Properties and Microstructure of Low-Carbon Whole-Tailings Cemented Paste Backfill Material Containing Steel Slag, Granulated Blast Furnace Slag and Flue Gas Desulphurization Gypsum

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Abstract

Using steel slag (SS), granulated blast furnace slag (GBFS) and flue gas desulphurization gypsum (FGDG) as cementing agents (CA) and iron ore tailings (IOT) as aggregate, a filling material for mine cemented paste backfill (CPB) material was prepared. The mixing ratio and properties of CPB were investigated. The hydration products and microstructure of CA were analyzed by X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FT-IR), and Scanning electron microscopy (SEM). The optimal proportion of CA is as follows: GBFS 58%, SS 29% and FGDG 13%. When binder sand ratio (CA/IOT) of CPB material is 1:4, and the slurry concentration is 80%, the slurry of meets the fluidity requirement of paste pumping. The compressive strength of the backfill at 28 d is 8.41 MPa, which meets the requirements of mine filling strength. After the hydration of the mineral phases in the raw materials, a large number of ettringite (AFt) and complex C-S-H gel with low crystallization degree are generated. They interweave together to make the system compact and have good mechanical properties.

Keywords: SS—GBFS—FGDG, Iron Ore Tailings, Cemented Paste Backfill, Ettringite, C-S-H

1. Introduction

Cemented paste backfill (CPB) refers to a certain proportion of cementitious materials and fine sand, tailings inert aggregate mixture mixing preparation water slurry cemented filling. The slurry is transported and stacked along the boreholes, pipes and grooves to the underground goaf, and the slurry gradually forms a backfill with certain strength and integrity in the goaf [1]. High quality cemented filling mining can improve the recovery rate
of resources by more than 30% compared with non-filling mining methods. As an effective mining technique for deep well, complex and special condition deposits, cementing filling has been widely used [2, 3].

The cementing and filling cost generally accounts for 25% ~ 40% of the total mining cost, and the cementing agent cost accounts for 70% ~ 80% of the filling cost [4, 5]. Cementing filling materials are mainly composed of aggregate and cementing agent. In the selection of cementing agent, most mines choose ordinary Portland cement [6-9]. However, due to its high price, many mines can only be deterred from cementing and filling. In order to reduce the cost of cementing and filling while satisfying the strength of backfill, it is undoubtedly the best way to find filling materials with wide sources and low prices. For this reason, many mining enterprises and researchers started to look for industrial byproducts with cementing properties to replace or partially replace cement, such as GBFS [10-14], SS [15], fly ash [16-19], red mud [20] and other additives [21-23]. GBFS and SS are the industrial waste residue discharged in the process of iron and steel metallurgy, which has good potential activity under the excitation of desulphurization gypsum [24-28]. From the perspective of effective utilization of resources, energy conservation and environmental protection, it is of great significance to select GBFS and SS as the main raw materials of mine filling cementing agent.

In this paper, GBFS is taken as the main raw material of the cementing agent, and the mixture of GBFS and SS is used to activate each other [29]. FGDG is used as the initiator. The industrial solid waste accounts for 100% of the total dry base of the cementing agent, which greatly reduces the filling cost and realizes the efficient utilization of GBFS and SS.

Because GBFS-SS-FGDG is a ternary system, hydration process is complex. In this paper, by means of XRD, FT-IR and SEM, the types and microstructures of the hydration products were analyzed and identified, and on this basis, the effects of the hydration reaction and the hydration products on the macroscopic properties were further discussed.

2. Materials and Methods

2.1. Materials

GBFS, SS, FGDG and IOT were the main raw materials used in the experiment. See Table 1 for the chemical composition and Fig. 1 for the mineral composition of the raw materials.

<table>
<thead>
<tr>
<th>Table 1. Chemical composition of raw materials (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>GBFS</td>
</tr>
<tr>
<td>SS</td>
</tr>
<tr>
<td>FGDG</td>
</tr>
<tr>
<td>IOT</td>
</tr>
</tbody>
</table>

GBFS. GBFS powder prepared by the laboratory itself is used, and the specific surface area (SSA) is 600 m² kg⁻¹. The calculated mass coefficient of GBFS powder is 1.572, which belongs to the active GBFS powder. According to mineral phase analysis (Fig.1(a)), the crystal diffraction peak intensity of GBFS powder is relatively low, and the GBFS powder mainly exists in the form of vitreous body.

SS. SS used was basic oxygen furnace SS without hot closed treatment technology which complies with the Chinese National Standard GB/T 20451-2006. Its main chemical composition is CaO (43.69%), followed by the level of residual iron in the SS (14.34%). Compared with the Portland cement, SS has higher contents of Fe and Mg and lower contents of Si and Ca. The content of MgO and CaO content in SS are 0.78% and 1.19%, respectively. Its activity can be partially reflected by the alkalinity calculated from the chemical composition. SS alkalinity is defined by Mason’s method [30]: CaO/(SiO₂+P₂O₅), and divided into three categories: low alkalinity SS (alkalinity <1.8), medium alkalinity SS (alkalinity = 1.8~2.5) and high alkalinity SS (alkalinity> 2.5). In this study, the alkalinity of SS is 2.67, which falls in the high range. The f-CaO content and alkalinity of SS satisfies the requirement in SS powder Used for Cement and Concrete (GB/T20491-2006) that f-CaO content should not exceed 3% and the alkalinity should not fall below 1.8. The main mineral phases of SS (see Fig.1(b)) are calcium silicate (C₃S), calcium silicate (C₃S) and RO phases (solid solutions of FeO, MnO and MgO). SS used in the test was SS powder after grinding, with a specific surface area of 580 m² kg⁻¹.

FGDG. FGDG is a wet desulphurization gypsum from the power plant, and its main component is calcium dihydrate sulfate (CaSO₄·2H₂O, Fig.1(c)). As shown in Table 1, the burning loss of FGDG is 8.28%, CaO and
SO$_3$ contents in FGD are 33.38% and 45.70% respectively. According to the calculation that all SO$_3$ comes from CaSO$_4$, the mass fraction of CaSO$_4$ in FGDG is 77.69%. The specific surface area of FGDG is 300 m$^2$ kg$^{-1}$.

IOT. IOT is used from Qian'an Dashihe Deposit mined by Shougang Mining Company. As can be seen from Table 1, SiO$_2$ content of Miyun IOT is high and it is belonging to high silicon type IOT. For the grading and screening of tailings, the particle size of about 97% of the tailings with mass fraction is less than 0.63 mm, the particle size of about 21% of the tailings is less than 0.08 mm, and the particle size of 0.08~0.63 mm accounts for 75.8%. The major minerals of IOT included: quartz, hornblende, biotite, plagipclase and a few amounts of chlorite, calcite and magnetite (see Fig.1 (d)).

Additive. PC water reducer produced by Beijing MuHu admixture Co., LTD.
2.2. Experimental Method

Firstly, GBFS, SS and FGDG were dried in oven at 105 ºC for 24 h to make moisture content less than 1 %, respectively. Then, crushed them using SM φ 500 mm × 500 mm laboratory ball mill at the speed of 48 r min⁻¹ to yield SSA of 600 m² kg⁻¹, 580 m² kg⁻¹, 300 m² kg⁻¹. The grinding media consists of several steel balls and a steel forging. The loading mass of the grinding media should be 100 kg. The steel balls add up to 40 kg, in which the φ70 mm ball takes up 19.7%, the φ60 mm ball takes up 33.1%, the φ50 mm ball takes up 29.6%, and φ40 mm ball takes up 17.6%; the φ25 mm × 30 mm steel forging weighs 40 kg.

Binder sand ratio (CA/IOT) was 1:4. IOT was added as aggregate, and 80% slurry concentration was added with water for stirring. Then pour into 4 cm×4 cm×16 cm of cement mortar joint test, in the cement paste compaction machine vibration molding, 24 h after demoulding curing, in the temperature of (20 plus or minus 1) ºC, humidity for more than 90% of the standard curing box maintenance, the final determination of different ages, the mechanical properties of block.

By measuring the compressive strength of the samples, a group of optimized proportions were obtained. XRD, FT-IR and SEM analysis were performed on the optimized proportions of the cementing agent CA.

The f-CaO of SS was determined by EDTA complexometric titration according to Methods of Chemical Analysis of SS (YB/T 140-2009) using ethylene glycol as extractant; the f-MgO was measured by using ammonium nitrate-ethanol as extractant.

According to the Chinese National Standard GB/T 19077.1-2008 Particle size analysis - Laser diffraction methods - Part 1: General principles, the particle size distribution of ground SS is analyzed using laser particle size analyzer (MASTER SIZER 2000, the analysis range is 0.02–2000.00 μm) with ethanol as the dispersant. The specific surface area is measured using dynamic specific surface area analyzer (SSA-3200).

The value of fluidity and slump in the test were determined in accordance with GB/t50080-2002 Performance test method standard for ordinary concrete mixtures. The initial and final coagulation tests of cementing agent were determined by vika apparatus in accordance with GB1346-1989 Test method for water consumption, setting time and stability of standard consistency of cement. The compressive strength test of samples was based on the Chinese National Standard GB/T 17671-1999 Method of testing cement-determination of strength. The strength was measured using hydraulic pressure testing machine (YES-300) with a maximum load of 300 KN and a loading rate of 2.0±0.5 kN/s.

The X-ray diffraction (XRD) spectra of the CA samples were performed using a D/Max-RC diffractometer (Japan) with Cu Ka radiation, voltage of 40 kV, current of 150 mA and 20 scanning ranging between 5° and 90°. The functional groups vibration of CA samples was qualitatively analyzed by NEXUS70 Fourier transform infrared (FT-IR, test range 350–4000 cm⁻¹). FE-SEM observation was performed to analyze the hydration products of the CA samples using a Zeiss SUPRA™55 scanning electron microscope coupled with a Be4-U92 energy spectrum.

3. Results

3.1. Properties of CPB material

The main purpose of this test is to satisfy properties of whole-tailings CPB material containing GBFS-SS-FGDG, and can make maximum use of GBFS and SS. The composition of GBFS phase is mainly glass phase and
has great activity. The content of $C_3S$ and $C_2S$ in SS is relatively high, and both of them have hydration activity. Such SS has certain hydraulicity and can be used as cementing material. Under the excitation of FGDG, GBFS and SS can be activated each other. Therefore, the initial ratio of the total content of GBFS and SS is temporarily determined as 87%, the content of FGDG is fixed as 13%, the water-reducing agent is 0.3%, the mass ratio of cementing agent (GBFS + SS + FGDG) and IOT in slurry is 1:4, and the slurry concentration is 80%. In this test, the activity of SS is less than that of GBFS, and the maximum content of SS is tentatively determined to be 58%. By continuously reducing the content of SS and increasing the content of GBFS, the mixing ratio is optimized, as shown in Table 2. GBFS, SS, FGDG and IOT are industrial solid waste, accounting for 100% of the total dry base, so the filling cost will be greatly reduced.

**Table 2. Mix proportion of whole-tailings CPB material containing GBFS-SS-FGDG**

<table>
<thead>
<tr>
<th>Number</th>
<th>CA additive/%</th>
<th>binder sand ratio</th>
<th>slurry concentration/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GBFS/%</td>
<td>SS/%</td>
<td>FGDG/%</td>
</tr>
<tr>
<td>A-1</td>
<td>28</td>
<td>59</td>
<td>13</td>
</tr>
<tr>
<td>A-2</td>
<td>38</td>
<td>49</td>
<td>13</td>
</tr>
<tr>
<td>A-3</td>
<td>48</td>
<td>39</td>
<td>13</td>
</tr>
<tr>
<td>A-4</td>
<td>58</td>
<td>29</td>
<td>13</td>
</tr>
<tr>
<td>A-5</td>
<td>68</td>
<td>19</td>
<td>13</td>
</tr>
</tbody>
</table>

Fig.2 shows the test results of the influence of different GBFS content on the fluidity of slurry filled with GBFS-SS-FGDG base whole tailings. As can be seen from Fig.2, the slurry fluidity gradually increases with the increase of GBFS content. When the slurry content is 60% and 70%, the slurry fluidity reaches 160 mm, which meets the requirements of paste pump transportation. Fig.3 shows the influence of different GBFS content on the compressive strength of GBFS-SS-FGDG cemented whole tailings filling block. As can be seen from Fig.3, with the increase of GBFS content, the compressive strength of test blocks at various ages gradually increases. The maximum strength occurs when the GBFS content is 58%, and the strength decreases when the GBFS content is 68%. When the content of GBFS is 60%, the early strength of the test block is low, and the late strength is greatly improved, reaching 8.41MPa at 28 d and 13.89 MPa at 60 d, and the fluidity reaches 160 mm. Therefore, the optimized formula is A-4, with the content of 58% GBFS, 29% SS, 13% FGDG and 0.3% water reducer as cementing agent, 80% slurry concentration and 1:4 binder sand ratio (CA/IOT).

Fig. 2. Influence of GBFS content on fluidity of slurry
Fig. 3. Influence of GBFS content on compressive strength of samples

The initial setting, final setting and slump tests were carried out on the ratio of the cementing agent of A-4, and the slurry was made according to binder sand ratio of 3:17 and water binder ratio of 1.2. The test results are shown in Table 3.

**Table 3.** Working performance of whole-tailings CPB material containing GBFS-SS-FGDG

<table>
<thead>
<tr>
<th>bleeding rate /%</th>
<th>initial setting /h</th>
<th>final setting /h</th>
<th>fluidity /mm</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>2.5</td>
<td>3.8</td>
<td>162</td>
</tr>
</tbody>
</table>

As can be seen from Table 3, A-4 CPB material has good water retention, which can ensure no bleeding or segregation during the filling process. Initial setting time is 2.5 h, which can provide sufficient time for the conveying and filling operations of the filling materials, and 3.8 h final setting can ensure rapid solidification after the completion of filling, which is conducive to improving the efficiency of cemented filling mining. Paste on fluidity (fluidity) 6.4 cm can be pumped in the pipe. In addition, the strength of A-4 is relatively surplus to the requirements of most mines for filling, so the water-cement ratio and fluidity can be more reasonable selection and adjustment according to the specific requirements of mines for strength, pumping conditions and setting time.

### 3.2. XRD analysis of hydration products

Fig.4 shows the XRD spectra of the cementing agent sample block with A-4 water binder ratio of 0.2 prepared according to the ratio of A-4, which was hydrated for 3 d, 7 d and 28 d.
As can be seen in Fig.4, 3 d, 7 d, 28 d (XRD spectrum diagram, in 20is 15.8, 22.9 and 32.4 ° where new diffraction peaks, for AFt, other diffraction peak greatly reduced, the presence of no hydration C2S, C3S and CaSO4·2H2O, RO and CaF. Except for the diffraction peak of AFt, no obvious crystallinity was observed in the hydration products. 20 ~ 50 ° shown is an obvious bulge phenomenon; show system contains a lot of gel and low degree of crystallinity of the material [101-33]. By comparing the XRD curve of the phase at 7 and 28 d, it can be seen that the diffraction peak of FGDW in the phase at 28 d is obviously weakened, while that of AFt is strengthened. The results show that the GBFS hydrates continuously under the excitation of gypsum sulfate. GBFS vitreous surface of Ca2+ and Mg2+ cation first to dissolve into the solution, the rest of the [SiO4]4- with [AlO4]3- a charge imbalance, cause [AlO4]3- alumina key (Al-O) fracture, on the aluminum acid group (AlO2-1) from the vitreous body surface in the form of dissolution, and tend to form the vitreous balance between the solution and the surface dissolved, in under the FGDW in free generate AFt, improved the strength of the gel system. With the continuous formation of AFt, the dissolution equilibrium between the vitreous surface of GBFS and the solution of AlO2- is constantly broken, which promotes the continuous migration of [AlO4]3- from the vitreous surface of GBFS and the continuous secondary hydration of GBFS. [AlO4]3- from the surface of GBFS vitreous body out, destroyed [SiO4]4- with [AlO4]3- connection, make the surface of GBFS vitreous silicon oxygen tetrahedron degree of polymerization (aluminum) falling fast, and residual [SiO4]4- and [AlO4]3- activity increased significantly, the slurry solution in the Ca2+ constantly form C-S-H gel, C-S-H gel deposition, to gradually thickening and hardening of the slurry, macroscopic strength increased rapidly.

3.3. FT-IR analysis of hydration products

Fig.5 is the FT-IR comparison diagram of the filling block made according to the ratio of A-4. It can be seen that the graphs of samples at different ages are relatively similar, showing basically the same characteristic absorption band, and each absorption peak moves towards the direction of wavelet number.

![Fig. 5. FT-IR spectra of CPB material samples at different ages](image)

In the Fig.5, the absorption peak at the wave number of 459 cm−1 belongs to the bending vibration of the Si-O bond, and about 795 cm−1 is the vibration absorption peak of quartz, which is caused by the residual quartz in the IOT. The absorption peak of wave number in 990 cm−1 is caused by the asymmetric vibration of Si-O in the 4-structure [SiO4]4-, where is the characteristic peak of C-S-H gel. The absorption band at 1427 cm−1 is an asymmetric stretching vibration band with CO3-2-, which may be due to the carbonization of the sample during the preparation process. The absorption band at 1645 cm−1 belongs to the bending vibration of the O-H bond in water. The band with wave number of 3425 cm−1 is the stretching vibration band of hydration product C-S-H gel structure water, indicating that C-S-H gel is generated continuously with the growth of age. As can be seen from the Fig.5, the absorption peak of 3635 cm−1 reflecting the stretching vibration of O-H bond is not obvious, which is because the hydroxyl groups in AFt and C-S-H gel are not typical hydroxyl groups, and they have no distinct boundaries with the hydrogen bond and molecular bond in the crystalline water, so they will be covered by the crystal water peak at 3425 cm−1. However, since most of the water in AFt is crystallized water, the absorption peak overlaps with that of C-S-H structure water at 3425 cm−1, showing a strong absorption peak. The strong absorption band at 1090 cm−1 belongs to the asymmetric stretching vibration of S-O bond, and its vibration peak is strengthened and
sharpened with the extension of curing time. After hydration for 3 d, AFt has been formed in a considerable number, indicating that AFt is formed at a relatively fast speed, which is consistent with the XRD analysis results in Fig. 4.

3.4 SEM analysis of hydration products

Fig. 6 is the SEM and EDS diagram of the filling test block made according to the ratio of A-4 on 3d, 7d and 28d. Fig. 6(a) is the SEM image of the hardened slurry on 3 d. It can be observed from the figure that the IOT particles at 2-10μm, the particles are not tightly packed, embedded in the hydration products, the pores are large, there are many flocculated C-S-H gel and club-shaped CaSO₄·2H₂O between the pores, they bond the particles together.

Fig. 6(b) is a partial enlargement of the gel. It can be seen from the figure that the flocculent and cluster-like colloid and the pin-stick CaSO₄·2H₂O agglomerate and fill in the IOT particles, so that the 3d hardened slurry has a certain strength.
Fig. 6. SEM images and EDS spectrum of CPB material samples at different ages. (a) and (b)-3 d, (c) and (d)-7 d, (e) and (f)-28 d.

Fig.6(c) is the SEM image of hardened slurry at 7 d. As can be seen from the figure, hydration products increase greatly, the boundary of tailings particles is blurred, hydration products connect a large number of particles together into a piece, the gap between particles is greatly reduced, so that the density of slurry increases.

Fig.6(d) is an enlarged image of the hole in Fig.6(c). It can be seen that CaSO$_4$·2H$_2$O in rod form is thicker and shorter than that in 3d hardened slurry.

Fig.6(e) is the SEM image of the hardened slurry at 28 d. At this time, IOT particles are no longer observed, and many small needle-like substances appear, as shown in Fig.7(f) after magnification. Semi-quantitative energy spectrum analysis (Fig.7(g)) of these needle-like substances is carried out, which is speculated to be Aft, which is also consistent with the analysis results of XRD (in Fig. 4). In the hardened slurry after hydration for 28 d, fine acicular Aft and gel are intertwined, making the structure very dense and no obvious large holes can be observed, which makes the specimen have good mechanical strength at the macro level.

4. Conclusions

(1) The filling material was made with the content of 58% GBFS, 29% SS and 13% FGDG, the ratio of colloidal sand was 1:4, the water-reducing agent was 0.3%, and the slurry concentration was 80%. The slurry fluidity was 162 mm, and the slurry fluidity met the requirements of paste pump conveying fluidity. The compressive strength of the filling material at 28 d and 60 d respectively reached 8.41 MPa and 13.89 MPa, meeting the requirements of mine filling.

(2) According to XRD, FT-IR and SEM analysis, the hydration products of CPB material are Aft and C-S-H gel. The presence of FGDG promoted the formation of Aft, which further promoted the fracture of [SiO$_4$]$^4-$ and [AlO$_4$]$^3-$ along the bridge oxygen in the GBFS. The continuous formation of C-S-H gel in Ca$^{2+}$ rich slurry solution resulted in the continuous deposition of C-S-H gel, which gradually thickened and hardened the slurry and rapidly increased the macroscopic strength. The interlacing of acicular Aft and C-S-H enhanced the compactness of backfill and made the system have good hydro-hard cementation performance.

(3) The superfine pulverized GBFS has strong activity, and the SS mixed with GBFS can activate each other and replace cement as the cementing filling for underground mining under the excitation of FGDG. 100% of the solid raw materials used are industrial wastes, which is conducive to reducing the filling cost. It also opens up a new way for the resource utilization of GBFS, SS, FGDG and IOT.

Acknowledgments

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