Assessment on the Potential of Volcano Ash as Artificial Lightweight Aggregates using Geopolymerisation Method

RAFIZA ABDUL RAZAK1,*, MOHD MUSTAFA AL BAKRI ABDULLAH2, KAMARUDIN HUSSIN, KHAIRUL NIZAR ISMAIL3, IOAN GABRIEL SANDU4, DJWANTORO HARDIJIT5, ZARINA YAHYA6, ANDREI VICTOR SANDU7*

1 Universiti Malaysia Perlis (UniMAP), Centre of Excellence Geopolymer & Green Technology (CEGeoGTech), School of Material Engineering, P.O. Box 77, D/A Pejabat Pos Besar, Kangar, Perlis 01000, Malaysia
2 Universiti Malaysia Perlis (UniMAP), Faculty of Engineering Technology, P.O. Box 77, D/A Pejabat Pos Besar, Kangar, Perlis 01000, Malaysia
3 Universiti Malaysia Perlis, School of Environmental Engineering, 02600, Jejawi, Perlis, Malaysia
4 Gheorghe Asachi Technical University of Iasi, Faculty of Materials Science and Engineering, 71 D. Mangeron Blvd., 700050, Romania
5 Civil Engineering Department, Petra Christian University, Jalan Siwalankerto 121-131, Surabaya, 60236, Indonesia

Keywords: geopolymer, volcano Ash, lightweight aggregates, alkaline activator, XRF, XRD, SEM

Following the Yogyakarta earthquake on May 27th, 2006, the subsequent eruption of a volcano mud has been closely observed and analyzed by the geological community. The volcano mud, known as LUSI (LU-lumpur, SI-Sidoarjo), began erupting near the Banjjarpanji-1 exploration well in Sidoarjo, East Java, Indonesia. LUSI offers a unique opportunity to study the genesis and development of a volcano mud. This paper summarizes the current knowledge about the potential of volcano ash as a raw material in geopolymer and as artificial aggregate. Previous experimental study shows that the volcano ash has a good performance when 5% and 10% OPC was replaced by volcano ash mixture. Volcano ash mixed with fly ash in certain composition has a potential to become a binder in geopolymer concrete. An effort to convert the volcano ash to artificial aggregate also shows good potential due to their specific gravity and water absorptions, and characterization of this material. The characterization of this material has been done through X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Scanning Electron Micrograph (SEM), and Fourier Transform Infrared Spectroscopy (FTIR), and then compared to other materials. Sintered volcano ash showed good performance in terms of strength as a cement replacement material with OPC and fly ash. Volcano ash also showed good performance for porosity. This material has a potential as a raw material due to high compounds of SiO2, and Al2O3 in producing geopolymer composites, and as new artificial aggregate to be used in concrete application.

Over the past five years, the volcano mud in Sidoarjo, East Java, Indonesia started to erupt on May 29th 2006 and has displaced 13,000 families with 30,000 people on this surrounding area. Controversy has begun whether the volcano mud was caused by drilling of the gas exploration well in the Porong area, Sidoarjo, East Java or due to the Yogyakarta earthquake that occurred at 03:54 am on the 27th May 2006 [1-3]. This eruption impacted an area of almost 3 square miles to a depth of 65 feet and thirty thousand people have been displaced which cost Indonesia $3.7 billion in damages and damage control [4, 5]. For 2012, the government has earmarked an initial amount of Rp 734 billion (US$80.01 million) to pay compensation for 61 hectares of the victims’ land. For 2013, the government expects to spend another Rp 1.1 trillion to purchase 164 hectares and Rp 1.3 trillion for 201.5 hectares in 2014 [6].

Figure 1 shows the map of gas explosion that was occurred at Sidoarjo, East Java, Indonesia. Volcano mud still active and contains highest in volume, duration and spatial extent when compared to some of the world most prominent and active volcano mud as mentioned in [1] and reviewed in [7]. As of June 2007, the average subsidence area was measured at 10.7 m [2]. Many efforts have been done to diminish damage. One of the efforts was by diverting the volcano mud to flow into nearby rivers and the ocean. Then, 300 kg concrete balls have been dropped in main conduits to tire the flow [1, 2, 4]. However, these efforts were not truly successful. Some researches have been done on utilizing the volcano mud as replacement material in producing concrete and geopolymer [8-10]. Some suitable compositions of the binders have been created and show good potential. Nuruddin et al. [9] stated that the concrete strength is affected by the percentage of LUSI mud inclusions. Study carried out by Ekaputri [8] shows that the wet and dry LUSI mud mixed with fly ash-alkaline activator give the good performance of geopolymer concrete.

Previous research also shows the approaches to convert fly ash into aggregates as replacements for natural aggregates. The reason of this approach is due to the demand for aggregates are large and increasing continuously while the natural aggregate resource is depleting. Many countries like USA, UK, Poland, Russia and Germany are producing aggregates commercially under different trade names. Aggregate may count for 70-80% by mass of concrete. Aggregates can also be used as soil conditioners, water savers, and soil and sand stabilizers [11]. Furthermore, the use of artificial aggregates has shown reasonable costs and produce better quality compared to conventional aggregates [12]. Niyazi and Turan [13] have chosen fly ash mixed with bentonite and glass powder as raw material in lightweight aggregate production. Ramamurthy and Harikrishnan [14] used fly ash mixed with ordinary Portland cement (OPC), Na-
bentonite and powdered limestone as binders for palletization. Study carried out in [15] used the fly ash mixed with sodium silicate (Na$_2$SiO$_3$) and sodium hydroxide (NaOH) as an oxidizing agent, MnO$_2$ used to improve strength, and the small amount of OPC was added to increase strength. However, Hamzah F. et al. [12] used concept of geopolymer material of fly ash mixed with Na$_2$SiO$_3$ and NaOH solutions as binder to form aggregates. These show that the volcano ash has a potential as raw material of geopolymer and also new approach of artificial lightweight aggregate can be done by using volcano ash. Further research need to be done to explore the characteristics, processing and performance of volcano ash as geopolymer material and artificial lightweight aggregate as an effort to reduce the quantity of currently available volcano ash [13-34].

**Experimental part**

*Sample Collection and Treatment*

There are very limited research data that currently available in published literature about this material. Most of the past research on the behaviour of geopolymeric material was based on the binder paste formed from fly ash and clay [35-39]. The volcano ash sample was directly collected from eruption site (in mud form) as shown in Figure 2. Study carried out by Nuruddin et al. [10] was first heated volcano mud at 105 °C for 24 h to remove the water content. Then the volcano mud was burnt until 600 °C for one hour. Next, the dried volcano mud was ground (3000 cycles) in a ball mill to increase its fineness as cement (range of 100 μm). Meanwhile, Ekaputri and Triwulan [8] used various ratio of wet or dry volcano mud as the filler in the binder composition, which fly ash as base material. Khandaker [16] used the volcanic ash from Rabaul area of the East New Britain Province of Mount Tavurvur as admixture in their research incorporating with OPC as main binder.

*Mixing Process and Curing Method*

*Volcano Ash as Pozzolanic Material*

Ekaputri and Triwulan [8] have used the volcano mud as filler (up to 50% by mass) in the production of fly ash based geopolymer concrete. Alkaline activator used in their study consist of sodium silicate and sodium hydroxide solutions. The alkaline activator-to-fly ash ratio was kept constant at 0.35. Volcano mud and fly ash was mixed in a bowl mixer for 2 min. The alkaline activator was added and mixed together for another 2 min. Then the paste was mixed with coarse and fine aggregate in producing geopolymer concrete. The aggregates-to-binder ratio was 7:3 or 3:1 by mass.

The mixing process described in [8] was similar to separate mixing which has been proposed by Rattanasak et al. [40] for fly ash but different in mixing time. Their study stated two types of mixing procedures, namely, separate mixing and normal mixing. For separate mixing, the NaOH solution was mixed with fly ash for the first 10 min, and then sodium silicate solution was subsequently added to the mixture. However, for normal mixing, fly ash, sodium hydroxide, and sodium silicate solution were mixed at the same time. From the results produced, separate mixing produced a slightly stronger mortar than normal mixing. The mixing process for volcano mud with fly ash should not mix in the long time to avoid the hardening process which happened too fast [8].

Nuruddin et al. [9] also used volcano ash as OPC replacement of 0, 5, 10, 15, and 20%. Water-to-cement ratio was taken as 0.5 and sand-to-cement ratio was taken as 1. Study carried out by Khandaker [16] has used the volcanic ash as a cement replacement up to 20% by mass with water-to-binder ratio of 0.30. However, superplasticizer was added in the concrete mixture in this study. The curing temperature may influence the compressive strength of geopolymer. The volcano ash incorporating with fly ash based geopolymer concrete was cured at ambient temperature for 24 h. The samples then were removed
and then cured in a waterproof cover for 2 days. Lastly, the samples were left at room temperature until testing day [8]. However, the study [16] cured their samples in a water tank at 25 °C for 28 days. Chanh et al. [41] stated that when the curing temperature increases, the setting time of the concrete decreases. Due to the increased temperature, polymerization becomes more rapid, and the concrete can gain 70% of its strength within 3 to 4 h of curing. Study carried out by Mustafa et al. [20] found that the optimum curing temperature of 60°C gives the highest compressive strength. Meanwhile, the 60°C curing temperature was also recommended in producing fly ash and kaolinite geopolymer. Further research need to be done on finding the best curing temperature for volcano ash geopolymer [42, 43].

Production of Artificial Aggregate

Nevertheless, for the production of fly ash based geopolymer artificial aggregate, the paste was moulded in a cylindrical mould with 2:1 height to diameter ratio [11]. After moulded in the mould, the samples were left in an oven at 60°C for 4 days to cure the geopolymer into aggregate pellets [11]. Study carried out by Byung-wan et al. [15] stated that the hardened paste of fly ash was granulated to produce the specified nominal maximum aggregate size. Other researcher [28] used the disc pelletizer machine to produce the fly ash lightweight aggregate, then sintered in furnace at temperature up to 1200°C. The pelletization disk was used to form the pellets of lightweight fly ash aggregates [13]. Water was added by spraying onto the powder mixtures with a quantity of 22-25% of the total material to form the spherical pellets which took about 20 min to rotate in the pelletizer pan. After that, the pellets were dried at 110°C, and then sintered for 1h at 1100, 1150 and 1200°C. Tommy et al. [44] produced the lightweight aggregate by pelletizing from clay and formed under high-temperature firing in a rotary kiln at 1300°C. Meanwhile, Markus et al. [45] used expanded clay as lightweight aggregate produced in a rotary kiln at 1120°C and manually in the laboratory which were rolled by hand, dried at 105°C, pre-heated for 2h at 250°C and finally fired for 8 min at 1120°C in a chamber furnace.

For the production of volcano ash artificial lightweight aggregate using geopolimerization method, the sodium hydroxide and sodium silicate was first mixed and stir until homogeneous solution was achieved to form as alkaline activator. Geopolymer paste was prepared by mixing volcano ash with the alkaline activator. The ratio of volcano ash/alkaline activator was 1.7. The mixing material was mixed for five minutes to obtain a homogeneous paste mixture. The paste need to be palleted as shown in figure 3 then dry at the temperature 80°C for 30 min to get the shape of the aggregate with 14-20 mm sizes. Then the pelletized artificial geopolymer aggregate was sintered at temperature 800 °C for 1 hour [48-49].

Results and discussions

Characterization of Volcano Ash

X-ray Fluorescent (XRF)

Table 1 shows the chemical composition of volcano ash from Nuruddin et al. [9] study compared to this study by using the same source. The volcanic ash from Rabaul, East New Britain also included to show the difference between these materials by using XRF equipment. There were differences in chemical composition between this study and Nuruddin et al. [9] which might be due to different location of sources during collecting the samples at eruption site. In addition, the are probabilities in difference of chemical composition of the sources for now and last 2 years. The volcano ash from Sidoarjo and volcano ash from Rabaul, East New Britain shows quite similar in terms of their chemical compositions of SiO₂ and Al₂O₃ and also comparable to the fly ash and kaolin. However, the chemical composition of Fe₂O₃ volcano ash in this study shows the highest composition compared to the other materials.

X-ray Diffraction (XRD)

X-Ray diffraction (XRD) analyses of volcano ash compared with Malaysia fly ash and kaolin are shown in
Figure 4. Volcano ash exhibit a peak at 2 theta where 2 theta = 26.8°, which is characteristic of structurally disordered compounds, corresponding to quartz, sulfur, feldspars, and kaolinite in the case of volcano ash [5]. However, the volcano ash has higher intensity compared to fly ash and kaolin. Geoffrey S. [5] stated that the volcano ash also dominated by smectite, illite, and mixed illite/smectite, with lesser kaolinite and chlorite.

Fly ash shows shifted peak to 27.0°, and a set of peaks corresponding to minor crystalline phases, i.e., quartz and faujasite, and mullite in the case of fly ash [17], meanwhile for kaolin exhibit a peak at 25.2° containing kaolinite as major mineral, some dickite and quartz [22].

Scanning Electron Microscopy (SEM)

The microstructure of raw material of volcano ash compared to Malaysia fly ash and kaolin are shown in figure 5. Initially, the raw kaolin has plate-like structure, where needle-like phase can be seen clearly and contributed smaller surface area compared to fly ash [19]. The volcano ash samples have similar smooth, dense and compacted surface [9]. The volcano ash has plate-like structure which is similar to kaolin structure [5, 19]. The overall particle size of volcano ash is dominated by particles less than approximately 10 μm [5]. The particle shape of fly ash is glassy, hollow and large surface area of spherical shape which is contradict to the volcano ash and kaolin. The particle size of fly ash was in the range of 1 – 20 μm [20, 21].

Fourier transform infrared spectroscopy (FTIR)

Figure 6 shows that the main FTIR adsorption bands of the raw materials of volcano ash compared to kaolin and fly ash [21, 22]. Volcano ash showed characteristic peaks at 3621 and 3407 cm⁻¹, corresponding to the OH- stretching vibrations. The depth of the volcano ash peak at 3621 cm⁻¹ showed higher than kaolin and fly ash. However, the bands at 2358 cm⁻¹ showed highest depth of intensity for fly ash compared to volcano ash and kaolin. This is due to highest OH- and HOH stretching vibrations in the fly ash represent higher composition of H₂O. The band at 1634 cm⁻¹ can be seen at volcano ash and fly ash but not in kaolin which assigned to HOH bending vibration. The band at 1430 cm⁻¹ did not appeared at kaolin but clearly appeared at volcano ash and fly ash which correspond to O-C-O stretching vibrations.

These three types of material showed the peak at 994, 986, and 1004 cm⁻¹ which were assigned to asymmetric stretching of Si-O-Si and Si-O-Al. Other peaks at 907 and 910 cm⁻¹ for kaolin and volcano ash, respectively showed the presence of kaolinite and OH bending which were assigned to Al-OH bending. Absorption at 799 and 795 for kaolin and volcano ash was assigned to symmetric stretching of Si-O-Si. The vibrational bands of volcano ash...
showed quite similar properties to kaolinite as can be proved by the FTIR results due to similar peak appeared in figure 6.

Properties of Volcano Ash as Geopolymer and Replacement Materials

Compressive Strength

The compressive strength result is affected by many parameters especially the design ratio, curing temperature and time and mixing procedure and the materials used. The study from [8] showed that geopolymer concrete with fly ash-to-volcano ash of 1:1 with NaOH molarity of 14 M, sodium silicate-to-sodium hydroxide ratio of 2.5, curing time for 5 days, and geopolymer paste-to-aggregate ratio by mass of 3:7 (diameter of aggregate was in the range of 0.5-1.0 cm) gave the best performance of 12 MPa at 28 days. However, the concrete strength achieved was still low compared to geopolymer with pure fly ash only which achieved 35 MPa at 28 days. Kong and Sanjayan [23] stated that the fly ash-based geopolymer concrete may achieve up to 72 MPa at 3 days.

Other study [10] using sintered volcano ash as a replacement material in OPC concrete showed 10% of volcano ash reacted well with the mixture and depict higher compressive strength of 53 MPa at 28 days. This shows that the volcano ash after sintered at 600 °C became more reactive which affect the results of compressive strength compared to Ekaputri and Triwulan’s study. [8] Heah et al. [24] stated that the fly ash-based geopolymer concrete may achieve up to 72 MPa at 3 days.

Other study [10] using sintered volcano ash as a replacement material in OPC concrete showed 10% of volcano ash reacted well with the mixture and depict higher compressive strength of 53 MPa at 28 days. This shows that the volcano ash after sintered at 600 °C became more reactive which affect the results of compressive strength compared to Ekaputri and Triwulan’s study. [8] Heah et al. [24] stated that the fly ash-based geopolymer concrete may achieve up to 72 MPa at 3 days.

Porosity

The vacuum saturation was conducted to measure the porosity of the sample. The replacement of OPC with 10% volcano ash can reduce the void in the mixture and showed the least porosity of 0.31 [9]. Other researcher found the decrease in porosity by addition of 15% of volcano ash in the OPC mixture. [16] Rafat S. [41] found that the replacement of OPC by 20% volcano ash can reduce the porosity with 0.15. The use of pozzolanic materials or supplementary cement materials can reduce the porosity of the concrete [26, 27]. It is evident that volcano ash can give the reduction in porosity of the concrete.

Fire Resistance

It is important to test the concrete under high temperature to investigate the fire resistance that considered very important to the safety of user. Study by Khandaker [16] showed that the use of volcano ash (incorporating up to 20% of volcano ash) in cement replacement materials was able to retain the strength and durability properties at elevated temperature from 200 to 800 °C. Bakharev [27] and Kong and Sanjayan [23] found that the fly ash-based geopolymer can remain mostly amorphous up to 1200 °C and improved the compressive strength after firing process. However, the results were controlled by alkaline activator and size aggregate used. Further research need to be done for fire resistance test at high temperature when using volcano ash as raw material in concrete.

Potential of Volcano Ash as Artificial Lightweight Aggregate

The natural aggregate resource now is depleting day by day. However, the demand for aggregates in the market is large and increasing continuously. So, the alternative of producing the aggregate with volcano ash will reduce the natural resource used with better properties and strength and may help the Indonesian government to reduce the cost of the damages.

Strength of lightweight aggregate

The crushing strength of lightweight aggregate made from clay was 4.13 MPa with 5 mm aggregate in size sintered at 1300°C and concluded that the aggregate strength does not directly relate to the size of the aggregate but much more related to the density and crushing strength of the aggregate [44]. For fly ash lightweight aggregate, the crushing strength found were 5.1, 8.6, and 19.3 MPa when sintered at 1100, 1150, and 1200°C [13]. This shows that the sintering temperature plays an important role in achieving the highest strength of aggregate. Byung-wan et al. [15] stated that the crushing strength of alkali-activated fly ash lightweight aggregate was 6.5 MPa.

Specific Gravity

Past research shows that the specific gravity of sintered fly ash aggregate is increases when a binder of lime is used. Aggregate with bentonite has a low specific gravity of 1.9 g/cm³. [28] Aggregate with fly ash and cement has a specific gravity of 2.1 g/cm³ meanwhile the aggregate containing fly ash and lime has a specific gravity of 2.3 g/
cm³ when sintered at 1100°C [14]. Byung-wan et al. [15] stated that the specific gravity of fly ash lightweight aggregate was 1.66 g/cm³ without involving the sintering process. The specific gravity of the expanded clays was 0.85 g/cm³ at sintering temperature of 1100-1250°C [47]. However, study carried out by Tommy Y.L. et al. [44] showed the lower specific gravity of 0.62 g/cm³ that sintered at 1300°C. It was hypothesized that the sintered artificial lightweight aggregate has a larger internal void that affect the specific gravity produced. In this study, the specific gravity of geopolymer volcano ash aggregate was in the range of 1.1 to 1.8 g/cm³. Figure 7 shows the porous interior of artificial lightweight aggregate from various materials.

Water Absorption
The water absorption of sintered fly ash aggregate without binders was in the range of 21-22%. With the addition of 20% bentonite as binder, water absorption reduced significantly to 15-16%. [28] In this study, the water absorption found from the geopolymer volcano ash lightweight aggregate was in the range of 12-16% which is lower than in the study by Ramamurthy [14]. However, the water absorption found by Byung-wan et al. [15] was much lower which is 11.8%. Artificial lightweight aggregates from diatomite aggregate, pumice aggregate, and recycled aggregate from autoclaved aerated concrete had high water absorptions of 114.1%, 60.3%, and 74.5%, respectively, due to their highly porous surfaces. Lightweight aggregates from clay showed the water absorption in the range of 8.2-9.3%. Past research also stated that the water absorption can be modulated by controlling the expansion temperature [29].

Conclusions
Volcano ash from Sidoarjo, East Java, Indonesia has a potential to be utilized as a geopolymer volcano ash artificial lightweight aggregate. This material contains high Si and Al as other pozzolan materials like fly ash and kaolin. Volcano ash correspond to quartz, feldspars, and kaolinite by XRD result. The volcanic ash samples have plate like structure which is similar to kaolin structure. FTIR result showed the OH-, HOH, O-C-O, Si-O-Si, Si-O-Al, and Al-OH bending vibrations appeared in this material. Sintered volcano ash as a replacement material in OPC concrete achieved higher compressive strength of 53 MPa at 28 days. Volcano ash also showed good performance for porosity. Geopolymer volcano ash aggregate has specific gravity of 1.1 to 1.8 and water absorption of 12 to 16%. However, studies on this volcano ash were very limited, so, further research need to be done to find the best mix design, curing temperature and fire resistance with new product in order to improve the understanding of the performance and properties of volcano ash.

References
17. SONGPIRIYAKIJ, S., Effect of Temperature on Compressive Strength of Fly Ash-based Geopolymer Mortar, King Mongkut’s Institute of Technology North Bangkok, Thailand, 2005, p. CON30-34.
41. CHANH, N.V., TRUNG, B.D., TUAN, D.V., Recent Research Geopolymer Concrete, in The 3rd ACF International Conference-ACF/VCA, Faculty of Civil Engineering - University of Technology Ho Chi Minh City, Vietnam, 2008.
42. SWANEPOEL J.C., STRYDOM C.A., Applied Geochemistry, 17, no. 8, 2002, p. 1143.
43. RANGAN, B.V., Low-Calcium Fly-Ash-Based Geopolymer Concrete, Faculty of Engineering, Curtin University of Technology, Perth, Australia, 2008, 1.

Manuscript received: 12.06.2013