Study on strength test and hydration mechanism of phosphogypsum based cemented backfill

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Abstract. In view of low early strength of phosphogypsum based slag cementitious material, exploration test of filling body strength is developed to get the optimal ratio of cementitious materials. Firstly, the physicochemical analysis of the test material was carried out; secondly, the cementitious material ratio and strength of waste rock coarse aggregate filling body was tested by orthogonal test and range analysis. In the end, the hydration products and microstructure of cementitious materials were analyzed by XRD and SEM. The results show that, for the slurry with waste rock coarse aggregate, 1:4 cement sand ratio and 80% mass concentration, the optimal ratio of cementitious materials is determined as phosphogypsum 30~33%, quicklime 5.5~6.0%, NaOH 1.5~2.0%, mirabilite 2.5~3.0%. The average particle size of cementitious material is -16μm, and the early strength agent or synergist must be added, which could meet the requirements of the Jinchuan mine.

1. Introduction
Industrial solid waste used for mine filling can effectively reduce costs and bring significant economic and environmental benefits [1]. Cemented filling mining is gradually adopted by mines because of its safety and environmental protection characteristics [2]. However, the cemented filling mining method is not only complex in technology, but also high in mining cost, especially the cost of cementitious materials, which accounts for about 75% of the filling cost [3]. Therefore, the use of solid waste to develop new cementitious materials instead of cement is the only way to reduce the filling cost and achieve safe and efficient mining [4-5]. Phosphogypsum is a kind of industrial waste residue produced when phosphate rock is treated with sulfuric acid in phosphoric acid production, which not only pollutes the environment, but also wastes land [6-7]. Aiming at the problem of low early strength of phosphogypsum slag cementitious material [8], through carrying out the exploration test of cemented filling body strength, constantly adjusting and optimizing the proportion, the proportion scheme of cementitious material meeting the requirements of mine filling design strength is obtained, and the maximization of solid waste resource utilization is realized.

2. Physicochemical analysis of test materials
Phosphogypsum (PP), slag (SL) and waste rock (WR) are used as main materials in the test. The Phosphogypsum is obtained from Wengfu Company in Gansu Province, with density of 2.29 g/cm³ and specific surface area of 260 m²/kg. The slag is obtained from Xijin Company by using blast furnace slag.
of Jiuquan Iron and Steel Co., Ltd., and its fineness (45 μm sieve residue) is 18.1%. Waste rock is used as coarse aggregate in the test, which is taken from the broken waste rock of Longshou Mine in Jinchuan, the fitting curve of particle size distribution is shown in Figure 1, the characteristic particle size is calculated by interpolation method, and the results are shown in Table 1. The uneven coefficient and curvature coefficient show that the grading of waste rock is good, but the uneven coefficient is too large. The chemical composition of the test material is shown in Table 2. It can be seen that phosphogypsum belongs to acidic activator and contains P₂O₅ impurities, which is not conducive to the hydration reaction of cementitious materials. Alkaline activator should be used for neutralization treatment to effectively stimulate the potential activity of slag. The alkali activators used in the test include quicklime (QL) and NaOH, and the additives include industrial mirabilite (IM), grinding aid (GA), early strength agent (ES), accelerator (AL) and synergist (SN).

Table 1  Particle size characteristic parameters of waste rock.

| d₁₀(μm) | d₃₀(μm) | d₅₀(μm) | d₆₀(μm) | d₉₀(μm) | Cₛ | Cᵤ |
|---------|---------|---------|---------|---------|----|----|
| 0.14    | 0.87    | 2.96    | 4.28    | 8.70    | 1.26| 30.57 |

Figure 1  Fitting curve of coarse aggregate size distribution of waste rock.

Table 2  Mineral components of test materials (%).

| Material | SO₃ | CaO | MgO | P₂O₅ | F⁻ | Fe₂O₃ | Al₂O₃ | SiO₂ | MnO | Fe |
|----------|-----|-----|-----|------|----|-------|-------|------|-----|----|
| PP       | 49.07 | 28.60 | 2.44 | 1.47 | 0.87 | 0.48 | 0.36 | —    | —   | —  |
| SL       | —   | 37.27 | 8.92 | —    | 0.46 | 11.68 | 39.18 | 0.36 | —   | —  |
| WR       | —   | 3.86 | 28.15 | —    | 0    | 3.39 | 36.31 | —    | 9.51 | —  |

3. Exploration test and analysis of early strength of backfill

3.1. Test plan

Based on the previous development experience and the optimized formula [8], the orthogonal test on the strength of cemented filling body of waste rock coarse aggregate with different composite activator formula of phosphogypsum cementitious material is carried out. The design of phosphogypsum level is 30%, 33% and 36%, quicklime level is 5.5%, 6.0% and 6.5%, NaOH level is 1.5%, 2.0% and 2.5%, mirabilite level is 2.0%, 2.5% and 3.0%. According to the filling system and filling process parameters of Jinchuan Mine, the cement sand ratio used in the test is 1:4. The 7.07 × 7.07 × 7.07 cm standard test block was prepared according to the standard experimental procedures, and the strength was tested after curing for 3 days and 7 days.
3.2. Strength test of cemented backfill with different slurry concentration

The orthogonal test on the strength of cemented filling body of phosphogypsum cementitious material waste rock coarse aggregate is carried out for three slurry concentrations of 78%, 80% and 82%. Through range analysis and comprehensive comparison, 3d and 7d strength analysis results are obtained, as shown in Table 3. Figure 2 shows the relationship curve between the maximum and average strength and the concentration of filling slurry in the orthogonal test.

| Age | Concentration (%) | Compressive strength (MPa) | Optimal ratio of activator (%) |
|-----|-------------------|-----------------------------|--------------------------------|
|     |                   | Maximum | Average | QL | PP | NaOH | IM |
| 3d  | 78                | 0.44    | 0.29    | 5.5 | 30 | 1.5  | 2.5 |
|     | 80                | 0.70    | 0.41    | 5.5 | 30 | 2.0  | 3.0 |
|     | 82                | 0.82    | 0.59    | 5.5 | 33 | 1.5  | 3.0 |
| 7d  | 78                | 2.52    | 2.01    | 6.0 | 30 | 2.0  | 3.0 |
|     | 80                | 3.80    | 3.24    | 5.5 | 33 | 2.0  | 3.0 |
|     | 82                | 5.28    | 4.03    | 5.5 | 30 | 1.5  | 3.0 |

Figure 2 Relationship between strength of backfill and slurry concentration.

It can be seen that: the 3d and 7d strength of filling body increase with the increase of slurry concentration, but the growth rate is different. The reaction speed of phosphogypsum cementitious material is slow in 0~3d, but the reaction speed is accelerated in 3~7d. The 3d strength of filling body is low, which does not meet the mine design strength (1.5 MPa), but the 7d strength can meet the design requirement (2.5 MPa). So improving the 3d strength of filling body is the basis of realizing the industrial application of phosphogypsum cementitious material.

The strength of cemented backfill depends not only on the characteristics of filling aggregate, the ratio of cement to sand and the concentration of slurry, but also on the quality and activity of slag itself, the fineness and gradation of slag powder and the formulation of activator. Under the condition that the properties and quality of slag can not be changed, the activity of slag can only be improved by two ways: on the one hand, improving the fineness of slag powder and optimizing the particle size distribution of powder. On the other hand, high efficient activators and composite admixtures compatible with slag characteristics are found to accelerate the hydration reaction rate of cementitious materials, so as to improve the strength of cemented backfill.
3.3. Strength test of cemented backfill with different cementitious materials fineness

The activity of low activity slag can be increased by increasing the fineness of slag powder. Aiming at undisturbed (UD) slag powder, medium fine (MF) slag powder (grinding for 1h) and ultra-fine (UF) slag powder (grinding for 1.5h), the strength test of cemented filling body of three fineness phosphogypsum filling cementitious materials with 80% slurry mass concentration was carried out, and range analysis and comprehensive comparison were carried out. The 3d and 7d strength analysis results of cemented filling body obtained are shown in Table 4. The results show that the 3d and 7d strength of cemented backfill increases with the decrease of the average particle size of cementitious powder, but the 3d strength still can not meet the design strength requirements.

| Age | Fineness | Average particle size (μm) | +45 μm content (%) | Compressive strength (MPa) | Optimal ratio of activator (%) |
|-----|----------|---------------------------|--------------------|---------------------------|-------------------------------|
|     |          |                           |                    | Maximum                  | Average                       |
|     |          |                           |                    | QL | PP | NaOH | IM |
| 3d  | UD       | 24.31                     | 18.1               | 0.70 | 0.41 | 5.5 | 30 | 2.0 | 3.0 |
|     | MF       | 15.88                     | 8.0                | 1.09 | 0.81 | 6.5 | 36 | 2.5 | 2.5 |
|     | UF       | 12.26                     | 3.9                | 1.26 | 1.05 | 5.5 | 36 | 2.5 | 3.0 |
| 7d  | UD       | 24.31                     | 18.1               | 3.80 | 3.24 | 5.5 | 33 | 2.0 | 3.0 |
|     | MF       | 15.88                     | 8.0                | 5.84 | 4.67 | 5.5 | 30 | 2.0 | 3.0 |
|     | UF       | 12.26                     | 3.9                | 6.65 | 5.99 | 5.5 | 33 | 1.5 | 2.5 |

3.4. Strength test of cemented backfill with different cementitious materials admixture

Choosing the appropriate admixture is another way to improve the early strength of cemented backfill. Considering the production cost and output of cementitious material, medium fineness (grinding 1h) is selected. The material ratio is quicklime 6%, phosphogypsum 34% (admixture is included in the proportion of phosphogypsum), slag powder 60%, and the slurry concentration is 80%. The orthogonal test of cemented filling body of phosphogypsum cementitious material with grinding aid, early strength agent, accelerator and synergist is carried out (early strength agent was designed according to three-level orthogonal design with three factors of mirabilite, NaOH and NaCl), so as to reveal the influence law of different admixtures on the characteristics of cementitious material, and select appropriate admixtures to improve the early strength of cemented filling body. Through orthogonal test and range analysis, the 3d and 7d strength analysis results of cemented backfill are obtained, which are shown in Table 5.

| Age | Admixture | Compressive strength (MPa) | Optimal ratio of admixture (%) |
|-----|-----------|---------------------------|-------------------------------|
|     |           | Maximum | Average | GA | AL | SN | IM | NaOH | NaCl |
| 3d  | GA        | 1.21    | 0.73    | 0.05 | 0 | 0 | 2 | 1 | 0 |
|     | ES        | 1.82    | 1.58    | 0.05 | 0 | 0 | 2 | 1.5 | 1.5 |
|     | AL        | 1.31    | 0.97    | 0.05 | 0.6 | 0 | 3 | 1 | 0 |
|     | SN        | 1.78    | 1.39    | 0.05 | 0 | 0.4 | 3 | 1.5 | 0 |
| 7d  | GA        | 3.57    | 2.98    | 0.05 | 0 | 0 | 3 | 0 | 0 |
|     | ES        | 5.59    | 4.10    | 0.05 | 0 | 0 | 1 | 1 | 1.5 |
|     | AL        | 3.39    | 2.32    | 0.05 | 0.4 | 0 | 3 | 0.5 | 0 |
|     | SN        | 3.28    | 2.82    | 0.05 | 0 | 0.4 | 3 | 0.5 | 0 |

By comparing the results, it can be seen that the early strength agent has the best effect on improving the 3d strength of cemented backfill, and the grinding aid has the worst effect. The 3d strength of cemented backfill with early strength agent and synergist is greater than 1.5 MPa, which meets the strength requirements. Only adding grinding aid and accelerator, the 3d strength is less than 1.5 MPa. Although the accelerator can accelerate the early setting of filling slurry, it is not ideal to improve the
early strength of cemented filling body. The 7d strength of cemented backfill with accelerator is less than 2.5 MPa, but with the other three admixtures is greater than 2.5 MPa, which meets the design requirements. The early strength agent is the best admixture to improve the early strength, and adding grinding aid synchronously can enhance the early strength of cemented backfill.

4. Hydration mechanism analysis of phosphogypsum cementitious material

In order to explore the hydration mechanism of phosphogypsum cementitious materials, XRD and SEM are used to analyze the hydration products and microstructure. The slag in cementitious materials has potential activity. Hydration reaction occurs under the excitation of alkali and salt. The main products are calcium silicate hydrate (C-S-H) and ettringite (AFt). The early strength agent creates suitable environment conditions for the early hydration reaction and makes the development rapid. A large amount of calcium silicate gel is produced and deposited. Ettringite is produced in large quantities. It absorbs the water in the paste, changes the composition of the filling body, makes the structure of the filling body compact, and improves the strength of the filling body.

The pure slurry was used in this test to prevent the unnecessary interference of aggregate to the XRD spectrum analysis. Figure 3 and Figure 4 are the XRD and SEM images of hydration products, respectively. XRD results show that phosphogypsum participates in hydration reaction. The content of phosphogypsum gradually decreases during hydration, while the content of calcium silicate hydrate and ettringite increases gradually. The formation of calcium silicate hydrate and ettringite can be observed by SEM test. With the increase of age, the production of both calcium silicate hydrate and ettringite gradually increased, and the structure gradually became dense. Calcium silicate hydrate play a filling role and ettringite play a supporting role in the filling body.

![XRD patterns of the hydration products of cementitious material.](image1)

![SEM images of the hydration products of cementitious material.](image2)

5. Conclusions

- The hydration reaction of phosphogypsum cementitious material is slow in 0–3d, and the reaction speed is accelerated with the increase of slurry concentration in 7d. Using undisturbed slag powder to develop cementitious material, the 3d strength of cemented filling body with waste rock is
less than 1.5 MPa, which does not meet the requirements. The 7d strength is greater than 2.5 MPa, which meets the requirements of Jinchuan mine.

- The early strength of cemented backfill increases with the increase of fineness of slag, but the 3d strength still does not meet the requirement. Compare with the grinding aid, early strength agent, accelerator and synergist, the early strength agent and synergist have the best enhancement effect, and the 3d and 7d strength can meet the requirements of Jinchuan mine.

- The optimum ratio of phosphogypsum cementitious material is: quicklime 5.5~6.0%, phosphogypsum 30~33%, NaOH 1.5~2.0%, mirabilite 2.5~3%, and the average particle size of cementitious material is -16 μm. For the slurry with waste rock coarse aggregate, 1:4 cement sand ratio and 80% mass concentration, adding early strength agent or synergist, the strength of cemented backfill can meet the design strength of Jinchuan Mine cemented backfill. This phosphogypsum cementitious material based on slag powder can be widely used.

- The main products of hydration reaction are calcium silicate hydrate and ettringite. Early strength agents have created suitable environmental conditions for early hydration reaction and made it develop rapidly. A large number of calcium silicate hydrate and ettringite are generated, which absorb the moisture in the slurry, change the composition of the filling body, make the structure compact, and increase the strength.

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References
[1] Wang, X.L., Yao, W.X., Wang, H., et al. (2011) Research status and development trend of full tailings filling of mine waste rock. China Mining Magazine, 20: 76-79.
[2] Li, X.B., Zhou J., Wang, S.F., et al. (2017) Review and practice of deep mining for solid mineral resources. The Chinese Journal of Nonferrous Metals, 27: 1236-1262.
[3] Wang, X.M., Zhao, J.W., Zhang, Q.L., et al. (2012) Optimal mining model of transition from open-pit to underground mining. Journal of Central South University, 43: 1434-1439.
[4] Wen, Z.J., Gao, Q., Wang, Y.D., et al. (2020) Development of composite cementitious material and optimization of slurry proportion based on fuzzy comprehensive evaluation. The Chinese Journal of Nonferrous Metals, 30: 698-707.
[5] Wei, H.B., Gao, Q. (2020) Experimental Study on Working Characteristics and Rheological Parameters of Filling Slurry of Waste Rock and Rod-mill Sand. Metal Mine, 534: 55-60.
[6] Li, G.M., Li, X., Jia, L., et al. (2012) Treatment and disposal of phosphogypsum at home and abroad. Inorganic Chemicals Industry, 44: 11-13.
[7] Mei, Y., Duan, D.C., Yang Y.B., et al. (2011) Comprehensive utilization and competitiveness analysis of phosphogypsum. Inorganic Chemicals Industry, 43: 1-5.
[8] Xiao, B.L., Yang, Z.Q., Gao, Q. (2015) Development of new filling cementitious material of phosphogypsum in Jinchuan Mine. Mining Research and Development, 35: 21-24.