Compressive Strength of Fly Ash Geopolymer Concrete by Varying Sodium Hydroxide Molarity and Aggregate to Binder Ratio

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Abstract. The concentration of sodium hydroxide solution increased the reaction rate during geopolymerisation process and thus enhanced the development of early strength of concrete. While the percentage volume of aggregates played a vital role in the strength development due to the better durability then paste alone and also filling and packing ability. The aim of the study is to determine the optimum molarity of sodium hydroxide and aggregate to binder ratio of geopolymer concrete towards high strength performance concrete based on compressive strength. The variable samples investigated include the sodium hydroxide (NaOH) concentration and aggregate to binder ratio at room temperature curing; the ratio of alkali activator solution and solid to liquid ratio remained constant. This resulted the presents work on the development of fly ash based geopolymer concrete having increment on the rate of compressive strength development from 7 to 28 days was found between 61 MPa and 82 MPa, respectively.

1. Introduction

The worldwide consumption of cement has risen to from year to year and the use of source materials in the production of cement have a negative impact on the environment. In addition, large amount of energy is consumed in the production of cement and as a result, cement production has become one of the largest emissions of carbon dioxide (CO2) [1-4]. Many research works on minimizing the use of cement through waste materials or earth source for instance clays, kaolin, metakaolin, fly ash, bottom ash, slag, rice husk ash and ground granulated blast furnace slag (GGBS) produced a positive impact [5-9]. This non-cementitious material is called geopolymer [10-11].

Geopolymers are inorganic binders have known as one of the possible alternatives to Portland cement binders for applications in concrete industry [12, 13]. It was well emerged that geopolymers can be produced amorphous aluminosilicates gels with good mechanical as well as chemical properties. The raw materials were rich in silica (Si) and alumina (Al) from by-product materials such as fly ash [14-18]. Further, the source materials of geopolymer might be activated by using alkaline solution [19]. The alkali liquids are usually sodium or potassium-based solutions as to balance the negatively charged and tetrahedrally coordinate Al atoms inside the network of these aluminosilicate gels [20-22]. Thus, the gels can be used to bind aggregates, such as sand or natural rocks, to produce mortars and concretes [23].

In this work, the low-calcium (ASTM Class F) fly ash based geopolymer is used as the binder instead of Portland cement, to high compressive strength concrete. Class F fly ash, which is relatively low
calcium, tends to have low setting time to which reduce the microcrack during the process of hardening [24]. The past research investigated the effects of aggregate content, solid to liquid ratio, sodium silicate to sodium hydroxide ratio, and curing method on fly ash based geopolymer concrete. Then, reported that geopolymer concrete can be produced with a 28-day compressive strength of 55 MPa [25]. Recently, the proposed mix design process is developed for low calcium Class F fly ash activated geopolymers using 16 M of sodium hydroxide as activator solutions [26]. Therefore, this study highlights on the use of a geopolymer binder for making green concrete which comprises waste materials of coal burning (fly ash), sodium silicate and sodium hydroxide solution, fine aggregates and coarse aggregate. The compressive strength of the fly ash geopolymer concrete were tested. The optimum mix design obtained will be beneficial for the future use of fly ash geopolymer for determining high compressive strength concrete which will lead to the excellent performance compared to ordinary Portland cement

2. Experimental Procedure

2.1. Raw Materials
The combination of raw materials in concrete mixing has a role in producing an optimum geopolymer concrete which was suitable for high performance concrete. The fly ash used from Manjung Power Plant, Perak, Malaysia, alkaline activator, fine aggregates and coarse aggregates. Alkaline activator was prepared by mixing sodium hydroxide (NaOH) solution and sodium silicate (Na₂SiO₃) solution. The sodium hydroxide solution is diluted with different molarities at 10 M, 12 M, 14 M and 16 M. One litre of distilled water is used to dissolve the NaOH pellets. Then, the NaOH stock is kept remain in volumetric flask at 24 hours to complete the reactions. While the sodium silicate has a 28.7 % silicate and 8.9% sodium, and comprises of 37.6% sodium silicate solids, and 62.4% water. Sodium hydroxide preparation for 1 litre of distilled water is detailed by calculating the molar mass of NaOH are 22.99 g/mol for Na, 16.00 g/mol for O and 1.008 g/mol for H. Total molar mass of NaOH is 40g. Therefore, 1M of NaOH is equal to 40 g of NaOH granules.

2.2. Mix Proportions and Samples Preparation
The proportions of coarse and fine aggregates used were 60% and 40% by total mass, respectively. Crushed granite and limestone aggregate between the sizes of 7 mm to 20 mm is used as coarse aggregate. While, fine aggregate is natural sand which had a size smaller up to 75 μm to 5 mm. 16 samples with the different mix proportion was prepared. The mix design for the specimen was shown in Table 1, with different NaOH molarity and binder to aggregates ratio. The constant variables were ratio solid to liquid 2.0 and ratio of sodium hydroxide solution to sodium silicate solution 2.5. The content of fly ash, alkaline activator and aggregates in cement composition varied according to the ratio. The density of the 100 mm concrete cube taken was 2400 kg/m³.

The aggregates and the fly ash were mixed dry in a mechanical mixer for 3 min. Then, add the alkaline solution and mixed thoroughly for 5-6 min to give the homogeneous mixture. The geopolymer concrete were cast into mould 100mm x 100mm after become homogeneous mix for being used in compressive test.

| Sample | Molarity (M) | Binder to aggregate ratio | Fly ash (g) | Fine aggregate (g) | Coarse aggregate (g) | Sodium hydroxide solution (g) | Sodium silicate solution (g) |
|--------|--------------|---------------------------|-------------|--------------------|----------------------|-----------------------------|-----------------------------|
| A1     | 10           | 40 : 60                   | 640         | 576                | 864                  | 91.4                        | 228.6                       |
| B2     | 10           | 35 : 65                   | 560         | 624                | 936                  | 80.0                        | 200.0                       |
| C3     | 10           | 30 : 70                   | 480         | 672                | 1008                 | 68.6                        | 171.4                       |
Table 1. Mix design for geopolymer concrete (Continued…)

| Sample | Molarity (M) | Binder to aggregate ratio | Fly ash (g) | Fine aggregate (g) | Coarse aggregate (g) | Sodium hydroxide solution (g) | Sodium silicate solution (g) |
|--------|--------------|----------------------------|-------------|--------------------|----------------------|-------------------------------|-----------------------------|
| D4     | 10           | 25:75                      | 400         | 720                | 1080                 | 57.0                          | 143.0                       |
| A1     | 12           | 40:60                      | 640         | 576                | 864                  | 91.4                          | 228.6                       |
| B2     | 12           | 35:65                      | 560         | 624                | 936                  | 80.0                          | 200.0                       |
| C3     | 12           | 30:70                      | 480         | 672                | 1008                 | 68.6                          | 171.4                       |
| D4     | 12           | 25:75                      | 400         | 720                | 1080                 | 57.0                          | 143.0                       |
| A1     | 14           | 40:60                      | 640         | 576                | 864                  | 91.4                          | 228.6                       |
| B2     | 14           | 35:65                      | 560         | 624                | 936                  | 80.0                          | 200.0                       |
| C3     | 14           | 30:70                      | 480         | 672                | 1008                 | 68.6                          | 171.4                       |
| D4     | 14           | 25:75                      | 400         | 720                | 1080                 | 57.0                          | 143.0                       |
| A1     | 16           | 40:60                      | 640         | 576                | 864                  | 91.4                          | 228.6                       |
| B2     | 16           | 35:65                      | 560         | 624                | 936                  | 80.0                          | 200.0                       |
| C3     | 16           | 30:70                      | 480         | 672                | 1008                 | 68.6                          | 171.4                       |
| D4     | 16           | 25:75                      | 400         | 720                | 1080                 | 57.0                          | 143.0                       |

3. Results and Discussions

3.1. Composition of Raw Materials

The class of fly ash was found from the chemical and mineral composition using X-Ray Fluorescence (XRF), which were obtained from the coal burning power plants in Manjung, Perak. The main composition of fly ash were alumina (Al$_2$O$_3$), silica (SiO$_2$) and iron oxide (Fe$_2$O$_3$), whereas magnesium oxide, sulphur trioxide, titanium dioxide, potassium dioxide, nickel and copper oxide were also exist in a lesser amount. Table 2 shows the chemical composition of fly ash. The result meets requirement as Class F fly ash because the chemical composition prescribed that the total amount of silica, alumina and iron oxide are 75.2% by mass percentage. According to (ASTM C 618, 2000), Class F fly ash was defined due to the total amount content of silica, alumina and iron oxide are more than 70 %.

The fly ash can be classified as Class F types and can be used as a replacement materials for cement. The calcium content in fly ash do influence towards higher degree of geopolymerization and give higher development in the mechanical strength [27]. Fly ash in high silica and alumina content are very good which can make it sufficient for synthesis zeolites as a starting material. The main purposes of the synthesized zeolites are they can be an absorbent and ion particles exchangers to remove the hazardous molecules towards atmosphere.

Table 2. Chemical composition of fly ash

| Elements | Al$_2$O$_3$ | SiO$_2$ | Fe$_2$O$_3$ | CaO | SO$_3$ | K$_2$O | TiO$_2$ | MnO | NiO | CuO |
|----------|-------------|---------|-------------|-----|--------|--------|---------|-----|-----|-----|
| Mass percentage (%) | 17.5 | 39.6 | 18.1 | 16.6 | 3.03 | 2.13 | 1.30 | 0.13 | 0.02 | 0.06 |

3.2. Compressive Strength at 7 Days of Curing

Figure 1 presents the compressive strength for 7 days of curing. There are difference in curing period, molarity of NaOH and aggregate to binder percentage. The value B25A75, B30A70, B35A65 and
B40A60 represent the percentage of the binder to aggregate in concrete density of 2400 kg/m$^3$. The compressive strength range between 38 MPa to 61 MPa within the first to seven days. In addition, among the aggregate to binder percentage, B35A65 which contains 35% of binder and 65% of aggregate shows the highest compressive strength in each molarity. Meanwhile, the concentration of sodium hydroxide at 14 M gives the highest compressive strength compared to 10 M, 12 M and 16 M.

The evidence of geopolymer concrete have high early compressive strength have been proved at 7 days of curing. At 14 M of NaOH, B35A65 have the highest compressive strength produced which is 61 MPa. Thus, it is beyond the requirements towards high strength concrete which is above 40 MPa of early compressive strength. Although a geopolymer was cured at shorter period of time, it can achieve the satisfactory results because geopolymer have high early compressive strength. The higher compressive strength in longer curing time can be obtained when it improves the polymerization process [23]. The geopolymerization process will occur in continuous action.

Figure 1. Compressive strength for 7 days of curing

3.3. Compressive Strength at 28 Days of Curing

Figure 2 shows the compressive strength for 28 days of curing. It shows the significant changes on curing time of geopolymer concrete at 7 and 28 days. The compressive strength range between 45 MPa to 82 MPa after 28 days of curing. From the results, the longer curing time produces high strength concrete which is 82 MPa, achieved in 28 days of concrete aging at B35A65 which contains 35% of binder and 65% of aggregate. At 10 M, 12 M and 16 M of NaOH, the compressive strength become lower than 14 M. The trends of the graph is same with curing day at 7 days but the value of the compressive strength becomes more higher due to longer time of curing. The curing time was importance for continuing the dehydration process in a matrix to eliminate water in geopolymer concrete. The percentage increment on compressive strength from 7 days to 28 days of curing is in the range of 4.1% to 19.6%.
The NaOH molarity at 10 M, 12 M, 14 M and 16 M throughout the 28 days resulted the compressive strength of 56 MPa, 72 MPa, 82 MPa and 69 MPa, respectively. The increased of molarity of NaOH higher the compressive strength of geopolymer concrete. The result supports the finding when 14 M achieves the compressive strength up to 82 MPa but not at 16 M. The presence of sodium ion in large amount can speed up the rate of dissolution of fly ash. Leaching of Al and Si ions can assist in gel formation. Consequently, the aluminosilicate gel formation gives a rise in compressive strength of geopolymer concrete as a binder bond tightly between the aggregates. At 16 M is beyond the optimum rate of geopolymerization process, the compressive strength decrease because of the excess of NaOH. The excess of Na+ ions results the polymer chain becomes unstable because of formation of sodium carbonate, thus affect the geopolymerisation and resulted in lower strength.

Aggregate to binder ratio is the biggest factor affecting the compressive strength of the geopolymer concrete. The increase of aggregate in the mixture contributes to a decrease in fly ash binder, resulting the low compressive strength. The excess of binder and lack of aggregates for B40A60 cause the interlocking shear in concrete decrease. An optimum percentage of aggregate to binder in each molarity is 35% of binder and 65% of aggregates with 82 MPa compressive strength. A higher aggregates content would lead to lower shrinkage and therefore to less damage to the bond between the aggregate and the paste. The optimum aggregate to binder ratio could decrease the amount of internal microcracks and porosity due to the reduced gel water to binder ratio thus lead to higher compressive strength of geopolymer concrete. Based on the result, the requirement towards high strength concrete is achieved because the compressive strength is higher than 70 MPa (ASTM C 39, 2009).

4. Conclusions
The results showed that the NaOH molarity and aggregate to binder ratio is an important factors in a mix design for developing and producing the high compressive strength geopolymer concrete. The optimum mix design gives the high compressive strength which beyond fulfill the requirement of high performance concrete based on ASTM C 39. The compressive strength up to 82 MPa with 14M sodium
hydroxide concentration and 65/35 aggregate to binder ratio at 28 days, was achieved at normal ambient air curing condition.

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