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ONE PART METHOD FOR MAKING GEOPOLYMER PASTE USING FLOCCULATED SIDOARJO MUD

Some efforts have proposed the utilization of Sidoarjo mud for geopolymer paste. However, the original dry mud in geopolymer concrete showed decreased compressive strength and increased required water. In this paper, the one-part method is proposed to reduce the water in the mixture. First, the mud was chemically flocculated. Then, the dry mud was mixed with fly ash, activated geothermal silicate, and sodium hydroxide mixture in solid form before then the distilled water was added. This reduced the required water to 50% compared to the two-part method. The flocculant sedimented heavy metal that resulted in higher compressive strength at a later age. At 28 days, dry flocculated mud showed higher compressive strength than the original dry mud, with a compressive strength of 13 MPa and 11 MPa, respectively. This is because of the increase of silica, alumina, and iron content from 70% in dry LUSI to 75% in dry flocculated mud.

Keywords: Sidoarjo mud; flocculation; geothermal silicate; one-part geopolymer, geopolymer paste

1. Introduction

Portland cement is known for its versatility, durability, and economic properties [1]. However, cement is associated with negative environmental impacts, responsible for 5% of the world's carbon dioxide emissions [2]. High production and demand for cement as a concrete material depletes natural resources and poses an environmental threat [3]. Thus, environmentally friendly cement substitute materials are needed. In addition, environmentally friendly concrete, or green concrete, where waste could be reused, is also in line with the Sustainable Development Goals (SDGs) [4].

Green concrete can be defined as concrete that uses alternative cement and waste material [3]. The waste used in this paper is Fly Ash (FA) and Sidoarjo mud (Lumpur Sidoarjo or LUSI) as binder and filler, respectively. LUSI is a mud volcanic erupted from a hydrocarbon exploration well near Sidoarjo, East Java, Indonesia [5]. Mud volcanic could also be used with FA to create geopolymer concrete [6]. LUSI sediment came from the Arjuno-Welirang Volcano Complex [7]. Therefore, it had excessive silica due to magma differentiation [8].

Based on XRF analysis, LUSI contains Silica and Alumina iron and calcium with a percentage of 51.14%, 14.16%, 5.54%, and 2.7%, respectively. The high amount of Silica, Alumina, and Iron makes LUSI similar to class F FA with 70% pozzolan as in ASTM C618 which chemically makes LUSI suitable for geopolymer materials [9]. Geopolymer materials required amorphous high aluminum and silica content [10]. However, particles of LUSI have a crystalline structure which made LUSI less suitable for geopolymers [11].To obtain an amorphous particle, LUSI was calcined. Calcined LUSI also contains metakaolin which showed excellent pozzolanic properties and was most reactive in clay [12]. In addition, geopolymer paste using calcined LUSI has higher compressive strength than the one without calcined LUSI [13]. However, calcined LUSI was less environmentally friendly because of the carbon footprint of the calcination process. Therefore, flocculated LUSI without the calcination process was utilized for geopolymer paste in this paper.

LUSI is considered a natural disaster by the Indonesian government. The mud is being discharged into the Porong river delta to minimize health and social impacts on the nearby community [14]. Discharge volume was estimated to be 5000-10,000 m^3/d [15]. However, mud materials are often not in demand because they have a high clay and water content [16]. Consequently, one treatment to reduce water content was using flocculants [17]. In addition, the flocculant also precipitated heavy metals and

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changed the pH value[18]. The flocculant attached small particles, forming flocs, which dewatered the liquid [19].

In common, flocculants that contain lime and silica are used. The lime generates new materials of cementitious nature and improves soil mechanical properties [20]. Silica neutralizes acid and separates the heavy metal from acid drainage [21]. The heavy metal, namely iron, increased compressive strength in a longer curing duration [22]. There is also evidence that the flocculant increased the compressive strength of mud [23].

Ekaputri et al. [24] found that adding Dry LUSI (DL) required 80%-100% additional water of the mud weight resulting in a 29.4% reduction in compressive strength. The additional water was needed due to the high water absorption mineral known as Halloysite, which has a similar XRD pattern to kaolinite [25]. Thus, a new method was needed to reduce the required water for the sample with DL.

Instead of the wet alkali activator, the Dry Alkali activator (DA) was used to reduce the required water. Mixture with a DA is called the one-part method because the pozzolanic materials, alkali activator, and filler are mixed in a solid state [26]. Fujiyama et al. [25] conducted a study using dehydrated sodium metasilicate nonahydrate resulted in a 62% increase in the compressive strength of a specimen with DL addition as a filler. The higher compressive strength is subjected to LUSI's high water absorption since the mixture using sodium metasilicate nonahydrate comprises 25% water. Therefore, the one-part method was better for mixing a geopolymer specimen using DL. However, sodium metasilicate nonahydrate is hard to obtain in Indonesia. Thus, an alkali activator from geothermal silica will be used as the activator replacement.

Petrus et al. [27] used a mixture of sodium hydroxide and geothermal sludge that contains 76% silica as the alkali activator, and then the mixture was calcined to obtain sodium metasilicate (Na_2SiO_3). Since all the waste and sodium hydroxide is easier to obtain in Indonesia, thus alkali activator from geothermal silica will be used in this paper.

This study used FA class F combined with an alkali activator from geothermal sludge and DL to obtain geopolymer cement. The DL was treated in two conditions: flocculated and unflocculated. Accordingly, the effect of DL on the compressive strength of geopolymer paste using one part method was studied.

2. Materials and method

2.1. Materials

LUSI is obtained from Sector 53 within the LUSI embankment, Porong, Sidoarjo, East Java, Indonesia. The LUSI was extracted 15 cm below the surface. Then, the LUSI was sun-dried for 3-days. Finally, the LUSI was crushed and labeled as DL. The specific gravity was obtained at 2.28 g/cm^3 and was measured using a pycnometer as in ASTM C188-95 [28]. The DL pH was obtained at 7.44 using the pH ohauss meter. The DL chemical composition was obtained using X-Ray Fluorescence (XRF), as shown in TABLE 1.

TABLE 1 also shows the chemical composition of the FA. The FA was obtained from the Tanjung Jati power plant. It was classified as F Class FA since the amount of Silica, Alumina, and Iron is 82.07%, which is over 70% as per ASTM C 618-19 with lime content being less than 18%. Then, the FA was pulverized to pass the No. 100 sieve with a diameter of 150 μm. The DA was a calcined mixture of geothermal silica and sodium hydroxide. The DA was obtained from Gadjah Mada university which was developed by Petrus et al. [27]. The Flocculant was a Commercial Flocculant from Japan that contained 52.63% lime and 24.85% Silica.

2.2. Flocculation process

The LUSI was treated using a Flocculant dose of 0.5 gr/L. First, the Flocculant was diluted in distilled water. Then DL was added by ¼ volume of water. After 24 hours, the water and LUSI mud slurry were separated. Finally, the LUSI was dried and crushed to pass the No. 100 sieve. The material was labeled as Dry Flocculated LUSI (DFL).

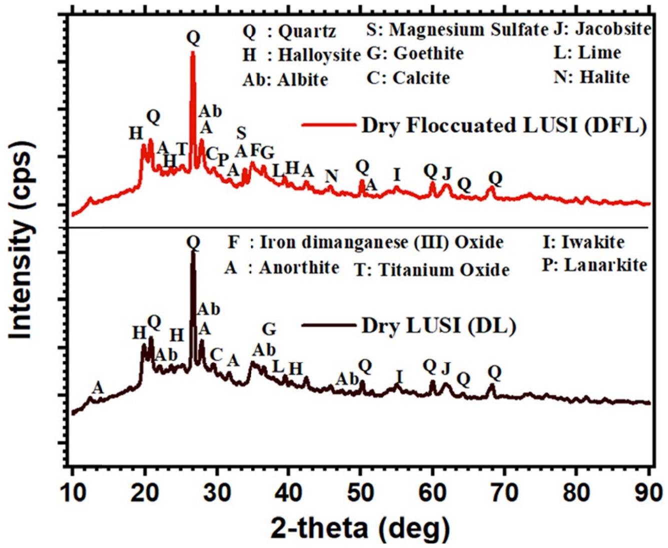
TABLE 1

Chemical Composition of Materials (% mass)

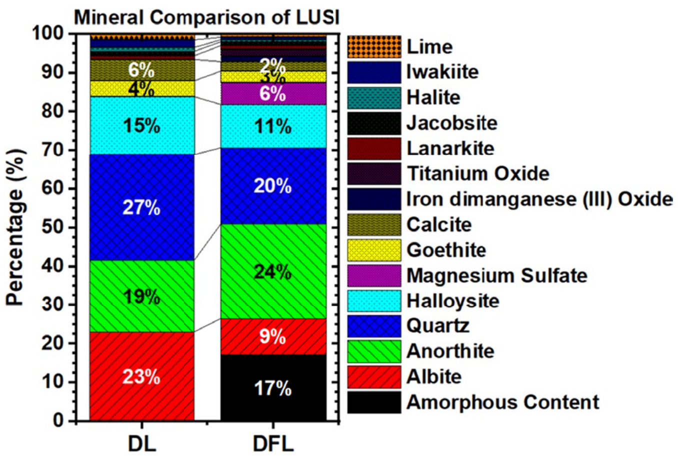
No.	Parameter	XRF Test Result			Test Method
		FA	DL	FL	
1	SiO_2	54.31	51.14	50.4	ASTM D 4326-13
2	Al_2O_3	17.62	14.16	17.73	
3	Fe_2O_3	10.14	5.54	7.48	
4	CaO	5.62	2.7	4.21	
5	MgO	2.98	2.51	3.28	
6	Na_2O	3.57	3.4	3.6	
7	K_2O	1.6	1.32	1.58	
8	TiO_2	0.67	0.6	0.73	
9	MnO_2	0.7	0.11	0.16	
10	P_2O_5	0.36	0	0.13	
11	Cr_2O_3	0.01	0.01	0.01	
12	SO_3	0.86	0	2.14	

The Flocculation process changed the chemical properties of LUSI, with the detail shown in TABLE 1. The XRF analysis found that the amount of silica decreased. Meanwhile, alumina, iron, and lime increased. So, it can be concluded that Flocculant sedimented heavy metal. The Flocculation process also increases Density and pH from 2.28 g/cm^3 to 2.49 g/cm^3 and 7.44 to 7.65, respectively.

The comparison of the XRD pattern between DL and DFL is shown in Fig. 1(a). The XRD analysis shows that DL and DFL have Feldspar as the main minerals. However, the Flocculant changes the feldspar minerals and percentage from 23% albite ($NaAlSi_3O_8$) and 19% anorthite ($CaAlSi_3O_8$) to 9% albite and 24% anorthite, which explains the higher Calcium content from DL to DFL as shown in Fig. 1(b).



(a) XRD Pattern



(b) Mineral Percentage

Fig. 1. Comparison of Dry LUSI and Dry Flocculated LUSI

The XRD analysis also showed that DL and DFL have Quartz and Halloysite as the main minerals. However, the flocculation process decreased Quartz and Halloysite percentages from 27% to 20% and 15% to 11%, respectively. In addition, the flocculant increased the amorphous content of the LUSI from 0% to 17%. The amorphous content was counted using a software. The Quartz and Halloysite minerals that have decreased are most likely to be amorphous content.

2.3. Method

The Geopolymer paste was mixed with the one-part geopolymer instead of the two-part geopolymer. The FA and LUSI were sieved with the No.100 sieve. Meanwhile, the DA was sieved with the No.200 sieve with a diameter of 75 μm. One-part geopolymer was chosen because of its simplicity and performance in a mixture using DL.

2.3.1. One-part geopolymer

Fig. 2 shows the making of the geopolymer paste. The FA and Alkali Activator were mixed in dry conditions (DA). After that, if additional filler was used, it was added to the sample. Thus, geopolymer cement was obtained. Finally, the geopolymer paste was created by mixing geopolymer cement and distilled water.

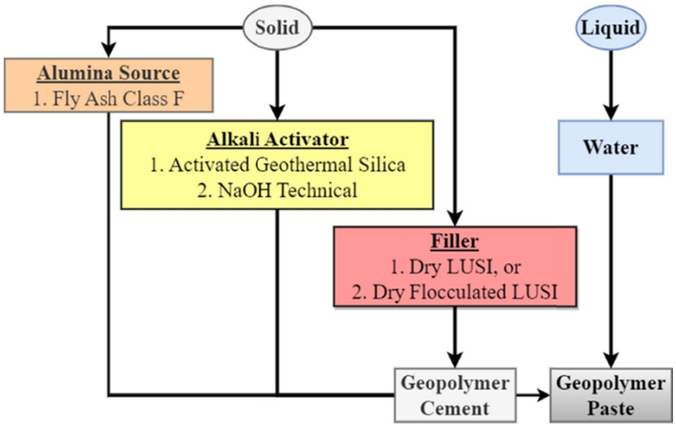


Fig. 2. One-part Geopolymer Process

Fig. 3 shows the mixtures of each geopolymer paste. DL and DFL were the mixtures with an additional filler of Dry LUSI and

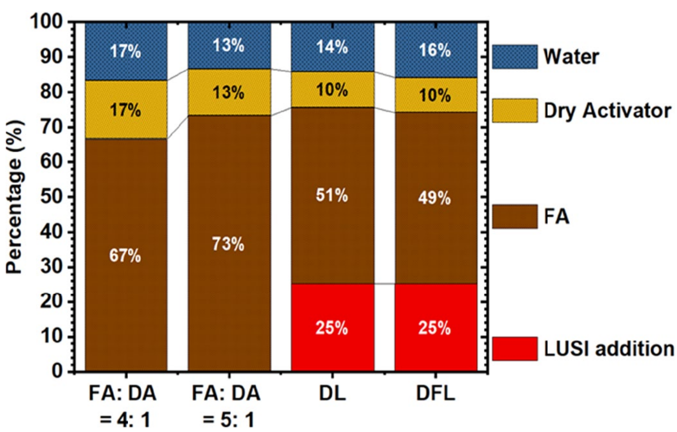


Fig. 3. Geopolymer Mixture

Dry Flocculated LUSI, respectively. The amount of additional LUSI was half of the FA. The paste with LUSI increases the required water by 1% and 3% for DL and DFL, respectively.

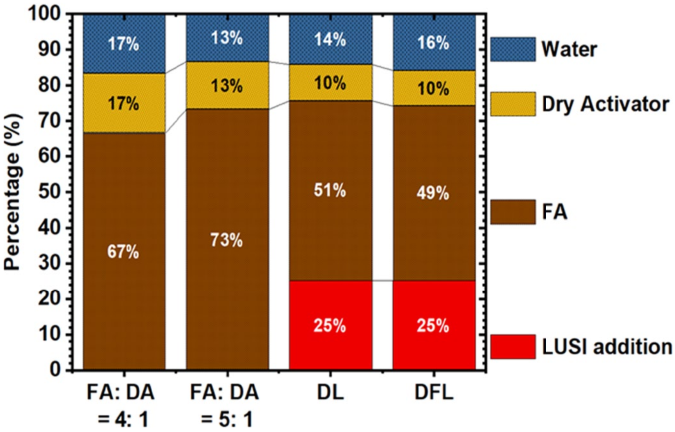


Fig. 3. Geopolymer Mixture

3. Results

3.1. Compressive strength

Fig. 4 shows that the increasing percentage of FA increases the compressive strength of the paste. This is subjected to an increase in the amount of Silica and Alumina in the mixture, with the comparison of Silica and Alumina, Si/Al, was 3.102 and 2.928 for the mixture with FA: DA = 4:1 and FA: DA = 5:1. Meanwhile, The Si/Al of DL and DFL sample was 2.955 and 2.916. However, a lower compressive strength was shown in both samples using DL and DFL. At 28 days, the sample without LUSI (FA: DA = 5: 1) has a compressive strength of 19.50 MPa. Meanwhile, DL and DFL have decreased the geopolymer paste compressive strength to 11.45 MPa and 12.63 MPa, respectively.

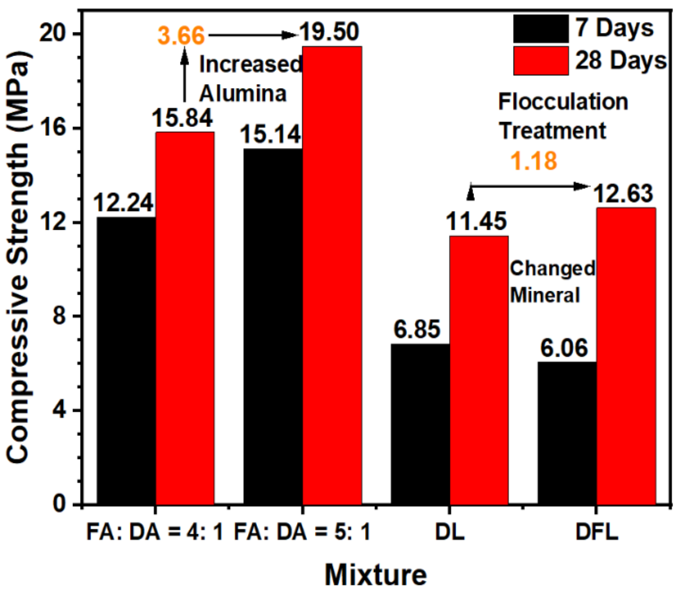


Fig. 4. Compressive Strength of Various Mixtures

Fig. 5 shows the decreasing percentage of the compressive strength in the geopolymer paste. The mixture with FA: DA = 5:1 is used as the 100% reference of the compressive strength as it has the highest compressive strength. FA: DA = 4: 1 decreased the compressive strength of geopolymer paste by 19% with the same percentage in both 7 days and 28 days. However, the sample with DL and DFL shows different percentage drops at 7 days and 28 days. The remaining compressive strength of DL was 45% and 59% at 7 days and 28 days, respectively. Meanwhile, DFL has the remaining compressive strength of 40% and 65% at 7 days and 28 days, respectively.

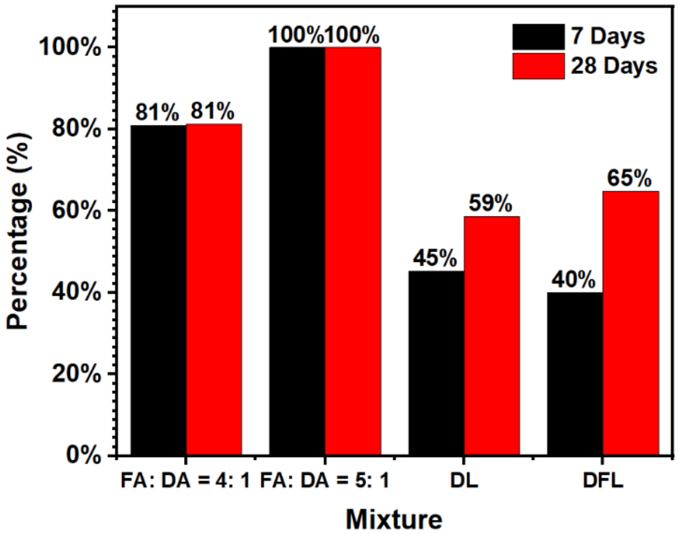


Fig. 5. Percentage Reduction of each mixture's compressive strength

4. Discussions

Geopolymer paste with DL required additional water for 80% to 100% of the LUSI weight, which decreases the compressive strength of the specimen [25]. It required additional water because DL contained Halloysite [26]. Fig. 6 shows the mixture comparison of this paper and other studies. The required water in DL and DFL was reduced because of the application of one-part method. This method allows the amount of water easily controlled. In addition, it required less water and alkali activators while using more FA and LUSI. The activator is divided into

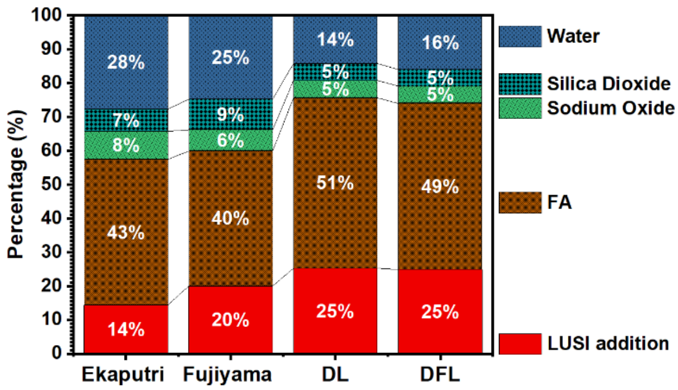


Fig. 6. The comparison of the mixture with the previous studies

Sodium Oxide (Na_2O) and Silica Dioxide (SiO_2) to determine the molarity of Sodium Hydroxide (NaOH). The amount of all the liquid compared to the amount of the Na flake will determine the molarity of the Sodium Hydroxide. The higher molarity of sodium hydroxide led to higher compressive strength [24].

The additional water in the two-part method decreased the Sodium Hydroxide molarity from 14 to 4.84 [24]. High sodium Hydroxide molarity shows the advantage of using the one-part method. The molarity was obtained from a comparison of sodium hydroxide and the water in the system. Therefore, the molarity of Sodium Hydroxide using one-part geopolymer in the sample without LUSI (FA: DA = 5:1), DL, and DFL was obtained at 10.23, 7.78, and 6.96, respectively.

The one-part method's advantage was mixing a higher percentage of LUSI and a lower percentage of alkali activator in a geopolymer paste. However, the lower alkali activator percentage decreased the compressive strength of the paste. The compressive strength of DL and DFL compared to Ekaputri et al. [24] and Fujiyama et al. [25] was 11.45 MPa, 12.63 MPa, 15.40 MPa, and 31.50 MPa, respectively. Although the one-part method could be used to create a geopolymer paste by utilizing more LUSI, this method shows lower compressive strength compared to the two-part method. However, the one-part geopolymer paste can utilize more LUSI. In addition, The DFL sample has higher compressive strength than the DL sample because of the sedimentation of heavy metal and dissolved particles by the flocculant. Therefore, the DFL sample contained higher silica, Alumina, and iron.

The flocculation process sedimented some heavy metals. One of them is iron complex molecules, which have a slight contribution to the compressive strength of the specimen at a later age since the iron oxide takes more time to react with the alkali solution [24]. In, addition, DFL has a 17% higher amorphous content than DL, which led to higher compressive strength at a later age. Therefore, DFL has a higher compressive strength than the DL with a compressive strength of 59% and 65% of the sample without LUSI, respectively in 28 days. However, DL has higher compressive strength than DFL at 7 days with a compressive strength of 45% and 40% of the sample without LUSI, respectively.

5. Conclusions

This study has compared the effect of DL and DFL in geopolymer paste. DL and DFL might become a geopolymer paste using the one-part method. The paste required more water percentage compared to the sample without LUSI. The following are some points:

1. The Flocculant changed the LUSI mineral. The XRD Analysis shows that the Feldspar was changed from Albite ($NaAlSi_3O_8$) to Anorthite ($CaAlSi_3O_8$).
2. Geopolymer paste with LUSI as the filler could be created. However, compared to the sample without LUSI, the compressive strength of the paste of DL and DFL was 59% and 65% of the sample without LUSI, respectively. Because of the higher water required in the geopolymer paste with LUSI.
3. DFL showed higher compressive strength than DL because the DFL contains higher Silica, Alumina, and Iron than those in DL. According to the XRF results, the total content of Silica, Alumina, and Iron in DL and DFL is 70% and 75%, respectively. In addition, flocculation made the DFL has a 17% higher amorphous percentage than the DL.

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