Research Article

The Effect of Calcium Formate, Sodium Sulfate, and Cement Clinker on Engineering Properties of Fly Ash-Based Cemented Tailings Backfill

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The influence of admixtures on the engineering properties of fly ash-based cemented tailings backfill (CTB) is a topic of significant practical interest, as it affects the backfilling cost and the environmental effect of mining operation. This paper presents results of an experimental study on the influence of different activators on the engineering properties of the CTB containing fly ash. CTB samples are mixed with different contents of calcium formate, sodium sulfate, and cement clinker (4%, 8%, and 12% by mass of total binder) and cured in a cubic chamber (at 20°C and RH 90 ± 5%) for 3, 7, and 28 days. Specimen tests were performed to assess the slump height, setting time, leaching water rate, vertical settlement, and strength development. Furthermore, the XRD analyses were conducted on the hydration products of fly ash-based CTB mixtures. The results show that activators can cause decrease in the slump height, leaching water rate, and vertical settlement of fly ash-based CTB mixtures. However, inclusion of cement clinker ranging from 8%–12% of total binder can reduce the slump height, setting time, leaching water rate, and vertical settlement to an acceptable range. Addition of calcium formate in the fly ash-based CTB caused negligible change in compressive strength. The compressive strength improved with higher content of sodium sulfate and cement clinker at the age of 28 days. XRD analyses showed considerable intensity counts of C-S-H gel, calcium hydroxide, and ettringite, resulting from the addition of sodium sulfate and cement clinker. This study also shows that an understanding of the effect of activators on the engineering properties of fly ash-based CTB is crucial for designing a cost-effective and workable CTB with reduced environmental impact.

1. Introduction

Mine tailings is the main waste from mineral processing with an annual output of about 300 million tons in China alone [1]. Therefore, safe disposal of tailings has been a big challenge in the mining industry, mainly due to its toxicity and potential risk to human health, ambient ecological environment, etc. The tailings storage facilities are the traditional method to dispose of these tailings, such as dams, embankments, and dry stacking on surface land. However, this surface disposal is associated with a risk of dam failure due to the rapid rising of pore pressure or seismic liquefaction. This can lead to unexpected catastrophic damage to people, equipment, and the environment in a very short time. There was such an accident on September 7th, 2008, in Shanxi Province, China, resulting in the death of 277 persons. Chinese government has issued much stricter requirements and regulation on surface tailings disposal since then [2]. Hence, applications for the tailings storage facilities on the surface became stricter and harder to approve. Consequently, compared with surface tailings disposal, backfilling has become significantly important in tailings disposal, for its potentials on improving ground stability conditions and reducing ecological impact. In addition, the cemented backfilling, such as cemented tailings backfill (CTB), can enhance ore recovery and reduce ore dilution. However, cemented backfilling mainly uses ordinary Portland Cement (OPC) as a binder to acquire strength, which significantly increases the cost of backfilling. The binder cost of cemented backfilling accounts for up to 75% of the total...
backfilling operation costs. Furthermore, the cement industry is one of the major emitters of CO$_2$, which gives rise to global warming. Based on a 2013 report, cement clinker production contributes up to 5% of the total amount of CO$_2$ emission globally [3]. To decrease the CO$_2$ emissions in relation to cement manufacturing and the binder cost associated with the cemented backfilling, utilization of artificial and natural minerals products for the partial replacement of OPC has aroused the attention of researchers around the world [4].

Fly ash is a potential pozzolanic material that can replace cement in views of its pertinent silica and alumina composition as well as its low water demand. The annual production of fly ash is predicted to be about 580 million tonnes in China, and the amount is estimated to increase in the future [5]. Fly ash can improve the engineering properties of concrete when used as a substitute for cement. The fly ash-based concrete cured at high temperature has been found to have good mechanical performance in both short- and long-term tests [6]. The structural property of fly ash-based concrete have also been reported to be similar or better than that of OPC concrete when tested for beams [7], reinforced columns [8, 9], bonding [10], and fracture behaviors [11]. However, the early strength gain of fly ash-based concrete is reportedly lower than traditional concrete [12–14]. The utilization of alkali-activated fly ash as substitute for OPC has drawn the attention of researchers in recent years. Katz found out that the activation of fly ash blended in cements not only depends on the pH of the activating ambiance but also affects by the ratio of the latter to the fly ash [15]. Another study revealed that the effect of NaOH activator solution concentration on pore solution alkalinity and subsequent alkali-silica reaction in fly ash-based concrete [16]. Shafigh et al. reported that the rate of compressive strength acquisition in fly ash-based concrete at 28 days age is significantly more than that without fly ash [3]. The addition of small size pozzolanic materials (e.g., silica fume) in fly ash-based concrete has also been studied. Barbhuiya et al. incorporated hydrated lime and silica fume into fly ash-based concrete to alter the early strength gain. The results indicated that the incorporation of silica fume and hydrated lime significantly increases the 28-day strength and improves the sorptivity of concrete [17]. Li presented an experimental research on the properties of high-volume fly ash concrete containing nanosilica. The significant strength increases of concrete containing nanosilica powder were observed as early as 3 days curing age [18]. Shaikh and Supit studied the influence of ultrafine fly ash on compressive strength and durability behaviors of concrete incorporating high-volume class F fly ash as partial replacement of cement. Their results show that the inclusion of 8 wt.% ultrafine fly ash significantly increased the early age as well as later age strengths of ordinary concrete with 100% cement [19]. Nath and Sarker also reported that the curing of fly ash-based concrete blended with a small proportion of OPC can be shortened instead of using elevated heat [5].

To date, the findings reported in the above studies illustrate that the proper alkali activator and appropriate proportion can significantly alter the mechanical properties of fly ash-based concrete. However, these observations mainly focused on the properties of modified concrete containing fly ash, and the results cannot be directly suitable for CTB. The size and nature of the aggregates as well as the water-to-cement ratio (w/c) have great effect on the fresh and hardened properties of concrete and CTB. In comparison to concrete, the CTB is different from concrete not only in views of the particle size used (the content of <20 micron is more than 20% by mass in CTB) but also on account of its high water-to-cement ratio (the w/c of CTB: >4.0, w/c of concrete: 0.3–0.6). To enhance the mechanical behavior of CTB, experimental researches have investigated the improvement the hydraulic behavior of binder used in CTB by blending OPC with fly ash, granulated slag, and silica fume [20, 21]. Cihangir et al. reported that CPB samples mixed with acidic blast furnace slag were found to acquire remarkably high compressive strength and workability over 360 days curing time [22]. Zheng et al. assessed the coupled effect of limestone powder and water-reducing admixture dosages on the mechanical properties of CTB with coarse copper mine tailings [23]. Presently, reports about the effect of activators on the engineering properties of CTB containing fly ash are scarce. Therefore, there is a need for further investigations on the effects of activators on the engineering properties of CTB containing fly ash.

This study aims to investigate the properties of alkali-activated fly ash-based cemented tailings backfill through various experimental tests, which assess the slump height, setting time, leaching water rate, settlement, and compressive strength. The proposed procedure cannot only mitigate the ecological impact of surface disposal of both mine tailings and fly ash but also can reduce the CO$_2$ emissions related to cement manufacturing. Above all, it will recycle fly ash as a binder for the cleaner production of mineral resource and reduce the binder cost of cemented backfilling.

2. Materials and Experimental Program

2.1. Materials. The materials used in this research include mine tailings, fly ash, cement, activators, and water.

2.1.1. Mine Tailings and Fly Ash. The tailings used for making CTB specimens in this study were from an iron ore-processing plant in Anhui Province, China. The grain sizes of the tailings were measured by a Microtrac S3500 laser particle size analyzer. The particle size analysis distribution of the tailings is shown in Figure 1, while the physical properties of the tailings are given in Table 1. The chemical compositions of the tailings were determined by the testing method of X-ray fluorescence (XRF) spectrometry, and the result is shown in Table 2.

The fly ash used is produced by the power plant of a coal mine in Sichuan Province, China. Its particle size distribution is also shown in Figure 1, and the physical properties in Table 1. The chemical composition of the fly ash is given in Table 2. It is mainly composed of SiO$_2$, Al$_2$O$_3$, CaO, and Fe$_2$O$_3$. The activity coefficient of the fly ash used is 0.68, and...
its alkalinity coefficient is 0.243 (<1), which indicates that it is an acidic fly ash.

2.1.2. Cement Type and Mixing Water. The cement used in all the CTB mixtures is the 42.5 R ordinary Portland cement (OPC). The chemical composition of the OPC is given in Table 2. Ordinary tap water was used to prepare the designed CTB mixtures.

2.1.3. Activators. Three types of activators—calcium formate, sodium sulfate, and cement clinker—were mixed as additives to improve the engineering properties of the CTB mixtures at different curing ages. Tables 1 and 2 show the physical properties and chemical composition of cement clinker, respectively. From Table 1, it is clear that the cement clinker has large quantities of fine particles and its particle size accounting for 50 wt.% in cement clinker is less than 13.69 μm.

2.2. Mix Proportions and Specimen Preparation. The CTB mixtures were proportioned to reveal the effect of activators on the CTB samples containing fly ash. Mix variables included the amount of fly ash as a replacement of OPC as well as the types and the amounts of activators. Fly ash was added by 48% of total binder according to the actual utilization in the iron mine. The binder-to-tailing ratio and solid content are set to 1/8 and 72% by mass, respectively. All of these mixtures blended with a constant amount of fly ash were activated with three levels of different types and amounts of activators. The calcium formate, sodium sulfate, and cement clinker were added as 4%, 8%, and 12% of total binder by mass, respectively. An additional specimen was used as a control mixture without fly ash. The detailed mixture proportions of CTB samples are presented in Table 3.

The tailings, binder, fly ash, and water with different proportions were prepared and thoroughly homogenized for about 12 minutes to produce the desired CTB mixtures. All mixtures have similar slump values between 220 and 250 mm. After mixing, the prepared CTB was poured into plastic cylindrical moulds that were 100 mm in height and 50 mm in diameter. Then, the well-prepared specimens were sealed to avoid the water loss and cured in a curing box of constant temperature (20°C) and humidity (relative

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**Table 1: Physical properties of tailings, cement clinker, and fly ash used.**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Gs (g·cm⁻³)</th>
<th>D₁₀ (μm)</th>
<th>D₃₀ (μm)</th>
<th>D₅₀ (μm)</th>
<th>D₆₀ (μm)</th>
<th>D₉₀ (μm)</th>
<th>Cc</th>
<th>Cc</th>
<th>SSA (m²/kg)</th>
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<tbody>
<tr>
<td>Tailings</td>
<td>2.9</td>
<td>55.27</td>
<td>135.32</td>
<td>178.28</td>
<td>200.79</td>
<td>233.11</td>
<td>3.63</td>
<td>1.657</td>
<td>135.36</td>
</tr>
<tr>
<td>Fly ash</td>
<td>2.3</td>
<td>3.93</td>
<td>15.38</td>
<td>35.62</td>
<td>45.87</td>
<td>110.34</td>
<td>11.672</td>
<td>1.310</td>
<td>229.70</td>
</tr>
<tr>
<td>Cement clinker</td>
<td>2.8</td>
<td>3.42</td>
<td>8.21</td>
<td>13.69</td>
<td>17.64</td>
<td>40.25</td>
<td>5.16</td>
<td>1.12</td>
<td>376</td>
</tr>
</tbody>
</table>

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**Table 2: Chemical composition of tailings and fly ash used.**

<table>
<thead>
<tr>
<th>Composition (wt.%)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>FeO</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>Na₂O</th>
<th>MnO</th>
<th>SO₃</th>
<th>Ignition loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tailings</td>
<td>79.99</td>
<td>2.54</td>
<td>8.04</td>
<td>2.04</td>
<td>2.78</td>
<td>1.16</td>
<td>—</td>
<td>—</td>
<td>0.31</td>
<td>—</td>
<td>—</td>
<td>3.127</td>
</tr>
<tr>
<td>Fly ash</td>
<td>43.77</td>
<td>19.05</td>
<td>5.85</td>
<td>4.41</td>
<td>10.84</td>
<td>0.71</td>
<td>2.46</td>
<td>1.38</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>8.45</td>
</tr>
<tr>
<td>Cement</td>
<td>20.34</td>
<td>5.02</td>
<td>3.11</td>
<td>1.09</td>
<td>64.78</td>
<td>0.35</td>
<td>0.26</td>
<td>0.10</td>
<td>—</td>
<td>2.20</td>
<td>1.73</td>
<td>—</td>
</tr>
<tr>
<td>Cement clinker</td>
<td>22.56</td>
<td>4.40</td>
<td>3.04</td>
<td>1.82</td>
<td>67.42</td>
<td>0.13</td>
<td>0.27</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.36</td>
</tr>
</tbody>
</table>
humidity of 90 ± 5%). CTB Specimens were separated from the mould after 24 h to ensure that it was not too soft. Finally, all CTB specimens were put into the curing box and cured continuously up to 3, 7, and 28 days.

2.3. Testing of Fresh CTB Mixtures. Slump height is a key fluidity index of fresh CTB mixtures. To determine this, three portions a fresh CTB mixture under uniform stirring were poured into an inverted conical slump cylinder (100 mm top diameter, 200 mm bottom diameter, and 300 mm of the height). All slump tests are carried out in accordance with ASTM C143 standard [24]. Then, the cylinder was lifted vertically upward; meanwhile, the fresh CTB mixture slumped under the action of self-weight. The slump height was calculated by the following equation (1):

\[ H_s = H_c - H_m, \]  

where \( H_s \) is the slump height of CTB, in mm, \( H_c \) is the height of the inverted conical slump cylinder (30 mm), and \( H_m \) is the center point height of CTB mixture after slump, in mm.

Setting times of the fresh CTB mixtures were determined in accordance with ASTM C191-08 [25]. The testing was conducted at a temperature of 21–23°C. The pastes were prepared by mixing the tailings, binder, and activators manually in a 500 ml beaker and tested for setting time by using a standard Vicat apparatus.

Bleeding rate is one of the main concerns of CTB technology, because the leached water can separate out the fine particle of cement added in cemented tailings slurry. Good fresh CTB slurry should behave very low leaching water. The leaching water was drained out rapidly with a straw and weighed after the slurry was mixed with binder, water, and tailings. The slurry was weighed every 20 minutes until the weight is constant and showed no further leaching water. The leaching water rate of slurry was determined according to the following equation (2):

\[ \alpha = \frac{m_w}{m_0} \times 100\%, \]

where \( m_0 \) is the initial weight of water prepared for the cemented tailings slurry and \( m_w \) is the mount of the leached water.

Water leaching from the slurry results in volume shrinkage. The shrinkage of the slurry induced vertical settlement of the slurry and generation of cracks in the upper layer of the slurry. The vertical settlement was measured in terms of settlement ratio in a column mould by a laser ranger apparatus. The settlement ratio represents the value of total amount of settlement \( (h_s) \) to the initial height \( (h_0) \), which may cause unfilled mined-out area in underground stope, as shown in Figure 2. The settlement ratio \( (\beta) \) is calculated as follows:

\[ \beta = \frac{h_s}{h_0} \times 100\%. \]  

2.4. Testing of CTB Specimens

2.4.1. Mechanical Tests. The unconfined compressive strength (UCS) test was performed on all CTB specimens by a loading apparatus in accordance with ASTM C 39-96 [26]. The load was applied at a displacement ration 0.5 mm per second and monitored until failure. All test data were recorded and saved by a computer acquisition system.

2.4.2. Microstructural Tests. All samples were dried in an electric blast oven (temperature: 50°C, time: 6 h) before microstructural tests to remove the free water until mass stabilization. A part of the dried sample was taken out and crushed by a mortar. Then, the hydration products types that formed in the CTB specimens were investigated by a D/Max 2500 X-ray diffraction (XRD). In addition, small pieces were obtained from the dried samples and sprayed with Au before scanning electron microscopy (SEM) observations. The microstructure morphology characteristics of the CTB specimens were investigated by a Quanta 250 FEG SEM with a solution of 1.0 nm and an accelerating voltage of 30 kV. The XRD and SEM tests were performed on the CTB samples CC4%, CC12%, and control cured for 28 days.

3. Results and Discussion

3.1. Effect of Activators on Slump Height. The tested slump heights of all the fly ash-based and non-fly ash CTB mixtures are shown in Figure 3. As illustrated in the graph, the
addition of activators reduced the slump height of fly ash-based CTB mixtures, and the value of slump height decreases with the increase in the activator content regardless of the activator type. The reduction of slump with sodium sulfate and cement clinker generated was more noticeable over the CTB mixtures with calcium formate and non-fly ash CTB mixtures (control), especially when the content level reached 12%. This fact may be attributed to the higher amount of fine particles in cement clinker and the filling effect induced by dispersing the voids among tailings particles, resulting in the inhibition of particles movement. However, the slump height of all CTB mixtures were found to be more than 180 mm, which is significantly higher than the threshold level that is required to produce the desired fluid slurry for backfilling in the mining industry [27].

3.2. Effect of Activators on Setting Time. The results of the initial setting and final setting time are shown in Figure 4. The setting times of CTB mixtures were observed to be shorter than that of the control which does not contain fly ash. The incorporation of 4%, 8%, and 12% calcium formate reduced the initial and final setting times of CTB mixtures by 1.7, 2.6, and 2.6 hours and 2.0, 3.3, and 3.2 hours, respectively. But the setting time increment for CF4%, CF8%, and CF12% mixtures were negligible in comparison with control mixture. The probable reason is that the calcium formate, being an organic admixture, is nonabsorbent. Slight decreases of the initial and final setting times were observed for the mixtures with sodium sulfate (e.g., SS4%, SS8%, and SS12%). The initial and final setting times for SS4%, SS8%, and SS12% mixtures were 25, 23.1, and 20.4 hours and 29.2, 26.2, and 22.0 hours, respectively. The addition of sodium sulfate relatively affects the setting times by accelerating both initial and final setting times with the increasing proportion of the content. The reason may be due to the presence of the strong cation in the mixture (i.e., Na⁺) that affects the solubility of a less strong cation (Ca²⁺) and anions of CTB mixture. However, from Figure 4, the reduction in the setting time of the mixtures with cement clinker are more pronounced than that containing equal amount of other two admixtures, and the effect of cement clinker is found severe compared to that of control mixture. The initial and final setting times were reduced, respectively, to 11.0, 9.9, and 6.8 hours and 14.0, 12.1, and 7.9 hours for CC4%, CC8%, and CC12%. A general decreasing trend in both initial and final setting times with the increase of the clinker can be observed. The probable cause is that clinker has larger fine particles and requires more water, and hence the setting time is shortened. The Ca(OH)₂ forms in the presence of water (CaO + H₂O → Ca(OH)₂), and this accelerates the hydration process. Furthermore, the results establish that the three types of activator admixture blended in CTB mixtures are found to improve the setting time. The magnitude of the setting time of the fresh CTB is in a descending order as follows: calcium formate > sodium sulfate > cement clinker. Cement clinker is more effective on the decreases of the initial and final settling time of CTB mixture. Thus, the required setting time for CTB mixture can be achieved by varying the clinker content of the fly ash-based binder.

3.3. Effect of Activators on the Bleeding Rate of CPB. Using equation (1), the bleeding rates of different fresh CTB mixtures were determined, and the results are plotted against time as shown in Figure 5. It illustrates that the curves follow a similar development pattern with time. The bleeding rate of different mixtures sharply increases to a certain value and then gradually remains constant with time. The mixtures blended with calcium and sodium sulfate have higher bleeding rate than that with cement clinker. The increasing period of bleeding could be prolonged to
150 minutes in mixtures with calcium and sodium sulfate, but the value only reached approximate 80 minutes in CC4%, CC8%, and CC12%. It is also found that the relative amplitude of bleeding peak increases with the content of activator, especially for the mixtures with cement clinker. It suggests that the CTB mixtures containing cement clinker have shorter separation phase in hardening transition process and better water-absorption than the other two activators. Thus, it can be inferred that fresh CTB mixtures with high content of activator may generate low amount water and contribute to the formation of CTB with good uniformity.

As discussed above, the type and content of activators significantly affect the bleeding rate of CTB mixtures. The final leaching rates of CTB mixtures are summarized and compared as shown in Figure 5(d). The final bleeding rate mainly ranges from 3.5% to 18.5%. By reference to the concrete standard, a segregation index of maximum 10% is considered as the limit for a concrete mixture to exhibit good resistance to segregation [28]. Based on this perspective, the CTB mixture blended with cement clinker by 8%∼12% of total binder shall be considered as a suitable activator material to alter the bleeding characteristic of CTB blended with fly ash.

3.4. Effect of Activators on Vertical Settlement. The leaching of water from CTB mixtures results in volume shrinkage, and this usually induces vertical settlement. Figure 6 shows the evolution of vertical settlement ratio of CTB mixtures with different activators over time. It illustrates that the settlement ratio of CTB mixtures increases as time elapses. The maximum settlement ratio was observed in the first 50 to 100 minutes after mixing. The settlement ratio development of the samples prepared with calcium formate and sodium sulfate is found to be in a constant growth after about 100 minutes, while the CTB mixtures with same content of clinker reach to the stable phase much earlier. Variation of the amount of activator also affects the settlement ratio of the CTB mixtures. Comparing the results shown in Figure 6(d), it can be seen that the magnitude of the final settlement of the fresh CTB is in a descending order as follows: calcium formate > sodium sulfate > cement clinker. The CTB mixtures with content of calcium formate and sodium sulfate show a much higher settlement than that made of cement clinker. It can be further observed that the final settlement generally decreases with the increase of admixtures. For instance, the final settlement for the CC8% and CC12% mixtures is noted to be 4% and 1.5%, respectively. The generation of the observed difference in CTB mixtures can be explained by the fact that the cement clinker has high content of calcium oxide and therefore reacts rapidly with water. The generated calcium hydroxide gel can fill the space and voids between the tailings particles, contributing to the compacting of mixtures and causing less shrinkage. The results also show that the bleeding and shrinkage have a similar trend as the time elapsed, comparing results of Figures 5 and 6.

3.5. Effect of Activators on UCS. The effect of different activators on UCS is apparent by comparing control mixture with other mixtures, as shown in Figure 7. The UCS of all CTB specimens, regardless of the type and content of the activators, increases with curing ages, which can be attributed to the improvement of the degree of hydration reaction in the CTB with the extension of curing time. To enable comparisons between the specimens with different activators, the UCS of CTB mixture without fly ash (control specimen) was chosen as a baseline level for reference in
At curing age of 3 days, the CTB specimens blended with calcium formate have the lowest UCS. In regard to CTB specimens blended with sodium sulfate, the UCS is significantly affected by the activator content. The UCS increased by 30% with an addition of 12% sodium sulfate as compared to the reference control specimen value. The main reason is that after hydrolysis of sodium sulfate, the content of SO$_4^{2-}$ in the CTB mixtures increased obviously. The Ca$^{2+}$ in the CTB mixtures was more likely to participate in the hydration reaction to form ettringite (Aft) under the action of SO$_4^{2-}$, which facilitates the strength gain of the CTB specimens [29]. Meanwhile, the structure of fly ash was destroyed by OH$^{-}$ in the CTB mixtures, which improves the activity degree of the fly ash and enhances its hydration reaction. The improvements noticed on the UCS are minor in CTB specimens with cement clinker. Moreover, for the specimens with calcium formate and cement clinker, the influence of the mixed activator content is negligible. Similar trend is obtained in comparison to the UCS of different specimens at curing age of 7 days, and the UCS values of different activator types and contents: (a) calcium formate; (b) sodium sulfate; (c) cement clinker; and (d) final bleeding rate.

Figure 5: Bleeding rate of fresh CTB mixtures with different activator types and contents: (a) calcium formate; (b) sodium sulfate; (c) cement clinker; and (d) final bleeding rate.
CTB specimens with sodium sulfate are still the highest, regardless of the activator content. At curing age of 28 days, the UCS values of CTB specimens added with sodium sulfate and cement clinker are all more than that of control specimen. However, the UCS of the CTB specimen blended with only 4% calcium formate is more than that of control specimen. Generally, the strength of CTB specimens increases with the increase in the content of sodium sulfate. Among the specimens blended with cement clinker, the UCS of the CC8% specimen is the highest, which means that the content of cement clinker with 8% of total binder in CTB works better than other two specimens (CC4% and CC12%). From the above observations, it can be concluded that the magnitude of the UCS of the CTB specimens is in a descending order as follows: sodium sulfate > cement clinker > calcium formate.

This comparison in compressive strength which is associated with the activator type and content is
experimentally supported by the results of the XRD analysis, as shown in Figure 8. From the figures, it can be noticed that the intensity of C-S-H, calcium hydroxide (CH), and ettringite (Aft) are comparatively higher in the CTB samples containing 12% sodium sulfate and 12% cement clinker than that in the fly ash-free CTB sample. This indicates that more C-S-H gel, Aft, and CH are formed in the samples containing activators. This increased formation of the hydration products has a positive effect on the strength gain of CTB mixtures with activator since C-S-H gel and Aft are the main bonding phases in hardened cement [30]. The formation of the hydration products also is confirmed by SEM observation, as shown in Figure 9. It can be seen from Figures 9(a) and 9(b) that a large amount of hydration products such as Aft and C-S-H gel are formed inside the CTB specimens with sodium sulfate content of 12%, cement clinker content of 12%, and cured for 28 days (CC4%) and fill in the microscopic pores of the CTB specimens, which are beneficial to the CTB specimens gaining higher UCS. Under the same magnification, the quantity of hydration products such as Aft and C-S-H gel of the CTB specimen blended without fly ash (Control) and cured for 28 days is significantly reduced, crystalline particle sizes are smaller, and the internal microscopic structure are relatively loose, as shown in Figure 9(c).

As mentioned above, the type and content of activators significantly affect the UCS of CTB specimens. Therefore, it can be concluded that the effect of calcium formate on UCS is negligible. Remarkably, the CTB specimens containing sodium sulfate and cement clinker have better strength enhancement than non-fly ash mixture. Therefore, from this standpoint, the CTB specimens blended with sodium sulfate and cement clinker can be considered as suitable activator materials to alter the UCS of fly ash-based CTB.

3.6. Further Discussions. The results on the slump height, setting time, leaching water rate, settlement, and strength development of the fly ash-based CTB sample mixed with different content and activators type with different curing age, which were presented and discussed above, give useful technical information for optimal choice and design of fly ash-based CTB and also have practical implications. It is observed that both the initial and final setting times of the fly ash-based CTB mixture with cement clinker are relatively shorter than that of the corresponding CTB samples containing other activators. Although the CTB mixtures with sodium sulfate have also shorter setting time compared with the CTB mixtures without fly ash (e.g., control samples), the final leaching water rate of mixtures with sodium sulfate could be prolonged to 150 minutes. According to the performance criteria of concrete and CTB, the optimal CTB mixtures should have a desired slump height, a limit leaching rate, settlement (i.e., maximum final segregation index of 10%), suitable setting time (i.e., minimum initial setting time of 60 min) [31], and high compressive strength (i.e., minimum 28 days compressive strength of 1.0 MPa for CTB) [32]. Therefore, the fly ash-based CTB mixtures with cement clinker replacement level from 8% to 12% of total binder can be suggested as optimal mixtures comparable to that of OPC CTB mixture. Fly ash-based binder modified with amount of cement clinker can be a suitable material for CTB at ambient curing condition. This is an energy and cost-saving alternative as it reduces not only the potential of the ecological impact of surface disposal of both mine tailings and fly ash but also the CO2 emissions related to cement manufacturing.

4. Conclusions

This paper presents the experimental results of research work that investigate the properties of fly ash-based cemented tailings backfill with various activator types and contents. The following conclusions are made based on the results obtained:

1. Presence of different activators shortened the initial and final setting time of fly ash-based CTB mixtures compared to that of traditional CTB mixture. The addition of sodium sulfate reduces the setting time proportionately with the increasing of content. However, the reduction in the setting time of the mixtures with cement clinker is more pronounced than that containing equal content of other two admixtures.

2. Increase of activators content in the fly ash-based CTB mixtures reduces the final leaching water rate. However, by reference to the concrete standard, if a segregation index of maximum 10% is considered as the limit for a concrete mixture to exhibit good resistance to segregation, the CTB mixture blended
with cement clinker by 8%–12% of total binder can be considered as a suitable activator material to alter the leaching characteristic of CTB blended with fly ash.

(3) The vertical settlement ratio of the fly ash-based CTB mixtures increases as time elapses. The amount of activator also affects the settlement ratio of the CTB mixtures. The final settlement ratio for the CC8% and CC12% mixture is noted to be 4% and 1.5%, respectively.

(4) Inclusion of calcium formate in the total binder caused negligible change in compressive strength. Increase of sodium sulfate in total binder improves the UCS of the fly ash-based CTB. Up to 28 days, the

Figure 8: XRD results of CTB with different additives cured for 28 days: (a) sodium sulfate content of 12%; (b) cement clinker content of 12%; (c) without fly ash.

Figure 9: SEM micrographs of CTB with different additives cured for 28 days: (a) sodium sulfate content of 12%; (b) cement clinker content of 12%; (c) without fly ash.
UCS values of CTB mixtures added with sodium sulfate and cement clinker are all more than that of control mixture and reach the requirement of minimum 28 days compressive strength of 1.0 MPa for CTB.

Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

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