Enhancing the Strength of Volcanic Mud-based Class C Fly Ash Geopolymer Specimen by Limestone Inclusion

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Abstract. Volcanic mudflow disaster has brought negative impacts in the area around the mudflow. The contents of mud are predominantly silicate and aluminates, which are the primary constituent materials of fly ash-based geopolymer specimen. However, the main issue of fly ash-based geopolymer is the requirement of heat curing due to the low calcium in fly ash precursor. The aim of this research is to identify the effect of limestone inclusion on strength properties of volcanic mud-based class C fly ash geopolymer mortar. The volcanic mud was obtained from Sidoarjo mud in East Java Indonesia. The alkaline activator solution was prepared by mixing 10 Molar sodium hydroxide with sodium silicate with the ratio of 0.67. The compressive strength test was carried out at the age of 28 days. The specimens were cured at room temperature. The results show that the addition of 30% limestone in volcanic mud-based class C fly ash geopolymer specimen gives the highest strength at 28 days. It also improves the setting time rate due to the calcium addition. However, further addition of limestone tends to reduce the strength. This might attribute to the decrease of silicate and aluminates contents in geopolymer specimen along with the limestone addition.

1. Introduction
The volcanic mudflow disaster has brought negative impacts around the affected environment both physically or materially. In 2006, a mud volcano emerged in Sidoarjo, Indonesia. The peak of mud eruption achieved in 2007 which released about 180,000 m3 of mud/day Although the eruption activity of mud volcano has been reported decreasing to be approximately 30,000 m3/day in 2012, it still continues until today and has resulted in an enormous volume of mud [1-3]. According to previous research, mud volcano contains a high silicate, aluminates, and ferrite contents [4, 5]. This mud volcano disaster has encouraged researchers to explore an alternative use of mud volcano material.

The environmental issues regarding to the Portland Cement (PC) production have become a major concern. Production of 1 ton cement releases approximately 0.8-1 ton of greenhouse gas (CO2) into the atmosphere as the result of limestone calcination and coal combustion process during PC manufacturing process [6-8]. One alternative to overcome this issue is by using fly ash, a waste product material from power station [9, 10]. The use of fly ash as fully cement replacement material, known as geopolymer, was first introduced by Davidovits [11]. The mechanism of geopolymerization reaction involves the polycondensation reaction between alumina-silicate oxide as a precursor and alkali polysiulrates producing polymeric Si-O-Al matrix [12]. Previous studies have shown that geopolymer made by fly ash and activated by alkaline activator demonstrates a comparable compressive strength to normal PC specimen [13-15]. However, the main problem of geopolymer is the need of high temperature to achieve...
its structural integrity [16]. The addition of high calcium content material is one alternative to overcome this problem [17].

The similarity chemical composition of mud volcano with geopolymer specimen provides an alternative to the geopolymer production based on fly ash and mud volcano. Previous research on the use of mud volcano as a partial replacement on sand or PC has been done by Handoko et al [3], Antoni et al [4], and Razak et al [18]. However, the use of mud volcano as a fully replacement has not been done. Thus, this research aims to investigate the strength properties of geopolymer made by fly ash and mud volcano as fully PC and sand replacement materials, respectively. The addition of limestone is used to overcome the requirement of high curing problems in geopolymer. Variation of limestone inclusion is carried out to investigate the fly ash/mud volcano geopolymer performance at normal temperature. The strength performance of specimen will be identified by compressive strength test at 28 days. The setting time test is performed to determine the effect of limestone addition. This research is expected to be able to solve the mud volcano volume problems and environmental problems caused by cement production process.

2. Methods

2.1. Materials
The main materials used in this research were volcanic-mud, fly ash and limestone. Volcanic-mud was collected from the eruption of mud-volcano Sidoarjo, Indonesia, while fly ash was obtained from Paiton power station. Limestone or calcium carbonate (CaCO₃) was purchased from material distributor. The chemical composition for all materials were identified by X-Ray Fluorescence (XRF) test using PANalytical Minipal test equipment. The chemical composition of volcanic-mud, fly ash and limestone are listed in Table 1.

| Chemical Composition | Fly Ash | Mud-Volcano | Limestone |
|----------------------|---------|-------------|-----------|
| CaO                  | 18.41   | 8.62        | 98.02     |
| SiO₂                 | 13.42   | 26.87       | -         |
| Al₂O₃                | 4.89    | 8.18        | -         |
| Fe₂O₃                | 54.63   | 46.52       | 0.33      |
| Mn₂O₃                | 0.54    | 0.64        | -         |

Fly ash used in this research was class C fly ash with CaO of 18.41% (>10%) and the total of SiO₂+Al₂O₃+Fe₂O₃ was 72.94% (>50%). This class C fly ash has satisfied the requirement of pozzolanic condition in accordance with ASTM C618 [19]. A mix of sodium silicate with SiO₂ to Na₂O ratio of 3.3 and 10 Molar NaOH were used as activators. A ratio of NaOH to sodium silicate of 0.67 was applied for this research.

2.2. Mix proportions
Details of mix proportions of volcanic mud/fly ash-based geopolymer specimens are shown in Table 2.
Table 2. Mix proportions of volcanic mud-based geopolymer.

| Mix | Fly ash | Lime stone | Mud-volcano | Sodium Silicate | NaOH |
|-----|---------|------------|-------------|----------------|------|
| 1   | 1       | -          | 3           | 0.21           | 0.14 |
| 2   | 0.9     | 0.1        | 3           | 0.21           | 0.14 |
| 3   | 0.8     | 0.2        | 3           | 0.21           | 0.14 |
| 4   | 0.7     | 0.3        | 3           | 0.21           | 0.14 |
| 5   | 0.6     | 0.4        | 3           | 0.21           | 0.14 |
| 6   | 0.5     | 0.5        | 3           | 0.21           | 0.14 |

Mix design proportions of volcanic mud/fly ash-based geopolymer (VMFAG) specimens were developed in accordance with ASTM C109 [20] with a water binder ratio of 0.45. However, due to a solid content on NaOH and sodium silicate activator solution and liquid characteristic of geopolymer specimen, a water solid ratio of 0.21 was preferably used compared to water binder ratio. The total quantity of solid in VMFAG specimens was determined as the sum of the mass of the solid content in activator solution, fly ash, limestone, and mud-volcano, while the quantity of water was measured from the sum of water in NaOH and sodium silicate [15]. Normal curing at room temperature was applied for VMFAG specimens.

2.3. Testing specimen
The compressive strength of 50 x 50 x 50 mm³ cube mortar VMFAG specimens were determined in accordance with ASTM C109 [20]. Three mortar specimens were tested for each data point. The mortar specimens were tested at 28 days after casting.

The depth penetration test (Vicat test) was carried out to identify the effect of limestone on the volcanic mud-based class C fly ash geopolymer paste setting time in accordance with ASTM C191 [21]. The test was performed on three (3) mix design with the best compressive strength value.

3. Results and discussion
Table 3 displays the compressive strength test results reported for the volcanic mud/fly ash-based geopolymer (VMFAG) specimens for all mixes.

Table 3. Compressive strength test results at 28 days.

| Mix | Compressive strength (kg/cm²) | Limestone inclusion (%) |
|-----|--------------------------------|-------------------------|
| 1   | 55.0 ± 5.0                     | 0                       |
| 2   | 63.3 ± 3.1                     | 10                      |
| 3   | 69.0 ± 2.7                     | 20                      |
| 4   | 88.3 ± 2.5                     | 30                      |
| 5   | 63.7 ± 2.1                     | 40                      |
| 6   | 52.1 ± 6.6                     | 50                      |
VMFAG Mix 4 (30% limestone inclusion) specimen demonstrates the highest compressive strength compared to all mixes with the strength of 88.3 kg/cm² at 28 days followed by VMFAG Mix 3 (20% limestone inclusion) with 69.0 kg/cm². The lowest strength was demonstrated by VMFAG Mix 6 with 50% limestone inclusion at 55.0 kg/cm² which only reached half (59%) of the VMFAG Mix 4 strength. It also exhibits a comparable strength to that VMFAG Mix 1 with no limestone addition.

Figure 1. Compressive strength of volcanic mud-based class C fly ash geopolymer at 28 days.

Figure 1 demonstrates that the inclusion of limestone significantly affects the strength of volcanic mud-based class C fly ash geopolymer specimens at 28 days. The limestone inclusion improved the strength performance of VMFAG as shown in VMFAG Mix 1 and Mix 2 with 0% and 10% limestone inclusion, respectively. There was a significant increase in strength from 55.0 kg/cm² to 63.3 kg/cm². A further increase in strength was shown along with limestone inclusion. A slight increase of 9% was demonstrated by VMFAG Mix 3 from 63.3 kg/cm² (10% limestone) to 69 kg/cm² with 20% limestone addition. The highest strength increase was shown from 20% to 30% limestone inclusion with the total increase of 19.3 kg/cm² as shown in VMFAG Mix 3 to VMFAG Mix 4, respectively. The highest strength was achieved by VMFAG Mix 4 with the strength of 88.3 kg/cm².

The limestone addition on volcanic mud-based class C fly ash geopolymer tended to provide additional strength. The polymerization reaction of geopolymer involves silicate and aluminate [12]. A high silicate content of class C fly ash and additional silicate from mud volcano tends to have un-reacted silicate remaining. This unreacted silicate reacts with calcium from limestone addition creates a hydration reaction similar to that PC concrete which leads to the strength addition to VMFAG mortar specimen. Similar finding was also found by Wardhono et al. [17, 22] According to the authors, the addition of slag with high calcium content significantly increase the strength development of class C fly ash geopolymer specimen.

However, a further limestone inclusion more than 30% tended to reduce the strength of VMFAG specimen. A significant strength reduction occurred in 40% and 50% limestone addition in VMFAG Mix 5 and Mix 6, respectively. The highest strength reduction was 28% from 88.3 kg/cm² (VMFAG Mix 4 with 30% limestone) to 63.7 kg/cm² (VMFAG Mix 5 with 40% limestone) at 28 days. This might attribute to the high calcium content in geopolymer specimen.

The calcium content in the volcanic mud-based class C fly ash geopolymer was obtained from the fly ash and mud volcano as primary material as shown in Table 1. High calcium content in geopolymer was able to overcome the heat curing problem during the hardening process. However, it still exhibited a low strength performance as shown in VMFAG Mix 1. The addition of limestone with high calcium compound at particular composition significantly increased the strength properties, however the addition of limestone in high proportions tended to decrease the strength performance of VMFAG. This might attribute to the unreacted calcium in geopolymer. The geopolymerization reaction occurs between silicate and aluminate forming geopolymer matrix, while the excess silicate will result in unreacted
The addition of calcium will react with the excess silicate to form C-S-H gel as in normal PC reaction, while the unreacted calcium will form Ca(OH)₂ through hydration reaction which might lead to an expansion and cracking [25]. This resulted in a decrease in strength along with the addition of calcium.

The depth penetration test results of volcanic mud-based class C fly ash geopolymer using vicat test apparatus are shown in Figure 2. The test was carried out at room temperature. The test was performed on three mix design with the best compressive strength value, i.e. VMFAG Mix 3, Mix 4, and Mix 5, with the strength of 69 kg/cm², 88.3 kg/cm², and 63.7 kg/cm², respectively.

![Figure 2. Depth penetration test of volcanic mud-based class C fly ash geopolymer at 28 days.](image)

The setting time of all VMFAG specimens exhibited a faster setting time compared to that normal PC. The setting time of VMFAG Mix 3 (20% limestone), VMFAG Mix 4 (30% limestone), and VMFAG Mix 5 (40% limestone) was 135, 75, and 60 minutes, respectively, which were faster than the setting time of normal PC. The setting time of normal PC was approximately 6th hours [22]. Further, the depth penetration test shows that the limestone inclusion affected setting time of VMFAG specimen (Figure 2). The addition of limestone significantly increased the setting time rate from 135 minutes (VMFAG Mix 3 with 20% limestone) to 75 minutes (VMFAG Mix 4 with 30% limestone). Further limestone addition in VMFAG Mix 5 slightly improved the setting time rate from 75 minutes to 60 minutes. This might attribute to the calcium content in limestone. The reaction of calcium based material produces a similar hydration product to normal PC concrete, i.e. calcium silicate hydrate (CSH) gel, which involving the reaction between calcium and silicate [25, 26]. Thus, the limestone inclusion in VMFAG specimens will cause two reactions, i.e. geopolymer reaction (silicate and aluminate) and calcium based reaction (calcium and silicate) which accelerate the setting time VMFAG specimens.

Based on this analysis, it can be suggested that mud volcano incorporating limestone can be used as fully sand replacement material due to the similarity silicate and aluminate content. Similar finding was also found by Amin et al. [27] using mud volcano as 70% cement replacement with the strength of 34.9 kg/cm².

4. Conclusions
This research investigates the effect of limestone addition on the strength and setting time of fly ash/mud volcano-based geopolymer mortar at normal curing temperature. Based on the finding, it can be concluded that:

- Mud volcano can be used as a fully sand replacement material in volcanic mud-based fly ash-based geopolymer mortar due to the similarity silicate and aluminate compositions.
- Limestone inclusion significantly affects the strength development of fly ash/mud volcano-based geopolymer mortar. The addition of 30% limestone demonstrates the highest compressive strength with the strength of 88.3 kg/cm² at 28 days.
The setting time of fly ash/mud volcano-based geopolymer was influenced by the addition of limestone. The addition of limestone accelerated the setting time and hardening process in normal curing temperature.

Limestone inclusion can overcome the high temperature requirement during curing process.

The utilization of mud volcano and fly ash in the development fly ash-based geopolymer can overcome the mud volcano high volume problem and global warming issue due to the PC production, respectively.

References
[1] Rudolph M L, Karlstrom L and Manga M 2011 Earth and Planetary Science Letters 308 (1-2) 124-130.
[2] Bakri A M M A, Rafiza A R, Hardjito D, Kamarudin H and Nizar I K 2012 Advanced Materials Research 548 82-86.
[3] Handoko L, Rifai’i A, Yasufuku N and Ishikura R 2015 Procedia Engineering 125 324-330.
[4] Antoni, Tjondro R G T, Anggono J and Hardjito D 2013 Advanced Materials Research 626 224-228.
[5] Krisnayanti B D and Agustawijaya D S 2014 Journal of Degraded and Mining Lands Management 1 (4) 207-210.
[6] Davidovits J 1994 World Resource Review 6 263-278.
[7] Berry M, Cross D and Stephens J 2009 Proceedings of The World of Coal Ash (WOCA) Conference, Lexington, USA.
[8] Meyer C 2009 Cement and Concrete Composites 31 (8) 601-605.
[9] Ahmaruzzaman M 2010 Progress in Energy and Combustion Science 36 (3) 327-363.
[10] Papadakis V G 1999 Cement and Concrete Research 29 (11) 1727-1736.
[11] Davidovits J 1994 Proceedings of First International Conference on Alkali Cements and Concretes, Kiev, Ukraine.
[12] Pacheco-Torgal F, Castro-Gomes J and Jalali S 2008 Construction & Building Materials 22 1308-1314.
[13] Hardjito D, Wallah S E, Sumajouw D M J and Rangan B V 2004 ACI Materials Journal 101 (6) 467-472.
[14] Hardjito D, Wallah S E, Sumajouw D M J and Rangan B V 2005 Australian Journal of Structural Engineering 6 (1).
[15] Wardhono A, Law D W and Molyneaux T C K 2016 Materials Science Forum 841 104-110.
[16] Kong D L Y and Sanjayan J G 2010 Cement and Concrete Research 40 334-339.
[17] Wardhono A, Law D W and Strano A 2015 Procedia Engineering 125 650-656.
[18] Razak R A, Abdullah M M A B, Hussin K, Ismail K N, Hardjito D and Yahya Z 2015 International Journal of Molecular Sciences 16 11629-11647.
[19] ASTM Standard, ASTM C618-03 2004.
[20] ASTM Standard, ASTM C109-02 2004.
[21] ASTM Standard, ASTM C191-04 2004.
[22] Wardhono A, Law D W, Sutikno and Dani H 2017 Proceedings of 1st Green Construction and Engineering Education Conference, Malang, Indonesia 1887.
[23] Collins F and Sanjayan J G 2001 Cement and Concrete Composites 23 345-352.
[24] Wardhono A 2015 Ph.D. Thesis. Royal Melbourne Institute of Technology (RMIT) University, Melbourne, Australia.
[25] Mindess S, Young J F and Darwin D 2003 Concrete (2nd ed.) (New Jersey: Prentice Hall).
[26] Peng J X, Huang L, Zhao Y B, Chen P, Zheng L and Zheng W 2013 Advanced Materials Research 610-613, 2120-2128.
[27] Amin M S, Ekaputri J J and Triwulan 2014 Jurnal Logic 14 (1) 54-59.