Setting time and compression strength of low-calcium fly ash geopolymer paste with non-calcined red soil substitution in ambient curing

P H Simatupang¹, V Nine¹ and A E Sinaga¹

¹ Civil Engineering Department, Faculty of Science and Engineering, University of Nusa Cendana, Kupang, Indonesia

partogihsimatupang@gmail.com

Abstract. This paper describes the research of the effects of non-calcined red soil substitution in low-calcium fly ash geopolymer paste in ambient curing. Mechanical characteristics observed were setting time and compression strength. The non-calcined red soil substitutions were varied i.e 0%, 5%, 25% and 50% of mass of fly ash. The alkaline solutions used were natrium silicate solution and natrium hydroxide solution 10 M with mass ratios 1:1 and 2:1. The results show that the higher the substitution of non-calcined red soil the longer the initial and final time setting of the geopolymer paste. Meanwhile, the higher the substitution of non-calcined red soil the lower the compression strength of the geopolymer paste. Furthermore, geopolymer paste with ratio of Na₂SiO₃ / NaOH = 2.0 will has longer initial and final setting than geopolymer paste with ratio of Na₂SiO₃ / NaOH = 1.0. Geopolymer paste with ratio of Na₂SiO₃ / NaOH = 2.0 will has higher compression strength than geopolymer paste with ratio of Na₂SiO₃ / NaOH = 1.0. All the relationships between the substitution of non-calcined red soil and setting time or compression strength of geopolymer paste can be drawn in exponential function.

1. Introduction

Geopolymer paste is a relatively new binder to make a solid material. This is the most promising binder to replace the cement paste. Low-calcium fly ash and other industrial by product based geopolymer material in Indonesia have been studied i.e: compression strength of geopolymer mortar [1], characteristics of geopolymer paste in sulphuric acid solution [2], pigment in geopolymer paste [3] and environmental aspects of geopolymer material [4].

Clay or soils based geopolymer materials studied were dominantly using calcination of the materials to get the amorphous silica-alumina precursor [5,6]. The calcination of raw material produced good geopolymer solidification. However, the researches on non-calcined clay or soil (including dredged soil and red soil/laterite soil) geopolymer material were relatively rare [7-11]. Several papers revealed that clays or soils have enough SiO₂ and Al₂O₃ to make geopolymer material i.e SiO₂ 47.49-70.23% and Al₂O₃ 11.79-35.69% [5], SiO₂ 31.7-46.7% and Al₂O₃ 10.6-23.04% [6] and SiO₂ 61.56% and Al₂O₃ 22.53% [7]. Meanwhile, in Nusa Tenggara Timur Province Indonesia, red soil is a raw material to make red fired brick. Red fired brick is always produced by burning the red soils in the furnace.

Several studies on the non-calcined red soils geopolymer mortar have presented sufficient compression strength i.e 7.73 MPa [7], 1.4-7 MPa [10]. However to increase its strength and durability of non-calcined red soil geopolymer material, it was recommended to use fly ash as a main precursor.
Until now, there were very few papers conducting research on the characteristics of setting time and compressive strength of low-calcium fly ash geopolymer paste with non-calcined red soils substitution. Therefore, this study focused on setting time and compressive strength of low-calcium fly ash geopolymer paste with non-calcined red soil substitution. Red soil used as solid substitution was non-treatment soil from Desa Obelo Kupang District, Nusa Tenggara Timur Province, Indonesia. To make the geopolymer paste, it was used Low-Calcium or Class F Fly Ash from Bolok-Kupang Coal Fired Power Plant as a rich silica-alumina of precursor material. Meanwhile, the mass ratio of natrium silicate solution to natrium hydroxide solution 10 M was 1:1 and 2:1. The mass ratio of solid (fly ash+non-calcined red soil) to liquid (alkaline activator solution) was 2.0. The characteristics of setting time and compressive strength of low-calcium fly ash geopolymer paste with non-calcined red soils substitution were obtained.

2. Experimental details
This subsection will present raw material used, sample made, and testing conducted. There was no treatment to fly ash and non-calcined red solid as raw materials. Testing conducted were: (1) the setting time testing and (2) compression strength testing.

2.1. Materials
Low-calcium fly ash from Power Plant Bolok Kupang was used as precursor material to make geopolymer paste. To substitute fly ash, it was used non-calcined red soil from Desa Obelo Tanah Merah in Kupang District-Nusa Tenggara Timur Province, Indonesia. These materials are shown in Figure 1. There is no treatment to fly ash. Before usage of non-calcined red soil, this soil should be dried in room temperature until 24 hours.

![Figure 1. Raw material used: Low-Calcium Fly Ash (left) and Non-Calcined Clay (right)](image)

The mixture composition of geopolymer paste was low-calcium fly ash, red soil and alkaline activator solution with certain mass ratios. Alkaline activator solution was a mixture of natrium silicate and 10 M sodium hydroxide solution with mass ratio 1:1 and 2:1. Class F or low-calcium fly ash from Power Plant Bolok Kupang was used as a precursor material to make geopolymer. This fly ash had CaO 3.64%, SiO$_2$ 57.47 % and Al$_2$O$_3$ 21.88 %. More detail oxide compositions by XRF (X-Ray Fluorescence) testing is given in Table 1. Meanwhile, XRD (X-Ray Diffraction) pattern of fly ash can be shown in Figure 2. Many minerals found in the fly ash were Quartz, Gypsum, Hematite and Magnitite. It was not conducted microscopic characteristics on non-calcined red soil.

Some text.
Table 1. Oxide Compositions of Fly Ash by XRF (X-Ray Fluorescence) Testing.

| Oxide | MgO | Al₂O₃ | SiO₂ | K₂O | Na₂O | CaO | TiO₂ | MgO | Fe₂O₃ | LOI |
|-------|-----|-------|------|-----|------|-----|------|-----|-------|-----|
| Wt (%) | 1.41 | 21.88 | 57.47 | 1.59 | 2.69 | 3.64 | 0.81 | 1.41 | 3.61 | 1.77 |

Figure 2. X-Ray Diffraction pattern of fly ash

2.2. Mixture compositions, mixing, and casting

Sample used were cylindric paste with diameter 2.5 cm and 5 cm height. After fresh geopolymer paste casted, the samples were cured in ambient curing. Composition of geopolymer paste studied is given in Table 2. The substitutions of non-calcined red soil to fly ash are 0%, 5%, 25% and 50%. Every mixture was prepared i.e 9 cylindric pastes (three samples for compression testing on 14 days, three samples for testing on 28 days and others for laboratory assets) and 1 sample of setting time.

The mixing and casting of geopolymer paste is shown in Figure 3. To make geopolymer paste, it was mixed fly ash, non-calcined red soil and alkali activator solution by using Paint Mixer with 1800 rpm for 2-3 minutes. After, geopolymer paste was ready, it was poured in plastic formwork. Then, samples were cured with ambient curing.

Table 2. Composition of geopolymer paste.

| Mixture | FA a (gr) | Non-Calcined Clay (gr) | NS b (gr) | NH c (10 M) (gr) | Ratio FA/ (NS+NH) | Ratio NS/NH | Substitution of Non-Calcined Clay to FA |
|---------|-----------|------------------------|---------|----------------|------------------|------------|----------------------------------------|
| A-AC-1  | 650       | 0                      | 162.5   | 162.5          | 2                | 1          | 0 %                                    |
| A-AC-2  | 600       | 0                      | 216.7   | 108.3          | 2                | 2          | 0 %                                    |
| B-AC-1  | 570       | 30                     | 162.5   | 162.5          | 2                | 1          | 5 %                                    |
| B-AC-2  | 570       | 30                     | 162.7   | 108.3          | 2                | 2          | 5 %                                    |
| C-AC-1  | 450       | 150                    | 162.5   | 162.5          | 2                | 1          | 25 %                                   |
| C-AC-2  | 450       | 150                    | 216.7   | 108.3          | 2                | 2          | 25 %                                   |
| D-AC-1  | 300       | 300                    | 162.5   | 162.5          | 2                | 1          | 50 %                                   |
| D-AC-1  | 300       | 300                    | 216.7   | 108.3          | 2                | 2          | 50 %                                   |

a Fly Ash
b Natrimum Silicate
c Natrimum Hydroxide
2.3. Testing

2.3.1. Setting time testing. The setting time of geopolymer paste was conducted using Vicat apparatus like setting time testing on cement paste in ASTM C191-13. The setting time testing is given in Figure 4. Every 15 minutes penetration test was taken using 1-mm Vicat needle until the final setting occurred. Then initial setting time could be found by determining 25 mm of penetration. The results of setting time were the mean of two observations of penetration depth on two different locations.

2.3.2. Compression strength testing. Hardened geopolymer pastes were tested using Compression Testing Machine with capacity 312.5 KN. The compression strength testing is given in Figure 5. Compression testings were conducted for 14 days and 28 days age of samples. The results of compressive strength were the mean of three samples for every variable.
3. Results and discussion

3.1. Setting Time

The results of setting time testing are given in Figure 6. Setting time testings were completely conducted except sample D-AC-2. The setting time of geopolymer paste D-AC-2 was not finished until 84 hours. So, the setting time testing was stopped and the end value of setting time was extrapolated. The results of initial and final setting time of geopolymer paste are shown in Figure 7. It is shown that the more the substitution of non-calcined red soil the high the initial and final setting time of geopolymer paste. The initial and final setting time depend on the ratio of Na$_2$SiO$_3$ to NaOH solution. Geopolymer paste with ratio of Na$_2$SiO$_3$ / NaOH = 2.0 (A-AC-2, B-AC-2, C-AC-2 and D-AC-2) will has longer initial and final setting than geopolymer paste with ratio of Na$_2$SiO$_3$ / NaOH = 1.0 (A-AC-1, B-AC-1, C-AC-1 and D-AC-1).
The relationships of setting time and substitution of non-calcined red soil are given in Figure 8. and Figure 9. Those relationships can be drawn as the exponential functions.

**Figure 7.** Initial and Final setting time of geopolymer paste

|                | A-AC-1 | A-AC-2 | B-AC-1 | B-AC-2 | C-AC-1 | C-AC-2 | D-AC-1 | D-AC-2 |
|----------------|--------|--------|--------|--------|--------|--------|--------|--------|
| initial setting time | 7      | 11.3   | 8.5    | 14     | 12.75  | 31     | 31     | 80.5   |
| final setting time    | 20.25  | 22.5   | 16     | 23.25  | 21     | 41.5   | 41.5   | 229.31 |

\[
y = 6.9534e^{0.0293x} \\
R^2 = 0.9853
\]

\[
y = 11.448e^{0.0392x} \\
R^2 = 0.9998
\]

**Figure 8.** Relationships of Initial Setting and substitution of non-calcined red soil.
3.2. Compression Strength

The results of compression strength testing are given in Figure 10 and Figure 11. It is shown that the more the substitution of non-calcined red soil the low the compression strength of geopolymer paste. The compression strengths also depend on the ratio of Na$_2$SiO$_3$ to NaOH solution. Geopolymer paste with ratio of Na$_2$SiO$_3$ / NaOH =2.0 (A-AC-2, B-AC-2, C-AC-2 and D-AC-2) will has higher compression strength than geopolymer paste with ratio of Na$_2$SiO$_3$ / NaOH =1.0 (A-AC-1, B-AC-1, C-AC-1 and D-AC-1).

![Figure 9. Relationships of Final Setting and substitution of non-calcined red soil](image)

![Figure 10. Compression strength of geopolymer paste with ratio Na$_2$SiO$_3$/NaOH = 1.0.](image)

|          | Compression Strength (MPa) |
|----------|-----------------------------|
|          | 14 days                     | 28 days                     |
| A-AC-1   | 13.58                       | 25.45                       |
| B-AC-1   | 12.73                       | 16.80                       |
| C-AC-1   | 11.88                       | 13.58                       |
| D-AC-1   | 7.08                        | 8.06                        |
Figure 11. Compression strength of geopolymer paste with ratio Na$_2$SiO$_3$/NaOH = 2.0.

The relationships of compression strength and substitution of non-calcined clay are given in Figure 12 and Figure 13. Those relationships can be also drawn as the exponential functions like the relationships between setting time and substitution of non-calcined clay.

Figure 12. Relationship between compressive strength and substitution of non-calcined red soil for age 14 days
The correlation between setting time and compressive strength of those mixtures can be described as follows. The longer the initial setting time of the paste, the lower the compressive strength of the paste. Similarly, the longer the final setting time of the paste, the lower the compressive strength of the paste. This correlation does not depend on the ratio of natrium silicate solution to natrium hydroxide solution.

4. Conclusions
It has been shown characteristics of setting time and compression strength of low-calcium fly ash geopolymer paste with non-calcined red soils substitution. The results show that the higher the substitution of non-calcined red soil the longer the initial and final time setting of the geopolymer paste and the higher the substitution of non-calcined red soil the lower the compression strength of the geopolymer paste. Furthermore, geopolymer paste with ratio of Na$_2$SiO$_3$ / NaOH =2.0 will has longer initial and final setting than geopolymer paste with ratio of Na$_2$SiO$_3$ / NaOH =1.0. Geopolymer paste with ratio of Na$_2$SiO$_3$ / NaOH =2.0 will has higher compression strength than geopolymer paste with ratio of Na$_2$SiO$_3$ / NaOH =1.0. All the relationships between substitution of non-calcined red soil and setting time or compression strength can be drawn in exponential function.

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Figure 13. Relationship between compressive strength and substitution of non-calcined red soil for age 28 days.
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