The Influence of Sodium Hydroxide Concentration on Physical Properties and Strength Development of High Calcium Fly Ash Based Geopolymer as Pavement Base Materials

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Abstract. This paper deals with the development of high calcium fly ash based geopolymers. Geopolymer paste was prepared from fly ash alkaline activator solutions using various mix design including molarity of sodium hydroxide used (6-14M) with solid-to-liquid ratio (1.0-3.0) and the sample were curing at ambient temperature. In this paper, flow value, setting time and unconfined compressive strength of high calcium fly ash based geopolymer paste was carried out using flow table equipment, Vicat’s apparatus and compression testing machine to measure the properties caused by high calcium fly ash. It was found that solid to liquid ratio of 2.0 and NaOH molarity of 12M was the best mix design to be applied due to its maximum unconfined compressive strength achieved (up to 19MPa at 28 days) as well as its flow ability of the fresh paste which shown better result compared to other mix designs. High calcium was also found to result in higher strength.

1. Introduction
Over the past few years, the world has seen the rapid growth on the development of road networks throughout the developing nations. However, this speedy development is having a bad consequence as the road construction consumes a massive amount of virgin aggregates or crushed aggregates, specifically for the construction of pavement based layer [1]. The worldwide production of cement rises each and every year and has revealed no signal of reducing down. Massive quantity of source from natural such as natural gas, limestone, electricity, and fossil fuels are required in cement manufacturing. In the production of cement in power plant, high temperatures are required, and this is the cause of large quantity of carbon dioxide released into the atmosphere. Another alternative pozzolanic raw materials such as fly ash, palm oil, slag, fuel ash, rice husk ash, and bagasse ash can be used to reduce the growth of cement consumption [2].
Geopolymer has developed a well-known environmental-friendly material. It was proven to have excellent properties. A precursor based material for geopolymer comprising aluminium (Al) and silicon (Si) that would react with highly alkaline activator solutions to form a geopolymer binder through a few processes [3-5]. Geopolymerization development occur when aluminosilicate materials for example fly ash (FA), blast furnace slag, and metakaolin, can be activated with concentrated alkaline activator solution. In the production of geopolymer cement and concrete, raw pozzolanic materials such as fly ash, has been the most broadly applied as aluminosilicate raw material. It can be used by total or partial replacement of ordinary Portland cement. From an eco-friendly and commercial viewpoint, fly ash application in cement is advantageous because it is a zero cost in the industrial byproduct which else compulsory to remain disposed [6,7].

A previous study proposed that fly ash can also be applied in clay bricks, tiles, admixture for producing concrete, ceramics and also as a soil stabilizer for sub-based layer in road construction [8]. Geopolymer composite has good physical and mechanical properties such as low water absorption, high early compressive strength, fire and heat resistant [9,10]. Geopolymer application also includes cement and concrete, lightweight concrete [11], fire resistance [12, 13], geopolymer bricks [14,15], fire resistant coatings on metal [16], excellent durability towards acidic attack [17] and machineability [18-19]. This paper reports the result of physical properties and strength development for unconfined compressive strength which is to produce high calcium fly ash based geopolymer paste. The utilization of high calcium fly ash as pavement material is one of the alternative low-carbon, low-cost replacement for conventional binders.

2. Experiment details

2.1 Materials

2.1.1 Fly Ash
High-calcium fly ash (FA) from Manjung Coal-Fired Power Station, Lumut, Perak Malaysia was used in this research. The color of fly ash was in brown and comprised of 30.8% SiO2, 13.1% Al2O3, 22.99% Fe2O3 and 22.3% CaO, which was examined by using X-ray fluorescence (XRF). Chemical composition of raw material fly ash is shown in table 1. In standard of practice ASTM C 618 Class C fly ash must contain a proportion of total sum of SiO2, Al2O3, and Fe2O3 contents equivalent to or larger than 50% by mass [20].

2.1.2 Alkaline Activators
Alkaline activator solutions in this research was made from sodium hydroxide (NaOH) and sodium silicate (Na2SiO3) with 97% purity. To produce NaOH solution, NaOH pellets were mixed together with distilled water and stirred up until the pellets were completely dissolved. The alkaline activator solution was then left for 24 hours before it can be used in the next process.

2.2 Mix proportions, Mixing Procedure, Casting and Curing Details

2.2.1 Mixing Procedures
Alkaline activator with sodium hydroxide (NaOH) and sodium silicate (Na2SiO3) was prepared earlier before mixing with fly ash to make sure the reactivity of the solution. The alkaline activator and fly ash were mixed in an automatic mixer up until a homogeneous paste was attained [21]. The procedure started with mixing sodium silicate and NaOH solution for 5 minutes. Fly ash was added into the bowl and mixed for another 5 minutes. Solid to liquid ratios (S/L) of 1.0, 2.0 and 3.0 and 2.5 ratio of sodium silicate to sodium hydroxide were used. The molarity concentrations of NaOH of 6, 8, 10, 12 and 14 M were also used.
2.2.2 Casting and curing of Specimens

For unconfined compressive strength, high calcium fly ash based geopolymer fresh paste was cast into 76 mm in height and 38 mm in diameter accordance to ASTM D1633 [22]. The paste was sealed with a thin plastic layer to avoid evaporation of water and cured at ambient temperature until they were tested. The samples were tested after 7 and 28 days using unconfined compressive strength test machine.

2.3 Testing of Specimen

Setting times of high calcium fly ash based geopolymer pastes were tested in accordance to ASTM C191-08 [23]. The test was conducted at an ambient temperature of 21–23 °C. By using Vicat’s apparatus, the paste was prepared by mixing the raw materials and the alkaline activator solutions in a bowl and tested for initial and final setting time. The outcome of setting time was obtained starting from the moment of the fly ash made an interaction with NaOH solution until the penetration of a 2 mm diameter needle was less than 10 mm. The flow ability of fresh paste of geopolymer was tested by flow table test. The flow of fresh geopolymer paste was performed in accordance to ASTM C124 [24]. The flow value of the geopolymer paste is measured when the fly ash based geopolymer fresh paste are activated by NaOH solutions with various concentrations. The flow value of the high calcium fly ash based geopolymer paste is investigated by measuring the flow value of the paste. Few tests were carried out right after mixing the paste. A conical mold with a bottom diameter of 10 cm was located at the center of the flow table and was filled with two layers of fresh geopolymer paste. Twenty tamps were applied per layer to ensure the mold was filled in uniformly. The mold was removed after extracting the excess paste, and the flow table was lowered for 25 times in 15 s. The increase in base diameter of the mold was recorded and the flow of the fresh paste was determined. Unconfined compressive strength test was conducted on the 7th and 28th days. The cylindrical specimens of fly ash based geopolymer paste were tested at a loading rate of 140 ± 70 kPa/s. The stated results were the average of three paste samples in this testing.

3. Result and Discussion

3.1 Flow Value

These results are presented in figure 1. Based on the figure, it can be confirmed that the flow value varied in the range between 93 to 143 %, depending on the types of raw material used which is fly ash and alkali activator solutions. The gradual increase in NaOH molarity concentration had made the viscosity increased and leaching of alumina and silica from fly ash elements and this indicates the reducing of the workability of the paste.

![Figure 1. Flow value at various NaOH concentration.](image-url)
Afterwards, the dissolution process of aluminosilicates of fly ash and alkali activator solution turns to be more viscous because of the increasing amount of the NaOH concentration. It is shown that the higher the concentration of alkali solution, the lesser is the flow. At lower NaOH molarity concentration, the flow value turns out to be higher due to the interaction of lubricating effect of alkaline activator solution. The effect of high molarity of concentrated alkaline solution increases the cohesiveness of the pore liquid that limits the flow and therefore decreases the flow value of the paste. In addition to the above-mentioned study, spherical particles of fly ash had encouraged the free flow of the paste as mentioned by Jang et al. [25].

3.2 Setting Time
The initial and final setting time of high calcium fly ash based geopolymer paste as presented in figure 2 were measured using Vicat’s needle apparatus. The initial setting times of the paste are found to vary from 10.3 minutes to 120 minutes whereas the final setting times vary between 15 to 330 minutes for different ratio for NaOH concentration (6 to 14M) and 1.0, 2.0 as well as 3.0 for solid to liquid ratio. This rate of setting time was influenced by NaOH molarity concentration and solid to liquid ratio. It is shown that the initial and final setting time slightly decreased as the solid to liquid ratio increased. It is also relatively little compared to other geopolymer produced from low calcium fly ash based. This is because of the slow chemical reaction of fly ash with time under an ambient temperature. The result is observed that an increased molarity of the concentration of the alkaline activator has contributed to a decrease in setting time. The decreasing of setting time is related with an increasing the content of fly ash geopolymer paste. The dissolutions of Al$^3+$ and Si$^4+$ ions from fly ash had increased from solid to liquid ratio (1.0 to 3.0) thus enhancing the geopolymerization and shortening the setting time when high calcium fly ash reacted with silicate to form calcium silicate hydrate gel.

![Figure 2. Initial setting time and final setting time at various NaOH concentration.](image)

3.3 Unconfined Compressive Strength
The experimental result can be seen in figure 3. The result shows that unconfined compressive strength for high calcium fly ash based geopolymer ranging from 3.49 to 10.8 Mpa for 7 days testing and for 28 days testing, the strength ranging from 5.3 to 21.01 Mpa for different NaOH concentration ratio 6, 8, 10, 12 and 14 MPa and solid to liquid ratio 1.0 to 3.0. At 7th and 28th days testing, the unconfined compressive strength value has increased from 8 to 12 M but started to decrease with higher NaOH molarity content. This is believed to occur due to the development of both CSH gels and geopolymer gels at relatively low NaOH molarity concentrations. The increase of NaOH concentration with the increasing alumina and silica content during geopolymization process can be explained by the increasing unconfined compressive strength value. As can be seen, once the NaOH molarity...
concentration is too high, however, the high alkalinity disturbs the formation of both CSH gels and geopolymer gels and hence the strength is reduced. However, at 14 M NaOH concentration, the strength started to decrease compared to a research conducted by Wongpa [26] which stated that the strength started to decrease at 20M NaOH concentration.

4. Conclusions
This paper presented the influence of sodium hydroxide concentration on physical properties and the strength development of high calcium fly ash based geopolymer as pavement-based materials. Based on the experimental research stated in this paper, the following summary are drawn:

- The ratio of the solid to liquid, is found to have a great effect on the unconfined compressive strength of the fly ash-based geopolymer. It can be summarized that the solid to liquid ratio of 2.0 has the optimum amount of it, which could activate the fly ash at the maximum rate of geopolymerization compared to ratio 1.0 and 3.0 with consideration of flow value and setting time of high calcium fly ash based geopolymer.
- It was also found that the best ratio of solid to liquid at 2.0, resulting in the highest unconfined compressive strength which is 19.56 MPa at day-28 of testing with NaOH molarity concentration 12M and ratio of sodium hydroxide to sodium silicate is 2.5.
- The highest unconfined compressive strength of fly ash based geopolymer meet the minimum strength requirement to be applied as pavement base material. The requirement was specified by Department of Public Works which has represented Malaysia road authority.

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References
[1] M Hoy, S Horpibulsuk and A Arulrajah 2016 Constr. Build Mater. 117 209-219
[2] P Topark-Ngarm, P Chindaprasirt and V Sata 2015 J. Mater Civil Eng. 27 04014198
[3] I H Aziz, M Abdullah, H Yong, L Ming, D Panias and K Sakkas 2017 IOP Conference Series: Materials Science and Engineering IOP Publishing pp. 012040
[4] Mohamed R, Razak A R, Abdullah M. M. A. B., Shuib R. K, Aida M M N, Wazien A Z W 2019 IOP Conf. Ser. Mater. Sci. Eng. 551 12093
[5] Romisuhani A, Albakri M M, Kamarudin H and Andrei S V 2017 In IOP Conf. Series: Mater. Sci. Eng. 267(1) 37-43
[6] M Jo, L Soto, M Arocho, J St John and S Hwang 2015 Constr. Build Mater. 93 1097-1104
[7] Ibrahim W M W, Hussin K, Abdullah M M A, Kadir A A and Deraman L M 2017 AIP Conference Proceedings 1885(1) 020011.
[8] N Nordin, M M A B Abdullah, M F M Tahir, A V Sandu and K Hussin 2016 Int. J. Conserv. Sci. 7
[9] I H Aziz, M M A B Abdullah, C-Y Heah and Y-M Liew 2019 Adv. Cem. Res. 1-11
[10] Jaya N A, Al Bakri Abdullah M M, Ghazali C M R, Binhuussen M, Hussin K and Ahmad R 2016 Key Eng. Mater. 700 3–11
[11] M A Faris, M Abdullah, A V Sandu, K N Ismail, L M Moga, O Neculai and R Muniaindy 2017 Mater. Plast 54 145-154
[12] M Abdullah, H Kamarudin, M Binhussain, I Khairul Nizar, A R Rafiza and Y Zarina 2011 Advanced Materials Research Trans Tech Publ pp. 1475-1482
[13] E Azimi, M Abdullah, L Ming, H Yong, K Hussin and I Aziz 2016 MATEC Web Conf. EDP Sciences pp. 01090.
[14] Razak, R. A., Mustafa, M., Bakri, A., Kamarudin, H., & Nizar, K. 2013 Revista de Chimie 64(6) 593-598
[15] Ibrahim W M W, Hussin K, Abdullah M M A B and Kadir A A 2017 AIP Conference Proceedings 1835(1) 020046
[16] N F Shahedan, M M A B Abdullah, N Mahmed, A Kusbiatoro, M Binhussain and S N Zailan 2017 AIP Conference Proceedings AIP Publishing LLC pp. 020046
[17] C Y Heah, H Kamarudin, A M Al Bakri, M Binhussain, M Luqman, I K Nizar, C M Ruzaidi and Y M Liew 2013 Int. J. Min. Met. Mater. 20 313-322
[18] P Y Fauziah, M Fathullah, M M A Abdullah, Meor Ahmad Faris, Faheem Tahir, Z Shayfull, S M Nasir, M Shazzuan and A Z W Wazien 2018 AIP Conference Proceedings. 2030 020067
[19] Fauziah P Y, Fathullah M, Abdullah M M A, Faris M A, Tahir F, Shayfull Z, Nasir S M, Shazzuan M and Wazien A Z W 2018 AIP Conf. Proc. 2030 020067
[20] A Pourkhorshidi, M Najimi, T Parhizkar, F Jafarpour and B Hillemeier 2010 Cem. Conr. Compos. 32 794-800
[21] L Sofri, M Abdullah, M Hasan and Y Huang 2018 AIP Conference Proceedings AIP Publishing LLC pp. 020993
[22] A D1633 2007 Standard test methods for compressive strength of molded soil-cement cylinders, ASTM West Conshohocken, PA, USA
[23] A C191-08 2008 Standard test methods for time of setting of hydraulic cement by Vicat needle,
[24] P Chindaprasirt, T Charerat and V Sirivivatnanon 2007 Cem. Conr. Compos. 29 224-229
[25] J G Jang, N Lee and H-K Lee 2014 Constr. Build Mater. 50 169-176
[26] J Wongpa, K Kiattikomol, C Jaturapitakkul and P Chindaprasirt 2010 Mater. Des. 31 4748-4754