Preparation of fly ash-granulated blast furnace slag-carbide slag binder and application in total tailings paste backfill

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Abstract. Based on activation and synergistic effect among various materials, a low-cost mine backfill cementing material, FGC binder, was prepared by using fly ash, granulated blast-furnace slag (GBFS), carbide slag and composite activator. The proper proportioning of FGC binder is obtained by response surface experiment optimization method: fly ash 62 %, GBFS 20 %, carbide slag 8 % and compound activators 10 %. Adjusting the material ratio obtains different cementing material which could satisfy requirements of different mined-out areas. With the mass ratio of cementing material and tailings 1:4 ~ 1:8, the concentration of total solid 70 %, the compressive strength values of total tailings filling body at 28 d reaches 1.64 ~ 4.14 MPa, and the backfilling cost is 20 % lower than using OPC cement.

1. Introduction
Backfilling not only can effectively prevent the surrounding rock movement and surface subsidence [1-4], but also realize sustainable development of mineral resources. However, the high filling cost restricts the application. According to the calculation, the backfilling cost is about 20% of the total cost of the mine operation, in which more than 75 % is the binder cost [5-6]. Therefore, the research and development of high-performance and low-cost backfill binder is the key to solve above problems.

The main way to reduce the cost of cementing materials is to maximize the use of industrial waste. Fly ash is a solid waste and a typical volcanic ash. Under certain conditions, when fly ash mixed with lime and other alkaline substances, hydrated calcium silicate, ettringite and zeolite substances form in the hardened paste, resulting in bonding strength [7-9]. As a kind of industrial by-product generated in iron-making process, blast-furnace slag (BFS) has experienced similar process as cement, including di-calcium silicate, tri-calcium silicate and RO phase, has the potential cementing activity. Experiments showed that there is a synergistic effect between fly ash and slag, which can improve the performance of cementing materials and reduce cost [10-11].

Alkaline materials are the most effective activating agents for fly ash and slag. Commonly used activating agents include alkali metal and alkaline earth hydroxide, carbonate, sulfate and silicate [12-13]. Calcium hydroxide and a small amount of calcium carbonate are the main components of calcium carbide residue (the waste residue of acetylene production process), which is currently abandoned, causing environmental pollution and waste of resources. If it is used for the activation of
fly ash and slag, it will be beneficial to reduce the cost of cementing materials and realize resourceful utilization.

2. Experimental

2.1. Materials.
Anhydrous sodium sulfate and anhydrous calcium chloride are bought from market. CF activator is provided by Hebei Zhongke Environmental Protection Co. lt. Modified gypsum is desulfurized gypsum calcined at 650-700 °C. OPC cement, Fly ash, BFS, carbide slag, tailings are provided by Shijiazhuang Jingxing Construction Material Corp. Ltd. Table 1 shows the chemical compositions of raw materials.

| Species   | SiO$_2$ (%) | MgO (%) | CaO (%) | Al$_2$O$_3$ (%) | Fe$_2$O$_3$ (%) | K$_2$O (%) | SO$_3$ (%) | Others (%) |
|-----------|-------------|---------|---------|-----------------|----------------|------------|-----------|-----------|
| Fly ash   | 49.82       | 0.66    | 5.96    | 33.90           | 4.40           | 1.24       | 2.05      | 1.97      |
| slag      | 39.05       | 8.47    | 30.98   | 2.53            | 13.65          |            |           |           |
| Modified  | 2.05        | 1.20    | 42.37   | 44.45           | 0.35           |            |           |           |
| gypsum    |             |         |         |                 |                |            |           |           |
| Carbide   | 3.82        | 0.14    | 92.02   | 2.72            | 0.50           |            |           |           |
| slag      |             |         |         |                 |                |            |           |           |
| Tailings  | 64.92       | 3.51    | 12.05   | 6.10            | 9.76           |            |           | 3.66      |

2.2. Methods.
The fine pulverized fly ash, GBFS, carbide slag and compound activator are mixed to form cementing material. Specimens with dimension of 40 mm×40 mm×160 mm were molded according to GB/T17671-1999. Quick test for cement paste is performed according to JC/T738-2004.

The cementing material is mixed with tailings and water to form the backfilling slurry, pouring into 70.7 mm × 70.7 mm × 70.7 mm mould, curing at (20 ± 2) °C & RH50 % for 48 h. Then the specimens were de-molded and cure at (20 ± 1) °C & RH90 % for desired age.
The mechanical strength test is performed using NYL-300A.

3. Results and discussion

3.1. Formula design of FGC binder.
On the basis of single factor experiments, CF activator (A), Sodium sulfate (B), calcium chloride (C) and modified gypsum (D) were used as control variables, the mechanical strength of the mortar (Y) as the response, response surface analysis was used for Formula design of FGC binder, the factors and levels are shown in Table 2, the results are shown in Table 3.

| Factors | Levels and coding |
|---------|-------------------|
| A/ (%)  | -1 2 3            |
| B/ (%)  | 1.5 2 2.5         |
| C/ (%)  | 0.5 1 1.5         |
| D/ (%)  | 6 9 12            |
Table 3  Response surface design and results

| Numbering | A/%  | B/%  | C/%  | D/%  | Compressive strength/MPa |
|-----------|------|------|------|------|--------------------------|
| U1        | 3.0  | 1.5  | 1.0  | 9.0  | 14.23                    |
| U2        | 2.0  | 1.5  | 1.0  | 12.0 | 14.28                    |
| U3        | 3.0  | 2.0  | 1.0  | 12.0 | 13.92                    |
| U4        | 1.0  | 2.0  | 0.5  | 9.0  | 15.73                    |
| U5        | 2.0  | 2.0  | 1.0  | 9.0  | 14.07                    |
| U6        | 3.0  | 2.5  | 1.0  | 9.0  | 13.05                    |
| U7        | 1.0  | 2.5  | 1.0  | 9.0  | 14.28                    |
| U8        | 2.0  | 2.0  | 1.5  | 6.0  | 14.00                    |
| U9        | 1.0  | 2.0  | 1.5  | 9.0  | 15.28                    |
| U10       | 2.0  | 2.0  | 0.5  | 6.0  | 14.38                    |
| U11       | 2.0  | 2.0  | 1.0  | 9.0  | 14.35                    |
| U12       | 2.0  | 2.0  | 1.0  | 9.0  | 13.87                    |
| U13       | 2.0  | 2.5  | 0.5  | 9.0  | 14.60                    |
| U14       | 2.0  | 2.0  | 1.0  | 9.0  | 14.80                    |
| U15       | 1.0  | 2.0  | 1.0  | 12.0 | 14.95                    |
| U16       | 2.0  | 2.0  | 1.0  | 9.0  | 14.80                    |
| U17       | 3.0  | 2.0  | 1.0  | 6.0  | 14.03                    |
| U18       | 2.0  | 1.5  | 0.5  | 9.0  | 14.68                    |
| U19       | 2.0  | 1.5  | 1.5  | 9.0  | 14.77                    |
| U20       | 2.0  | 2.0  | 0.5  | 12.0 | 15.48                    |
| U21       | 2.0  | 2.5  | 1.0  | 6.0  | 14.63                    |
| U22       | 3.0  | 2.0  | 1.5  | 9.0  | 13.47                    |
| U23       | 3.0  | 2.0  | 0.5  | 9.0  | 13.45                    |
| U24       | 2.0  | 2.0  | 1.5  | 12.0 | 14.68                    |
| U25       | 1.0  | 1.5  | 1.0  | 9.0  | 15.78                    |
| U26       | 2.0  | 2.5  | 1.5  | 9.0  | 15.17                    |
| U27       | 2.0  | 1.5  | 1.0  | 6.0  | 15.80                    |
| U28       | 2.0  | 2.5  | 1.0  | 12.0 | 15.30                    |
| U29       | 1.0  | 2.0  | 1.0  | 6.0  | 16.32                    |

Multiple regressions fitting of experimental data is performed using Design-Export software. The regression model is obtained.

\[ Y = 14.66 - 0.89A - 0.16B - 0.079C - 0.046D \]  \( (1) \)

The proportioning of the composite activator was obtained using the optimization function of Design-Export software: CF activator 1 %, Sodium sulfate 1.5 %, calcium chloride 0.51 %, and modified gypsum 6 %. In this case, the compressive strength is up to 15.84 MPa. After further adjustment tests, the optimized proportioning of the cementing material was obtained: composite activator 10 %, carbide slag 8 %, GBFS 57.4 %, fly ash 24.6 %.

3.2. Mechanical properties test of total tailings backfilling slurry.

FGC binder was prepared by the optimal ratio of the optimized proportioning of the cementing material, and thus the backfilling mortar by mixing it with tailings and proper amount of water. The mortar was molded in 70.7 mm × 70.7 mm × 70.7 mm, de-molding and curing till desired age, and the compressive strength values were tested. The ratio of binder to tailings is 1:4 ~ 1:8 and the concentration of slurry is 70%. The results are shown in Figure 1.
It can be seen from Figure 1 that the compressive strength of the filling body increases with the increase of the binder/tailings ratio. When the binder/tailings ratio is 1:4 ~ 1:8 and the concentration of the slurry was 70%, the 3d strength value of filling body reaches 1.06 ~ 2.39 Mpa, and the strength values of 28 d reaches 1.64 ~ 4.1 Mpa. According to the literature, the compressive strength values of P. O. 42.5 cement filling body was 0.51 Mpa and 2.20 MPa at 3 d and 28 d, respectively, when the cement sand ratio is 1:4 ~ 1:8 and the concentration of the slurry was 70%. It is obviously that the strength of filling body with FGC binder is much higher than that of Portland cement. FGC binder can meet the filling requirements of different mining areas by controlling the ratio of FGC binder and tailings.

It is estimated that the cost of FGC binder is 20 % lower compared to ordinary Portland cement. Considering the raw materials of FGC binder are mostly industrial waste residue (fly ash and calcium carbide slag) and by-products (BFS), the carbon dioxide emission is lower and the environmental benefit is remarkable.

4. Summary

(1) The synergistic effect of fly ash and BFS, carbide slag and composite accelerator is the key to the preparation of FGC binder. Mechanical grinding and chemical activation strengthens the hydration process of the system, enhancing the strength of the binder and the backfilling body. The optimal proportioning of FGC binder is obtained: fly ash 62 %, BFS 20 %, carbide slag 8 %, composite activator 10 %.

(2) Total tailings backfilling application showed that when binder/tailings ratio is 1:4 ~ 1:8, and the slurry concentration is 70 %, the 3d compressive strength of the filling body is 1.06 ~ 2.39 Mpa, and the 28 d compressive strength reaches 1.64 ~ 4.14 MPa MPa. The binder can meet the filling requirements of different mining areas by adjusting the ratio of FGC binder and tailings.

(3) FGC binder, when used for total tailings backfilling, the cost in cementing material is 20% lower than the case of ordinary Portland cement. Besides, large amount of solid wastes such as fly ash and calcium carbide slag, are used, thus remarkably reducing carbon dioxide emissions.

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