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Research Article

Fineness Effect on Pozzolanic Activity of Cu-Ni Slag in Cemented Tailing Backfill

Wenyuan Xu[1,2,3] **Xiaocong Yang,**[2,3] **Wenchen Li,**[2,3] **and Lijie Guo**[2,3]

[1]*Civil and Resource Engineering School, University of Science and Technology Beijing, Beijing, China*
[2]*BGRIMM Technology Group, Beijing, China*
[3]*National Centre for International Research on Green Metal Mining, Beijing 102628, China*

Correspondence should be addressed to Lijie Guo; guolijie@bgrimm.com

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This paper presents the experimental results of the fineness effect on the pozzolanic activity of Cu-Ni slag in cemented tailing backfill. Cement paste and cemented tailing backfill samples that without or contain Cu-Ni slag with various grinding times were made and cured at 20°C for 7, 28, and 150 days. Mechanical test and microstructural analyses are performed. In general, the pozzolanic activity of Cu-Ni slag increases with the fineness of particle size. The strength of cemented tailing backfill samples decreased with the addition of Cu-Ni slag. It was found that the pozzolanic activity of Cu-Ni slag used in this study is relatively low. According to the fineness, the Cu-Ni slag will make the cemented tailing backfill samples looser or denser. For the sample containing ground Cu-Ni slag ground for 30 min to 50 min, the sample becomes dense gradually as the particle size of Cu-Ni slag becomes finer.

1. Introduction

The nonferrous slag is the waste produced in the smelting process of metal minerals, which has a huge storage in China, causing environmental problems such as land occupation and groundwater pollution [1–3]. According to the 2013 Annual Report on Comprehensive Utilization of Chinese Industrial Resources, 128 million tons of smelting slag had been output from the nonferrous metal industry, only 17.5% of which (i.e., 22 million tons) had been recycled for the production of cement admixture, minefill and building materials, etc. A large amount of nonferrous slag has become one of the main sources of environmental pollution. With more and more attention paid to environmental protection in the world, mining and metallurgical enterprises begin to pay more attention to the comprehensive disposal and resource utilization of solid wastes.

The existing research [4–6] shows that the nonferrous smelting slag has certain pozzolanic activity or potential hydraulic property. Compared with the water-quenched blast furnace slag [7–12], the nonferrous smelting slag has the problem of the relatively low pozzolanic activity or potential hydraulic property, and the comprehensive utilization added value is low. Therefore, the relevant research and application are relatively few, and the overall utilization rate is not high.

The low-cost filling cementitious materials prepared by using nonferrous smelting slag and other solid wastes can promote the resource utilization of smelting slag and other solid wastes and reduce the filling mining cost, which has certain economic and environmental benefits. Sun [13] carried out an experimental study on the preparation of alkali-activated cementitious materials by using the lead-zinc smelting slag as the main silicon aluminum raw material and the sodium silicate as the basic activator; Xue [14] prepared a new type of filling cementitious materials by using the tailings and the lead-zinc smelting slag and studied the effect of the hydration products on the mechanical properties of the composite cementitious materials. However, there is no report on the preparation of cementitious materials from Cu-Ni slag.

In this paper, the effect of grinding fineness on the pozzolanic activity of water-quenched Cu-Ni slag produced by a Cu-Ni smelter in Xinjiang was studied, and the feasibility of producing cementitious materials from the slag was explored.

2. Experimental

2.1. Materials

2.1.1. Water-Quenched Cu-Ni Smelting Slag. The Cu-Ni slag used in this study is the waste slag discharged from a Cu-Ni mine in Xinjiang through smelting in a dilution electric furnace. Its chemical element analysis results are shown in Table 1. According to GB-T18046-2008, the basicity coefficient, activity coefficient, and quality coefficient of the Cu-Ni slag used in this study can be calculated as 0.2, 0.06, and 0.31, respectively, belonging to low activity acid slag. The electric oven was used to dry the Cu-Ni slag, and then, the ball mill was used for grinding. The grinding time was set to 10 min, 20 min, 30 min, 40 min, 50 min, and 60 min. After grinding, the Cu-Ni slag was tested and analyzed by laser particle size test. The particle size distribution (PSD) results are shown in Figure 1, and the particle size characteristic values are shown in Table 2.

2.1.2. Cement. The cement used in this experiment was ordinary Portland PO 42.5 cement. The main chemical properties of the cement used are shown in Table 3.

2.1.3. Tailing. The tailings used in this experiment were the unclassified tailings produced by the Cu-Ni ore beneficiation. The element analysis results are shown in Table 4, and the particle size distribution is shown in Figure 2.

2.1.4. Mixing Water. Distilled water was used.

2.2. Sample Preparation. The compositions of cemented paste (CP) samples and cemented tailing backfill (CTB) samples are shown in Tables 5 and 6. Weighted tailings, binder, and mixing water were mixed in a food mixer for about 5 min. The prepared CTB was poured into a plastic cubic mold sized 4 cm in side length. After compacting by manual vibration, all samples were cured at 20C until the ages of 7, 28, and 150 days. Cubic molds sized 1 cm in side length were used for CP samples, which were prepared for microstructural analysis. After curing was carried out for the required length of time, various tests were performed on the CPB and the CP samples.

2.3. Tests

2.3.1. Mechanical Tests. Uniaxial compressive strength (UCS) tests were performed on the CTB specimens, and the CTB specimens are shown in Figure 3. The loading capacity and load rate are 50 kN and 1 mm/min, respectively. Each test was repeated at least three times, and the average was chosen as the strength of the tested sample.

2.3.2. Microstructural Analysis. To assess the sulphate effect on binder hydration products in the CTB, X-ray diffraction analysis (XRD) and differential thermal gravity analysis (DTG) were conducted on CP samples. To acquire information about the sulphate influence on pore structure, mercury intrusion porosimetry (MIP) tests were conducted on CTB samples. All samples for microstructural analysis were first dried in an oven at 45°C to remove the free water.

3. Results

3.1. The Strength of CTB Decreased with the Addition of Cu-Ni Slag. The UCS results of CTB samples with slag of different grinding times cured for 7, 28, and 150 days are presented in Figure 4. From this figure, it can be observed that the strengths of CTBs are significantly decreased with the addition of Cu-Ni slag. This is due to the reduction of cement content caused by the addition of copper and nickel slag, which leads to the reduction of cement hydration products. This judgment can be supported by SEM results shown in Figure 5. Figure 5 shows the SEM results of CP, CP-30, and CP-50. The microstructure of AFT, CSH, and CH is generally needle-like, fiber or gel-like, and hexagonal sheet, respectively. By comparing CP-10 and CP-50, it can be found that the hydration products of cement in CP samples are mainly calcium silicate hydrate (CSH), ettringite (AFT), and calcium hydroxide (CH), which are more than those in CP-30 and CP-50. When the curing time is 7 days, 28 days, and 150 days, the average strength of CTB samples containing copper and nickel slag is 38%, 50%, and 56% lower than that of CTB samples without copper and nickel slag, respectively. This shows that, with the increase of curing time, the strength growth rate of CTB with Cu-Ni slag is slower than that of CTB without Cu-Ni slag. It can be concluded that the pozzolanic activity of Cu-Ni slag is relatively low.

3.2. The Pozzolanic Reaction of Cu-Ni Slag Was Activated by Cement. Pozzolanic activity refers to the property that some materials do not have hydration, but can react with water under the action of activator, thus forming hydration products with gelling and hydraulic properties. Due to the high temperature in the smelting process and quenching by water when discharged, the Cu-Ni slag may have certain potential activity. It can show pozzolanic activity under the excitation of CH, the hydration product of cement. This judgment can be supported by the microscopic test results of CP and CTB samples. It can be seen from Figure 5(a) that the CP sample contains hexagonal lamellar CH crystal, which is one of the main products of cement hydration. No CH crystal was found in CP-30 and CP-50 samples. This is due to the pozzolanic reaction between the milled smelting slag and CH formed by cement hydration. CH is consumed in this reaction. This judgment can be confirmed by the XRD results in Figure 6. XRD results of CP, CP-10, CP-30, and CP-50 samples are shown in Figure 5. From this figure, it can be seen that the diffraction peak of CH can appear obviously in the results of CP sample. However, there is no CH diffraction peak in the XRD of CP-10, CP-30, and CP-50 with Cu-Ni slag.

The same conclusion can be summarized in Figure 7. Figure 7 shows the DTG results for CP, CP-10, CP-30, and CP-50 specimens. Typical weight loss or peaks located in the 50–200°C, 400–450°C, and 600–750°C temperature ranges can be seen in this figure. It is well known that the weight loss

Table 1: The main chemical properties of the Cu-Ni water quenching smelting slag (wt.%).

Element	CaO	SiO_2	Al_2O_3	MgO	TFe	MnO	P_2O_5	K_2O	Na_2O	SO_3	C	TiO_2
Percentage	2.2	34.6	3.2	5.3	39.0	0.1	0.1	0.3	0.6	3.7	0.1	0.2

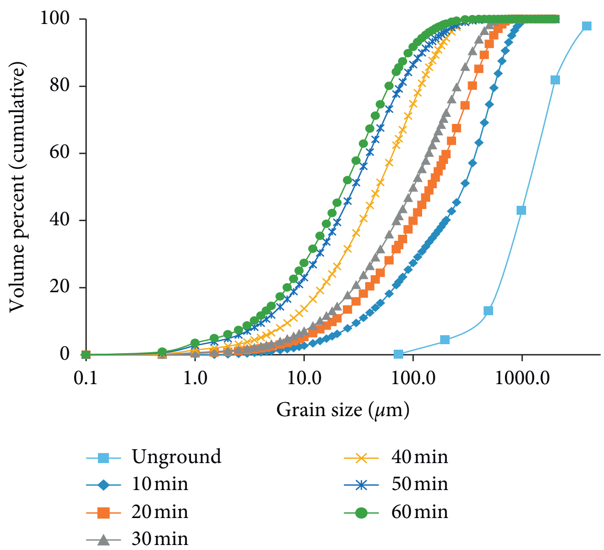

Figure 1: PSD of unground and ground Cu-Ni slag.

Table 2: The particle size characteristic of ground Cu-Ni slag with different grinding times.

Grinding time (min)	D (0.1) (μm)	D (0.5) (μm)	D (0.9) (μm)
10	31.6	290	690
20	18.5	146	460
30	13.9	101	344
40	7.4	48	164
50	4.2	28	120
60	3.4	23	91

Table 3: The main chemical compositions of the cement used (wt.%).

Element	SO_3	Fe_2O_3	Al_2O_3	SiO_2	CaO	MgO	Rel. density
	3.56	2.420	4.27	18.59	62.14	2.35	3.01

or peak situated in the 50–200°C temperature range results from the dehydration of C-S-H, ettringite, carboaluminates, and gypsum [15], whereas the weight loss or a peak located at 400–450°C and 600–750°C is mainly caused by the decomposition of CH and calcite, respectively [16, 17]. In substantial agreement with the mechanism described in [18, 19], it can be seen from Figure 7 that more weight loss of CP sample than that in CP-10, CP-30, and CP-50 samples is detected in the 400–450°C and 600–750°C temperature ranges. This indicated that more CH is detected in CP sample, which means the CH in CP-10, CP-30, and CP-50 samples was consumed by the pozzolanic reaction of the Cu-Ni slag.

The reaction of pozzolanic materials is generally that the active parts SiO_2, Al_2O_3, and $Ca(OH)_2$ react with pozzolanic materials in the following form [10]:

$$SiO_2 + m_1 Ca(OH)_2 + nH_2O \longrightarrow m_1 CaO \cdot SiO_2 \cdot nH_2O \quad (1)$$

$$Al_2O_3 + m_2 Ca(OH)_2 + nH_2O \longrightarrow m_2 CaO \cdot Al_2O_3 \cdot nH_2O \quad (2)$$

In the system containing sulphate, calcium aluminate can further form ettringite:

$$\begin{aligned} &3CaO \cdot Al_2O_3 \cdot 6H_2O + 3CaSO_4 + 26H_2O \\ &\longrightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \end{aligned} \quad (3)$$

However, in the microanalysis results of CP-10, CP-30, and CP-50 samples containing ground Cu-Ni slag, no more AFT was observed than that of CP samples. The pozzolanic reaction of Cu-Ni slag mainly comes from the hydration of active SiO_2.

3.3. The Influence of Fineness of Cu-Ni Slag on CTB Strength. From Figure 4, it can also be seen that the fineness of Cu-Ni slag has a significant effect on the strength of CTB sample. Moreover, the influence of the fineness of Cu-Ni slag on the strength of CTB samples is different at different curing times. The strength of CTB decreased with the increase of grinding time when the curing time was 7 days and the grinding time was in the range of 10 min–40 min. The strength of the two groups of samples with grinding time of 50 min and 60 min was higher than that of the other four groups. However, when the curing time is 28 days, the strength of CTB sample increases with the increase of grinding time. The strength of CTB-20, CTB-30, and CTB-40 has been inversely higher than that of CTB-10. This shows that the finer the Cu-Ni slag, the higher the strength of the CTB sample made from it. When the curing time is 150 days, the strength of CTB-50 exceeds that of CTB-60, and it becomes a group of samples with the highest strength. This phenomenon can reflect that for the expression of pozzolanic activity, the finer the Cu-Ni slag is, the higher the strength of the sample is. There is an optimum grinding fineness for Cu-Ni slag in CTB. Under the experimental conditions of this study, the best grinding time of Cu-Ni slag is 50 min, and the corresponding fineness indexes D (0.1), D (0.5), and D (0.9) are 4.2 μm, 28 μm, and 120 μm, respectively.

3.4. Fineness Effect on the Pozzolanic Activity of Cu-Ni Slag. From Figure 7, it can be seen that less weight loss of CP-50 sample than that in CP-10, and CP-30 samples is detected in the 400–450°C and 600–750°C temperature ranges. This indicated that less CH is detected in CP-50 sample, which means the CH in CP-50 sample was consumed more by the pozzolanic reaction of the Cu-Ni slag than that in CP-10 and CP-30 samples. It can be concluded that in the range of 10°min–50 min, with the prolongation of grinding time, that is, with the fineness of Cu-Ni slag particle size, the

Table 4: The main chemical compositions of the tailings used (wt.%).

Element	CaO	SiO_2	Al_2O_3	MgO	TFe	MnO	P_2O_5	K_2O	Na_2O	SO_3	C	TiO_2
	4.2	43.4	10.4	11.5	16.5	0.2	0.2	1.1	2.2	12.1	0.0	0.8

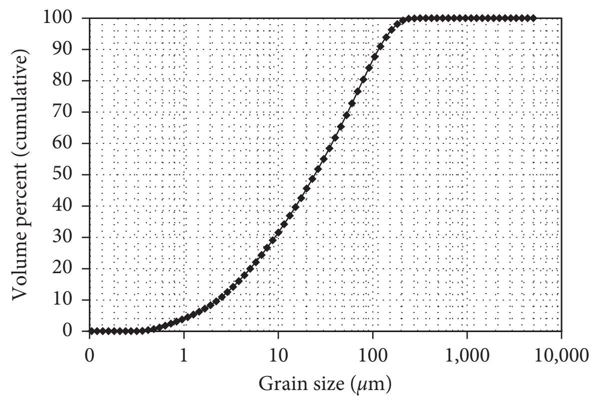

Figure 2: Particle size distribution of tailings.

Table 5: The composition of the cemented paste samples.

No.	Binder		Grinding time of the slag (min)	Concentration (%)
	Cement (%)	Ground slag (%)		
CP	100	0	—	66
CP-10	70	30	10	66
CP-20	70	30	20	66
CP-30	70	30	30	66
CP-40	70	30	40	66
CP-50	70	30	50	66
CP-60	70	30	60	66

Table 6: The composition of the cemented tailing paste samples.

No.	Binder		Grinding time of the slag (min)	Binder/tailing ratio	Concentration (%)
	Cement (%)	Ground slag (%)			
CTP	100	0	—	1 : 4	66
CTB-10	70	30	10	1 : 4	66
CTB-20	70	30	20	1 : 4	66
CTB-30	70	30	30	1 : 4	66
CTB-40	70	30	40	1 : 4	66
CTB-50	70	30	50	1 : 4	66
CTB-60	70	30	60	1 : 4	66

Figure 3: CTB samples.

pozzolanic activity of Cu-Ni slag also increases gradually, which means that the hydration reaction is more sufficient.

3.5. The Influence of Fineness of Cu-Ni Slag on CTB Compactness. Different fineness of Cu-Ni slag will also lead to different compactness of CTB sample containing smelting slag. This phenomenon can be clearly observed from the SEM results in Figure 5. As can be seen from Figure 5, CP-50 samples are denser than CP and CP-30 samples. This judgment can also be supported by the MIP results in Figure 8. Figure 8shows the MIP test results of CTB, CTB-10, CTB-

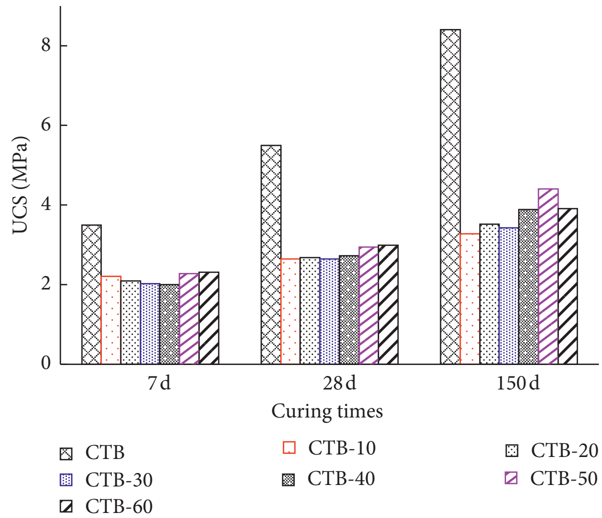

Figure 4: UCS of CTB samples with slag of different grinding times.

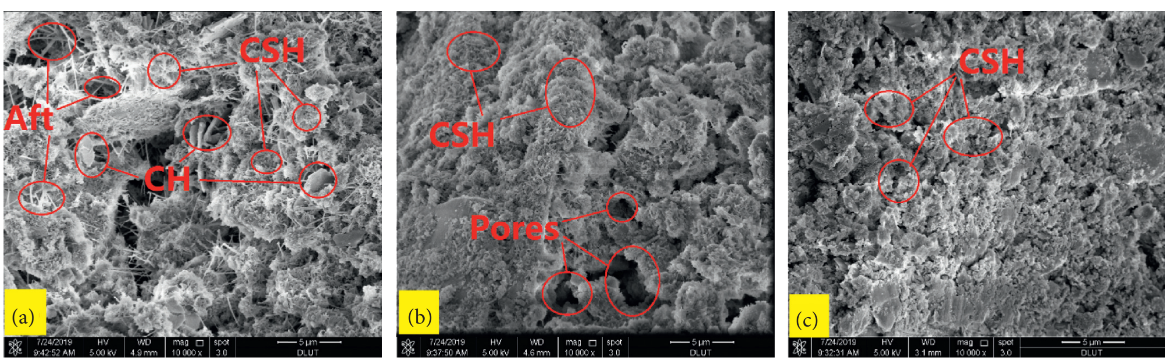

Figure 5: SEM results of CTB samples with slag of different grinding times and curing for 150 days: (a) CTB; (b) CTB-30; (c) CTB-50.

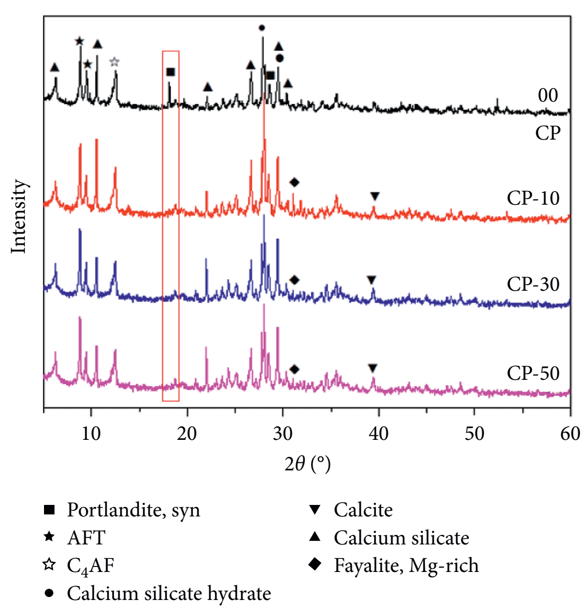

Figure 6: XRD results for CP samples cured for 150 days.

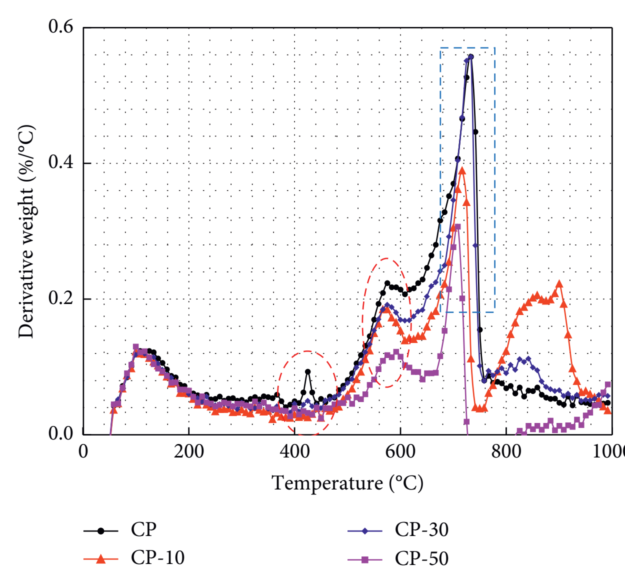

Figure 7: DTG diagrams for cement paste of CP samples cured for 150 days.

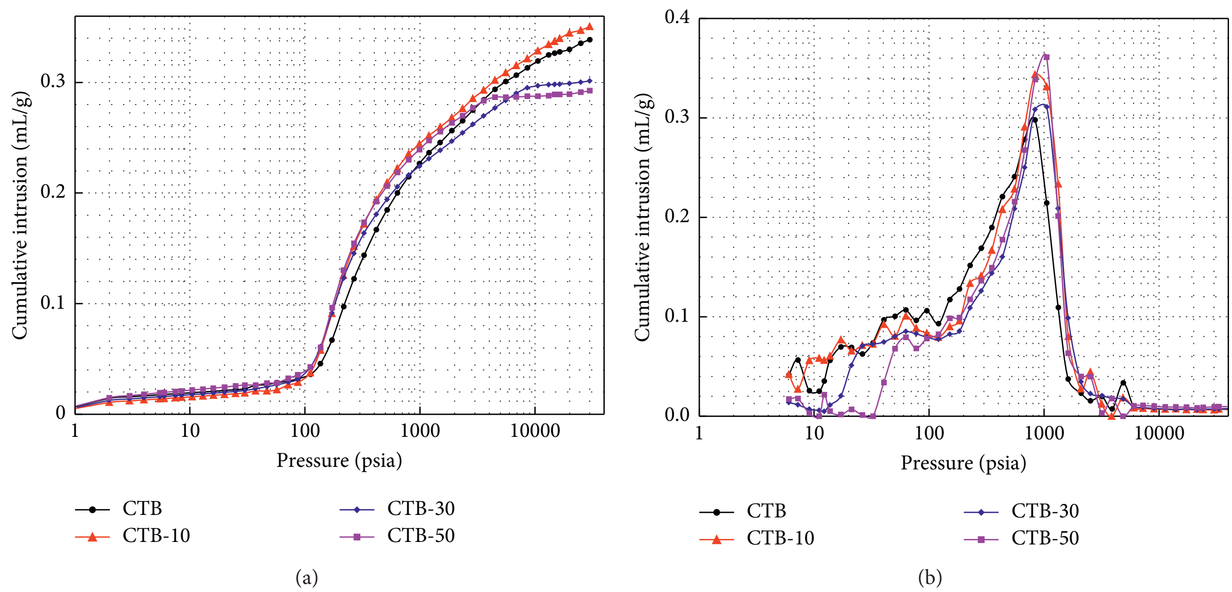

FIGURE 8: MIP test results for CTB samples curing for 150 days: (a) total pore volume; (b) pore distribution.

30, and CTB-50. It can be seen from Figure 8(a) that the total amount of pores in CTB-10 sample is larger than that in CTB sample, which indicates that the addition of Cu-Ni slag with a grinding time of 10 min makes the samples looser. However, the total porosity of CTB-30 and CTB-50 samples is less than that of CTB samples, which means that the addition of Cu-Ni slag with grinding time of 30 min and 50 min makes the CTB samples denser. Compared with CTB-10, CTB-30, and CTB-50, the total porosity of the three groups of samples can be found that the compactness of the corresponding samples increases with the increase of grinding time. In addition, the fineness of the Cu-Ni slag also has a significant effect on the pore size distribution of the sample, which can be seen in Figure 8(b).

4. Further Discussion

The high cost of cement in filling mining is a problem faced by many mines. Using smelting slag and other solid wastes to prepare low-cost filling cementitious materials can not only realize the resource utilization of nonferrous smelting slag and other solid wastes, but also effectively reduce the mining cost of filling, with significant economic and environmental benefits.

According to the test results of this paper, some industrial tests are being carried out in a copper-nickel mine in Xinjiang, China. In this project plan, copper-nickel smelting slag is ground and mixed with cement as filling cementing material. It can reduce the cost of filling cementitious materials and dispose and utilize the copper-nickel smelting slag which is used as solid waste.

5. Conclusions

It is found that the strength of CTB decreased with the addition of Cu-Ni slag, and the pozzolanic activity of Cu-Ni slag is relatively low. With the increase of curing time, the strength growth rate of CTB with Cu-Ni slag is slower than that of CTB without Cu-Ni slag.

It is demonstrated that the Cu-Ni slag can show pozzolanic activity under the excitation of CH, the hydration product of cement.

The fineness of Cu-Ni slag has a significant effect on the strength of CTB sample; moreover, this influence shows different conditions at different curing times.

In the range of 10 min–50 min, with the fineness of Cu-Ni slag particle size, the pozzolanic activity of Cu-Ni slag increases gradually, which means that the hydration reaction is more sufficient.

According to the fineness, the Cu-Ni slag will make the CTB sample looser or denser. For the sample containing ground Cu-Ni slag ground for 30 min to 50 min, the sample becomes dense gradually as the particle size of Cu-Ni slag becomes finer.

Data Availability

All data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

There are no conflicts of interest in this publication.

Acknowledgments

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