

Article

# Rational Utilization of Fine Unclassified Tailings and Activated Blast Furnace Slag with High Calcium

Yanlong Zhou <sup>1,2,\*</sup>, Hongwei Deng <sup>1,2,\*</sup> and Jixiang Liu <sup>1,2,3</sup>

<sup>1</sup> School of Resources and Safety Engineering, Central South University, Changsha 410083, China; csuliujiexiang@126.com

<sup>2</sup> Hunan Key Laboratory of Mineral Resources Exploitation and Hazard Control for Deep Metal Mines, Changsha 410083, China

<sup>3</sup> Lanzhou Engineering & Research Institute of Nonferrous Metallurgy Co., Ltd., Lanzhou 730000, China

\* Correspondence: zhylcsu@csu.edu.cn (Y.Z.); denghw208@126.com (H.D.); Tel.: +86-731-8883-0960 (Y.Z.)

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**Abstract:** The utilization of cemented tailings/paste backfill (CPB) by the mining industry is becoming increasingly important. However, it has been difficult to analyze the economic usage of CPB for fine unclassified tailings. Therefore, the physical and chemical properties of fine unclassified tailings, sampled from the Sijiaying Mine, were first analyzed in this study. After this, active excitation of blast furnace slag was examined, with a cement mixture made up of slag, lime, plaster and cement being used to conduct the physicochemical evaluations and proportioning tests. These results were compared with those from ordinary cement. It was revealed that the cement mixture can effectively harden the unclassified tailings. The cement mixture specimens have good performance in early strength, with the seven-day strength being about twice as high as ordinary cement, which meets the requirements for efficient continuous mining. This strength was reduced after 10 days due to expansion and complicated reactions, with an average reduction of 11.8% after 28 days under recommended and better conditions. In addition, analysis of the microstructures was carried out to observe the hydration products and the change in strength. Furthermore, fluidity characteristics of the slurry were measured, with the slurry found to have a mass fraction of 70%–72% in addition to containing an ideal fluidity and a paste-like flow state. Considering the mining conditions, the aggregates with a tailings-cement ratio of 6:1 and a mass fraction of 70%–72% are recommended as high-strength CPB, which should be used for the surface layer and safety pillars. In addition, backfilling materials with a tailings-cement ratio of 15:1 and a mass fraction of 70%–72% are recommended as low-strength CPB, which should be used as ordinary CPB to achieve economic benefits. The application cases showed that the cement mixture is suitable for utilization of unclassified tailings with regards to safety, economics and efficiency.

**Keywords:** fine unclassified tailings; slag; high calcium; early strength; strength reduction

## 1. Introduction

A very large number of tailings are produced by mining operations each year, with serious environmental problems occurring consequently, such as underground goaf [1], land occupation [2] and heavy metals [3,4]. Filling the goafs with tailings seems to be an ideal solution [5], with cemented paste backfill (CPB) being widely and intensively employed in the global mining industry [6–8]. The physicochemical properties of unclassified tailings play an important role in the application of CPB [9–11], such as strength, hardening performance and pipeline transportation. Having a large proportion of fine particles makes it difficult to harden the tailings backfill body. With the rapid

development of mineral processing, it is an inevitable trend for finer tailings to be produced, with the usage of CPB based on unclassified tailings being more reasonable in this sense.

In order to improve the usage of tailings, a host of explorations have been carried out by some scholars, with an extensive development of this research field. The effect of particle gradation on properties of fresh and hardened CPB in addition to the effect of the fineness of tailings on the pore structure development of CPB were analyzed by Ke et al. [12,13]. It was found that increasing the fineness of tailings is good for the mechanical performance of CPB, although it is detrimental to the workability of fresh CPB and leads to a higher moisture content in hardened CPB. In addition, this increase in fineness also resulted in a decrease in the critical pore diameter of large pores. Yi et al. [14] found that the CPB is much more ductile than the unreinforced tailings once 0.5% Adfil-Ignis polypropylene fibers by weight of total solids in CPB were added. Kesimal et al. [15] found that the strength of the deslimed tailings ranged from being 12% to 52% higher than the original mill tailings. Additionally, Ercikdi et al. [16] studied the effect of desliming sulfide-rich mill tailings on the long-term (224 days) strength of CPB composed of sulfide-rich mill tailings, finding that the long-term unconfined compressive strength (UCS) development of CPB is similar to that of the short-term (7 and 28 days) specimens. This means that desliming can improve the strength and stability in the long term as well as potentially being able to reduce binder consumption. It can be noted that if classified disposal is conducted, coarse aggregates can easily be hardened, while disposing finer aggregates provide more challenges [17,18]. Therefore, finding cheap material to get a hardened result for unclassified tailings has significant research and practical significance.

Sijiaying Iron Mine is a large iron mine in Hebei Province, China. The average ore grade of mined ore is about 28%, with simple ingredients found in the ore. Magnetite, hematite and false hematite account for the majority of this ore, with other components including magnetic hematite, pyrite and siderite (Table 1). The production capacity of mining and mineral processing is 20 million tons of iron ore each year. At the same time, 11.982 million tons of tailings are produced in the mineral processing plant per year. Apart from being an environmental threat, the tailings have potential value if reasonably used. Taking underground goafs and land occupation into account, the application of CPB based on unclassified tailings has drawn people's attention. Therefore, the research on the application of unclassified tailings backfilling is advocated. If feasible, economic and environmental benefits can be obtained simultaneously.

**Table 1.** Main ingredients of iron ore.

Material	Magnetite	Siderite	Red Limonite	Pyrite	Ferric Silicate	Iron Concentrate
Mean mass fraction (%)	27.99	0.56	2.23	0.12	1.99	32.89

This article attempts to develop useful knowledge in the rational application of CPB based on unclassified tailings. Therefore, the physicochemical analysis, proportioning test, investigation of micro-structures, fluidity measure and application evaluation were carried out to support the research. Given the problems mentioned above, the main objectives of this study are as follows:

- to evaluate the particle gradation and the chemical composition of the unclassified tailings;
- to analyze the hardened effects of binder mixture and ordinary cement;
- to investigate flowability of the backfilling slurry for finding better proportion parameters; and
- to recommend reasonable structural application of cemented unclassified tailings backfill.

## 2. Experimental Setup

Considering the background, the unclassified tailings were first sampled from sites in Sijiaying to carry out the research. After this, the physicochemical properties of unclassified tailings were

measured, followed by analysis using the proportioning and micro-structure tests. Finally, the fluidity test was conducted.

## 2.1. Materials Characteristics

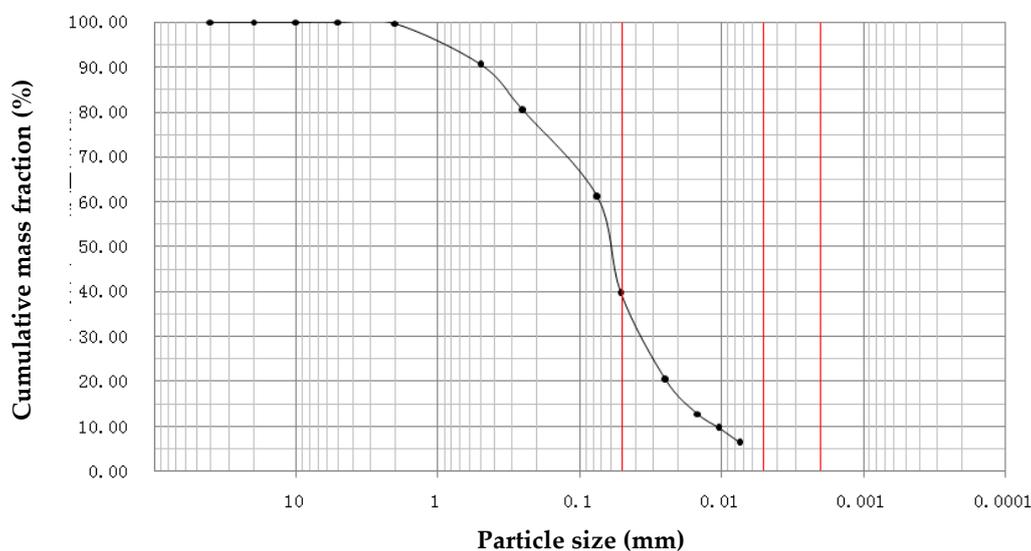
### 2.1.1. Tailings

After sampling, the drying [19] of unclassified tailings was carried out under standard conditions, before being kept in a safe space (Figure 1).



**Figure 1.** Preparation of unclassified tailings. (a) Field sampling; (b) drying; (c) preparation.

It is known that the physicochemical properties of unclassified tailings play an important role in the application of CPB [9–11]. Hence, the chemical composition was measured by the titrimetric method and particle size distribution was tested by one laser particle size analyzer (Malvern Instruments Ltd., Malvern, UK), which was conducted in Chemical Composition Analysis Center, Central South University. The particle size distribution, main chemical composition and physical properties are shown in Figure 2 and Tables 2 and 3.



**Figure 2.** Curve of particle size distribution.

**Table 2.** Particle size distribution of unclassified tailings.

Particle (mm)	5–2	2–0.5	0.5–0.25	0.25–0.075	0.075–0.05	0.05–0.005	0.005–0.002
Mass Fraction (%)	0.3	9.1	10.2	19.2	22.2	34.8	4.1

**Table 3.** Main chemical composition of unclassified tailings.

Material	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MgO	FeS <sub>2</sub>	Others
Mass Fraction (%)	1.14	0.37	9.11	32.65	13.02	-	43.71

We defined  $d_{50}$  as the median particle size [20], which reflects the particle size when the accumulative mass fraction reaches 50%.

We defined  $Cu$  as the non-uniform coefficient [21], which is equal to the ratio value of the particle size with accumulative mass fraction of 60% and the particle size with cumulative mass fraction of 10%.

In accordance with Figure 2 and Table 2,  $d_{50} = 0.062$  and  $Cu = 6.8$  were calculated.

The unclassified tailings are fine, with a median particle size of 0.062 mm. The non-uniform coefficient of 6.8 showed no advantage in terms of particle size distribution. The fine particles, that are smaller than 0.075 mm and account for 62% of the samples, may cause harm to the efficiency of dehydration and hardening of the CPB.

A CaO content of 32.65% is beneficial for forming ettringite in addition to also contributing to the pipeline transportation of the backfill slurry and the strength of CPB [22]. High CaO content is conducive to the improvement of fluidity, early strength, mortar density and the reduction of dry shrinkage, based on a reasonable excitation of activity [23]. A high CaO content might be able to expand the application of high calcium fly ash. However, in certain circumstances, it may have a negative impact on volume stability. SiO<sub>2</sub>, which accounts for 9.11% of the mixture, only seems to make up a slightly smaller proportion of CPB. High-activity Al<sub>2</sub>O<sub>3</sub> accounts for 0.37%, while the content of MgO being 13.02% needs to be noted because it may have a harmful effect [24] on volume stability. Additionally, pyrite is not detected due to having very little content.

Furthermore, the specific gravity (Gs) of unclassified tailings was measured as 2.83, with the color of the drying tailings powder being light gray. This showed the mineralogical properties in one perspective.

The results proved that the unclassified tailings are not ideal materials for CPB from the traditional perspective.

### 2.1.2. Cement Materials

A host of explorations have been made by mining engineers to examine the appropriate usage of tailings. It was found that the performance of blast furnace slag can cause effective hardening of unclassified tailings [25]. Therefore, when mixed with lime, plaster and cement, blast furnace slag has been considered as the main material for treating the unclassified tailings for the following reasons:

There is a large amount of blast furnace slag discharged every year in China and it is widely available in addition to having a lower price and significance for environmental protection. The slag has the potential to be active and have early strength, but needs to be stimulated [26].

Mechanical activation can be used to stimulate the activity of blast furnace slag, by grinding this substance finer using a high-energy ball-mill behavior, although stability is hard to guarantee. Relatively speaking, chemical activation [27] is more convenient and practical. The activity of slag is easily excited by alkali ions and sulfate [28], with lime and plaster also potentially being useful due to being widely available.

Blast furnace slag containing more SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> offsets the defects in composition of unclassified tailings.

Blast furnace slag was studied in a similar situation and it was found that the aggregates are ideal if there is a mass fraction of 4% of cement, 18% of lime, 8% of plaster and 70% of slag. Therefore, the experimental cement mixture was produced based on the ratio, with their physicochemical properties being tested and shown in Table 4. Similarly, there was a relatively high content of CaO.

**Table 4.** Chemical composition of cement mixture (%).

Material	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>	S <sup>2-</sup>	Others
Slag	38.16	33.38	16.23	10.10	0.62	0.44	0.17	0.90
Lime	86.06	-	-	12.61	-	-	-	1.33

In addition, the mass fraction of CaSO<sub>4</sub> in lime accounts for more than 93%, while there is almost no sulfur in the lime. Tested using the laser particle size analyzer, the particle size of slag shows that 95% of the particles are smaller than 60 μm, showing that the material has high activity. It can be concluded that there is a high content of Ca and Mg, which may raise expansion in cement mixture.

Composite Portland Cement (Grade 325), consisting of the Portland cement clinker, several mixed materials and an appropriate amount of cement, was used for comparison. The main ingredients of the ordinary cement are Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO and SiO<sub>2</sub>.

### 2.1.3. Water

Discharge water from the ore concentrator has a good quality after high quality disposal, with the pH value being between 6 and 7 (basically neutral). Knowing this, we hypothesized that this water could support CPB [29] and subsequently used this water to carry out the experiment.

## 2.2. Specimens and Curing Conditions

The proportion of CPB plays an important role in strength and other characteristics [30,31]. The specimens were prepared by mixing a binder mixture, ordinary cement, unclassified tailings and neutral water timely. The preparation was conducted according to the National Standard [32] and traditional practice, which is based on some auxiliary tests.

Mixing the unclassified tailings and the cement mixture, a host of specimens were produced, with tailings-cement ratios of 4:1, 6:1, 8:1, 10:1, 12:1 and 15:1 respectively. At the same time, the mixed slurry with mass fractions of 68%, 70% and 72% were used in order to get better strength. Grade 325 Portland cement with a mass fraction of 70% was used for comparison.

Standard tri-unit models (7.07 cm × 7.07 cm × 7.07 cm) [33] were used to produce the specimens. After intensive mixing, the mixed slurry was poured into the models, followed by a rest period to obtain cubic specimens. Following this, the specimens were cured in a conservation room for a period of time. The curing conditions are that the constant temperature is about 20 °C and the humidity is greater than about 90%. The calculation (calculated by mass fraction) of the proportions of each sample is shown in Table 5.

**Table 5.** Proportion calculation of experimental specimens.

Tailings-Cement Ratio		4:1				6:1				8:1			
Mass fraction of solid (%)		68	70	72	70	68	70	72	70	68	70	72	70
Mass fraction (%)	Water	32	30	28	30	32	30	28	30	32	30	28	30
	Tailings	54.40	56.00	57.60	56.00	58.29	60.00	61.71	-	60.44	62.22	64.00	62.22
	Cement mixture	13.60	14.00	14.40	-	9.71	10.00	10.29	70.00	7.56	7.78	8.00	-
	Ordinary cement	-	-	-	14.00	-	-	-	60.00	-	-	-	7.78
Tailings-Cement Ratio		10:1				12:1				15:1			
Mass fraction of solid (%)		68	70	72	70	68	70	72	70	68	70	72	70
Mass fraction (%)	Water	32.00	30.00	28.00	30.00	32.00	30.00	28.00	-	32.00	30.00	28.00	-
	Tailings	61.82	63.64	65.45	63.64	62.77	64.62	66.46	-	63.47	65.33	67.20	-
	Binder mixture	6.18	6.36	6.55	-	5.23	5.38	5.54	-	4.53	4.67	4.80	-
	Ordinary cement	-	-	-	6.36	-	-	-	-	-	-	-	-

### 2.3. Strength Test

The strength of CPB is one of the most important factors in the application of CPB [34], with strength analysis conducted timely in this study. In accordance with mining cycle of stopes,

traditional practice and the consensus of mining operators, the curing period was determined as 7 and 28 days. After this, the UCS of specimens were tested by the WDW-2000 rigid hydraulic pressure servo machine (Ruite, Guilin, China).

Seven-day and 28-day strength of specimens were mainly performed, with several auxiliary tests being conducted as a supplement. In order to ensure accuracy, 2–3 specimens for each set were tested.

#### 2.4. Microscopic Test

To reveal the quality of strength, it is necessary to conduct an analysis at the microscopic level [35,36]. Therefore, microscopic tests were carried out through commissioned tests using the X-ray spectrometer (EDAX/AMETEK EDAX, EDAX Inc., Mahwah, NJ, USA) in Experimental Teaching Center of Materials Science and Engineering, Central South University.

#### 2.5. Fluidity Test

The fluidity characteristics of filling slurry are very important for transportation and subsequent spreading out across a surface. On the basis of the above and auxiliary tests, it is recommended to have a slurry of aggregates with a mass fraction of 70%–72% (tailings-cement ratio of 6:1 and 15:1). For achieving better application of the backfilling, a series of fluidity parameters were measured, including collapsed slump [37], consistency [38], threshold concentration [39] and bleeding rate [40].

### 3. Results and Discussion

#### 3.1. Strength Evaluation

The strength of CPB is one of the most important factors in the application of CPB [34], which can mainly be affected by activity of the binder [41], component proportions [42] and slurry concentration.

##### 3.1.1. Test Results of Unconfined Compressive Strength

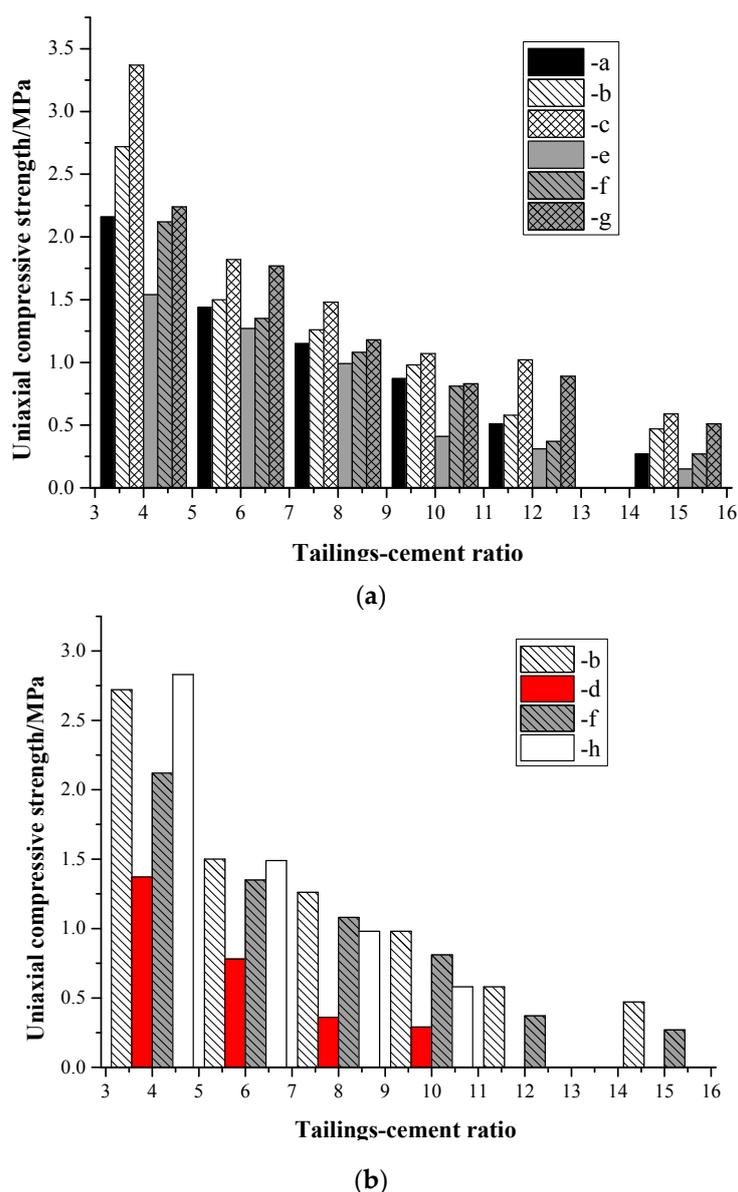
The results of UCS are shown in Table 6 and Figure 3.

**Table 6.** Results of unconfined compressive strength (UCS) of cemented paste backfill (CPB) with different proportions (MPa).

Numbering	a	b	c	d	e	f	g	h	
Conservation period	7-day	7-day	7-day	7-day	28-day	28-day	28-day	28-day	
Binder type	Cement mixture			Ordinary cement	Cement mixture			Ordinary cement	
Mass fraction (%)	68	70	72	70	68	70	72	70	
Tailings-cement ratio	4:1	2.16	2.72	3.37	1.37	1.54	2.12	2.24	2.83
	6:1	1.44	1.5	1.82	0.78	1.27	1.35	1.77	1.49
	8:1	1.15	1.26	1.48	0.36	0.99	1.08	1.18	0.98
	10:1	0.87	0.98	1.07	0.29	0.41	0.81	0.83	0.58
	12:1	0.51	0.58	1.02	-	0.31	0.37	0.89	-
15:1	0.27	0.47	0.59	-	0.15	0.27	0.51	-	

##### 3.1.2. Evaluation of Test Results

The cement mixture can have a beneficial effect on the UCS of CPB. It was revealed that the UCS increased as the mass fraction increased, while the UCS also declined when there was an increase in the tailings-cement ratio. The content of cementitious material has an important influence on the strength, but this effect is weakened after the tailings-cement ratio is equal to 10. The hardening ability of ordinary cement is comparatively poor, as the UCS increased slowly and there was almost no strength when the tailings-cement ratio was higher than 10.



**Figure 3.** Test results of UCS. (a) Specimens of cement mixture; (b) specimens of the cement mixture and ordinary cement.

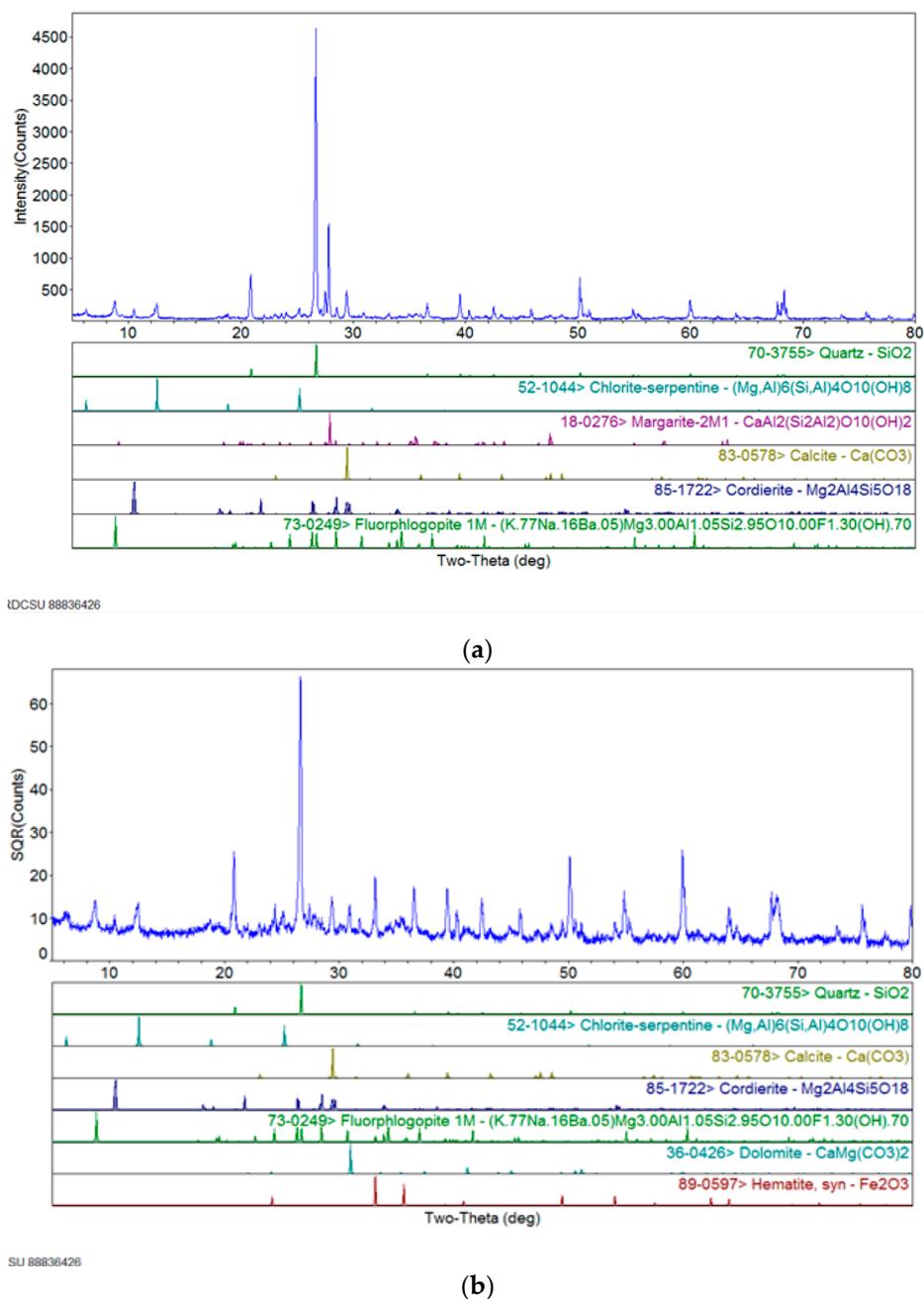
The cement mixture has the advantage of early strength, with 7-day strength being about twice as high as ordinary cement. However, there is a phenomenon of strength retraction after 28 days. The strength increases rapidly during the first few days. On the 10th day, the strength reaches its peak, with subsequent decline in strength after this time. Finally, the strength remains basically stable after 28 days. For ordinary cement, the improvement of UCS is consistent and slow, with the strength remaining basically stable after 28 days. Additionally, the UCS of ordinary cement is mostly lower than that of the cement mixture, with only the 28-day UCS being a little higher when the tailings-cement ratio is equal to 4:1.

According to the conditions in mining sites, apparent concentration of slurry and test results, there are two types of specimens that could be handy. The specimens with a mass fraction of 70%–72% and tailings-cement ratio of 6:1 have significant strength and are thus recommended as high-strength CPB. The high-strength CPB is used to carry out efficient continuous mining in addition to producing the surface layer and pillar, due to it being able to satisfy the requirement of early strength. The specimens

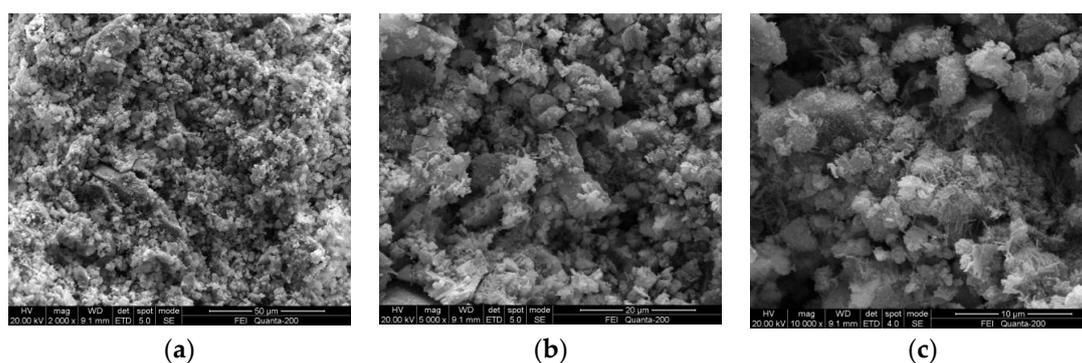
with a mass fraction of 70%–72% and tailings-cement ratio of 15:1 can satisfy the conditions for common uses of CPB and are thus recommended as low-strength CPB. The low-strength CPB is taken into account for economic purposes and is designed to fill the most of the goaf.

### 3.2. Analysis of Microscopic Results

A series of hydration of products and micro structures were observed, with a set comparison diagram of X-ray diffraction (XRD) patterns shown in Figure 4. Figure 5 shows a set of scanning electron microscope (SEM) images of the cement mixture specimen with a mass fraction of 68% after curing for 28 days. In general, the micro-structure characteristics and the hydration products of the cement mixture specimens are close to those of ordinary cement, but there are some obvious differences.



**Figure 4.** X-ray diffraction (XRD) patterns of backfilling materials. (a) Specimens of ordinary cement; (b) specimens of the cement mixture.



**Figure 5.** Scanning electron microscope (SEM) images of the backfilling: (a) 2000 times; (b) 5000 times; (c) 10,000 times.

The main hydration products of the cement mixture specimens are quartz, chlorite, calcite, cordierite, fluorophlogopite, dolomite and iron oxide. Quartz accounts for the highest proportion, with the other products being found in similar proportions to those in ordinary cement. However, specimens of the cement mixture contain more dolomite.

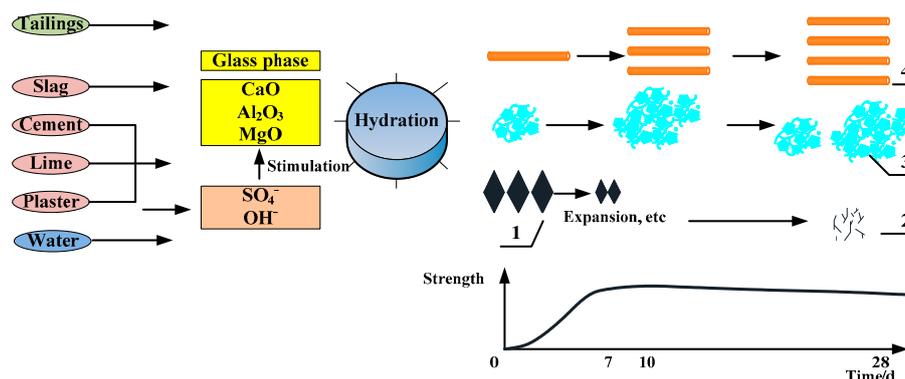
The phenomenon of a large amount of ettringite being formed earlier in the cement mixture specimens was found in the State Key Laboratory of High-Efficient Mining and Safety of Metal Mine.

According to the analysis of material composition, it is known that there is relatively more MgO in the cement mixture, with the effects of MgO being mainly represented in two aspects. One is a certain degree of expansion, which is conducive to the improvement of early strength by compressing pores inside the backfill body during the early period of hydration, although this can also be detrimental for later strength. The expansion [43] is limited as  $\text{Mg}(\text{OH})_2$  and granite were not found in the hydration products, which have obvious features of volume expansion. The other aspect is that as an active component, MgO can promote the activity and vitrification of slag by reducing the viscosity of the solution to some extent.

Additionally, a high content of CaO contributes to the early strength if activated fully, although it can adversely affect volume stability.

Furthermore, the stimulation of alkali ions and  $\text{SO}_4^-$  allow for significant activity of slag. In perfect cooperation with the physicochemical properties of unclassified tailings and the micro-expansion of MgO and CaO at the same time, the cement mixture causes a significant hardening of unclassified tailings.

Hence, the development process of strength is clear. In the beginning,  $\text{OH}^-$  and  $\text{SO}_4^-$  emerge and excite the glass phase in slag after being mixed with neutral water. When combined with the active component (CaO,  $\text{Al}_2\text{O}_3$ , and MgO), a hydration phenomenon of high activity is realized. After this, C-S-H gels and ettringite form earlier due to being influenced by the environment. Furthermore, pores shrink and are affected by micro-expansion of MgO and CaO, resulting in the strengthening of the mixture. On the 10th day, the positive effect of expansion and the reaction reach their critical values, with the UCS reaching its climax. With continuance of the micro-expansion coupled with physicochemical interference, a little less damage appears, accompanied by slowing down of the physicochemical reaction. Finally, a new balance is reached. The strength changes with the hydration process (Figure 6).



**Figure 6.** Hydration process of the cement mixture. 1 = Pores; 2 = Strength damage; 3 = C–S–H gels; 4 = Ettringite.

### 3.3. Fluidity Evaluation

From multiple perspectives, the recommended slurry parameters were measured and listed in Table 7. These parameters [37–40] are considered superior with regards to pipeline transportation and ability to spread out over surfaces.

We defined  $C'$  as the concentration of apparent ratio, which can directly reflect the apparent morphology of the slurry. The closer to 1  $C'$  is, the thicker the apparent state of the slurry is. Concentration of the apparent ratio is calculated by the following equation:

$$C' = \frac{C_w}{C_{wm}} \tag{1}$$

where  $C_w$  is mass fraction of the slurry and  $C_{wm}$  is the threshold concentration.

**Table 7.** Results of the main slurry parameters that are recommended.

Parameters	Values			
Tailings-cement ratio	6:1	6:1	15:1	15:1
Mass fraction (%)	72	70	72	70
Threshold concentration (%)	76.9	76.9	77.3	77.3
Concentration of apparent ratio (%)	93.6	91	93.1	90.6
Consistency (cm)	10.1	11.9	10.1	11.3
Collapsed slump (cm)	27.6	28.7	27.4	28.3
Diffusion degree (cm)	91	108	86.3	99.7
Slurry density ( $t \cdot m^{-3}$ )	1.91	1.86	1.79	1.76
Bleeding rate (%)	6.48	6.66	6.77	7.89

The tests of the main slurry parameters show that the recommended proportions have good performance with regards to fluidity, while stratification and segregation are hard to create when transported through the pipeline.

The value of  $C'$  being between 90% and 95% proves that the slurry has a proper structure, a small bleeding rate and a better fluidity than paste backfill.

Showing features of “Structural Flow” when transported, the recommended slurry is consistent with having a paste-like flow state [44].

The fluidity parameters show that the recommended slurry is very conducive to pipeline transportation and spreading out in goafs.

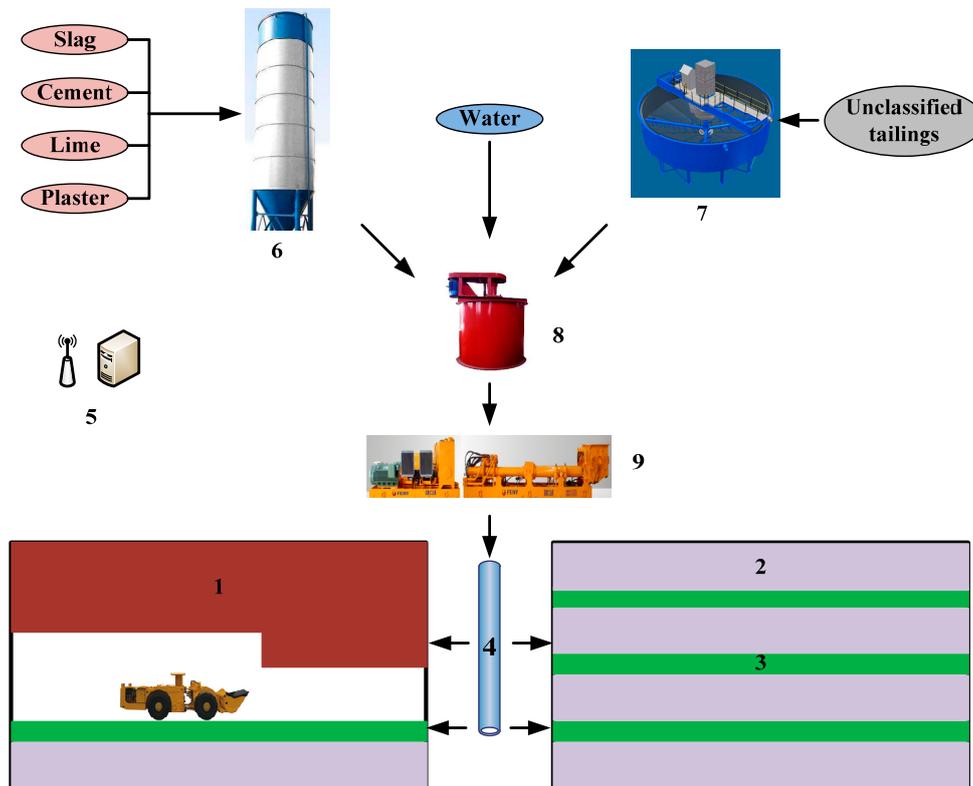
### 3.4. Application of Backfill

#### 3.4.1. Backfilling System

There are several common problems in the mining operations of CPB in underground mines, such as low speed of solidification of backfilling body, roof-contacted technique and filling costs. It is clear that the cement mixture is very suitable for backfill in the studied mine due to micro-expansion being helpful in contacting the roof of stopes, early strength being high, and raw material being cheap and widely available.

According to the research results, the optimal aggregates, with a mass fraction of 70%–72% and tailings-cement ratio of 6:1 and 15:1, are recommended for CPB in Sijiaying Mine. The backfilling application is realized depended on a backfilling system. First, unclassified tailings are poured into a deep-cone thickener by pipeline transportation from the dressing plant, with a high efficiency of dehydration being necessary. The cement mixture is transported and unloaded in the cement warehouse after intensive mixing. Another cement warehouse for storing ordinary cement is recommended. After this, the cement mixture, unclassified tailings and neutral water are accurately measured and then mixed using mixing equipment with high performance. After five minutes of mixing, the backfilling slurry is transported into stopes through pipelines with the help of pumps.

Most of the goaf is filled by low-strength CPB, with the surface layer being made up of high-strength CPB. Combined with the required pillars that are formed by high-strength CPB, it is confirmed that high-strength CPB accounts for 46% of the structure, in order to achieve safety and economic benefits. The process of crafting the backfilling system is shown in Figure 7.



**Figure 7.** Backfilling process. 1 = Ore body; 2 = High-strength CPB body; 3 = Low-strength CPB body; 4 = Backfilling pipeline; 5 = Control system; 6 = Cement warehouse; 7 = Thickener; 8 = Mixing equipment; 9 = Pump.

### 3.4.2. Application Evaluation

The price of the cement mixture is 74% [45] of the ordinary cement price and has better strength and practicality. The scale of high-strength CPB accounts for about 46% and the scale of low-strength CPB accounts for about 54%. The integrated price of backfill is \$5.99/m<sup>3</sup>, which is calculated based on the market price.

The added scale of goaf is about 6 million cubes each year. If an effective coefficient of 80% is taken into account for rough calculation, then there will be a cost of 7.73 million tons of tailings and 0.86 million tons of blast furnace slag for backfill per year. Simultaneously, the utilization rate of tailings will reach 64.5%.

Under the recommended parameters, the slurry has good collapsed slump, diffusion degree, bleeding rate and concentration of apparent ratio, which are very conducive to pipeline transportation.

The cement mixture can cause effective hardening of the unclassified tailings. First, the CPB can be provided with 7-day strength of 1.5 MPa under high-strength CPB. Following this, a micro-expansion is conducive to the improvement of the roof contacting, which provides significant stability. Apart from this, the early strength can safeguard efficient continuous production, without a long period of conservation. Several application cases prove that this method is feasible, with economic and environmental benefits possibly being obtained by using the cement mixture.

## 4. Conclusions

To study the application of CPB based on unclassified tailings, the cement mixture composed of slag, lime, plaster and cement was analyzed. Physicochemical evaluation, proportioning tests and fluidity evaluation were conducted to study the feasibility of CPB. From which, following conclusions can be drawn:

- (1) The tailings in Sijiaying Mine are fine and difficult to be hardened by ordinary cement, if not classified. However, the cement mixture (mixing slag, lime, plaster and cement) can cause effective hardening of the unclassified tailings. The 7-day UCS of specimens of the cement mixture is 1.5 MPa, which is about twice as high as those of ordinary cement.
- (2) The cement mixture has a good performance with regards to early strength and meets the requirements for continuous and efficient mining. A large amount of ettringite and C–S–H gels forming early is the key for early strength, which is affected by the hydration environment. There is a phenomenon of strength decline after 10 days due to the effect of volume expansion and complicated reactions.
- (3) The slurry of aggregates can satisfy pipeline transportation under the recommended parameters, with an ideal fluidity feature of “Structural Flow” and a paste-like flow state.
- (4) Based on the production conditions, two types of CPB are recommended. The high-strength CPB is used for the surface layer and safety pillars for pursuing efficient continuous mining, with a mass fraction of 70%–72% and tailings-cement ratio of 6:1. The low-strength CPB is used at a low price, with a mass fraction of 70%–72% and tailings-cement ratio of 15:1. Economic and environmental benefits can be obtained by using the cement mixture.

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## References

1. Huang, Y.L.; Zhang, J.X.; Zhang, Q. Backfilling technology of substituting waste and fly ash for coal underground in China coal mining area. *Environ. Eng. Manag. J.* **2011**, *10*, 769–775.
2. Rico, M.; Benito, G.; Salgueiro, A.R. A review of the European incidents in the worldwide contest. *J. Hazard. Mater.* **2008**, *152*, 846–852. [[CrossRef](#)] [[PubMed](#)]
3. Rodriguez, L.; Alonso-Azcarate, J. Heavy metal distribution and chemical speciation in tailings and soils around a Pb-Zn mine in Spain. *J. Environ.* **2009**, *90*, 1103–1116. [[CrossRef](#)] [[PubMed](#)]
4. Macur, R.; Wheeler, J.; McDermott, T. Microbial populations associated with the reduction and enhanced mobilization of arsenic in mine tailings. *Environ. Sci. Technol.* **2001**, *35*, 3676–3682. [[CrossRef](#)] [[PubMed](#)]
5. Widisinghe, S.; Sivakugan, N. Vertical stress isobars for trenches and mine stopes containing granular backfills. *Int. J. Geomech.* **2014**, *14*, 313–318. [[CrossRef](#)]
6. Ercikdi, B.; Cihangir, F.; Kesimal, A. Utilization of water-reducing admixtures in cemented paste backfill of sulphide-rich mill tailings. *J. Hazard. Mater.* **2010**, *179*, 940–946. [[CrossRef](#)] [[PubMed](#)]
7. Aldhafeeri, Z.; Fall, M.; Pokharel, M. Temperature dependence of the reactivity of cemented paste backfill. *Appl. Geochem.* **2016**, *72*, 10–19. [[CrossRef](#)]
8. Belem, T.; Benzaazoua, M. Design and application of underground mine paste backfill technology. *Geotech. Geol. Eng.* **2008**, *26*, 147–174. [[CrossRef](#)]
9. Fall, M.; Benzaazoua, M.; Ouellet, S. Experimental characterization of the influence of tailings fineness and density on the quality of cemented paste backfill. *Miner. Eng.* **2005**, *18*, 41–44. [[CrossRef](#)]
10. Kesimal, A.; Yilmaz, E.; Ercikdi, B. Effect of properties of tailings and binder on the short-and long-term strength and stability of cemented paste backfill. *Mater. Lett.* **2005**, *15*, 3703–3709. [[CrossRef](#)]
11. Klein, K.; Simon, D. Effect of specimen composition on the strength development in cemented paste backfill. *Can. Geotech. J.* **2006**, *43*, 310–324. [[CrossRef](#)]
12. Ke, X.; Zhou, X.; Wang, X.S.; Wang, T.; Hou, H.B.; Zhou, M. Effect of tailings fineness on the pore structure development of cemented paste backfill. *Constr. Build. Mater.* **2016**, *126*, 345–350. [[CrossRef](#)]
13. Ke, X.; Hou, H.B.; Zhou, M.; Wang, Y.; Zhou, X. Effect of particle gradation on properties of fresh and hardened cemented paste backfill. *Constr. Build. Mater.* **2015**, *96*, 378–382. [[CrossRef](#)]
14. Yi, X.W.; Ma, G.W.; Fourie, A. Compressive behaviour of fibre-reinforced cemented paste backfill. *Geotext. Geomembr.* **2015**, *43*, 207–215. [[CrossRef](#)]
15. Kesimal, A.; Ercikdi, B.; Yilmaz, E. The effect of desliming by sedimentation on paste backfill performance. *Miner. Eng.* **2003**, *16*, 1009–1011. [[CrossRef](#)]
16. Ercikdi, B.; Baki, H.; İzki, M. Effect of desliming of sulphide-rich mill tailings on the long-term strength of cemented paste backfill. *J. Environ. Manag.* **2013**, *115*, 5–13. [[CrossRef](#)] [[PubMed](#)]
17. Wang, F.H.; Cao, W.Q.; Kang, R.H. Whole tailings cement filling test and system transformation at Nanjing Lead-zinc-silver Mine. *Met. Min. China* **2003**, *328*, 16–17.
18. Liu, Z.X.; Li, X.B. Chaotic optimization of tailings gradation. *J. Cent. South Univ.* **2005**, *36*, 2868–2874.
19. Mishra, D.P.; Sahu, P.; Panigrahi, D.C.; Jha, V.; Patnaik, R.L. Assessment of <sup>222</sup>Rn emanation from ore body and backfill tailings in low-grade underground uranium mine. *Environ. Sci. Pollut. Res.* **2014**, *21*, 2305–2312. [[CrossRef](#)] [[PubMed](#)]
20. Huang, X.F.; Wang, C.; Peng, J.F.; He, L.Y.; Cao, L.M.; Zhu, Q.; Cui, J.; Wu, Z.J.; Hu, M. Characterization of particle number size distribution and new particle formation in Southern China. *J. Environ. Sci.* **2017**, *51*, 342–351. [[CrossRef](#)]
21. Qi, J.X.; Zhao, X.J.; Liu, Y.; Zhang, Z.Y.; Zhang, G.Y. A statistical analysis of seepage deformation type of noncohesive soil with uniformity coefficient  $C_u \leq 5$ . *Chin. J. Rock Mech. Eng.* **2014**, *33*, 2554–2561.
22. Chindapasirt, P.; Chareerat, T.; Sirivivatnanon, V. Workability and strength of coarse high calcium fly ash geopolymer. *Cem. Concr. Res.* **2007**, *29*, 224–229. [[CrossRef](#)]
23. Hanjitsuwan, S.; Phoo-ngernkham, T.; Damrongwiriyanupap, N. Comparative study using Portland cement and calcium carbide residue as a promoter in bottomash geopolymer mortar. *Constr. Build. Mater.* **2017**, *133*, 128–134. [[CrossRef](#)]
24. Sherir, M.A.A.; Hossain, K.M.A.; Lachemi, M. Self-healing and expansion characteristics of cementitious composites with high volume fly ash and MgO-type expansive agent. *Constr. Build. Mater.* **2016**, *127*, 80–92. [[CrossRef](#)]

25. Wei, W.; Yang, Z.Q.; Gao, Q. Cementing action of neotype whole-tailing cementitious material. *J. Build. Mater. China* **2013**, *16*, 881–887.
26. Yang, Y.P.; Gao, Q. Experimental study of a new cementing material using tailings. *Chin. J. Rock Mech. Eng.* **2012**, *31*, 2906–2911.
27. Zhang, F.W.; Yang, J.T.; Liu, W.X.; Shen, L.F. Microscopic experiment of consolidating tailings by slag cementing materials. *J. Univ. Sci. Technol. Beijing* **2012**, *34*, 738–743.
28. Kourounis, S.; Tsivilis, S.; Tsakiridis, P.E.; Papadimitriou, G.D.; Tsibouki, Z. Properties and hydration of blended cements with steelmaking slag. *Cem. Concr. Res.* **2007**, *37*, 815–822. [[CrossRef](#)]
29. Ercikdi, B.; Kesimal, A.; Cihangir, F.; Deveci, H.; Alp, I. Utilization of industrial waste products as pozzolanic material in cemented paste backfill of high sulphide mill tailings. *J. Hazard. Mater.* **2009**, *168*, 848–856. [[CrossRef](#)] [[PubMed](#)]
30. Fall, M.; Benzaazoua, M.; Saa, E.G. Mix proportioning of underground cemented tailings backfill. *Tunn. Undergr. Space Technol.* **2008**, *23*, 80–90. [[CrossRef](#)]
31. Hamberg, R.; Maurice, C.; Alakangas, L. The use of low binder proportions in cemented paste backfill—Effects on As-leaching. *Miner. Eng.* **2015**, *78*, 74–82. [[CrossRef](#)]
32. *Test Method for Strength of Hydraulic Cement Mortar*; Chinese National Standard: GB/T 17671-1999; The State Bureau of Quality and Technical Supervision: Beijing, China, 1999.
33. Liu, Z.X.; Lan, M.; Xiao, S.Y.; Guo, H.Q. Damage failure of cemented backfill and its reasonable match with rock mass. *Trans. Nonferr. Met. Soc. China* **2015**, *25*, 954–959. [[CrossRef](#)]
34. Benzaazoua, M.; Fall, M.; Belem, T. A contribution to understanding the hardening process of cemented pastefill. *Miner. Eng.* **2004**, *17*, 141–152. [[CrossRef](#)]
35. Vespa, M.; Daehn, R.; Grolimund, D. Co speciation in hardened cement paste: A macro- and micro-spectroscopic investigation. *Environ. Sci. Technol.* **2007**, *41*, 1902–1908. [[CrossRef](#)] [[PubMed](#)]
36. Ouellet, S.; Bussiere, B.; Aubertin, M. Microstructural evolution of cemented paste backfill: Mercury intrusion porosimetry test results. *Cem. Concr. Res.* **2007**, *37*, 1654–1665. [[CrossRef](#)]
37. Shen, H.M.; Wu, A.X.; Jiang, L.C.; Wang, Y.M.; Jiao, H.Z.; Liu, X.H. Small cylindrical slump test for unclassified tailings paste. *J. Cent. South Univ. Sci. Technol.* **2016**, *47*, 204–208. (In Chinese).
38. Yilmaz, T.; Ercikdi, B. Predicting the uniaxial compressive strength of cemented paste backfill from ultrasonic pulse velocity test. *Nondestruct. Test. Eval.* **2016**, *37*, 247–266. [[CrossRef](#)]
39. Garcia, V.; Francois, R.; Carcasses, M.; Gegout, P. Potential measurement to determine the chloride threshold concentration that initiates corrosion of reinforcing steel bar in slag concretes. *Mater. Struct.* **2014**, *47*, 1483–1499. [[CrossRef](#)]
40. Yilmaz, E.; Belem, T.; Benzaazoua, M. Study of physico-chemical and mechanical characteristics of consolidated and unconsolidated cemented paste backfills. *Min. Resour. Manag.* **2013**, *29*, 81–100. [[CrossRef](#)]
41. Cihangir, F.; Ercikdi, B.; Kesimal, A.; Turan, A.; Deveci, H. Utilisation of alkali-activated blast furnace slag in paste backfill of high-sulphide mill tailings: Effect of binder type and dosage. *Miner. Eng.* **2012**, *30*, 33–43. [[CrossRef](#)]
42. Yin, S.H.; Wu, A.X.; Hu, K.J.; Wang, Y.; Zhang, Y.K. The effect of solid components on the rheological and mechanical properties of cemented paste backfill. *Miner. Eng.* **2012**, *35*, 61–66. [[CrossRef](#)]
43. Heidberg, B.; Bredow, T.; Littmann, K. Ceramic hydration with expansion. The structure Ceramic hydration with expansion. The structure and reaction of water layers on magnesium oxide. A cyclic cluster study. *Mater. Sci. Pol.* **2005**, *23*, 501–508.
44. Chen, Q.S.; Zhang, Q.L.; Wang, X.M.; Xu, D.; Xiao, C.C. Pipeline hydraulic gradient model of paste-like unclassified tailings backfill slurry. *J. China Univ. Min. Technol.* **2016**, *45*, 902–905.
45. Dong, L.; Gao, Q.; Nan, S.Q.; Du, J.Q. Performance and hydration mechanism of new super fine cemented whole-tailings backfilling materials. *J. Cent. South Univ.* **2013**, *44*, 1571–1577.

