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Preparation of High-Performance Cementitious Materials from Industrial Solid Wastes †

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Abstract: Based on coal gangue, sintered red mud, and fly ash, which are primary industrial waste products, a high-performance cementitious material was developed that considered its composition, physical and chemical properties, and microstructure. The optimal ratio of the materials with an appropriate exciter content was determined through the production and testing of samples composed of various ratios. It was found that the compressive strength reached its maximum when the ratio of coal gangue: red mud: fly ash was 40:40:20 and the exciter content was 8%. The synergistic effect of the waste-based cementitious material and the exciter content was confirmed, which lays a foundation for the development of diverse waste-based industrial materials. The use of such materials helps reduce abandoned industrial waste and encourages the recycling of materials for various purposes.

Keywords: coal gangue; red mud; fly ash; solid-waste-based cementitious materials

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1. Introduction

The shortage of resources such as cement and gravel and the environmental effect of using them has been a concern for road construction for a long time. Therefore, the research on the curing agent based on recycled solid wastes has received a lot of attention. Solid waste used in construction is mainly collected from wasted rocks from mining, beneficiation, and tailings, as well as from waste slag from fuel production or smelting [1,2]. Liu [3] et al. prepared a highway pavement subgrade material using red mud waste from Bayer process waste products, coal gangue, and fly ash. The material was found to have appropriate mechanical and environmental properties that met the national standards. Liu [4] et al. studied the effects of fly ash addition on the early strength and volumetric stability of a mixture of desulfurization gypsum, lime, and the exciter of red-mud-filled materials. They found that the desulfurization gypsum promoted the generation of calcium alumina, the lime enhanced the effect of the fly ash, and the exciter accelerated the process of the hydration reaction of red mud and fly ash. The synergistic effect of the three materials improved the strength of the red-mud-filled body.

Wei [5] pointed out that coal gangue and red mud could be used in road construction, and Wang et al. [6] prepared alkali-activated cementitious materials with fly ash, titanium gypsum, and carbide slag; they found the optimal ratio of the mixture to have the best mechanical property as a cementitious material. Wang et al. [7] selected coal gangue and fly ash as base materials to prepare geopolymer foaming materials. The compressive strength, density, porosity, and thermal conductivity of the foaming materials prepared under different blending ratios of coal gangue and fly ash were studied to find an appropriate blending ratio to satisfy the expected engineering effects. Ye et al. [8] tested aluminosilicate solid waste as cementitious materials and found that the performance of the materials was enhanced significantly when red mud and coal gangue were mixed in a ratio of 39 and

26 wt.%, respectively. Gao [9] developed multi-source solid-waste-based marine grouting materials using Bayer red mud, calcium carbide slag, and silica fume as raw materials and proved that the compressive requirements of the material met the industrial standard. In an indoor test, Wang et al. [10] found that the solid-waste-based soil curing agent composed of ISW and Portland cement improved mechanical properties and durability compared to solidified clay, expansive soil, solidified silty soil, and fine sandy soil. The mixture's unconfined compressive strength after 28 days reached above 3.3 MPa. By comparing the soil curing agent made from a mixture of industrial wastes, including fly ash, tailings, slag, and slaked lime and PF32.5, Wang [11] proved that the industrial-waste-based soil curing agent was effective for curing clay soils of a low liquid limit. Wei [12] optimized the ratio and performance of grouting material that was prepared with alkali-excited cement-based material for mines and road construction. They found that, as the ratio of slag powder/fly ash increased, the precipitation rate gradually decreased, and the compressive strength gradually increased and stabilized.

Referring to the previous study results of various cementitious materials using industrial wastes, we developed a high-performance waste-based cementitious material using coal gangue, sintered red mud, and fly ash. Coal gangue is one of the most-produced industrial solid wastes in China due to the enormous use of coal, and red mud is a well-known material for its great potential as a new alkali-inspired cementitious material [13]. Cement production requires a huge amount of various raw materials. Thus, if coal gangue and red mud are used in cement production, abandoned coal gangue and red mud can be reused to save production costs and increase product reliability, as well as to support environmental protection [14]. In this study, the physical and chemical properties, as well as the microstructure of a waste-based cementitious material, were investigated to understand its mineral synergy and excitation characteristics. The optimal ratio of each raw material and an exciter was determined by experimenting with the performance. The result provides a reference for recycling and using industrial wastes for various purposes to develop diverse, environment-friendly construction materials.

2. Materials and Methods

2.1. Analysis Method

The major component of raw materials was analyzed using X-ray fluorescence analysis (XRF) and X-ray powder diffraction (XRD) analysis methods. In XRD analysis, the powder method was adopted with a Rigaku Ultima type IV ray diffractometer. The conventional wide angle was 10–80°, and the conventional test rate was 2°/min. The size of the particles of the materials did not exceed 75 μm, and 0.5 g of each material was used for the analysis. The fluidity was measured with the conventional spiral fluidity test method for cement slurry. The penetration resistance test (ASTM C803) was carried out for compressive strength with 4 × 4 × 4 cubes made from cementitious materials with various mixing ratios (explained in Section 3.2).

2.2. Coal Gangue

In this study, burned coal gangue was selected as the main component of the high-performance composite gel material and was collected from the Jinan Huaiyin western heat source plant. The analyzed content of metals and minerals are shown in Tables 1 and 2. Rare metals such as gallium, vanadium, titanium, and cobalt were contained in the coal gangue. The content of titanium was the highest (110.9670 mg/kg on average). The average contents of gallium, vanadium, and cobalt were 44.0505, 4.7352, and 4.8384 mg/kg, respectively. In the coal gangue, the content of titanium was about 2.5 times higher than that of gallium and about 23 times higher than those of vanadium and cobalt, while the content of vanadium and cobalt was similar. It is important to know their contents, as they may cause environmental pollution and radioactivity, which requires continuous environmental monitoring to use them.

Table 1. Metal contents of coal gangue used for producing high-performance waste-based cementitious material.

Sample Number	Gallium (mg/kg)	Vanadium (mg/kg)	Titanium (mg/kg)	Cobalt (mg/kg)
1	45.1848	5.2487	109.7672	5.0205
2	42.8322	3.9336	117.7885	4.5892
3	44.1345	5.0234	105.3452	4.9056
Average	44.0505	4.7352	110.9670	4.8384

Table 2. Mineral contents of coal gangue used for producing high-performance composite gel material.

Analysis Number	Mineral (Chemical Formula)	Content (wt%)			Average Content (wt%)
		Sample 1	Sample 2	Sample 3	
1	Silicate (SiO_2)	27.9	25.6	28.0	27.2
2	Muscovite ($(KF)_2(Al_2O_3)_3(SiO_2)_6$)	7.0	6.2	8.0	7.1
3	Titanium oxide (TiO_2)	0.4	1.0	0.9	0.8
4	Albite ($NaAlSi_3O_8$)	7.3	5.7	8.6	7.2
5	Kaolinite ($2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$)	28.2	27.5	26.4	27.4
6	Iron oxide (Fe_2O_3)	5.6	3.5	4.9	4.7
7	Chlorite ($(Mg,Fe)_5Al(Si_3Al)O_{10}(OH)_8$)	7.2	13.5	6.4	9.0
8	Montmorillonite ($(Na,Ca)_3(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot n(H_2O)$)	16.5	17.0	16.8	16.8
	Total (weight %)	100	100	100	100

In the coal gangue, kaolinite was the most abundant (27.4% on average), followed by silicate (27.2%), while iron oxide was the least abundant (4.78%). Kaolinite, silicate, montmorillonite, chlorite, and muscovite were major minerals in the coal gangue. SiO_2 and Al_2O_3 comprised 55% of the coal gangue. TiO_2 is a harmful substance that causes environmental pollution and radioactivity, and it plays a role as a main control factor for pollution. The montmorillonite content was 16.8% on average. It reacts chemically with rainwater, which expands gangue particles, as it changes Al_2O_3 into $Al(OH)_3$. The reaction also attenuates the mechanical strength of coal gangue in general. Thus, attention needs to be paid to the leakage of coal gangue in use.

2.3. Red Mud

The red mud was obtained from three sources, including the second stockpile of Chinalco Shandong Branch (Shandong red mud) and Shandong Weiqiao Aluminum Company (Weiqiao red mud) after the sintering process and the red mud stockpile of Shandong Aluminum (Zibo red mud) after the Bayer process. The samples were stored and dried for over half a year. The average moisture content of the red mud was between 40.7 and 44.5%. The average liquid limit, plastic limit, and plasticity index values were 45.2–50.9%, 31.4–44.0%, and 6.9–14.6%, respectively. There were significant differences in those properties for different red mud samples, as shown in Table 3 below.

Table 3. Several properties of red mud collected from three sources.

Samples	Average Moisture Content (%)	Average Liquid Limit (%)	Average Plastic Limit (%)	Average Plasticity Index
Shandong red mud	41.4	50.9	44.0	6.9
Weiqiao red mud	40.7	48.0	33.4	14.6
Zibo red mud	44.5	45.2	31.4	13.8

The typical particle composition of red mud is shown in Figure 1. In general, the red mud particles smaller than 75 μm (in diameter) comprised more than 80% of the red mud. The particles smaller than 10 μm amounted to about 10% of the content, while the sizes of the rest ranged between 20 and 50 μm. The average unevenness coefficient was 29.0, and the curvature coefficient was 0.31. A large unevenness coefficient results in a wide particle size distribution, a better gradation, and a small curvature coefficient. In this case, particles were easy to compact, as the red mud lacked large particles. The curvature coefficient of the samples in this study was small, thus indicating that the red mud lacked large particles.

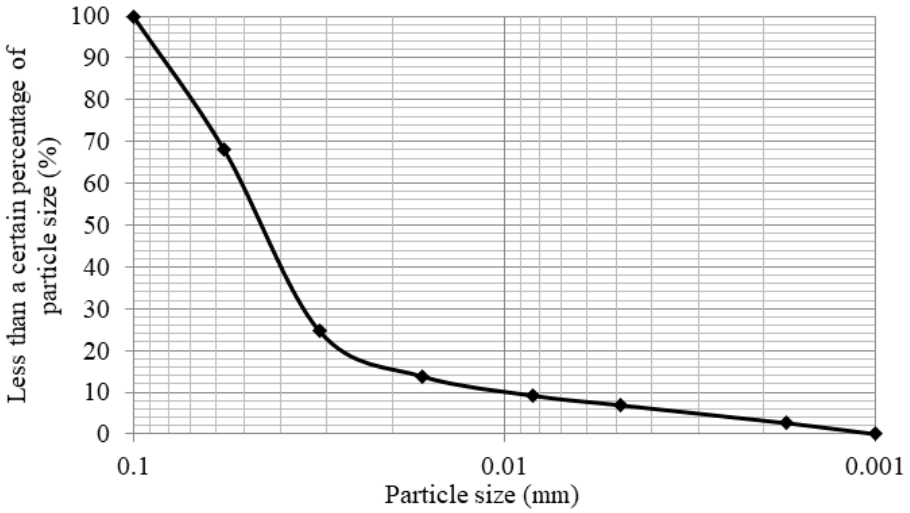


Figure 1. Conventional particle composition of red mud.

The red mud samples were analyzed with XRF to identify their compositions after being dried at 105 °C. The chemical compositions of Shandong red mud and Weiqiao red mud after the sintering process were similar in the content of chemical elements (carbon, sodium, magnesium, phosphorus, sulfur, chloride, potassium, titanium, vanadium, and manganese). The contents of silicon, calcium, aluminum, and iron were different in the two red mud samples. Shandong red mud contained higher contents of iron and aluminum than Weiqiao red mud. In particular, the iron content of Shandong red mud was 33.3% higher than that of Weiqiao red mud. Zibo red mud produced after the Bayer process showed higher contents of Al_2O_3, Fe_2O_3, SiO_2, and other oxides than those of Shandong red mud and Weiqiao red mud but a lower content of CaO. This difference in the chemical composition led to the difference in the color of Zibo red mud, which was dark red. Sintered red mud had higher CaO and SiO_2 contents and lower Fe_2O_3 content than the Bayer-processed red mud, which made it mostly white or gray in color. The differences in the chemical compositions of the red muds with different processes are shown in Figure 2. The analysis result showed a significant difference in the contents of SiO_2, Al_2O_3, CaO, and Fe_2O_3. Considering the environmental effect and cementing performance, the red mud with the sintering process calcined at 1200 °C was used in this study.

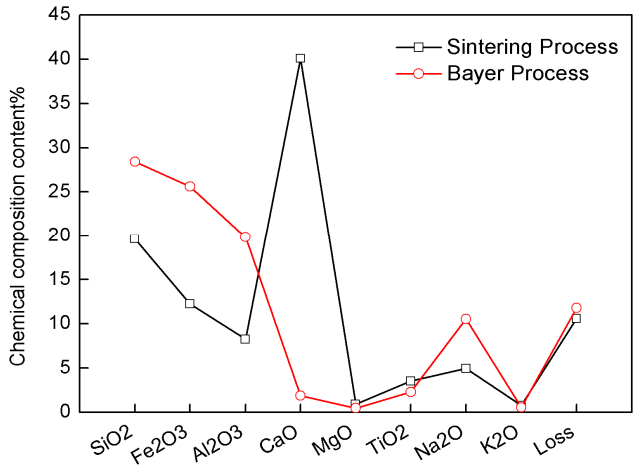


Figure 2. Comparison of chemical compositions of red mud samples produced with the sintering process (the black line) and the Bayer process (the red line).

2.4. Fly Ash

The fly ash was obtained from Jinan Thermal Power Company. XRF analysis of fly ash collected from the landfill site was performed to determine its chemical composition as shown in Table 4. The main components of the fly ash were SiO_2 (50.76%) and Al_2O_3 (20.12%). In general, more SiO_2 increases the activity of the fly ash regarding the mixture of cementitious materials.

Table 4. Chemical composition of fly ash collected from the landfill site in this study.

Composition	SiO_2	CaO	SO_3	Fe_2O_3	Al_2O_3
Content (wt.%)	50.76	16.8	6	6.22	20.12

The SEM image in Figure 3 shows that the fly ash was composed of a variety of particles, of which spherical particles accounted for more than 50% of the total particles, and irregular-shaped particles accounted for about 35% of the total particles. It is known that irregular-shaped particles have higher chemical reactivity in high-temperature calcination. However, all particles store high chemical energy after high-temperature calcination, so fly ash maintains a high activity. As the total content of SiO_2, Al_2O_3, CaO, and Fe_2O_3 reached 80%, and the particle size was small enough at the micrometer level, the fly ash turned out to have a high possibility of synergistic polymerization with the C-S-H gel structure.

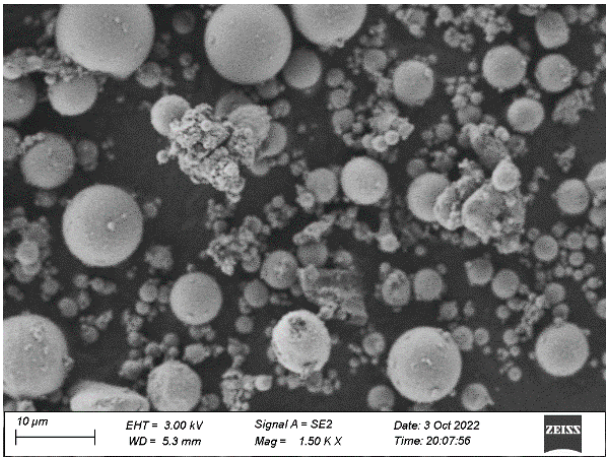


Figure 3. SEM image of fly ash collected from landfill site.

3. Preparation and Characterization of Waste-Based Cementitious Material

3.1. Preparation of Exciter

To prepare the high-performance waste-based cementitious material, we used sodium silicate, triterpene saponin, polymerized aluminum sulfate, magnesium fluorosilicate, sodium hydroxide, hydroxypropyl methylcellulose, carboxymethyl starch ether, sodium tripolyphosphate, and sulfonated melamine formaldehyde resin at the pure reagent level. A total of 35 g sodium silicate was dissolved in distilled water, and sodium hydroxide was added when the temperature was raised to 70–80 °C. The modulus of the sodium silicate was controlled at about 1.5, and the temperature was cooled to 60–65 °C after stirring for 1–2 h. Then, 6.4 g of polymerized aluminum sulfate, 35 g of triterpenoid saponins, 3 g of magnesium fluorosilicate, and 0.3 g of sulfonated melamine formaldehyde resin were added to the solution. After stirring for 1–2 h and leaving it to cool down to room temperature, 0.8 g hydroxypropyl methylcellulose, 0.4 g carboxymethyl starch ether, and 2 g sodium tripolyphosphate were added to the solution and dissolved completely. The solution was dried to obtain the alkaline composite exciter.

3.2. Preparation of Material

The alkaline composite exciter was added to the mixture of coal gangue, red mud, and fly ash in various ratio quantities (Table 5). First, the exciter was dissolved in distilled water according to the designated content shown in Table 5. After the exciter was completely dissolved, the solution was cooled to a room temperature of 20 °C. Then, coal gangue, red mud, and fly ash were added to the solution while the solution was stirred continuously so that the materials could be fully mixed until the color became uniform and no longer changed. The prepared solution was poured into the net slurry mixer container to obtain 4 × 4 × 4 cm cubes. The cubes (samples) were cured for 1 day to be hardened. The samples were hydrated in anhydrous ethanol before being used for the experiment. A total of 10 different samples were produced according to the different mixing rates of coal gangue, red mud, fly ash, and different exciter contents, which were determined through preliminary experiments.

Table 5. Coal gangue/red mud/fly ash ratio.

Sample Number	Ratio in Weight (Coal Gangue:Red Mud:Fly Ash)	Water-to-Solid Ratio	Exciter Content (%)
A0	0:0:100	0.4	6
A1	5:5:90	0.4	6
A2	10:10:80	0.37	8
A3	10:20:70	0.35	10
A4	20:20:60	0.4	6
A5	20:30:50	0.37	8
A6	30:30:40	0.35	10
A7	30:40:30	0.4	6
A8	40:40:20	0.37	8
A9	40:50:10	0.35	10
A10	50:50:0	0.4	6

3.3. Performance Assessment and Proportional Optimization

With reference to the preliminary experiments of this study, the mechanical property was tested, and microscopic characterization was conducted within 28 days after curing. Experiments were carried out to optimize the coal gangue/red mud/fly ash ratio and exciter content and to obtain the waste-based cementitious material with optimal performance using eleven different samples with different mixing ratios and exciter contents (Table 5).

Figures 4 and 5 show the degrees of fluidity and the compressive strengths of the samples, respectively. With the increase in amounts of coal gangue and red mud, the degree of fluidity decreased, but the compressive strength increased. The compressive strength

increased until the ratio of coal gangue and red mud reached 40% in the composite (A0–A8). A higher ratio of coal gangue and red mud decreased the compressive strength. Sample A8 showed the highest compressive strength, with a ratio of 40:40:20 (coal gangue: red mud: fly ash) and an exciter content of 8%. Thus, the ratio and exciter content allowed for the best synergistic performance among the samples tested.

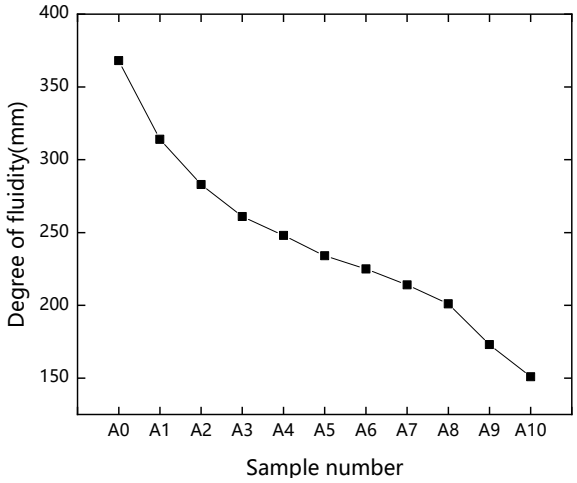


Figure 4. Effect of ratios of coal gangue, red mud, and fly ash and exciter content on degrees of fluidity of cementitious materials.

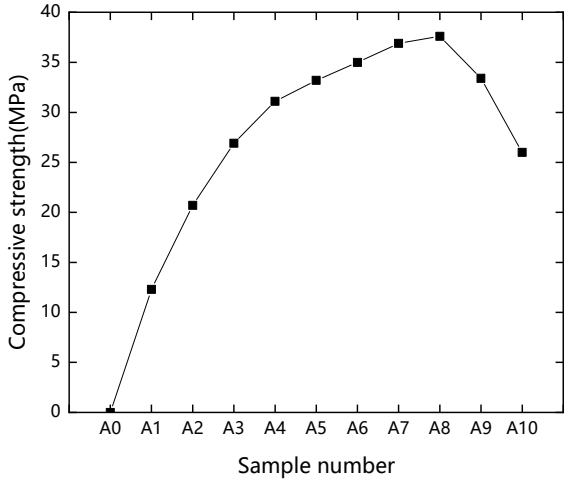


Figure 5. Effect of ratios of coal gangue, red mud, and fly ash and exciter content on compressive strengths of cementitious materials.

When coal gangue, red mud, and fly ash were used as the sole cementitious material, their hydration was too low to have enough cementation reaction. When the three materials were combined, the compressive strength increased considerably. When the contents of coal gangue and red mud were between 0–20% (A0–A4), the compressive strength increased greatly, which corresponded to a decrease in the degree of fluidity. With the contents of 30–40% of coal gangue and red mud, the compressive strength growth still increased but tended to be stabilized at a plateau. The compressive strength reached a maximum value of 37.6 MPa with the contents of coal gangue and red mud at 40%.

The influence of the exciter on the compressive strength was also observed. When the summed content of coal gangue and red mud exceeded 50% (A5–A8), the compressive strength increased, regardless of the exciter content. When the summed content was higher than 90%, the compressive strength decreased, even with a higher content of the exciter. However, the exciter content did not affect the degree of fluidity significantly, as the degree

kept decreasing with the higher content of the exciter. The cross-section image shows white coarse dots with an uneven distribution in the samples with higher contents of coal gangue and red mud. This indicates a fast-setting phenomenon and incomplete reaction, which leads to reduced internal stress and mechanical properties.

In summary, the optimal ratio of coal gangue, red mud, and fly ash was found to be 40:40:20 with an exciter content of 8%, wherein the compressive strength reached a maximum value of 37.6 MPa, and the degree of fluidity was below 200 mm. This indicates that the three materials had a synergistic effect, which is appropriate as a cementitious material.

4. Conclusions

With the increase in the use of natural resources such as coal and aluminum for various industrial activities, the amount of waste from using them also increases considerably. The construction of roads also has been increasing due to the development of industry and society, which demands an enormous amount of construction materials. To reduce the amount of abandoned industrial wastes and newly exploited materials, various waste-based materials have been developed for industrial use, but many of them do not have the appropriate mechanical property to be used. Therefore, we proposed a new cementitious material made from coal gangue from mining, red mud from aluminum production, and fly ash from incineration processes. With an alkaline exciter, the optimal ratio of the materials was determined through the experiment of testing the compression strength and degree of fluidity. The chemical compositions and microstructure of the new material with various mixture ratios and exciter content were analyzed and observed with XRF, XRD, SEM, and other methods. The result showed that the material of the mixture ratio of 40:40:20 (coal gangue: red mud: fly ash) with an exciter content of 8% had the optimal mechanical property, wherein it showed a compressive strength of 37.6 MPa and a degree of fluidity that was less than 200 mm. The newly developed cementitious material can be used as a reference for the study of the curing mechanism and performance analysis of the solid-waste-based binder, as well as the development of waste-based industrial materials.

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