Research Article
Mechanism on Activation of Coal Gangue Admixture

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Coal gangue, an industrial waste, is rich in silicon and aluminum phase and may be used as a mineral admixture in concrete after moderately stimulating activity, allowing for efficient solid waste utilization. This study used a mortar strength and activity evaluation method to investigate single or compound activation methods to find the optimum activation method of coal gangue. FLIR, XRD, and SEM were used to investigate the activation mechanism of different modes, providing a theoretical foundation for the study of coal gangue as a concrete admixture. Results showed that mechanical ball milling, microwave, and chemical activator could activate coal gangue, and the composite activation effect was the best. The fineness of the coal gangue powder was more than 300 mesh, according to the optimal compounding method. Accordingly, the particle surface was smooth, the internal defects were reduced, and the microwave irradiation temperature was 700°C–800°C, causing the coal gangue particles to form a bonding surface and gradually agglutinate and densify. Meanwhile, the layered structure of kaolin minerals was destroyed, and a significant amount of glassy active SiO2 and Al2O3 was produced, enhancing the gel ability and activity of coal gangue. Finally, 8% Ca(OH)2 was added in the production of mortar specimens, which increased the alkalinity of the slurry, stimulated the rapid cracking and secondary hydration of the coal gangue, and enhanced the strength of mortar. At this time, the activity rate of coal gangue powder reached the highest, which was 90.5%.

1. Introduction
Coal gangue is a solid waste produced during coal mining and washing, and it is responsible for the majority of global emissions in the world [1]. Long-term coal gangue storage not only takes up space, pollutes the environment, and degrades water quality, soil, and atmosphere but also endangers public safety and has a great influence on people’s lives [2]. However, coal gangue also has resource properties, and its inorganic components are mainly silicon, aluminum oxides, and some rare metals, which are similar to fly ash and slag [3, 4]. Nonetheless, coal gangue has low self-activity, it must be treated to stimulate its potential activity. The activated coal gangue can be used as mineral admixture in concrete, and concrete is currently the most important building material with huge consumption. Coal gangue can be utilized as mineral admixture to minimize the amount of cement needed and the environmental and economic problems associated with by coal gangue accumulation. Therefore, it is very important to explore the activation of coal gangue and use it as an admixture to replace cement [5–7].

Mineral admixtures have an important influence on the working properties of cement mortar [8, 9], mechanical properties [10, 11], and durability [12–14]. At present, the mineral admixtures that are widely used are mainly fly ash [15], slag [16], silica fume [17], and limestone [18], and research on coal gangue is rare. Only few studies have shown that coal gangue can improve its activity through mechanical activation, chemical activation, thermal activation, and microwave activation [7]. The effect of mechanical force in grinding would change the crystal structure and physical properties of minerals in coal gangue; the structures of the Al-O, Al-O-Si, and Si-O bonds on the particle surface are broken, and the surface hydroxyl is eliminated; this situation results in many chemical active points on the particle surface, increasing the surface activity and free energy of live materials [19–21].
Different types of chemical activators have been used in the trial of active excitation of coal gangue, and the commonly mixed activators are Ca(OH)\textsubscript{2} and Na\textsubscript{2}O\textsubscript{nSiO\textsubscript{2}}, which could make coal gangue cementitious materials achieve high mechanical properties by mixing them individually or in combination [22, 23]. The single addition of CaCl\textsubscript{2} and Na\textsubscript{2}SO\textsubscript{4} improved the strength of mortar. The addition of NaCl and NaOH provided a strong alkaline solution environment, promoted the precipitation of alumina in coal gangue, and improved its reaction rate [24, 25]. When NaOH and Na\textsubscript{2}O\textsubscript{nSiO\textsubscript{2}} were mixed to stimulate coal gangue-slag mortar, the unhydrated coal gangue particles in the mortar played a role of filling and framework, and the flocculent C-S-H gel and network N-A-S-H gel produced by the polymerization reaction compound increased the strength of mortar, thus inhibiting drying shrinkage [26]. However, a high concentration of NaOH would prevent the production of hydration products C-S-H, AFT, and CH, and hydration products have considerable pores; accordingly, the strength of the system would diminish [27]. Therefore, the choice and dosage of chemical activator are vital factors in simulating the activity of coal gangue.

Microwave is more environmentally friendly compared with the traditional calcination technology; thus, it is gradually applied to the field of thermal modification of materials. Simultaneously, microwave irradiation has several advantages, such as short heating time, high efficiency, and no secondary pollution. Microwave can directly heat coal gangue through energy dissipation inside it, remove free water and mineral structure water inside it, enhance the solubility of SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}, and ameliorate the reaction activity and gelling performance of coal gangue [28–31]. However, the role of various activation methods of coal gangue is not absolutely independent, and many factors affect the activity. Therefore, the activation effect of mechanical, microwave, and chemical activation on the coal gangue activity must be analyzed by single or compound methods. However, relatively few studies have been conducted worldwide on the combined activation of coal gangue, and extensive research on the activation mechanism of coal gangue is scarce.

In this study, mechanical, chemical, and microwave activation methods were employed, and single or compound methods were used to stimulate the activity of coal gangue. The effects of the fineness of coal gangue powder, microwave temperature, and type and amount of chemical activator on the activity and cementitious properties of coal gangue were explored. The phase composition and microstructure of mortar specimens were analyzed by XRD and SEM. The influential regularity and mechanism of different activation methods on the properties of coal gangue were revealed, providing a theoretical basis for the study of coal gangue as concrete admixture.

2. Experiment

2.1. Raw Materials and Mix Proportion. The cement used was an ordinary P-O 42.5 Portland cement from Xi’an, China. Table 1 shows the specific properties of the cement. River sand was selected as sand with a moisture content of 5% and a bulk density of 1280 kg/m\textsuperscript{3}. The curve of particle grading is shown in Figure 1. Coal gangue was dredged from the northern part of China, with a maximum particle size of 25 mm, bulk density of 1191.3 kg/m\textsuperscript{3}, and water absorption rate of 8.23% (Figure 2). The chemical composition of coal gangue and other mature admixtures (such as slag and fly ash) were analyzed by XRF. Table 2 illustrates the results. The three admixtures are similar in chemical composition and have more silicon and aluminum oxides; thus, coal gangue has potential activity, which is worthy of excitation and research. The coal gangue mortar specimens are mixed with Portland cement at a mass ratio of 3:7. The cement to mortar ratio is 1:3, and the water-cement ratio is 0.5.

2.2. Method

2.2.1. Mechanically Activated Coal Gangue and Fineness Detection

(i) Mechanically activated coal gangue

Coal gangue will produce varying particle sizes depending on the machine grinding instruments used, resulting in diverse mineral crystals, giving the particles activity. Therefore, the machine grinding process of coal gangue is particularly vital, and the grinding steps in this study are as follows:

- After the coal gangue was dried, 500 g coal gangue was placed into the GJ-1000B type grinding machine, and the grinding time was set to 4 min.
- The ground powder was placed into the grinding tank of the GMB/B ball mill with 3:1 ratio of materials and steel balls, and the lid of the tank was sealed. The grinding tank was placed on the corresponding rubber shaft, the time was set to 30 min, and grinding was commenced.
- After grinding, the material was subjected to natural cooling. Then, the fine powder was taken out. The specific process flowchart is shown in Figure 3.

(ii) Fineness and specific surface area of coal gangue powder

- Fineness of coal gangue powder: the sample weighed 25 g, and it was placed in a clean negative pressure screen. The screening time was set to 120 s. Turn on the power of the cement fineness negative pressure sieve analyzer (FSY-150B). The negative pressure was set to 400–6000 Pa, and 20–100, 100–180, 180–300, 300–400, and 400 mesh were taken above the five stages of coal gangue powder (60 g each).

- Specific surface area of coal gangue powder: (a) the coal gangue powder with different mesh sizes was dried at 110°C ± 5°C for 1 h; then, it was cooled to...
room temperature in a sealed environment; (b) anhydrous kerosene was poured into Lee’s flask to 0 mL scale line, the stopper was covered, and it was placed into a thermostatic water bath (XMTD-7000) with water temperature controlled at 20°C ± 1°C for 30 min, until the scale line was stable; (c) Lee’s bottle was taken out, 45 g coal gangue sample was put into the bottle with a medicine spoon, it was shaken repeatedly to expel the bubbles, then Lee’s bottle was put in thermostatic water bath and let to stand for 30 minutes, the reading was recorded, and the density of the coal gangue sample was calculated; (d) the U-type liquid level and air tightness of the specific surface area meter (FBT-9) were checked, and the amount of samples needed in the ventilated cylinder was calculated by using the measured coal gangue powder sample density; (e) a layer of vaseline was applied to the outer cone of the breathable cylinder containing the sample, and it was inserted to the upper cone of the U-shaped press to measure the breathable time and record the specific surface area data. The process was repeated twice. If the results of the two tests were less than 2%, then the average value was taken; if the value was greater than 2%, then it was retested and remeasured until the error was eliminated. The test instrument is shown in Figure 4, and the test results are illustrated in Table 3.

2.2.2. Microwave Activation of Coal Gangue. The coal gangue powder of more than 300 mesh was placed into a hemispherical crucible with a loading amount of 1 kg each time. Then, the surface of the powder in the crucible was flattened and placed into a microwave oven (ORW10S-3T, 2450 MHz, 380 V). The coal gangue powder was set to 1.33 kw and irradiated for 25–30 min. Subsequently, the crucible was taken out, and the infrared temperature measuring meter (FLIR T420) was turned on. The temperature range was set to 250°C–1200°C, measurement was carried out at a distance of 1 m, and the red laser button was pressed. The laser was aimed at the coal gangue powder inside the crucible and slowly moved to determine the high temperature point. The coal gangue powder with the highest temperatures of 400°C–500°C, 500°C–600°C, 600°C–700°C, and 700°C–800°C was selected. The test equipment is shown in Figure 5.

2.2.3. Chemically Activated Coal Gangue. Different types of chemical activators were added to investigate the activation effect of chemical activators on coal gangue powder at the same water-binder ratio. The details of the activators are illustrated in Table 4. The dosage of the chemical activator was added according to the mass percentage of coal gangue powder, and the dosage rates were 2%, 4%, 6%, 8%, and 10%. The optimal activator and dosage of coal gangue powder were finally selected by comparing their excitation effects.
2.3. Production of Mortar Specimens. Thirty groups of mortar samples were prepared according to the compressive strength test of Chinese standard GB17671-1999 [33]. The blank group with full cement and the unactivated coal gangue powder group with 30% substitution rate were used as the control group. The production steps of this test sample are as follows: ① the amount of raw materials was weighed according to the design of the mix ratio; ② the mixer was prewet, and coal gangue powder, cement, and chemical activator of different mass ratios were poured into the mixer for 120 s. Subsequently, sand was added to continue stirring for 60 s. Then, water was

| Mesh   | Density (g/cm³) | Specific surface area (m²/kg) |
|--------|----------------|-----------------------------|
| 20–100 | 2.446          | 58.30                       |
| 100–180| 2.406          | 121.15                      |
| 180–300| 2.394          | 230.21                      |
| 300–400| 2.378          | 361.07                      |
| Over 400| 2.366          | 438.28                      |

Note. GB/175-2007 [32] stipulated that the specific surface area of cement should not be less than 300 m²/kg. Hence, the coal gangue powder of more than 300 mesh was selected for microwave and chemical activation in the later stage.
slowly added. After all the water is added, mixing was continued for 2 min. The mixture was placed into a mold of 70.7 mm × 70.7 mm × 70.7 mm for molding. After curing with the mold for 24 h, the mold was removed and soaked into water at 20°C ± 1°C for curing until each age (3 d, 7 d, and 28 d). The compressive strength of mortar samples was measured at a loading rate of 0.24 ± 0.2 kN/s, and the average values of three specimens in each group were taken.

2.4. Macro-Test Method.

(1) Strength test method: the strength of coal gangue mortar was tested with a YES-2000B testing machine according to GB/T17671-1999 [33]. Figure 6 shows the experimental method of compressive resistance of specimens. Compressive strength \( R_c \) takes Newton per square millimeter (MPa) as the unit and is calculated according to the following equation:

\[
R_c = \frac{F_c}{A},
\]

where \( F_c \) is the maximum load at the time of failure, and \( A \) is the compressed area.

(2) Coal gangue activity test method: the activity of coal gangue can be evaluated by the strength method in GB/T12957-2005 [34], and the activity index \( K \) can be calculated according to the following equation:

\[
K = \frac{R_1}{R_2},
\]

where \( R_1 \) is the compressive strength of the coal gangue mortar at 28 d, and \( R_2 \) is the compressive strength of the cement mortar for 28 d.

2.5. Microscopic Test Method.

(1) Sampling method: the coal gangue powder samples with different mesh sizes were placed into glass dishes after microwaving, dried in a vacuum drying box at 25°C for 24 h, bagged, and sealed. The specimens of mortar sand produced after compound activation were split on a press, and the mortar skin was removed. The sheet and internal block mortar samples of approximately 3–5 mm were selected and soaked in anhydrous ethanol for 3 d to stop the hydration. Then, the samples were placed into a vacuum drying oven at 60°C for 24 h. The flake mortar samples were bagged and sealed. Meanwhile, the mortar samples were ground in a ceramic mortar to 20 mesh, bagged, and sealed.

(2) Test method: X-ray diffraction (D8 Advance) operation steps: the sample was loaded onto the sample plate with a spoon, and the surface was flattened with a glass sheet and placed into the instrument. The diffraction pattern was obtained in the 2θ range of 10° to 80° by setting the step length of 0.02 (2θ) per second. Operating procedure of the scanning electron microscope (JSM-6460LV): the sample surface was gilded to increase the electrical conductivity, and the sample was...
fixed in the sample room with conductive black tape. After the vacuum treatment was completed, the focusing knob was adjusted in the high vacuum mode until the image was clear.

3. Results and Discussion

3.1. Effect of Mechanical Activation on the Activity of Coal Gangue

3.1.1. XRD Analysis of Coal Gangue after Grinding. Mineralogical characterizations of different meshes of coal gangue powder were analyzed by XRD (Figure 7). The main components of coal gangue powder are quartz, kaolin, and Al₂O₃. When coal gangue powder was milled to 20–100 mesh, 100–180 mesh, and 180–300 mesh, the crystallization peak of kaolin (2θ = 12.370°, 2θ = 26.535°) and the crystal peak of quartz (2θ = 54.613°, 2θ = 59.660°, and 2θ = 68.046°) were sharp, which indicated that they have a good degree of crystallization and less amorphous substances and were not easy to react with alkali hydration. So, it was difficult for them to generate hydration product to provide strength. When the coal gangue powder was milled from 300 to 400 mesh and more than 400 mesh, the characteristic peak of kaolin (2θ = 12.370°) was dispersed, and the peak became steamed bread peak. Moreover, the crystal structure of kaolin was destroyed and transformed into partially ordered semicrystalline metakaolin.

From the perspective of dynamics, mechanical activation would deform the lattice of coal gangue and produce various structural defects, thus increasing the energy storage of crystal. The increased energy of crystals in coal gangue due to mechanical activation was $\Delta E_{a1} > 0$. Then, the relationship between the actual reflected activation energy $\Delta E_{a2}$ after activation and the reaction activation energy $\Delta E_{a3}$ of the unactivated ideal crystal was

$$\Delta E_{a2} = \Delta E_{a3} - \Delta E_{a1}, \quad (3)$$

$\Delta E_{a2}$ was less than $\Delta E_{a3}$ according to the Arrhenius equation.

$$\ln k = -\frac{E_a}{RT}, \quad (4)$$

$$k = \frac{k_3}{k_2}, \quad (5)$$

$$E_a = \Delta E_{a1}, \quad (6)$$

where $k$ is the reaction rate constant, $k_2$ is the reaction rate constant after mechanical activation, $k_3$ is the reaction rate constant before activation, $E_a$ is the activation energy of the reaction, $R$ is the gas constant, and $T$ is the absolute temperature. The mechanical activation is carried out at the same temperature.

Substituting (3) and (4) into (2) yields

$$\frac{k_2}{k_3} = \exp \left( \frac{\Delta E_{a1}}{RT} \right), \quad (7)$$

because $\Delta E_{a1}$ was greater than 0, and $\exp (\Delta E_{a1}/RT) > 1$.

The reaction rate constant after mechanical activation was greater than the reaction rate constant before activation. Then, $k_2 > k_3$; that is, the reaction rate constant after mechanical activation was greater than that before activation. Accordingly, mechanical activation attenuates the characteristic peak of coal gangue minerals.

3.2. Morphological Analysis of Coal Gangue with Machine Grinding. Figure 8 shows the micromorphology of coal gangue powder with different meshes without and after machine grinding. In Figure 8(a), the raw coal gangue had a smooth wall and dense shape, which was made up of layers of lamellar structures. The dense structure of coal gangue reduced its surface tension and weakened the adsorption capacity of the solid surface. Accordingly, the contact area with liquid was reduced, and the solid surface was uneasy to be wetted, further weakening the chemical reaction rate of coal gangue. During the mechanical ball milling for 30 min, the raw coal gangue was impacted by many steel balls, the
material was broken, and many material particles with different particle sizes were produced. The external morphology of coal gangue was also transformed into irregular shapes with multiple edges and corners of different sizes (Figures 8(b)–8(f)). The coal gangue powder with granular structure, the structural micropores, and the internal voids and cracks of the particles increased with the increase in the mesh number. Accordingly, the surface area of coal gangue powder expanded, the free energy of surface particles was improved, and the surface adsorption capacity of coal gangue particles was enhanced.

In summary, mechanical activation could increase the specific surface area of coal gangue powder and the free energy of surface particles, improving the activity of coal gangue powder to a certain extent. However, the mechanically activated coal gangue powder had many voids. Although the surface activation energy of the particles was high, the internal active substances were not released. It was
not easy to participate in the hydration. The irregular flake shape of the powder was difficult to fill into the base phase of cement paste, which cannot be completely hydrated, and its pozzolanic activity is complicated to demonstrate. Therefore, the activity must be further simulated.

3.3. Effect of Microwave Activation on the Activity of Coal Gangue

3.3.1. Thermal Imaging Analysis of Coal Gangue Powder after Irradiation. The temperature of unmicrowaved coal gangue powder was close to room temperature, and its color was gray. After microwave radiation, the coal gangue powder rapidly absorbed and reflected heat due to its high emissivity (0.95), and its temperature sharply increased, especially in the central part. Heat was transferred outward in a circular radial shape. According to the thermal imaging in Figure 9, the coal gangue powder has reached the melting state at 400°C–500°C with the increase in microwave temperature, the coal gangue powder was gray-black, and no sintered matter was generated. When the temperature was between 500°C and 600°C, the formation of small sintered particles could be observed. When the temperature was above 600°C, a massive substance of approximately 4-5 cm was observed at the center of the coal gangue powder. The coal gangue powder was also mixed with grayish black and yellow. This phenomenon occurred because the carbon oxidation in the coal gangue powder during the microwave process needs a substantial amount of oxygen. However, the closed cavity had insufficient oxygen, and the carbon inside the coal gangue powder was difficult to oxidize and remove, so it was gray-black. The longer the microwave time was, the more partially oxidized the colorants in coal gangue powder were, resulting in mixed colors. The longer the microwave time was, the more partially oxidized the coloring material in the coal gangue powder was, resulting in mixed colors. The indirect contact surface of coal gangue particles increased with the raise in the microwave temperature. The grain boundary area increased, and the coal gangue powder was rearranged. The grain boundary slipped. Thus, the viscous flow and plastic flow of particles were induced to the mass transfer, resulting in the particles getting close to each other and gradually forming grain boundaries, reducing pore volume and holes, and forming part of the hard polycrystalline sintered body.

3.3.2. Composition Analysis of Coal Gangue after Microwave Activation. In the XRD analysis of different microwave temperatures in Figure 10, many sharp peaks and high crystal strength can be observed in the original crystal diffraction peaks of coal gangue powder. First, the characteristic diffraction peaks of kaolin were found at 2θ = 12.36°, 19.86°, 21.27°, 39.23°, 42.37°, and 59.76°. The four diffraction peaks between 2θ = 18° and 2θ = 25° form a mountain shape, which fully showed that the crystallinity of kaolin was great. Second, the crystal diffraction peak of coal gangue powder after microwave was significantly changed compared with the initial sample. The characteristic diffraction peak of kaolin was diffused, and the fuzzy steamed bun peak appeared at 2θ = 10°–20°. This phenomenon indicated that the hydrogen and oxygen bond between the [SiO4] tetrahedral layer and [AlO2(OH)4] octahedral layer in kaolin was broken, and the layered structure was destroyed, and the grain was finely broken [35]. Kaolin in coal gangue powder was transformed into metakaolin, accompanied by the formation of amorphous substances SiO2 and Al2O3. Finally, the diffraction peaks of quartz at 2θ = 20.77°, 26.47°, 27.80°, 36.38°, 49.98°, and 59.76° also began to disperse, resulting in the formation of more glass SiO2, which had a higher activity.

3.3.3. Micromorphological Changes of Coal Gangue after Microwave Activation. Figure 11 shows the micromorphology of coal gangue particles after different microwave temperatures. In the absence of microwave radiation, the large particles of coal gangue were irregular flakes, and the small particles were similar to thin pieces of paper. With the increase in microwave temperature, the solid particles of coal gangue powder caused the particles in the coal gangue powder bond to rearrange, the grains would polymerize and grow, the small particles moved close to each other, and the grain boundaries were connected with the voids. The edges and corners of the coal gangue particles appeared smooth at 472.3°C and 574.8°C. At 687.0°C and 765.7°C, the large particles became thicker and regularized due to the coal gangue particles, while the small particles appeared spherical and tend to be glassy. The internal voids and cracks of coal gangue particles at 765.7°C were also increased, and the surface adsorption capacity of coal gangue particles was enhanced. Moreover, the glassy state easily adsorbed CH to react with it. The results showed that the particle morphology of coal gangue powder activated by microwave was closer to that of vitreous body to improve its pozzolanic activity.

3.3.4. Activity Analysis of Coal Gangue after Microwave Activation. Figure 12 shows the activity rate of coal gangue at different temperatures. The activity index of coal gangue mortar activated by microwave was higher than that of mechanical coal gangue mortar. The activity index of coal gangue powder reached 0.887 when the microwave irradiation temperature reached 700°C–800°C. Therefore, microwave can greatly improve the activity of coal gangue.

Figure 13 shows the mechanical strength of the mortar mixed with different activation degrees of coal gangue powder. After microwave activation, the strength of coal gangue mortar was higher than mechanically activated coal gangue mortar. The optimum microwave irradiation temperature of coal gangue powder was 765.7°C. At this temperature, the mortar strength reached 15.47 MPa in 3d, 23.89 MPa in 7d, and 31.38 MPa in 28d, which were 8.0%, 35.8%, and 39.6% higher than initial (0°C). The reason is that the coal gangue powder had many voids by mechanical activation, and although the surface activation energy was high, the internal active substances were not released, and it was not easy to participate in hydration. In addition, the
irregular flake shape of the coal gangue power was difficult to fill into the voids of the cement paste, so it was hard to exert strength. The coal gangue powder activated by microwave contained more amorphous active SiO$_2$ and Al$_2$O$_3$, which further reacted with the CH formed by cement hydration to form C-S-H and C-A-S-H, improved the compactness of the overall framework, and increased the strength of the mortar. Moreover, the strength growth rate of the unactivated coal gangue mortar was similar and only approximately 20% in 3–7 d and 7–28 d. The mortar at 472.4°C had the highest strength growth rate in 3–7 d, which was 57.36%, and the mortar at 765.7°C had the highest strength growth rate in 7–28 d, reaching 31.33%. This is because mechanical grinding could not release the active substances in the coal.
gangue power, and the hydration of coal gangue powder was relatively gentle. The high temperature generated by the microwave could decompose the kaolin in the coal gangue powder. The higher the microwave temperature, the more thorough the decomposition of kaolin. The more reactive SiO₂ and Al₂O₃ in coal gangue powder, the stronger the hydration capacity. Therefore, coal gangue powder at 765.7°C had more active SiO₂ and Al₂O₃ than at 473.2°C. In the early stage of hydration, such as 3–7 d, most of the free SiO₂ and Al₂O₃ in the coal gangue powder reacted secondary hydration reactions with the CH in the slurry, which consumed Ca²⁺ and OH⁻ ions in the slurry to generate hydration products. In the late stage of hydration, the residual active SiO₂ and Al₂O₃ in the coal gangue powder continue to hydrate, and the rate slowed down. Therefore, the strength growth rate in the later stage of hydration was relatively weak.

3.4. Effect of Chemical Activation on the Activity of Coal Gangue. The effect of chemical activator and its content on the compressive strength of the specimen is shown in Figure 14. In Figure 14(a), the strength growth rate of mortar is higher in 3–7 and 7–28 d when the coal gangue was mixed with 4% CaCl₂. The strength was the highest in each age, and the strength reached 19.93 MPa in 28 d. When the content reached 8%, the strength in 28 d was...
8.25 MPa, and the strength growth rate in 7–28 d was 13.68%. This phenomenon was attributed to CaCl₂, which was a colorless cubic crystal block, easily soluble in water, and released a large amount of heat when combined with hydration. A small amount of calcium chloride increased the local temperature of the paste, provided a large amount of cement hydration heat energy, shortened the setting time of cement, and promoted the formation of strength. However, an excessive amount of Ca²⁺ would lead to high calcium, and competition for OH⁻ in the solution would lead to the weakening of the local alkalinity of the liquid phase, instability, and precipitation of the solution. Thus, the increase of intensity must be restrained.

In Figure 14(b), growth rate of the compressive strength of the specimen first decreased and then increased when the concentration of Na₂O·nSiO₂ increased from 2% to 10%. The curing age prolonged, and the compressive strength rapidly developed in the early 3–7 d and slowly in the late 7–28 d. The slurry thickening rate accelerated with the increase in Na₂O·nSiO₂ content and OH⁻ concentration. The hydration products generated failed to spread and cover the surface of coal gangue particles to form a protective film, which hindered the outward dissolution of internal ions and inhibited the hydration process, leading to the slow growth rate of the strength of coal gangue in the later period. When the Na₂O·nSiO₂ content was 10%, the compressive strength of gangue specimens at 3 d, 7 d, and 28 d was the highest.

Figure 14: Compressive strength development of geopolymers with different chemical activators and their contents.
which was caused by the “concentration effect,” and there was enough [SiO$_4$]$_{4-}$ and dissolved Ca$^{2+}$ to form C-S-H gel, resulting in a highly compact mortar structure.

In Figure 14(c), the compressive strength of the specimen prolonged with the increase in Na$_2$SO$_4$ content. When the content of Na$_2$SO$_4$ was 10%, the strength of the specimen rapidly increased in the later period of 7–28 d. In the alkaline environment of cement hydration, OH$^-$$^-$ rapidly increased in the later period of 7–28 d. In the alkaline environment of cement hydration, OH$^-$$^-$ rapidly increased in the later period of 7–28 d.

3.5. Effect of Compound Activation on the Activity of Coal Gangue

3.5.1. Cementitious Properties of Coal Gangue after Compound Activation. Many factors affect the activity of coal gangue. However, the role of various activation methods is not absolutely independent. Therefore, mechanical activation, microwave activation, and chemical activation must be simultaneously used, and their excitation effects on the activity of coal gangue must be analyzed.

Figure 15 shows the activity index and compressive strength of different types of mortar specimens. In Figure 15(a), the activity index of coal gangue in the case of compound activation is as follows: M7H8 > M7C4 > M7G10 > M7S10. The activity index of M7H8 was as high as 0.905 (microwave activation index). Consequently, the activation effect of M7H8 was optimal under compound activation.

In Figure 15(b), when Na$_2$O·nSiO$_2$ and Na$_2$SO$_4$ were mixed into the mortar, the pH value of solution could be provided in the early stage of hydration, which would further corrode the vitreous body of coal gangue power and would hydrate with the active SiO$_2$ and Al$_2$O$_3$ in the coal gangue powder to form AFt, N-A-S-H, and C-S-H gel, etc. At the same time, a large amount of Ca(OH)$_2$ was formed. However, in 28 d, the strength of coal gangue mortar shrank, and the growth rate of M7H10 and M7G10 from 7–28 d was as low as 7%. Compared with M7, its 28 d strength decreased by 40.63% and 35.59%, respectively. That is because the alkalinity inside the mortar was high in the later stage. The free water with a high concentration of Ca(OH)$_2$ in the structure gradually migrated outward along the internal capillaries to the surface of the mortar. Ca(OH)$_2$ reacted with CO$_2$ and water in the air, resulting in a white precipitated CaCO$_3$ insoluble in water and attached to the surface of mortar. In Figure 16, the mortar of M7S10 and M7G10 groups demonstrated alkali flooding on the surface at the age of 28 d, resulting in white flocs, and a considerable number of white crystals were found inside after crushing. Secondly, a large amount of molecular water would be combined with the hydration process when [SiO$_4$]$_{4-}$ and SO$_2^-$ ions invade the coal gangue mortar, which increased the absolute volume of the solid phase and filled the pores. Consequently, the early compressive strength of the mortar rapidly reached the maximum value, and the hydration product continued to squeeze the pore wall. Moreover, pore tensile stress was experienced, some microcracks appeared on the surface of the mortar, and the compressive strength was difficult to increase.

When the appropriate amount of CaCl$_2$ and Ca(OH)$_2$ was added, the coal gangue powder after microwave activation contained more active SiO$_2$ and Al$_2$O$_3$, which could preferentially react with the Ca$^{2+}$ and OH$^-$$^-$ ions in the solution to make the coal gangue powder fully hydrated. Therefore, the mortar strength of M7C4 and M7H8 was higher than M7S10 and M7G10. However, the incorporation of CaCl$_2$ would introduce Cl$^-$ ions, and the mortar was prone to chloride salt erosion. And the mortar strength of M7C4 was lower than M7H8 group. When the curing age reached 28 d, the 28 d mortar strength of M7H8 was 2.09% higher than M7, and the growth rate of M7H8 group from 7–28 d reached 40%–50%. Most of the cement and coal gangue powder have been hydrated. Therefore, the intensity of M7H8 was higher than that of all activation groups.

3.5.2. Phase Analysis of Gangue Mortar after Composite Activation. The XRD spectra of hydration products of coal gangue mortar samples of different ages are shown in Figure 17. The main mineral phases in mortar include cement, coal gangue, and hydration products. The hydration products include AFt, AFm, CH, N-A-S-H, and C-S-H gel.

With the continued hydration reaction, the mineral composition content of each sample varies, mainly as follows: (i) when the hydration age was 3 d, the intensities of the amorphous diffraction peak (2$\theta$ = 13°–17° and 2$\theta$ = 65°–70°) in M7S10 and M7G10 were lower than those in M7H8 and M7. Sharp diffraction peaks of metakaolin and C$_2$S were still observed in M7S10 and M7G10. This phenomenon shows that coal gangue in M7H8 and M7 had undergone secondary hydration reaction to form C-S-H and N-A-S-H, which was consumed. (ii) When the hydration age was 7 d, Al$^{3+}$ and Si$^{4+}$ precipitated from the coal gangue, and the slurry formed a SiO$_2$·Al$_2$O$_3$·Na$_2$O ternary system. Moreover, Al$^{3+}$ occupied the tetrahedral position of alkaline feldspar to form a more stable and ordered microplagioclase. Accordingly, the five samples had albite diffraction peaks at 2$\theta$ = 27°–28°. (iii) When the hydration age was 28 d, the peak of AFt diffraction (2$\theta$ = 25°–28°) of M7H8 was the sharpest, the diffraction peak of calcium silicate hydrate and calcium aluminosilicate hydrate (2$\theta$ = 18°–22°) of M7H8 was the strongest, and the mechanical strength of M7H8 sample was the highest. (iv) A substantial amount of metakaolin was observed in M7S10 after 28 d, thus indicating that Na$_2$O·nSiO$_2$ provided a large amount of SO$_2^-$ reaction to
form C-S-H during cement hydration. When the crystal lattice of kaolin was damaged by strong alkali corrosion, the bond breakage at the outermost edge of kaolin led to charge imbalance. The H⁺ outside of kaolin structure was replaced by Na⁺, which complemented the mineral structure of kaolin in the coal gangue and formed a new metakaolin. Accordingly, the secondary hydration of coal gangue was hindered, and the pozzolanic activity of coal gangue powder was difficult to exert.

3.5.3. Microstructural Analysis of the Composite Activated Coal Gangue Mortar. In Figures 18 and 19, unreacted coal gangue particles were present in the paste, and AFt, C-S-H, and C-A-S-H gel were formed by hydration reaction. The gel covered the surface of coal gangue particles and AFt. The strength of mortar mainly depends on the structure formed by the AFt and C-S-H crystals. The 3 d mortar specimens showed less AFt and C-S-H gel, more macropores and through pores, and a loose structure. As the age increased, the activated coal gangue powder reacted with the cement hydration product Ca(OH)₂; and a hydration film was formed on its surface, which grew and condensed with each other, forming hydration products to fill cement-based pores, reducing the macropores and through pores in the mortar specimens, densifying the structure, and increasing the strength. The hydration process is shown in Figure 20.

In Figures 18(a), 18(b), and 19(a), the coal gangue powder was translucent flake, and a certain portion of the surface and edge of the active coal gangue powder were covered with some hydration products, thereby indicating that its surface had participated in the secondary hydration reaction. Meanwhile, the surface of some active coal gangue powder was smooth, indicating that it was basically not...
involved in the reaction. These unreacted and partially reacted coal gangue particles were filled in the cement hydration products. The aforementioned particles intertwined with the hydration products to exert the “filling effect” for reducing the porosity of cement matrix and improving the compactness of colloid. In Figure 19(b), the active coal gangue powder was eroded by Ca(OH)$_2$, resulting in secondary hydration and C-S-H and C-A-S-H, which wrapped

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**Figure 17**: XRD patterns of the different types of specimens at various ages. 1—dickite; 2—calcium tecto-alumosilicate; 3—ettringite (AfT); 4—calcium silicate hydroxide (C-S-H); 5—calcium chloride (CaCl$_2$); 6—calcium hydroxide (Ca(OH)$_2$); 7—quartz; 8—albite; 9—C$_2$S; 10—C$_3$S; 11—sodium aluminum silicide (N-A-S-H). (a) 3 d. (b) 7 d. (c) 28 d.

**Figure 18**: Micromorphology of the M7 block at different ages. (a) 3 d. (b) 7 d. (c) 28 d.
the sand and filled in the gap between sand and cement paste, thereby demonstrating the “microaggregate effect” and improving the compactness between sand and cement paste. In Figures 18(c) and 19(c), no coal gangue powder was observed when the specimens were cured for 28 d. This result showed that the active coal gangue powder demonstrated the “pozzolanic activity” and produced a dense cement paste structure due to the long age and sufficient hydration time. A small number of cracks in the cement matrix after loading could be observed in Figure 18(c). Meanwhile, dense cementitious and plate-like calcium hydroxide is observed in Figure 19(c), which showed that the hydration products of coal gangue powder developed well after compound activation.

![Figure 19: Micromorphology of the M7H8 block at different ages. (a) 3 d. (b) 7 d. (c) 28 d.](image)

![Figure 20: Secondary hydration process of coal gangue.](image)

![Figure 21: Activation process of coal gangue.](image)
3.5.4. Mechanism Analysis of Compound Activated Coal Gangue. Under the activation mode of the M7H8 group, the activation effect of coal gangue is great. The activation of coal gangue is shown in Figure 21. The reasons are as follows:

First, the specific surface area, granular structure, structural micropores, and internal voidage and cracks increased after the coal gangue was mechanically ground. Accordingly, the surface area and free energy of surface particles of coal gangue were improved, and the surface adsorption capacity of its particles was enhanced. Second, the coal gangue particles gradually changed from irregular sheet to round and glassy state under the microwave radiation at 700°C–800°C, and the surface activity was improved. The content of the internal amorphous active SiO$_2$ and Al$_2$O$_3$ increased. The pozzolanic activity of coal gangue powder was enhanced.

Finally, after the coal gangue powder activated by mechanical microwave was added with 8% Ca(OH)$_2$ as the activator, the film outside the coal gangue particles was rapidly hydrolyzed in alkaline environment to form Ca-Si-Al amorphous film. The internal active material was also rapidly released, which reacted with Ca$^{2+}$, SO$_2^-$, and Al$^{3+}$ in the solution to form C-S-H, C-A-S-H, and AFt, to promote the development of strength. Accordingly, the pozzolanic activity of coal gangue powder could be demonstrated.

4. Conclusion

Coal gangue, a concrete admixture, has a high economic and environmental value. How to effectively stimulate the pozzolanic activity of coal gangue and promote the formation of hydration products with strong cementitious ability of coal gangue is of great significance. In this study, the activity of coal gangue under different activation modes was studied by the combination of macro and micro. The conclusions were as follows:

(1) When the coal gangue was milled to more than 300 mesh, the layered structure showed a flaky or granular structure, which increased the adsorption capacity of the particle surface and accelerated the surface hydration reaction rate.

(2) When the microwave temperature reached 700°C–800°C, a large number of active SiO$_2$ and Al$_2$O$_3$ of coal gangue powder was formed, and the particle pores were reduced. The activity index of the coal gangue mortar specimen reached 0.887, and the 28d strength reached 31.38 MPa, which was 39.6% higher than that of pure mechanically activated coal gangue mortar.

(3) The strength of coal gangue mortar was related to the choice of chemical activator and its content. When a single chemical activator was incorporated, the optimal dosage of CaCl$_2$ was 4%; the optimal dosages of Na$_2$O·nSiO$_2$ and Na$_2$SO$_4$ were both 10%, and the optimal dosage of Ca(OH)$_2$ was 8%. Among them, 8% Ca(OH)$_2$ had the best excitation effect, and the 28d strength of mortar reached 21.24 MPa.

(4) The activity index of the M7H8 specimen reached 0.905, and the 28d strength attained 32.03 MPa. Compound activated coal gangue could efficiently stimulate its pozzolanic activity and accelerate the secondary hydration reaction. The resulting hydration products were filled with cement-based pores, making the structure densified and improving the mechanical strength of coal gangue as a cementitious material.

Data Availability

The data used to support the findings of this study are included within the article and are available from the corresponding author upon request.

Additional Points

(1) The activity of coal gangue was assessed using different activation methods. (2) The layered structure of coal gangue was mechanically destroyed, and the surface activity was improved. (3) Microwave caused the grains in coal gangue powder to polymerize and grow, the grain boundary was connected with pores, and the pores were reduced. (4) The pozzolanic activity of coal gangue was activated by using calcium hydroxide. (5) The activity of compound activated coal gangue was better than that of single activated coal gangue.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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