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Factors Affecting the Setting Time of Fly Ash-Based Geopolymer

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Abstract. Fly ash is a waste from coal burning, that are generated with fluctuation both in its physical and chemical characteristics. This characteristics of fly ash when used in the making of geopolymer concrete will greatly affect the final products obtained. The pH value measured in fly ash, according previous research, can influence the setting time of geopolymer and fly ash with high pH values can cause flash-setting in the concrete. Understanding more clearly about the factors that affect the setting time of fly ash based geopolymer is important for further progress and development of the material. It was found that factors that influence the setting time of geopolymer was not only from the physical and chemical properties of the fly ash itself. Other factors such as composition and mix design, manufacturing process and environmental conditions can also affect its setting time. The experimental results showed that fly ash particle size, CaO and MgO content, in addition to ratio of sodium silicate and sodium hydroxide in the alkali solution, molarity of NaOH, initial temperature of the mixture, curing temperature, and mix volume could potentially influence the setting time of the geopolymer mixture.

Introduction

In the manufacturing of geopolymer concrete, the fly ash are to be used both its physical and chemical properties to be reacted with the alkaline solution and be compacted to make a dense matrix. In general, its physical properties is closely related to the type of coal burning equipment, combustion conditions and techniques in the collection while the chemical composition is related to the source of the coal, unit energy obtained and the burning temperature [1]. Therefore, any different fly ash can produce different geopolymer characteristic depending on its physicochemical properties.

According Davidovits [2], pH value measured in fly ash can affect setting time of fly ash based geopolymer concrete. Fly ash as a raw material which has a pH value above 11 have high possibility of flash-set that is harden after 5 minutes of mixing, while those with a pH value between 8 and 11 tend to experience rapid setting. The pH value was closely associated with CaO content in fly ash [3,4]. Also stated in another study [5], that fresh geopolymer concrete has a tendency to have a short setting time, especially on geopolymer-based high calcium fly ash. Yet it was also found that the high levels of CaO in the fly ash actually have an advantage because it can produce a high compressive strength concrete [6]. This could be because high calcium fly ash based geopolymer would have both polymerization and hydration reaction [7]. For comparison, geopolymer concrete made with low calcium fly ash does not have indication of setting time up to 120 minutes after mixing [8].

This study aims to investigate the factors in causing the difference in setting time of the fly ash based geopolymer by using fly ash from different sources. Factors that are investigated includes the physical and chemical properties and the mixing composition and condition. If the factors causing flash-set that occurs in fly ash-based geopolymer can be identified and addressed, then the use of fly ash with a high pH can be possible so as to produce geopolymer concrete with high compressive strength.

Experimental Method

Materials. This study used five samples of fly ash from different coal fired power plant, the fly ash code and its physical properties are listed in Table 1. Alkalinity of the fly ash (pH) is measured on 20 gr fly ash in 80 ml deionized water solution. Particle size analysis (PSA) was carried out on the fly ash with to see the gradation distribution of fly ash type. Fig. 1 showed the distribution of particle size of the fly ash. It was shown that fly ash P10.3 and R9.6 had larger particle size compared to other fly ash samples. Apparently different plant origin, might produce a different particle shapes and gradation.

Chemical compounds from each fly ash samples were tested using x-ray fluorescence (XRF) and the results are shown in Table 2. For all fly ash, the cumulative of SiO_2, Fe_2O_3 and Al_2O_3 compound were greater than 70%, and only one fly ash (Y11.2) have CaO content higher than 10%. Making the fly ash Y11.2 can be classified as high calcium fly ash (type C) while others can be classified as type F fly ash. Amount of Lost on Ignition (LOI) is also shown in the table.

Table 1. Physical properties and measured pH of the fly ash sample.

Fly ash code	Source	pH	SSA (kg/m²)	$D_v(90)$ (μm)	$D_v(50)$ (μm)	$D_v(10)$ (μm)	Specific Gravity
FA Y11.2	Paiton unit 5 & 6	11.2	2618	60.8	6.98	1.13	2.630
FA J10.6	Tanjung Jati	10.6	2078	63.5	8.03	1.46	2.915
FA P10.3	Paiton unit 1&2	10.3	1370	136	20.1	2.38	2.489
FA Y9.8	Paiton unit 5 & 6	9.8	1785	84.3	10.3	1.73	2.360
FA R9.6	Rembang	9.6	1169	104	19.2	3.08	2.245

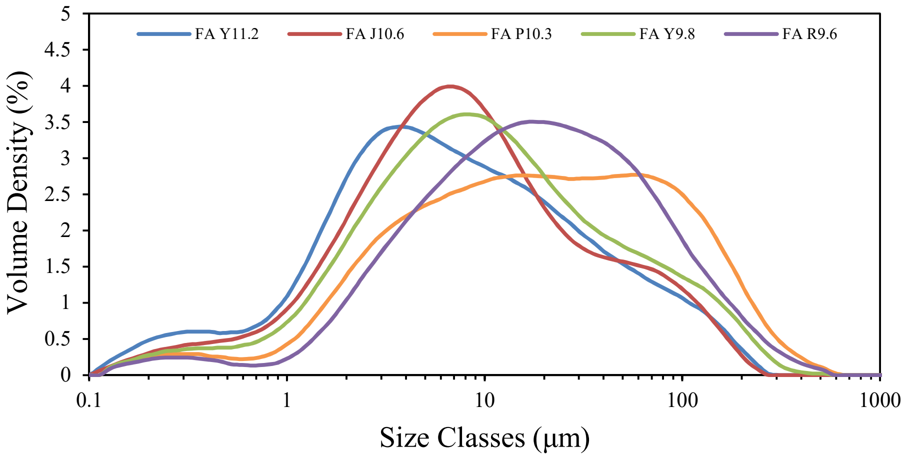


Figure 1. Particle Size Analysis of the fly ash sample

Table 2. XRF test result of the fly ash sample.

Oxide (%)	Fly ash Y11.2	Fly ash J10.6	Fly ash P10.3	Fly ash Y9.8	Fly ash R9.6
SiO_2	39.78	38.24	51.03	51.12	50.14
Al_2O_3	17.87	15.28	25.13	18.9	29.08
Fe_2O_3	15	24.28	9.66	17.71	9.66
CaO	15.47	9.15	5.49	5.54	4.03
K_2O	1.32	0.78	1.58	0.82	1.53
MgO	6.45	5.19	3.25	3.17	1.11
SO_3	1.32	0.61	0.51	0.47	0.77
LOI	0.49	3.9	1.44	6.96	0.63

The alkaline activator for geopolymerization process used sodium hydroxide solution mixed with sodium silicate solution at predetermined ratio. Sodium hydroxide solid is dissolved in distilled water one day prior making the mixture. Fine aggregate used is sand from Lumajang, East Java with water absorption of 1.37% and a fineness modulus of 2.52. Distilled water was used in the mix to prevent impurities that can affect the level of acidity.

Mix Proportion. Study of the setting behavior of geopolymer concrete was conducted on mortar mixture. Fly ash and fine aggregate's ratio of 1:2 and water to binder ratio of 0.25 was used for all mixture. Concentration of sodium hydroxide solution used are 8M, 10 M and 12 M. Ratio between of sodium silicate solution and sodium hydroxide solid (S/N) was 1; 1.5; and 2. Other variable of the experiment include curing temperature, alkaline activator ratio and concentration and mix volume. When the mixture and curing method is not specifically mentioned in the discussion, the proportion used are 8 M of sodium hydroxide solution, S/N ratio of 2 and curing was done at oven temperature of 60°C.

Mixing and setting time. Geopolymer mortar-making process begins with the manufacture of alkaline solution in accordance with a predetermined ratio. Fine aggregate and fly ash mixed in dry condition and then alkaline activator was added, and all material were thoroughly mixed. The mixture was then poured into 150 mm cube mould and the measurement of setting time was conducted on the sample at 60°C oven cured temperature or at room temperature, until initial and final setting time is obtained. Testing of setting time testing was done using penetrometer testing according to ASTM C403 [9]. Initial setting time is reached when the penetration resistance shows the pressure of 500 psi (3.5 MPa) and for 4000 psi (27.6 MPa) for the final setting time.

Result and Discussion

From making of geopolymer mortar with different fly ash source materials, several factors that affect the setting time of the mixture can be identified. The changes of setting time can be seen from the internal factors which are its physical and chemical properties and from external factors such as the mixture composition and manufacturing method and temperature.

Particle size and distribution is related to the specific surface area (SSA) and mean particle size measured from PSA analysis. The initial setting time from different fly ash based geopolymer and its relation to SSA and Dv50 is shown in Fig. 2. There seem to be correlation with the setting time with exception of fly ash R9. There was an indication that fly ash with finer particle size tends to have accelerated initial setting time.

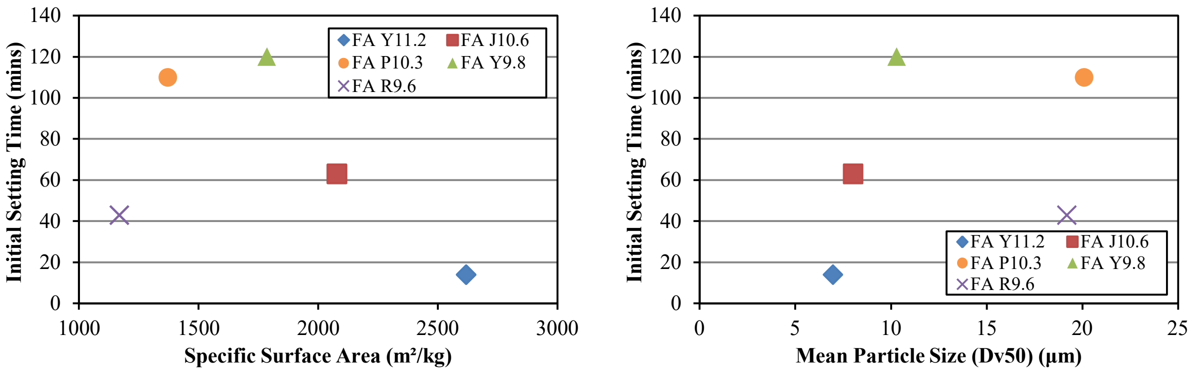


Figure 2. Relationship of initial setting time of fly ash with (a) specific surface area, (b) mean particle size of the sample.

Chemical compound of fly ash could also have an effect on its setting time. It can be seen from Fig. 3 that higher content of CaO and MgO would produce increasingly faster initial setting time. However, the effect of MgO content in fly ash is still not known whether gives a direct influence on setting time because until now the effect of Mg is known only to reduce shrinkage in geopolymer [11]. As mentioned [2], the pH level of fly ash could have great influence on the setting time of the mixture. Fly ash Y11.2 with pH level of 11.2, the highest of all fly ash have very short initial setting time.

Carbon content (LOI). High carbon content affects the absorption of liquid the mixture and making more stiff mix. Fig. 4 shows the initial setting time of the geopolymer mortar with its carbon content and SiO_2/Al_2O_3 ratio. There seem to be no seem to correlate of both properties with its initial setting time for higher carbon content. However for fly ash with a carbon content below 1%, there are indication of flash-set. Further research is needed to determine the mechanism.

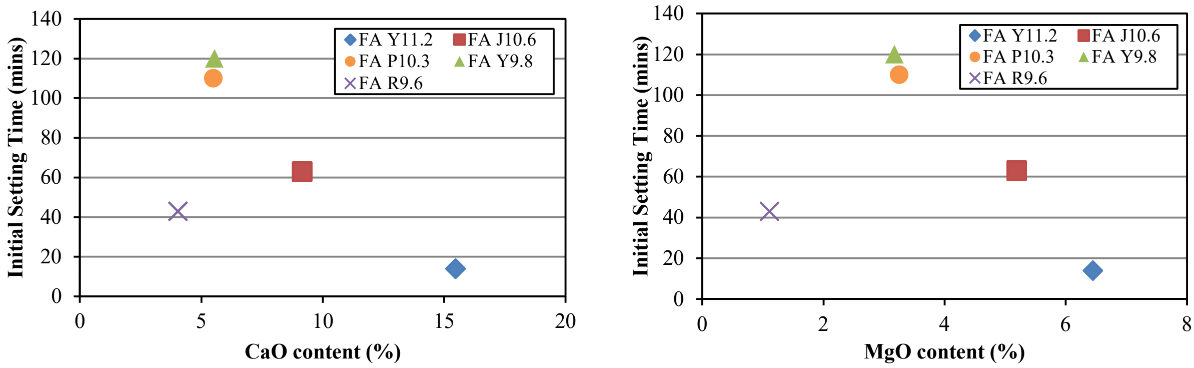


Figure 3. Relationship of initial setting time of fly ash with
(a) CaO content, (b) MgO content.

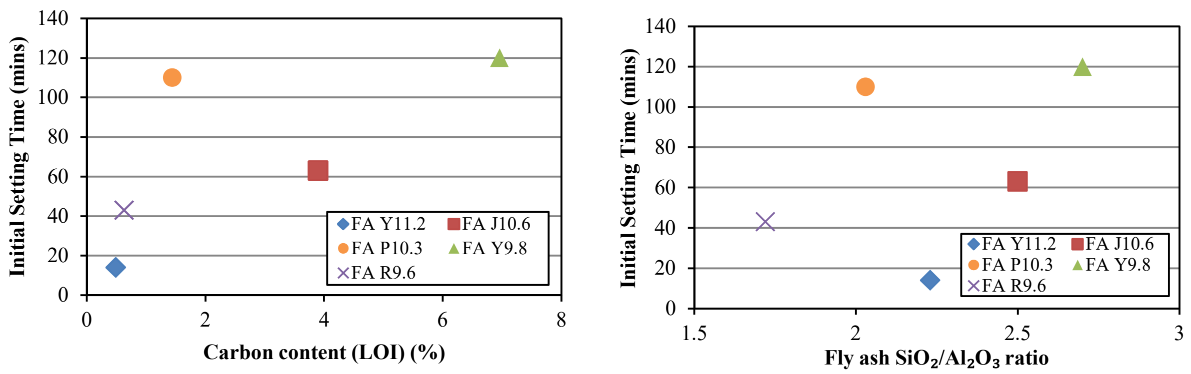


Figure 4. Relationship of initial setting time of fly ash with (a) Carbon content (LOI),
(b) SiO_2/Al_2O_3 ratio of the fly ash sample.

Sodium hydroxide concentration. The strength of alkaline solution to dissolve fly ash have significant effect in the process of setting of geopolymer mortar. Fig. 5 shows initial and final setting time for fly ash from the same source but taken at different time, Y11.2 and Y9.8. Different NaOH molarity (8M, 10M, and 12M) seem to have different time, however this could be due to the constant ratio of sodium silicate and sodium hydroxide ratio, making higher molarity of NaOH also have higher content of silicate and thus making longer setting time. It also should be noted that the time scale of the two fly ash are significantly different. Initial setting of fly ash Y11.2 were achieved at about 15 minutes from the start of mixing while fly ash Y9.8 have more than 2 hours of initial setting time.

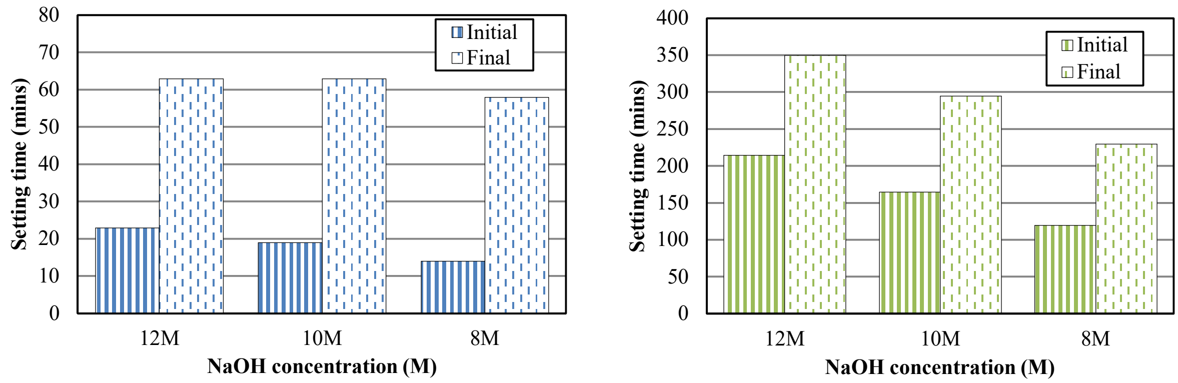
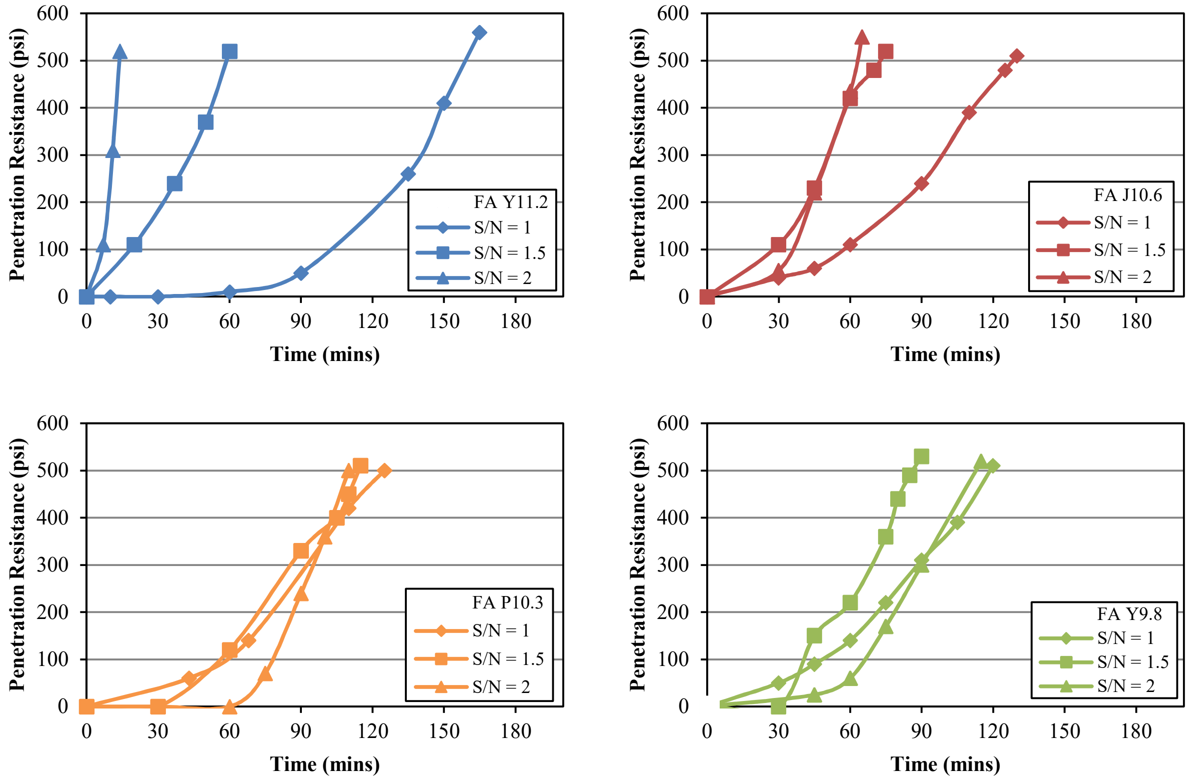


Figure 5. Setting time of geopolymer mortar for (a) fly ash Y11.2 and (b) fly ash Y9.8, with molarity variation in the NaOH solution.

Sodium silicate to sodium hydroxide ratio. Fig. 6 showed the increase of penetration resistance with time for all fly ash with different sodium silicate solution to sodium hydroxide solid ratio (S/N). Molarity of NaOH solution used were 8 M. the result showed that with increase of S/N ratio the setting time was faster, showing that the geopolymer reaction rate was faster with higher S/N ratio up to 2. Fly ash with a higher pH level have a tendency to experience fairly more rapid setting time compared to the others, especially fly ash on S/N ratio of 1.5 and 2. However there is one fly ash R9.6 that did not follow the trend. Despite having a low pH value it also have a fast setting time. This could be due to the particle shape of fly ash that absorb the alkaline liquid and making the mixture more stiff, hence causing faster initial setting time.



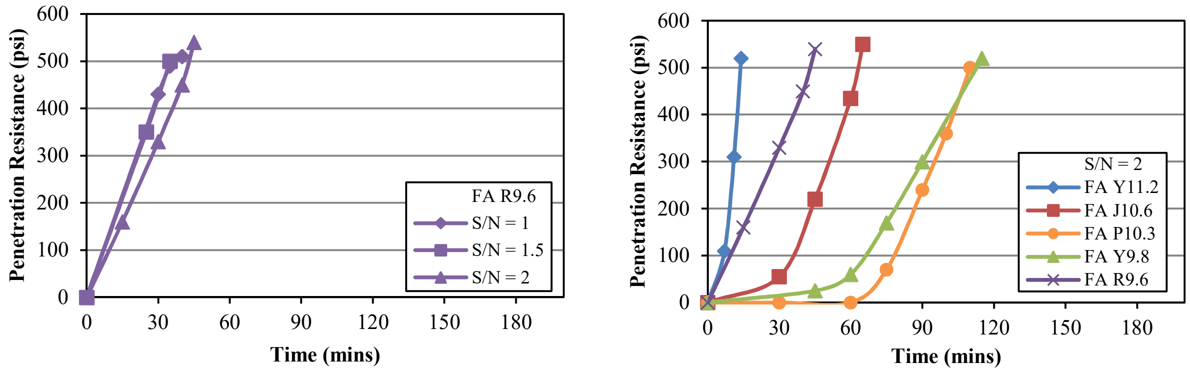


Figure 6. Penetration resistance of geopolymer mortar made for fly ash
(a) Y11.2, (b) J10.6, (c) P10.3, (d) Y9.8, (e) R9.6 and (f) all fly ash with S/N = 2

Curing and initial temperature. Three initial mixture temperature was conditioned for fly ash Y11.2 and Y9.8 by keeping all the material at constant temperature of 20°C, 30°C and 40°C. Oven curing and room curing was done to see the effect of curing temperature. Fig. 7 shows the initial setting time results. Lower initial temperature of the mixture would have longer setting time and the trend was true for both samples of fly ash, however the scale was significantly differs. Fly ash Y11.2 have a very short setting time compare to fly ash Y9.8. Curing temperature also have great effect on increasing the setting time but only for fly ash Y9.8, and no influence on the fly ash Y11.2. Fly ash Y11.2 was still experiencing flash-set. So it can be said that the occurrence of flash-set is not affected by curing temperature, and lowering the initial temperature will make longer initial setting time.

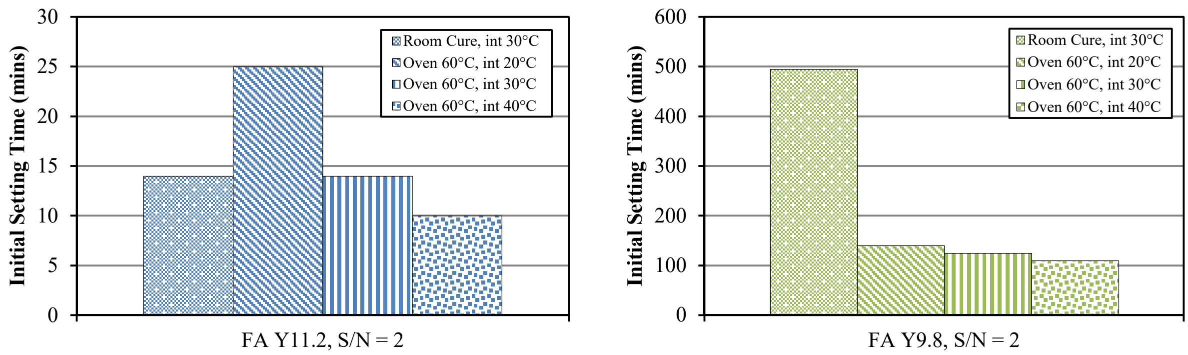


Figure 7. Initial setting time of geopolymer mortar for fly ash (a) Y11.2 and (b) Y9.8
with different initial and curing temperature.

Volume of casting could have cumulative effect on the setting of the geopolymer mortar. Larger volume would have significant cumulative temperature increase and thus resulting faster setting time. Fig. 8 shows the penetration resistance of fly ash Y9.8 with different volume batch. Larger batch 3 times the original volume, have slightly faster initial time (± 10 minutes). This showed that larger mixing volume would have potential of faster setting time. Larger mixture could have higher initial temperature and have faster setting time as discussed previously.

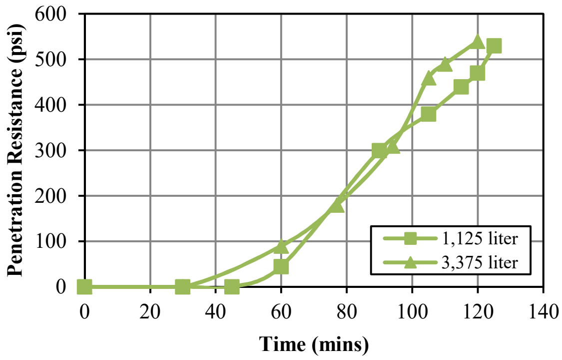


Figure 8. Penetration resistance of fly ash Y9.8 with different volume batch.

Conclusions

Setting time of fly ash-based geopolymer it can be affected by various factors both from internal material aspect such as physical and chemical composition, and from external aspect such as mixture composition, initial and curing temperature and mixture volume. From this study several conclusions were found which are:

- Source of the fly ash have great effect on the setting time of the geopolymer concrete. Fly ash from different source have significantly different physical and chemical composition.
- Both physical and chemical composition of fly ash affect the setting time of the geopolymer mixture. Physical properties include particle size distribution, surface area while the chemical composition include CaO content and LOI.
- CaO content in the fly ash have significant effect on the setting time of geopolymer concrete. Higher CaO content could be detected by measuring pH level of the fly ash solution.
- Initial temperature of the mixture also have significant effect on the setting time of the geopolymer mortar mix. For fly ash with high potential of flash setting, lowering the initial temperature would prolong the initial setting time.
- Caution should be taken when making large volume of geopolymer concrete, especially for fly ash with high tendency of fly setting.

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References

[1] M. Thomas, "Optimizing the use of fly ash in concrete," Portl. Cem. Assos., 2007.

[2] J. Davidovits, Geopolymer chemistry and applications, 2nd ed. Saint-Quentin, France: Institute Géopolymère, 2008.

[3] M. Izquierdo and X. Querol, "Leaching behaviour of elements from coal combustion fly ash: An overview," Int. J. Coal Geol., vol. 94, no. 5, pp. 54–66, May 2012.

[4] Antoni, R. Gunawan and D Hardjito, "Rapid Indicators in Detecting Variation of Fly Ash for Making HVFA Concrete" Appl. Mech. Mater. Vol. 815 (2015) pp 153-157

[5] T. Phoo-ngernkham, P. Chindaprasirt, V. Sata, and T. Sinsiri, “High calcium fly ash geopolymer containing diatomite as additive,” Indian J. Eng. Mater. Sci., vol. 20, no. 8, pp. 310–318, 2013.

[6] J. J. Ekaputri, U. M. Bahrul, R. Bayuaji, S. T. Eddy, M. M. Al Bakri, and M. I. Triwulan, “A comprehensive characterization and determination of fly ashes in Indonesia using different methods,” Appl. Mech. Mater., 2015.

[7] D. Hardjito, “Studies on fly ash-based geopolymer concrete,” Curtin University of Technology. Perth, Australia, 2005.

[8] D. Hardjito, C. C. Cheak, and C. H. Lee Ing, “Strength and Setting Times of Low Calcium Fly Ash-based Geopolymer Mortar,” Mod. Appl. Sci., vol. 2, no. 7, pp. 3–11, 2008.

[9] ASTM C403, Standard test method for time of setting of concrete mixtures by penetration resistance. ASTM International, 1999.

[10] L. U. Duyou, Z. Yanzeng, L. I. U. Yongdao, and X. U. Zhongzi, “Effect of Light-burned Magnesium Oxide on Deformation Behavior of Geopolymer and its Mechanism,” J. Chinese Ceram. Soc., vol. 40, no. 11, pp. 1625–1630, 2012.