

Research Article

Performance of Coal Gangue-Based Cemented Backfill Material Modified by Water-Reducing Agents

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Coal gangue-based cemented backfill material (CGCBM) is developed for backfilling the goaf in coal mines. As fresh CGCBM slurry is generally transported into underground openings through a pipeline, and after hardening, it plays the role of supporting the overlying strata. The fluidity, stability, and mechanical (compressive strength) of CGCBM become the most important properties. Adding water-reducing agents (WRAs) is considered to improve the fluidity, stability, and mechanical properties of CGCBM, but there is a risk of increased bleeding. So, two types of WRA (naphthalene series (WRA1) and poly carboxylic acid (WRA2)) are used at different contents (1.0%–2% for WRA1, 0.2%–0.6% for WRA2) by mass of binder. Slump, slump flow, yield stress, and plastic viscosity test are used to evaluate the fluidity properties of CGCBM after adding WRA. Bleeding rate test is used to evaluate the stability of CGCBM after adding WRA. Compressive strength is the most important factor in measuring the mechanical properties. SEM and XRD tests are used to analyse the mechanism of strength change. Results show that the slump, slump flow, and plastic viscosity increase after adding WRA, which reduces the yield stress and improves the fluidity. The bleeding rate increases with the increase of WRA content, leading to a decrease in stability. Adding WRA increases the compressive strength, and it increases first and then decreases with the increase of the content at the later stage. Considering the effects of WRA on the fluidity, stability, and compressive strength properties of CGCBM, the reasonable content of WRA1 and WRA2 is 1.5% and 0.4%, respectively. The research results provide guidance for the design and preparation of CGCBM with favourable performance in practical production.

1. Introduction

Underground coal mining produces a large amount of coal [1] and also generates a large number of underground openings and discharges a large amount of coal gangue. It is reported that about 4.5 billion tons of coal gangue are piled up in China [2], causing serious environmental concern. On one hand, coal gangue stacking occupies a lot of arable land, and coal gangue contains a large amount of sulfide, which will infiltrate and then pollute the land and groundwater [1, 3]. On the other hand, coal gangue may cause auto ignition and generate a large amount of sulfide gas, which damage the atmospheric environment and threaten human health [4, 5]. At the same time, a large number of

underground openings will cause surface subsidence, which will cause the village to relocate and cause a lot of economic losses. Coal gangue-based cemented backfill material (CGCBM), which is an engineered mixture of crushed coal gangue, fly ash, cement, and water, is designed for mine backfill [6–8]. It effectively solves the problems of coal gangue stacking and surface subsidence [9, 10].

Although CGCBM technology has certain environmental and economic benefits, the cost and transportation of filling slurry preparation are still worrying. The report suggested that the slurry filling method consumes a large amount of binder (10^5 tons per year), accounting for backfilling eighty percent of the cost. Generally, filling slurry is prepared at the ground mixing station and then

transported to the underground openings, so it needs to be mixed with enough water to ensure good fluidity [11]. However, the increase in the amount of water in the backfill material increases the water-to-cement ratio, resulting in a decrease in the strength and durability of the backfill material after hardening [12].

In the view of this challenge, scholars have referenced the research of concrete technology to add water-reducing agents (WRAs) to the backfill material to reduce the amount of mixed water and to improve the strength and durability of the backfill material on the premise of ensuring flow performance [13, 14]. A lot of researches have been done on the effect of water-reducing agents on the properties of backfill material. Ercikdi et al. reported that adding the superplasticizer to the cemented paste backfill (CPB) formulation can reduce the amount of binder and enhance CPB durability [15]. Indeed, Ercikdi et al. confirmed that superplasticizers have some chemical admixtures that meet the fluidity and also the increasing strength and durability of the backfill material with reduced water content. The amount of superplasticizer for lignosulfonate, naphthalene sulfonate, and polycarboxylate was 7%, 6%, and 5.4% (by dry binder mass), respectively, to reach the designed slump (7 inches). The authors reported that superplasticizers reduced water content (~6.6%), enhanced mechanical properties (20–50%), and improved durability [16]. Huynh et al. defined these additives as organic polymer molecules and found that they have the ability to adsorb on cement and coal gangue particles and therefore disperse them by internal electrostatic and spatial forces, affecting CPB rheological properties [17]. Papayianni et al. reported that superplasticizers will significantly reduce CPB porosity and permeability, thereby affecting the microstructure of CPB [18]. Uchikawa et al. found that binding energy of the calcium atoms on the surface of cement particles have a certain degree of chemical shift when naphthalene series WRA and the poly carboxylic acid WRA mixed into the materials, which indicated that the chemical reaction occurred between calcium and the active group of WRA and can enhance strength [19]. Ercikdi et al. studied the effect of the WRA on CPB material with a high content of sulphur tailings and concluded that mixing of WRA has optimized effect on the flowability, compressive strength, and long-term stability of CPB and poly carboxylic acid WRA was more effective for the enhancement of strength [20].

Although the above studies on CPB have achieved important results, however, additional data is required, because these results cannot be directly applied to CGCBM, CPB is very different from CGCBM in material composition, CPB uses tailings as aggregate and has a large amount of cement, and CGCBM uses coal gangue with different particle sizes as aggregates and has a small amount of cement. Therefore, it is necessary to obtain more data on the amount of WRA in CGCBM, which is related to the cost of filling and the effect of water reducer on the fluidity, stability, and mechanical properties of CGCBM.

In this research, effect of WRA types and dosage on the CGCBM performance is studied by measure rheological property, bleeding rate, and compressive strength for

different ages of CGCBM. The change of microstructure characteristics in hydration products of specimens was observed by scanning electron microscopy (SEM), and X-ray diffraction (XRD) technology was used to determine the reddish-brown substance of specimen. Determine the reasonable amount of WRA according to the fluidity, stability, and mechanical properties of the CGCBM.

2. Materials and Methods

2.1. Materials and Mix Proportion

2.1.1. Coal Gangue. The coal gangue used in this study was collected from Xinyang coal mining located in eastern China, and the mineral content is shown in Table 1. The sampled coal gangue was reprocessed to create two grain size classes corresponding to fine aggregate (the particles diameter <5 mm) and coarse aggregate (the particles diameter is 5–15 mm). The proportion of fine and coarse aggregate is 3:7.

2.1.2. Binder. Ordinary Portland cement (P.O42.5) with the compression strength of 6.5 MPa and the flexural strength of 48.0 MPa and fly ash were used as the binder in this study (Tables 2 and 3).

2.1.3. Water-Reducing Agents. Two different water-reducing agents (WRA1 and WRA2) were used to modify the performance of backfill materials. WRA1 and WRA2 are naphthalene series water-reducing agent and poly carboxylic acid water-reducing agent, and the recommended dosages are 0.5%–2.0% and 0.2%–0.6% by mass of binder, respectively.

2.1.4. Mix Proportion. In this study, the control mass ratio cement: fly ash: coal gangue is 1:2:5 and water-binder ratio is 0.67, which is on the previous research [21]. When a WRA is admixed, the water-binder ratio decreased to 0.6 and the dosage of WRA1 and WRA2 are 1.0%, 1.25%, 1.5%, 1.75%, 2.0% (numbered N1–N5) and 0.2%, 0.3%, 0.4%, 0.5%, 0.6% (numbered J1–J5) by weight of cement, respectively. The dosage is in the recommended range.

2.2. Methods

2.2.1. Rheological Behaviour Test. In this study, four different indexes, i.e., slump, slump flow, yield stress τ_0 , and plastic viscosity η were measured to describe the fluidity of fresh CGCBM. The former two indexes were determined by the slump and spread diameter test, which is currently the most used method [22], and can be conveniently used in the field, and it was conducted according to ASTM C143 [23]. The latter two were measured by a concrete rheometer (as shown in Figure 1), which is composed of a container to hold the fresh CGCBM, a four-blade vane that is held by the chuck on the driver, a frame to attach the driver/vane assembly to the top of the container, a laptop computer to

TABLE 1: The main mineral content in Xinyang coal gangue of Fenxi Coal Mine group (%).

Composition	$\text{Ca}_{2.87}\text{Fe}_{0.13}(\text{SiO}_3)_3$	$\text{Fe}_3(\text{Si, Fe})_2\text{O}_5(\text{OH})_4$	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	SiO_2
Content (%)	34.3	26.8	23.9	14.9

TABLE 2: The chemical component of cement.

Composition	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Others
Content (%)	65.08	22.36	5.53	3.46	1.27	2.3

TABLE 3: The main mineral content in fly ash.

Composition	SiO_2	MgO	$(\text{Fe}_{0.807}\text{Al}_{0.193})(\text{Al}_{1.807}\text{Fe}_{0.193})\text{O}_4$	Fe_2O_3	CaO
Content (%)	63.8	26.3	4.4	4.0	1.5



FIGURE 1: Concrete rheometer.

operate the drive, record the torque during the test, and calculate the flow peters.

2.2.2. Bleeding Rate Test. Bleeding rate test is conducted according to ASTM C 232-14 [24].

The apparatus used in the bleeding test are container, a cylindrical container of approximately 14L (1/2 ft³) capacity, having an inside diameter of 255 ± 5 mm ($10 \pm 1/4$ in) and an inside height of 280 ± 5 mm ($11 \pm 1/4$ in), scale, pipet, glass graduate, tamping rod, metal beaker, and hot plate.

During the test, maintain the ambient temperature between 18 and 24°C (65 and 75°F). Immediately after trowelling the surface of the specimen, record the time. Place the specimen and container on a level platform or floor free of noticeable vibration, and cover the container to prevent evaporation of the bleed water. Keep the cover in place throughout the test, except when drawing off the water. Draw off (with pipet or similar instrument) the water that has accumulated on the surface at 10 min intervals during the first 40 min and at 30 min intervals thereafter until cessation of bleeding, recording the time of last observation. To facilitate the collection of bleed water, tilt the specimen carefully by placing a block approximately 50 mm (2 in) thick under one side of the container 2 min prior to each time the water is withdrawn.

After the water is removed, return the container to a level position without jarring. After each withdrawal, transfer the water to a 100 mL graduated cylinder. Record the accumulated quantity of water after each transfer. If it is desired to determine the mass of the bleed water and to exclude the material present other than the water, carefully decant the contents of the cylinder into a metal beaker. Determine the mass and record the mass of the beaker and its contents. Dry the beaker and its contents to constant mass and record the final mass. The difference between the two masses, D , is equal to the mass of the bleed water. The mass of the sludge shall also be obtained. Calculate the accumulated bleed water, expressed as a percentage of the net mixing water contained within the test specimen, as

$$C = \left(\frac{w}{W} \right) \times S, \quad (1)$$

$$\text{bleeding, \%} = \left(\frac{D}{S} \right) \times 100\%,$$

where C is mass of net mixing water in the test specimen, g; W is the total mass of the batch, kg; w is the mass of net mixing water in the batch (the total amount of water minus the water absorbed by the aggregates), kg; S is the mass of the specimen, g; D accumulated mass of the bleed water, g, (total volume with drawn from the test specimen in multiplied by 1 g/mL).

2.2.3. Samples Preparation and Compressive Strength Test. Compressive strength test is conducted according to GB/T 50081-002 [25].

A number of CGCBM samples (150 in total) were prepared to measure the compressive strength for different mix proportions and different ages (1 d, 3 d, 7 d, 14 d, 28 d). The raw materials were mixed and poured into steel modules of 100 mm × 100 mm × 100 mm in size. After 24 h, the steel modules were removed, and the samples were placed in a humid room for curing. The temperature and humidity of the room are kept constant ($20 \pm 2^\circ\text{C}$ and 95%) to ensure the curing condition similar to the underground coal mine. The CGCBM samples were prepared to measure compressive strength for different ages following a predetermined curing period. Based on the previous work, it was predicted that the

compressive strength of samples was not more than 10 MPa. Therefore, compressive strength test was conducted with a YAW-200B-type compression-testing machine, and the displacement speed is 0.3 kN/s, and cube compressive strength should be calculated as

$$f_m = \frac{F}{A} \quad (2)$$

where f_m is cube compressive strength, MPa; F is the specimen failure load, N; and A is the pressure area of the test piece, mm^2 .

2.2.4. SEM and XRD Studies on CGCBM Samples. The microstructure and texture of some fractured samples obtained from compressive strength tests after 28 days were examined under a JSM-7001F thermal field emission scanning electron microscope (TFSEM) which also can be used to measure energy dispersive spectrometry (EDS). SEM was operated at an accelerating voltage of 15 kv. Powder samples we soaked in alcohol to cease further hydration and dried in an oven. Then, they were put on the rotating observation deck under SEM to be measured. XRD was used determine the product of fractured section.

3. Results and Discussion

Based on Sections 2.2.1, 2.2.2, and 2.2.3 to test slump, slump flow, yield shear stress τ_0 , plastic viscosity η , bleeding rate, and compressive strength, the test results are shown in Table 4.

3.1. Rheological Behaviour of Fresh CGCBM. Changes of yield stress τ_0 , plastic viscosity η , slump, and slump flow for fresh mixture with different dosages of WRA are shown in Figures 2~4. Because the binder ratio of control group (NO. 0) is different from others, the result of the control group is not shown in the figures.

Especially for J1, τ_0 dropped from 634.4 to 384.7, nearly to 40%.

3.1.1. Yield Shear Stress. Compared with the control group NO. 0, yield shear stress of the fresh mixture with WRA significantly decreased, which means that the mixing of WRA contributed to the decrease of τ_0 and the fresh paste is more flexible. The trend of τ_0 with the dosage is similar for the two WRs, i.e., with the increase of dosage, τ_0 declined. But some distinction exists as shown in Figure 2. For WRA1, the rangeability of τ_0 is large when the dosage increased from 1.0% to 1.5%, then τ_0 decreased slowly. When the dosage increased from 1.75% to 2.0%, the reduction of τ_0 is only 8.1 Pa which is much less than 153.0 Pa corresponding to that of the same addition from 1.0% to 1.25. Diversely, the yield shear stress roughly linearly cut down with the dosage increase of WRA2. Obviously, the effect of WRA2 on τ_0 is more remarkable, when 0.2% WRA2 were mixed (NO. J1), τ_0 dropped from 634.4 to 384.7, nearly to 40% that is a small result because the decrease of water-binder ratio is not considered. In the process of test, it was observed that

segregating occurred when the dosages are 2% for WRA1 and 0 for WRA2, and the latter is more sensitive to water and less prone to be controlled. So, 2% and 0.6% are the upper values.

3.1.2. Plastic Viscosity. The dosage of WRA has important influence on plastic viscosity η of fresh mixture as shown in Figure 3. Obviously, the trend of η with the dosage of WRA is averse to that of τ_0 . η grows rapidly when the dosage of WRA1 varies from 1% to 1.5% (by weight of binder), and the increase is inconspicuous when the dosage is greater than 1.5%. Compared with the group NO. 0, when the dosage of WRA1 is 1.0%, η decreases from 7.9 Pa·s to 2.3 Pa·s, reduced by 70.9%. η is greater than NO. 0 when the dosage of WRA1 varies from 1.25% to 2.0%, when the dosage of WRA1 is 1.5%, η increases from 7.9 Pa·s to 12.1 Pa·s, increased by 53.2%. η is only increased 0.3 Pa·s than NO. N3 when the dosage of WRA1 varies from 1.5% to 2.0%. Therefore, when the dosage of WRA1 is greater than 1.5%, the improvement effect of η is not significantly changed. The effect of WRA2 is more obvious, compared with the group NO. 0, η is lower than NO. 0 when the dosage of WRA2 is 0.2% and 0.3%, η drops from 7.9 Pa·s to 1.7 Pa·s and 5.9 Pa·s, respectively. η is greater than NO. 0 when the dosage of WRA2 varies from 0.4% to 0.6%, when the dosage of WRA2 is 0.5%, η increases from 7.9 Pa·s to 17.6 Pa·s. However, when 0.6% WRA2 was added, it drops to 10.5 Pa·s. In this case, the coarse aggregate submerged for the intense dispersion effect of WRA2 and the lower slurry tightly stick to the container bottom of the rheometer (i.e., the so-called “scratch ground” phenomenon). The measured plastic viscosity is the dilute liquid of the upper layer material, and the viscosity is small. Therefore, it is recommended to control the WRA1 and WRA2 doses to within 1.5% and 0.5%. In contrast, WRA1 performance is relatively stable. Therefore, it is recommended to control the WRA1 and WRA2 doses to within 1.5% and 0.5%. In contrast, WRA1 performance is relatively stable.

Both WRA1 and WRA2 can significantly improve the rheological properties of fresh materials. Add 1.5% WRA1 and 0.4% WRA2 to the filling slurry, τ_0 is decreased from 634.4 Pa to 301.6 Pa and 314.7 Pa, respectively. η is increased from 7.9 Pa·s to 12.1 Pa·s and 8.5 Pa·s.

3.1.3. Slump and Slump Flow. Slump and slump flow indicate the ability of flow under gravity action, which is the macroindex describing the rheological property of fresh paste and more conveniently be obtained in practice. The more the slump and slump flow are, the better the rheological property of fresh paste is. The two indexes show a growing tendency with the increase of WRA1 in Figure 4(a). In Figure 4(b), the variation of slump and slump flow is complex. When the dosage varies from 0.2% to 0.5%, the two indexes roughly first rise and then decrease. And when the dosage is 0.6%, the indexes are abnormal and the reason is described in the above section. Compared with the control group, not only the dosage of water was saved by 10.4%, but also the rheological property of fresh paste was dramatically

TABLE 4: Performance indicators of CGCBM.

No.	Performance index of rheology				Bleeding rate / %	Cube compressive strength (MPa)				
	Slump (cm)	Slump flow (cm)	τ_0 (Pa)	η (Pa·s)		1 d	3 d	7 d	14 d	28 d
0	20	30	634.4	7.9	4.9	2	1.2	2.7	4.6	6.5
N1	22	33	563.6	2.3	1.3	0.4	1.5	3.0	5.0	8.3
N2	23	40	410.6	9.6	2.5	0.4	1.6	3.1	5.5	8.4
N3	23.5	43	301.6	12.1	4.0	0.5	2.0	3.2	6.4	9.3
N4	24	50	252.6	12.7	4.4	0.5	2.0	3.1	5.8	8.7
N5	27	62	244.5	12.4	6.4	0.6	2.0	3.1	5.7	8.0
J1	25	52	384.7	1.7	0	0.3	1.8	3.3	6.3	8.5
J2	25.5	66	319.3	5.9	0	0.4	2.2	3.6	7.2	8.7
J3	27	64	314.7	8.5	0.5	6	2.3	4.0	7.5	9.5
J4	27.5	43	216.9	17.6	1.1	0.8	2.5	4.1	7.5	9.2
J5	25.5	83	163.9	10.5	2.5	0.6	2.0	3.3	6.0	8.1

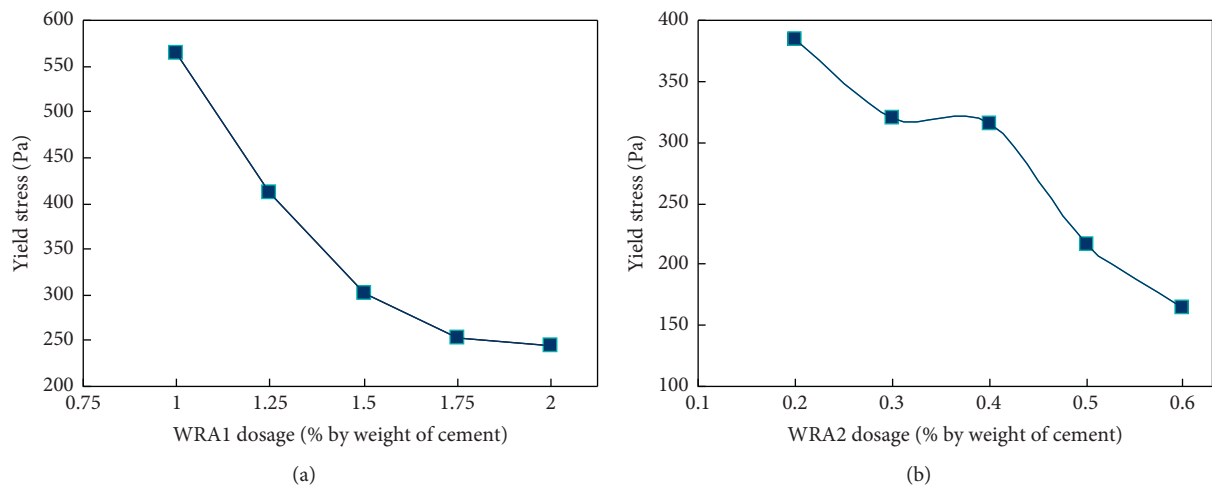


FIGURE 2: Shear yield stress of CGCBM mixed with different dosage of WRA.

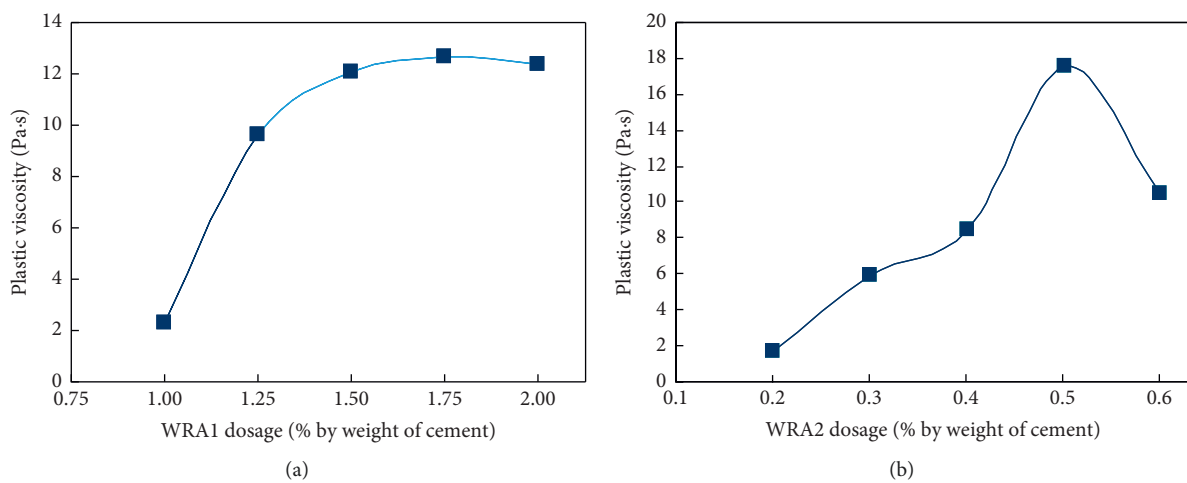


FIGURE 3: Plastic viscosity of CGCBM mixed with different dosage of WRA.

improved when the water reducers were added. In the test, all slumps >230 mm and slump flows >400 mm, which meet the technological requirements.

Variation of four indexes manifests that the mix of WRA effectively improved the workability of fresh CGCBM for the mixing of WRA which contributes to increase the

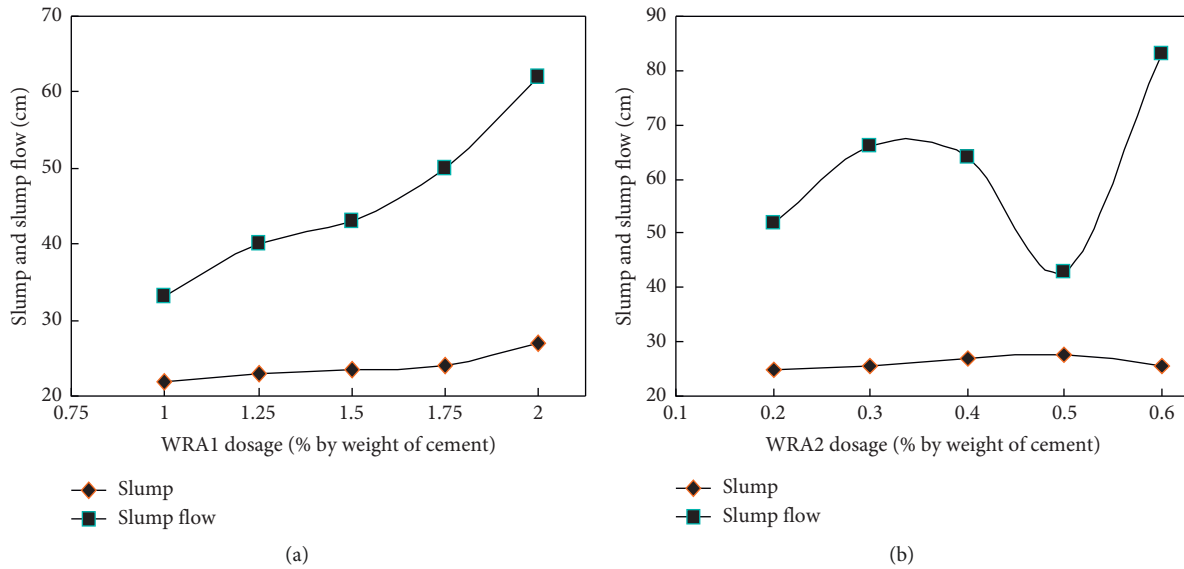


FIGURE 4: Slump and slump flow of CGCBM mixed with different dosage of WRA.

electrostatic repulsion between molecules, decrease surface tension of interface between solid and liquid, and decrease the wetting angle. In this test, the two WRAs are strong electrolytes with negative charges; if they were mixed, the lipophilic group will actively adhere to the surface of cement and fly ash particles, and the hydrophilic group will direct to water molecules [26–30]. This directional arrangement of WRA molecules makes the surface of cement and fly ash particles absorbed with like charge and form water film with a certain thickness which prevent forming flocculated structure. Solid particles were dispersed and lubricated of fresh mixture for the mixing of WRA, so yield shear stress τ_0 reduced and slump enhanced and the degree is relating with the dosage of WRA. Meanwhile, WRAs are viscous, salvation film will form when they dissociate in water film between particles which enhance the viscosity of mixture. Therefore, plastic viscosity η increased.

To prepare desired fresh CGCBM mixture with good flowability, homogeneity, segregation resistance, pumpability, yield shear stress τ_0 , and plastic viscosity η , slump and slump flows should keep in a certain range [31]. The range of slump and slump flow are often determined according to experience, for CGCBM, they are >230 mm and 400 mm, respectively. The range of τ_0 and η is not reported in related literatures.

3.2. Bleeding Rate of Fresh CGCBM. For fresh paste, the cemented material (cement and fly ash) particles with different charges will absorb each other to form a flocculated structure in the early stage of hydration and the water was enclosed in it. In the standing process, the enclosed water will bleed through the capillary pore which has some side effect on the property of paste [32]. So, a lower bleeding rate is favoured in practice. In the test, water reduced was added to cut down the dosage of water to decrease the bleeding rate. It can be found that in Table 4 and Figure 5, except N5, all

bleeding rates are less than 4.9% that of the control group. But because the water was cut down by 10.4% for N1–N5 and J1–J5, their bleeding rate is larger than that of the control group and increases with the dosage of WRA. The reason is that part of mixed water was dispersed by active substance when WRA was added and bleeding out through communication pore. WRA2 has more branches to conjugate water molecules, and water retaining capacity is better; consequently, the bleeding rate of the corresponding mixture is lower.

3.3. Cube Comprehensive Strength of Hardened CGCBM.

The test results of CGCBM compressive strength are shown in Table 4 and Figure 6, compared with the group NO. 0, mixing of WRA1 is helpful to enhance the early age strength. The compressive strength of the cube at 1 day was above 0.4 MPa, which was twice the strength of the group NO. 0. And the compressive strength increases with the increase of WRA1 content. At 3 days, the compressive strength of the cube increased with the increase of the WRA1 content, but the compressive strength no longer increased after the content was 1.5%. At 7 days, the compressive strength of the cube did not change much with the increase of the WRA1 content, and remained at the level of 3 MPa. At 14 days and 28 days, the compressive strength of the cubes changed similarly, showing a trend of increasing first and then decreasing. When the WRA1 content was 1.5%, the compressive strength of the cubes at 14 days and 28 days was the largest, which were 1.39 times and 1.43 times of the group NO. 0 cubes, respectively. WRA2 strengthens the early compressive strength of CGCBM more obviously. Cube compressive strength increased up to 4 times at 1 day. The compressive strength of CGCBM cubes at all ages increased first and then decreased with the increase of WRA2 content. At 1, 3, and 7 days, the compressive strength of the cube reached the maximum when the WRA2 content was 0.5%. Cube compressive strength is 0.8 MPa, 2.5 MPa,

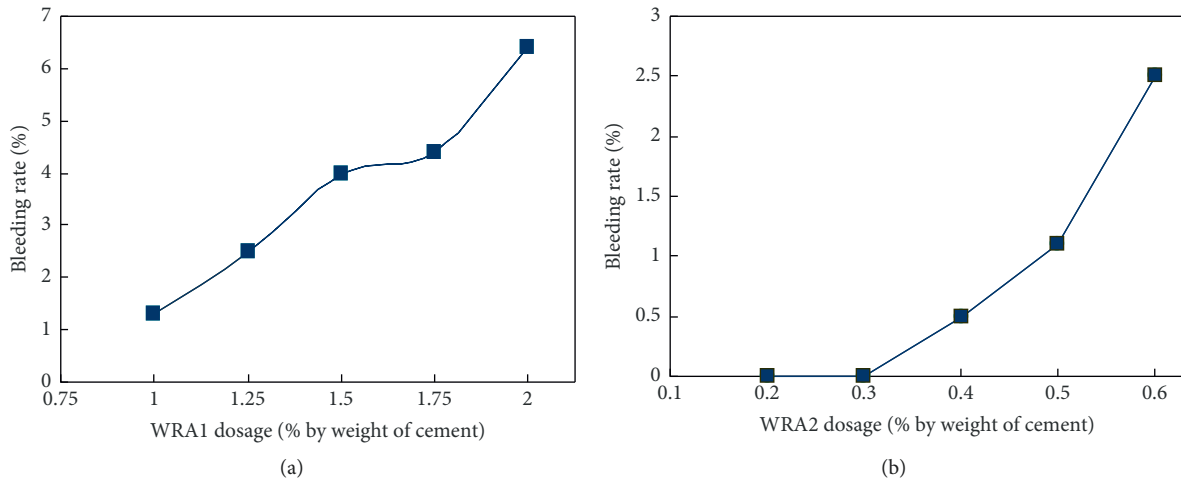


FIGURE 5: Bleeding index of CGCBM mixed with different dosage of WRA.

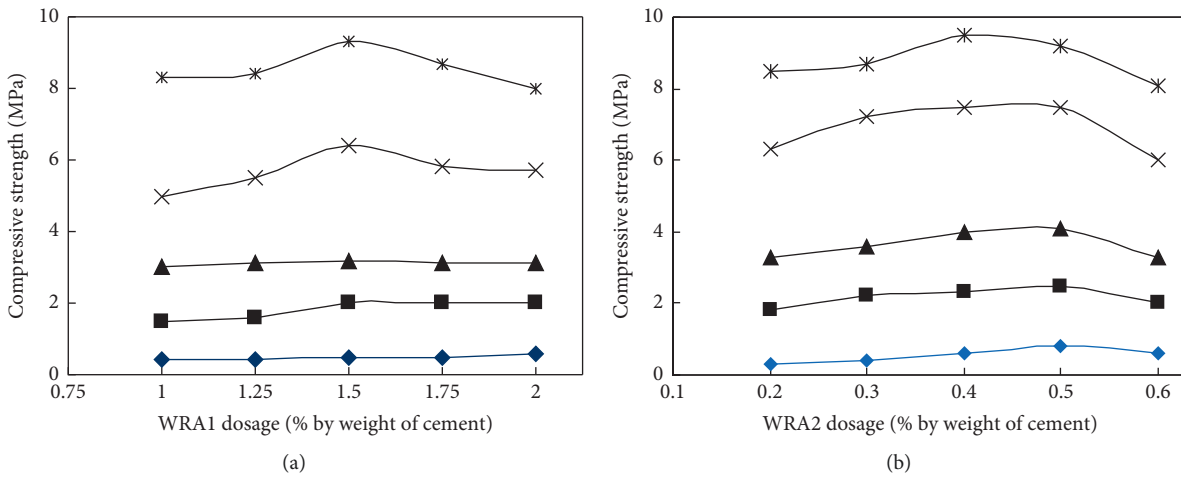


FIGURE 6: Cube compressive strength of CGCBM mixed with different dosages of WRA.

and 4.1 MPa, respectively. The compressive strength of the cube is 4 times, 2.08 times, and 1.52 times that of the NO. 0 group, respectively. At 14 and 28 days, the compressive strength of the cube reached the maximum when the WRA2 content was 0.4%. Cube compressive strength is 7.5 MPa and 9.5 MPa, respectively. The compressive strength of the cube is 1.63 times and 1.46 times that of the NO. 0 group, respectively.

In summary, both types of water-reducing agents have a continuous enhancement effect on the compressive strength of the CGCBM. The overall performance of the material is better, when the dosage of WRA1 alone is 1.5% or the dosage of WRA2 alone is 0.4%. WRA1 is affected by physical factors, because the WRA reduces the amount of water used in mixing, at the same time, the water bleeding rate is reduced, so the cracks and voids caused by a large amount of water bleeding during the material hardening process are reduced, and the density is enhanced [33]. WRA2 is affected by chemical factors, because WRA can not only uniformly disperse the interfacial cementing material (Fe(OH)₃) (by

SEM and XRD tests, as shown in Figures 7 and 8) and avoid the agglomeration of iron oxide gel, but also promote the hydration and pozzolanic reaction of gelling materials, enhancing the thermal movement between fine particles, so that fine minerals not participating in the reaction are filled into the interface transition zone, and the structure of the transition zone is optimized, thereby improving the interface structure and the CGCBM strength.

3.4. SEM and XRD of CGCBM Sample. To explore the mechanism of water reducer on the strength of paste, the damaged sections of samples were analysed by TFSEM, as shown in Figure 7, in which images A–C are the pictures of damaged sections, and images D–F is the SEM picture amplified 1000 times.

It was detected in images A–C of Figure 7 that (1) some coal gangue was covered by rufous solid matters in the damage section, and the colour in images B and C is lighter. XRD (Figure 8) confirmed that it is Fe(OH)₃. The reason is

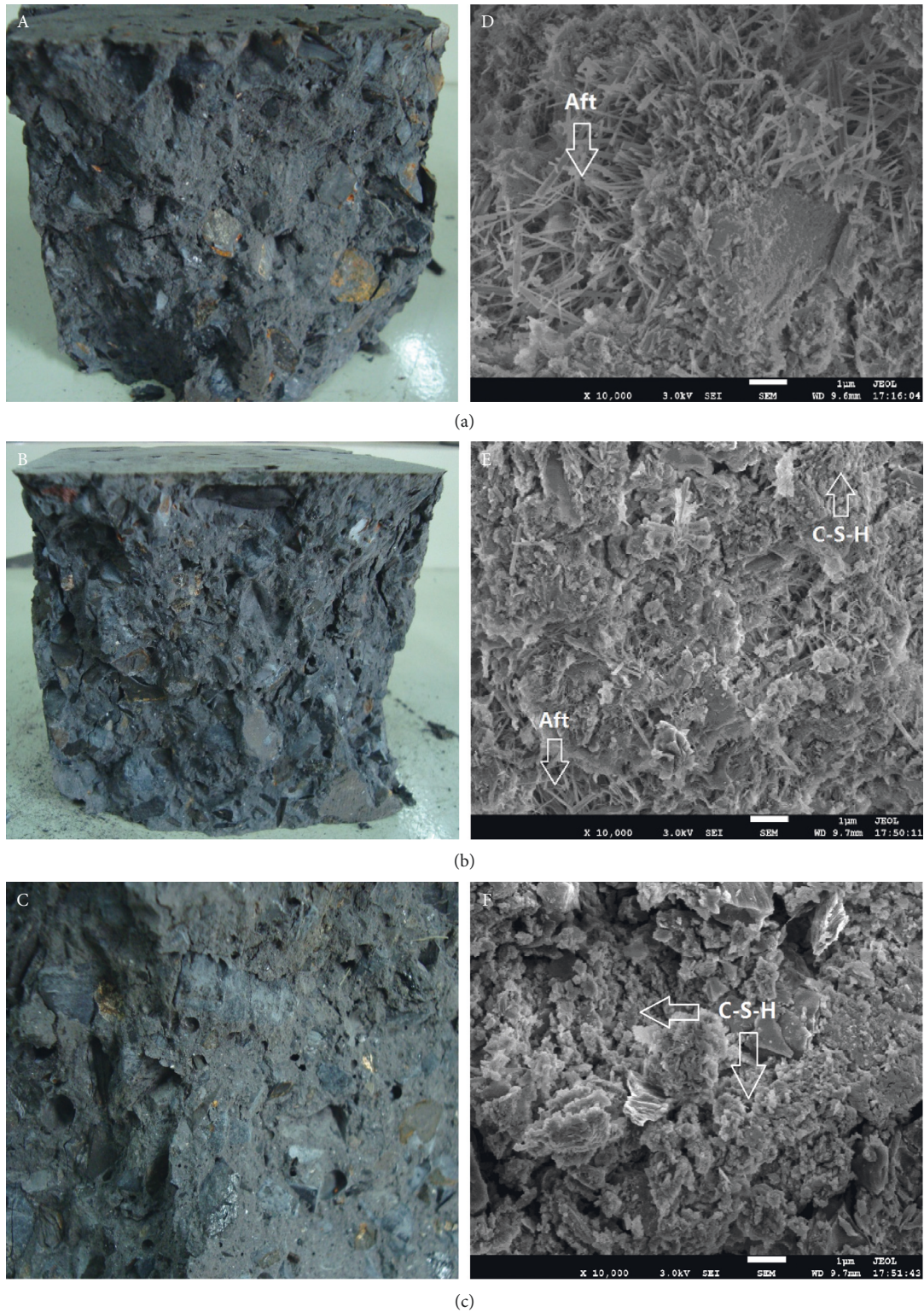


FIGURE 7: Damaged sections and SEM picture of (a) 0, (b) N3, and (c) J3.

that the coal gangue collected from Gao Yang coal mining contains active iron-rich minerals (as shown in Table 1) that are prone to ooze out of coal gangue in moisture circumstance and the Fe^{3+} and Fe^{2+} will combined with hydroxyl ions and form $\text{Fe}(\text{OH})_3$ gel and $\text{Fe}(\text{OH})_2$, then $\text{Fe}(\text{OH})_2$ was

oxidized to form $\text{Fe}(\text{OH})_3$ gel. During drying, the gel will dehydrate and become rufous powder. This powder is harmful to the interface strength. For the dispersive action of water reducer, the iron-rich minerals evenly distribute over the surface of coal gangue which lead to the $\text{Fe}(\text{OH})_3$ powder

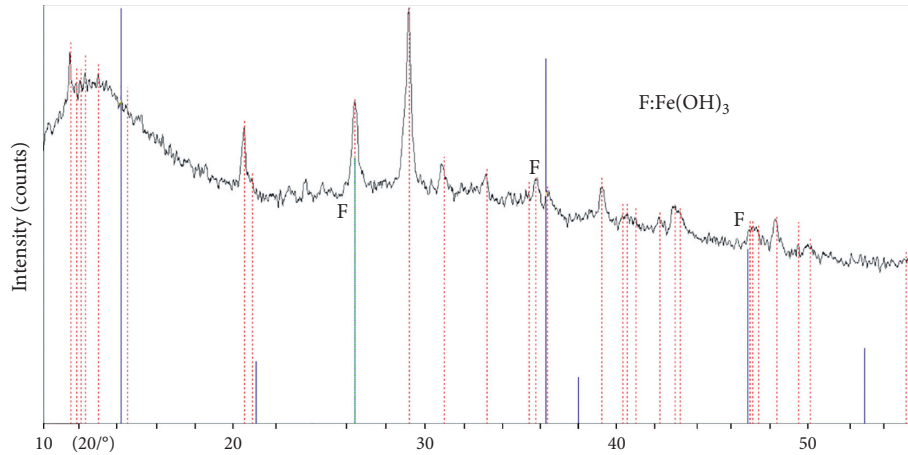
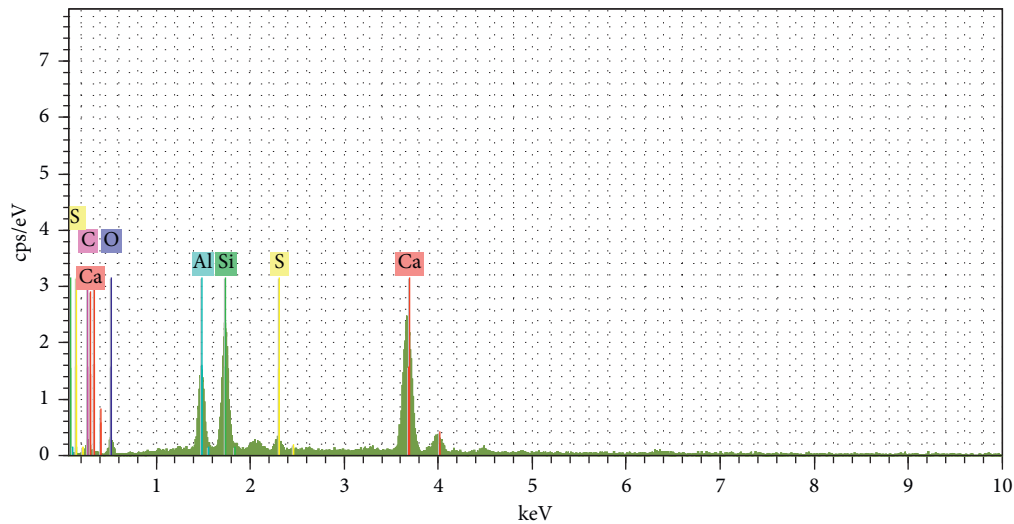


FIGURE 8: XRD analysis for reddish-brown powder.



High voltage: 15.0kV Pulse: 1.20kcps

El AN Series	unn. (wt.%)	C norm. (wt.%)	C atom. (at. %)	C error (1 Sigma) (wt.%)
Ca 20 K-series	23.83	39.63	24.66	0.78
Si 14 K-series	12.73	21.18	18.81	0.59
Al 13 K-series	8.15	13.54	12.52	0.44
O 8 K-series	7.82	13.00	20.26	2.00
C 6 K-series	6.44	10.70	22.23	1.78
S 16 K-series	1.18	1.95	1.52	0.09
Total:	60.14	100.00	100.00	

FIGURE 9: EDS for hydration products.

layer thin and colour light. For control group, $Fe(OH)_3$ gel gathered in the interface between coal gangue and binder for bleeding and form a weak point. Because of accumulation of $Fe(OH)_3$ gel, it is dark. (2) From images A and C, it can be found that adding WRA2 can reduce microporous and increase CGCBM compactness.

From SEM pictures, the needle products in Figure 7(a)-D were less than that in Figure 7(b)-E, and the particles size diminished from 0.1-0.2 μm to 0.05-0.06 μm . It almost

disappears in Figure 7(c)-F. Inversely, the sheet products increased in Figures 7(a)-D and 7(c)-F and the size increased. By EDS (as shown in Figure 9), it was found that the needle products and sheet products are ettringite (Aft) and C-S-H gel, respectively. Also, it can be found that the connection of cemented material transit from cross linking of needle products to stacked linking of sheet products. It was illustrated that the surface tension of solid/liquid interface was decreased after the WR was added, and the inner

active matter of cemented material particle is subject to strip. So, the hydration and pozzolanic reaction were promoted to generate more compact C-S-H gel; then, the interface bonding was strengthened. Meanwhile, the connection manner of hydrated products was changed making the paste denser.

To sum up, the contribution of WRA is (1) uniformly dispersing interface binding material, avoiding the accumulation of $\text{Fe}(\text{OH})_3$, and improving interface structure, (2) promoting hydration and pozzolanic reaction and increasing the bond strength, and (3) improving the connection manner of cemented material to increase the density.

WRA2 (polycarboxylate superplasticizer) is of a special molecular structure, which is not only combined with the electrostatic repulsion and space steric hindrance, intensifying thermal motion between particles to promote reaction, but also is of many combining positions, strengthening the interface connection. However, WRA1 (naphthalene water reducer) promotes the hydration only by electrostatic repulsion. Thus, WRA2 is more effective for the increasing of compressive strength.

4. Conclusions

This study reveals the influence of the addition of naphthalene series (WRA1) and poly carboxylic acid (WRA2) based water-reducing admixtures (WRA) on the rheological and mechanical properties of CGCBM produced from coal gangue. The addition of these WRA appeared to improve the fluidity, stability, and the strength development of CGCBM. After adding WRA, the water-to-cement ratio of CGCBM decreased from 0.67 to 0.6 without increasing binder dosage. Adding WRA can reduce yield stress (τ_0), increase plastic viscosity (η), not make any significant change in slump, increase the slump flow significantly, and improve the fluidity of CGCBM effectively. The bleeding rate increases with the increase in the amount of WRA, leading to a gradual decrease in stability. WRA can effectively improve the compressive strength of CGCBM, and the strength at the later stage increases first and then decreases with the increase of the dosage. Considering the effects of WRA on the fluidity, stability, and compressive strength properties of CGCBM, the reasonable content of WRA1 and WRA2 is 1.5% and 0.4%, respectively.

Data Availability

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

Disclosure

Only abstracts of this paper have been published in 2015 International Conference on Human Health and Medical Engineering.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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References

- [1] H. Liu and Z. Liu, "Recycling utilization patterns of coal mining waste in China," *Resources Conservation and Recycling*, vol. 54, no. 12, pp. 1331–1340, 2010.
- [2] G. Wang, Y. Xie, Y. Qin et al., "Element geochemical characteristics and formation environment for the roof, floor and gangue of coal seams in the Gujiao mining area, Xishan coalfield, China," *Journal of Geochemical Exploration*, vol. 190, no. 4, pp. 336–344, 2018.
- [3] D. Wu, B. Yang, and Y. Liu, "Transportability and pressure drop of fresh cemented coal gangue-fly ash backfill (CGFB) slurry in pipe loop," *Powder Technology*, vol. 284, pp. 218–224, 2015.
- [4] F. G. Bell, T. R. Stacey, and D. D. Genske, "Mining subsidence and its effect on the environment: some differing examples," *Environmental Geology*, vol. 40, no. 1–2, pp. 135–152, 2000.
- [5] J. Szczepanska and I. Twardowska, "Distribution and environmental impact of coal-mining wastes in Upper Silesia, Poland," *Environmental Geology*, vol. 38, no. 3, pp. 249–258, 1999.
- [6] T. Qi and G. Feng, "Resistivity and AE response characteristics in the failure process of CGB under uniaxial loading," *Advances in Materials Science and Engineering*, vol. 2017, Article ID 7857590, pp. 1–11, 2017.
- [7] X. Du, G. Feng, Y. Guo, T. Qi, Y. Zhang, and J. Guo, "Failure analyses of unconfined CCWBM body in uniaxial compression based on central pressure variation," *Waste Management & Research*, vol. 36, no. 2, pp. 159–168, 2018.
- [8] X. Zhang, J. Lin, J. Liu, F. Li, and Z. Pang, "Investigation of hydraulic-mechanical properties of paste backfill containing coal gangue-fly ash and its application in an underground coal mine," *Energies*, vol. 10, no. 9, p. 1309, 2017.
- [9] T. Qi, G. Feng, Y. Li, Y. Guo, J. Guo, and Y. Zhang, "Effects of fine gangue on strength, resistivity, and microscopic properties of cemented coal gangue backfill for coal mining," *Shock and Vibration*, vol. 2015, Article ID 752678, 11 pages, 2015.
- [10] D. Wu, Y. Hou, T. Deng, Y. Chen, and X. Zhao, "Thermal, hydraulic and mechanical performances of cemented coal gangue-fly ash backfill," *International Journal of Mineral Processing*, vol. 162, pp. 12–18, 2017.
- [11] P. Sandeep, D. Debasis, and T. Sreenivas, "Variability in rheology of cemented paste backfill with hydration age, binder and superplasticizer dosages," *Advanced Powder Technology*, vol. 29, no. 9, pp. 2211–2220, 2018.
- [12] A. Kesimal, E. Yilmaz, B. Ercikdi, I. Alp, and H. Deveci, "Effect of properties of tailings and binder on the short-and long-term strength and stability of cemented paste backfill," *Materials Letters*, vol. 59, no. 28, pp. 3703–3709, 2005.
- [13] Q. Jiang, X. Z. Xia, and Q. Zhang, "The influence of the air-entraining water-reducing agent on the mechanical properties

- of the recycled concrete,” *Materials Research Innovations*, vol. 19, no. 5, pp. S5–514, 2015.
- [14] N. Zhou, S. Y. Ouyang, Q. Q. Cheng et al., “Experimental study on mechanical behavior of a new backfilling material: cement-treated marine clay,” *Advances in Materials Science and Engineering*, vol. 2019, Article ID 1261694, 8 pages, 2019.
- [15] B. Ercikdi, F. Cihangir, A. Kesimal, H. Deveci, and İ. Alp, “Effect of natural pozzolans as mineral admixture on the performance of cemented-paste backfill of sulphide-rich tailings,” *Waste Management & Research*, vol. 28, no. 5, pp. 430–435, 2010.
- [16] B. Ercikdi, F. Cihangir, A. Kesimal et al., “Utilization of water-reducing admixtures in cemented paste backfill of sulphide-rich mill tailings,” *Journal of Hazardous Materials*, vol. 179, no. 1–3, pp. 940–946, 2010.
- [17] L. Huynh, D. A. Beattie, D. Fornasiero, and J. Ralston, “Effect of polyphosphate and naphthalene sulfonate formaldehyde condensate on the rheological properties of dewatered tailings and cemented paste backfill,” *Minerals Engineering*, vol. 19, no. 1, pp. 28–36, 2006.
- [18] I. Papayianni, G. Tsohos, N. Oikonomou, and P. Mavria, “Influence of superplasticizer type and mix design parameters on the performance of them in concrete mixtures,” *Cement and Concrete Composites*, vol. 27, no. 2, pp. 217–222, 2005.
- [19] H. Uchikawa, S. Hanehara, T. Shirasaka, and D. Sawaki, “Effect of admixture on hydration of cement, adsorptive behavior of admixture and fluidity and setting of fresh cement paste,” *Cement and Concrete Research*, vol. 22, no. 6, pp. 1115–1129, 1992.
- [20] B. Ercikdi, F. Cihangir, A. Kesimal, H. Deveci, and İ. Alp, “Utilization of water-reducing admixtures in cemented paste backfill of sulphide-rich mill tailings,” *Journal of Hazardous Materials*, vol. 179, no. 1–3, pp. 940–946, 2011.
- [21] A. Ren, G. Feng, Y. Guo et al., “Influence on performance of coal mine filling paste with fly ash,” *Journal of China Coal Society*, vol. 39, no. 12, pp. 2374–2380, 2014.
- [22] O. H. Wallevik and J. E. Wallevik, “Rheology as a tool in concrete science: the use of rheographs and workability boxes,” *Cement and Concrete Research*, vol. 41, no. 12, pp. 1279–1288, 2011.
- [23] ASTM C 143, *Standard Test Method for Slump of Hydraulic-Cement Concrete*, ASTM International, West Conshohocken, PA, USA, 2008.
- [24] ASTM C 232-14, *Standard Test Methods for Bleeding of Concrete*, ASTM International, West Conshohocken, PA, USA, 2004.
- [25] GB/T50081-2002, *Standard for Test Method of Mechanical Properties on Ordinary Concrete*, China Architecture & Building Press, Beijing, China, 2005.
- [26] J. Peng, D. Deng, H. Huang, Q. Yuan, and J. Peng, “Influence of superplasticizer on the rheology of fresh cement asphalt paste,” *Case Studies in Construction Materials*, vol. 3, pp. 9–18, 2015.
- [27] X. Kong, Y. Zhang, and S. Hou, “Study on the rheological properties of Portland cement pastes with polycarboxylate superplasticizers,” *Rheologica Acta*, vol. 52, no. 7, pp. 707–718, 2013.
- [28] T. U. Mohammed, T. Ahmed, S. M. Apurbo et al., “Influence of chemical admixtures on fresh and hardened properties of prolonged mixed concrete,” *Advances in Materials Science and Engineering*, vol. 2017, Article ID 9187627, 11 pages, 2017.
- [29] A. Papo and L. Piani, “Effect of various superplasticizers on the rheological properties of Portland cement pastes,” *Cement and Concrete Research*, vol. 34, no. 11, pp. 2097–2101, 2004.
- [30] E.-S. M. Negim, M. Ramli, B. Saad, L. Bekbayeva, and M. I. Saleh, “Effects of surfactants on the properties of styrene/methacrylate-type superplasticizer in cement paste,” *Polymer-Plastics Technology and Engineering*, vol. 50, no. 9, pp. 941–946, 2011.
- [31] J. Zhu, G. Zhang, Z. Miao, and T. Shang, “Synthesis and performance of a comblike amphoteric polycarboxylate dispersant for coal-water slurry,” *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 412, pp. 101–107, 2012.
- [32] J. Liu and R. H. Guo, “Applications of steel slag powder and steel slag aggregate in ultra-high performance concrete,” *Advances in Civil Engineering*, vol. 2018, Article ID 1426037, 8 pages, 2018.
- [33] F. Deschner, F. Winnefeld, B. Lothenbach et al., “Hydration of Portland cement with high replacement by siliceous fly ash,” *Cement and Concrete Research*, vol. 42, no. 10, pp. 1389–1400, 2012.

