Design and Properties of Coal Gangue-Based Geopolymer Mortar

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Abstract: The feasibility of preparing coal gangue-based geopolymer mortar (CGBGM) with composite-activated coal gangue was experimentally explored in this paper. The effects of water-to-binder ratio (W/B), alkali content (A), and slag content (S) on the fluidity and performances of the CGBGM were experimentally investigated. The ANOVA method was employed to evaluate the significance level of influenced factors. Moreover, the microstructure, element compositions, and qualitative microanalysis of the CGBGM at various curing ages were verified by ESEM-EDS. Test results denoted that the mechanical properties of the CGBGM are superior to that of ordinary Portland cement mortar (OPCM). The flexural and compressive strength of the CGBGM rapidly increases before 7 d and then tends to slow afterward. According to the impact degree on the flexural and compressive strength of the CGBGM, the S is ranked first, followed by the A, and finally the W/B. The flexural and compressive strength of specimens with 40% slag increased by 45.97% and 90.75%, respectively, compared to the control group. However, the A and W/B have little effect on flexural strength. In addition, the hydration productions filled in the crevice and healed the entrapped microcracks in the hardened paste with the increase in curing ages, forming a dense microstructure. The Ca/Si decreased from 0.5 at 3 d to 0.06 at 28 d, and the Ca/Al decreased from 0.25 at 3 d to 0.05 at 28 d. Finally, the difference in drying shrinkage behavior between the CGBGM and OPCM was systematically analyzed.

Keywords: coal gangue; coal gangue-based geopolymer mortars; mechanical properties; drying shrinkage

1. Introduction

Coal gangue is the associated solid waste of coal and one of the largest solid industrial wastes worldwide. It was reported that coal gangue occupies approximately 15~20% of the total coal output, and its emission exceeds 7 billion in China [1,2]. Over time, such non-biodegradable wastes occupy land, pollute air, water, and soil, and even induce geological disasters [3,4]. Hence, the utilization of coal gangue as a recyclable resource has attracted the attention of global scholars [5–11].

In the meantime, as the most used construction material, manufacturing cement consumes high content of non-renewable clay minerals and limestone, producing 800 kg to 1000 kg CO₂ per ton [12,13]. In comparison, the CO₂ emissions can reduce by 25~50% when fabricating identical amounts of coal gangue-based geopolymer [14,15]. Meanwhile, state-of-the-art research implies that the chemical and mineral compositions of coal gangue are highly similar to the low-calcium fly ash. Given that, coal gangue can be considered a novel eco-friendly cementitious binder that partially or entirely replaces conventional Portland cement (OPC) after proper treatment [16–18]. Therefore, the question arises of how to boost the activity of raw coal gangue. Extensive attempts have been conducted by global scholars to address this universal concern. Zhang et al. [19] summarized that...
the composite activation method is an effective measure to trigger the pozzolanic activity of coal gangue. In particular, Zhao et al. [20] systematically revealed the influences and mechanisms of mechanical, thermal, and chemical activation on the pozzolanic activity of coal gangue. Ma et al. [21] found that the CGBG concretes have high early strength and good durability. Ye et al. [22] and Peter Duxson et al. [15] discovered that the CGBG has low hydration heat release and high chemical attack resistance. Currently, the research on the activation method and mechanism of coal gangue, hydration reaction and mechanism, mixture proportion design, and microstructure characteristics of the CGBG has attracted a lot of attention from scholars in various regions. However, it is rarely reported that the coal gangue after appropriate treatment is used as a partial or entire substitute for ordinary Portland cement. Additionally, the utilization rate of coal gangue in building materials is less than 30%, while that of slag and fly ash exceeds 85%.

In this paper, composite-activated coal gangue (CACG) was employed as a primary cementitious material to fabricate coal gangue-based geopolymer mortars (CGBGMs). The effects of alkali content (11%, 12%, 13%, and 14%), slag content (0, 10%, 25%, 30%, 35%, and 40%), and water-to-binder ratio (0.45, 0.50, 0.55, and 0.60) on the fluidity and mechanical properties of the CGBGM were experimentally investigated. The significance level of each factor was also systematically analyzed with a one-way analysis of variance (ANOVA). Moreover, the microstructure, element types, and qualitative microanalysis of the CGBGM at different curing ages were compared and analyzed by advanced inspection techniques. Finally, the difference in drying shrinkage behavior between the CGBGM and ordinary Portland cement mortar (OPCM) was systematically analyzed.

2. Experimental Section

2.1. Raw Materials

The raw coal gangue was derived from the Ordos in China. The S95 grade granulated blast furnace slag was used as supplementary cementitious material, whose specific surface area and density were 450 m$^2$/kg and 2.9 g/cm$^3$, respectively. The primary compositions of Portland cement (PO 42.5), slag, and raw coal gangue are collectively shown in Table 1. Compared with the compositions of Portland cement (PO 42.5) and slag, the coal gangue has higher SiO$_2$ and Al$_2$O$_3$ contents and lower CaO content. Moreover, the loss on ignition (IOI) of raw coal gangue is up to 15.33%, indicating high organic carbon content in coal gangue.

<table>
<thead>
<tr>
<th>Component</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>Al$_2$O$_3$</th>
<th>MgO</th>
<th>Fe$_2$O$_3$</th>
<th>SO$_3$</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw coal gangue</td>
<td>55.14</td>
<td>0.41</td>
<td>40.96</td>
<td>0.30</td>
<td>1.23</td>
<td>0.43</td>
<td>0.20</td>
<td>0.09</td>
<td>15.33</td>
</tr>
<tr>
<td>Slag</td>
<td>36.10</td>
<td>35.58</td>
<td>16.32</td>
<td>11.32</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.30</td>
</tr>
<tr>
<td>PO 42.5</td>
<td>21.08</td>
<td>60.20</td>
<td>7.10</td>
<td>2.11</td>
<td>60.20</td>
<td>3.85</td>
<td>1.16</td>
<td>0.214</td>
<td>2.1%</td>
</tr>
</tbody>
</table>

Coal gangue displayed low pozzolanic reactivity due to its stable crystallized structure and high organic carbon content [23]. Therefore, a composite activation approach was introduced to enhance the pozzolanic activity of raw coal gangue, including mechanical activation and thermal activation. According to extensive findings [19,24,25], the calcination temperature, particle size, and calcination time were determined as 700 °C, 200 mesh, and 2 h, respectively. The XRD spectra and microstructures of raw coal gangue and composite-activated coal gangue (CACG) are displayed in Figures 1 and 2.
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Gradation curve of sand.

Metastable high-reactivity silica and alumina [20,26,27]. Moreover, calcination can remove the organic carbon in raw coal gangue. The loose microstructure of raw coal gangue transformed into a tight microstructure after calcination at 700 °C for two hours. Figure 2 clearly demonstrates that the loose microstructure of raw coal gangue transformed into a tight microstructure after calcination at 700 °C for two hours. It can be seen from Figure 1 that coal gangue is primarily composed of kaolinite (K), illite (I), quartz (Q), chlorite (C), and muscovite (M). The kaolinite peaks nearly disappeared after calcination at 700 °C for two hours. Figure 2 clearly demonstrates that the loose microstructure of raw coal gangue transformed into a tight microstructure after composite activation. It demonstrated that those stable kaolinite crystals gradually turned into metastable high-reactivity silica and alumina [20,26,27]. Moreover, calcination can remove the organic carbon in raw coal gangue.

The test sand with a fineness modulus of 2.62 is taken from Nanjing in China, whose detailed gradation curve is shown in Figure 3. Moreover, the apparent density and bulk density of test sand are 2585 kg/m³ and 1627 kg/m³.

![Figure 1](image1.png)

**Figure 1.** XRD spectra of raw coal gangue and CACG.

![Figure 2](image2.png)

**Figure 2.** Microstructure of various samples: (a) raw coal gangue; (b) CACG.

![Figure 3](image3.png)

**Figure 3.** Gradation curve of sand.
Previous studies have shown that compared with sodium hydroxide, gypsum, and other activators, sodium silicate (Na$_2$SiO$_3$) could efficiently activate the pozzolanic activity of coal gangue [28,29]. When the sodium silicate modulus was 1.2, the alkali-activated coal gangue cementing materials exhibited outstanding properties [20]. Therefore, Na$_2$SiO$_3$ with a modulus of 1.2 was obtained by adding sodium hydroxide and employed in this research. Among them, the initial modulus of sodium silicate (59.6% SiO$_2$, 21.6%Na$_2$O) was 2.85, and the purity of sodium hydroxide was 99.8%.

2.2. Mixture Proportions

Thirteen groups were conducted to study the effects of water-to-binder ratio (W/B), alkali content (A), and slag content (S) on the fluidity and performances of CGBGM. The ordinary Portland cement mortar (OPCM) was chosen for the blank group. The detailed mixing proportions of the CGBGM and blank group are displayed in Table 2.

<table>
<thead>
<tr>
<th>NO.</th>
<th>A/%</th>
<th>S%</th>
<th>W/B</th>
<th>CACG/g</th>
<th>Slag/g</th>
<th>Cement/g</th>
<th>Sand/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>A11</td>
<td>11</td>
<td>30</td>
<td>0.55</td>
<td>700</td>
<td>300</td>
<td>-</td>
<td>3000</td>
</tr>
<tr>
<td>A12</td>
<td>12</td>
<td>30</td>
<td>0.55</td>
<td>700</td>
<td>300</td>
<td>-</td>
<td>3000</td>
</tr>
<tr>
<td>A13</td>
<td>13</td>
<td>30</td>
<td>0.55</td>
<td>700</td>
<td>300</td>
<td>-</td>
<td>3000</td>
</tr>
<tr>
<td>A14</td>
<td>14</td>
<td>30</td>
<td>0.55</td>
<td>700</td>
<td>300</td>
<td>-</td>
<td>3000</td>
</tr>
<tr>
<td>S0</td>
<td>12</td>
<td>0</td>
<td>0.55</td>
<td>1000</td>
<td>0</td>
<td>-</td>
<td>3000</td>
</tr>
<tr>
<td>S10</td>
<td>12</td>
<td>10</td>
<td>0.55</td>
<td>900</td>
<td>100</td>
<td>-</td>
<td>3000</td>
</tr>
<tr>
<td>S25</td>
<td>12</td>
<td>25</td>
<td>0.55</td>
<td>700</td>
<td>250</td>
<td>-</td>
<td>3000</td>
</tr>
<tr>
<td>S35</td>
<td>12</td>
<td>35</td>
<td>0.55</td>
<td>650</td>
<td>350</td>
<td>-</td>
<td>3000</td>
</tr>
<tr>
<td>S40</td>
<td>12</td>
<td>40</td>
<td>0.55</td>
<td>600</td>
<td>400</td>
<td>-</td>
<td>3000</td>
</tr>
<tr>
<td>W/B0.45</td>
<td>12</td>
<td>30</td>
<td>0.45</td>
<td>700</td>
<td>300</td>
<td>-</td>
<td>3000</td>
</tr>
<tr>
<td>W/B0.50</td>
<td>12</td>
<td>30</td>
<td>0.50</td>
<td>700</td>
<td>300</td>
<td>-</td>
<td>3000</td>
</tr>
<tr>
<td>W/B0.60</td>
<td>12</td>
<td>30</td>
<td>0.60</td>
<td>700</td>
<td>300</td>
<td>-</td>
<td>3000</td>
</tr>
<tr>
<td>OPC</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1000</td>
<td>3000</td>
</tr>
</tbody>
</table>

In each group, eighteen prismatic specimens (160 mm × 40 mm × 40 mm) were fabricated for the flexural and compressive strength test according to the ASTM C192 [30] and JGJ/T70-2009 standards [31], respectively. All specimens were removed from the molds after 24 h and cured in a standard curing chamber.

2.3. Experimental Methods

2.3.1. Fluidity Test

According to the GB/T2419-2005 standard, a mortar fluidity tester was employed to measure the fluidity of the CGBGM. First, a wet rag was used to wipe the mortar fluidity tester. Second, the CGBGM was poured into the mold twice. The fresh CGBGM was poured into two-thirds of the mold for the first time and tamped fifteen times with a tamping rod. Then, the second layer of the CGBGM was poured into the mold and tamped ten times. Finally, the molds were removed, and the mortar fluidity tester was started. After the mortar fluidity tester jumped 25 times, the widths in both vertical directions were recorded. The average value is taken as the fluidity of the CGBGM.

2.3.2. Mechanical Test

According to the GB/T17671-1999 standard, a three-point bending method and YDW-10 microcomputer mortar flexure tester were adopted to study the flexural strength of the CGBGM, and the loading rate was 50 N/s. A WAW-300 compression testing machine was used to determine the compressive strength of the CGBGM, and the loading rate was 0.5 MPa/s.
2.3.3. Drying Shrinkage Test

According to the JTGE30-2005 standard, the differences in drying shrinkage behavior between the OPCM and CGBGM were investigated. Three standard test samples with a cross-section of 25 mm × 25 mm and a length of 280 mm were poured into each group. The molds of all specimens were removed after one day and were placed in a constant temperature (20 ± 2 °C) and relative humidity (50 ± 4%) tank. The mass \( m_0 \) and length \( L_0 \) of the AACGC and OPCC were recorded according to reference [21]. The mass-loss ratio \( \Delta m \) and drying shrinkage \( \varepsilon_{st} \) of all specimens were calculated as Equations (1) and (2), respectively:

\[
\Delta m = \frac{m_0 - m_t}{m_0} \times 100\% \quad (1)
\]

\[
\varepsilon_{st} = \frac{L_0 - L_t}{L_0} \quad (2)
\]

where \( m_0 \) and \( m_t \) are the weight of the sample on the first and \( t \) days, respectively; correspondingly, \( L_0 \) and \( L_t \) are the lengths of the sample on the first and \( t \) days, respectively.

3. Results and Discussion

3.1. Fluidity

Figure 4 indicates that the fluidity of the CGBGM increases with the increase in the A. Compared with the A11 group, the fluidity of the A14 group increased by 16.85%. It is apparent that the amount of silicate ions in an alkali solution with the increase in alkali content and silicate ions improves the fluidity of CGBGM [32]. The S and the fluidity of the CGBGM exhibit overall ascending trends. The fluidity of the S40 group was 1.58 times that of the S0 group. The slag contains a large number of glass microbeads and acicular glass bodies with dense and smooth surfaces, which struggle to absorb water molecules and generate a smooth sliding surface in the slurry, thereby improving its fluidity.

![Figure 4. Fluidity of the CGBGM with different parameters.](image)

Moreover, slag has a smaller particle size than coal gangue, and it fills the voids between coal gangue particles and improves the fluidity of the CGBGM. Compared with the W/B 0.45 group, the fluidity of the W/B 0.60 group increases by 44.06%, indicating that the W/B has a significant impact on the fluidity of the CGBGM because the free water content of CGBGM increases along with the increase in W/B, which improves the fluidity of the CGBGM.

3.2. Mechanical Properties

3.2.1. Flexural and Compressive Strength

Figure 5 displays the flexural and compressive strength of the CGBGM with different parameters. It can be observed that the effects of the A on the flexural and compressive strength of specimens display an inflection point when the A is 12%, which indicates that
there is an optimum alkali content. The result is consistent with previous findings [32]. This is because it does not meet the conditions of the polymerization reaction when the alkali content is too low. However, excess alkali content contributes to higher dimensional shrinkage and cracking potentials, herein decreasing the strength of the CGBGM [21,33]. Meanwhile, the S and the flexural and compressive strength of the CGBGM exhibit overall ascending trends. Compared with the S0 group, the 28 d flexural strength of the S10, S25, S30, S35, and S40 groups increased by 22.15%, 38.59%, 43.62%, 44.97%, and 45.97%, respectively; the 28 d compressive strength of the S10, S25, S30, S35, and S40 groups increased by 51.86%, 69.69%, 74.81%, 83.03%, and 90.75%, respectively, because the concentration of calcium ions in the system increases gradually along with the increase in the S. Moreover, calcium ions can replace sodium ions in N-A-S-H gels to produce C-A-S-H with higher density [34], which leads to an increase in the strength of the CGBGM. In stark contrast, the W/B exhibits a noticeably contradictory tendency compared to the conventional Portland-based concrete. Compared with the W/B0.45 group, the flexural and compressive strength of the W/B0.60 group decreased by 47.89% and 31.48%, respectively. This is attributed to the alkali concentration in the CGBGM system gradually decreasing, thereby restarting the hydration reaction rate. Furthermore, the free water in the CGBGM system also dramatically increased, which could produce a water film on the aggregate surface. Therefore, the local increases in the W/B inevitably compromise the compactness of the aggregate/matrix interface, thereby degrading the macroscopic strength of the CGBGM.

Additionally, it is also found that the tension/compression performances of the CGBGM are superior to the OPCM, irrespective of the W/B. In particular, when the W/B is 0.5, the flexural and compressive strength of the geopolymer-based composites were 1.42 times and 1.23 times that of the standard Portland-based group. This phenomenon was attributed to the fact that the primary hydration products of geopolymer-based composites were (Ca, N)-A-S-H gels, which were filled with each other to form a more compact structure [18].

![Flexural strength comparison](attachment:figure5.png)

Figure 5. Cont.
3.2.2. Relative Strength

The relative flexural and compressive strength of the CGBGM is displayed in Figure 6. It can be observed that the flexural and compressive strength of the CGBGM increases rapidly before 7 d and then tends to slow afterward. The average relative flexural strength of the CGBGM at 3 d and 7 d reached 80.73% and 91.90% at 28 d, respectively. The average relative compressive strength of the CGBGM at 3 d and 7 d reached 74.19% and 90.49% at 28 d, respectively. Additionally, the early flexural and compressive strength (≤7 d) of the CGBGM was greater than that of the OPCM. This is consistent with the results in the literature [21,35]. This is attributed to the rapid hydration reaction of geopolymer in the early stage.

Figure 5. Mechanical properties of CGBGM with different parameters: (a) flexural strength; (b) compressive strength.

Figure 6. Cont.
Figure 6. Relative strength of the CGBGM: (a) relative flexural strength; (b) relative compressive strength.

3.2.3. Influence of the $f_{cf}/f_{cu}$ Ratio

Figure 7 displays the comparison results of the $f_{cf}/f_{cu}$ ratio of the CGBGM at each curing age. The $f_{cf}/f_{cu}$ ratio gradually declined with increasing curing ages, indicating that the development of the compressive strength at the later stage was superior to that of flexural strength. The effect of the $A$ on the $f_{cf}/f_{cu}$ ratio was opposite to that on the $f_{cf}$ (or $f_{cu}$), and the $f_{cf}/f_{cu}$ ratio was the smallest when the $A = 12\%$. The $f_{cf}/f_{cu}$ ratio reached the maximum value when the $S = 30\%$. In addition, the $f_{cf}/f_{cu}$ ratio reached the maximum value when the $W/B = 0.50$, which was similar to slag content.

Figure 7. $f_{cf}/f_{cu}$ of the CGBGM.

3.3. One-Way Analysis of Variance (ANOVA)

The above results have shown that the $A$, $S$, and $W/B$ were the critical factors affecting the mechanical properties of the CGBGM. In order to evaluate the level of significance for each factor, a one-way analysis of variance (ANOVA) method was employed, which is the variance model of only one dependent variable [36]. Based on the ANOVA method,
the value of $F$ can reflect the influence of each factor on the various performances of the CGBGM, and significant analyses are displayed in Table 3.

**Table 3.** Criteria of significant analysis.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Level of Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F &gt; F_{0.01}$</td>
<td>Highly significant effect</td>
</tr>
<tr>
<td>$F_{0.01} &gt; F &gt; F_{0.05}$</td>
<td>Significant effect</td>
</tr>
<tr>
<td>$F_{0.05} &gt; F &gt; F_{0.10}$</td>
<td>Little effect</td>
</tr>
<tr>
<td>$F &lt; F_{0.10}$</td>
<td>Very little effect</td>
</tr>
</tbody>
</table>

3.3.1. Significant Analysis of the Impact Factors for Flexural Strength

According to the data in Figure 5a, an ANOVA method was employed to evaluate the level of significance of each influence factor on the flexural strength of the CGBGM at 28 days. The criteria and results of the significant analysis were displayed in Table 4. As can be seen from Tables 3 and 4, three factors were ranked according to the impact degree ($F$ value) on the flexural strength of the CGBGM, concluding that $S$ is ranked first, followed by $A$, and finally $W/B$. The level of significance of $S$ was a highly significant effect, indicating slag could dramatically enhance the flexural strength of the CGBGM. However, the levels of significance of $A$ and $W/B$ showed little effect. This is because slight changes in variables have less impact on the flexural strength of the CGBGM.

**Table 4.** Variance analysis of the flexural strength.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Sum of Squares of Deviations</th>
<th>Degree of Freedom</th>
<th>Mean Square Deviation</th>
<th>$F$</th>
<th>$F_s$</th>
<th>Level of Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S$</td>
<td>$S_A = 17.62$</td>
<td>5</td>
<td>3.52</td>
<td>22.99</td>
<td>$F_{0.01}(5,8) = 4.34$</td>
<td>Highly significant effect</td>
</tr>
<tr>
<td></td>
<td>$S_E = 1.84$</td>
<td>12</td>
<td>0.15</td>
<td></td>
<td>$F_{0.05}(3,8) = 2.81$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_T = 19.46$</td>
<td>17</td>
<td>-</td>
<td></td>
<td>$F_{0.10}(3,8) = 2.22$</td>
<td></td>
</tr>
<tr>
<td>$A$</td>
<td>$S_A = 21.89$</td>
<td>3</td>
<td>7.30</td>
<td>6.80</td>
<td>$F_{0.01}(3,8) = 27.49$</td>
<td>Little effect</td>
</tr>
<tr>
<td></td>
<td>$S_E = 8.58$</td>
<td>8</td>
<td>1.07</td>
<td></td>
<td>$F_{0.05}(3,8) = 8.84$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_T = 30.47$</td>
<td>11</td>
<td>-</td>
<td></td>
<td>$F_{0.10}(3,8) = 5.25$</td>
<td></td>
</tr>
<tr>
<td>$W/B$</td>
<td>$S_A = 1.34$</td>
<td>3</td>
<td>0.45</td>
<td>3.62</td>
<td>$F_{0.01}(3,8) = 27.49$</td>
<td>Little effect</td>
</tr>
<tr>
<td></td>
<td>$S_E = 0.99$</td>
<td>8</td>
<td>0.12</td>
<td></td>
<td>$F_{0.05}(3,8) = 8.84$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_T = 2.32$</td>
<td>11</td>
<td>-</td>
<td></td>
<td>$F_{0.10}(3,8) = 5.25$</td>
<td></td>
</tr>
</tbody>
</table>

3.3.2. Significant Analysis of the Impact Factors for Compressive Strength

According to the test results in Figure 5b, an ANOVA method was adopted to evaluate the level of significance of each influence factor on the compressive strength of the CGBGM at 28 d. The criteria and results of the significant analysis are shown in Table 5. From Tables 3 and 5, the levels of significance of $A$, $W/B$, and $S$ showed a highly significant effect, highly significant effect, and significant effect, respectively. According to the impact degree ($F$ value) on the flexural strength of the CGBGM, the $S$ is ranked first, followed by the $A$, and finally the $W/B$. Therefore, the compressive strength of the CGBGM could be dramatically enhanced by adding slag and selecting the optimal $A$ and $W/B$. However, excessive alkali and slag will dramatically accelerate the hydration reaction rate and increase the drying shrinkage of geopolymer.
### Table 5. Variance analysis of the compressive strength.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Sum of Squares of Deviations</th>
<th>Degree of Freedom</th>
<th>Mean Square Deviation</th>
<th>F</th>
<th>F&lt;sub&gt;x&lt;/sub&gt;</th>
<th>Level of Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>S&lt;sub&gt;A&lt;/sub&gt; = 957.10</td>
<td>5</td>
<td>191.42</td>
<td>58.62</td>
<td>F&lt;sub&gt;0.01&lt;/sub&gt;(3,8) = 4.34</td>
<td>Highly significant effect</td>
</tr>
<tr>
<td></td>
<td>S&lt;sub&gt;E&lt;/sub&gt; = 39.19</td>
<td>12</td>
<td>3.27</td>
<td></td>
<td>F&lt;sub&gt;0.05&lt;/sub&gt;(3,8) = 2.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S&lt;sub&gt;T&lt;/sub&gt; = 996.29</td>
<td>17</td>
<td>-</td>
<td></td>
<td>F&lt;sub&gt;0.10&lt;/sub&gt;(3,8) = 2.22</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>S&lt;sub&gt;A&lt;/sub&gt; = 473.78</td>
<td>3</td>
<td>157.93</td>
<td>33.54</td>
<td>F&lt;sub&gt;0.01&lt;/sub&gt;(3,8) = 27.49</td>
<td>Highly significant effect</td>
</tr>
<tr>
<td></td>
<td>S&lt;sub&gt;E&lt;/sub&gt; = 37.67</td>
<td>8</td>
<td>4.71</td>
<td></td>
<td>F&lt;sub&gt;0.05&lt;/sub&gt;(3,8) = 8.84</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S&lt;sub&gt;T&lt;/sub&gt; = 511.45</td>
<td>11</td>
<td>-</td>
<td></td>
<td>F&lt;sub&gt;0.10&lt;/sub&gt;(3,8) = 5.25</td>
<td></td>
</tr>
<tr>
<td>W/B</td>
<td>S&lt;sub&gt;A&lt;/sub&gt; = 105.15</td>
<td>3</td>
<td>35.05</td>
<td>16.03</td>
<td>F&lt;sub&gt;0.01&lt;/sub&gt;(3,8) = 27.49</td>
<td>Significant effect</td>
</tr>
<tr>
<td></td>
<td>S&lt;sub&gt;E&lt;/sub&gt; = 17.49</td>
<td>8</td>
<td>2.19</td>
<td></td>
<td>F&lt;sub&gt;0.05&lt;/sub&gt;(3,8) = 8.84</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S&lt;sub&gt;T&lt;/sub&gt; = 122.65</td>
<td>11</td>
<td>-</td>
<td></td>
<td>F&lt;sub&gt;0.10&lt;/sub&gt;(3,8) = 5.25</td>
<td></td>
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</table>

#### 3.4. Microstructure Analysis

The microstructure, morphology, element types, and qualitative microanalysis of the CGBGM were investigated and analyzed by a scanning electron microscope (SEM) and X-ray energy dispersive spectrometer (EDS), as shown in Figure 8. A large number of microcracks and pores were randomly distributed on the sample at 3 d. However, those pores and cracks nearly disappeared after 28 d. The polymerization reactions of the CGBGM produced higher proportions of intersected sodium aluminosilicate hydrate (N-A-S-H) and calcium aluminosilicate hydrate (C-A-S-H) gels and smaller proportions of orientated calcium hydroxide (CH) and needle ettringite (AFt) [18]. The hydration productions filled in the crevices and healed the entrapped microcracks in the hardened paste. Therefore, the CGBGM exhibits a more refined microstructure and superior mechanical properties than OPCM with the same water-to-binder ratio.

![SEM and EDS results of the CGBGM: (a) 3 d; (b) 28 d.](image)
Moreover, the EDS results indicated that the primary elements of the hydration products detected in the CGBGM were oxygen, calcium, sodium, aluminum, and silicon elements. With the increase in curing ages, the calcium-to-silicon ratio (Ca/Si) decreased from 0.5 to 0.06, and the calcium-to-aluminum ratio (Ca/Al) decreased from 0.25 to 0.05. Therefore, many aluminosilicate products are generated during the curing process, which is consistent with the conclusion in the literature [32,35].

3.5. Drying Shrinkage

Figure 9 displays the differences in the mass-loss rate and drying shrinkage of the OPCM and CGBGM. It can be seen that the mass-loss rate and drying shrinkage of the OPCM and CGBGM exhibit a positive correlation with curing age. The curve of the mass-loss rate and drying shrinkage with curing age can be divided into the rapid increase, slow increase, and stabilization stages. Compared to the OPCM, the CGBGM has a higher mass-loss rate and drying shrinkage. The mass-loss rate and drying shrinkage of the CGBGM at 180 d increased by 95.20% and 78.08%, respectively. This is because the geopolymer system contains more free water than the cement-based material system [21]. Previous studies found that the drying shrinkage of low-calcium geopolymers was primarily caused by the evaporation of internal water [37,38]. Moreover, the low-calcium geopolymers are denser than cement-based materials, and there are many capillary pores. Therefore, the free water will rapidly evaporate when it is placed in a dry environment after hardening, leading to greater capillary pressure and more significant drying shrinkage [39,40]. The high drying shrinkage was an important factor limiting the wide application of the CGBGM. Ma et al., found that the dry shrinkage of the CGBGM is 2.01–3.05 times that of the OPCM [21]. Wang et al., implied that fly ash and MgO expansive agent could effectively reduce the drying shrinkage of face slab concrete [41-43]. Thereby, several methods of reducing drying shrinkage were recommended to be applied in the preparation of the CGBGM, such as shrinkage-reducing admixture, fibers, expansive admixture, and water-retaining admixture [44-46].

![Figure 9. Difference in drying shrinkage behavior of the OPCM and CGBGM: (a) mass-loss rate; (b) drying shrinkage.](image)

4. Conclusions

The following crucial conclusions could be drawn:

1. Compared with the OPCM, the CGBGM has higher compressive strength, flexural strength, and early strength. The flexural and compressive strength of the W/B0.50 group increased by 42.13% and 22.60%, respectively. The flexural and compressive strength of the CGBGM rapidly increases before 7 d and then tends to slow afterward. In addition, the $f_{\text{cf}}/f_{\text{cu}}$ ratio gradually declined as the curing time developed.
(2) According to the impact degree on the mechanical properties of the CGBGM, the A is ranked first, followed by the W/B, and finally the S. The slag can dramatically enhance the mechanical properties of the CGBGM. The flexural and compressive strength of specimens with 40% slag increased by 45.97% and 90.75%, respectively, compared to the control group. However, the A and W/B have little effect on flexural strength.

(3) With the increase in curing ages, the hydration productions filled in the crevice and healed the entrapped microcracks in the hardened paste, forming a dense microstructure. In addition, the calcium-to-silicon ratio (Ca/Si) decreased from 0.5 at 3 d to 0.06 at 28 d, and the calcium-to-aluminum ratio (Ca/Al) decreased from 0.25 at 3 d to 0.05 at 28 d.

(4) Compared with the OPCM, the mass-loss rate and drying shrinkage of the CGBGM were greater than those of the OPCM. The mass-loss rate and drying shrinkage of the CGBGM at 180 d increased by 95.20% and 78.08%, respectively. Additionally, the drying shrinkage behavior curve of the CGBGM includes three stages: rapid increase, slow increase, and stabilization.

Author Contributions: Conceptualization, Y.Z.: Writing—original draft, Y.Z.: Supervision, C.Y. (Caiqian Yang) and Z.W.; Project administration, C.Y. (Caiqian Yang) and Z.W.; Resources, C.Y. (Chengyu Yan) and J.Y.; Data curation, C.Y. (Chengyu Yan) and J.Y. All authors have read and agreed to the published version of the manuscript.

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References
1. Li, Y.; Yao, Y.; Liu, X.M.; Sun, H.H.; Ni, W. Improvement on pozzolanic reactivity of coal gangue by integrated thermal and chemical activation. Fuel 2013, 109, 527–533. [CrossRef]
2. Peng, B.; Li, X.; Zhao, W.; Yang, L. Study on the release characteristics of chlorine in coal gangue under leaching conditions of different pH values. Fuel 2018, 217, 427–433. [CrossRef]
10. Ivanikov, A.L.; Kongar-Syuryun, C.; Rybak, J.; Tyulyaeva, Y. The reuse of mining and construction waste for backfill as one of the sustainable activities. IOP Conf. Ser. Earth Environ. Sci. 2019, 362, 012130. [CrossRef]


33. Fractal Fract. 2015, 2, 335. [CrossRef]


41. Fractal Fract. 2015, 2, 335. [CrossRef]


44. Fractal Fract. 2015, 2, 335. [CrossRef]


46. Fractal Fract. 2015, 2, 335. [CrossRef]

47. Fractal Fract. 2015, 2, 335. [CrossRef]

48. Fractal Fract. 2015, 2, 335. [CrossRef]

49. Fractal Fract. 2015, 2, 335. [CrossRef]