Research Article
Study on Rheological Mechanism of Cement-Coal Gangue Cementitious Material (CGCM) Slurry

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To explore the rheological mechanism of cement-coal gangue cementitious material (CGCM) slurry, the effects of the activation temperature (500°C-900°C) of coal gangue on the initial fluidity, plastic viscosity (η₀), and yield stress (τ₀) of CGCM slurry were considered, the variation laws of rheological parameters of CGCM slurry at different hydration ages were compared, and the rheological equations of CGCM slurry were established in this study. The results show that the rheological law of the CGCM slurry conforms to the modified Bingham model, and the significant shear thinning occurs in the CGCM slurry at low-shear speed, and relatively weak shear thickening occurs in the CGCM slurry at high-shear speed; under the thermal activation temperature of 800°C, the pozzolanic activity of coal gangue reaches the highest, the hydration reaction is the fastest, and the initial fluidity of CGCM slurry at 800°C is the lowest; the plastic viscosity of CGCM slurry increases gradually with the increase of thermal activation temperature of coal gangue, and the yield stress of the CGCM slurry reaches the maximum at 800°C; the flow law of CGCM slurry has significant time-varying characteristics, and the plastic viscosity and yield stress of CGCM slurry increase gradually with the extension of hydration time. This study shows that the fluidity of coal gangue cement slurry has significant time-varying characteristics, which can provide effective theoretical support for the accurate application of coal gangue cement in grouting engineering.

1. Introduction

Grouting reinforcement of surrounding rock/broken rock is inevitable in the underground engineering such as tunnel construction and roadway support [1–4]. In the research of grouting theory, the flow law of slurry in cracks and crevices of rock and soil is a key scientific problem. The physical and mechanical properties of slurry largely determine the diffusion radius, grouting time, and other key grouting parameters. According to the rheological theory, the properties of slurry change with the change of flow time [5] and stress state. Therefore, the rheological properties of slurry properties should be considered in the iterative calculation of the model, so as to greatly narrow the gap between theoretical calculation and engineering practice [6].

Cement-based material is the most widely used grouting material at present. It has the advantages of great fluidity, adjustable time setting, and strong adaptability, but it also has the disadvantages of poor slurry stability and easy precipitation [7]. In addition, the cement-based material is easily stuck at small cracks due to the large diameter of cement particles [8]. At present, composite cement-based materials have been made by adding industrial by-products (such as fly ash and slag) into cement-based material to further reduce the grouting cost [9, 10]. To improve the grouting performance, in-depth research on cement-based grouting materials has been widely conducted. Through the preparation of grouting materials with sulfoaluminate cement, Wang found that adding 1.0% nano-SiO₂ can significantly improve the fluidity of grouting materials and better meet the engineering requirements [11]. Liang studied the strength of cement-based grouting material with different nanosilica contents at a certain age. The results show that when the content of nanosilica is low, the flexural strength and compressive strength of cement-based grouting materials increase with the increase of the nanosilica content;
however, with the increase of the nanosilica content, the flexural strength and compressive strength of cement-based grouting materials decrease [12]. Zhang researched the mechanical properties of the cement-based grouting material reinforced with the plasma-functionalized graphene fiber (PGF). It is reported that the compressive strength and flexural strength of aluminum sulfate cement grouting materials with the water-cement ratio of 0.8 and PGF dosage of 0.3% are increased by 1.1 times and 1.3 times, respectively, and the electrical conductivity of this composite material is also significantly improved [13]. Taking cement, polyethylene glycol (PEG) 200, sodium silicate, and polycarboxylate superplasticizer (PS) as raw materials, Zhang developed a novel grouting material with a water-cement ratio of 1, the PEG200 content of 2%, the sodium silicate content of 10%, and the PS content of 0.2%. In the modified cement-sodium silicate grouting material (C-S-P), a three-dimensional network structure is formed with high stability, good pumpability, great initial compressive strength, and relatively low permeability [14]. Zhang designed the ultra-fine cement-based grouting mixed with ultra-fine fly ash (MFA), nanocalcium carbonate (NC), and superplasticizers (SP). Through the test, it is found that adding MFA and 1.5% SP can prolong the setting time and improve the fluidity and spreading capacity of fresh slurry. The addition of NC can increase the yield stress and plastic viscosity of the fresh slurry and reduce the fluidity and spreading ability of the fresh slurry, but it significantly improves the stability of slurry and shortens the setting time of slurry. The addition of MFA and 1.5% SP reduces the compressive strength of the hardened grouting, while the addition of NC improves the mechanical properties of the material [15]. He claimed that the mechanical properties of cement-based iron-tailings grouting material (ICGM) decrease with the increase of the water-cement ratio. When the water-cement ratio reaches 0.31, the early strength of the ICGM slurry decreases significantly; therefore, it is determined that the reasonable water-cement ratio should be 0.30 [16].

Traditional grouting theories, including spherical diffusion theory, cylindrical diffusion theory, and sleeve casing method theory, aim to establish the relationship between grouting pressure, flow, setting time, and grouting time [17]. In these classical theories, the slurry is simplified as a Newtonian fluid, and the viscosity of the slurry is considered to be a constant under certain environmental conditions. With the deepening of research, it is found that the viscosity of slurry changes with time, shear rate, and other factors [18]. Through numerical simulation method, Xiang-yang et al. simulated the flow law of cement-sodium silicate grout (C-S) in splitting grouting based on the Bingham model and fully considered the variation law of C-S slurry viscosity with time [19]. Yuan believed that the grouting flow pattern and rheological parameters determine the grouting pressure transmission process of the annular tail tunnel and the filling rate of the shield tail tunnel and performed the research by using the orthogonal experimental design method. It is found that the flow mode of cement mortar is basically consistent with the Bingham fluid, and the plastic viscosity changes within 1-4 Pa-s, and the shear yield stress changes within 10-40 Pa. Water-binder ratio and the water content of bentonite are the key factors affecting the rheological parameters of slurry. With the increase of the water-binder ratio and the decrease of the water content of bentonite, the plastic viscosity and shear yield stress of slurry decreases [20]. Rahman believed that the rheological properties of the cement-based grouting change with the change of water-cement ratio and time during hydration and measured the rheological properties of common cement grouting by ultrasound velocity profiling combined with the pressure difference (UVP + PD) method. The results obtained are consistent with those obtained by the Bingham and the Herschel-Bulkley rheological models [21]. Therefore, it is necessary to consider the rheological and time-varying characteristics of slurry viscosity in the theoretical model to improve the accuracy and practicability of the grouting theory.

However, there are few reports on coal gangue cement as grouting material in relevant research. By means of thermal activation, mechanical activation, and chemical activation, the considerable pozzolanic activity can be obtained from coal gangue and then used as a substitute for cement. This is of great significance to effectively consume coal gangue and alleviate the environmental harm caused by coal gangue accumulation. Taking the grouting of broken rock as the research background, coal gangue was mechanically and thermally activated and used to substitute some ordinary Portland cement in this study, and then the rheological properties of cement-coal gangue cementitious material (CGCM) slurry were investigated under different calcination temperatures. This study aims to demonstrate the characteristics of coal gangue as grouting material from the perspective of rheology.

2. Materials and Methodology

2.1. Raw Materials. According to common Portland cement (GB175-2007), the ordinary Portland cement (OPC) with a strength grade of 42.5 produced by Xuzhou Zhonglian Cement Co., Ltd. was used, and the unburned coal gangue (CG) taken from Xuzhou Longdong Coal Mine was selected in this test. The fixed carbon content was 3.54%, and the calorific value was 1620 KJ/Kg. The unburned coal gangue provided part of the energy source during the calcination process. Table 1 shows the chemical compositions of OPC and CG. Tap water was used in the test.

At the same time, an appropriate amount of water-reducing agent (Sika ViscoCrete 3301c) produced by Sika Jiangsu Building Material Ltd. was used to ensure the fluidity of the slurry when measuring the time fluidity.

The particle sizes of OPC and CG were measured by the Winner 802 nano-laser particle sizer. As shown in Figure 1, the fine particle content of CG is significantly higher than that of OPC. The existence of fine particles can promote the early hydration reaction.

2.2. Preparation of Cement Paste. To study the effect of thermal activation temperature on the fluidity of CGCM slurry, coal gangue was crushed, ground, and calcined at 500°C,
During the calcination process, the heating rate was 5°C/min, and the temperature was kept for 3 hours after reaching the set temperature. Subsequently, the materials were taken out of the furnace, quenched in air, and sealed for standby. Figure 2 shows the apparent characteristics of CG after different calcination.

<table>
<thead>
<tr>
<th>Materials</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
<th>Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC (%)</td>
<td>25.59</td>
<td>7.49</td>
<td>3.49</td>
<td>52.62</td>
<td>2.58</td>
<td>0.30</td>
<td>1.45</td>
<td>2.16</td>
<td>2.7</td>
</tr>
<tr>
<td>CG (%)</td>
<td>60.24</td>
<td>18.50</td>
<td>2.58</td>
<td>1.48</td>
<td>0.52</td>
<td>0.14</td>
<td>1.53</td>
<td>0.61</td>
<td>12.41</td>
</tr>
</tbody>
</table>

**Table 1: Chemical composition of raw materials/(wt%).**

![Cumulative curve](image1.png)

**Figure 1:** Particle size distribution of OPC and CG.

![Distribution curve](image2.png)
temperatures. With the increase of calcination temperature, the apparent color of CG gradually transits from dark brown to milky white.

CG at different calcination temperatures of 500°C, 600°C, 700°C, 800°C, and 900°C were fully mixed with OPC at a mass substitution rate of 30wt% and named as CGCM 500°C, CGCM 600°C, CGCM 700°C, CGCM 800°C, and CGCM 900°C, respectively. The pure OPC slurry was set as the control group. The water-cement ratio was set at 0.5, the powder content of each group of the slurry was 600g, and 1.0 g water-reducing agent was added into the slurry. The slurry was mixed in the JJ-5 cement mortar mixer. Firstly, water containing water reducer was poured, then CGCM was added, mixed at a low speed (revolution speed: 62 ± 5 r/min; rotation speed: 140 ± 5 r/min) for 1 min, and then mixed at a high speed (revolution speed: 125 ± 10 r/min; rotation speed: 285 ± 10 r/min) for 1 min. Then, the mixer was rested for 0.5 minutes. During this period, a rubber wedge was used to scrape off the material adhered to the side wall of the mixing container. After that, the CGCM slurry was stirred in high-speed mode for 1 minute further, and then the fresh grouting sample was prepared. All samples were prepared at the temperature of (20 ± 2) °C and the humidity of (70 ± 5)%.

2.3. Methodology

2.3.1. Flow Characteristics. According to Method for Testing the Uniformity of Concrete Admixtures (GB/T8077-2012), the fluidity of the fresh slurry was measured by truncated cone circular mold test (upper diameter: 36 mm; lower diameter: 60 mm; and height: 60 mm) to characterize the fluidity difference of the slurry. The initial fluidity of fresh slurry was measured at the ambient temperature of (20 ± 2 ) °C. The mixed slurry was quickly poured into the truncated cone circular mold and scraped with a scraper; the truncated cone circular mold was lifted in the vertical direction, and the timing was started. When the slurry flowed on the glass plate for 30s, a ruler was used to measure the maximum diameters in two directions perpendicular to each other, and the average value was taken as the freshly mixed fluidity.

2.3.2. Rheological Test. The Brookfield rheometer was used in the rheological test, and the spindle VT-60-30 was used. The shear rate was increased from 0 to 100 rpm within 150 s, and the shear rate of 100 rpm was kept for 30 s; then the shear rate was decreased to 0 rpm within 150 s. During the whole test process, one data point was taken at an interval of 2 s. After the test of fresh slurry was completed, the rheological test was carried out again after slurry standing for 30 min and 60 min. The shear stress-shear rate curve of slurry can be obtained by rheological tests. The rheological parameters of yield stress (τ₀) and plastic viscosity (η₀) are widely used to characterize the rheological properties of cement paste. These two parameters can be obtained by fitting the intercept and slope of the curve, and the relationship between shear stress and shear rate can be expressed by the Bingham model:

\[ \tau = \tau_0 + \eta_0 \gamma, \]

where \( \tau \) is the shear stress (Pa), \( \gamma \) is the shear rate (s⁻¹), \( \tau_0 \) is the yield shear stress (Pa), and \( \eta_0 \) is the plastic viscosity (Pa·s).

The research has shown that with the increase of the shear rate, the relationship of shear stress and shear rate of some cement-based materials mixed with superplasticizers gradually deviate from the linear relationship, showing the rheological characteristics of shear thickening. Therefore, an improved Bingham model is proposed as follows:

\[ \tau = \tau_0 + \eta_0 \gamma + c \gamma^2, \]

where \( \tau \) is the shear stress (Pa), \( \gamma \) is the shear rate (s⁻¹), \( \tau_0 \) is the yield shear stress (Pa), \( \eta_0 \) is the plastic viscosity (Pa·s), and \( c \) is the constant.

When the Bingham model or the improved Bingham model is used for curve fitting, the down curve is usually employed for curve fitting.

2.3.3. Particle Micromorphology Test. The microstructure of ordinary Portland cement (OPC) and thermal activated coal gangue (CG) were observed by scanning electron microscope in this study. The Hitachi SU8220 was used as the tungsten lamp scanning electron microscope.

3. Results and Discussion

3.1. The Effect of CG on the Fluidity of CGCM. The effect of calcination temperature on the initial fluidity of CGCM slurry is obtained, as shown in Figure 3. It can be seen that the fluidity of pure OPC slurry is 213 mm. With the addition of 30% calcined coal gangue at 500°C, the initial fluidity of CGCM slurry decreases by 10.3% compared with the pure OPC slurry; with the increase of calcination temperature of coal gangue, the initial fluidity of CGCM slurry further decreases. When the calcination temperature is 800°C, the initial fluidity of CGCM slurry is the lowest (155 mm); compared with OPC slurry, the initial fluidity of CGCM slurry with the coal gangue at a calcination temperature of 800°C decreases by 27.2%. When the calcination temperature of coal gangue is 900°C, the initial fluidity of CGCM slurry increases to 164 mm, which is about 6% higher than the minimum initial fluidity of CGCM slurry with the coal gangue at a calcination temperature of at 800°C.
3.2. Effect of CG on Rheological Properties of CGCM Slurry

3.2.1. Rheological Curve and Time-Dependent Rheological Curve of Fresh Slurry. Figure 4 shows the time-dependent rheological curves of CGCM slurry mixed with CG at different calcination temperatures. Specifically, there are rheological curves at three time nodes: 5-minute hydration (fresh slurry), 30-minute hydration (end of induction period), and 60-minute hydration (before initial setting of slurry). As shown in Figure 4(a), it can be seen from the rheological curve of 5-minute hydration that the shear stress of CGCM slurry increases with the increase of shear rate. When the calcination temperature of CG is in the range of 500°C-800°C, the shear stress of CGCM slurry at the same shear rate increases gradually with the increase of calcination temperature, and it is greater than that of the pure OPC slurry. When the shear rate is less than 50 rpm, the shear stress of CGCM slurry mixed with CG at 900°C is lower than that of CGCM slurry mixed with CG at 800°C but higher than that of other groups. This is because with the increase of activation temperature, the activity of coal gangue gradually increases and reaches a peak at 800°C [22, 23]. At this time, the hydration reaction of fresh composite slurry is the fastest; the formation of a large number of flocculent structures leads to the rapid thickening of slurry and the increase of shear stress of slurry. However, when the thermal activation temperature of CG exceeds 800°C, the activity of CG decreases significantly, the interaction force between particles in the fresh slurry decreases greatly, and the shear stress of the slurry decreases. When the shear rate exceeds 50 rpm, the shear stress of the CGCM slurry mixed with CG at 900°C increases rapidly, which is significantly higher than that of other groups; its shear rate-shear stress curve shows a nonlinear trend.

When the shear rate is less than 70 rpm, the change law of the rheological curve of the CGCM slurry after 30-minute hydration is consistent with that of the CGCM slurry after 5-minute hydration. When the shear rate exceeds 70 rpm, the shear stress of CGCM 900°C exceeds that of CGCM 800°C. The shear stress curves of the CGCM slurry mixed with CG at 500°C, 600°C, and 700°C intersect and have similar values, and the growth of shear stress shows a nonlinear trend.

When the hydration time is extended to 60 min and the calcination temperature is less than 900°C, the shear stress of CGCM slurry increases gradually with the increase of calcination temperature at the same shear rate, and the growth law is basically consistent with that of CGCM slurry after
Figure 4: Continued.
5-minute and 30-minute hydration. When the shear rate exceeds 80 rpm, the shear stress of CGCM 900°C exceeds that of the CGCM 800°C. Similarly, the shear stress curves of CGCM slurry at 500°C, 600°C, and 700°C show a nonlinear trend.

3.2.2. Viscosity Curve and Time-Varying Viscosity Curve of Fresh Slurry. Figure 5 shows the time-varying viscosity curves of CGCM slurry. It can be seen from the figure that the apparent viscosity of CGCM slurry decreases with the increase of shear rate, and its variation is characterized by “sharply decrease at a low shear rate and be stable at a high shear rate”; the apparent viscosity of CGCM slurry is greater than that of OPC slurry in the control group. Due to the action of the water-reducing agent, the fluidity of OPC slurry after 5-minute hydration is too high, the viscosity of the fresh slurry is almost zero, and the effective data at low speed are not collected. The apparent viscosity of OPC slurry does not change significantly with the increase of shear rate, and the curve is almost parallel to the horizontal coordinate axis. When the calcination temperature of CGCM slurry with hydration age of 5 min is in the range of 500°C-800°C, the apparent viscosity curves of CGCM slurry at different hydration ages are basically consistent; that is, at the same shear rate, the apparent viscosity increases gradually with the increase of calcination temperature of CG. However, the apparent viscosity of CGCM 900°C shows different development laws. When the hydration age is 5 min and the shear rate is less than 5 rpm, the apparent viscosity of CGCM 900°C is lower than that of CGCM 700°C and CGCM 800°C. When the shear rate is in the range of 5 rpm-50 rpm, the apparent viscosity of CGCM 900°C is medium between those of CGCM 700°C and CGCM 800°C; with the increase of shear rate, the viscosity of CGCM 900°C is higher than that of CGCM 800°C, but the change tends to be gentle, and shear thickening occurs. This is because after the thermal activation temperature exceeds 800°C, the activity of coal gangue decreases obviously, and the water-reducing agent can be fully adsorbed on the surface of particles, so that the particles of cementitious materials are evenly dispersed in the slurry. Therefore, at a low shear rate, the shear thinning of slurry is significantly weakened compared with that in other groups. Due to the shear stress at high shear rate, the ordered distribution state of cementitious material particles are changed into a disordered distribution, the “particle clusters” are formed by particle combinations, and the “ion clusters” are easily generated and quickly developed. As a result, the slurry consumes more energy during flow, and the apparent viscosity increases and presents the phenomenon of shear thickening.

With the extension of hydration time, the apparent viscosity of CGCM slurry at the same calcination temperature and shear rate gradually increases. The change rule of rheological curves of CGCM slurry after 30-minute (Figure 5(b)) and 60-minute (Figure 5(c)) hydration are basically consistent with those of CGCM slurry after 5-minute hydration; that is, the plastic viscosity increases with the progress of hydration and the increase of flocculation structure in the slurry.

3.2.3. The Rheological Model of CGCM Slurry. With the simplest calculation, the Bingham model is a common model of cement-based materials and can better meet the requirements of the measurement accuracy of rheological parameters in engineering. However, it is found that (I) in the case of large fluidity,
Figure 5: Continued.
the yield stress fitted by the Bingham model will have a negative value and lose its physical significance. (II) The shear rate and shear stress of cement-based materials mixed with superplasticizer gradually deviate from the linear relationship. Therefore, the modified Bingham model is adopted in processing the test data, and the obtained rheological curve of CGCM slurry is consistent with the measured curve. The plastic viscosity (\(\eta_0\), Pa·s) and yield stress (\(\tau_0\), Pa) of slurry can be obtained from the fitted curve equation in Table 2. These two parameters are important indexes to characterize the rheological properties of the slurry.

![Graph showing apparent viscosity vs. shear rate for different groups](image)

**Figure 5:** Time viscosity curve of fresh slurry mixed with heated-activated coal gangue.

**Table 2:** Fitting results of the modified Bingham rheological model of CGCM slurry.

<table>
<thead>
<tr>
<th>Group</th>
<th>Fitting formula</th>
<th>(R^2)</th>
<th>(\eta_0)/Pa·s</th>
<th>(\tau_0)/Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC-0 min</td>
<td>(y = 0.0022x^2 + 0.0018x + 0.0112)</td>
<td>0.9984</td>
<td>0.0018</td>
<td>0.0112</td>
</tr>
<tr>
<td>OPC-30 min</td>
<td>(y = 0.002x^2 + 0.0075x + 0.8654)</td>
<td>0.9997</td>
<td>0.0075</td>
<td>0.8654</td>
</tr>
<tr>
<td>OPC-60 min</td>
<td>(y = 0.0024x^2 + 0.0162x + 1.0732)</td>
<td>0.9993</td>
<td>0.0162</td>
<td>1.0732</td>
</tr>
<tr>
<td>CGCM 500°C-0 min</td>
<td>(y = 0.0037x^2 + 0.0028x + 3.1987)</td>
<td>0.9994</td>
<td>0.0028</td>
<td>3.1987</td>
</tr>
<tr>
<td>CGCM 500°C-30 min</td>
<td>(y = 0.0041x^2 + 0.0189x + 7.7544)</td>
<td>0.9969</td>
<td>0.0189</td>
<td>7.7544</td>
</tr>
<tr>
<td>CGCM 500°C-60 min</td>
<td>(y = 0.003x^2 + 0.1322x + 10.569)</td>
<td>0.9954</td>
<td>0.1322</td>
<td>10.569</td>
</tr>
<tr>
<td>CGCM 600°C-0 min</td>
<td>(y = 0.0039x^2 - 0.0034x + 7.281)</td>
<td>0.997</td>
<td>0.0034</td>
<td>7.281</td>
</tr>
<tr>
<td>CGCM 600°C-30 min</td>
<td>(y = 0.0033x^2 + 0.0642x + 9.9746)</td>
<td>0.9924</td>
<td>0.0642</td>
<td>9.9746</td>
</tr>
<tr>
<td>CGCM 600°C-60 min</td>
<td>(y = 0.0022x^2 + 0.1671x + 11.958)</td>
<td>0.9941</td>
<td>0.1671</td>
<td>11.958</td>
</tr>
<tr>
<td>CGCM 700°C-0 min</td>
<td>(y = 0.0038x^2 + 0.0191x + 8.1484)</td>
<td>0.9959</td>
<td>0.0191</td>
<td>8.1484</td>
</tr>
<tr>
<td>CGCM 700°C-30 min</td>
<td>(y = 0.0029x^2 + 0.0962x + 11.196)</td>
<td>0.992</td>
<td>0.0962</td>
<td>11.196</td>
</tr>
<tr>
<td>CGCM 700°C-60 min</td>
<td>(y = 0.0017x^2 + 0.2199x + 13.142)</td>
<td>0.9965</td>
<td>0.2199</td>
<td>13.142</td>
</tr>
<tr>
<td>CGCM 800°C-0 min</td>
<td>(y = 0.0008x^2 + 0.277x + 16.041)</td>
<td>0.9937</td>
<td>0.277</td>
<td>16.041</td>
</tr>
<tr>
<td>CGCM 800°C-30 min</td>
<td>(y = 0.0003x^2 + 0.4067x + 19.427)</td>
<td>0.997</td>
<td>0.4067</td>
<td>19.427</td>
</tr>
<tr>
<td>CGCM 800°C-60 min</td>
<td>(y = 0.0003x^2 + 0.4462x + 21.624)</td>
<td>0.9976</td>
<td>0.4462</td>
<td>21.624</td>
</tr>
<tr>
<td>CGCM 900°C-0 min</td>
<td>(y = 0.0026x^2 + 0.3879x + 6.1112)</td>
<td>0.9986</td>
<td>0.3879</td>
<td>6.1112</td>
</tr>
<tr>
<td>CGCM 900°C-30 min</td>
<td>(y = 0.0013x^2 + 0.4984x + 7.586)</td>
<td>0.9998</td>
<td>0.4984</td>
<td>7.586</td>
</tr>
<tr>
<td>CGCM 900°C-60 min</td>
<td>(y = 0.0014x^2 + 0.5292x + 8.1296)</td>
<td>0.9995</td>
<td>0.5292</td>
<td>8.1296</td>
</tr>
</tbody>
</table>
3.2.4. Effect of Thermally Activated Coal Gangue on the Yield Stress of CGCM Slurry. Figure 6 shows the variation law of yield stress of the pure OPC slurry in the control group and CGCM slurry mixed with coal gangue at different calcination temperatures. As shown in Figure 6, when the hydration age is 5 min, the yield stress of the pure OPC slurry in the control group is very small (0.01112 Pa), and the OPC slurry after 5-minute hydration can be considered as a Newtonian fluid. The yield stress of CGCM slurry with calcined CG at 500°C is 3.1987 Pa, which is about 287% higher than that of the pure OPC slurry. It indicates that the addition of calcined CG has a significant effect on the rheological properties of the slurry. Compared with the CGCM 500°C, the yield stress of CGCM 600°C slurry increases from 3.1987 to 7.281, increasing by about 128%. Compared with CGCM 600°C, the CGCM 700°C increases by about 11.9%, and the growth tends to be flat. The yield stress of CGCM 800°C increases to the peak value (16.041 Pa). When the calcination temperature is raised to 900°C, the yield stress of CGCM decreases significantly to 6.1112 Pa, decreasing by about 61.9%.

With the extension of hydration time, the yield stress of the pure OPC slurry in the control group increases, and the slurry is transformed from Newtonian fluid to non-Newtonian fluid. However, the yield stress of CGCM slurry at the calcination temperature of 800°C also reaches the peak; compared with the yield stress of CGCM slurry after 5-minute hydration, the yield stress of CGCM slurry after 30-minute and 60-minute hydration increases by 21.1% and 34.8%, respectively.

3.2.5. Effect of Thermally Activated Coal Gangue on Plastic Viscosity of CGCM Slurry. Figure 7 shows the variation law of plastic viscosity of the pure OPC slurry in the control group and CGCM slurry mixed with CG at different calcination temperatures. It can be seen from the figure that the plastic viscosity of OPC slurry and CGCM slurry increases with the extension of hydration age. At the same hydration age, the plastic viscosity of CGCM slurry increases with the increase of the calcination temperature of CG, and the plastic viscosity of CGCM slurry increases significantly at 800°C compared with that at 700°C. Specifically, the apparent viscosity of CGCM 700°C after 0-minute, 30-minute, and 60-minute hydration is 0.0191, 0.0962, and 0.2199 and that of CGCM 800°C is 0.277, 0.4067, and 0.4462, increasing by about 0.26 Pa·s (+1350%), 0.31 Pa·s (+323%), and 0.23 Pa·s (+103%), respectively. When the CG calcination temperature continues to increase to 900°C, the plastic viscosity of CGCM slurry increases gently.

4. Mechanism Analysis

4.1. Rheological Property Mechanism of Cement. After the cement is mixed with water, a large number of flocculation structures are formed between various particles due to the attraction of anisotropic charges, thermal movement, mutual collision and adsorption, van der Waals gravity, and other reasons. These flocculation structures are connected with each other to form a continuous whole, and they are wrapped with a lot of mixing water when they are formed. When the test rotor in the rheometer is rotating, the fresh slurry is subjected to shear force, and the flocculation structure is constantly damaged. At the beginning of the test, the shear rate is low, the flocculation structure is less damaged, and the shear stress increases.
rapidly with the increase of rotating speed; with the increase of shear rate, the damaged flocs increase, the resistance of flocs to the rheometer rotor is reduced, and the shear stress changes gently with the change of shear rate (as shown in Figure 4). At the same time, because there are many floculation structures in the initial stage, the apparent viscosity of the slurry is high, and the number of the damaged floculation structures after the running of the rheometer rotor increases, and the apparent viscosity of the slurry decreases sharply, which is characterized by shear thinning. Subsequently, with the increase of shear rate, most of the floculation structure has been destroyed, and the apparent viscosity of the slurry changes gently with the speed (as shown in Figure 5).

The main reason for the shear thinning of cement-based materials is that the network floculation structure produced by hydration in the slurry is gradually destroyed under shear, resulting in the decrease of apparent viscosity. In addition, the Brownian motion of particles with particle size below microns in the system increases the repulsive force between particles. Under the action of shear force, the particles are arranged into a layered structure (which is most conducive to fluid motion), and then shear thinning can be caused.

4.2. Mechanism of CG Effect on the Rheological Properties of CGCM Slurry. Thermal activation makes coal gangue have certain pozzolanic activity, and the activity produced by different calcination temperatures is quite different. The main mineral phase of coal gangue is kaolinite with high content [24–26]. Kaolinite is dehydrated at 500°C-800°C to form amorphous metakaolinite, which contains a large amount of amorphous active Al₂O₃ and SiO₂. These amorphous silicon aluminum oxides undergo hydration reaction under the action of Ca(OH)₂, CaSO₄, and water to coagulate and harden the slurry, which is the main source of activating the activity of coal gangue.

The addition of thermally activated coal gangue accelerates the rate and volume of floculation structure in the fresh slurry to varying degrees. At the same time, there is a high content of ultra-fine particles of activated coal gangue (as shown in Figure 1), which also promotes the generation of floculation structure in fresh slurry. Compared with the pure OPC slurry, the yield stress and plastic viscosity of the CGCM slurry mixed with activated coal gangue increase to different degrees. With the increase of activation temperature, the activity of coal gangue gradually increases and reaches the peak at 800°C. At this time, the hydration reaction of fresh composite slurry is the fastest. The formation of a large number of floculent structures leads to the rapid thickening of slurry and the increase of shear stress of slurry. However, when the thermal activation temperature exceeds 800°C, the activity of coal gangue decreases significantly, the amount of floculation structure of fresh CGCM slurry also decreases, the interaction between particles decreases greatly, and the shear stress of slurry decreases.

4.3. Effect of Particle Morphology on the Rheological of the Cement Paste. It is well known that the shape and surface roughness of particles have an important influence on the rheological properties of the slurry. Figure 8 shows the
micromorphology of OPC, CG, and thermally activated CG particles. As shown in Figure 8, the sphericity of cement particles is low, but the structure is dense, and the surface is smoother. The coal gangue particles have a certain layered structure, namely, the surface is rough, and the surface roughness of the particles is deepened under the action of thermal activation. With the increase of calcination temperature, the surface roughness of particles is further deepened. The main reason is that in the process of thermal activation, the coal in the particles is gradually oxidized and volatilized, the mineral phase bonding water is lost, then the occupied space is released, and the particle surface roughness is increased. In the 500× SEAM image of thermally activated CG, the hollow structural particles are observed, which is also caused by the volatilization of coal components. The increase of surface roughness and hollow structure greatly increases the surface area of particles, thereby more free water are absorbed in particle surface at the initial hydration stage of CGCM slurry. Finally, the water-cement ratio in the slurry is reduced, and the initial fluidity is decreased. This also confirms the analysis of initial flow reduction in 3.1. When the slurry is stirred, the internal particles produce relative motion, collision, and friction. The collision and friction of particles above micron level are the main factors affecting their motion. The increase of spherical particles can reduce the apparent viscosity and yield stress of the slurry, while the added thermally activated CG is rough nonspherical particles, which increases the friction resistance between the particles and hinders the flow of the slurry, resulting in the increase of apparent viscosity and yield stress. Therefore, the addition of thermally activated coal gangue has an adverse effect on the fluidity of the slurry.

Figure 8: The micromorphology of OPC, CG, and thermally activated CG particles.
5. Conclusions

In this study, the coal gangue after mechanical activation and thermal activation was used to replace some cement in preparing cement coal gangue-mixed cementitious material, and the rheological test on CGCM slurry was carried out. The following conclusions are obtained:

(1) After mechanical activation, the fine particle content of coal gangue is higher than that of OPC, which increases the particle surface area, adsorbs more free water, reduces the water-cement ratio, and reduces the initial fluidity of CGCM slurry. Under the thermal activation temperature of 800°C, the pozzolanic activity of coal gangue reaches the highest, the hydration reaction is the fastest, and the initial fluidity of CGCM slurry at 800°C is the lowest.

(2) CGCM slurry is a typical non-Newtonian fluid, and its flow law conforms to the modified Bingham model. Significant shear thinning occurs during low-speed shear, and relatively weak shear thickening occurs during high-speed shear. The main factor causing the rheological effect is the flocculent structure produced in the early stage of hydration. Under the action of shear, the flocculent structure is gradually damaged, and the apparent viscosity decreases.

(3) The thermal activation temperature of coal gangue has a significant effect on the rheological parameters of the CGCM slurry. The plastic viscosity of slurry increases gradually with the increase of thermal activation temperature of coal gangue, and the yield stress of CGCM slurry at mixed with CG at the calcination temperature of 800°C reaches the maximum. At the same time, the flow law of slurry has significant time-varying characteristics; that is, the plastic viscosity and yield stress of slurry gradually increase with the extension of hydration time.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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