GEOPOLYMERISATION OF VOLCANIC MUD

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ABSTRACT

This paper presents the results of geopolymerisation of volcanic mud. The mud is taken from a mud volcano in Sidoarjo, East Java, Indonesia; and thus, locally it is called Sidoarjo mud or LUSI mud. The mud volcano started to erupt since May 2006, and to date there is no sign that the eruption will end in the near future. Currently, the daily discharge of mud is about 30,000m^3*. More than 640 hectares of productive land, housing and industrial areas, and infrastructural facilities have been submerged. The height of the cover dam right now is not less than 12.00 meters. The mud is rich in* SiO_2, Al_2O_3 *and CaO. In its original form, its microstructure is crystalline. The SEM results revealed that the mud has plate-like shape, dominated by particles with less than 20μm in dimension. The total amount of* SiO_2, Al_2O_3 *and CaO is more than 80%, with* SiO_2 *content about 57% and* Al_2O_3 *about 23%. After pre-treatment in the form of calcinations and grinding, the mud is proven to be a potential raw material for geopolymer. In this study, a combination of sodium hydroxide solution and sodium silicate solution is used as the alkaline activator. The particle size of the calcined mud affects the reactivity of the material, whereby the finer the particle size, the higher the compressive strength of the geopolymer. The compressive strength of volcanic mud-based geopolymer mortar at 7*th *day is more than 30 MPa.*

Keywords: Calcination, geopolymer, particle size, Sidoarjo/LUSI mud, volcanic mud.

1. INTRODUCTION

Since May 2006, a mud volcano in Sidoarjo, East Java, Indonesia, has been erupting; continuously discharging mud, and submerging its surrounding. After six years of eruption, not less than 640 hectares of productive land, housing and industrial areas, schools and infrastructure facilities have been submerged. The height of the cover dam is currently about 12 meters, although some of the discharge has been channeled to the nearby river; causing a newly formed island in its mouth. In its peak in 2007, the discharge was about 180,000m^3 daily, while nowadays it is about 30,000m^3. There is no sign that the eruption will end in the near future. Rudolph et al. predicted that the eruption will last at least for a few more decades [1].

The volcanic mud is brownish in colour and it contains mostly SiO_2, Al_2O_3 and CaO in a more crystalline microstructure. Treatment in the form of calcinations and grinding have shown that the material is suitable for use as pozzolanic material, even in the case of semi high volume pozzolanic mortar with up to 40% of cement replacement [2, 3]. From the SEM observation, it was found that the particle of the mud has a plate-like structure, whereby the particle size is mostly less than 20μm [4, 5].

Geopolymer requires raw materials high in SiO_2 and Al_2O_3 in amorphous form. The use of this volcanic mud in original form, for both pozzolanic and geopolymer raw material, was unsuccessful, especially due to its crystalline form [6]. This study aims to further investigate the potential of volcanic mud from Sidoarjo, Indonesia, as geopolymer precursor, following the success in using it as pozzolanic materials.

2. MATERIALS AND EXPERIMENTAL DETAILS

The fresh volcanic mud was obtained directly from the eruption site of the mud volcano in Sidoarjo, East Java, Indonesia. Calcinations was performed to improve the reactivity of the mud, which is in a more crystalline microstructure in its original for [2, 3]. Before calcinations, the mud was dried in the oven to expel the moisture. Calcinations was performed in a local roof tile manufacturer furnace at 910^{0}C for five hours duration. Grinding was performed by using bar-milled grinding machine to obtain four different particle sizes, *i.e.*, <63μm, 63–150μm, 150–300μm and 300–600μm. Characterization of the volcanic mud was performed by using X-ray fluorescence (XRF) and X-ray diffraction analysis.

Table 1 shows the chemical composition of calcined mud as measured by XRF. The composition is dominated by SiO_2, Al_2O_3 and Fe_2O_3. The total content of these three components is more than 87%. Figure 1 shows the X-ray diffraction pattern of the calcined mud, characterized by a set of peaks at 2 thetha, especially where 2 thetha is in between 21^0-28^0.

Table 1. The chemical composition of calcined volcanic mud as measured by XRF (% by mass)

SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	CaO	K_2O	SO_3	TiO_2	MnO_2	Cr_2O_3	LOI
56.75	23.31	7.37	2.95	2.70	2.13	1.04	0.96	0.38	0.14	0.01	1.20

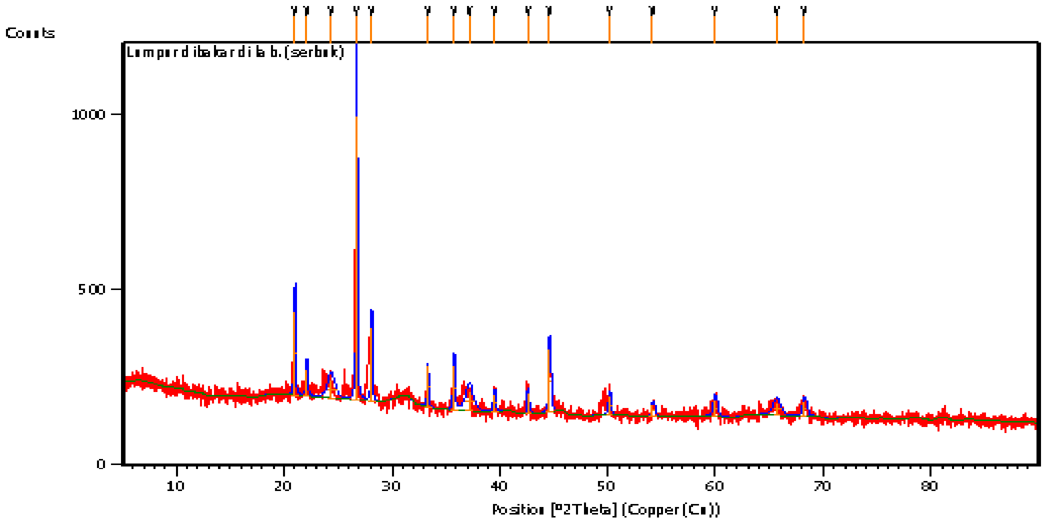

Figure 1. The XRD pattern of calcined volcanic mud

River sand in saturated surface dry condition with fineness modulus (FM) of 2.16 was used as the fine aggregate for the geopolymer mortar. As for the alkaline activator, a combination of sodium hydroxide and sodium silicate solution was employed. Sodium silicate solution utilized throughout the study contained 17.14% Na_2O and 36.17% SiO_2 with the ratio between SiO_2 and Na_2O as 2.14. NaOH of industrial grade was obtained in a flake form with 98% purity. Added water was taken from the tap water available in the laboratory.

Sodium silicate solution and sodium hydroxide solution were mixed together beforehand. Calcined mud and sand were mixed thoroughly, and then the alkaline solution was added. Mixing was continued until the homogeneity of the fresh mix was achieved. The workability of fresh volcanic mud-based geopolymer mortar was evaluated based on its flow diameter using the Flow Table Apparatus. Mortar was cast into 50x50x50mm cube moulds. The fresh geopolymer mortar was then sent to an oven for curing at 100^0C for 24 hours. The geopolymer cubes were left in the ambient temperature until the day of testing at the age of 7 days. Each compressive strength data presented here is a mean value of testing results of three cubes. All tests were performed in accordance to relevant ASTM Standards.

Altogether, there were four series of experiments have been carried out in the study. The first two series were aimed to investigate the influence of particle size of calcined mud on the strength and workability of geopolymer mortar. The last two series was designed to evaluate the impact of water to mud ratio (by mass) and NaOH concentration on the properties of volcanic mud-based geopolymer mortar.

Calcined volcanic mud to sand ratio, by mass, was kept constant at 1:2 for all series. For the first three series, NAOH solution of 10M was used, while for the last series the molarity of NaOH solution was varied as 8M, 10M, 12M and 14M. Ratio of NaOH solution to sodium silicate solution, by mass, was 5:8. The other details of the mixture composition are shown in Tables 2 to 5.

3. RESULTS AND DISCUSSION

3.1. The Influence of Particle Size of Volcanic Mud on the Compressive Strength of Geopolymer Mortar

In this series, four mixes were prepared. The main parameter is the particle size of the calcined mud, i.e. between 300-600 μm, 150-300 μm, 63-150 μm and < 63 μm. Water to mud ratio was kept constant at 0.4, by mass, while the solution to mud ratio was 0.7143. The amount of water was the sum of water in the sodium silicate and sodium hydroxide solution. The term solution means the total amount of sodium silicate and sodium hydroxide, by mass.

Table 2. The influence of particle size of mud on compressive strength

Specimen	Particle Size	Compressive Strength at 7-day (MPa)
P600_WM.40_10M	300-600 μm	5.4
P300_WM.40_10M	150-300 μm	9.4
P150_WM.40_10M	63-150 μm	13.8
P063_WM.40_10M	< 63 μm	14.5

Table 2 shows the influence of particle size of calcined volcanic mud on the compressive strength of geopolymer mortar at the age of 7-day. It can be seen clearly that the finer the particle size of the mud, the higher the compressive strength, suggesting the more reactivity of the mud when the particle size is finer. This agrees with the previous report on fly ash-based geopolymer [7].

The compressive strength of the geopolymer mortar in this series is considered low, especially for those manufactured using bigger sizes mud particle, larger than 150μm. Apparently, the water-to-mud ratio was too large. To improve the compressive strength, the following series applies reduction of water-to-mud ratio, by mass, from 0.40 to 0.30, and subsequently also lowering the solution-to-mud ratio, by mass, from 0.71 to 0.54.

3.2. The Influence of Particle Size of Volcanic Mud on the Workability of Fresh Geopolymer Mortar

In this series, the amount of mud and sand were kept the same as in the first series. The main feature of this series is the lower water-to-mud ratio, i.e. 0.3. The main parameter is particle size of the mud. Table 3 shows the flow diameter of the fresh geopolymer mortar as measured after applying strokes using the Flow Table Apparatus in accordance to the relevant ASTM Standard, and the compressive strength at the age of 7 days.

Table 3. The influence of particle size of mud on compressive strength

Specimen	Particle Size	Flow Diameter (mm)	Compressive Strength at 7-day (MPa)
P600_WM.30_10M	300-600 μm	190	2.0
P300_WM.30_10M	150-300 μm	169	6.2
P150_WM.30_10M	63-150 μm	120	27.6
P063_WM.30_10M	< 63 μm	117	29.5

On the compressive strength, the results shown in Table 3 confirm those presented in Table 2, whereby the finer the particle size of the mud, the higher the compressive strength. With smaller water-to-mud ratio, and subsequently lower solution-to-mud ratio, the compressive strength increases significantly, especially with mud smaller than 150μm. For the next two series, the mud used was the one with particle size less than 63μm.

Mixture with bigger particle size of volcanic mud exhibits larger flow diameter, indicating higher workability of the fresh geopolymer mortar. This can be explained as, with bigger particle size, the surface area of the mud is smaller. This causes the area covered by the solution is smaller, ends up with higher workability. On the other hand, the bigger the particle size, the lower the compressive strength, due to the less reactivity of the bigger particles.

3.3. The Influence of Water-to-Mud Ratio on Workability and Compressive Strength

Water-to-mud ratio, by mass, was chosen as the parameter for this series. The particle size of mud was smaller than 63μm, as it ends up with the highest compressive strength in the preceding series. The ratio between NaOH solution and sodium silicate solution was kept constant at 5:8. The amount of mud and sand were also kept unchanged. Table 4 shows the four mixtures prepared for this series, as well as the flow diameter and the compressive strength of the mortar.

Table 4. The influence of water-to-mud ratio on workability and compressive strength

Specimen	Water/Mud Ratio	Solution/Mud Ratio	Flow Diameter (mm)	Compressive Strength at 7-day (MPa)
P063_WM.25_10M	0.25	0.45	106	30.0
P063_WM.30_10M	0.30	0.54	117	29.5
P063_WM.35_10M	0.35	0.63	139	27.9
P063_WM.40_10M	0.40	0.71	176	21.5

Compressive strength of volcanic mud-based geopolymer mortar decreases as the water-to-mud ratio increased. This is similar to the one applies to the normal OPC mortar, whereby in the latter the water-to-cement ratio is the main parameter affecting the compressive strength. The highest compressive strength achieved in this series is about 30MPa at the age of 7 days, i.e. for mixtures with water-to-mud ratios of 0.25 and 0.3. Water-to-mud ratio as well as the solution-to-mud ratio play important role in determining compressive strength of volcanic mud-based geopolymer mortar.

On the flow diameter, the higher water-to-mud ratio resulted in the bigger flow diameter. With the constant mud content, the change in the ratio indicates the change in the water content. As in the case of normal OPC mortar, water content apparently also the main contributor to the workability of fresh geopolymer mortar. The more the water content, the bigger the flow diameter.

3.4. The Influence of NaOH Molarity on Workability and Compressive Strength

In the last series in this study, the NaOH molarity is chosen as the parameter. Four mixes with NaOH molarity of 8M, 10M, 12M and 14M were prepared. Water-to-mud ratio, by mass, was kept constant at 0.30, while the particle size of the mud was smaller than 63μm. The ratio between NaOH solution and sodium silicate solution was kept constant at 5:8. The amount of mud and sand were also kept unchanged. Although the water-to-mud ratio is constant, the solution-to-mud ratio slightly varies. With different molarity of NaOH solution, the amount of NaOH solids and the water content were also different.

Geopolymer cubes from these four different mixes showed similarity in compressive strength, i.e. about 30 MPa at the age of 7 days. With constant water-to-mud ratio, apparently the variation of NaOH molarity does not affect both workability and compressive strength of volcanic mud-based geopolymer mortar. Flow diameters were about 120-130mm for all four mixes.

Table 5. The influence of NaOH molarity on workability and compressive strength

Specimen	Molarity of NaOH	Solution/Mud Ratio	Flow Diameter (mm)	Compressive Strength at 7-day (MPa)
P063_WM.30_08M	8 M	0.51	128	30.1
P063_WM.30_10M	10 M	0.54	116	30.4
P063_WM.30_12M	12 M	0.56	128	30.6
P063_WM.30_14M	14 M	0.57	120	31.5

4. CONCLUSIONS

This study reveals that the calcined volcanic mud from Sidoarjo, East Java, Indonesia, is a suitable precursor for geopolymeric materials. The SiO_2 and the Al_2O_3 content in the volcanic mud, which is about 57% and 23%, respectively, indicating that the mud possesses the required contents for the raw materials for geopolymer. Several more detail conclusions are listed here:

a. The finer the particle size of the calcined volcanic mud, the higher the compressive strength and the lower the flow diameter of the geopolymer mortar. The particle size of the calcined volcanic mud should be less than 150μm to enable its use as raw materials for geopolymer.

b. The water-to-mud ratio significantly influences the compressive strength of the hardened geopolymer mortar, whereas the water content in the mix is the important parameter determining the workability of the fresh geopolymer.

5. REFERENCES

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