Research Article

Fly Ash/Blast Furnace Slag-Based Geopolymer as a Potential Binder for Mine Backfilling: Effect of Binder Type and Activator Concentration

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1. Introduction

Portland cement is a par excellent construction material and is critical to the world economy. The manufacture of it, however, is energy intensive and has other environmental penalties of great significance [1–5]. It has been reported that the production of Portland cement constitutes at least 8% of global CO₂ emissions because its production requires high kiln temperature (1450°C–1550°C) [6–9]. On the contrary, Portland cement industry consumes a large amount of raw materials, such as limestone, and results in significant overexploitation of natural reserves [2, 10]. In consequence, there is an urgent need to develop new alternative binders with lower environmental and energy costs.

The concept of geopolymer, which was coined to describe a class of solid materials, was introduced in 1970s by Professor Joseph Davidovits. Generally, the synthesis of geopolymer involves mixing an alkali solution with an aluminosilicate powder, which results in a discorded alkali aluminosilicate gel. Compared with Portland cement, geopolymer enjoys quick compressive strength development [7, 11], lower permeability [12, 13], lower shrinkage [14, 15], and good resistance to acid and fire attack [16, 17]. Moreover, geopolymer can be synthesized at a lower temperature than Portland cement since the geopolymerization reaction can be conducted at room temperature [18]. Furthermore, almost no SOₓ, NOₓ, or CO are generated in the process of geopolymer preparation [10]. All these merits contribute to a great interest in the study and development of geopolymer worldwide. At present, geopolymer has been used in various applications, i.e., new-type building materials [19, 20], soil stabilization [21–23], immobilization of heavy metals [24–26], novel catalyst [27, 28], and adsorbent [29, 30].

FA and BFS are commonly used materials for the preparation of geopolymer. Chi and Huang [31] investigated the binding mechanism and properties of alkali-activated FA/BFS with various ratios of FA to BFS through the compressive strength test, flexural strength test, and SEM and XRD analysis. They found that the fly ash/slag ratio is a significant factor influencing the binding mechanism and properties of AAFS mortars. Abdalqader et al. [32] used sodium carbonate (Na₂CO₃) as the alkali activator for the fly FA/BFS blends. The influences of activator dosage and FA/BFS on the strength of alkali-activated mortar were examined. They found that the inclusion of 25% FA gave
comparable or even higher strength than mixes containing only BFS, after 90 days of curing. However, increasing the content of FA to 50% led to the decrease of the strength significantly. Phoo-ngernkham et al. [33] investigated the effects of NaOH and Na₂SiO₃ on the properties of FA/BFS geopolymer. The results indicated that the properties of geopolymer depended on the types of source materials and alkali activators. The increase in BFS content improved the compressive strength of geopolymer due to the formation of additional CSH. Sankar et al. [34] studied five Na₂SiO₃-activated slag-fly ash binders and explored their compressive and flexural strengths. It was found that increasing the slag/fly ash ratio accelerated the strength development due to the formation of CSH, CASH, and Ca- and Na-based geopolymer. However, to the authors’ knowledge, there are few and very limited researches on the utilization of geopolymer to mine backfilling. In the present study, blast furnace slag (BFS) and fly ash (FA) were used as raw materials activated by sodium hydroxide (NaOH) solution with different concentrations to prepare geopolymer. The effects of FA/BFS mass ratio and the concentration of NaOH solution on the properties of the prepared geopolymer were explored using XRD, FTIR, TG-DTG, and SEM.

2. Materials and Methods

2.1. Source Materials. Materials used in this research are blast furnace slag (BFS) and fly ash (FA), obtained from Jinfeng Materials Co., Ltd in Henan, China, with a specific gravity of 2.84 and 2.37, respectively. The chemical compositions of BFS and FA are presented in Table 1. Fine aggregate used was mine tailings (MTs), which were collected from a gold mine located in the Shandong, China. MTs are dried at 105°C for 24 hours before being used. The particle-size distribution of MT, BFS, and FA is presented in Figure 1.

2.2. Alkali Activator. Sodium hydroxide (NaOH) solution is used as an alkaline activator because it is widely available and less expensive. NaOH pellets of 98% purity are dissolved in distilled water to obtain NaOH solution of required molarity and stored at room temperature for 24 h before its use.

2.3. Geopolymer Paste. FA and BFS, with different proportions by weight, are mixed in dry condition in a mixer. The mixture is activated by adding NaOH solution at the activator/binder mass ratio of 0.4 and mixed for 3 min. The fresh pastes are then quickly casted into molds (40 × 40 × 40 mm) and vibrated for 2 min on an electrical vibrating table. After that, the molds are sealed in plastic bags and cured at room temperature until the testing age. A series of geopolymer pastes (Table 2) are prepared by varying the proportions of FA and BFS and different concentrations of NaOH solution.

2.4. BM Mortar. The mass ratio of FA/BFS to MT is fixed as 1:6, and the NaOH solution to binder mass ratio is fixed as 0.4. MT, FA, and BFS are dry-mixed for 5 min in a mixer. NaOH solution is then added and mixed for another 5 min to ensure homogeneity. After that, the mortars are poured into molds (40 × 40 × 40 mm) and vibrated for 2 min. The molds are then sealed in plastic bags and cured at room temperature until the testing age. The summary of the experimental conditions is shown in Table 2.

2.5. Characterization. Samples were broken into small pieces and immersed into acetone for 24 hours to stop the geopolymerization process. The samples were then dried under vacuum at 40°C before being grinded to a fine, homogeneous powder, using XRD, TD-DTG, and FTIR tests. X-ray diffraction (XRD) analysis is carried out using an X’Pert Pro XRD (Philips, Holland) at a scanning rate of 0.1 deg·s⁻¹ in the 2θ range of 10 to 80°. TD-DTG analyses are performed using Diamond TG-DSC (Netzsch STA 409 PC/PG, Germany). The temperature is raised up from 25°C to 1000°C at a heating rate of 10°C/min in an alumina crucible under N₂ atmosphere. Fourier-transform infrared (FTIR) spectroscopy tests are performed by NEXUS 470 (America) with a wavenumber of 4000–400 cm⁻¹ to identify the functional group of the materials.

The setting time of BM fresh mortars is tested using Vicat apparatus. Setting ratio (ΔH) of BM mortars is investigated using the following equation:

\[ \Delta H = \frac{H_2 - H_1}{H_1} \times 100\% \]  

where \( H_1 \) and \( H_2 \) are the height of BM samples before and after hardening.

Slump of BM fresh mortars are tested using the slump meter, conducting in accordance with the Chinese standard specification (GB/T 2419-2005) [35]. Determining the compressive strength of BM mortars, UCS tests are performed by using a computer-controlled mechanical press with a loading capacity of 50 kN and a displacement loading speed of 1 mm per minute, according to the ASTM D2166/D2166M-16 standard [36]. For each mix formulation, triplicate tests are conducted and the average values are recorded.

Microtopography is determined by scanning electron microscopy (SEM) using a Philips XL30 SEM (Philips, Holland) with an accelerating voltage of 20 kV electrical pulses for the characterization of the surface morphology. Samples were impregnated using acetone for 24 hours and then dried under vacuum at 40°C. The samples were consequently gold coated prior to electron microscopy observations.

3. Results and Discussion

3.1. X-Ray Diffraction (XRD) Analysis. The XRD patterns of the raw materials and FA/BFS-based geopolymer pastes are presented in Figure 2. It is obvious that there are distinct differences in the mineral composition of FA and BFS. The phase of FA is mainly composed of quartz, albite, and mullite (Figure 2(a)), which are highly crystalline. Also, a hump
between $2\theta = 18-25^\circ$ is observed, indicating that there are some amorphous phases in FA. However, the BFS is mainly composed of the amorphous phase due to the abrupt cooling, except from traces of quartz, calcite, and akermanite, which are reported to be contained in most slags. After activating by NaOH solution, some obvious changes are noticed from Figures 2(b) and 2(c). For the series of N8 (F100B0N8, F50B50N8, and F0B100N8), the F100B0N8 paste consisted of crystalline phases of quartz, mullite, and albite with their intensity decreased due to the activation by NaOH solution. On the contrary, the presence of sodium aluminum silicate hydration (N-A-S-H) suggested some geopolymers [37–39]. However, FA is reported [40–42] to be less reactive at room temperature with low alkali concentration because crystalline materials remaining in fly ash could not be dissolved in alkali solution.

For the mix with increased BFS dosage (F50B50N8 and FOB100N8), the XRD pattern shows both amorphous and crystalline phases. The peak of the crystalline phase, i.e., quartz, albite, and mullite, and albite with their intensity decreased due to the activation by NaOH solution. On the contrary, the presence of sodium aluminum silicate hydrate (N-A-S-H) suggested some geopolymers [37–39]. However, FA is reported [40–42] to be less reactive at room temperature with low alkali concentration because crystalline materials remaining in fly ash could not be dissolved in alkali solution.

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[40, 43, 44]. A relatively lower intensity peak at $2\theta = 11.5^\circ$ is also observed assigned to the hydroxalcite phase. Hydroxalcite phase is usually detected in the alkali-activated slag when there is enough MgO content [45]. Traces of calcium carbonate are also identified, resulting from the absorption of carbon dioxide from air when the samples were analyzed [46]. It is obvious that the amount of geopolymerization product enhances with the increase of BFS. BFS has been reported to contain a larger amount of soluble CaO and MgO, which could enhance the geopolymerization process and generate more gel [47, 48].

For the series of N16 (F100B0N16, F50B50N16, and F0B100N16), less crystalline phases such as quartz, albite, and mullite are observed due to the higher concentrations of NaOH solution. At the same time, the amount of N-A-S-H and C-S-H increases, which could be noticed from their intensity from the XRD patterns. The dissolution of the FA and BFS accelerates because the concentration of OH$^-$ is sufficient in high molar concentrations [49], resulting in a better geopolymerization. Similar results have been reported by other literatures [33, 50]. Generally speaking, a strong alkaline medium is necessary to increase the leaching of Si$^{4+}$, Al$^{3+}$, Ca$^{2+}$, and other minor ions to some extent, which is reported to be important for the formation of geopolymerization gel and the enhancement of mechanical properties of the geopolymer [51]. On the contrary, the surface hydrolysis of the aluminosilicate particles is very much dependent on the concentration of alkali solution concentration [52].
in the BFS is related to the asymmetric stretching of AlO$_4$ groups in the glass phases [32], while the shoulder at 800 cm$^{-1}$ identified in FA is associated with the symmetric stretching vibrations of Si-O-T (T=Si or Al). The strong band between 1400 and 1500 cm$^{-1}$ is related to stretching vibration of the O-C-O group [53], suggesting the presence of carbonate minerals (such as calcite) in BFS. Bands at 1650 cm$^{-1}$ and 3420 cm$^{-1}$ correspond to the O-H stretching vibration, which are attributed to water present in the raw material [54].

After alkali activation by NaOH solution, asymmetric stretching vibration of Si-O-T bonds (T=Si or Al) shift to lower frequencies (997 cm$^{-1}$) in the FTIR spectra of FAGA, indicating the formation of a new product (N-A-S-H) [55]. The appearance of new bands between 780 and 580 cm$^{-1}$ relates to the symmetric stretching vibrations of T-O-Si (T=Al or Si), which are referred to the formation of N-A-S-H [56, 57]. All these changes are similar in all the pastes, both series N8 and series N18. However, the series of N16 represents a sharper vibration, suggesting more products are generated. This phenomenon is in agreement with the XRD analysis, and similar results have been reported in previous studies [7, 51]. Furthermore, it is obvious that the incorporation of OH$^-$ from NaOH solution leads to the increase of the intensity of the bands, resulting from O-H stretching vibration (1650 cm$^{-1}$ and 3420 cm$^{-1}$).

**Figure 2:** XRD patterns of (a) FA and BFS and geopolymer pastes with (b) 8 M NaOH solution and (c) 16 M NaOH solution.
3.3. TG-DTG Analysis. The differential thermogravimetric (DTG) curves with TG data are shown in Figure 4. The weight loss accumulated before 200°C is an indicator of the interlayer water weight of CSH and NASH for FA/BFS geopolymer systems. Figure 4(b) illustrates that the quantity of geopolymerization products (CSH and NASH) increases with the increase of BFS content, and the higher NaOH concentration also leads to more CSH and NASH, possibly resulting in higher compressive strength. In addition, very small peaks of the hydrotalcite phase, which were only seen in the XRD patterns of BFS-based geopolymer, are noticed. Similar to the quantity of CSH and NASH, the amount of hydrotalcite increases with the BFS content and NaOH concentration. However, calcite is not detected in the TG, resulting from its small amounts.

3.4. Slump, Final Setting Time, and Setting Ratio. The slump, setting time, and setting ratio of BM are presented in Table 3. When the concentration of NaOH solution is 8 M, the slump for F100B0N8 was 286 mm, whereas that of F0B100N8 is only 142 mm, which is lower than the standard requirement of backfilling. This result contributes to the spherical shape of the FA, which reduces flow resistance. An increase in BFS content reduces the slump of BM mortar due to the higher water demand of BFS resulted from the higher specific

![Figure 3: FTIR of (a) FA and BFS and geopolymer pastes with (b) 8 M NaOH solution and (c) 16 M NaOH solution.](image-url)
BFS is an irregular particle and more abrasive during its flow. Similar results were also reported by previous studies [58, 59]. Therefore, a proper content of BFS should be selected and considered when using FA/BFS in backing filling to meet the requirement of pipelines. On the contrary, the slump of BM fresh mortar decreases by 8.37%, from 203 mm (F50B50N8) to 186 mm (F50B50N16) when increasing the concentration of NaOH solution to 16 M. This can be explained by the fact that increasing the concentration of NaOH solution leads to the increase of the viscosity of fresh BM mortar and then reduces the flow ability.

The final setting time of different mixes considered in this study varied from 0.69 to 9.33 h. It is found that increase in the concentration of NaOH solution and decrease in the FA content resulted in decreased final setting time. When FA content in the mix is 100%, the final setting time decreases from 9.33 h (with NaOH solution of 8 M) to 8.05 h (with NaOH solution of 16 M). An increase in the concentration of NaOH solution accelerates the geopolymerization process, which contributes to the faster setting. Partial replacement of FA by BFS by 25% reduced the final setting time from 9.33 h to 6.17 h when the molarity of the NaOH is 8 M. This phenomenon clearly indicates that the BFS readily reacts with the NaOH solution compared with FA, which is in accordance with the isothermal calorimetry test. The final setting time has drastically reduced from 8.05 h to 0.69 h when the FA is totally replaced by BFS for 16 M of NaOH solution. Such fast setting behavior is not convenient for BM mortar to be transported to the worked-out section through pipeline self-flowing transportation or pipe transfer process.

Setting ratio of F100B0N8 is the largest, exceeding 7%. When BFS is added, the setting ratio dropped sharply with the increase of BFS content but do slow when the BFS content exceeded 50%. On increasing the concentration of NaOH solution, the setting ratio is also found to reduce. For example, the setting ratio of F100B0N16 was only 3.07% compared with 7.53% for F100B0N8. Both adding BFS and enhancing the concentration of NaOH solution could lead to more geopolymerization products (CSH and NASH), which would make denser microstructure and reduce the setting ratio.

3.5. Compressive Strength. Figure 5 compares compressive strength of BM samples with different binder types and NaOH solution concentration at ages of 3, 7, 28, and 60 d. It could be seen from Figure 5 that the compressive BM samples decreases with the increase of FA content. On enhancing the content of FA from 0% to 100%, the 28 d compressive strength of BM samples decreases from 5.25 MPa to 1.98 MPa at a NaOH concentration of 8 M. Similarly, at NaOH concentration of 16 M, addition of FA from 0% to 100% associates with the reduction of 28 d compressive strength of BM samples by 69.62%.

Fly ash is a commonly used material for geopolymer synthesis due to its easy availability, aluminosilicate...
composition, low water demand, and high workability. The limiting factor, which has hindered the use of fly ash in geopolymers, is low strength development with ambient temperature curing [60, 61]. Several researchers [62, 63] found that the incorporation of calcium could enhance the strength development of fly ash geopolymer, which could result from the oxide constituents and mineralogy of the BFS. BFS contains higher amount of basic oxides, such as CaO and MgO, which are more soluble during the process of geopolymerization [47, 48]. On the contrary, the hydration products obtained by CaO and MgO could magnify the dissolution of BFS and FA and then render a driving force for the geopolymerization process [48]. Therefore, the incorporation of BFS to FA geopolymer resulted in the improvement of the mechanical properties and microstructure of geopolymer [33, 60, 64].

However, some researchers [31, 65] also found positive effect on the compressive strength by inclusion of FA. The difference in these studies could be explained by the differences in the activator type and concentration and the physical and chemical properties of raw materials. On the contrary, microfiller effect could influence the behavior of the alkali-activated materials, considering the more fine-grained BFS, which refers to the theory of granularity. On the contrary, the coexistence of NASH gel and C(A)SH gel has reported to be helpful to bridge the gaps between the different hydrated phases and unreacted particles, thereby resulting in a matrix to be denser and homogeneous [66].

Increasing the NaOH concentration from 8 M to 16 M results in the strength increase of all samples. For example, the 28 d compressive strength of the BM sample with 50 FA content increases by 31.49%, from 2.98 MPa to 4.35 MPa. In the process of the alkali-activated process, NaOH was found to have a significant effect on both the compressive and structure of alkali-activated materials [67]. Leaching of Si⁴⁺, Al³⁺, Ca²⁺, and other minor ions begins when the raw materials come into contact with NaOH, and the amount of leaching is dependent on NaOH concentration [49, 51]. The compressive strength of alkali-activated materials is related to the degree of the hydration reaction, which is strongly affected by the soluble ions of the alkali-activated system [55].

However, some studies [68] also reported that a higher concentration of NaOH had resulted in a decrease in compressive strength of geopolymer. One of the possible reasons could be attributed to the high viscosity of NaOH solution, disrupting the leaching of Si, Al, and other ions. On the contrary, excess OH⁻ may lead to the precipitation of geopolymerization gel at early ages, thus resulting in lower mechanical properties [69]. However, this phenomenon is not found in the present study, which could be the result of various raw materials, and the concentration of the NaOH solution is not high enough.

Table 4 summarizes the percentage increase in compressive strength at different time intervals. As seen from Table 4, the BM samples tend to gain compressive strength in the later curing days with the increase of FA content. For the group of 8 M of NaOH solution, the BM samples acquired 94.94% of the final compressive strength at 7 d of curing using 100% BFS. However, the number decreases to 50.98% when BFS is replaced by 50% of FA. This may indicate that the geopolymerization reaction of FA starts at later ages due to its low reactivity compared to BFS. The long-term enhancement in compressive strength by the addition of FA was also reported in other studies [32].

3.6. SEM Analysis. The results of SEM analyses of the BM samples are shown in Figure 6. As seen from Figure 6, in general, the microstructure is the heterogeneous matrix, consisting of geopolymerization gel and unreacted or partially reacted FA and BFS particles. The unreacted particles
Table 4: Percentage increase in compressive strength at different time intervals.

<table>
<thead>
<tr>
<th>FA content (%)</th>
<th>3d (%)</th>
<th>7d (%)</th>
<th>28d (%)</th>
<th>60d (%)</th>
<th>3d (%)</th>
<th>7d (%)</th>
<th>28d (%)</th>
<th>60d (%)</th>
</tr>
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<tr>
<td>0</td>
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<td>94.94</td>
<td>100.00</td>
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<td>84.96</td>
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<td>66.76</td>
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<td>37.61</td>
<td>67.52</td>
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<td>61.76</td>
<td>100.00</td>
<td>14.47</td>
<td>31.51</td>
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Figure 6: Continued.
are found to increase with the increase of FA content, due to the lower reactivity of FA. This finding is further supported by the above study results, which show that the higher amount of geopolymerization products generate in the BFS rich samples. Pores with the size from micron to submicron are observed in the matrix. In general, increasing the FA content leads to a rather loose matrix. The F100B0N8 sample shows low density and many nonreacted FA particles which embed in the matrix. Similar results were also reported in [70, 71]. With the increase of BFS content, like F50B50N8 and F0B100N8, the matrix seems to be slightly denser than F100B0N8 with more geopolymer products (CSH and NASH) generated and less unreacted FA particles. This is in line with the analyses of XRD, FTIR, and TG-DTG. Noticeable difference is found with the F50B50N16 compared to that of F50B50N8. The matrix appears denser and more homogeneous. As mentioned above, more CSH and NASH from the reaction of FA/BFS and NaOH solution formed, which modified the microstructure of the matrix.

4. Conclusion

The purpose of this paper was to study the properties of NaOH-activated FA/BFS-based backfill material in terms of slump, final setting time, setting ratio, reaction products, and microstructure. The conclusions from this paper set a foundation for the utilization of FA/BFS-based geopolymer in mine backfilling in view of the present situation of the large number of tailings and worked-out section, as well as the potential safety hazards. The critical influencing factors on the properties of FA/BFS-based geopolymer were scrutinized: NaOH concentration and FA/BFS ratio. The main conclusions and perspectives this paper are summarized as follows:

(1) From the results of microstructure analyses, more geopolymerization products (CSH/NASH) are produced with the increase of BFS content and NaOH concentration, leading to a higher compressive strength.

(2) The slump of BM mortar increases as a function of FA content due to the special sphere particles of FA. While, at the same time, the increase of FA content increases the final setting time and setting ratio, resulting from the low reactivity of FA compared to BFS. Increasing the NaOH concentration reduces the slump, final setting time, and setting ratio.

(3) The influence of NaOH concentration and FA/BFS ratio on the properties of FA/BFS-based geopolymer was scrutinized; however, the characteristics of FA and BFS are various in different plants. Therefore, the relationship between the content of FA/BFS and the properties of FA/BFS geopolymer should be explored in the future, and such studies are being carried out by our team.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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