Mechanical Properties and Microstructure of Iron Tailings Cemented Paste Backfills Using Carbide Slag-Activated Ground Granulated Blast-Furnace Slag as Alternative Binder

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Abstract: For rational disposal of solid wastes, low-cost cemented paste backfills (CPB) were prepared with iron tailings, ground granulated blast-furnace slag (GGBS), and calcium carbide slag (CS). To ensure that CPB can be effectively utilized in mine backfill projects, the effects of solid contents, GGBS content, CS/GGBS ratio, and mixing water on the workability and mechanical properties of CPB were investigated. The results indicated that when the solid content was 70%, the GGBS content was 14%, the CS/GGBS ratio was 0.4, the mixing water was tap water, the fluidity of fresh CPB slurry was 167 mm, and 28d unconfined compressive strength (UCS) of CPB reached 2.89 MPa, at which time the effect of the activation of the GGBS with CS was optimal. The analysis of X-ray diffraction (XRD), scanning electron microscopic imaging (SEM), thermogravimetric analysis (TG-DTG), and Fourier transform infrared spectroscopy (FTIR) demonstrated that the hydration products are mainly C-S-H gels, C-A-S-H, hemicarbonate, and hydrotalcite in CS-GGBS cementitious material. The C-S-H gel content gradually increased with increasing curing time and CS content (15%–35%). When the CS content was increased to 25%, the C-S-H gel content significantly increased, which improved the overall structural compactness and increased the UCS of CPB.

Keywords: cemented paste backfills; calcium carbide slag; iron tailing; alkali-activated materials; unconfined compressive strength; fluidity

1. Introduction

Mine surface subsidence, tailings reservoir dam-break, and severe damage resulting from solid wastes are major environmental disasters facing metal mines in China [1]. In particular, substantial mining wastes in terms of tailings and waste rocks, which can be sources of environmental and geotechnical problems, such as acid mine drainage and failure of tailings dams, are produced during the underground mine process [2]. Backfill mining is one of the core technologies of green mining, which is employed to achieve large-scale safe disposal of waste while effectively controlling rock movement and surface subsidence [3,4]. Ordinary Portland cement (OPC) has been the most widely used binder to produce cemented paste backfills (CPB). It is estimated that mine backfill accounts for about 20% of underground mining operational costs and, from this total amount, 75% is the binder cost when OPC is utilized as a singular binder [5]. In addition, cement production not only consumes extensive non-renewable resources but also emits a significant quantity of particulate matter and harmful gases. In particular, its carbon dioxide emissions account...
for approximately 7% of the total emissions, exacerbating the global greenhouse effect [6]. The application of backfill mining technology is restricted by the high economic and environmental costs of cementitious materials such as OPC.

The effective approach for developing high-performance and low-cost filling cementitious material is to use industrial waste. Alkali-activated materials (AAM), whose mechanical properties are similar to those of OPC [7,8], have excellent properties, such as a high strength, a low heat of hydration, a high resistance to attack of salt ions, and high-temperature and frost [9], and the carbon footprint of AAM is 40%–80% lower than those of similar products prepared with ordinary Portland cement (OPC) [10], which remains a potential alternative binder [11,12] in backfill mining. The common alkaline activators include alkali metal, alkaline earth hydroxide, carbonate, sulfate, and silicate [13,14]. Currently, sodium hydroxide and sodium silicate are the most widely utilized; however, they are expensive, and the pollutants discharged in their production process can severely damage the environment. For example, the most employed method for preparing sodium hydroxide is the electrolysis of sodium chloride, which consumes a significant amount of electricity and produces toxic compounds containing chlorine [15]. Calcium carbide slag (CS) is a by-product of acetylene production and approximately $5.6 \times 10^7$ tons are produced in China per year [16], which causes environmental pollution and wastage of resources. The main component of CS is Ca(OH)$_2$ [17]. The pH of CS is generally above 12 [18], which indicates CS can be utilized as potential alkaline activator. Granulated blast-furnace slag (GGBS) is a by-product obtained from the steel industries and is mainly composed of CaO, Al$_2$O$_3$, and SiO$_2$ [19], which remain potential cementitious activity. The alkali-activated GGBS were indicated to perform at a high strength [20].

Previous studies have demonstrated that CS-GGBS cementitious materials present excellent compressive strength. Kou et al. [21] utilized Taihu Lake sediment with CS, GGBS, and OPC to prepare cementitious materials. When the proportions of sediment, CS, GGBS, and OPC were 60%, 10%, 10%, and 20%, respectively, the 28d unconfined compressive strength (UCS) could reach 10 MPa. Zhang et al. [16] determined that the 28 d UCS of cementitious materials could reach 34.1 MPa with 10% CS and 90% GGBS. Li et al. [22] utilized CS-activated GGBS and determined that the compressive UCS of cementitious materials reached 23 MPa with 5% CS and 95% GGBS. Chu et al. [23] determined that when the mass ratio of dredged river sediment, iron tailings, OPC, and CS was 6:4:10:1, the fluidity of the filling materials was approximately 160 mm and the 7 d UCS of CPB was approximately 2.8 MPa. Yi et al. [19] used CS to stimulate GGBS to stabilize marine soft clay and found that when the mass ratio of CS, GGBS, and dry clay was 3:30:100, the 90 d UCS of the stabilized clay sample reached 1 MPa. Yi et al. [24] investigated the resistance of CS-activated GGBS stabilized clay to magnesium sulfate corrosion. They showed that when the mass ratio of CS to GGBS was 1:9 and their total mass accounted for 30% of the dry clay mass, the specimens still had a UCS of 2.4 MPa after 90 d of immersion in magnesium sulfate solution. Arulrajah et al. [25] prepared specimens using 5% CS, 5% GGBS, and 90% crushed brick, which showed a 7 d UCS of specimen reached 4.2 MPa. Lang et al. [26] stabilized dredged sludge with CS, GGBS, and dry sludge at a mass ratio 1:4:10, and the 28 d UCS of the specimens reached 350 kPa. Seo et al. [27] prepared mortar specimens using a 1:9:10 mass ratio of CS, GGBS, and river sand, and the 28 d UCS reached a peak value of 32.4 MPa. Therefore, the preparation of low-cost CPB using CS and GGBS has potential application prospects and promotion value in backfill coal mining. In addition, the uniqueness of the CPB matrix from the mix composition and proportion and the performance requirement points of view mean that the previous research results on alkali-activated pastes, mortars, and bricks may be not suitable or reliable for the ultimate design and application of CPB matrix with alkali-activated binders. However, there are few detailed studies addressing the performance of the alkali-activated system on workability and UCS performance of CPB matrix made up of iron tailings, CS, and GGBS, even though they are of significance for the application of filling materials in practical engineering.
In this study, the CS slurry was the activator, the GGBS was the binder, and iron tailings as aggregate were used to prepare CPB. The effects of solid content, GGBS content, CS/GGBS ratio, and mixing water on the workability and UCS of CPB were investigated. We also prepared the CPB with iron tailings as the aggregate and studied the effects of the solid content, GGBS content, CS/GGBS ratio, and mixing water composition on the workability and UCS of CPB. The microstructure and hydration products of CS-GGBS cementitious material specimens were analyzed via the analysis of X-ray diffraction (XRD), scanning electron microscopic imaging (SEM), thermogravimetric analysis (TG-DTG), and Fourier transform infrared spectroscopy (FTIR) tests. The aim was to develop CPB that can replace OPC and realize “treating waste with waste and turning waste into treasure”. The results provide a theoretical basis and scientific guidance for the utilization of solid wastes in mine backfill.

2. Experimental Process

2.1. Raw Materials

The main raw materials utilized in this study included CS as the alkaline activator, GGBS as the binder, iron tailings as the aggregate, and mixing water. CS was derived from an alkali plant in Tangshan, Hebei. The initial water content of CS was higher than 90%, which was required standing stratification for 5–7 days before use. The solid deposits were taken for use, and the water content was about 50%. The S95 grade GGBS was from Qinhuangdao Municipal Construction Group Co., Ltd., and iron tailings were obtained from an iron ore plant in Qinhuangdao, Hebei. Tap water was acquired from the laboratory, and deionized water was obtained from Qinhuangdao Zhisheng Trading Co., Hebei, China.

The particle size distributions of GGBS, CS, and iron tailings were measured using the BT-9300H laser particle sizer, the results of which are shown in Figure 1. After GGBS, CS, and iron tailings were dried, crushed, and sieved by a 200# sieve, their chemical compositions were determined using an X-ray fluorescence spectroscopy (XRF); the results are presented in Table 1. The phase composition was determined by an X-ray diffractometer (XRD); the results are illustrated in Figure 2. The average particle size (D50) of CS was 7.494 µm, and its specific surface area was 719.9 m²/kg. Its main chemical composition was CaO (89.50%), followed by Al₂O₃ (2.99%) and SiO₂ (5.17%). The crystalline compound was mainly calcium hydroxide. The average particle size (D50) of the S95 grade GGBS was 14.48 µm, and the specific surface area was 419.5 m²/kg. Its chemical composition was mainly CaO (31.30%), Al₂O₃ (17.60%), and SiO₂ (35.20%). The average particle size (D50) of iron tailings was 45.05 µm with a specific surface area of 200.1 m²/kg. Its composition was dominated by SiO₂ (67.3%), followed by Fe₂O₃ (16.80%), Al₂O₃ (7.14%), and CaO (3.48%).

![Figure 1. Particle size distribution curves of GGBS, CS, and tailings.](image-url)
Table 1. Chemical composition of raw materials (wt.%).

<table>
<thead>
<tr>
<th>Material</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>MgO</th>
<th>SO₃</th>
<th>Na₂O</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>Cl</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGBS</td>
<td>31.30</td>
<td>17.60</td>
<td>35.20</td>
<td>8.00</td>
<td>3.00</td>
<td>0.71</td>
<td>0.80</td>
<td>0.57</td>
<td>2.32</td>
<td>-</td>
<td>-</td>
<td>0.50</td>
</tr>
<tr>
<td>CS</td>
<td>89.50</td>
<td>2.99</td>
<td>5.17</td>
<td>0.45</td>
<td>0.53</td>
<td>0.27</td>
<td>0.22</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.73</td>
<td>0.14</td>
</tr>
<tr>
<td>Tailings</td>
<td>3.48</td>
<td>7.14</td>
<td>67.3</td>
<td>1.89</td>
<td>0.40</td>
<td>0.31</td>
<td>16.80</td>
<td>2.10</td>
<td>0.20</td>
<td>0.11</td>
<td>-</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Figure 2. XRD patterns of GGBS, CS, and tailings.

2.2. Test Procedure

The solid content, GGBS content, CS/GGBS ratios, and mixing water were treated as the influence factors to design the CPB test protocols. The CPB specimens were prepared by mixing CS, GGBS, iron tailings, and tap water according to the proportion of mixture and were poured into a 70.7 × 70.7 × 70.7 mm³ tri-mold. GGBS in S-D-70% was replaced by PII cement in equal amounts as a blank control experiment (S-S-14). The test protocols are presented in Tables 2 and 3.

Table 2. Mixture proportions of specimens.

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Mass Concentration (%)</th>
<th>GGBS Content (%)</th>
<th>Activator/Binder</th>
<th>Mixing Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect of Solid Content</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-D-72%</td>
<td>72</td>
<td>14</td>
<td>0.4</td>
<td>tap water</td>
</tr>
<tr>
<td>S-D-71%</td>
<td>71</td>
<td></td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>S-D-70%</td>
<td>70</td>
<td></td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>S-D-69%</td>
<td>69</td>
<td></td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>S-D-68%</td>
<td>68</td>
<td></td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Effect of GGBS content</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-K-10%</td>
<td>70</td>
<td>10</td>
<td>0.4</td>
<td>tap water</td>
</tr>
<tr>
<td>S-K-12%</td>
<td>72</td>
<td>12</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>S-K-14%</td>
<td>74</td>
<td>14</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>S-K-16%</td>
<td>76</td>
<td>16</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>S-K-18%</td>
<td>78</td>
<td>18</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>S-K-20%</td>
<td>80</td>
<td>20</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Effect of activator to binder ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-C-0.2</td>
<td>70</td>
<td>14</td>
<td>0.2</td>
<td>tap water</td>
</tr>
<tr>
<td>S-C-0.3</td>
<td>72</td>
<td>14</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>S-C-0.4</td>
<td>74</td>
<td>14</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>S-C-0.5</td>
<td>76</td>
<td>14</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>S-C-0.6</td>
<td>78</td>
<td>14</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Cont.

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Mass Concentration (%)</th>
<th>GGBS Content (%)</th>
<th>Activator/Binder Mixing Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect of mixing water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-W-T</td>
<td>70</td>
<td>14</td>
<td>0.4 tap water</td>
</tr>
<tr>
<td>S-W-Q</td>
<td></td>
<td></td>
<td>deionized water</td>
</tr>
<tr>
<td>S-W-S</td>
<td></td>
<td></td>
<td>supernatant</td>
</tr>
</tbody>
</table>

Note: The mass concentration is the mass ratio of solid raw materials, and the solid includes CS, GGBS, and tailings; the GGBS content is the mass ratio of GGBS to tailings; the activator is CS; and the binder is GGBS. Supernatant refers to calcium carbide slag supernatant.

Table 3. Mixture proportions of OPC specimen.

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Mass Concentration (%)</th>
<th>OPC Content (%)</th>
<th>Mixing Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-S-14%</td>
<td>70</td>
<td>14</td>
<td>tap water</td>
</tr>
</tbody>
</table>

The specimens of CS-GGBS cementitious material were prepared with the water-to-binder ratio fixed at 0.5, which followed the Chinese standard GB/T17671. The mix proportions are presented in Table 4. The CS mass content ranged from 15% to 35%, and the GGBS mass content ranged from 85% to 65%, which were recorded as D1, D2, D3, D4, and D5. The specimens were demolded after being maintained at room temperature (20–25 °C) for 48 h. After 48 h, the specimens were demolded and kept in a curing box at (20 ± 1) °C and humidity of not less than 95% until the specified age to obtain the CPB specimens and the specimens of CS-GGBS cementitious materials.

Table 4. Mixture proportions of CS-GGBS cementitious material specimens.

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>CS (%)</th>
<th>GGBS (%)</th>
<th>Water-Binder Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>15</td>
<td>85</td>
<td>0.5</td>
</tr>
<tr>
<td>D2</td>
<td>20</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>D3</td>
<td>25</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>D4</td>
<td>30</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>D5</td>
<td>35</td>
<td>65</td>
<td></td>
</tr>
</tbody>
</table>

2.3. Test Methods

The workability of fresh CPB slurry was evaluated by measuring the fluidity. The fluidity of fresh CPB slurry was tested using a micro-slump cone, according to ASTM C143 standard procedure. The diameter of the CPB slurry in two vertical directions was measured three times each with calipers [5]. The UCS of the specimen was tested by using a mechanical press which has a normal loading capacity of 50 kN and a displacement rate of 1 mm/min [28]. Three specimens were tested for each curing age, and the average value and standard deviation were determined.

XRD analyses of the cemented paste specimens of the specified curing age were performed using a D/MAX-2500/PC X-ray diffractometer with a copper target, tube voltage of 40 kV, and a tube current of 40 mA. The scanning angle was from 5° to 65°, scanning speed was 2°/min, and total scanning time was 30 min. The thermogravimetry-derivative thermogravimetry (TG-DTG) test was performed using an STA449C integrated thermal analyzer with argon as the protective gas and a controlled heating rate of 10 °C/min. The temperature ranged from room temperature to 1000 °C. A Czech VEGA3 XMU scanning electron microscope (SEM) was utilized to analyze the hydration products and microstructure, and the elemental composition of the hydration products was determined by EDS spectrometry. Infrared spectroscopy was performed using an E55+FRA106 FTIR spectrometer with a wave number range of 4000–400 cm\(^{-1}\) and resolution of 2 cm\(^{-1}\).
3. Results and Discussion

3.1. Effect of Solid Contents

The fluidity of the filling slurry and UCS of specimens at 3 d, 7 d, 14 d, and 28 d with various solid contents are illustrated in Figure 3. The fluidity of the fresh CPB slurry is generally controlled between 150 and 250 mm [29], and UCS of CPB is controlled between 0.4 and 4.0 MPa [30]. S-D-68%, S-D-69% and S-D-70% can meet the requirements.

From Figure 3a, the fluidity of specimens increased with decreasing solid contents. As the solid content decreased from 71% to 70%, the fluidity increased by 37 mm, which denoted an increase of 30.5%. This is because decreasing solid contents led the water content increases, and the distance between particles in the specimen increased, thus reducing the direct particle-to-particle contact. In addition, solid particles tended to slide against each other during shear in an environment with a higher water content [31].

Figure 3b shows that the UCS of all specimens continuously increased with an increase in the curing time. The UCS of specimens increased significantly within 14 d, whereas the growth in the UCS slowed down from 14 d to 28 d. This is because initial pores exist in the specimens, and the generated hydration products fill the pores as the hydration reaction proceeds. Moreover, the hydration reaction was basically completed within 14 d, the formation rate of hydration products slowed down between 14 and 28 days. As the solid contents increased, the UCS of specimens continuously increased. The UCS of S-D-72% at 3 d, 7 d and 14 d were lower than that of S-D-70% at 3 d, 7 d, and 14 d due to experimental errors and the lack of uniformity in the particle size distribution of the raw material. When the solid content was increased from 69% to 70%, the 3 d UCS increased by 37.4%, and the 14 d UCS increased by 22.4%, reaching 2.42 MPa, which had met the filling material UCS requirements [30]. This is because the specimens with higher solid contents have lower initial porosities, which is conducive to improving their compactness [14]. In addition, the main component in CS is calcium hydroxide. Hence, a decrease in water content increases the concentration of calcium hydroxide and the solution viscosity, which promotes the alkali-activated reaction [32]. Compared with S-S-14, the fluidity of the filling slurry of S-D-70% was reduced 14.0%, while the 28 d UCS of S-D-70% was significantly increased 39.6%, and the use of CS and GGBS is more conducive to cost reduction and environmental protection, demonstrating the viability of the CS-GGBS cementitious materials as alternative binder.

3.2. Effect of GGBS Contents

The fluidity of the filling slurry and UCS of the specimens at 3 d, 7 d, 14 d, and 28 d with various GGBS contents are illustrated in Figure 4.
Figure 4. Effects of GGBS content on (a) fluidity and (b) compressive strength of specimens.

Figure 4a shows that with an increase in the GGBS content, the fluidity first decreased and when the GGBS content exceeded 14%, and the fluidity remained at approximately 169 mm. This is because the irregular and angular microstructure of GGBS weakens the fluidity of the fresh CPB slurry [33].

Figure 4b indicated that the UCS of specimens gradually increased with an increase in the GGBS content. When the GGBS content was 10% and 12%, the 3 d UCS of the specimen reached 1.00 MPa, which indicated improved early performance. When the GGBS content was 14%, the 28 d UCS reached 2.89 MPa. As the GGBS content increased from 10% to 20%, the 28 d UCS increased by 5.6%, 24.5%, 1.4%, 2.8%, and 6.1%. In addition, the most significant increase was observed at a GGBS content of 14%; however, the intensity of increase in the UCS was significantly reduced after the GGBS content exceeded 14%. The hydration products generated during the alkali-activated reaction were the primary sources of UCS. With an increase in the GGBS content, the hydration products kept increasing, gradually enhancing the specimen compactness and UCS [21]. When GGBS content exceeded 14%, the fluidity remained at approximately 169 mm and the UCS of CPB increased limitedly. Therefore, the appropriate GGBS content is 14%.

3.3. Effect of CS/GGBS Ratios

The variation in the fluidity of the filling slurry and UCS of specimens at 3 d, 7 d, 14 d, and 28 d with various CS/GGBS ratios are illustrated in Figure 5.

Figure 5. Effect of CS/GGBS ratio on (a) fluidity and (b) compressive strength of specimens.
From Figure 5a, the fluidity of the fresh CPB slurry first decreased, then increased, and eventually decreased as the CS/GGBS ratio increased. This may be because the specific surface area of CS (719.9 m$^2$/kg) is much larger than that of GGBS (419.5 m$^2$/kg), and the addition of CS absorbed more water of the freshly mixed slurry, thus reducing the fluidity. As the CS/GGBS ratio increased to 0.5, the content of the fluid medium in the system reached the peak. Thus, the number of direct contacts between particles reduced and the fluidity improved [5,31].

From Figure 5b, the UCS first increased, and then remained constant with the increase in CS/GGBS ratio. The 28 d UCS significantly increased as the ratio increased from 0.3 to 0.4, with an increase of 14.3%. When the ratio exceeded 0.4, the 28 d UCS slightly decreased. This may be because when the CS/GGBS ratio was below 0.4, the amount of hydration products is limited, resulting in a greater amount of GGBS residue. Nevertheless, when the CS/GGBS ratio exceeded 0.4, the increase of the content of hydration product leaded the structure of specimens become more compacted, thereby increasing the UCS. Simultaneously, the content of calcium hydroxide crystals increased. Excessive calcium hydroxide hinders the development of the UCS of specimens to a certain extent [18], and the final UCS converged to become stable.

3.4. Effect of Mixing Water

The variation in the fluidity of the filling slurry and UCS of specimens at 3 d, 7 d, 14 d, and 28 d with different types mixing water are illustrated in Figure 6.

As shown in Figure 6a, minor differences exist between the fluidity of specimens with different types of mixing water. The fluidity of the fresh CPB slurry mixed with tap water, deionized water, and CS supernatant decreased in the given order. Thus, with appropriate alkali concentrations in water, the viscosity between particles after a hydration reaction can be reduced, and the fluidity can be improved [34].

From Figure 6b, the 28 d UCS of CPB using tap water, deionized water, and calcium carbide slag supernatant were 2.89 Mpa, 2.45 Mpa, and 2.56 Mpa respectively, while the 28 d UCS of CPB mixed with tap water was relatively higher. The 7 d UCS of the specimens prepared with CS supernatant, deionized water, and tap water decreased in the given order. This may be because CS supernatant and deionized water can provide a relatively high alkaline environment. The higher alkalinity was conducive for the formation of hydration products, which can improve the UCS of specimens [35]. However, when the CS supernatant and deionized water were employed, the growth rate of the specimen UCS at 14 d and 28 d slowed down. This may be due to the formation of coatings on the surface of the GGBS particles in a relatively high alkaline environment, which prevented the
continuous hydration of the particles, thus slowing down the process of UCS development of specimens [36].

3.5. XRD Analysis

To determine the hydration products and further investigate the impact of CS and GGBS contents on the hydration reaction, the 3 d, 7 d, 14 d, and 28 d specimens of the D2 group, and the 28 d specimens of D1, D2, D3, D4, and D5 were tested by XRD, as illustrated in Figure 7.

![Figure 7. XRD patterns of D2 specimens (a) and all 28 d specimens (b).](image-url)

The crystalline materials of specimens in the D2 group primarily included hydrotalcite (6 MgO·Al2O3·CO2·12 H2O), hemicarbonate (8 CaO·Al2O3·CO2·24 H2O), quartz (SiO2), portlandite (Ca(OH)2), and calcite (CaCO3). Portlandite (Ca(OH)2) was obtained from unreacted CS particles, and quartz (SiO2) was obtained from unreacted GGBS particles. Diffraction peaks of hydrotalcite and hemicarbonate were clearly detected, similar to the results reported in previous studies [16,22]. The formation of calcite could be attributed to the carbonation of calcium hydroxide during specimen preparation and curing [16]. With an increase in the curing time, the diffraction peaks of calcite decreased slightly and those of hydrotalcite and hemicarbonate increased continuously. This may be because the addition of CS continuously promoted the hydration reaction of GGBS, and partially dissolved calcite promoted the formation of hydrotalcite and hemicarbonate. The “hump” within 20°–40° is the characteristic of C-S-H, indicating that the hydration reaction formed the amorphous hydration product of C-S-H [37]. The “hump” became more prominent with increasing curing time, indicating a further increase in the amount of C-S-H produced. In addition, the characteristic of C-A-S-H may result from that part of free Al3+ entering the C-S-H structure and forming C-A-S-H [38].

The test results of the 28 d specimens of D1, D2, D3, D4, and D5 were analyzed, and new hydration products were not observed. Among them, the degree of protrusion of the “hump” of C-S-H gels in the 28 d specimen of D5 was more pronounced, indicating a higher content of C-S-H. The degree of protrusion of “hump” of C-S-H in the D3 specimen was significantly increased compared with that of the D2 specimen. When the CS content exceeded 25%, the hydration reaction of GGBS activated by CS was more sufficient. The degree of protrusion of “hump” C-S-H in the D4 and D5 specimens indicated a slightly increase compared with that of D3, while the intensity of Ca(OH)2 diffraction peaks significantly increased. With the continuous increase in CS content, “excessive” calcium hydroxide appeared. The results of XRD analysis showed that CS can effectively promote the hydration reaction of GGBS, and the synergistic effect of multiple hydration products, mainly C-S-H, ensures the UCS of CPB.
3.6. SEM-EDS Analysis

To further characterize the hydration products, the 3 d, 14 d, and 28 d specimens of D2 and the 28 d specimens of D1–D5 were subjected to SEM tests, and the D5 28 d specimen was subjected to the EDS test, as illustrated in Figures 8 and 9.

From the SEM images of the 3 d, 14 d, and 28 d specimens of D2, when the curing age was 3 d, a small amount of C-S-H gel was generated, and there were many pores in overall specimen structure. With the prolongation of curing time, the C-S-H gels were continuously generated and filled the pores; therefore, the overall structure of the specimens was more compact. After the curing age reached 14 d, the amount of the C-S-H gels in the specimens significantly increased, the gel distribution became more uniform, and the compactness of the overall structure was significantly improved [39]. When the curing age was 28 d, the large amount of the C-S-H gels in the specimens significantly improved the overall structural densities of the specimens. The amount of Ca(OH)$_2$ with a hexagonal lamellar crystal significantly decreased between 14 d and 28 d, while the presence of Ca(OH)$_2$ could be observed in all 28 d specimens, indicating that Ca(OH)$_2$ remained after participation in hydration reactions. The structures of the D3–28 d and D5–28 d specimens were significantly more compacted than those of the D1–28 d and D2–28 d specimens, indicating when the CS content exceeded 25% (CS/GGBS ratio was 0.4), the UCS of CPB was significantly improved, which was consistent with the XRD results.

![SEM images of D2 specimens: 3 d (a); 14 d (b); 28 d (c).](image)

![Figure 8. SEM images of D2 specimens: 3 d (a); 14 d (b); 28 d (c).](image)

![Figure 9. Cont.](image)
Figure 9. EDS results of specimens at 28 d: D1 (a); D3 (b); D5 (c,d).

The EDS results for the D1–28 d, D3–28 d, and D5–28 d specimens revealed the presence of Ca, Si, Al, Mg, and C elements in Area 1-spot 1, Area 2-spot 2, and Area 3-spot 3. The presence of Mg and may be due to the possible overlapping of hydrotalcite, hemicarbonate, and C-S-H gels at these sites. Hydrotalcite and hemicarbonate can fill the pores of structure to improve the densification of specimens. Al can partially replace Ca and Si and enter the structure of C-S-H gels to form C-A-S-H gels [40,41], which was consistent with the XRD results. On Area 4-spot 1, Ca and O were the most abundant, indicating a higher probability of Ca(OH)$_2$ crystals at these locations.

3.7. TG-DTG Analysis

TG-DTG analysis was performed on 3 d, 7 d, and 14 d specimens of D2 and 28 d specimens of D1–D5. The results of TG-DTG analysis and weight loss are respectively shown in Figures 10 and 11.

Figure 10. TG–DTG curves of D2 specimens and all 28 d specimens.
Five distinct weight loss peaks were observed in Figure 10, which corresponded to C-S-H, hemicarbonate, hydrotalcite, Ca(OH)$_2$, and calcite. The weight loss in the range of 30–250 °C was due to the dehydration and decomposition of C-S-H [42] and was also associated with the decomposition of hemicarbonate [16]. The decomposition of C-S-H occurred in the entire temperature range of the test; thus, significant horizontal segments of the TG curve were not observed. In the range of 300–400 °C, the appearance of the weight loss peak could be attributed to the loss of CO$_2$ and water from hydrotalcite [43]. The weight loss in the range of 400–500 °C can be attributed to the decomposition of Ca(OH)$_2$ [44]. The calcite can be decarburized and decomposed between 700 °C and 800 °C [45], produced by carbonization of part of Ca(OH)$_2$. Within 14 d, the weight loss rate of C-S-H, hemicarbonate, and hydrotalcite significantly increased. The synergistic effect of multiple hydration products, mainly C-S-H, promoted the UCS of CPB developed rapidly within 14 d. From 14 d to 28 d, the weight loss peak intensity of C-S-H, hemicarbonate, and hydrotalcite limitedly increased, indicating that the hydration reaction was basically completed within 28 d.

Comparing the TG-DTG curves of the 28 d specimens of D1–D5 (Figure 10), the C-S-H weight loss peak intensities of D5, D4, D3, D2, and D1 increased in turn. The variation trend of the weight loss peak intensity of hemicarbonate and hydrotalcite was similar to that of C-S-H. Compared with D2 specimens, the C-S-H weight loss peak intensity of the D3 specimens was significantly increased, whereas that of the D4 specimens was slightly higher than that of the D3 specimen, demonstrating that when the CS/GGBS ratio was close to that of D3, the UCS of CPB obviously increased. This was consistent with the results of SEM-EDS. The presence of Ca(OH)$_2$ could be found in all 28 d specimens, indicating that the Ca(OH)$_2$ in all CS content was not completely reacted after the CS content increased beyond 15%.

3.8. FTIR Analysis

The FTIR results for 3 d, 7 d, and 14 d specimens of D2 and 28 d specimens of D1–D5 are illustrated in Figure 12.
Figure 12. FTIR curves of D2 specimens (a) and all 28 d specimens (b).

The absorption peak at 3644 cm$^{-1}$ corresponded to the O-H vibrations in Ca(OH)$_2$ [46]. The absorption peaks near 450 cm$^{-1}$, 664 cm$^{-1}$, and 972 cm$^{-1}$ can be attributed to the in-plane bending vibrations of the Si-O bonds and the stretching vibrations of Si-O-Si and Si-O bonds. They were all characteristic peaks of C-S-H gels [47]. As illustrated in Figure 12a, with an increase in curing time, the absorption peak intensity of Ca(OH)$_2$ gradually decreased, whereas the characteristic peak intensity of C-S-H gels continuously increased, indicating the hydration reaction was continuously promoted by CS. Figure 12b illustrated the absorption peaks of Ca(OH)$_2$, which indicated that there was Ca(OH)$_2$ remaining after the hydration reaction. The results were consistent with those of XRD and TG-DTG. The bands at 3464 cm$^{-1}$ and 1643 cm$^{-1}$ were generated by H-O-H bending vibrations, and the formation of these bands might have originated from the chemically bound water in the C-S-H gels of the hydration products [48]. The out-of-plane bending vibrations of CO$_3^{2-}$ corresponded to the absorption peaks at 875 cm$^{-1}$, and the bands at 1417 cm$^{-1}$ were attributed to the symmetric stretching vibrations of C-O bonds. This indicated the formation of hydrotalcite and calcite [49]. The absorption peak near 664 cm$^{-1}$ also indicated the presence of Al-O or Mg-O bonds, further demonstrating the formation of hydrotalcite [50]. The aforementioned analysis further validated the XRD and TG-DTG results.

3.9. Discussion

Previous studies generally used OPC [51,52] or strong alkali to stimulate GGBS [5] as a cementitious material for the production of CPB, but few studies used CS to stimulate GGBS as a cementitious material to prepare CPB. The effects of solid content, GGBS content, CS/GGBS ratio, and mixing water on the workability and UCS of CPB were investigated in our study. When the ratios were a solid content of 70%, GGBS content of 14%, and CS/GGBS ratio of 0.4, the fluidity of the fresh slurry was 167 mm, and the mixed water was tap water, then both fluidity and the UCS of CPB (S-D-70%) were optimal. The fluidity of the cemented paste backfills is generally controlled between 150 and 250 mm [29], and UCS is controlled between 0.4 and 4.0 MPa [30]. Compared with S-S-14 (CPB produced by PII cement), the 28 d UCS of S-D-70% was significantly increased 39.6% (Figure 3) when S-D-70% and S-S-14 could meet the requirements. In terms of cost, the price of 595 GGBS is USD 31–46/ton [53], CS is used directly after storage and removal of the supernatant, whose cost was negligible, and the price of PII cement is USD 75–79/ton. The aforementioned statement demonstrated that the application of CS and GGBS for CPB is more advantageous in terms of UCS and cementitious material cost, indicating that CS-GGBS can be used as an alternative cementitious material to OPC for the production of CPB. In addition, CS is cheaper, more accessible, and less polluting than traditional alkali activators (e.g., NaOH).
4. Conclusions

(1) CS, GGBS, and iron tailings were utilized to prepare CPB. The results indicated that when the ratios were a solid content of 70%, GGBS content of 14%, CS/GGBS ratio of 0.4, and the mixed water was tap water, the fluidity of the fresh slurry was 167 mm, and the 28 d UCS of CPB reached 2.89 MPa, at which time the effect of the activation of the GGBS with CS was optimal.

(2) The XRD, SEM-EDS, TG-DTG, and FTIR results revealed that the hydration products of the CS-GGBS cementitious material system were mainly C-S-H gels, C-A-S-H, hemicarbonate, and hydrotalcite. As the curing time increased, the amount of C-S-H increased. The synergy of the hydration products, mainly C-S-H gels, ensured the UCS of the CPB.

(3) In the process of the CS activation of GGBS, with addition in the CS proportion, the hydration product content increased. The amounts of the hydration products significantly increased when the CS content was 25%, confirming that the hydration reaction of CS-activated GGBS was optimal under this ratio. When the CS content was 15% or higher, different degrees of CH remained after participating in the hydration reaction.

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References


