

Review Article

CHARACTERIZATION OF SIDOARJO MUD AS BASE MATERIAL IN GEOPOLYMER

<sup>1</sup>Rizal Syahyadi, <sup>2</sup>Syarwan, <sup>3</sup>Fajri, <sup>4</sup>Amir Fauzi

Politeknik Negeri Lhokseumawe, Lhokseumawe, Indonesia  
[amirfauzi@pnl.ac.id](mailto:amirfauzi@pnl.ac.id)

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**Abstract:** Sidoarjo mudflow (SM) is an alternative source material in the construction which is generated from natural disasters of volcano mudflow in Porong, Sidoarjo, East Java, Indonesia. This source material is classified as replacement cementing material (RCM) due to rich of Si, Fe and Al content. In addition, high Si and Al contents in SM material are considered to be able to replace FA as a base material in geopolymer binder. However, the calcination temperature is required to reduce volatile and impurities in SM material. The source material after calcination process is termed as volcanic meta ash (VMA). This study aims to investigate the feasibility of VMA material as an alternative source material in geopolymer binder. The results mention that Si and Al contents of VMA material are 1.5 and 1.3 times higher than fly ash (FA) material. The crystalline of quartz and mullite and chemical bonding of Si-O-Si and Si-O-Al in VMA material is more than FA material. VMA material has the particle of irregular agglomerate shape and rough surface.

**Keywords:** Sidoarjo mud, calcination temperature level, XRF, XRD, TGA, FTIR, SEM/EDS.

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Introduction

Geopolymer binder is an inorganic polymer that can utilize several types of aluminosilicate wastes. Recently, geopolymer binder is considered as an alternative method to replace conventional binder in the construction. It is due to the conventional binder contributes to release CO<sub>2</sub> emission in the atmosphere through OPC production. It is recorded that every ton of OPC production released one ton of CO<sub>2</sub> in the atmosphere [1], so that OPC production has an issue in the air environment pollution.

Geopolymer binder used the source material was the waste or by-product material that had high Si and Al content in its material such as fly ash (FA), metakaolin and slag [2]. Furthermore, Sidoarjo mudflow (SM) is considered as an alternative source material in geopolymer binder due to rich in Si and Al content. It is known that SM material is a natural disaster caused by the technical error of gas drilling in Sidoarjo, Surabaya, East Java, Indonesia. The volume of SM material in 2007 was 180,000 m<sup>3</sup>/day and it is predicted to flow until next 25 to 30 years [3]. This volume of SM material caused the tremendous impact on the society (Figure 1).

The utilization of SM as a base material in geopolymer binder is considered to be able to reduce the negative impact of SM in the society and at the same time, it can reduce utilization of OPC material in the construction [4]. However, the impurities in SM material should be reduced by a calcination process. This study is investigated to evaluate the feasibility of VMA material as an alternative source material in geopolymer binder.



(a)



(b)

Figure 1. SM; (a) source of SM and (b) impact of SM

Literature Review

The production of OPC faces several challenges including environmental concerns. Increased production of OPC contributed to release carbon dioxide (CO<sub>2</sub>) emission in the atmosphere [5, 6]. It is a critical issue in the environment especially the greenhouse effect. It is known that the release of CO<sub>2</sub> emission increased the global temperature causing climate changes. So that, it was required an alternative material to replace the OPC as the binder.

A few decades ago, an alternative binding material was found from by-product or waste material such as fly ash (FA) from the combustion of pulverized coal in electric power generating plants, ground granulated blast furnace slag (GGBFS) from combustion of metal production, silica fume (SF) from combustion of silicon and ferrosilicon alloys, rice husk ash (RHA) from incineration of rice husk, kaolin from the mineral kaolinite on the earth's crust. In addition, an alternative binding material can also be produced by certain treatment such as metakaolin (MK) that was produced from calcination of kaolin [7].

The feasibility of waste or by-product material as an alternative source material in the concrete industry was attributed to the chemical content of silica (Si), alumina (Al), and calcium (Ca) [8]. These chemical contents are able to react with calcium

hydroxide [Ca(OH)<sub>2</sub>] and water (H<sub>2</sub>O) to generate C-S-H (calcium silicate hydrate) and C-A-H (calcium aluminate hydrate) gels. These gels are termed as a pozzolanic reaction that contributed to the compressive strength. In addition, alternative source material also reacted with the alkaline solution to generate Si-O-Si (siloxo), Si-O-Al (sialate), C-A-S-H (calcium aluminosilicate hydrate) and N-A-S-H (sodium aluminosilicate hydrate) gels. These gels are termed as a geopolymer reaction which the Si-O-Si and Si-O-Al gels contributed to the compressive strength, whereas the C-A-S-H and N-A-S-H gels contributed to the final setting time [9, 10].

Furthermore, the sharp peaks in the XRD pattern indicates that the material of FA presented the crystalline phases in quartz (SiO<sub>2</sub>), mullite (Al<sub>2</sub>O<sub>3</sub>), amorphous phases, calcined silica, and alumina [11, 12]. Susan et al mentioned that the weight loss on the material of FA happened through water evaporation that affected the hydroxyl groups OH at a temperature range of 700<sup>o</sup>-1000<sup>o</sup>C. However, the temperature of 110 °C was considered as pre-drying material. [13].

The fourier transform infrared spectroscopy (FTIR) showed that the material of FA had six peak band areas. The peak band in the area range of 450-470 cm<sup>-1</sup> indicates molecular vibration in the bending of Si-O-Si, the peak band in the area range of 980-1040 cm<sup>-1</sup> indicates the molecular vibration in the stretching of Si-O-Si and Si-O-Al, the peak band in the area of 1450 cm<sup>-1</sup> indicates the molecular vibration in a type of carbonate groups, the peak band in the area range of 1640-3460 cm<sup>-1</sup> indicates the molecular vibration in the stretching and deformation of OH and H-O-H, and the peak band in the area of 3690 cm<sup>-1</sup> indicates the molecular vibration in the stretching of O-H in Ca(OH)<sub>2</sub>. However, the peak band in the area ranges of 450-470 cm<sup>-1</sup> and 980-1040 cm<sup>-1</sup> are the concerned area to indicate the source material of geopolymer. It is due to these areas indicate the richness of the alumina silicate [14, 15]. Finally, the scanning electron microscope (SEM) showed that the particle size of FA is microspheres, amorphous, glassy and sleek with the size range of 1 to 20 μm [11]. Whereas, the strong signal intensities in the material of FA are aluminum (Al), silica (Si) and oxygen (O).

## Research Methods

### Materials

The source material used in this study was FA class C that was from electric power generating plants, Manjung, Perak, Malaysia. Whereas, SM material was from Sidoarjo, Surabaya, East Java, Indonesia. The material of SM was calcined at high temperature to reduce volatile and impurities in its material. Figure 2 shows the calcination process of VMA material that was begun with drying of fresh SM in the oven with the temperature of 100°C for 24 hours. It was conducted to reduce the water content of fresh SM so that it reduced the amount of smoke during the calcination process. The drying of SM was calcined by the temperature of 400°C to 900°C within 5 hours and followed by grinding for 2 hours to obtain the fine particle size referring to FA particle size. The production of new source material was termed as volcanic meta ash (VMA) material.

Characterization of source material and geopolymer binder was measured by X-ray fluorescence (XRF), thermogravimetric analysis (TGA), Fourier transform infrared spectrometer (FTIR), scanning electron microscope (SEM) and Energy dispersive spectrometer (EDS). The alkaline solution used in this study was the combination of sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) and sodium hydroxide (NaOH) solution with the ratio of 2. The specific gravity of Na<sub>2</sub>SiO<sub>3</sub> was 1.53 g/cc and the concentration of NaOH solution was 10M.

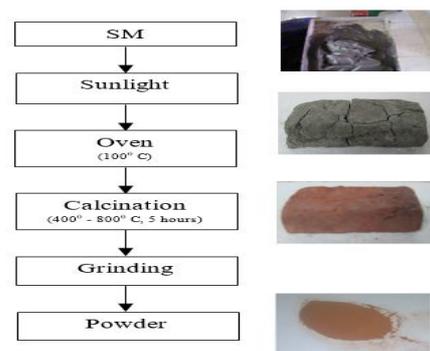


Figure 2. Sidoarjo Mud Production Process.

## Results and Discussion

### Chemical Composition

The chemical composition is a basic investigation in the characterization of the new material, which is analyzed by X-Ray Fluorescence (XRF) analysis. Table 1 shows the chemical composition of FA, SM, and VMA with the calcination temperature of 400°C to 900°C. This level of calcination temperature was applied to evaluate its effect on the chemical composition of VMA referring to FA. It shows that the Cl content of SM material is about 5.31% of total masses which it does not meet ACI 201 standards. However, the Cl content gradually decreases with the increase of calcination temperature level. It is obvious that the calcination temperature of 700°C (VMA) is able to reduce the Cl content up to 0.34% of the total mass and it is stagnant in the higher calcination temperature.

Table 1. The chemical composition of CFA, MV raw materials at calcination temperatures level

Chemical Composition	FA	SM calcination temperature						
		0	400	500	600	700	800	900
SiO <sub>2</sub>	24.9	32.5	34.4	35.5	36.5	37.2	38.0	38.3
Fe <sub>2</sub> O <sub>3</sub>	32.2	26	26.4	26.9	27	27.8	28	28.2
Al <sub>2</sub> O <sub>3</sub>	10.3	11.1	11.6	11.6	12.1	12.5	12.8	13.1
CaO	20.9	7.63	7.63	7.63	7.46	7.46	6.89	6.85
Cl <sub>2</sub> O	0	5.31	3.78	3.23	2.03	0.34	0.34	0.34
K <sub>2</sub> O	2.8	4.25	4.34	4.29	4.22	4.12	4.06	3.88
SO <sub>3</sub>	0.7	1.24	1.20	1.16	1.16	1.11	0.88	0.49
MgO	2.08	1.07	1.11	1.16	1.2	1.27	1.3	1.33
LOI	6.12	8.3	9.54	8.53	8.33	8.20	7.73	7.51

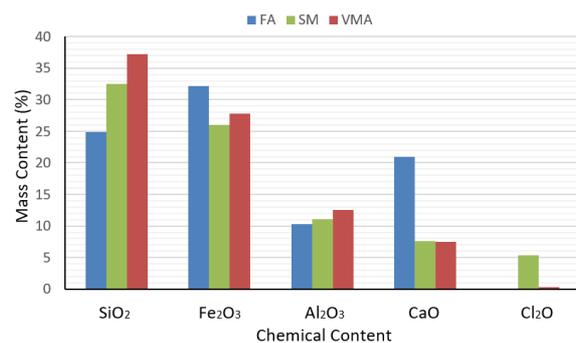


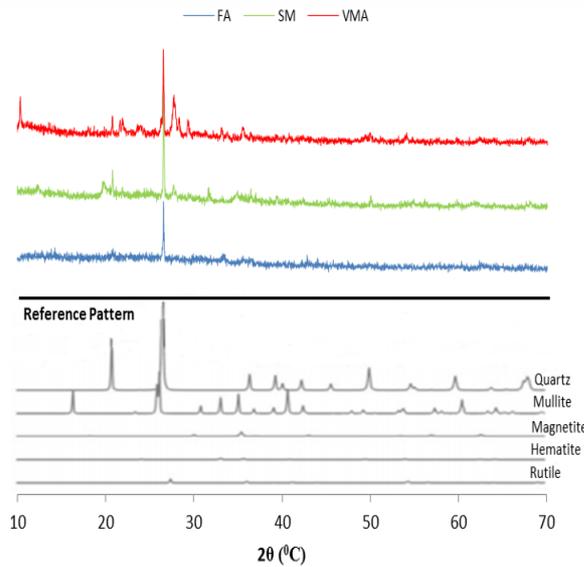
Figure 3: The concern chemical composition of FA, SM and VMA materials.

Figure 3 shows concern chemical content of FA, SM and VMA materials. It is recorded that the total chemical contents of Si, Fe, and Al in FA, SM, and VMA materials are 67.4%, 69.6%, and 77.5%, respectively. In addition, the Si and Al contents of VMA are 1.5 and 1.3 times more than FA. It means that SM and VMA materials produce more gel of Si-O-Si and Si-O-Al in geopolymer binder compared to FA material which these gels contribute to the mechanical properties such as compressive strength. It is considered that the calcination temperature was able to reduce the gas element, volatile and impurities so that increases the crystalline content of its material. Furthermore, the presence of Ca content in SM and VMA materials is classified as low Ca content whereas FA is classified as high Ca content. It means that SM and VMA materials generate N-A-S-H gel that causes

prolong setting time in geopolymer binder whereas FA material generates C-A-S-H gel that provides short setting time.

**Crystalline identification**

The crystalline identification of FA, SM and VMA materials is measured by X-ray Powder Diffraction (XRD) analysis pattern as illustrated in Figure 4. The XRD spectrum of materials refers to the similar dispersion peaks of the reference pattern to identify the main mineral constituent in the material. The XRD spectrum shows a surge peak in the range of 15 to 30° 2θ that indicates the presence of a crystalline phase from quartz, mullite, magnetite, hematite, and rutile. However, quartz and mullite are identified as the main crystalline in the material. In addition, there is another peak in the range of 15 to 30° 2θ and this peak is only present in SM and VMA materials. It indicates that the crystalline of quartz and mullite in SM and VMA materials is presented more compared to FA material. It confirms the chemical composition result mentioning that the contents of Si and Al in SM and VMA materials are more than FA material.

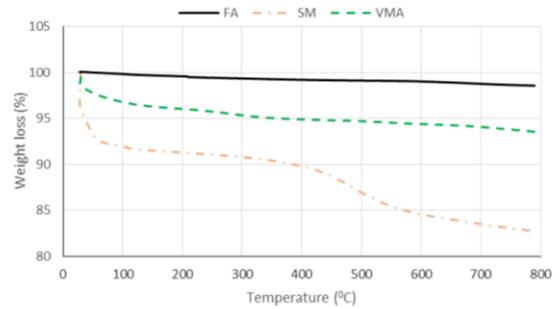


**Figure 4. The crystalline identification of FA, SM and VMA materials.**

**Weight loss**

Figure 5 displays the weight loss of FA, SM and VMA materials by thermal gravimetric analysis (TGA). There are three weight losses range areas in TGA due to a temperature level of less 20-100°C, 100-300°C, and above 300°C. The range area of 20-100°C indicates the physically bonded water evaporation. The weight loss of FA, SM and VMA materials is 0.15%, 8.17%, and 3.37%, respectively. It means that the weight loss of VMA material is lower than SM material. It is attributed to the high calcination temperature has evaporated the water content to its full potential in VMA material.

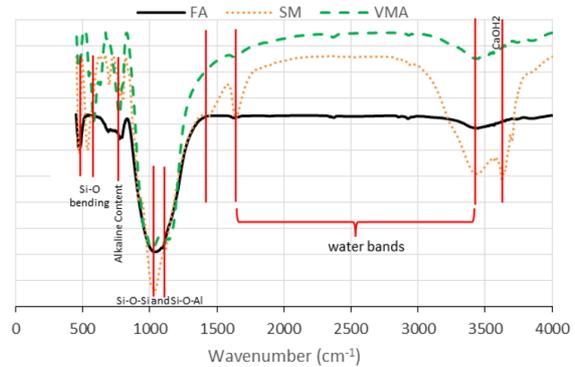
The second range area of 100-300°C indicates chemically bonded water evaporation. The weight loss of FA, SM and VMA materials about 0.47%, 1.34%, and 1.3%, respectively. This range area shows that the weight loss of SM is similar to VMA materials. It is attributed to the amount of water lost in SM material during the range area of 20-100°C so that the rest water evaporation in the second area is in a small amount. The third area above 300°C indicates the dihydroxylation of OH groups with the subsequent polycondensation into siloxo bond Si-O-Si and linking neighboring the geopolymer chain. The weight loss of FA, SM and VMA materials is about 0.77%, 8.77%, and 1.88%, respectively. It shows that the weight loss of VMA material is lower than SM material. It is attributed to the high temperature of compelled water content in SM material to evaporate causing water evaporation as much as possible whereas the water content of VMA material was evaporated by high calcination temperature in the large quantity.



**Figure 5. The weight loss of FA, SM and VMA materials.**

**Chemical bonding identification**

Figure 6 shows the chemical bonding identification of FA, SM and VMA materials by Fourier-transform infrared spectroscopy (FTIR). Table 2 shows the indication of the peak in each band area that presented in Figure 6. They are the range area of 3600-3700 cm<sup>-1</sup> indicates the stretching of Ca(OH)<sub>2</sub>, 1630-3440 cm<sup>-1</sup> indicates the stretching and bending of H-O-H, 1380-1450 cm<sup>-1</sup> indicates the stretching of CaCO<sub>3</sub>, 880-1140 cm<sup>-1</sup> indicates the stretching Si-O-Si and Al-O-Si, 680-800 cm<sup>-1</sup> indicates the presence of alkali content and below 680 cm<sup>-1</sup> indicates the bending of Si-O.



**Figure 5. The bonding chemical identification of FA, SM and VMA materials.**

**Table 2. The comparison of FTIR analysis of FSM and SMC700 powder refer to FA.**

Band range (cm <sup>-1</sup> )	Type of bond/indication	Number of peak		
		FA	SM	VMA
3600-3700	Stretching of Ca(OH) <sub>2</sub>	0	1	0
1630-3440	Stretching of H-O-H and Bending of H-O-H	2	2	2
1380-1450	Stretching of CaCO <sub>3</sub> (carbonate)	0	1	0
880-1140	stretching of Si-O-Si and Al-O-Si	1	1	2
680-800	Presence of alkali content	2	2	2
Below 680	Bending of Si-O	1	2	2
Total band point		6	9	8

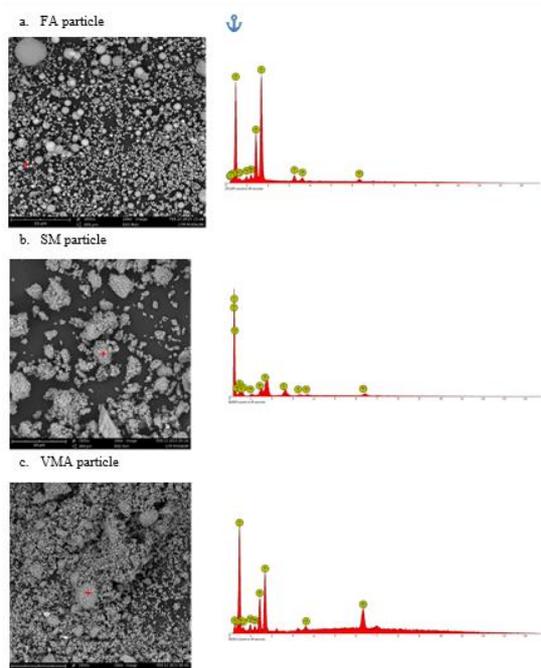
Peak band area of 880-1140 cm<sup>-1</sup> and below 680 cm<sup>-1</sup> show the feasibility of material to be used in the geopolymer binder. It is due to these band areas shows the presence of Si and Al contents which contribute to generate Si-O-Si and Si-O-Al gel in geopolymer binder. In addition, it is seen that the peak number of VMA material in these band areas is more than FA material. It confirms the XRF and XRD results mentioning that the chemical content of VMA material is more than FA material.

**Surface image and chemical identification**

The particle shape of FA, SM, and VMA materials are measured by scanning electron microscope (SEM) as illustrated in Figures 6a, 6b, and 6c. The properties of FA particle are an amorphous

sphere, glassy and sleek. These properties have some advantages in geopolymer binder. The amorphous sphere shape serves as a filler in the concavity of geopolymer binder whereas the glassy and sleek surfaces retain the alkaline solution in the surface of FA which it is good to maintain the workability in fresh geopolymer mixture. The strong signal intensity shows that the main proportion of FA is in Si and Al content. It means that FA material is able to generate Si-O-Si and Si-O-Al gels in geopolymer binder.

Furthermore, particle properties of SM have irregular agglomerate shape and rough surface which the irregular agglomerate shape of SM is not able to fill the concavity of geopolymer binder as good as FA while the rough surface of SM absorbs the alkaline solution and it causes the reduction of workability in the fresh mixture. The strong signal intensity shows that the main proportion of SM is not in Si and Al content. It is due to Si and Al content is hindered by volatile and impurities so that the calcination temperature is considered to be able to reduce the volatile and impurities. It can be confirmed by the strong signal intensities of VMA particle in Si and Al content. However, the calcination temperature does not change the particle properties of VMA so that VMA provides similar properties of geopolymer binder to SM.



**Figure 6. Surface image and chemical identification of FA, SM, and VMA particle.**

### Conclusion

Based on the results of source material and geopolymer binder, the following conclusions are highlighted.

1. The calcination temperature improved the total chemical content of Si, Fe, and Al from 69.6% to 77.5% of total mass content but it did not change the surface and shape of the SM particle.
2. The crystalline of quartz and mullite in VMA material were more than FA material.
3. The weight loss of water content in VMA material was 3.4% and FA material was 1.56%.
4. Peak number of VMA material in the range area of 880-1140  $\text{cm}^{-1}$  had more Si-O-Si and Si-O-Al gels compared to FA material.
5. The surface image of FA was an amorphous sphere, glassy and sleek whereas the surface images of SM and VMA were irregular agglomerate and rough.

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