Engineering and Applied Science Research April – June 2018;45(2):89-94 Research Article

EASR

Engineering and Applied Science Research

https://www.tci-thaijo.org/index.php/easr/index

Published by the Faculty of Engineering, Khon Kaen University, Thailand

Setting time, compressive strength and sulfuric acid resistance of a high calcium fly ash geopolymer containing borax

Athika Wongkvanklom[1)], Vanchai Sata[1)], Jay G. Sanjayan[2)] and Prinya Chindaprasirt*[1, 3)]

[1)]Sustainable Infrastructure Research and Development Center, Department of Civil Engineering, Faculty of Engineering, Khon Kaen University, Khon Kaen 40002, Thailand
[2)]Centre for Sustainable Infrastructure, Faculty of Sciences, Engineering and Technology, Swinburne University of Technology, Melbourne, Victoria 3122, Australia
[3)]Academy of Science, The Royal Society of Thailand, Dusit, Bangkok 10300, Thailand

Received 6 January 2017
Accepted 7 March 2017

Abstract

The objective of this research was to study the influence of borax on setting time and other properties viz., workability, compressive strength and sulfuric acid resistance of a high calcium fly ash (HCFA) geopolymer. Four borax types viz., deca-hydrate borax, deca-hydrate borax heat-treated for 5-minutes and 10-minutes and anhydrous borax were used to replace fly ash. A liquid to binder ratio (L/B) of 0.60, a 10M NaOH solution, and Na_2SiO_3/NaOH at a ratio of 1.0 were used in the formulation of the geopolymer. The results indicated that the replacement of fly ash with borax accelerated the initial setting time but retarded the final setting time of the geopolymer paste. The flow of mortar with deca-hydrate borax remained unaffected by the increase in the amount of borax. For other borax types, the mortar flow was reduced and this was related to the water molecules in the borax. The compressive strength of the mortar tended to decrease with increasing borax content. The resistance of the mortar to 3% sulfuric acid was reduced with increased borax content. The use of borax should be around 2.5% to control the setting of a high calcium fly ash geopolymer and to obtain good strength and resistance to acid.

Keywords: Geopolymer, High calcium fly ash, Borax, Workability, Compressive strength, Sulfuric acid resistance

1. Introduction

Geopolymers are an alternative binder in the concrete industry. Their synthesis involves a smaller CO_2 emission than ordinary Portland cement (OPC) [1] due to the use of industrial by-product materials that do not require heating of calcareous materials. A raw material containing high silica and alumina is activated with an alkali solution [2]. Fly ash is a waste from burning of coal in generating electricity. It can be used as a raw material for the synthesis of geopolymers [3-7]. The annual output of fly ash from Mae Moh power station in the north of Thailand is around 3 million tonnes [5]. It has a high calcium content and can be used in making high quality geopolymers. The calcium content has a significant effect on the properties of geopolymers, especially by reducing their setting times [8-11].

To control the setting times of fly ash geopolymer, bentonite or potassium salts can be used to prolong the setting time, whereas mayenite or calcium and magnesium salt were reported to shorten these times [12]. Metakaolin can also be incorporated to improve the strength and setting time of geopolymers [13]. The replacement of fly ash with silica fume [14] or OPC [15] also has a significant effect on setting time. The incorporation of nano-SiO_2 as an additive in the mixture also decreases the setting time of geopolymers [16]. Conventional set control additives such as calcium chloride and sucrose affect the setting time of high calcium fly ash in a similar manner to that of Portland cement mixtures [17]. The content of calcium [18-20] and water [21] can thus modify the setting time of geopolymers.

Incorporation borax into an alumino-silicate raw material resulted in boroaluminosilicate, which is another form of geopolymer. This slows the setting time with little influence on workability [22]. The use of borax and lithium pyroborate in conventional Portland cement has also been shown to increase the setting time of this material [23]. When used, borax can form borosilicate inorganic polymers [24] and boroaluminosilicate geopolymers [25], which have different setting characteristics than normal geopolymers.

This research examines the influence of borax as an additive for controlling setting time. Other properties, viz., flow, compressive strength and sulfuric acid resistance of high calcium fly ash geopolymers were investigated. Borax deca-hydrate, dehydrated borax deca-hydrate produced by microwave heating and anhydrous borax were used in the current investigation. This study provides some basis for the future use of an alternative material, i.e., borax, as a set control additive in fly ash geopolymer mixtures. Normally, the setting time of high calcium fly ash geopolymer paste is

---

*Corresponding author. Tel.: +66 4320 2355
Email address: prinya@kku.ac.th
doi: 10.14456/easr.2018.20

quite short [5]. In the current study, the initial and final setting times of fly ash geoploymers were 274 and 395 mins, respectively, which were highly desirable. Incorporation of various forms of borax was done to determine their effects and their possible use for controlling the setting times of these geopolymers.

2. Materials and methods

2.1 Materials

High calcium fly ash (HCFA) from the Mae Moh power plant in northern Thailand with a chemical composition as shown in Table 1 was used as the starting material. A 10M sodium hydroxide solution and sodium silicate solution (Na_2SiO_3) with Na_2O 12.53%, SiO_2 30.24% and H_2O 57.23% were used as alkali activators. It has been shown that borax can be dehydrated with microwave heating [26]. In this study, four varieties of borax forms were thus used as a set retarder as follows:

1. BRA: $Na_2B_4O_7.10H_2O$ (sodium tetraborate deca-hydrate),
2. BRB: 5-min microwave heated BRA,
3. BRC: 10-min microwave heated BRA, and
4. BRD: $Na_2B_4O_7$ (anhydrous borax).

The borax was in the powder form with a white color and passed a No. 200 sieve. Williams and van Riessen [24] suggested to heat deca-hydrate borax to 150 ◦C for 30 min followed by further dehydration at 300 ◦C for 15 h to produce anhydrous borax. Microwave heating was thus employed to shorten the time required for the dehydration. The river sand with fineness modulus of 2.50 in saturated surface dry state and sodium hydroxide solution prepared with distilled water were used.

2.2 Mix proportions

A ratio of liquid activator to binder materials (L/B) of 0.60 and a Na_2SiO_3/NaOH ratio of 1.0 were used for the production of HCFA geopolymer paste. For mortar, the same mix design was used with a binder to sand ratio of 1:2.75.

2.3 Preparation and testing of geopolymer paste and geopolymer mortar

For the determination of setting time, the BRA, BRC and BRD geopolymer pastes with 0, 2.5 and 5.0 % replacement of fly ash were tested. HCFA and borax were mixed to obtain a uniform mixture. NaOH was added and the samples mixed for 5 min. After that, sodium silicate solution was added and mixed for another 5 min. The fresh pastes were tested for setting times using a Vicat needle in accordance with ASTM C191 [27]. The test was done in a 25 °C controlled room.

For the geopolymer mortars, 0, 2.5, 5.0 and 7.5 wt % of BRA, BRB, BRC and BRD were used to replace HCFA. The mix proportions are shown in Table 2. The mixing sequence was the same as that of paste, except sand was added after mixing in the NaOH solution. It was then mixed for 5 min, followed by addition of sodium silicate and mixed for another 5 min. The flow of fresh mortar was tested in accordance with ASTM C1437 [28]. The mortar was cast in 50x50x50 mm^3 molds. They were wrapped with plastic sheets to protect against moisture loss. The samples were cured in an oven at 60˚C for 48 h and then demolded and left in a climate controlled room at 50% R.H. and 25˚C. The samples were tested for compressive strength after 7 and 28 days in accordance with ASTM C109/109M [29]. The reported results are the average of three samples.

For sulfuric acid resistance, the fly ash geopolymer mortar containing borax series BRD had a relatively high compressive strength and long final setting time. It was selected for this test. BRD geopolymer mortars with 0, 2.5, 5.0 and 7.5% replacements were tested in accordance with the modified test method B of ASTM C267-01 [30] using a 3% sulfuric acid solution. The weight loss of samples immersed in this solution after 7, 14, 28 and 56 days were determined. The reported results are the average of three samples.

Table 1 Chemical composition of fly ash (mass %)

SiO_2	Al_2O_3	CaO	Fe_2O_3	SO_3	K_2O	MgO	Na_2O	Other	LOI
39.4	19.8	18.0	11.4	3.9	2.42	2.33	1.67	0.68	0.4

Table 2 Mix proportion of HCFA geopolymer mortar in kg/m^3

Mix ID	Fly ash	NaOH	Na_2SiO_3	Sand (SSD)	Borax
Control	666.7	200	200	1833	0.0
2.5BRA	650.0	200	200	1833	16.7
5.0BRA	633.3	200	200	1833	33.3
7.5BRA	616.7	200	200	1833	50.0
2.5BRB	650.0	200	200	1833	16.7
5.0BRB	633.3	200	200	1833	33.3
7.5BRB	616.7	200	200	1833	50.0
2.5BRC	650.0	200	200	1833	16.7
5.0BRC	633.3	200	200	1833	33.3
7.5BRC	616.7	200	200	1833	50.0
2.5BRD	650.0	200	200	1833	16.7
5.0BRD	633.3	200	200	1833	33.3
7.5BRD	616.7	200	200	1833	50.0

3. Results and discussion

3.1 Setting time of HCFA geopolymer paste

Figure 1 shows the setting times of HCFA geopolymer pastes containing BRA, BRC and BRD. The BRB borax was not tested for the setting time as the flow results indicated that the behavior of BRB was intermediate between BRA and BRC. The results showed that the initial setting time of the pastes tended to decrease with the increasing borax content. The final setting time increased with the increasing borax content. The effects on both the initial set and final set were significant. For example, the use of 5.0% BRA, BRC and BRD resulted in a reduction of the initial setting times to 191, 187 and 169 min, respectively, compared with 274 min for the control paste. This also resulted in an increase of the final setting times to 472, 510 and 563 min compared with 395 min for the control paste. The incorporation of borax into an alumino-silicate medium resulted in boroaluminosilicate, which is another form of a geopolymer [25]. This borax was recommended for use as a set retarder in fly ash geopolymer mixtures [22]. It is notable that in a study of high calcium fly ash geopolymer paste, Songpiriyakij et al. [14] showed that the incorporation of silica fume resulted in an increase in the initial setting time, but a reduction of the final setting time. This is the opposite of the results found in the current experiment with the incorporation of borax. The addition of silica rich material into the system changed the silica to alumina ratio of geopolymer paste. It was reported that the setting time of high calcium fly ash depended on the silica to alumina ratio [31]. Incorporation of borax, however, did not change the silica to alumina ratio, but increased the $Na_2B_4O_7$ content of the system with some influence on the chemical reactions and the setting time. As illustrated in Figure 1, the initial setting time decreased as the water content of the borax decreased. The reduced initial setting time was primarily due to the reduced water content of the mixture in this case. The reduction in the water content implied an increase in borax content. Borax is usually used as a set retarder in a geopolymer system [22]. However, the varying amounts of water in the borax impacted the setting time of the geopolymer. The slight reduction in initial setting time was primarily due to the reduced water content of the mixture in this case. The reduction in the water content implied an increase in other gel forming elements and thus resulted in a slight acceleration of initial setting time. As shown in Figure 1, the final setting time was retarded with the incorporation of borax and the retarding effect was increase when the borax compound had a lower water content. The results in Figure 1 indicated that the final setting time increased with the reduction in the water content of the borax compound and thus with the increase in amount of borax. The results thus implied that the reaction of boron and alumino-silicate had a significant effect on the final setting time of this system, i.e., it prolonged setting through the reaction of boron and alumino-silicate [22]. Since the replacement of fly ash with borax influenced the setting times of HCFA geopolymer inversely with the use of silica fume suggested that the incorporation of silica fume and borax could thus be used for adjusting the setting behavior of HCFA geopolymer pastes.

3.2 Flow of mortar

The flow characteristics of HCFA geopolymer mortars are shown in Figure 2. With incorporation of BRA, the flows of mortar were relatively unaffected. Incorporation BRB, BRC and BRD clearly reduced the flow of mortars. The reduction in the flow was related to the type of borax used. BRA, $Na_2B_4O_7 \cdot 10H_2O$, with 10 molecules of water, helped to maintain the flow of mortar with increasing BRA content. The water molecules in BRA increased the total water content of the mixture and thus helped increase the workability and flow of mixture. Incorporation of BRA thus had a very small effect on the flow of mortars. For the other mixes, the water content of borax was less and thus resulted in a reduction in the flow of the mixture. For BRD, the reduction in flow of the mortar was clearly observed and this was due to a reduced water content as BRD contained anhydrous borax. For BRB and BRC, intermediate reductions in flow were observe that were related to the amount of water in the borax.

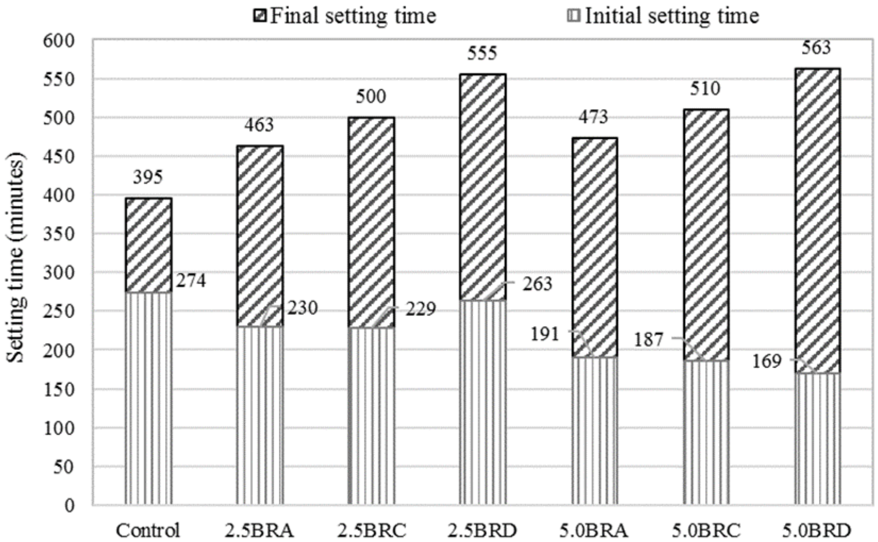

Figure 1 Setting times of HCFA geopolymer pastes

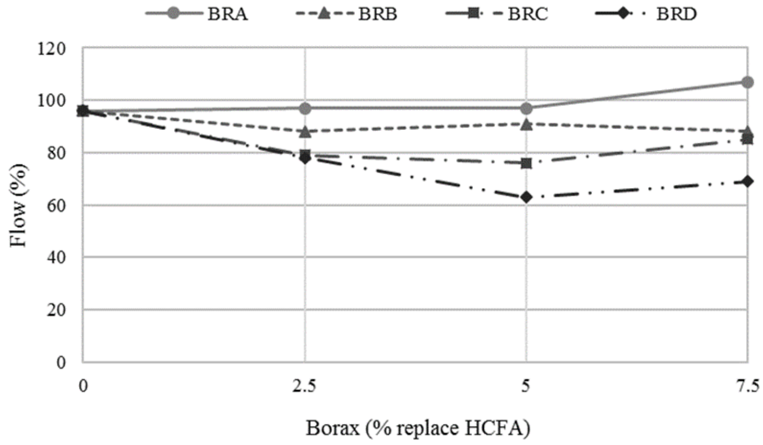

Figure 2 The flow of HCFA geopolymer mortars

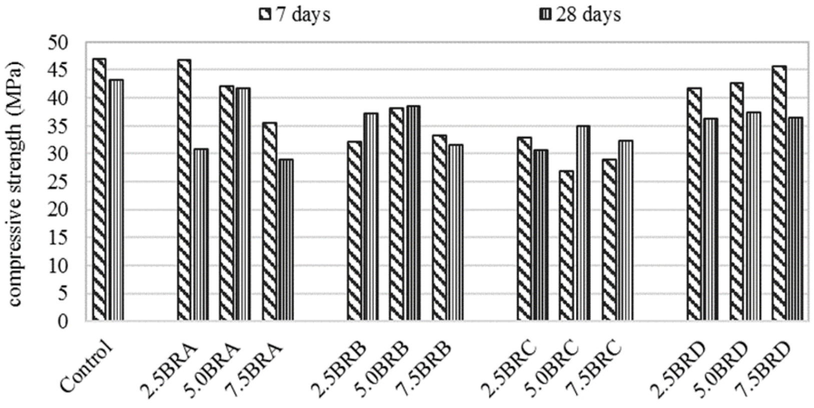

Figure 3 The compressive strengths of HCFA geopolymer mortars

3.3 Compressive strength of mortar

The results of compressive strength testing of HCFA geopolymer mortars containing borax are shown in Figure 3. These results indicated that the compressive strength tended to decrease with the increased borax content for BRA, BRB and BRC geopolymer mortars. Although the BRD geopolymer mortars had lower compressive strengths than the control mortar, their strengths tended to increase with the increased borax content from 2.5% to 7.5%. The strength reduction of the BRD mix was a result of the reduction of fly ash content due to the incorporation of borax. This resulted in a reduction in the alumina and silica content of the system. Thus, a slight reduction in strength was obtained. The reduction in strength with the increased borax content was primarily due to the reduction in fly ash content, which was the main source of silica and alumina. However, for the case of dehydrated BRA, the trend was reversed as the water content of mixture was affected by the use of dehydrated borax. The mix was stiffer with a lower total liquid to binder ratio. This resulted in a possible increase in the compressive strength of mix. The compressive strengths were in the range of 27.0-47.0 MPa after 7 days and 29.0-42.0 MPa after 28 days. For a number of mixes, the compressive strengths at 28 days were lower than their 7 day values. This was related to the formation of micro-cracks as a result of shrinkage of the fly ash pastes of the geopolymers containing additives. An adverse effect on the long-term strength resulted [20]. These strengths were sufficiently high for general uses of these materials.

3.4 Sulfuric acid resistance

The BRD geopolymer mortar was selected for testing its resistance to sulfuric acid as this series of mix showed good strength characteristics. The results of sulfuric acid resistance tests are shown in Figure 4. The weight loss of the BRD geopolymer mortar increased with increased borax content. The weight loss values after immersion in 3% sulfuric acid for 56 days of 0, 2.5, 5.0 and 7.5% BRD mortars were 2.60, 4.05, 5.47 and 5.28%, respectively. It was reported that Portland cement mortars immersed in 3 % sulfuric acid for 56 days resulted in a 67% weight loss [32]. This suggested that although incorporation of BRD resulted in a significant increase in weight loss in an acidic environment, the loss was still relatively low.

In a small quantity, borax can be effectively used for adjusting setting time. For example, the use of 2.5% borax in a BRD geopolymer paste could lengthen the final setting time from 395 to 555 min. The compressive strength of mortar of the same mix was 36.0 MPa, which is a good strength for a geopolymer. The weight loss in a 3% sulfuric acid solution was 4.05%, which was still low compared to Portland cement.

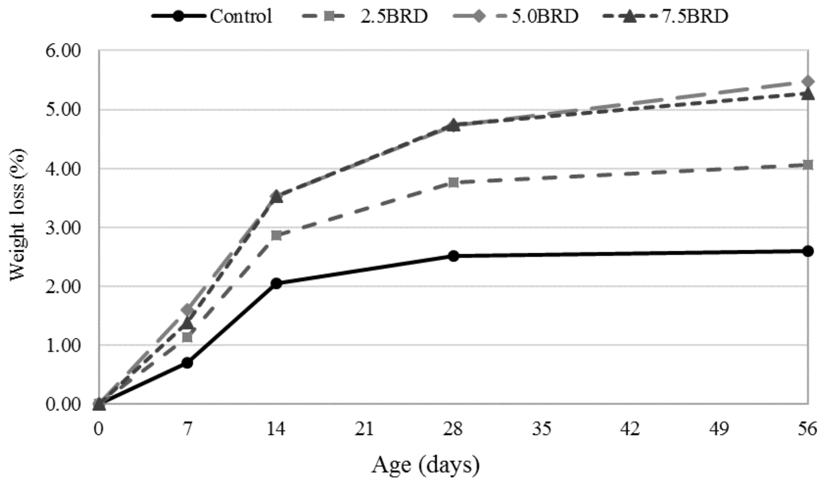

Figure 4 Sulfuric acid resistance of HCFA geopolymer mortars

4. Conclusions

From the experimental results, the following conclusions were drawn:

1. Replacement of fly ash with borax had a significant effect on the setting time of HCFA geopolymer pastes. The initial setting times of geopolymer pastes were shortened and the final setting times were prolonged with increasing levels of borax replacement. The reduction in the initial setting time was due to the reduction in available water molecules related to the type of borax used. The increase in final setting time was due to the slow reaction of boron and alumino-silicate.
2. The flow of the mortars was affected by the type of borax and was also related to the amount of water in the borax powder. For BRA with 10 molecules of H_2O, the flow remained relatively unaffected with increased borax content. For BRD, which contained anhydrous borax, the flow was reduced. For BRB and BRC, the flows of mortars were intermediate between the BRA and BRD samples.
3. The compressive strength of the mortars tended to decrease with increased borax content. For BRD, the strength was slightly decreased due to the reduced water content and flow of the mixture. Additionally, the compressive strengths after 28 days of several mixes were lower than their 7 day strengths. This was related to the formation of micro-cracks as a result of shrinkage.
4. The resistance to sulfuric acid of mortars containing borax was reduced with increased borax content. However, the weight loss of samples after immersion in 3% sulfuric acid was only slightly more than 5% which was still quite low.

5. Acknowledgements

The authors would like to acknowledge the financial support of the Thailand Research Fund (TRF), Khon Kaen University under the Royal Golden Jubilee Ph.D. Program (Grant No. PHD/0066/2557). The support of Kasetsart University, Chalermphrakiat Sakon Nakhon Province Campus is also gratefully acknowledged.

6. References

[1] Rickard WDA, Temuujin J, van Riessen A. Thermal analysis of geopolymer pastes synthesised from five fly ashes of variable composition. J Non-Cryst Solids. 2012;358(15):1830-9.

[2] Silva PD, Sagoe-Crenstil K, Sirivivatnanon V. Kinetics of geopolymerization: role of Al_2O_3 and SiO_2. Cement Concr Res. 2007;37(4):512-8.

[3] Chindaprasirt P, Chareerat T, Sirivivatnanon V. Workability and strength of coarse high calcium fly ash geopolymer. Cement Concr Compos. 2007;29(3):224-9.

[4] Nematollahi B, Sanjayan J. Effect of different superplasticizers and activator combinations on workability and strength of fly ash based geopolymer. Mater Des. 2014;57:667-72.

[5] Pangdaeng S, Phoo-ngernkham T, Sata V, Chindaprasirt P. Influence of curing conditions on properties of high calcium fly ash geopolymer containing Portland cement as additive. Mater Des. 2014;53:269-74.

[6] Xie J, Kayali O. Effect of superplasticiser on workability enhancement of class F and class C fly ash-based geopolymers. Construct Build Mater. 2016;122:36-42.

[7] Chindaprasirt P, Chareerat T, Kunawanakit W. Geopolymer from Mae Moh fly ash. KKU Eng J. 2005;32(5):715-24.

[8] Canfield GM, Eichler J, Griffith K, Hearn JD. The role of calcium in blended fly ash geopolymers. J Mater Sci. 2014;49(17):5922-33.

[9] Winnefeld F, Leemann A, Lucuk M, Svoboda P, Neuroth M. Assessment of phase formation in alkali activated low and high calcium fly ashes in building materials. Construct Build Mater. 2010;24(6):1086-93.

[10] Temuujin J, van Riessen A, Williams R. Influence of calcium compounds on the mechanical properties of fly ash geopolymer pastes. J Hazard Mater. 2009;167(1-3):82-8.

[11] Guo X, Shi H, Chen L, Dick WA. Alkali-activated complex binders from class C fly ash and Ca-containing admixtures. J Hazard Mater. 2010;173 (1-3):480-6.

[12] Rashad AM. A comprehensive overview about the influence of different admixtures and additives on the properties of alkali-activated fly ash. Mater Des. 2014;53:1005-25.

[13] Zhang Z-h, Yao X, Zhu H-j, Hua S-d, Chen Y. Preparation and mechanical properties of polypropylene fiber reinforced calcined kaolin-fly ash based geopolymerJ Cent S Univ Tech. 2009;16:49-52.

[14] Songpiriyakij S, Pulngern T, Pungpremtrakul P, Jaturapitakkul C. Anchorage of steel bars in concrete by geopolymer paste. Mater Des. 2011;32(5):3021-8.

[15] Phoo-ngernkham T, Chindaprasirt P, Sata V, Hanjitsuwan S. Influence of portland cement replacement in high calcium fly ash geopolymer paste. KKU Eng J. 2014;41(1):19-27.

[16] Phoo-ngernkham T, Chindaprasirt P, Sata V, Hanjitsuwan S, Hatanaka S. The effect of adding nano-SiO_2 and nano-Al_2O_3 on properties of high calcium fly ash geopolymer cured at ambient temperature. Mater Des. 2014;55:58-65.

[17] Rattanasak U, Pankhet K, Chindaprasirt P. Effect of chemical admixtures on properties of high-calcium fly ash geopolymer. Int J Miner Metall Mater. 2011;18(3):364-9.

[18] Nath P, Sarker PK. Effect of GGBFS on setting, workability and early strength properties of fly ash geopolymer concrete cured in ambient condition. Construct Build Mater. 2014;66:163-71.

[19] Tennakoon C, Nicolas RS, Sanjayan JG, Shayan A. Thermal effects of activators on the setting time and rate of workability loss of geopolymers. Ceram Int. 2016;42(16):19257-68.

[20] Lee NK, Lee HK. Setting and mechanical properties of alkali-activated fly ash/slag concrete manufactured at room temperature. Construct Build Mater. 2013;47:1201-9.

[21] Diaz EI, Allouche EN, Eklund S. Factors affecting the suitability of fly ash as source material for geopolymers. Fuel. 2010;89(5):992-6.

[22] Nicholson CL, Fletcher RA, inventors. Geopolymers and methods for their production. New Zealand patent WO 2005/019130 A1. 2005.

[23] Provis JL, van Deventer JSJ. Geopolymers Structure, processing, properties and industrial applications. USA: Wood head publishing limited and CRC Press LLC; 2009.

[24] Williams RP, van Riessen A. Development of alkali activated borosilicate inorganic polymers (AABSIP). J Eur Ceram Soc. 2011;31(8):1513-6.

[25] Nazari A, Maghsoudpour A, Sanjayan JG. Characteristics of boroaluminosilicate geopolymers. Construct Build Mater. 2014;70:262-8.

[26] Kocakusak S, Koeroglu JH, Ekinci E, Tolun R. Production of anhydrous borax using microwave heating. Ind Eng Chem Res. 1995;34(3):881-5.

[27] American Society for Testing and Materials (ASTM) C191. Standard test methods for time of setting of hydraulic cement by Vicat Needle. Conshohocken, PA: ASTM; 2013.

[28] American Society for Testing and Materials (ASTM) C1437. Standard test method for flow of hydraulic cement mortar. Conshohocken, PA: ASTM; 2013.

[29] American Society for Testing and Materials (ASTM) C109/109M. Standard test method for compressive strength of hydraulic cement mortars (Using 2-in. or [50-mm] Cube Specimens). Conshohocken, PA: ASTM; 2013.

[30] American Society for Testing and Materials (ASTM) C267. Standard test methods for chemical resistance of mortars, grouts, and monolithic surfacings and polymer concretes. Conshohocken, PA: ASTM; 2012.

[31] Chindaprasirt P, De Silva P, Sagoe-Crentsil K, Hanjitsuwan S. Effect of SiO_2 and Al_2O_3 on the setting and hardening of high calcium fly ash-based geopolymer systems. J Mater Sci. 2012;47(12):4876-83.

[32] Sata V, Sathonsaowaphak A, Chindaprasirt P. Resistance of lignite bottom ash geopolymer mortar to sulfate and sulfuric acid attack. Cement Concr Compos. 2012;34(5):700-8.