Preparation of Self-leveling Mortar Based on Anhydrite-II Phosphogypsum

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Abstract: The construction material from anhydrite-II phosphogypsum is dense in structure and has good water resistance. But its disadvantages are low hydration activity and long setting time. In this work, anhydrite-II phosphogypsum is modified by adding a composite activator, which is made of sulfuric acid modified steel slag, β-hemihydrate gypsum and calcium aluminate cement. With this, the hydration rate of anhydrite-II phosphogypsum is clearly increased and setting time shortened. The performance of self leveling mortar prepared is as per JC/T 1023-2021, with softening coefficient of 0.8.

1. Introduction
Phosphogypsum is a by-product of the phosphate fertilizer industry. About 4~5 tons of phosphogypsum are produced for 1 ton of phosphate fertilizer. According to statistics in 2019, phosphogypsum production is 75 million tons in China, the comprehensive utilization rate is only 40%[1]. At the same time, the accumulated stock exceeds 500 million tons[2]. The main component of phosphogypsum is calcium sulfate dihydrate, which is difficult to use because of free phosphoric acid, fluoride and other impurities. It not only occupies land and wastes resources, but also pollutes soil, groundwater and atmosphere, increasing the environmental burden[3].

At present, the production of self leveling mortar from phosphogypsum is an important approach which can realize its high value utilization[4-6]. The self leveling mortar has high fluidity, good performance, short construction period and low cost. Besides, it has the advantages of high ground flatness and stabilized size[7-9]. However, the current self leveling mortar is largely made from hemihydrate phosphogypsum, which has the disadvantages of poor water resistance and high content of harmful components[10-12]. The material from anhydrite-II phosphogypsum has good water resistance, but with low hydration activity and long setting time. Feng Yang[13] used anhydrite-II that was obtained by calcining phosphogypsum at high temperature to prepare self leveling mortar, with high dosage of α-hemihydrate. The setting time can be shortened obviously. However, the cost is high.

In this paper a low-cost modification scheme for anhydrite-II phosphogypsum is proposed with the sulfuric acid modified steel slag, β hemihydrate gypsum and calcium aluminate cement; then the setting performance, mechanical strength and water resistance of cementing materials are investigated; and finally, low-cost self leveling mortar is prepared.
2. Materials and Methods

2.1. Raw materials
Anhydrite-II was prepared by calcining phosphogypsum at 750℃ for 2h. The chemical composition is shown in Table 1. Calcium aluminate cement, polycarboxylate superplasticizer (PCE) and hydroxypropyl methylcellulose (HPMC) are bought from market. Steel slag and granulated blast furnace slag (GBFS) were from Shijiazhuang Orsen Iron and Steel Co. Fly ash were from Pingshan Power Plant, Hebei, China.

| Composition | CaO | MgO | SiO₂ | Fe₂O₃ | Al₂O₃ | SO₃ | Others |
|-------------|-----|-----|------|-------|-------|-----|--------|
| Content     | 40.06 | 5.10 | 9.07 | 5.09  | 0.54  | 40.01| 0.13   |

2.2. Modification of steel slag
The steel slag is dried at 110–120 ℃ and ground to the specific surface of 420–460 m²/kg, add dilute sulfuric acid, dried, to obtain the modified steel slag.

2.3 Test Methods

2.3.1 Performance test of cementitious materials
The water requirement of normal consistency of gypsum is determined according to GB/T 17669.4-2008. Gypsum paste is prepared according to the water requirement, and the setting time, flexural and compressive strength of cementitious materials are tested.

2.3.2. Performance test of self leveling mortar
The initial fluidity water requirement of self leveling mortar is measured according to JC/T 1023-2021, then the setting time, mechanical strength and fluidity are measured. The softening coefficient is calculated according to JC/T 698-2010.

3. Results & Discussion

3.1. Preparation of cementitious materials

3.1.1. Initial proportion of cementitious material
With calcium aluminate cement, β hemihydrate gypsum and modified steel slag being the factors, the orthogonal experiment is designed and the initial cementitious material is obtained: calcium aluminate cement 0.5%, β hemihydrate gypsum 2%, modified steel slag 4% and anhydrite-II 93.5%. At this time, the initial and the final setting time are 3h 5min and 5h 59 min, respectively.

3.1.2. Effect of GBFS on water resistance
The influence of GBFS on softening coefficient is investigated. The results are shown in Figure 1.

![Figure 1. Effect of GBFS on water resistance](image)
With the increase of GBFS content, it can be seen that the softening coefficient of gypsum increases first and then decreases. At the same time, the compressive strength is significantly improved. At the dosage of 25%, the softening coefficient increases to 0.8.

3.2. Preparation of self-leveling mortar
The fluidity of self leveling mortar can be improved by adding superplasticizer, but bleeding will occur when the content is high. The effects of PCE and HPMC on the fluidity are investigated. The results are shown in Figure 2.

![Figure 2. Effect of additives on fluidity](image)

It can be seen that the appropriate HPMC content can reduce the fluidity loss of mortar. When the gypsum based self leveling mortar contains 0.3% PCE and 0.1% HPMC, the fluidity after 30 minutes meets JC/T 1023-2021, with little fluidity loss.

The material proportion of self-leveling mortar is shown in Table 2. The main performance is shown in Table 3.

| Material                               | Dosage, wt% |
|----------------------------------------|-------------|
| Anhydrite-Ⅱ                           | 43.33       |
| Modified steel slag                   | 3.98        |
| β-Hemihydrate gypsum                  | 1.99        |
| Calcium aluminate cement              | 0.50        |
| Steel slag sand                       | 19.92       |
| GBFS                                   | 24.90       |
| Fly ash                               | 4.98        |
| Superplasticizer                      | 0.30        |
| Hydroxypropyl methylcellulose         | 0.10        |

| Performance                            | JC/T1023-2007 | Test  |
|----------------------------------------|---------------|-------|
| Setting time                           |               |       |
| Initial setting /h:min                 | ≥1            | 02:17 |
| Final setting /h:min                   | ≤6            | 04:49 |
| Mechanical strength                    |               |       |
| Flexural/MPa                           | ≥7.5          | 8.7   |
| Compressive/MPa                        | ≥20.0         | 24.1  |
| Fluidity after 30 minutes /mm          | ≥140          | 143   |

4. Conclusions
(1) In order to reduce the setting time of anhydrite-Ⅱ phosphogypsum based cementitious materials...
the composite modifier is prepared, which is composed of sulfuric acid modified steel slag, β hemihydrate gypsum and calcium aluminate cement. With this, the hydration rate of anhydrite-II phosphogypsum is clearly increased and setting time shortened.

(2) Granulated blast furnace slag has remarkable effect on water resistance of anhydrite-II phosphogypsum based cementitious materials. At the dosage of 25%, the softening coefficient of the cementious material reaches 0.8.

(3) Anhydrite-II phosphogypsum based self leveling mortar is prepared with the proportion: GBFS 24.9%, β hemihydrate gypsum 1.99%, modified steel slag 3.98%, calcium aluminate cement 0.5%, fly ash 4.98%, anhydrite-II 43.33%, steel slag sand 19.92%, hydroxypropyl methylcellulose 0.1% and superplasticizer 0.3%. The performance is as per JC/T 1023-2021, with softening coefficient reaching 0.8. The initial setting time is 2h 17min, final setting time is 4h 49min, and compressive strength is 22MPa.

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