Characterization of Fresh Sidoarjo Mud as Material on Geopolymer System

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Abstract. Sidoarjo mud is the alternative cementitious material which derived from a volcano mud eruption in Porong, Sidoarjo, East Java, Indonesia. The calcination of fresh sidoarjo mud in high temperature was known rich in the content of Si and Al that has similar chemical content with the material of OPC. However, the calcination process had caused the consumption of energy, time duration and cost in the production. To solve the problem, this study was required to investigate the fresh sidoarjo mud without the calcination process. However, material of FSM was analyzed to understand its feasibility as a material in geopolymer referring to the material of fly ash. The results showed that the material of FA consisted of quartz (SiO₂), mullite (3Al₂O₃ 2SiO₂ or 2Al₂O₃ SiO₂) and hematite. While, the material of FSM consisted of quartz (SiO₂), mullite (3Al₂O₃ 2SiO₂ or 2Al₂O₃ SiO₂), magnetite (Fe₃O₄), hematite (Fe₂O₃), and rutile (TiO₂). The particle of FA was amorphous and sphere with the misty surface that caused the absorption of alkaline solution and reduced the workability on fresh geopolymer mortar. While the particle of FSM was the agglomerate irregular shape with the rough surface that also caused the absorption of alkaline solution and reduced the workability on fresh geopolymer mortar. The analysis of FTIR identified that the material FA and FSM had the stretching in the gel of Si-O-Al and Si-O-Si. The compressive strength reached optimum at the replacement of 5% FSM.

1. Introduction

Ordinary Portland Cement (OPC) is a famous material that is often used in the construction as the binder. The production of OPC was known to have increased pollution in the environment. There were more million tons of OPC production in the world that played an important role in the increase of CO₂ emission, exploitation the natural resources and consumed the energy. It was required to solve this problem with the use of alternative material that was from the waste material such as fly ash (FA), silica fume (SF), ground granulated blast furnace slag (GGBFS), metakaolin, rice husk dust.

Geopolymer is a green technology formed by polymerization of silicon, alumina, and oxygen in the triangle structure consisted of Si-O-Al and Si-O-Si which is one of the most stable covalent bonds is the nature. The constituent of geopolymer is the cementitious material from waste material that the rich in the content of Si and Al and alkaline solution derived from soluble alkali metal that is the combination of NaOH and Na₂SiO₃ solution with the certain ratio.

Sidoarjo mud (SM) is a volcano mud eruption caused by drilling gas exploration in Porong, Sidoarjo, East Java, Indonesia. The eruption had released the mud as 18x10⁴ m³ per day in 2007 and it is considered to continue for the next 25 to 30 years. To date, the volume had impacted the environment and society. The previous research was investigated with the calcination of SM at a high temperature. The results showed that the material of SM was categorized as a cementitious material due to rich in Si...
and Al content, but it was lower in the content of Ca. The material of SM was an amorphous phase with a crystalline peak of quartz and silicon dioxide (SiO₂). The analysis of FTIR showed that the material of SM formed the gel of Si-O-Si and Si-O-Al on geopolymer binder. Whereas, the particle of SM has an irregular agglomerate shape with the rough surface.

Furthermore, it was mentioned that the finer particle size of SM caused the low flowability that caused the absorption of alkaline solution and reduction of viscosity in geopolymer mixture. The low Ca content in the source material of SM brings to prolong setting time in the geopolymer binder. It was due to the low Ca content generated N-A-S-H gel retarding the reaction of geopolymer which it debilitated the mechanical properties at an early age. Finally, the calcination of SM at the temperature of 800°C provided the highest compressing strength in geopolymer mortar.

However, the calcination process of sidoarjo mud caused the consumption of energy, time duration and cost in the production. To solve the problem, this study was required to investigate the fresh sidoarjo mud without the calcination process. So that, the characterization of fresh sidoarjo mud as material on geopolymer system is investigated in this study.

2. Material and experimental program
This study used the material of FSM that was from Porong, Sidoarjo, East Java, Indonesia whereas the material of fly ash was from power plantation in Nagan Raya, Aceh, Indonesia. Furthermore, the alkaline solution was generated by a combination of NaOH and Na₂SiO₃ solution with a certain ratio which was obtained from CV. Rudang Jaya company in Medan, Indonesia. The material was evaluated by XRD to analyze the particle structure of the material, FTIR to indicate the geopolymer binder gel and SEM to indicate the shape and surface of the particle. The mix proportion was designed based on the constituent material of geopolymer, whereas the mixing procedure followed the conventional method which referred to the standard of ASTM C305. The fresh and hardened properties of geopolymer mortar were evaluated by workability, setting time and compressive strength.

3. Results and discussion
3.1. Characterization of material
3.1.1. Chemical composition
Chemical composition is one of analysis in the characterization of material linking to the condition of fresh and hardened properties on geopolymer system. Table 1 shows the chemical composition of FA and FSM that is known rich in content of Si and Al. Yet, the contents of Ca in the material of FSM and FA are categorized as low Ca and moderate Ca content. The content of Si and Al formed a gel of Si-O-Si and Si-O-Al that contributed to the mechanical properties of geopolymer mortar. The low Ca content formed a gel of N-A-S-H that caused prolong the setting time in fresh geopolymer mortar whereas the medium Ca content formed a gel of C-A-S-H that bring the short setting time in fresh geopolymer mortar. Furthermore, the contents ratio of Si and Al in the material of FSM and FA is 2.93 and 2.11, respectively. It means that the content ratio of Si and Al of 2.93 caused the worse chemical stability in the air compared to the content ratio of Si and Al of 2.11 that indicated the presence of efflorescence on the surface due to the higher residual free K⁺.

| Table 1. Chemical composition of fly ash and FSM |
|-----------------------------------------------|
| FA and FSM                                     |
| Si    | Al  | Ca    |
| 52.32 | 17.43 | 12.29 |
| 48.64 | 15.92 | 14.75 |
| 2.93  | 2.11 |      |

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3.1.2. Crystalline analysis of material.
The crystalline identification of FA and FSM particle was investigated by X-ray diffraction test (XRD) as seen in Figure 1. The spectrum in the particle of FA and FSM follows the similar peak of dispersion refers to the database of XRD. The trend of the graph indicates the similarity of dispersion peak in the material of FA and FSM. It means that both of material consists of quartz (SiO$_2$), mullite (3Al$_2$O$_3$ 2SiO$_2$ or 2Al$_2$O$_3$SiO$_2$) and hematite (Fe$_2$O$_3$). However, the maximum dispersion peak is at 20º-30º that indicates the amorphous material.

![Figure 1](image.png)

**Figure 1.** Identification material of FA and FSM by the analysis of XRD

3.1.3. Surface image of material
Figure 2 shows the scanning electron microscope (SEM) image to analyze the particle image of the material. Figure 2a shows the spherical shape of FA particle with the misty surface. The surface of FA in this study was in contrast with the surface of common FA that is a spherical shape with a sleek surface. The misty surface was considered absorbing the alkaline solution on fresh geopolymer mortar so that caused the reduction of workability. Also, the spherical shape of FA was indicated to be able to fill the concavity of geopolymer binder.

Furthermore, figure 2b shows irregular agglomerate shape of FSM particle with the rough surface. Irregular agglomerate shape of FSM caused the particle to be unable to fill the concavity on the geopolymer binder as good as the particle of FA. It brought up the small concavity on the geopolymer binder. Nevertheless, the big concavity was reduced and replaced with the small concavity. Furthermore,
the rough surface of FSM absorbed the alkaline solution from the fresh mixture of geopolymer mortar that caused the reduction of workability on fresh geopolymer mortar.

2a. The image of FA particle           2b. The image of FSM particle

**Figure 2.** The surface image of FA and FSM particle

4. **Chemical bonding identification of material**

Figure 3 shows the FTIR result of FA and FSM particle that identifies the chemical bonding structure of a material. Peak band at a wavenumber of 3600 cm\(^{-1}\) is presented by the material of FSM that indicated stretching and bending of H-O-H. It means that the material of FSM contained more water in its material. It is attributed to the calcination process that was not applied to fresh geopolymer mortar so that it was water buildup in the material. Peak band at a wavenumber of 3400 cm\(^{-1}\) is presented by the material of FA and FSM that indicates the presence of Ca (OH)\(_2\) in its material. However, material of FSM had deeper peak band compared to the material of FA. It indicates that the presence of more efflorescence on the surface of FSM based geopolymer mortar compared to FA based geopolymer mortar. Peak band in the wavenumber range of 3440 cm\(^{-1}\)-1380 cm\(^{-1}\) is presented by the material of FSM that indicated the stretching and bending of water band and CaCO\(_3\) (carbonate) in its material. Peak band at wavenumber range of 880-1140 cm\(^{-1}\) is presented by the material of FA and FSM that indicated the stretching of Si-O-Si and Al-O-Si in the crystalline of quartz and mullite. This wavenumber area determines what the material can be as geopolymer material or not. Furthermore, there was not found the presence of alkali content in the material of FSM. Yet, it was a presence in the material of FA. It is seen through peak band in the wavenumber of 680 cm\(^{-1}\)-800 cm\(^{-1}\). Finally, peak band in the wavenumber below 680 cm\(^{-1}\) is presented by the material of FA. It indicates that the bending of Si-O was only presented by the material of FA. It means that the gel of Si-O was found in the material of FA that contributed to a high compressive strength of geopolymer mortar.
5. Workability
Rheology properties in fresh geopolymer mixture were measured by the workability and setting time. The workability of the fresh mixture was conducted by the flow table apparatus with measuring the diameter flow after a certain number of cycling. The workability was affected by the surface of the material that contacted with the water-cement in the conventional concrete or alkaline solution in the geopolymer concrete. It was known that the glassy surface of material did not absorb the water-cement or alkaline solution in a short time. Whereas the rough surface of material absorbed them by a direct time that caused the loss of workability on the fresh mixture of geopolymer mortar. It can be seen in Figure 4 which the increasing replacement of FSM in the FA based geopolymer mixture caused the reduction of workability. It is attributed to the surface of FSM as mentioned in the SEM section which in the agglomerate and rough surface.

![Figure 4. Workability of FSM on FA mortar geopolymer](image)

The particle shape of FSM was an irregular agglomerate shape with the rough surface. Irregular agglomerate shape of FSM was considered not able to fill the concavity as good as the particle of FA. However, the rough surface of the FSM particle caused the absorption of the alkaline solution on the fresh mixture of geopolymer mortar that impacted on the reduction of workability. Figure 6 shows that the increase of FSM replacement causes the reduction of workability. It was attributed with the increase of FSM particle developed the rough surface of FSM that absorbed more alkaline solution on fresh geopolymer mortar.

6. Setting Time
Figure 5 shows the initial and final setting time of FSM replacement on the fresh mortar geopolymer. It is noted that the trend of initial and final setting time is consistent to increase. The figure shows that the increase of FSM replacement caused the reduction of FA in the binder. It means that the percentage of Ca content in the binder will be reduced so that caused the increase of setting time. The initial setting time indicated the plastic condition of fresh geopolymer mixture which was 80% reaction of geopolymer. Whereas, the final setting time indicated the static condition which was rest reaction of geopolymer.
7. Compressive strength

Compressive strength of FSM replacement on FA based geopolymer is shown in Figure 6. It is seen that the replacement of 5% and 10% FSM provides higher compressive strength compared to the other replacement. However, it was still lower than the compressive strength of FA based geopolymer. It was attributed to the content of Si and Al in the material of FSM. It was known that the chemical content of Si and Al in the material of FSM was lower than the material of FA. The increase of FSM replacement on FA based geopolymer caused the reduction of Si and Al content that impacted on the reduction of gel Si-O-Si and Si-O-Al in the binder. Even, the compressive strength of FSM was lower than the compressive strength of FA. Yet, it was still acceptable to be used as the material in the geopolymer binder. Furthermore, the reduction of compressive strength in the FSM replacement was also caused by retarding of reaction impacting to the prolong setting time. There is a correlation between the compressive strength and setting time which the presence of FSM on the FA based geopolymer mortar retarded the setting time and also reduced the compressive strength.
8. Conclusion
The study had been investigated with the following conclusion:

1. The material of FSM was rich in the content of Si and Al but poor in the Ca content compared to the material of FA.
2. The analysis of SEM showed that the particle of FSM was irregular agglomerate with the rough surface. While the particle of FA was spherical with the misty surface.
3. The analysis XRD showed that the material of FSM and FA consisted of quartz (SiO₂), mullite (3Al₂O₃ 2SiO₂ or 2Al₂O₃ SiO₂) and hematite (Fe₂O₃).
4. Peak band at wavenumber range of 880-1140 cm⁻¹ was presented by the material of FA and FSM that indicated the stretching of Si-O-Si and Si-O-Al in the crystalline of quartz and mullite.
5. The increase of FSM replacement in the FA based geopolymer mortar caused the reduction of workability, increase the setting time and it did not improve the compressive strength.

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