Compressive strength of geopolymer concrete with fly-ash from Paiton Steam Power Plant and variations of substitution sodium silicate (Na$_2$SiO$_3$) with natural zeolite

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Abstract. Geopolymer concrete is one of the technological innovations of concrete without cement. It was prepared using fine aggregates, coarse aggregates, fly-ash, sodium hydroxide (NaOH), and sodium silicate (Na$_2$SiO$_3$). In the production of geopolymer concrete, sodium silicate and sodium hydroxide serve as an alkaline activator. One of the natural materials that can be used as an alternative material is natural zeolite. Zeolite contains high silica and alumina, that expected to increase the compressive strength of geopolymer concrete. This research aims to develop geopolymer concrete technology by understanding the setting time behaviour and compressive strength by substitution sodium silicate (Na$_2$SiO$_3$) with natural zeolite. The percentage of zeolite that substitute for sodium silicate is 0%, 2.5%, 5%, and 7.5 %. The molarity of NaOH is 12 M. Meanwhile, the ratio of sodium hydroxide and sodium silicate is 1:2.5. Compressive strength testing is carried out on cylindrical specimens 10 cm x 20 cm. The results show that natural zeolite can accelerate the setting time of geopolymer paste. The fastest initial setting time is 48 minutes. Meanwhile, the final setting time is 60 minutes in geopolymer paste with substitution sodium silicate using 7.5 % zeolite. In addition, for compressive strength results, zeolite can increase compressive strength. The highest average of compressive strength results is 46.07 Mpa in substitution of Na$_2$SiO$_3$ with 7.5 % zeolite.

1. Introduction
Cement production is one of the main contributors to the greenhouse effect. One ton of cement production can produce one ton of carbon dioxide (CO$_2$) too into the atmosphere [1]. As the main material of concrete, cement is one important material for concrete construction. This encourages new research about alternative materials for replacing cement which more environmentally friendly.

Geopolymer concrete is an innovative construction material that not uses cement as a binder. The main material used is fine aggregates, coarse aggregates, fly-ash, and alkaline activator. Fly-ash is pozzolanic material from power plant waste. It used with alkaline activator as geopolymer binder for the alternative of portland cement. Its contains 45.59 % silica (Si) and 25.08 % alumina (Al) [2]. Fly ash is reacted with an alkali-activator (NaOH and Na$_2$SiO$_3$) to form a polymerization reaction. Sodium hydroxide and sodium silicate greatly affect the mechanical properties of geopolymer concrete, especially in terms of mass ratio and molarity. The mass ratio between sodium silicate and sodium hydroxide is affected for setting time. The higher the mass ratio makes the initial setting longer but
speeds up the final setting. Meanwhile, the higher molarity of sodium hydroxide used makes setting time and compressive strength increase [3]

Geopolymer material has a chemical composition similar to natural zeolite but has an amorphous microstructure [4]. Zeolite is crystalline aluminosilicates with structure composed of tetrahedral units of silicon-oxygen (SiO4) and aluminium oxygen (AlO4) [10]. Its contains 60.9 % of silica (Si), 8.7 % of alumina (Al), and 11.7 % of Calcium (Ca) [5]. Zeolite is often used as a substitute for cement because it is rich in active SiO2 and Al2O3, such as other pozzolanic materials [6]. With similar chemical composition, zeolite is expected to be one of the materials that can be used in the manufacture of geopolymer concrete. Besides having similar chemical composition, zeolites are also able to increase the compressive strength of concrete up to 15% at 28 days [6].

Zeolite reaction with alkali can form polymerization of inorganic materials/geopolymerization [7]. Alkaline concentrations can affect the dissolution of Si4+ and Al3+ from zeolites to form sodium-alumino-silicate. For geopolymer concrete production, alumino-silicate is the main material [9]. This compound makes the compressive strength increase. In addition, a large content of Calcium (Ca) in zeolites can also react to form CSH (calcium silicate hydrate) which is the same as the reaction of portland cement forming [7].

This study aims to determine the mechanical properties of geopolymer concrete based on compressive strength and setting time generated on geopolymer concrete with substitution of Na2SiO3 with zeolite. With its chemical composition and properties, zeolites are expected to be an alternative use for geopolymer concrete.

2. Material and method

2.1. Material

The material used in this research is fly-ash, alkaline solution (NaOH and Na2SiO3), fine aggregates, coarse aggregates, and natural zeolite.

| Table 1. Material used for specimen test |
|-----------------------------------------|
| Type | Type of Fly-Ash | Zeolite (%) | NaOH (Molarity) | Na2SiO3/NaOH |
|------|-----------------|-------------|-----------------|--------------|
| 1    | F               | 0           | 12              | 2.5          |
| 2    | F               | 2.5         | 12              | 2.5          |
| 3    | F               | 5           | 12              | 2.5          |
| 4    | F               | 7.5         | 12              | 2.5          |

2.2. Method
The mix design used in this research is referred to Pavithra et al., 2016 "A mix design procedure for geopolymer concrete with fly ash". The specimens used were cylinders Ø10 x 20 cm totalling 36 test specimens. The curving process is wrapped with plastic within 7 days in ambient temperature. The test carried out are setting time and compressive strength.

3. Result and analysis

3.1 Material testing
The purpose of material testing is to find out the specifications of the material used. Material test results must suitable with the material specification requirements that regulated in ASTM. Materials that tested are fly-ash, fine aggregates, and coarse aggregates.
Table 2. Physical properties of fine and coarse aggregate

| Aggregate      | Specific Gravity | Particle Density (g/cm³) | Water Absorption (%) |
|----------------|------------------|--------------------------|----------------------|
| Fine Aggregates| 2.65             | 1.45                     | 2.28                 |
| Coarse Aggregates| 2.76            | 1.30                     | 1.97                 |
| Fly-Ash        | 2.59             | 1.11                     | -                    |

3.2 Setting Time

Vicat needle apparatus is used to find out the setting time of geopolymer paste. The test of setting time is carried out for all proportion used. Geopolymer paste prepared according to the standard universal testing method guidelines. The result of Initial setting time is showed when vicat needle dropped at 25 mm. Meanwhile, the final setting time is showed when the vicat needle dropped at 0 mm (figure 3). The initial setting and final setting that occurred in geopolymer paste with substitution of sodium silicate with natural zeolite are shown in figure 2.

Figure 1. Material testing

Figure 2. Initial setting and final setting of geopolymer paste with substitution of sodium silicate with natural zeolite.
The fastest initial setting time occurred in the proportion of Na$_2$SiO$_3$ substitution with 7.5 % of zeolite is 48 minutes. Meanwhile, the longest initial setting time is normal geopolymer paste with 0% substitution of zeolite which is 94 minutes. The longest final setting time occurs in geopolymer paste with substitution of 0 % zeolite is 135 minutes while the fastest final setting time occurs in geopolymer cement with substitution of 7.5 % zeolite which is 60 minutes.

In this case, the setting time of geopolymer paste is getting faster, linear with increasing substitution sodium silicate with natural zeolite. According to Wang Ru and Wang Gaoyong [11], zeolite can accelerate the setting time because it could transform become C-S-H gel. In addition, according to Ismuyanto [7], C-S-H from zeolite is form by reaction of calcium oxide with silicate compound.

3.3 The proportion of material mixture
The proportion of the material mixture is designed for normal concrete (Table 3).

| Type | Zeolite | Zeolite | Fly-ash | NaOH | Na$_2$SiO$_3$ | Coarse Aggregate | Fine Aggregate |
|------|---------|---------|---------|------|--------------|-----------------|---------------|
|      | %       | kg      | kg      | kg   | kg           | 1-5 mm (kg)     | 5-10 mm (kg)  | kg            |
| 1    | 0       | 0.00    | 6.50    | 0.97 | 2.42         | 8.04            | 8.04          | 15.43         |
| 2    | 2.5     | 0.06    | 6.50    | 0.97 | 2.36         | 8.04            | 8.04          | 15.43         |
| 3    | 5       | 0.12    | 6.50    | 0.97 | 2.30         | 8.04            | 8.04          | 15.43         |
| 4    | 7.5     | 0.18    | 6.50    | 0.97 | 2.24         | 8.04            | 8.04          | 15.43         |

3.4 Slump test
Fresh concrete testing performed for normal concrete is slump testing using an abrams cone (figure 4). The result of the slump test for all proportion is shown in Table 4. The slump test result is getting smaller along with the increase of substitution of zeolite. It is due to the fast setting time of proportion that can affect the workability of concrete.
Table 4. The result of the slump test

| Type | Proportion of Zeolit | Slump Test (cm) |
|------|----------------------|-----------------|
| 1    | 0%                   | 12              |
| 2    | 2.5%                 | 12              |
| 3    | 5%                   | 11              |
| 4    | 7.5%                 | 10.5            |

3.5 Compressive strength test
The curring process is done in ambient temperature for 7 days with plastic as a membrane to resist evaporation of the concrete (Figure 5).

Figure 4. Abrams cone

Figure 5. Curring process in ambient temperature

Figure 6. Compressive strength test
The compressive strength test is carried out for all specimens at 7, 14, and 28 days (figure 7).

After curing process for 7 days, the compressive strength test is done for specimens test. Based on the result (Figure 7), for 7, 14, and 28 days, it can be seen that geopolymer concrete without zeolite is the lowest average compressive strength. The largest average compressive strength value is shown by geopolymer concrete with 7.5% zeolite as substitution for sodium silicate, which is 46.07 Mpa.

According to Ismuyanto [7], zeolite reaction with sodium hydroxide form sodium-alumino silicate, it can increase the compressive strength of geopolymer concrete. In addition, according to Emam and Yehia [12], zeolite reaction with calcareous material can form calcium silicoaluminate hydrates which contribute for compressive strength result of concrete. It showed that zeolite affects compressive strength for geopolymer concrete and can react with fly-ash and alkaline solution. In this research, zeolite can replace Na$_2$SiO$_3$ up to 7.5%.

3. Conclusion
1. Zeolite substitution for sodium silicate can accelerate the setting time and increase the compressive strength.
2. Zeolite substitution in sodium silicate accelerates the setting time. The fastest setting time occurs in geopolymer paste with 7.5% zeolite as substitution for sodium silicate, i.e 48 minutes for initial setting time and 60 minutes for final setting time.
3. The average of compressive strength results from the proportion of zeolite substitution is getting bigger along with the increase of zeolite substitution.

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