table 2.

Table 2
Extra water, SP and flow of geopolymer mortar

Sodium silicate to NaOH ratio	NaOH (M)	Flow (%)	Water (% of fly ash)	or SP (% of fly ash)
0.67	10	135 ± 5	0	0
1	10	125 ± 5	0	0
1.5	10	110 ± 5	0	0
3	10	110 ± 5	2.3	3
0.67	15	135 ± 5	3.4	3
1	15	125 ± 5	3.4	4
1.5	15	110 ± 5	3.4	5
3	15	110 ± 5	4.5	6
0.67	20	135 ± 5	6.8	12
1	20	125 ± 5	6.8	8
1.5	20	110 ± 5	6.8	10
3	20	110 ± 5	7.9	10

Table 1
Chemical compositions of fly ash

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	TiO_2	MgO	K_2O	P_2O_5	SO_3	LOI
Percent	38.7	20.8	15.3	16.6	1.2	0.4	1.5	2.7	0.1	2.6	0.1

2.3.2. Methods of curing

Heat curing is important for the activation of fly ash, because of the activation barrier that needs to be overcome for the reaction to take place [13]. NaOH with concentration of 10 M and sodium silicate to NaOH ratio of 0.67 were used. The mortar flow of 135 ± 5% was used, as this is the base flow of the mix without additional water or SP. In this series, the methods of heat curing viz., duration of heat curing, delay time and temperature of heat curing were therefore studied.

1. *Duration of heat curing*
   In this test, the duration of heat curing of 1, 2, 3 and 4 days were used. The specimens were put in the oven at 60 °C after wrapping with vinyl sheet with no delay time.
2. *Delay time*
   The delay time is the time duration where specimens were left at the room temperature (25–28 °C) after they were wrapped with vinyl sheet and the time of placing them in the oven. In this test, the delay time of 0, 1, 3 and 6 h were used. After the delay time, the specimens were put in the oven at 60 °C for a period of 24 h.
3. *Temperature of heat curing*
   The temperature of heat curing of 30, 45, 60, 75 and 90 °C were used in this test. The specimens were put in the oven after casting and wrapping with vinyl sheet. The time duration in the oven was 24 h.

2.3.3. Concentration and dosage of NaOH and sodium silicate

In this series, the optimum delay time, temperature of heat curing and duration of heat curing obtained from Section 2.3.2 were selected and used for the preparation of the geopolymer. The mixes described in Section 2.2.1 were used with extra water incorporated to obtain similar flow with the control mix as shown in Table 2.

2.3.4. Effect of extra water and SP on strength

In this series, the optimum delay time, temperature of heat curing and duration of heat curing obtained from Section 2.3.2 were also used. After the determination of flow, the mortars were moulded, cured and tested for compressive strength to compare the effect of addition of extra water and SP.

3. Results and discussions

3.1. Workability

The workability of the geopolymer mortar depended on the concentration of NaOH and the ratio of sodium silicate to NaOH ratio as shown in Table 2. For the 10 M NaOH, the flow of geopolymer mortar decreased with an increase in the ratio of sodium silicate to NaOH. The flows of the mortar with 0.67, 1.00, and 1.50 sodium silicate to NaOH ratio were 135 ± 5, 125 ± 5 and 110 ± 5%, respectively. When the sodium silicate to NaOH ratio was increased to 3.00, the flow became lower than 110 ± 5%. In order to obtain the 110 ± 5% flow, extra water of 2.3% by weight of fly ash was needed. Alternatively, the addition of 3% of SP also produced the mortar with a flow of 110 ± 5%. An increase in sodium silicate concentration thus reduces the flow of geopolymer mortar.

For the 15 M NaOH mortar, the mixture was thicker in comparison to the 10 M NaOH mortar. Slightly more water was required to produce mortar with similar flow pattern. In order to obtain similar flow with those of 10 M NaOH series, extra water of 3.4% by weight of fly ash was needed for the mortars with 0.67, 1.00, and 1.50 sodium silicate to NaOH ratio and 4.5% was needed for the 3.00 sodium silicate to NaOH ratio mortar. Alternatively, 3, 4, 5 and 6% of SP were needed to produce similar flow pattern of the 10 M NaOH mixes.

For the 20 M NaOH mortar, the mixture was much thicker than those of the 10 M and 15 M NaOH mortars. In order to obtain similar flow with the other series, extra water of 6.8% by weight of fly ash was needed for the mortars with 0.67, 1.00, and 1.50 sodium silicate to NaOH ratio and 7.9% of water was needed for the 3.00 sodium silicate to NaOH ratio mortar. This again was achieved with the addition of SP of 12, 8, 10 and 10% as shown in Table 2. An increase in NaOH concentration thus reduces the flow of geopolymer mortar.

In general, increases in the concentration of NaOH and the amount of sodium silicate solution decrease the workability of the mixes. An increase in the NaOH concentration increases the viscosity of the solution and thus reduces the flow of the mortar. The sodium silicate solution is itself a solution of very high viscosity and hence an increase in the amount also reduces the flow of the mortar. To obtain the mixes with suitable flow, extra water or SP are needed.

3.2. Strength

3.2.1. Method of curing

In this test, NaOH with concentration of 10 M and sodium silicate to NaOH ratio of 0.67 were used without additional water or SP. The sand to fly ash ratio of 2.75 and the flow of 135 ± 5% were used. There were altogether three tests in this series.

(a) *Duration of heat curing and strength*
    The result of the duration of heat curing and strength is shown in Fig. 1. In this test there was no delay time and the curing temperature was 60 °C. The strength increases with an increase in the curing time. A good strength of 48.5 MPa could be obtained with a minimum of two days heat curing. A little higher strength of 52.0 MPa was obtained with the three days heat curing. An increase in the curing time beyond this did not increase the strength. Similar strength development with high temperature curing has been

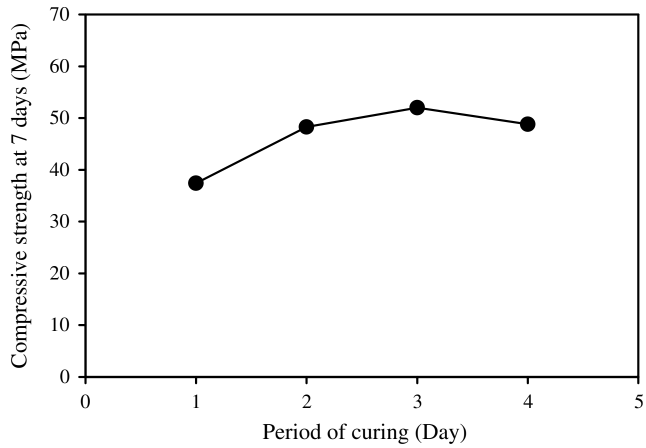

Fig. 1. Duration of heat curing and strength cured at 60 °C with no delay time.

reported [4,5]. An increase in the curing duration is expected to improve the strength characteristics of the geopolymer. It has, however, been suggested that curing for long periods of time at elevated temperature of fly ash-based geopolymeric materials appeared to weaken microstructure [14]. The results obtained from this study did appear to support this suggestion. The trend is not yet definite and more work needs to be done on this.

(b) *Delay time and strength*
The result of the strength of geopolymer for various delay time is shown in Fig. 2. The curing temperature of this test was 60 °C with the time of heat curing of 24 h. The strength of 37.5 MPa was obtained with sample cured in the oven right after the wrapping of the sample with no delay time. When the delay time was 1 h, the strength increased slightly to a maximum of 43.5 MPa. Increase in the delay time to 3 and 6 h resulted in no significant change in strength. The delay time adopted by various researchers varies considerably [4,6]. For fly ash concrete, the delay time of up to 60 min was found to have no effect on the compressive strength [4]. On the contrary for class F fly ash paste, delay time of 24 h was found to be beneficial to the strength development [6]. Some delay time allows the dissolving of silica and alumina which are main ingredients for the alumino–silicate geopolymerization. In this experiment, it was shown that delay time had no adverse effect on the strength of mortar. For practical purposes, this is rather convenient as some delay time before heat application is generally needed in the manufacturing process.

(c) *Temperature of heat curing and strength*
The results of the curing temperature and strength are given in Fig. 3. In this test, the geopolymer were placed in the oven right after casting and wrapping with vinyl sheet with no delay time. The optimum temperature was 75 °C and the maximum strength of 50.0 MPa was obtained. An increase in the temperature of curing from 30 °C to 75 °C increased the strength. However, when the temperature was 90 °C, the strength started to drop. Normally, it is expected that the strength of geopolymer increases with the curing temperature. The increase in the strength with curing temperature has been reported for concrete specimens [4]. However, for the study of the geopolymer paste with smaller 50 mm cube specimens, the optimum curing temperature was 60 °C [5]. This suggested that the small specimen with high surface to volume ratio is more susceptible to the heat of curing and to the loss of moisture in comparison to that of the large specimen. This could result in the reduction in strength for curing at high temperature.

An examination of the sample revealed that specimens with curing temperature of 90 °C were relatively dry. When the curing temperature was high, the sample would

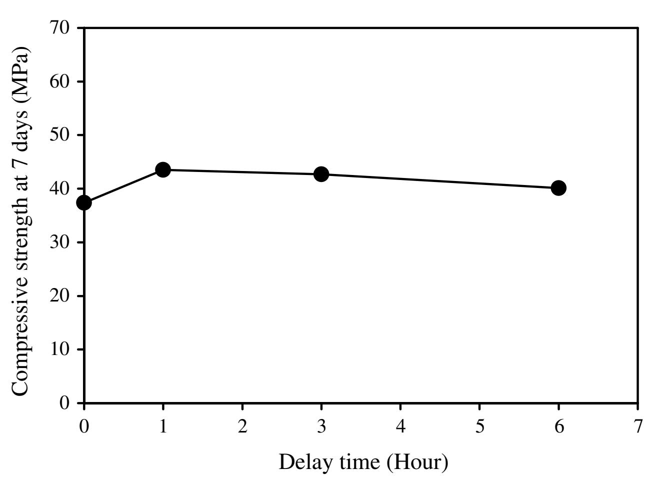

Fig. 2. Strength and delay time of geopolymer mortar with 60 °C heat curing for 24 h.

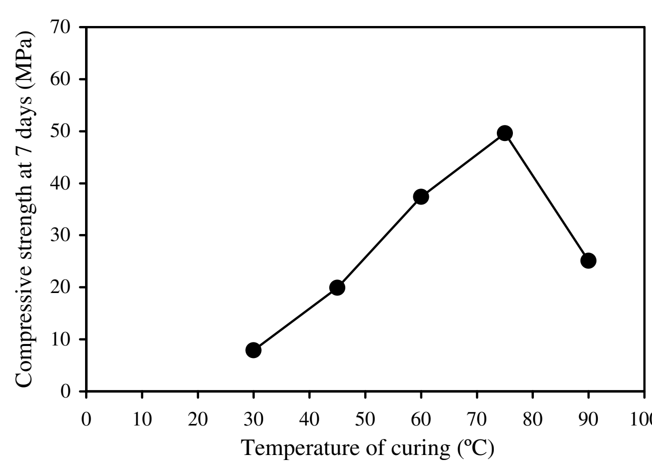

Fig. 3. Strength and temperature of curing of geopolymer with no delay time before heat curing.

experience a substantial loss of moisture. It has been shown that deterioration of strength would result if moisture evaporation is allowed [6]. The result thus suggested that the geopolymer reaction requires the presence of moisture in order to develop good strength. Water is an integral part of the geopolymer as shown in the empirical formula:

$$M_n[-(SiO_2)_z - AlO_2]_n \cdot wH_2O$$

where z is 1, 2 or 3 M is alkali cation; and n is the degree of polymerization [15].

3.2.2. Concentration and dosage of NaOH and sodium silicate and strength

In this series, the optimum curing conditions viz., a delay time of one hour and curing at 75 °C for three days were used for the preparation of the geopolymer. No superplasticizer was used in this series. Only extra water was incorporated for some mixes to obtain a similar flow pattern. It is of interest to note that similar optimum conditions with slightly lower heat curing of 60 °C and slightly shorter period of heat curing of 48 h were recommended in manufacturing of fly ash and kaolinite geopolymer [5]. The strength result of geopolymer with various concentrations and dosages of NaOH and sodium silicate is shown in Fig. 4. The effect of the concentration of NaOH on strength was not clear. The average strengths of 10, 15 and 20 M NaOH mortars were 48.4, 49.1 and 50.2 MPa, respectively. It should however be pointed out here that the water content and the workability of the mixes were not the same and the comparison was done with this limitation. It is, however, quite clear that the strength of mortars with sodium silicate to NaOH ratio of 0.67 and 1.00 were significantly higher than those with sodium silicate to NaOH ratio of 1.5 and 3.0. This is rather unexpected as the literatures on the case of low calcium fly ash indicated that the high sodium silicate to NaOH ratio provided a higher compressive strength [4]. The variation in the ratio of sodium silicate to NaOH ratio affects the pH conditions and thus would have some effects on the strength development of the geopolymer.

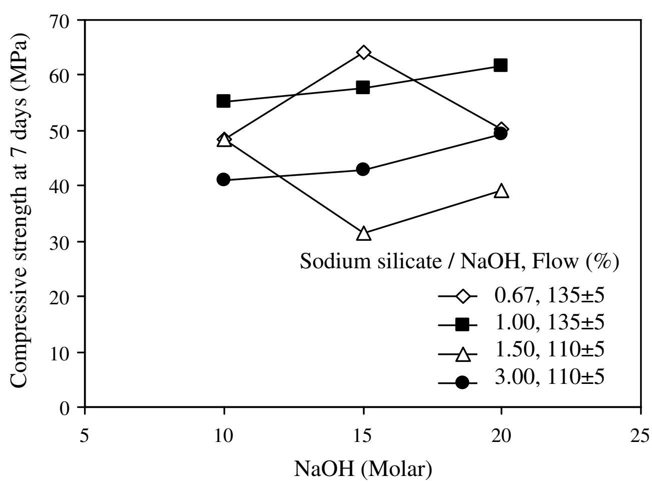

Fig. 4. Strength and concentration of NaOH and sodium silicate.

3.2.3. Extra water and superplasticizer

The strength result of geopolymer with extra water or superplasticizer is shown in Fig. 5. The strengths of mortars with extra water were consistently higher than those of the mortars with SP. The strength reductions of mortar with SP in comparison to those of mortar with extra water were dependent on the sodium silicate to NaOH ratio. At low sodium silicate to NaOH ratio of 0.67 and 1.0, the reductions in strength were relatively large. The average reductions in strength of the 0.67 and 1.0 sodium silicate

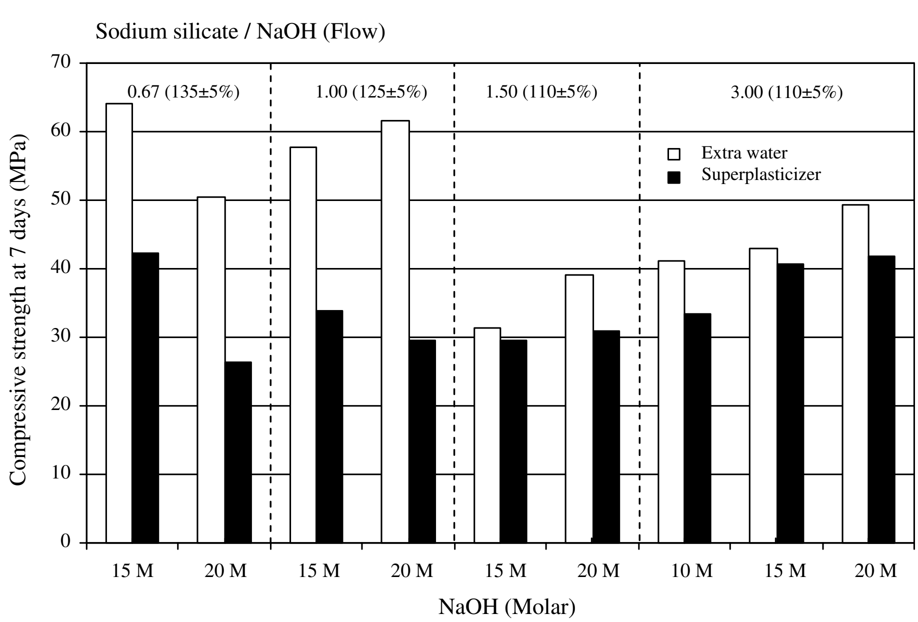

Fig. 5. Strength of mortar with extra water or superplasticizer.

to NaOH ratio mortars were 41 and 47%, respectively. For the high sodium silicate to NaOH ratio of 1.5 and 3.0, the reductions in strength were relatively small. The average reductions in strength of the 1.5 and 3.0 sodium silicate to NaOH ratio mortars were lower but still significant at 13% both. It has been reported that the strength of geopolymer concrete started to reduce when the dosage of superplasticizer by weight of fly ash was greater than 2% [4].

It is likely that the use of fly ash as the base material for making geopolymer does not require the SP to improve the workability as fly ash itself is spherical and can disperse easily in the sodium silicate and NaOH environment with extra water. The use of SP therefore is not beneficial in reducing the water content as in the case of Portland cement. In this case, the solid part as well as the integral water of SP consistently lowered the strength of the mortars.

4. Conclusions

Based on the obtained data, it can be concluded that the flow of coarse lignite high calcium fly ash geopolymer mortar depended on the concentration of NaOH and sodium silicate. Increases in NaOH and sodium silicate concentrations reduced the flow of mortar. The workable flow of geopolymer mortar was in the range of 110 ± 5–135 ± 5%. Improvements in the workability of the mortar could be achieved with addition of water or superplasticizer. However, the use of superplasticizer had an adverse effect on the strength of geopolymer.

With the NaOH of 10, 15 and 20 M, the sodium silicate to NaOH ratios of 0.67, 1.00, 1.50, and 3.00; and the extra water or superplasticizer contents of 2–8 and 3–12% by weight of fly ash, respectively, geopolymer mortars with compressive strength up to 65 MPa were obtained. The use of extra water to improve the workability of the fly ash geopolymer was found to give a higher strength than the addition of SP. The test results indicated that the optimum sodium silicate to NaOH ratio was 0.67–1.00 in order to produce a high strength geopolymer. The effect of the concentration of NaOH between 10 and 20 M on strength was small. The delay time before heat application had no adverse effect on the strength of mortar. This is important as in the manufacturing process, some delay time is needed. The geopolymer samples with a high strength were obtained using the delay time after moulding and before subjecting the sample to heat of 1 h with heat curing in the oven at 75 °C of not less than two days.

Acknowledgement

The authors acknowledge the financial support from Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program (Grant No. PHD/0074/2548).

References

[1] Maholtra VM. Introduction: sustainable development and concrete technology. ACI Concr Int 2002;24(7):22.
[2] Davidovits J. Chemistry of geopolymeric systems, terminology. In: Davidovits J, Davidovits R, James C. (Eds.) Geopolymer '99 international conference, France; 1999. p. 9–40.
[3] Palomo A, Grutzeck MW, Blanco MT. Alkali-activated fly ashes, a cement for the future. Cem Concr Res 1999;29(8):1323–9.
[4] Hardjito D, Wallah SE, Sumajouw DMJ, Rangan BV. On the development of fly ash – based geopolymer concrete. ACI Mater J 2004;101(6):467–72.
[5] Swanepoel JC, Strydom CA. Utilisation of fly ash in a geopolymeric material. Appl Geochem 2002;17(8):1143–8.
[6] Bakharev T. Geopolymeric materials prepared using class F fly ash and elevated temperature curing. Cem Concr Res 2005;35(6):1224–32.
[7] Fernandez-Jimenez A, Palomo A, Criado M. Microstructure development of alkali-activated fly ash cement: a descriptive model. Cem Concr Res 2005;35:1204–9.
[8] Davidovits J, Davidovics M. Geopolymer room temperature ceramic matrix for composites. Ceram Eng Sci Proc 1988;9:842–53.
[9] Palomo A, Macias A, Blanco MT, Puertas F. Physical, chemical and mechanical characterization of geopolymers. In: Proceedings of the 9th International Congress on the Chem of Cem; 1992. p. 505–11.
[10] American Society for Testing and Materials. ASTM C494/C494M-99a: Standard specification for chemical admixtures for concrete, Annual book of ASTM standards, Philadelphia; 04.02, 2001. p. 261–9.
[11] American Society for Testing and Materials. ASTM C124-71: Standard test method for flow of Portland cement concrete by use of the flow table, Annual book of ASTM standards, Part 10, Philadelphia; 1973. p.75–7.
[12] American Society for Testing and Materials. ASTM C109/C109M-99: Standard test method for compressive strength of hydraulic cement mortars (Using 2-in or [50 mm] cube specimens), Annual book of ASTM Standards, Philadelphia; 04.01, 2001. p. 83–8.
[13] Jiang W, Roy D. Hydrothermal processing of new fly ash cement. Ceram Bull 1990;71(4):642–7.
[14] Van Jaarsveld JGS, Van Deventer JSJ, Lukey GC. The effect of composition and temperature on the properties of fly ash and kaolinite-based geopolymer. Chem Eng J 2002;89(1–3):63–73.
[15] Davidovits J. Properties of geopolymer cements. Proceedings first international conference of alkali cements and concretes, vol. 1. Kiev, Ukraine: SRIBM; 1994. pp. 131–49.