LADLE FURNACE SLAG REPLACEMENT ON THE FLEXURAL STRENGTH OF THIN FLY ASH GEOPOLYMER

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Abstract

This article reports the investigation on the effect of ladle furnace slag replacement on the flexural strength of thin fly ash-based geopolymer. The thin fly ash/slag geopolymers were prepared with the replacement of various percentages of ladle furnace slag (0%, 10%, 20%, 30% and 40%) into fly ash geopolymers with dimension of 160 mm × 40 mm × 10 mm. The thin geopolymer was synthesised using 12M sodium hydroxide (NaOH) solution with solid-to-liquid (S/L) ratio of 2.5 and Na₂SiO₃/NaOH ratio of 4.0. The curing temperature and time of samples were 60°C and 6 hours respectively. The mechanical properties of thin geopolymers was revealed using flexural test after 28 days. Several characterisation tools have been used including Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD) to correlate the flexural properties with the microstructure and phases of fly ash/slag geopolymers. Results obtained reported that a positive effect on flexural strength was observed with the increasing amount of slag. The thin fly ash geopolymers replaced with 40% of ladle furnace slag showed the highest flexural strength of 7.8 MPa. The rich CaO content in ladle furnace slag boosted the C-S-H gels formation which increased the flexural strength of thin geopolymers.

Keywords: thin geopolymer, ladle furnace slag, replacement, fly ash, flexural strength.

Introduction

Geopolymers are inorganic polymers with SiO₄ and AlO₄ frameworks. They are produced by mixing aluminosilicates and alkaline silicate solution [1]. The solid aluminosilicate precursors could be categorised into two types such as industrial by-products (fly ash and slag) and natural materials (kaolin and metakaolin) [2]. The mixed aluminosilicates and alkaline silicate produced a short-range ordered amorphous gel arranged in three-dimensional structure exhibits excellent physical and mechanical properties [3]. Besides, geopolymers are environmental friendly with low energy consumption production process and low carbon footprint [4].

The flexural strength of thin fly ash geopolymers could be improved by incorporating slag as the aluminosilicate source during the mixing process. Slag is rich in CaO content and the Ca²⁺ from slag favours the formation of C–S–H (Calcium Silicate Hydrate) and C–(A)–S–H (Calcium Aluminosilicate Hydrate) gels which increased the mechanical properties and durability of geopolymers [5]. Sankar et al. [6] investigated the mechanical strength of slag-fly ash based geopolymers and reported that as the slag/fly ash ratio increased, the strength development of geopolymer was accelerated due to the formation of C–S–H gels and C–(A)–S–H gels in the structure of geopolymer which results in the formation of Ca- and Na-based geopolymer. Chi and Huang [7] investigated the relationship of different sets of fly ash/slag ratios with the binding mechanism and properties of fly ash/slag geopolymers. Their results showed that the fly ash/slag...
ratio plays a significant role in affecting the binding mechanism and properties of geopolymers. Puligilla et al. [8] investigated the role of slag in fly ash/slag based geopolymers and observed that the reaction products were mainly dominated by C–S–H gel which coexisted with the aluminosilicate geopolymeric gels. This caused the setting time for geopolymerisation was shortened and increased the mechanical strength of geopolymers.

Thus far, researches regarding the flexural properties of geopolymers are mainly focused on precast concrete elements such as beams, columns. In comparison, flexural properties of thin neat (without addition of fillers or aggregates) geopolymers is less explored. Moreover, past studies reported that the flexural strength of geopolymers were always low (<20 MPa) in comparison with its compressive strength [9]. Therefore, this knowledge gap should be filled to further explore the field of utilisation of thin geopolymers in terms of flexural properties.

Ground-granulated blast furnace slag (GGBFS) was more well-known slag used in the geopolymers’ research. However, in this study, ladle furnace slag (LFS) is proposed to be incorporated into the fly ash geopolymers as it possesses similar chemical composition (high calcium content) to GGBFS. The smaller particles size of ladle furnace slag could fill up the pore in the structure and produce a more compact geopolymer body [10]. This make ladle furnace slag has better potential in improving the flexural strength of thin geopolymers than ground-granulated blast furnace slag. This paper studied the effect of ladle furnace slag replacement in the thin fly ash geopolymers. The paper focussed on the correlation of the slag replacement ratio and the flexural properties of thin geopolymers.

**Methodology**

**Materials**

The aluminosilicate source of this study was fly ash collected from Manjung Coal-fired Power Plant, Malaysia. Ladle furnace slag (LFS) collected from Southern Steel Berhad Penang, Malaysia was partially replaced into thin fly ash geopolymers to investigate the effect of slag replacement. Table 1 depicts the chemical composition of fly ash and ladle furnace slag obtained via XRF analysis. The fly ash was made up of mainly SiO$_2$ and Al$_2$O$_3$ of 56.30% and 28.00% respectively while the ladle furnace slag had the high amount of CaO with the percentage of 63.59%. The fly ash used was considered as Class F fly ash according to ASTM C618 as it consisted of only 3.89% of CaO which is less than 20%. The SEM micrographs of fly ash and ladle furnace slag particle are shown in Figure 1. The fly ash particles had a spherical microstructure with smooth surfaces while ladle furnace slag has the microstructure of irregular and angular in shape and the grains are sharp-edged and partly dense. The alkaline activator used in this study was prepared by mixing the liquid sodium silicate (Na$_2$SiO$_3$) with sodium hydroxide (NaOH) solution. The chemical composition for liquid Na$_2$SiO$_3$ contained 60.5% of H$_2$O, 30.1% of SiO$_2$ and 9.4% of Na$_2$O with SiO$_2$/Na$_2$O modulus of 3.2, viscosity and specific gravity of 0.4 Pa·s and 1.4 respectively at 20°C. Caustic soda pellets with the assay of 97.0% by the brand of HmbG® Chemicals was used to prepare the NaOH solution.

**Table 1. Chemical composition of fly ash and ladle furnace slag**

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
<th>TiO$_2$</th>
<th>K$_2$O</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly Ash</td>
<td>56.30</td>
<td>28.00</td>
<td>3.89</td>
<td>6.86</td>
<td>-</td>
<td>2.17</td>
<td>1.49</td>
<td>1.29</td>
</tr>
<tr>
<td>Ladle Furnace Slag</td>
<td>21.30</td>
<td>2.30</td>
<td>63.59</td>
<td>8.08</td>
<td>2.60</td>
<td>0.50</td>
<td>-</td>
<td>1.63</td>
</tr>
</tbody>
</table>
Ladle Furnace Slag Replacement on the Flexural Strength of Thin Fly Ash

Thin Geopolymer Formation

The thin geopolymers were synthesised using 12M NaOH, 2.5 S/L ratio and 4.0 Na$_2$SiO$_3$/NaOH ratio. The percentage of ladle furnace slag substitute into fly ash was set as 10%, 20%, 30% and 40%. Fly ash and ladle furnace slag were mixed together with liquid alkali activator until homogenous slurry was achieved. Then, the slurry was rapidly poured into the moulds with dimension of 160 × 40 × 10 mm and compaction was done. The samples were then sent into oven with the curing temperature and time of 60°C and 6 hours. After that, the samples were cured at room temperature for another 24 hours. The cured thin geopolymers (Figure 2) were sealed with plastic wrap and kept for 28 days at room temperature before testing.

Testing and Analysis

Several testing and analyses were conducted to investigate the effect of ladle furnace slag replacement on the flexural properties of thin fly ash geopolymers. The bulk density of thin geopolymers were determined by measuring the mass and the dimensions of samples according to BS EN 12390-7. Water absorption was measured using the dry mass (heated in oven at 100°C for 24 hours) and wet mass (immersion of samples in water for 24 hours). Meanwhile, the apparent porosity was determined using the dry mass, wet mass and suspended mass (samples suspended in water after 24 hours immersion) in accordance to ASTM C642. Instron Machine Series 5569 Mechanical Tester was used to access the flexural strength of thin geopolymers using
ASTM C348. The span length was fixed at 110 mm with 1 mm/min crosshead speed. The microstructure of thin geopolymers at fracture surface was revealed using JSM-6460LA model Scanning Electron Microscope (JEOL). Model of D2 Phaser, Bruker X-Ray Diffractometer was used to access the phase of fly ash, slag and geopolymers with the scan range of 10-80° and scan rate was 2° per minute.

**Results and Discussion**

**Bulk Density, Apparent Porosity and Water Absorption**

Figure 3 displays the bulk density of thin fly ash/slag geopolymers with various percentages of ladle furnace slag replacement. In general, the fly ash/slag geopolymers has higher bulk density than the fly ash geopolymer and the bulk density of the samples increases as the slag replacement amount increases. This is because the density of ladle furnace slag (1238 kg/m³) is higher than fly ash (1168 kg/m³). The highest bulk density recorded is fly ash slag geopolymer replaced by 40% of ladle furnace slag which is 2273 kg/m³ whereas the fly ash geopolymer possesses the lowest bulk density of 2060 kg/m³. This can be explained by the fact that the incorporation of slag which is calcium-rich leads to the formation of a denser microstructure [11]. Besides, Zawrah et al. [12] observed that different chemical reactions could occur with the incorporation of ladle furnace slag into the fly ash geopolymers system and thus produced different products as compared to fly ash geopolymers with no addition of slag. These different products caused the increment in bulk density and thus increased the strength development of geopolymers.

![](image)

**Fig. 3.** Bulk density of thin fly ash/slag geopolymers with different percentages of ladle furnace slag replacement

Figure 4 illustrates the apparent porosity and water absorption of thin fly ash geopolymers partially replaced by different percentages of ladle furnace slag replacement. As the slag content increases, both the apparent porosity and water absorption decrease. Ghosh et al. [13] reported similar trend of decreasing in both apparent porosity and water absorption as slag content increased. They reported that the increase in slag content could favour the occurrence of different chemical reactions which led to different products formed in geopolymer system. C–A–S–H gels which is more densified are formed and coexisted with the geopolymeric gel causes the decrease in water absorption and porosity [14]. Besides, the unreacted ladle furnace slag particles would
act as a reinforcement and enhance the pore structure of the geopolymer matrix, which causes the porosity decreases and hence increases the strength of geopolymers [15].

![Fig. 4. Apparent porosity and water absorption of thin fly ash/slag geopolymers with different percentages of ladle furnace slag replacement](image)

**Flexural Strength**

Figure 5 represents the flexural strength of thin fly ash/slag geopolymers with different percentages of ladle furnace slag replacement. Generally, thin fly ash/slag geopolymers possess higher flexural strength compared to thin fly ash geopolymer. This increment in flexural strength is contributed by the more reactive nature of slag particles. The improvement in flexural strength could be attributed to the incorporation of ladle furnace slag into the fly ash geopolymers. The highest flexural strength of 7.8 MPa is obtained by the fly ash/slag geopolymer replaced by 40% of ladle furnace slag where it shows approximately 26% improvement of flexural strength as compared to the fly ash geopolymers with no slag replacement (6.2 MPa). Similar flexural trend was observed by Al-Majidi et al. [15] where they also reported that 40% of slag replacement contributed to the most increment in flexural strength. This could be related to the lower reactivity nature of fly ash as compared to ladle furnace slag which normally had slower setting time and present a weaker strength [16, 17].

The high content of CaO from ladle furnace slag could improve the strength of geopolymers as the soluble Ca\(^{2+}\) ions are introduced into the geopolymer system, and facilitate the formation of C–S–H gel (Calcium Silicate Hydrate), C–A–S–H (Calcium Aluminosilicate Hydrate) gel alongside N–A–S–H (Sodium Aluminosilicate Hydrate) gel [18-20]. The formation of these gels produced a more compact microstructure and has been reported to show an increment in the mechanical strength of geopolymers [21, 22]. Kathirvel et al. [23] and Pilehvar et al. [24] investigated the effect of slag replacement on the properties of fly ash geopolymers. Through their investigations, they observed that the presence of C–S–H gels coexisted with the N–A–S–H gels in the geopolymer matrix. These two species would promote the development of complex C–(N)–A–S–H geopolymer gels. This complex species could accelerate the setting rate of geopolymers enhance the mechanical strength of geopolymers. Similar trends were observed by Khale and Chaudhary [25] as the strength of fly ash/slag geopolymers increased with the C–(N)–A–S–H gels formation from the higher slag amount, which caused the porosity decreased and favoured the densification in the geopolymers’ microstructure.
On the other hand, a slight decrement in the flexural strength could be observed in the fly ash/slag geopolymer replaced with 20% of ladle furnace slag as compared to other percentages of slag replacement. However, the flexural strength is still higher as compared to the fly ash geopolymer with no slag replacement. It is believed that the drop in strength is related to the bulk density and porosity of the fly ash/slag geopolymer as the flexural strength results obtained is in aligned with the bulk density and apparent porosity obtained in Figure 4, respectively. Lower bulk density exhibits a looser geopolymeric structure with pores and thus shows lower value of flexural strength.

![Graph](image)

**Fig. 5.** Flexural strength of thin fly ash/slag geopolymers with different percentages of ladle furnace slag replacement

**Microstructural Analysis**

Figure 6 shows the microstructure of the fracture surface of fly ash/slag geopolymers replaced with different amount of ladle furnace slag under SEM. As the slag amount increases from 10% to 40%, more densified and compact structure is observed with the formation of more C–S–H gel coexists with the geopolymer matrix. Figure 7 depicts the SEM micrograph of C–S–H gel present in fly ash geopolymer replaced by 40% ladle furnace slag with 2000× magnification. Zawrah et al. [12] observed the same phenomena in the microstructure of geopolymers with increasing slag content. They reported that increasing the slag content exhibited more C–S–H gel as dominant products and coexisted with geopolymeric gel, and hence produced a more compact microstructure which could enhance the strength of geopolymer.

Furthermore, the increasing amount of CaO from slag reduced the microstructural porosity as more amorphous structure Ca–Al–Si gels were formed [26, 27]. This complied with the apparent porosity results obtained in Figure 4 in which the fly ash/slag geopolymers have lower porosity than the fly ash geopolymers with no slag replacement. Murri et al. [28] observed that the fly ash/ladle furnace slag geopolymers with higher CaO content had denser matrices and lesser number of unreacted spherical fly ash particles. Besides, Phair et al. [29] stated that the increasing slag content promoted polysialate network formation and hardening of the geopolymer matrix. The substitution of slag into fly ash geopolymers could accelerate the reaction rate and promote strength development as the reactivity of fly ash is relatively slow at room temperature [30]. Hence, the flexural strength of thin fly ash geopolymers improved with the substitution of slag into the system as shown in Figure 5.
In addition, Qiu et al. [31] reported that more geopolymerisation products were produced in the samples with higher slag content. In contrast, higher amount of fly ash produces a rather loose matrix. From Figure 6 (a) to (c), a more loosely packed structures with large amount of
partially-reacted or unreacted fly ash and slag particles are observed. Besides, more pores are observed when compared to the higher amount of slag replacement (Figure 6d and e).

**Phase Analysis**

Figure 8 displays the XRD pattern of fly ash and ladle furnace slag using X-ray diffractogram. Based on Figure 8(a), there is a broad hump of diffraction in fly ash between 15° and 35° indicating the amorphous phases of fly ash [32]. Fly ash showed an intense diffraction peak of quartz (SiO$_2$) with other diffraction peaks of mullite (3Al$_2$O$_3$·2SiO$_2$) and hematite (Fe$_2$O$_3$). For ladle furnace slag, the intense peak of belite (Ca$_2$SiO$_4$) was observed with the presence of glassy phase of larnite (Ca$_2$SiO$_4$), merwinite (Ca$_3$MgSi$_2$O$_8$), magnetite (Fe$_3$O$_4$) and calcium aluminium oxide (CaAl$_2$O$_4$).

![Figure 8](https://example.com/figure8.png)

**Fig. 8.** XRD pattern of (a) fly ash and (b) ladle furnace slag

Figure 9 displays the XRD diffractogram of fly ash slag geopolymers replaced with various percentages of ladle furnace slag. It could be observed that fly ash geopolymers have the major peaks of quartz (SiO$_2$) and mullite (3Al$_2$O$_3$·2SiO$_2$). The vitreous phase of the original ash, which is represented by the broad hump, shifted slightly from 15-30° to 20-40° (2θ) values. The alkaline activation of ladle furnace slag causes the geopolymerisation process accelerates and some new phases that could contribute to the strength development of are formed. Secondary peaks of belite (Ca$_2$SiO$_4$), calcium silicate hydrate (C–S–H) gel and calcite (CaCO$_3$) are observed as the slag amount increases [33]. Previous studies also observed that the main binding phase of alkali-activated slag materials is C–S–H gels [34]. These peaks appear along with the primary peaks of quartz and mullite. Besides, the intensity of the broad hump reduces with increasing slag.
amount. This is because more crystalline phases are formed associated with the rich amount of calcium in slag [35].

![XRD diffractogram of fly ash/slag geopolymers with different percentages of ladle furnace slag replacement](image)

Fig. 9. XRD diffractogram of fly ash/slag geopolymers with different percentages of ladle furnace slag replacement

Besides that, the intensity of quartz and mullite decreases and even disappears when the percentage of slag replacement increases from 10% to 40%. The peak intensity for C–S–H gel and calcite becomes more apparent due the alkali activation of slag. The high CaO content promoted the C–S–H gel development of and the excess CaO would react with CO₂ to form calcite [36]. The high intensity of belite is attributed from the major phase present in the ladle furnace slag as shown in Figure 8. Apart from that, the highest intensity of C–S–H gel and calcite could be observed in the fly ash/slag geopolymer replaced by 40% of ladle furnace slag. The coexistence of belite, calcite and C–S–H gel alongside with aluminosilicate gel helped improving the mechanical properties of geopolymers [19]. This observation is in parallel with the flexural strength data obtained in Figure 5.

**Conclusion**

This paper studied the effect of ladle furnace slag replacement on the flexural properties of thin fly ash geopolymers. Correlation of physical and flexural properties of thin fly ash/slag geopolymers was made via bulk density measurement, apparent porosity and flexural test. Results obtained showed that the amount of slag replacement plays a significant role in improving the flexural properties of thin fly ash geopolymers as the flexural strength of geopolymers increased as the amount of slag replacement increased. The thin fly ash geopolymers were replaced with 40% of ladle furnace slag was observed to have the highest flexural strength of 7.8 MPa. The CaO present in the ladle furnace slag eased the C–S–H gels formation in the geopolymer structure. This C–S–H gels formation produced a more compact microstructure which could be observed

http://www.ejmse.ro
in the SEM micrographs helps improved the flexural strength of thin geopolymers. XRD results also further proved that the flexural properties of thin fly ash geopolymers was enhanced by the higher amount of slag.

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