Research Article

Effect of Calcined Hard Kaolin Dosage on the Strength Development of CPB of Fine Tailings with Sulphide

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This study presents the effect of calcined hard kaolin (CHK) as replacement (15–50 wt.%) to Portland cement (PC) on the strength development of cemented paste backfill (CPB) of fine tailings containing sulphide. PC is used as binder at 20 wt.% dosage. The results show that CPB sample containing 30 wt.% CHK replacements produces the desired strength and durability (i.e., 26.1% increase in strength over the curing period between 28 d and 360 d). CPB without CHK does not produce the desired strength and durability (i.e., 32.8% losses in strength over the curing period between 90 d and 360 d). The quantity of expansive gypsum of CPB containing 30 wt.% CHK is obviously less than that of CPB without CHK. The porosity of the fine pore for pore diameter < 0.3 μm is obviously higher in CPB containing 30 wt.% CHK than in CPB without CHK, regardless of curing time. It can be concluded that CHK can be suitably exploited for CPB of fine tailings with sulphide to improve the strength and stability in short and long terms.

1. Introduction

The tailings are usually separated to fine tailings (average particle size less than 0.037 mm) and coarse tailings by hydrocyclones in China. The fine parts are generally stored in a surface impoundment [1], whereas the coarse tailings mixed water and a hydraulic binder are transported by gravity into underground voids [2, 3]. The lead-zinc tailings are often rich in pyrite and contain toxic metals such as arsenic (As), cadmium (Cd), lead (Pb), zinc (Zn), and copper (Cu). The oxidation of pyrite in presence of water and oxygen generates acidity and facilitates the release of toxic metals contained in the tailings [4, 5]. The finer the granularity of tailings is, the lower the water permeability is, the harder the drainage consolidation is, and the easier the spill of the storage tailings dam is [6]. The spill of the storage tailings dam will lead to increasing the heavy metal content in the downstream soil, acidizing the soil, reducing organic matter content in the soil, and hardening the soil [7, 8]. In recent years, cemented paste backfill (CPB) of potentially hazardous mill tailings into underground and surface disposal practices has gained importance for the environmental management of such wastes [9, 10]. Environmental problems associated with the storage of sulphide-rich wastes under atmospheric conditions (i.e., the formation of acid mine waters and the release of heavy and toxic metals with the concomitant risk of contamination of soils and underground/drinking waters) can be considerably reduced by the placement of such wastes safely in underground.

CPB is essentially an engineered mixture of wet fine mill tailings (75–85% solids by weight), a hydraulic binder (3–7% by dry total paste weight), and mixing water. However, some potentially long-term durability problems of CPB may be encountered when mill tailings with high sulphide (especially pyrite) content are used. Oxidation products (i.e., acid and sulphate) of sulphide minerals present in the tailings could lead to chemical reactions with hydration products and binder phases, such as calcium hydroxide (CH) and calcium aluminate (C3A) and, concomitantly, to the formation of expansive phases such as ettringite and gypsum [11–15]. These could then culminate in the reduced backfill strength and potential collapse of the backfill. The incorporation of pozzolanic wastes such as granulated blast furnace slag (GBFS) and silica fume (SF) into the binder phase appeared
to mitigate the strength losses in the long term although the initial rate of development of strength of CPB samples tended to slow down with increasing the dosage of these pozzolanic wastes in the binder phase [13, 14]. Therefore, binder properties, that is, its sulphate resistance, are of practical importance for CPB of sulphide-rich tailings. Metakaolin (MK) replacement of cement was found to be effective in improving the resistance of concrete to sulphate attack [16]. “Lower Ca/Si ratios indicate the improvement of compressive strength [17].” The MK used in this study shows lower Ca/Si ratio. However, reports about the effect of calcined hard kaolin (CHK) with metakaolin on the short- and long-term strength and stability of CPB of fine tailings with sulphide (mainly pyrite) (19.07 wt.% S) are scare.

Given the problems mentioned above, the main objectives of this study are as follows:

(1) To investigate the effect of CHK replacement to PC on the properties of CPB mixtures.

(2) To investigate the effect of CHK replacement to PC on unconfined compressive strength (UCS) development of CPB.

(3) To investigate the mechanism of the short- and long-term strength and stability of CPB of fine tailings with sulphide.

2. Materials and Methods

2.1. Tailings and Binder. The fine tailings sample used in this study is obtained from an underground lead-zinc mine located in the south of China. The fine tailings are quartz, pyrite, calcium carbonate, dolomite, and muscovite, in which pyrite is the major sulphide mineral (Figure 1(a)).

The binder used in this study is Portland cement (PC). The PC consisted of silicate cement that satisfied the Chinese standards for “Universal Portland Cement” (GB 175-2007). The chemical compositions and physical properties of the PC are shown in Tables 1 and 2. The main materials in the PC are cement clinker (i.e., tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite) and gypsum (Figure 1(b)).

2.2. Admixtures. One type of calcined hard kaolin (CHK) is used as mineral admixture in this study. Pozzolanic activity index can be reflected by the absorption ability of calcium hydroxide. The CHK used in this study is commercially available and with the absorption ability of 1050 mg Ca(OH)$_2$/g CHK. The CHK is obtained by calcining coal-measure hard kaolinite and grinding. China is rich in coal hard kaolinite reserves, which belong to sedimentary kaolinite and occur in the coal seam roof and floor and mezzanine. The chemical and physical properties of the CHK are shown in Tables 1 and 2. The main crystal minerals in the CHK are kaolinite and quartz, while the amorphous form mineral (i.e., metakaolin, MK) in the CHK is also obvious (Figure 1(c)).

2.3. Mixing Water. Tap water is used in this study. The effect of the sulphate ions in tap water can be neglected.

2.4. Slump and Wet Density Tests. The workability of CPB mixtures is measured by the slump of CPB mixtures. The high slump and low bleeding rate value of CPB mixtures indicate that the CPB mixture has good workability. The bleeding rate value of all CPB mixtures in this study is all ≤2 wt.%.

The slumps of the samples are tested according to the Chinese standard (GB/T 50080-2002). The desired slump value in this study is 180 mm.

2.5. Preparation and Testing of CPB Samples. The UCS criteria to be achieved in this study are to produce the desired 28-day strength of ≥2.0 MPa and the maintenance of the stability (i.e., ≥2.0 MPa UCS at curing 360 d) according to requirement of mining technology.

Table 1: Chemical properties of tailings, PC, and CHK used.

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>Pb</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>S</th>
<th>Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tailings</td>
<td>25.37</td>
<td>5.88</td>
<td>21.28</td>
<td>14.47</td>
<td>0.15</td>
<td>0.84</td>
<td>0.009</td>
<td>1.58</td>
<td>19.07</td>
<td>19.97</td>
</tr>
<tr>
<td>PC</td>
<td>25.26</td>
<td>6.38</td>
<td>4.05</td>
<td>54.67</td>
<td>2.68</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.06</td>
<td>—</td>
</tr>
<tr>
<td>CHK</td>
<td>43.13</td>
<td>45.17</td>
<td>1.25</td>
<td>1.75</td>
<td>0.10</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>7.70</td>
</tr>
</tbody>
</table>

Table 2: Physical properties of tailings, PC, and CHK used.

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>SSA (m$^2$/kg)</th>
<th>$G_c$</th>
<th>$&gt;90 \mu\text{m}$ (%)</th>
<th>$&gt;45 \mu\text{m}$ (%)</th>
<th>$D_{10}$ (μm)</th>
<th>$D_{50}$ (μm)</th>
<th>$D_{60}$ (μm)</th>
<th>$C_w$ (%)</th>
<th>$C_c$ (%)</th>
<th>$&lt;20 \mu\text{m}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tailings</td>
<td>633.8</td>
<td>3.0</td>
<td>1.07</td>
<td>7.28</td>
<td>1.50</td>
<td>4.55</td>
<td>14.68</td>
<td>9.8</td>
<td>0.94</td>
<td>73.67</td>
</tr>
<tr>
<td>PC</td>
<td>461.9</td>
<td>3.1</td>
<td>—</td>
<td>5.67</td>
<td>5.12</td>
<td>9.19</td>
<td>18.28</td>
<td>3.6</td>
<td>0.90</td>
<td>65.65</td>
</tr>
<tr>
<td>CHK</td>
<td>588.1</td>
<td>2.6</td>
<td>1.44</td>
<td>13.11</td>
<td>1.31</td>
<td>4.8</td>
<td>17.97</td>
<td>13.72</td>
<td>0.98</td>
<td>68.69</td>
</tr>
</tbody>
</table>
Figure 1: XRD profiles of tailings (a), PC (b), and CHK (c).

Table 3: Mix proportions and partial properties of CPB mixture.

<table>
<thead>
<tr>
<th>Number</th>
<th>Tailings slurry/g</th>
<th>Mix proportions</th>
<th>Partial properties of CPB mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PC/g</td>
<td>CHK/g</td>
</tr>
<tr>
<td>1</td>
<td>1000</td>
<td>92.5</td>
<td>157.5</td>
</tr>
<tr>
<td>2</td>
<td>1000</td>
<td>92.5</td>
<td>133.9</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>92.5</td>
<td>110.25</td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td>92.5</td>
<td>78.75</td>
</tr>
</tbody>
</table>

(1) Tailings slurry has 63 wt.% solid concentration; (2) RL is CHK replacement to PC. Binder (including PC and CHK) dosage is kept constant at 20 wt.% of total solids.

Binder (including PC and CHK) dosage in this study is kept constant at 20 wt.% of total solids. The required amounts (see Table 3) of CPB ingredients (tailings slurry, PC, CHK, and mix water) are thoroughly mixed in a double spiral mortar mixer for about 5 min to ensure paste homogeneity. Immediately after mixing, samples are poured into 70.7 mm x 70.7 mm x 70.7 mm iron molds. Excess water (i.e., drain away water) in the samples could separate out from the seam between the broadsides and the baseboard of the iron molds. Then, the open-top samples are placed in a humidity chamber set at 20 ± 1 °C and 90% RH for curing. In total, 84 samples were made and cured for 7, 28, 56, 90, 150, 210, 270, and 360 days. Then the CPB samples are tested for unconfined compressive strength (UCS) according to the Chinese standard (JGJ/T 70-2009), in which the loading rate is 0.25–1.5 KN/s. Prior to a UCS test, the sizes of a sample are...
rectified to get valid press surfaces. UCS tests are performed using a computer-controlled mechanical press, which had a load capacity of 100 KN.

2.6. XRD and MIP Studies. After compression testing, representative samples are taken from locations as far as possible from the shear plane to avoid stress concentration effects. The representative samples are treated with acetone and then dried in an oven maintained at 60°C to halt further hydration prior to X-ray diffraction (XRD) and mercury intrusion porosimeter (MIP) studies.

The XRD analysis is performed using a D/max-2500PC X-ray diffractometer from Japan with a copper target with a 2θ range of 4° – 60° and a scanning speed of 2° /min to examine the mineralogical compositions of CPB samples after the curing process.

The MIP used in this study is an AutoPore IV 9500 V1.05. Applying pressures ranged from 0 to 414 MPa (60,000 psi), allowing throat pore diameter measurements down to 0.003 μm. MIP is analyzed according to the ISO 15901-1: 2005 standard. In this study, mercury surface tension σ and mercury contact angle θ are taken as 485 dynes/cm and 130°C, respectively.

3. Results and Discussion

3.1. Effect of CHK on the Workability of CPB Mixtures. The influence of CHK replacement level to PC on the workability of CPB mixtures is illustrated in Table 3. Table 3 shows that the slump of CPB mixture tends to decrease with increasing CHK replacement level to PC at the same solids content. However, the wet density of CPB mixture tends to increase with increasing CHK replacement level to PC at the same solids content. Fineness and surface characteristic of CHK can be main influence factors.

3.2. Effect of CHK on the Strength Development of CPB Mixtures. The effect of CHK replacement level to PC on the strength development of CPB samples over a curing period of 360 days is illustrated in Figure 2. Mix proportions and partial properties of CPB mixtures in Figure 2 are shown in Table 3.

Figure 2 shows that the UCS of the control sample (i.e., no CHK in binder) and the samples of 15 wt.% CHK and 50 wt.% CHK in binder tend to increase over a curing period of 90 d, 28 d, and 28 d, respectively; thereafter, the UCSs tend to decrease. The control sample has 32.8% losses in strength over the curing period between 90 days and 360 days. The samples of 15 wt.% CHK and 50 wt.% CHK in binder have 38.6% and 57.2% losses in strength over the curing period between 28 days and 360 days, respectively. The 28 d UCS of CPB sample containing 30 wt.% CHK in binder achieves the desired 28-day strength of ≥ 2.0 MPa. In addition, the CPB samples containing 30 wt.% CHK in binder are observed to develop consistently over a curing period of 360 days and have 26.1% increase in strength over the curing period between 28 days and 360 days. These findings suggest that 20 wt.% binder in total solids and 30 wt.% CHK in binder are extremely effective for increasing the strength and stability in short and long terms of CPB of fine tailings with sulphide (19.07 wt.% S).

When the fine tailings with pyrite (FeS₂) mix with binder and water, a series of complex chemical reactions happen. First of all, the hydration reaction between PC and water produces hydrated calcium silicate gel (C–S–H), portlandite (Ca(OH)₂), and so forth. Secondly, the sulphide phases such as pyrite present in CPB could undergo oxidation under the curing conditions in the presence of air and moisture. The oxidation of pyrite yields acid and sulphate (1). The former can attack and destruct C–S–H bonds while the latter can react with portlandite (Ca(OH)₂) and tricalcium aluminate (C₃A) to form secondary gypsum (2) and ettringite (3) with these leading to the expansion and development of microcracks in cured CPB. The formation of secondary gypsum and ettringite with expansive properties was claimed to be responsible for the reduction of strength of CPB samples after 56 and 90 days. However, the formation of secondary ettringite is not observed by XRD analyses in the CPB samples in this study (see Figures 3(a) and 3(b)).

\[
4\text{FeS}_2 + 15\text{O}_2 + 8\text{H}_2\text{O} \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_4^{2-} + 16\text{H}^+ \quad (1)
\]
\[
\text{Ca} (\text{OH})_2 + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{OH}^- \quad (2)
\]
\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 3\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 3\text{H}_2\text{O} \quad (3)
\]

Figure 3 shows that the quantity of expansive gypsum of CPB with 100% PC (a) is obviously higher than that of CPB with 70% PC + 30% CHK (b) at 360 days. The results can be explained by the following mechanisms. First, the replacement of a portion of PC with CHK reduces the total amount of PC cinder in binder of CPB samples. The second mechanism is through the pozzolanic reaction between the MK in CHK and calcium hydroxide released during the hydration of PC, which consumes part of the calcium hydroxides leading to decreasing the quantity of expansive gypsum [15].
Figure 3: XRD profile of CPB with 100% PC (a) and 70% PC + 30% CHK (b) at 360 days.

It is well known that pore structure can cause significant effects on the strength of CPB. Figure 4 shows that relationships between MIP total porosity and curing time of CPB samples. For CPB samples with the same mixing proportion, the lower the MIP total porosity, the greater the UCS. For CPB samples with different mixing proportion, UCS is not strictly correlated with the MIP total porosity.

Figure 5 shows the changes in incremental pore size distribution (PSD) curves for 28 and 360 cured CPB samples. According to the definition of the capillary pore, pores ≥0.3 μm correspond to the main interconnected capillary porosity network. The porosity of the fine pore for pore diameter < 0.3 μm is obviously higher in CPB sample with CHK than in CPB without CHK, regardless of curing time. The reason of gaining the result is that the formation of secondary hydrated calcium silicate gel (C–S–H) by the pozzolanic reaction is effective in filling and segmenting large capillary pores into small, discontinuous capillary pores through pore size refinement, which increases the UCS of CPB samples. An additional potential reason of more finer pores in CHK is the filler effect role of the admixture.

Figure 6 shows visual appearance of CPB samples. In visual appearance of CPB samples, the surface cracks of CPB sample with 100% PC at 360 days can be clearly identified while no surface cracks can be detected in CPB sample with 70% PC + 30% CHK at 360 days.

Figure 7 shows schematic diagram of bonding strength and expansion stress development in CPB samples. The bonding strength of CPB sample increases with increasing curing times due to the increase of hydration products and the porosity of the fine pore for pore diameter < 0.3 μm. The expansion stress of CPB sample increases with increasing the quantity of secondary gypsum and ettringite within CPB sample. When the expansion stress (ES1 in Figure 7) produced by forming secondary gypsum and ettringite in CPB sample exceeds the bonding strength (BS in Figure 7) of CPB sample, the sample cracks and MIP total porosity increase, which lead to the decrease of the UCS of the samples such as number 1, number 2, and number 4 in Table 3. However, the secondary gypsum in certain quantity could also fill the voids within CPB. The expansion stress (ES2 in Figure 7) is always less than the bonding strength (BS in Figure 7) within CPB. This in turn leads to a decreased porosity and higher short- and long-term strength of CPB sample such as number 3 in Table 3. This is a conclusion in this study that CPB sample containing 30% CHK replacement level to PC shows excellent short- and long-term mechanical performances.

4. Conclusions

This study presents the results for effect of calcined hard kaolin with metakaolin on the short- and long-term strength and stability of CPB of fine tailings with sulphide. Based on the results obtained from this study, the following conclusions may be warranted:
(1) CPB containing 30 wt.% CHK replacement to PC achieves the desired strength value (i.e., ≥2.0 MPa UCS at curing 360 d).

(2) CPB without CHK has 32.8% losses in strength over the curing period between 90 days and 360 days. CPB containing 30 wt.% CHK replacement level to PC has 26.1% increase in strength over the curing period between 28 days and 360 days.

(3) The quantity of expansive gypsum of CPB containing 30 wt.% CHK replacement to PC is obviously less than that of CPB without CHK. The porosity of the fine pore for pore diameter < 0.3 μm is obviously higher in CPB containing 30 wt.% CHK replacement to PC than in CPB without CHK, regardless of curing time.

(4) When the expansion stress produced by forming secondary gypsum and ettringite in CPB samples exceeds the bonding strength of CPB samples, the
sample cracks and MIP total porosity increase, which lead to the decrease of the UCS of the sample, and vice versa.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

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References