Effect of Solid-to-Liquid Ratio on Thin Fly Ash Geopolymer

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Abstract. The present work studies the effect of solid-to-liquid (S/L) ratio on the properties of thin fly ash-based geopolymer. The fly ash geopolymers with dimension of 160 mm × 40 mm × 10 mm were synthesised by using various S/L ratios (1.5, 2.0, 2.5, 3.0 and 3.2). The alkali activator was prepared by mixing 10M sodium hydroxide (NaOH) solution and sodium silicate (Na2SiO3) with the Na2SiO3/NaOH ratio of 2.5. The samples were cured at 60°C for 6 hours. The performance of fly ash geopolymers was evaluated by testing the flexural strength after 28 days. Results showed that the S/L ratio had an effect on flexural strength. The optimum flexural strength of 5.1 MPa was achieved by the fly ash geopolymer with S/L ratio of 2.5. However, the flexural strength dropped with higher S/L ratio as the workability decreases. However, further experimental lab work should be carried out as there is less knowledge in the study on the flexural strength of thin fly ash geopolymer.

1. Introduction
Geopolymer is an inorganic aluminosilicate polymer synthesised by the alkali activation of the solid aluminosilicate base materials with the mixture of an alkali metal hydroxide and silicate solution [1, 2]. The types of solid aluminosilicate base materials could be divided into natural materials such as such as kaolin and metakaolin [3] or industrial by-products such as fly ash and slag [4]. Geopolymers is getting widespread attraction recently as it is sustainable with low carbon footprint [5, 6] and exhibits a wide range of properties such as high mechanical strength, low shrinkage, low water absorption, fast setting time and low thermal conductivity [7-13].

Geopolymerisation involves several processes including the dissolution of solid aluminosilicate oxide in alkali activator, followed by the diffusion of dissolved Al and Si species to an interparticle space, the gelation process of polymerisation between silicate solution and Al and Si species, and eventually the hardening that occurs in the gel phase [14]. The geopolymerisation process is affected by various factors such as raw materials, molarity of alkali solution used, alkali activator ratio, curing regime and solids-to-liquids ratio.

The solids-to-liquids (S/L) ratio indicated the aluminosilicate raw materials-to-alkaline activator solution ratio. The S/L ratio is crucial for homogenous mixing as it controls the quantity of solids and
liquid. These compositional amount would directly influence the workability, dissolution, setting and most importantly, the strength of the geopolymers [15, 16].

The rate of geopolymerisation is affected by initial solids content. Increasing the S/L ratio leads to the larger formation of alkaline aluminosilicate as the reactant species are increasing dissolved [17]. Yao et al. [18] reported that the geopolymerisation reaction would be slower and take longer time with lower S/L ratio as large amount of liquid content decreased the interfacial connection between the precursor materials. In contrast, Fernandez-Jimenez and Palomo [19] reported a lower workability for high S/L ratio fly ash geopolymers.

Besides, Rahim et al. [20] reported that the mechanical strength of fly ash geopolymers increased with the increasing S/L ratio. However, the strength dropped once the S/L ratio exceed its optimum ratio of 4. This decrement in strength was associated with the faster setting time resulting in faster hardening of gel phase and more rapidly bonding of the geopolymeric structure when S/L ratio increased [21]. Thus, the optimum solid-to-liquids ratio for geopolymer formation is significant in determining the properties of geopolymer. In this study, the influence of solids-to-liquids ratio on the thin fly ash geopolymer was investigated. The study focused on the relationship of this parameters between the physical properties and flexural strength of thin geopolymers.

2. Methodology
2.1. Materials
Fly ash collected from Cement Industries of Malaysia Berhad (CIMA) Perlis Plant, Malaysia was used as the source of aluminosilicate. Table 1 shows the chemical composition of the fly ash obtained through XRF analysis. The fly ash contains total composition of SiO₂ and Al₂O₃ of 84.30%. According to ASTM C618, the fly ash used was classified as Class F fly ash as the CaO content is 3.89% which is less than 20% The SEM micrograph of fly ash particle is revealed in Figure 1. The morphology of fly ash particles sieved with siever 68μm was spherical in shape with smooth surfaces. The alkaline activator used was a mixture of liquid sodium silicate (Na₂SiO₃) and sodium hydroxide (NaOH). The technical grade Na₂SiO₃ has chemical composition of 30.1% SiO₂, 9.4% Na₂O and 60.5% H₂O with modulus SiO₂/Na₂O of 3.2, specific gravity at 20°C = 1.4 and viscosity at 20°C = 0.4 Pa·s. The NaOH pellets used was classified as caustic soda pellets by the brand of HmbG® Chemicals supplied by Sigma-Aldrich, Germany with assay of 97.0%.

| Compound | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | TiO₂ | K₂O | Others |
|----------|------|-------|-------|-----|------|-----|--------|
| Mass (%) | 56.30| 28.00 | 6.86  | 3.89| 2.17 | 1.49| 1.29   |

Figure 1. SEM micrograph of fly ash particles.
2.2. Formation of Thin Geopolymer

The alkaline activator was mixed with the Na$_2$SiO$_3$/NaOH ratio of 2.5 and the concentration of NaOH solution was fixed at 12M. Then, the fly ash was mixed well with the alkaline activator at a S/L ratio ranging from 1.5 – 3.2. S/L ratio of 3.2 was set as the upper boundary of this experimental work as the mixing process beyond that was undesirable. The fresh paste was then rapidly moulded and compacted into a 160 × 40 × 10 mm moulds. The moulded geopolymer samples were cured at 60°C in oven for 6 hours and then left at room temperature for another 24 hours. The cured samples were kept at room temperature for 28 days before testing.

2.3. Testing and Analysis

The bulk density measurement was obtained by measuring the mass and dimension of the samples. The water absorption was measured by the wet mass (immersed in water for 24 hours) and dry mass (heated 100°C in oven for 24 hours) while apparent porosity was measured by the wet mass, dry mass and suspended mass (after immersed in water for 24 hours) according to ASTM C642. The flexural test was carried out using Instron Machine Series 5569 Mechanical Tester according to the ASTM C348 with a span length of 110 mm at a crosshead speed of 1 mm/min.

3. Results and Discussion

3.1. Physical Observation

Figure 2 shows the physical image of fly ash geopolymers synthesised with different S/L ratio. The fly ash geopolymers were grey in colour and the surface condition was comparatively similar. However, the fly ash geopolymer mixed using S/L ratio of 1.5 bended in a curvature shape as shown in Figure 3 after 28 days. This is due to the higher liquid content which lead to the formation of less viscous slurry during mixing process [22]. The high liquid content in the system creates tension force on the surface of samples and causes the occurrence of curvature in sample.

![Figure 2. Physical images of fly ash geopolymers prepared with S/L ratio of (a) 1.5, (b) 2.0, (c) 2.5, (d) 3.0 and (e) 3.2.](image-url)
3.2. Bulk Density, Apparent Porosity and Water Absorption

Figure 4 shows the bulk density of fly ash geopolymers with different S/L ratios. It was observed that the bulk density of fly ash geopolymers increased from ratio 1.5 to 2.5, but followed by a decrement with S/L ratio of 3.0 and 3.2. The highest bulk density obtained was 2020 kg/m$^3$ with S/L ratio of 2.5 whereas the fly ash geopolymers mixed with S/L ratio of 2.0 had the lowest bulk density of 1868 kg/m$^3$. However, when the solid content was in excess (S/L ratio of 3.0 and 3.2), the bulk density of fly ash geopolymers reduced. This is because the liquid content is insufficient for geopolymerisation reaction as the flow of mixture is hindered [18]. The fly ash particles could not interact fully with the limited amount of liquid during geopolymerisation process, and hence reduced the bulk density and less reaction products were formed.

Rahim et al. [21] observed a similar trend in the bulk density of fly ash geopolymers cured with one day with S/L ratios of 3 to 5. The bulk density first increased the S/L ratio increased from 3 to 4 but then decreased when the S/L ratio reached 5. However, the density obtained was higher (ranges from ~2900 kg/m$^3$ to ~3600 kg/m$^3$. This difference in bulk density might be due to data collection at different curing day.

![Figure 4. Bulk density of fly ash geopolymers with varying S/L ratios.](image)

Figure 5 depicts the apparent porosity and water absorption of fly ash geopolymers with different S/L ratios. Generally, both the apparent porosity and water absorption shared the similar trend where the apparent porosity and water absorption decreased when S/L ratio increased from 1.5 to 2.5, but followed by an increment when the S/L ratio was beyond 2.5. This data was in parallel with the bulk density measurement obtained in Figure 4 as the lower percentage of porosity would contribute to the lower water absorption and more densified structure which lead to higher bulk density.

The fly ash geopolymers synthesised using S/L ratio of 2.5 had the lowest apparent porosity and water absorption of 19.9% and 10.6% respectively. Furthermore, fly ash geopolymers prepared with S/L ratio of 3.2 had the highest apparent porosity and water absorption of 22.2% and 11.5%. This is
because the precursor materials could not fully react with alkaline activator when the S/L was too high. This led to the water retained in the geopolymer matrix and promoted the pore formation and hence increased the percentage of water absorption [24].

Figure 5. Water absorption and apparent porosity of fly ash geopolymers with varying S/L ratios.

3.3. Flexural Strength
Figure 6 depicts the flexural strength of fly ash geopolymers synthesised using different S/L ratios. It was observed that the flexural strength of fly ash geopolymers increased with increasing S/L ratios from 1.5 to 2.5, and then decreased as the S/L ratio increased until 3.0 and 3.2. The highest flexural strength was denoted by fly ash geopolymer synthesised using S/L ratio of 2.5 with the value of 5.12 MPa whereas the fly ash geopolymer prepared with S/L ratio of 3.2 had the lowest flexural strength of 3.61 MPa.

At lower S/L ratio, the intermolecular contact between the precursor materials with the activating solution was hindered and became limited as the volume of fluid medium was too large [25]. The rate for the aluminosilicate materials to be dissolved was decelerated and thus lower the flexural strength of fly ash geopolymers. As the S/L ratio was increased to 2.5, the solid content in system was increased. The probability for the contact between the precursor materials with activating solution was increased and thus increase the flexural strength of fly ash geopolymers.

However, the flexural strength of fly ash geopolymers dropped at high S/L ratios of 3.0 and 3.2. This is because the workability of fly ash geopolymers decreases when the S/L ratio is too high. The excess solid content makes the mixing becomes undesirable and faces the difficulty in compaction for moulding process [18]. Besides, the excess solid contents would retard the geopolymerisation reaction and consequently lower the flexural performance of fly ash geopolymers as the extent for the binder formation is hindered [23, 26].

Furthermore, the flexural results were in parallel with the bulk density measurement and apparent porosity results as shown in Figure and

Figure respectively. The lower the porosity content, the higher the bulk density, the higher the compressive strength. Some researchers evaluated that the S/L ratio could be influence the volume of voids and porosity in the slurry which directly affect the mechanical strength of geopolymer [27, 28]. In overall, the optimum S/L ratio for the fly ash geopolymers synthesis was 2.5, as it exhibited the highest flexural strength among the other specimens. However, further research activities should be
implemented in order to enhance the performance of thin geopolymer and get better flexural properties.

![Figure 6. Flexural strength of fly ash geopolymers with varying S/L ratios.](image)

4. Conclusion
This paper investigated the effect of various S/L ratios (1.5 to 3.2) on thin fly ash geopolymers. Physical and mechanical properties of thin geopolymers indicated with bulk density, apparent porosity and flexural strength reported that, ratio of solids-to-liquids plays an important role in enhancing the properties of thin fly ash geopolymer. The optimum S/L ratio of 2.5 produced thin fly ash geopolymer with the highest flexural strength of 5.12 MPa. It was believed that the contact between the alkaline activator and the reacting materials were improved and thus produced denser geopolymer sample. The flexural strength results were complied with the density, porosity and water absorption values. However, further experimental lab work should be carried out to enhance the flexural strength of thin fly ash geopolymer.

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