DEVELOPING GEOPOLYMER PASTES USING DRY MIXING TECHNIQUE

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Abstract: A geopolymer is a cement-free binder produced with the help of industrial waste products and alkaline reagents. This paper presents fresh-state and strength properties of geopolymer pastes prepared using dry mixing technique. The pastes were made by incorporating supplementary cementitious materials (SCMs) and powder-based activators with ambient curing. The performance of geopolymer paste mixes was assessed in terms of slump flow characteristics and compressive strength. The setting times (initial and final) of the best performing paste mix were also measured to investigate its suitability to produce geopolymer mortar/composites. The influence of SCMs types/dosages and activator types/dosages/combinations is presented and discussed to evaluate the tentative optimum combination of SCMs and activators to produce geopolymer based blended composites. The mix combination of fly ash (Class C) and ground granulated blast furnace slag (GGBS) activated with powder-based reagent combination of calcium hydroxide and sodium metasilicate was inferred to be the superior geopolymer paste in terms of compressive strength and workability parameters. This geopolymer binder obtained a slump flow spread of 195 mm, relative slump of 2.8 and achieved a compressive strength of 55.45 MPa at 56 days. The initial and final setting time for this mix were determined to be 119 and 259 minutes, respectively.

1   INTRODUCTION

The main binding material of the concrete construction industry is Portland cement, the most widely used binder among all the binding materials (Abo El-Wafa and Fukuzawa, 2018). Moreover, ongoing urbanization is causing rapid development of cement concrete industries to keep pace with the growing need for construction (Elyamany *et al.*, 2018). Each ton of cement production releases about one ton of carbon-dioxide, 1 kg of sulphur dioxide (SO_2), 2 kg oxides of nitrogen (NO_x) and 10 kg dust into the atmosphere (Zhang *et al.*, 2018). Thus, cement production leads to a total of approximately 4 billion tonnes of green house gas emissions annually which is about 7% of the global green house gas emissions (Bhutta *et al.*, 2017). On the other hand, the ever-growing population and the subsequent industrialization have led to the shortfall of landfill sites for the disposal of industrial and domestic wastes. The increasing waste disposal costs has led to the illegal disposal of untreated wastes in the landfills which has raised large social concerns and poses a great threat to the environment (Abo El-Wafa and Fukuzawa, 2018).The partial replacement of cement with industrial waste products can be one of the options to address such environmental issues. But, the complete substitution of cement with domestic, agricultural and industrial wastes by incorporating geopolymer technology appears to be a more sustainable solution to reduce carbon emissions. A geopolymer is a cement free binder formed as a result of alkali activation of aluminosilicate rich materials (source materials) such as ground granulated blast furnace slag (GGBS), fly ash, etc. (Zhang *et al.*, 2018). The most common alkaline reagents used to activate the source materials are a combination of sodium hydroxide or potassium hydroxide and sodium silicate or potassium silicate in solution form (Shaikh and Fairchild, 2018). The process of geopolymerisation involves the dissolution of various types of

silica and alumina under highly alkaline conditions from the surface of source materials (Görhan, Aslaner and Şinik, 2016), thus results in free [SiO4]- and [ALO4]- in the solution. These tetrahedral units are alternatively linked to the polymeric precursor by sharing oxygen atom forming polymeric Si-O-Al-O linkages (Komnitsas, 2011, Davidovits, 1991). The development of binders using this technique results in 50-80% lower carbon emissions than that of from the production of ordinary Portland cement (OPC) (Ding *et al.*, 2016).

Considering the material greenness of the geopolymer binders, their applications in large scale construction and infrastructure industries is still very limited. This can be attributed to many reasons associated with the conventional two-part production technique of such binders (Nematollahi *et al.*, 2015a). The use of the solution-based reagents to activate the source materials creates a difficult environment for the workers. More importantly, handling such huge quantities of highly corrosive alkaline reagents would be practically cumbersome and less feasible for large scale construction projects than the use of conventional concrete (Nematollahi *et al.*, 2015b). Also, the requirement of heat curing of the geopolymer composites hinders its large scale applications (Nematollahi *et al.*, 2017a). All these issues can be resolved by using powder-based reagents to activate the aluminosilicate rich materials, thus facilitating the process of commercialization of the material. Also, these powder-based reagents or solid activators are used in smaller quantities as compared to their counterparts alkaline solutions thus reducing the production costs of the geopolymer binders (Nematollahi *et al.*, 2017b, Alrefaei and Dai, 2018).

There has been considerable amount of research on the development of geopolymers using the conventional two-part production technique, but the one-part or dry mix technique is relatively less explored. Neupane *et al.*, (2016) investigated the development of compressive strength and drying shrinkage of geopolymer concretes produced through the activation of Class F fly ash and ground granulated blast furnace slag (GGBS) using a multi-component powder-based activator combination of sodium silicate and sodium hydroxide. It was inferred that concrete incorporating geopolymer binders required significantly less water for the same workability and 28 days compressive strength. Also, the gain (15-20%) in the compressive strength with age was considerably higher from 28 days to 90 days period as compared to their OPC counterparts. The influence of high range water reducing admixtures (HRWRA) on sodium metasilicate-anhydrous activated geopolymer pastes incorporating Class F fly ash and GGBFS as precursors was assessed in terms of relative slump by Alrefaei*et al.*, (2019). It was found that polycarboxylate based super-plasticizer performed better for higher water/binder ratios (w/b ≥ 0.36) while the naphthalene-based admixture was better for lower water/binder ratios (w/b ≤ 0.36). Also, reducing the water content did not have considerable effect on the compressive strength as it may decrease the solubility of the powdered based activator. Moreover, the alkalinity of the mix increases as the mixing water is reduced which in turn may influence the stability of the super-plasticizers. Similar binding phases or gels-calcium silicate hydrate (C-A-S-H) and sodium aluminosilicate hydrate (N-A-S-H) were observed in both the two-part and one-part geopolymers. The release rate of silica and alumina ions was inferred as a major difference between the two techniques of production of alkali-activated materials (Luukkonen *et al.*, 2017).

This paper further contributes to the limited existing database of literature on the novel dry-mix ("just add water") technique of alkali-activated materials production. The research presented in this paper focusses on the improvements in compressive strength of geopolymer pastes by varying the associated parameters i.e. types/dosages of activators, activator components ratio and water to binder ratio. The slump flow in terms of relative slump and the setting times (initial and final) of the selected optimized paste mixes based on compressive strength has also been documented in this article. The selected optimum paste components can be further used to develop geopolymer mortar/composites.

2   MATERIALS AND EXPERIMENTAL METHODS

2.1   Materials

High calcium fly ash-Class C (FA(C)), low calcium fly ash-Class F (FA(F)) and GGBFS were used as the industrial bi-products or source materials. Two types of powder-based reagents/multi-component activators were used to activate the source materials. The components of the first type of reagent consisted of a combination of calcium hydroxide (Ca (OH)$_2$) and sodium meta-silicate (Na$_2$SiO$_3$.5H$_2$O). The second

reagent consisted of a combination of calcium hydroxide (Ca (OH)$_2$) and sodium sulfate (Na$_2$SO$_4$). The sodium metasilicate had a modulus ratio (MS) of 1 (where MS= SiO$_2$/Na$_2$O) and a specific gravity of 1.81. The purity and specific gravity of calcium hydroxide was 96.5% and 2.24, respectively. Sodium sulfate had a purity of 99% and a specific gravity of 2.7. All the chemicals/reagents used in this research were of lab-grade being cheaper in price and were supplied by our industrial partner Westlab, Canada.

2.2   Mix Proportions

The mix proportions were developed based on the fundamental concepts of activator to source materials ratio, activator components ratio and water to binder ratio used in both conventional two-part geopolymers and the novel dry mix geopolymers in the existing research studies. Six different mixes were developed as provided in the Table 1.

Table 1: Mix proportions of geopolymer pastes

Binder*	Mix Designation**	Activator	Activator/ Binder	Activator component ratio	Water/Binder	HRWRA***
FA(C)+ GGBS	M1A1	Ca(OH)$_2$+ Na$_2$SiO$_3$.5H$_2$O	0.09	Na$_2$SiO$_3$.5H$_2$O/ Ca(OH)$_2$=2.5	0.35	0
	M1A2	Ca(OH)$_2$+ Na$_2$SO$_4$	0.12	Ca(OH)$_2$/ Na$_2$SO$_4$=2.5	0.35	0.01
FA(F)+ GGBS	M2A1	Ca(OH)$_2$+ Na$_2$SiO$_3$.5H$_2$O	0.09	Na$_2$SiO$_3$.5H$_2$O/ Ca(OH)$_2$=2.5	0.3	0
	M2A2	Ca(OH)$_2$+ Na$_2$SO$_4$	0.12	Ca(OH)$_2$/ Na$_2$SO$_4$=2.5	0.35	0
GGBS	M3A1	Ca(OH)$_2$+ Na$_2$SiO$_3$.5H$_2$O	0.09	Na$_2$SiO$_3$.5H$_2$O/ Ca(OH)$_2$=2.5	0.35	0
	M3A2	Ca(OH)$_2$+ Na$_2$SO$_4$	0.12	Ca(OH)$_2$/ Na$_2$SO$_4$=2.5	0.35	0.02

All numbers are mass ratios of binder

*Binder denotes supplementary cementitious materials (SCMs)

** Mix Designation: M-mix, A-activator

*** HRWRA: Poly-carboxylate based super-plasticizer

2.3   Casting, Specimen Preparation and Testing

The source materials and the activators required for each mix were weighed as per the proportions given in the Table 1. The activator components were first mixed thoroughly to form a multi-component activator. This multi-component activator was then added to the binder and was dry mixed for about 3 minutes in a shear mixer. After 3 minutes of dry mixing, required water was gradually added to the mixer. Then super-plasticizer (if required as per the mix design) was gradually added for a period of 2-3 minutes after the addition of water. The total mixing operation lasted about 10-12 minutes. For each mix, at least 12 cube specimens having dimensions of 50 mm × 50 mm × 50 mm were cast. The cube molds were kept in the curing room maintained at a temperature of 23±3°C and 95 ± 5% relative humidity (RH). All specimens were demolded after 24 hours and were kept in the curing room until the day of testing. The compressive strength for each mix was tested at 7, 14, 28, and 56 days as per ASTM C109/C109M-2016 (2016). The workability in terms of slump flow for each mix was observed and measured using a mini-slump cone in compliance with ASTM C1437-2015 (2015).

The relative slump for each mix was determined from the flow measurements using the following equation (Nematollahi and Sanjayan, 2014) :

$$[1] \quad T = \left[\left(\frac{d}{d_0} \right)^2 \right] - 1$$

where d = average of two measured diameters of the matrix spread; and d_0 = bottom diameter of the conical cone.The setting times (initial and final) was determined as per ASTM C 191-2018a (2018) for the best performing paste mix of the study. The best performing paste mix was determined in terms of compressive strength and slump flow results.
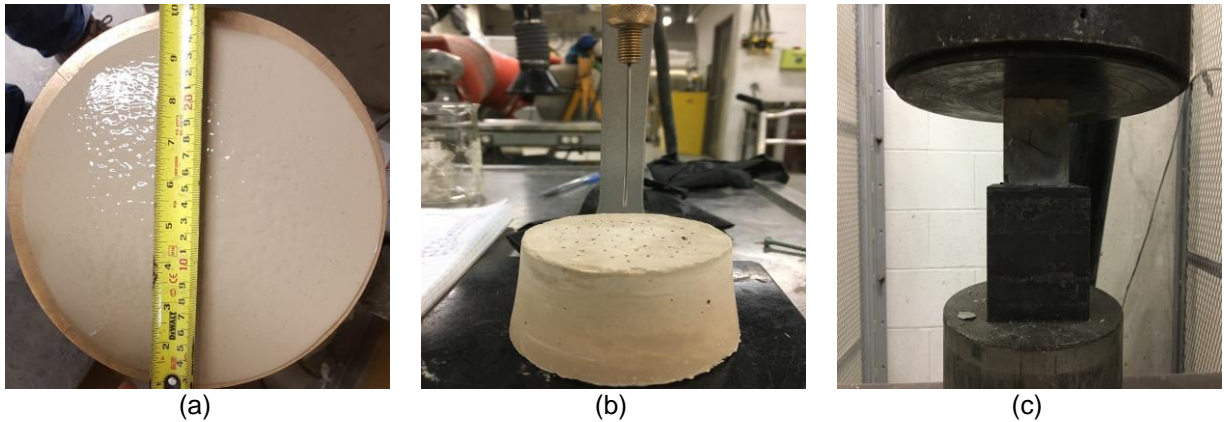

| (a) | (b) | (c) |

Figure 1- (a) slump flow spread, (b) setting time test, (c) compressive strength test

3   RESULTS AND DISCUSSIONS

3.1   Compressive Strength

The test results of all six different mix combinations at different days are tabulated in Table 2. The influence of the two types of activator combinations (A1 and A2) on a binary source material (FA(C)+GGBS) in terms of compressive strength can be seen in Figure-2a. Both the types of multi-component activator resulted in a steady gain of strength with age. It can be seen from Figure 2-a that the strength remained almost constant for mix (M1A1) till 14 days which may be due to slower process of geopolymerisation in comparison to the mix (M1A2). The mix (M1A2) exhibited the highest compressive strength of 64.2 MPa at 56 days. The effect of activation of GGBS can be seen from Figure-2b. There is a decrement in strength of about 15% for mix (M3A1) at 14 days with respect to the strength at 7 days which can be due to initial coagulation of some part of the geopolymeric (Si-Al) gels. A gradual reduction in strength can be seen for mix (M3A2) after 14 days which may be attributed to the in-compatibility arising between the two types of gels (calcium silicate hydrate and Si-Al) being formed due to the presence of high calcium content in the mix. However, a detailed microscopic study of the microstructure is needed to quantify the formation of geopolymeric/calcium silicate hydrate (CSH) gels or products.

A steady gain in strength can be seen for mix M2A1 till 28 days as shown in Figure 3. However, the strength remains constant after 28 days. This can be attributed to comparatively lower activation of fly ash (Class F) by this combination of activators. Thus, fly ash (Class F) mainly acted as a filler in the mix and hence resulted in a lower compressive strength. Also, this combination of FA(F)+GGBS did not get activated by the second multi-component activator (Ca(OH)$_2$+ Na$_2$SO$_4$) as evident from 7 days compressive strength result.

Table 2: Density and Compressive Strength

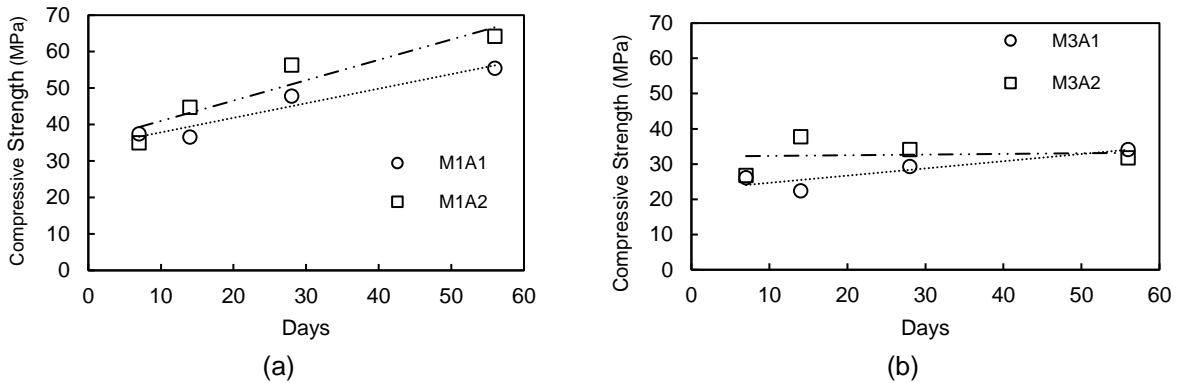| Binder*	Mix Designation	Water/Binder	Days	Density (g/cm^3)	Compressive Strength (MPa)
FA(C)+ GGBS	M1A1	0.35	7/14/28/56	2.1/2/1.97/2.03	37.5/36.6/47.8/55.45
	M1A2	0.35	7/14/28/56	2.14/2.02/2.02/2	35/44.72/56.3/64.2
FA(F)+ GGBS	M2A1	0.3	7/14/28/56	1.85/1.86/1.86/1.87	20.5/25.67/34.05/34.12
	M2A2	0.35	7/14/28/56	1.75/N.A.	8.4/N.A.
GGBS	M3A1	0.35	7/14/28/56	2.08/2/2.02/2	26.15/22.4/29.3/34.1
	M3A2	0.35	7/14/28/56	2.03/2/2.01/2.03	26.75/37.8/34.11/31.77

(a)

(b)

Figure 2- (a) Influence of two types of activators on mix-1, (b) Influence of two types of activators on mix-3
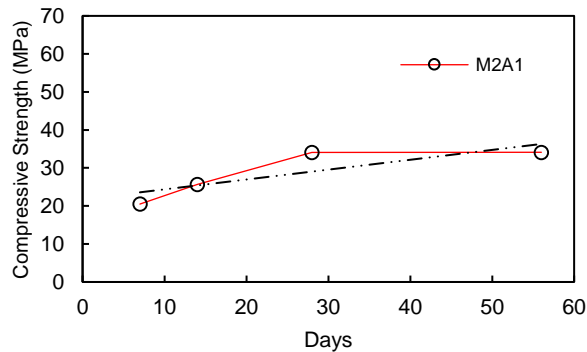

Figure 3: Compressive strength for mix (M2A1)

The effect of reagent/activator (Ca(OH)$_2$+ Na$_2$SiO$_3$.5H$_2$O) on three different types/combinations of source materials/SCMs can be seen from Figure 4-a. Also, the variation in compressive strength for two mixes (M1A2, M3A2) activated with second type of reagent (Ca(OH)$_2$+ Na$_2$SO$_4$) is shown in Figure 4-b. It can be inferred that reagent-A1 performed significantly better than reagent-A2 based on the analysis of compressive strength results. A gradual gain in compressive strength can be seen for all the mixes (M1A1, M2A1 and M3A1) activated with reagent-A1. This may be due to better compatibility of the reagent-A1 with the source materials and because of the higher ions-dissolution potential of sodium-metasilicate from the SCMs.
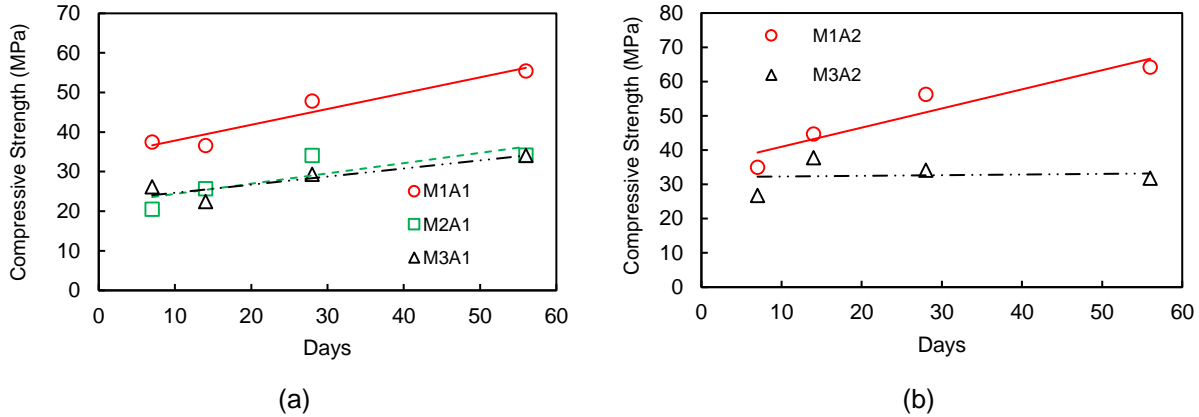
Figure 4- Effect of activator on different source materials, (a) A1, (b) A2

3.2 Workability and Setting Time

The workability of all the six mix combinations was determined in terms of slump flow and relative slump as presented in the Table 3. Figure 5 shows the relative slump values of different mixes in terms of both mix variations and activator variations. It was observed that slag-based binder had lower slump values than a binary binder (FA(C)+GGBS) activated with reagent A1 (Ca (OH)$_2$+ Na$_2$SiO$_3$.5H$_2$O). This may be due to the rounded particle shape of fly ash (Class C) which induces a ball bearing like effect thus improving the flowability of the mix and hence, the relative slump. Also, GGBS might not have been partially activated by the reagent A1 thus reducing the slump flow spread. The low slump flow spread for mix (M2A1) as indicated in Table 3 can be attributed to slow geopolymerisation reaction for fly ash (Class F). The geopolymer mix M1A1 appeared to perform superior as compared to all the mixes of this study considering both strength and flow values. Also, the strength and workability parameters obtained in this study were found to be well in comparison to the conventional OPC binder and two-part activators based geopolymer composites (Nematollahi *et al.*, 2015b, Ranjbar *et al.*, 2016).The initial and final setting time of the superior geopolymer paste mix (mix designation-M1A1) was determined to be 119 minutes and 259 minutes, respectively.
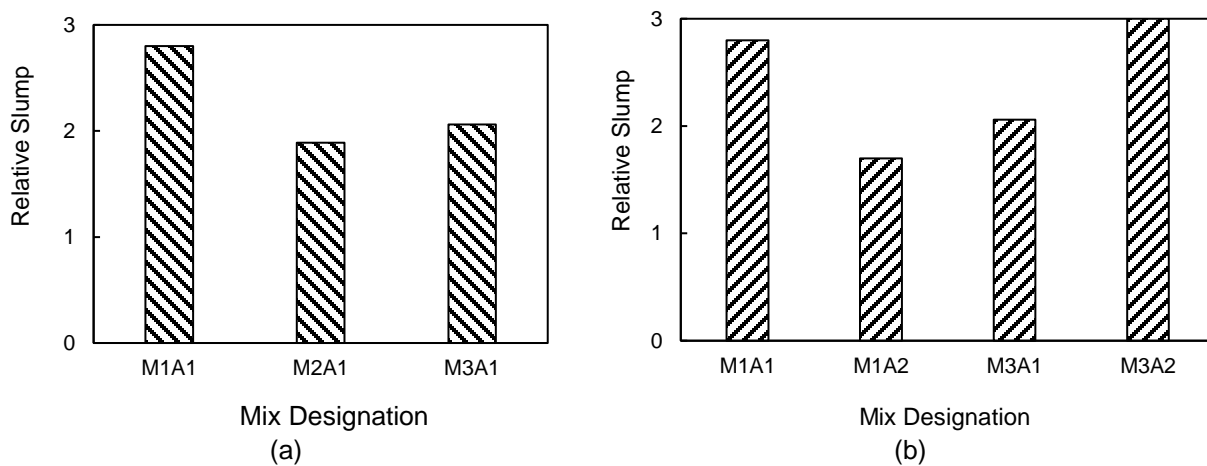

Figure 5- (a) Relative slump of different mixes for activator A1, (b) influence of activators (A1 and A2) on relative slump of different mixes

Table 3: Workability

Binder*	Mix Designation	Water/Binder	HRWRA**	Avg. Flow Dia. (mm)	Relative Slump
FA(C)+ GGBS	M1A1	0.35	0	195	2.8
	M1A2	0.35	0.01	165	1.7
FA(F)+ GGBS	M2A1	0.3	0	170	1.89
	M2A2	0.35	0	N.A.	N.A.
GGBS	M3A1	0.35	0	175	2.06
	M3A2	0.35	0.02	200	3

4   CONCLUSIONS

The mix combination (M1A2) achieved the highest compressive strength of 64.2 MPa at 56 days. However, the relative slump for this combination (M1A2) was determined to be less than the relative slump of the mix (M1A1). The mix M1A1 exhibited a comparable compressive strength of 55.45 MPa at 56 days with respect to the mix M1A2. Therefore, considering strength and flow characteristics, the mix M1A1 having a compressive strength of 55.45 at 56 days, slump flow spread of 195 mm and relative slump of 2.8 was inferred to be the best performing geopolymer paste in this study. The initial and final setting time of this optimized mix combination was obtained as 119 minutes and 259 minutes respectively. The strength and workability parameters of the mix M1A1 were comparable to their conventional OPC binder and two-part geopolymer counterparts. Therefore, the dry mix technique used for geopolymers' production in this research is capable of producing geopolymer composites with desirable properties. Such dry mix technique of geopolymer binder production has immense potential to facilitate the application of alkali activated materials in construction and building industries as it eliminates the need for heat curing and handling large quantities of powders is practically easier and more feasible than handling corrosive alkaline solutions being used in conventional two-part production technique. Moreover, the strength and workability parameters achieved in this research further reinforces this fact of on-site practical applications.

5   REFERENCES

El-Wafa, M. A. and Fukuzawa, K. 2018. Early-Age Strength of Alkali-Activated Municipal Slag-Fly Ash-Based Geopolymer Mortar. *J. Mater. Civ. Eng.,* 2018, 30(4): 04018040 (1-9).

Alrefaei, Y. and Dai, J.-G. 2018. Tensile behavior and microstructure of hybrid fiber ambient cured one-part engineered geopolymer composites. *Construction and Building Materials,* 184: 419–431.

Alrefaei, Y., Wang, Y.-S. and Dai, J.-G. 2019. The effectiveness of different superplasticizers in ambient cured one-part alkali activated pastes. *Cement and Concrete Composites,* 97(2019): 166–174.

Bhutta, A., Farooq, M., Zanotti, C. and Banthia, N. 2017. Pull-out behavior of different fibers in geopolymer mortars: Effects of alkaline solution concentration and curing. *Materials and Structures/Materiaux et Constructions,* 50:80 (1-13).

Davidovits, J. 1991. Geopolymers. *Journal of Thermal Analysis,* 37(8):1633–1656.

Designation: C191 − 18a Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle 1' (2018). doi: 10.1520/C0191-18A.

Ding, Y., Dai, J.-G. and Shi, C.-J. 2016. Mechanical properties of alkali-activated concrete: A state-of-the-art review. *Construction and Building Materials*, 127:68–79.

Elyamany, H. E., Elmoaty, A, E. M. A. and Elshaboury, A. M. 2018. Setting time and 7-day strength of geopolymer mortar with various binders. *Construction and Building Materials*, 187:974–983.

Görhan, G., Aslaner, R. and Şinik, O. 2016. The effect of curing on the properties of metakaolin and fly ash-based geopolymer paste. *Composites Part B: Engineering. Elsevier,* 97:329–335.

Komnitsas, K. A. 2011. Potential of geopolymer technology towards green buildings and sustainable cities. *Procedia Engineering*, 21:1023–1032.

Luukkonen, T., Abdollahnejad, Z., Yliniemi, J., Kinnunen, P. and Illikainen, M. 2017. One-part alkali-activated materials: A review. *Cem. & Conc. Res.,* 103:21-34.

Nematollahi, B., Sanjayan, J. and Shaikh, F. U. A. 2015a. Synthesis of heat and ambient cured one-part geopolymer mixes with different grades of sodium silicate. *Ceramics International*, 41:5696–5704.

Nematollahi, B., Sanjayan, J. and Shaikh, F. U. A. 2015b. Tensile Strain Hardening Behavior of PVA Fiber-Reinforced Engineered Geopolymer Composite. *Journal of Materials in Civil Engineering*, Vol. 27, Issue 10.

Nematollahi, B., Sanjayan, J., Qiu, J. and Yang, E.-H. 2017a. High ductile behavior of a polyethylene fiber-reinforced one-part geopolymer composite: A micromechanics-based investigation', *Archives of Civil and Mechanical Engineering.* 17(3):555–563.

Nematollahi, B., Sanjayan, J., Qiu, J. and Yang, E.-H. 2017b. Micromechanics-based investigation of a sustainable ambient temperature cured one-part strain hardening geopolymer composite. *Construction and Building Materials,* 131:552–563.

Nematollahi, B. and Sanjayan, J. 2014. Effect of different superplasticizers and activator combinations on workability and strength of fly ash based geopolymer. *Materials and Design*, 57:667–672.

Neupane, K., Kidd, P., Chalmers, D., Baweja, D. and Shrestha, R. 2016. Investigation on compressive strength development and drying shrinkage of ambient cured powder-activated geopolymer concretes. *Australian Journal of Civil Engineering*, 14(1).

Ranjbar, N., Mehrali, M.,Behnia, A., Javadi, P., Alireza, M., Mohammad, A., Johnson,U. and Jumaat,Z. 2016. A Comprehensive Study of the Polypropylene Fiber Reinforced Fly Ash Based Geopolymer.*PloS one*, 11(1):1-20

Shaikh, F. and Fairchild, A. 2018. Strain hardening behaviour of polyethylene fibre reinforced ambient air cured geopolymer composite. *RILEM Bookseries*, 15:162-171.

Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens)1' (ASTM, 2016). doi: 10.1520/C0109_C0109M-16A.

'Standard Test Method for Flow of Hydraulic Cement Mortar 1' (ASTM, 2015). doi: 10.1520/C1437.

Zhang, J., Zhang, P., Zheng, Y. and Wang, K. 2018. A review on properties of fresh and hardened geopolymer mortar. *Composites Part B*, Volume 152.