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# Effects of Alkaline Solution on Properties of the HCFA Geopolymer Mortars

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**Abstract**

Geopolymers are novel binding materials produced by the alkaline activation of rich aluminosilicate materials. Geopolymer binders are considered as green building materials that have increasing potential to replace the ordinary Portland cement in the concrete industry. This study investigated the alkali solution effects on the physical and mechanical properties of the high calcium fly ash based geopolymers. The parameters involved in this study were the NaOH solution molarity and the $Na_2SiO_3$/NaOH ratio. Three NaOH concentrations (8, 10, and 12 molars) were investigated. The $Na_2SiO_3$/NaOH ratio was varied between 1 and 2.5. The results showed that the studied parameters significantly affected the properties of the produced geopolymer mortars. The workability and setting time were found to decrease by increasing the NaOH concentration or by increasing the $Na_2SiO_3$/NaOH ratio. The influence of the NaOH concentration was higher on the workability and setting time while the $Na_2SiO_3$/NaOH ratio highly affected the compressive strength. The initial setting time was in the range of 45-105 minutes while the final setting occurred quickly after that within 70-115 minutes. Oven curing method resulted in high strength at early ages where all of the mixes were able to achieve more than 75% of the 28 days strength within the first 3 days. The 28-days compressive strength ranged between 60-85 MPa, which promotes the use of the high calcium fly ash for the production of early high strength geopolymer concrete.


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*Keywords:* Geopolymer; High Calcium Fly Ash; Compressive Strength; Setting Time; Workability

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## 1. Introduction

Geopolymer is a term that was firstly used by Davidovits [1] to describe the aluminosilicate binders, which formed by the alkali activation of a source material that is rich in content of aluminum and silicon. These binders have superior properties that promote them as cement replacement materials. Geopolymers can utilize precursors from many industrial byproducts such as, fly ash (FA), rice husk ash, and granulated blast furnace slag. These byproducts are usually disposed to landfills, which create serious environmental concerns. Additionally, many researchers have described that geopolymer binders can reduce the carbon dioxide ($CO_2$) emissions by 80-90% compared to the ordinary Portland cement (OPC), which contributes to 5-7% of the global $CO_2$ emissions [1-3].

Geopolymer consists of a three-dimensional network of the aluminosilicate tetrahedral that are connected together by co-sharing of the oxygen atoms. The presence of the alkali cations is essential to neutralize the negative charge of the $[AlO_4]^-$ group in the geopolymer frameworks. Also, the alkali cations are perceived to act as reaction catalysts which promote the dissolution reactions. These reactions are considered as the main player in determining the geopolymer binder properties [4].

The geopolymer formation mechanisms are still not clearly understood; however, these reactions mainly involve three processes: dissolution, reorientation and oligomers formation, and polycondensation and setting [5, 6]. These reactions are occurring simultaneously; therefore, it is difficult to distinguish between them. However, further research is required in this area since these reactions have the main role in determining the properties of the produced binder. Geopolymerization reactions start by the dissolution process where the aluminosilicate precursors dissolve in the alkali solution, and then hydrolyzed to produce the aluminate $[AlOH_4]^-$ and silicate $[SiOH_4]^-$ monomers. These monomers are going through reorientation and rearrangement processes to form oligomers of the Si-O-Al and Si-O-Si that are covalently bonded by co-sharing of the oxygen atoms. It is worth mentioned that the covalent bonding mechanism controls these oligomers, not the ionic bonding mechanism; since the atoms cannot move freely within the structure which results in the stronger geopolymer framework. The final stage is the polycondensation and setting stage, which starts after reaching a supersaturated solution state, where these oligomers precipitate forming the main geopolymer binder.

Geopolymerization reactions are influenced by several parameters including; the aluminosilicate precursor properties such as the Si/Al ratio, calcium content, presence of impurities, Si and Al speciation, particle size distribution, curing temperature, curing time, and alkaline solution type, proportions, and quantity. Each of these parameters has a different role in determining the properties of the produced geopolymer binder. This study aims to investigate the alkali solution effects on the physical and mechanical characteristics of the high calcium content fly ash (HCFA) based geopolymer mortars.

## 2. Materials and Methods

Geopolymer mortars were prepared based on the HCFA for the aluminosilicate source and mixture of sodium hydroxide (NaOH) and sodium silicate ($Na_2SiO_3$) solutions for the alkaline solution. The HCFA was supplied from the Manjung power plant, Perak, Malaysia. Table 1 presents the chemical composition of this HCFA as obtained by the X-ray fluorescence (XRF) analysis. The NaOH solution was prepared by dissolving the NaOH solids in the form of pellets in potable water. Three different solutions of 8M, 10M, and 12M concentration were prepared and equilibrated to room temperature overnight prior to use. The $Na_2SiO_3$ solution ($SiO_2$ = 29.43%, $Na_2O$ = 14.26%, and water = 56.31% mass ratios) was supplied by the Malay-Sino Chemical Industries, Malaysia. The NaOH solution and the $Na_2SiO_3$ solution were mixed together in different mass ratios just before using in the mortar preparation. Locally available river sand of 2.52 specific gravity and 2.69 fineness modulus was used as a fine aggregate.

Table 1: Chemical composition percentage of the HCFA.

| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $Na_2O$ | $K_2O$ | LOI | Median particle size |
|---|---|---|---|---|---|---|---|---|---|
| 25.9% | 12.3% | 32.3% | 20.9% | 2.08% | 0.7% | 0.26% | 2.8% | 3.6% | 17 μm |

The mortars were prepared with the FA to sand ratio of 1 to 2. The alkali solution/ FA ratio of 0.55 was used for all of the mixes. The details of mixes are shown in Table 2. The mixing procedures were similar to that specified for the OPC mortars by the ASTM standards C305 [7]. The fresh mortars were cast in 50mm cubes and then cured in an oven for 24 hours at a temperature of 60°C. Then, the specimens were de-molded and tested for compressive strength at different ages. At least 3 specimens were tested and the average values were recorded at each age. Also, fresh mortars were tested for the setting time and flowability according to the ASTM standards C807 [8] and C230 [9], respectively.

Table 2: Mix parameters and proportions of the FA based geopolymer mortars.

| Sample | FA [g] | Sand [g] | $Na_2SiO_3$ [g] | NaOH [g] | $Na_2SiO_3$:NaOH | NaOH Molarity [Molar] | Molar Ratio | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Si/Al | $H_2O$/Si | Na/Si |
| N1 | 300 | 600 | 82.5 | 82.5 | 1:1 | 8 | 2.76 | 1.10 | 0.29 |
| N2 | 300 | 600 | 99 | 66 | 1.5:1 | 8 | 2.90 | 1.01 | 0.27 |
| N3 | 300 | 600 | 110 | 55 | 2:1 | 8 | 2.98 | 0.96 | 0.25 |
| N4 | 300 | 600 | 117.9 | 47.1 | 2.5:1 | 8 | 3.05 | 0.91 | 0.24 |
| N5 | 300 | 600 | 82.5 | 82.5 | 1:1 | 10 | 2.76 | 1.07 | 0.32 |
| N6 | 300 | 600 | 99 | 66 | 1.5:1 | 10 | 2.90 | 0.99 | 0.29 |
| N7 | 300 | 600 | 110 | 55 | 2:1 | 10 | 2.98 | 0.94 | 0.27 |
| N8 | 300 | 600 | 117.9 | 47.1 | 2.5:1 | 10 | 3.05 | 0.91 | 0.26 |
| N9 | 300 | 600 | 82.5 | 82.5 | 1:1 | 12 | 2.76 | 1.05 | 0.34 |
| N10 | 300 | 600 | 99 | 66 | 1.5:1 | 12 | 2.90 | 0.98 | 0.30 |
| N11 | 300 | 600 | 110 | 55 | 2:1 | 12 | 2.98 | 0.93 | 0.28 |
| N12 | 300 | 600 | 117.9 | 47.1 | 2.5:1 | 12 | 3.05 | 0.90 | 0.27 |

## 3. Results and Discussion

### *3.1. Workability of Fresh Mortars*

Flow table was used to measure the mortar flow diameter as an indicator of workability. In general, the OPC mortars show higher workability than geopolymer binder mortars, this may refer to the higher viscosity if the liquids used in geopolymer production [10, 11]. Fig. 1 shows the effect of the NaOH molarity on workability. Increasing of the NaOH molarity resulted in reducing of the mortar flowability. This could be ascribed to the enhanced reaction rates. Increasing of the NaOH concentration has increased the pH of the mix and resulted in a higher dissolution rate, which enhanced the geopolymerization processes [12]. On the other hand, the higher molarity of the NaOH solution has increased its viscosity and reduced the mixture workability. Also, this may be drawn by noting the reduction in the $H_2O$/Si ratio in the case of higher molarity solutions.

Increasing the $Na_2SiO_3$/NaOH ratio has reduced the mortar flowability. On the other hand, the effect of the $Na_2SiO_3$/NaOH ratio seems to be dependent on the NaOH solution molarity. It was observed that changing of the $Na_2SiO_3$ content has a higher effect in the case of lower NaOH molarity. At 8 molar solution, changing the $Na_2SiO_3$ content from 50% to 71% of the total solution has reduced the flowing diameter by 33%; however, this ratio was about 10% in the case of the 12 molar NaOH solution. This may attribute to the higher viscosity of the $Na_2SiO_3$ solution compared to the NaOH solution, hence increasing the $Na_2SiO_3$ content will increase the mix viscosity and reduces the flowability. However, as the NaOH molarity increased the variation in the $H_2O$/Si ratio reduced and a similar amount of water available for the mixture.

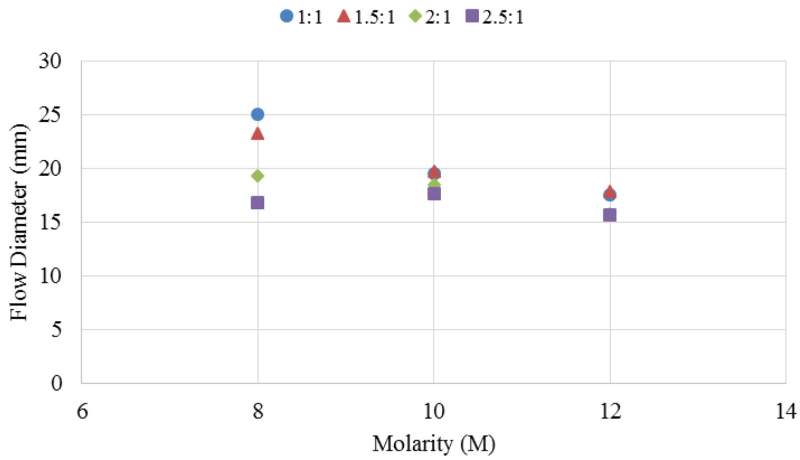


Fig. 1: Effect of the NaOH molarity and $Na_2SiO_3$/NaOH ratio on the flowability of geopolymer mortar.

*3.2. Setting Time*

The setting time of the geopolymer mortars was measured using the modified Vicat needle apparatus under controlled temperature of 22-25°C. The results of the initial setting time and the final setting time are shown in Fig. 2. The initial setting time for the different mixes ranged from 45-105 minutes. Compared to the OPC (around 30 min) geopolymer can offer flexible ranges of initial setting time, where the material is still workable. The final setting has occurred faster than the initial setting time. The final setting time ranged from 75-115 minutes, which is about 10-20% of the time required for the final setting of the OPC (around 600 min). Hence, this HCFA can develop strength in the early ages. This may consider as an advantage in case of repairing works and other conditions where the fast setting is required. Compared to other types of FA, the faster setting time of this FA refers to its high content of calcium (20.9%) [13].

The effect of the NaOH solution on the setting time is shown in Fig. 2. This figure displays that the initial setting time and the final setting time was increased by increasing of the NaOH solution molarity. In addition, the NaOH solution molarity has a higher effect on the initial setting time more than the final setting time. Referring to the mixing proportions (Table 2), it can be seen that for different molarity solutions the Si/Al ratio and the $H_2O$/Si ratio remain almost the same. However, changing of the solution molarity will change the Na/Si ratio. Hence, it can be concluded that the Na content is the main factor influencing the setting time. This may be attributed to the fact that the Na cations work as a reaction catalyst [4]. At lower NaOH molarity, the geopolymer setting was controlled by leaching of the calcium ions, which is directly available for the reaction compared to the silicon and aluminum ions that are controlled by the dissolution processes. Sufficient amounts of the calcium ions were available to react with water forming the C-S-H and C-A-H gels. However, for the higher concentrations, the presence of higher $Na^+$ and $OH^-$ increase the dissolution rate of the aluminosilicate precursors, which hinders the leaching of the calcium ions [14]. The reactions become controlled by the geopolymerization processes which they are slower than the hydration reactions of the calcium [15].

Increasing the $Na_2SiO_3$/NaOH ratio has increased the initial and final setting times. Both setting times were observed to increase significantly when this ratio was more than 1.5. This could be related to the higher viscosity of the alkali solution besides the higher Si/Al ratio [16]. The higher content of Si will motivate the geopolymerization reactions and hinders the calcium hydration reaction, which will increase the setting time. However, further investigations are required regarding this area.

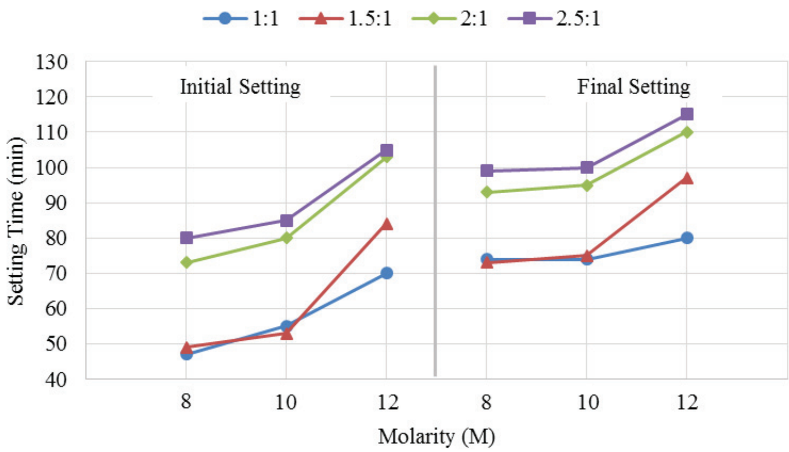


Fig. 2: Effect of the NaOH molarity and $Na_2SiO_3$/NaOH ratio on the setting time of geopolymer mortar.

### 3.3. Compressive Strength

The compressive strengths of the geopolymer mortar based on the HCFA are tabulated in Table 3 at different ages. Table 3 shows that all of the geopolymer mixes were able to develop high compressive strength during the early ages. The compressive strength ranged between 49-75MPa within the first three days. All the geopolymer mixes have achieved more than 75% of their 28-day strength during the first three days. Moreover, some of the mixes (N3, N4, N7, N9, N11, and N12) were able to achieve more than 90%. This can be attributed to the fast geopolymerization reactions due to the act of heat curing. Applying of the heat curing has increased the reactivity of the aluminosilicate precursors and most of the geopolymerization reactions were able to occur during the early ages [17].

Table 3: Physical and mechanical properties of the geopolymer mixes.

| Sample | Compressive strength [MPa] | | | Flowing diameter | Initial setting time | Final setting time |
|---|---|---|---|---|---|---|
| | 3days | 7days | 28days | [mm] | [min.] | [min.] |
| N1 | 49.7 | 53.3 | 61.2 | 25.0 | 47 | 74 |
| N2 | 57.7 | 65.3 | 74.1 | 23.3 | 49 | 73 |
| N3 | 69.5 | 78.0 | 74.4 | 19.3 | 73 | 93 |
| N4 | 71.2 | 76.1 | 78.2 | 16.8 | 80 | 99 |
| N5 | 59.7 | 64.3 | 71.1 | 19.5 | 55 | 74 |
| N6 | 65.3 | 71.0 | 79.9 | 19.8 | 53 | 75 |
| N7 | 69.1 | 75.1 | 75.9 | 18.5 | 80 | 95 |
| N8 | 75.1 | 79.3 | 84.3 | 17.6 | 85 | 100 |
| N9 | 65.2 | 68.1 | 70.2 | 17.5 | 70 | 80 |
| N10 | 69.3 | 75.1 | 77.2 | 17.9 | 84 | 97 |
| N11 | 71.6 | 73.6 | 77.9 | 15.8 | 103 | 110 |
| N12 | 77.2 | 79.0 | 79.1 | 15.6 | 105 | 115 |

The effects of the Si/Al ratios on the compressive strength are shown in Fig. 3. This figure displays that the compressive strength of the geopolymer mortars is directly proportioned to the Si/Al ratio. Increasing of the Si/Al ratio by 10% were able to increase the strength by 20%-40% referring to the 3-days strength; however, lower effect

(10%-25%) was observed on the later strength at 28-days. This may refer to the effect of the additional soluble silicate (supplied by the higher content of the $Na_2SiO_3$ solution) that was directly available for the geopolymerization reactions [18]. The dissolution of the aluminosilicate precursors is slow and depends on several factors. However, the dissolution of the aluminate is much easier when compared to the dissolution of the silicate. Hence, the presence of the soluble silicate will enhance the reactions, especially in the early ages [19]. Therefore, increasing the $Na_2SiO_3$/NaOH ratio will improve the geopolymerization processes and results in higher strength.

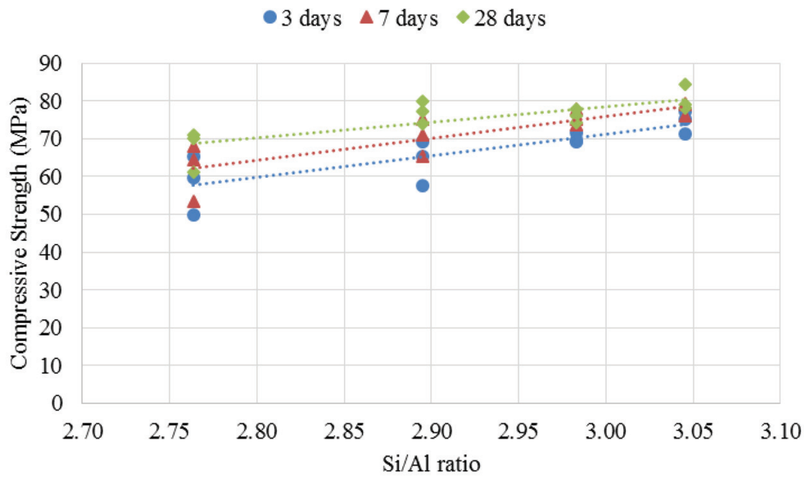


Fig. 3: Effect of Si/Al ratio on geopolymer mortar strength at different ages.

Fig. 4 displays the effect of the Na/Si ratio on the compressive strength. The compressive strength seems to be inversely proportioned to the Na/Si ratio. Increasing the NaOH molarity has increased the Na/Si ratio; however, the strength was reduced. This can be ascribed to the formation of the sodium carbonate, which was evident as efflorescence over the cubes surface. The excess of the Na cations has reacted with the carbon dioxides from the atmosphere which interrupted the polymerization reactions [16]. It is worth mentioned that this behavior is opposite to the known behavior of low calcium fly ash, where the strength usually increases as the NaOH solution molarity increases [20, 21]. This may be attributed to the fact that increasing of the NaOH solution molarity has introduced more OH ions to the mix, which may react with the calcium content forming $Ca(OH)_2$ and decrease the geopolymer strength. However, more investigations are required to prove this phenomenon.

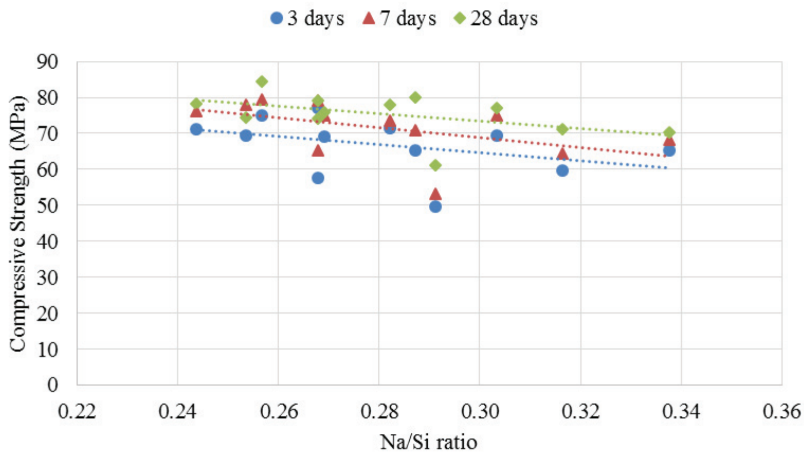


Fig. 4: Effect of Na/Si ratio on geopolymer mortar strength at different ages.

Fig. 5 displays the effect of the $H_2O/Si$ ratio on the compressive strength. The compressive strength decreased as the $H_2O/Si$ ratio increased. Increasing this ratio by about 20% resulted in strength reduction by more than 25% depending on the other variables. It is known that water has no role in the geopolymerization reactions; nevertheless, it acts as a transition medium for the ions during the reaction processes and after polycondensation processes it is expelled from the geopolymer structure [14]. However, the higher water contents the higher the porosity, which will reduce the strength. Also, it can be noted that the higher $H_2O/Si$ ratio had more effects on the strength at later ages. When the ratio was less than 1, the variation between the 3-days and the 28-days strength ranged from 2.5-12.5%; however, when the ratio was higher than 1, the variation ranged from 19-28%.

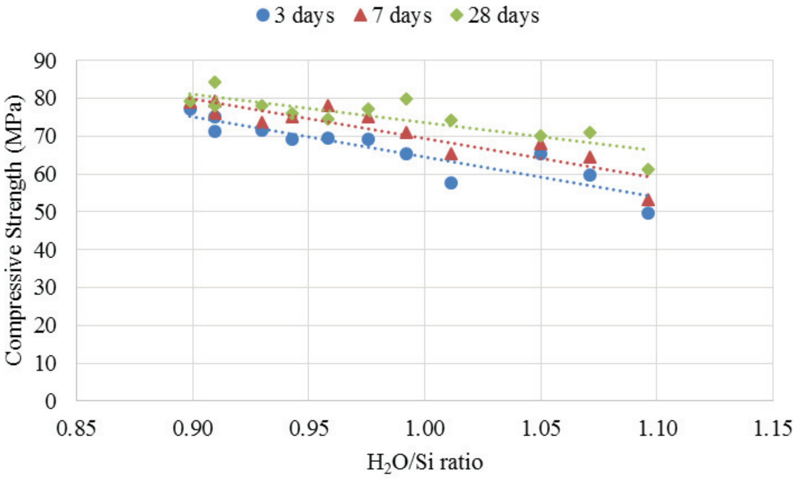


Fig. 5: Effect of $H_2O/Si$ ratio on geopolymer mortar strength at different ages.

## 4. Conclusions

The effect of the alkaline solution on the HCFA based geopolymer mortar was investigated in this study. The results showed that changing of the alkaline solution proportions and concentration could provide a geopolymer mixture with a wide range of properties in terms of the workability, setting time, and compressive strength. The NaOH concentration and the $Na_2SiO_3/NaOH$ ratio have a similar effect on the workability and setting time of the geopolymers mixes, where increasing these ratios resulted in lower workability and longer setting times. On the other hand, the NaOH concentration has the highest effect on the workability and setting time, while the $Na_2SiO_3$ content has a higher influence on the later strength characteristics. The HCFA based geopolymers showed a good range of initial setting time; however, the final set occurred within a short time after the initial setting. This promotes the use of this material in repairing works and other works where the fast setting condition is required. On the other hand, the oven curing of the HCFA based geopolymers provided a very high rate of strength development, where more than 75% of the 28-days strength was obtained within the first three days.

The effect of the NaOH molarity on the properties of the geopolymer mortars seems to be different depending on the $Na_2SiO_3$ content. This introduces the presence of an interaction effect between them, where the effect of each parameter will vary and depends on the other parameter.

Using higher concentrations of the NaOH solution resulted in lower compressive strength. This is contrary to the known behavior in the case of the low calcium FA based geopolymers. This is may refer to the reactivity and the composition of the source material. However, more investigations are required.

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## References

[1] Davidovits, J., Geopolymer Chemistry and Applications. 3 ed. 2011, Saint-Quentin, France: Institut Géopolymère.
[2] Davidovits, J., Global warming impact on the cement and aggregates industries. World Resource Review, 1994. 6(2): p. 263-278.
[3] van Deventer, J.S.J., et al., Chemical Research and Climate Change as Drivers in the Commercial Adoption of Alkali Activated Materials. Waste and Biomass Valorization, 2010. 1(1): p. 145-155.
[4] BOKSITA, G.R., GEOPOLYMERIZATION OF LOW-GRADE BAUXITE. Materiali in tehnologije, 2014. 48(1): p. 39-44.
[5] Khale, D. and R. Chaudhary, Mechanism of geopolymerization and factors influencing its development: a review. Journal of Materials Science, 2007. 42(3): p. 729-746.
[6] Pathak, A., S. Kumar, and V.K. Jha, Development of Building Material from Geopolymerization of Construction and Demolition Waste (CDW). Transactions of the Indian Ceramic Society, 2014. 73(2): p. 133-137.
[7] ASTM C305-14, Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency, ASTM International, West Conshohocken, PA, 2014, www.astm.org.
[8] ASTM C807-13, Standard Test Method for Time of Setting of Hydraulic Cement Mortar by Modified Vicat Needle, ASTM International, West Conshohocken, PA, 2013, www.astm.org.
[9] ASTM C230 / C230M-14, Standard Specification for Flow Table for Use in Tests of Hydraulic Cement, ASTM International, West Conshohocken, PA, 2014, www.astm.org.
[10] Deb, P.S., P. Nath, and P.K. Sarker, The effects of ground granulated blast-furnace slag blending with fly ash and activator content on the workability and strength properties of geopolymer concrete cured at ambient temperature. Materials & Design, 2014. 62: p. 32-39.
[11] Thokchom, S., K.K. Mandal, and S. Ghosh, Effect of Si/Al Ratio on Performance of Fly Ash Geopolymers at Elevated Temperature. Arabian Journal for Science and Engineering, 2012. 37(4): p. 977-989.
[12] Görhan, G. and G. Kürklü, The influence of the NaOH solution on the properties of the fly ash-based geopolymer mortar cured at different temperatures. Composites Part B: Engineering, 2014. 58: p. 371-377.
[13] Nath, P. and P.K. Sarker, Use of OPC to improve setting and early strength properties of low calcium fly ash geopolymer concrete cured at room temperature. Cement and Concrete Composites, 2015. 55: p. 205-214.
[14] Karakoç, M.B., et al., Mechanical properties and setting time of ferrochrome slag based geopolymer paste and mortar. Construction and Building Materials, 2014. 72: p. 283-292.
[15] Temuujin, J., R. Williams, and A. Van Riessen, Effect of mechanical activation of fly ash on the properties of geopolymer cured at ambient temperature. Journal of Materials Processing Technology, 2009. 209(12): p. 5276-5280.
[16] Al Bakri, A.M., et al., Effect of Na2SiO3/NaOH ratios and NaOH molarities on compressive strength of fly-ash-based geopolymer. ACI Materials Journal, 2012. 109(5): p. 503-508.
[17] Castel, A. and S.J. Foster, Bond strength between blended slag and Class F fly ash geopolymer concrete with steel reinforcement. Cement and Concrete Research, 2015. 72: p. 48-53.
[18] Phoo-ngernkham, T., et al., Effects of sodium hydroxide and sodium silicate solutions on compressive and shear bond strengths of FA–GBFS geopolymer. Construction and Building Materials, 2015. 91: p. 1-8.
[19] Risdanareni, P., J.J. Ekaputri, and Triwulan, The Influence of Alkali Activator Concentration to Mechanical Properties of Geopolymer Concrete with Trass as a Filler. Materials Science Forum, 2015. 803: p. 125-134.
[20] Balczár, I., T. Korim, and A. Dobrádi, Correlation of strength to apparent porosity of geopolymers – Understanding through variations of setting time. Construction and Building Materials, 2015. 93: p. 983-988.
[21] Sayyad, A.S. and S.V. Patankar, Effect of Steel Fibres and Low Calcium Fly Ash on Mechanical and Elastic Properties of Geopolymer Concrete Composites. Indian Journal of Materials Science, 2013. 2013: p. 1-8.