Effect of limestone powder on mechanical properties and microstructure of phosphogypsum

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Abstract. In order to enhance the large-scale and high-quality application of limestone powder (LP) and phosphogypsum in the construction industry. Therefore, this paper mainly studies the effect of LP on the physical and mechanical properties of phosphogypsum-based composites, and clear the mechanism of action from the micro level. Based on the results, the conclusions were as follows: LP has the effect of reducing the standard consistency water requirement and shortening the setting time of fresh phosphogypsum-based composites slurry; LP can increase the bulk density and reduce 24-hour water absorption of hardened phosphogypsum-based composites matrix; In addition, the strength of the matrix increases first and then decreases with the increase in the amount of LP and the recommended amount of LP is 5%-10%. Microscopic tests have shown that when the amount of LP is less than 10%, it can effectively reduce the porosity, refine the pore size, and play the role of a dense hardened matrix. In addition, the appropriate amount of LP particles can be adsorbed on the surface of dihydrate crystals, increasing the bonding force between the crystals, which is conducive to increasing the strength of the composite matrix.

1. Introduction

The global resource crisis and the shortage of natural raw materials are becoming increasingly serious. Resources such as high-quality fly ash and slag are increasingly scarce. Moreover, the general trend of low-carbon and green development has brought great challenges to the construction industry [1-2]. It is imperative to find new mineral admixtures. Limestone powder (LP) has become a research and application hotspot in recent years due to its rich natural resources, wide distribution, convenient local material acquisition, and high quality and low price [3-6]. At present, LP has been used in self-compacting concrete, high fluidity concrete and high-performance grouting at domestic and foreign, and has achieved significant economic benefits [8]. It is generally believed that after mixing LP, its particle shape effect, particle filling effect and particle surface state effect will affect the rheology, strength, impermeability and durability of cement slurry, and great progress has been made[9-10]. The research on the effect of LP on the hydration characteristics of cement system shows that: LP can react with C₃A to form calcium carbon aluminate hydrate (mainly monocarbon calcium aluminate hydrate) [11-12]. LP can be used as a heterogeneous nucleation site to reduce the nucleation barrier, accelerate the adsorption of Ca²⁺ in the system, and accelerate the hydration reaction of C₃S [13-14]. Yang et al. studied the effects of LP modified with nano-CaCO₃ on the hydration products and pore structure of cement system by means of differential thermal, thermogravimetric, and backscattered electron imaging. The results show that the addition of modified LP can reduce the system porosity, optimize the pore structure, and improve the compressive and flexural strength of the sample [15].
Building gypsum is one of the three major traditional cementitious materials. Because of its advantages such as fast setting and hardening, light weight, wide source of raw materials, low production energy consumption, low carbon emissions, and heat insulation, it has become an internationally respected green building material, especially suitable for indoor non-load-bearing structures[16-19]. However, compared with cement, because the standard consistency of building gypsum requires much more water than theoretically required for complete hydration in the later period, the hardened matrix is loose and porous, resulting in defects such as low strength, large water absorption, and poor water resistance, which seriously restrict its application rate and application level[20-23]. Therefore, research on improving the strength and water resistance of building gypsum has become a hot spot.

Related research has shown that LP has superior particle shape effects, particle filling effects, and particle surface state effects, which can effectively improve the rheological properties, compactness, and impermeability of cement-based cementitious materials [7-15]. However, the influence of LP on the physical and mechanical properties of gypsum-based cementitious materials and its mechanism of action are vague. Therefore, it is necessary to systematically study the influence of LP on the fluidity, setting time, strength and microstructure of hardened matrix of gypsum slurry. This can provide theoretical guidance and technical support for high value-added applications of LP and industrial by-product gypsum.

2. Experimental study

2.1. Raw materials
Phosphogypsum powder selected from Sichuan Landing New Materials Co., Ltd. which was industrial by-product phosphorus gypsum. Particle size was 80% sieve with 0.06% remaining. LP was selected from Sichuan Esheng Cement Group Co., Ltd. and has a specific surface area of 387.4 m²/g. The three-phase composition of the phosphogypsum powder is shown in Table 1, and the main chemical components of LP are shown in Table 2. In addition, the microscopic morphology of phosphogypsum powder and LP is shown in Figure 1. From Figure 1, it can be seen that the crystal form of phosphogypsum powder is dense cuboid plate shape, the particle sphericity is poor; The sphericity of LP particles is good, and the surface is dense and smooth, and the edges and corners are obvious. It is well known that good sphericity of the particles of the gelling material is conducive to reducing the water requirement of the standard consistency and improving the strength of the matrix.

| Sample  | Anhydrous phase/% | Semi-aqueous phase/% | Dihydrate phase/% | Adhering water/% |
|---------|-------------------|----------------------|------------------|-----------------|
| gypsum  | 0                 | 91.25                | 1.13             | 1.71            |

| Sample | CO₂ | CaO | SiO₂ | Fe₂O₃ | Cr₂O₃ | Al₂O₃ | SrO₂ | K₂O | LOSS |
|--------|-----|-----|------|-------|-------|-------|------|-----|------|
| LP     | 42.16 | 53.66 | 0.33 | 0.26 | 0.17 | 0.22 | 0.064 | 0.04 | 3.1  |

Figure 1. SEM images of phosphogypsum powder and LP: (a) Phosphogypsum powder, (b) LP.
2.2 Test procedures
In the test, the LP content was 0%, 5%, 10%, 15%, and 20% of the mass of the phosphogypsum powder, and then the two mineral materials were mixed uniformly to prepare for related performance tests. The physical and mechanical properties of standard consistency water consumption, setting time and strength of phosphogypsum are tested in accordance with GB/T 9776-2008 Standard for Phosphogypsum. Use a cylinder with an inner diameter of 50mm and a height of 100mm to measure the consistency of the slurry. When the expanded diameter is 180 ± 5mm, it is the standard thick water demand; The time elapsed from the time when the semi-aqueous gypsum was in contact with water, the time elapsed until the steel needle first hit the glass bottom plate was recorded as the initial setting, and the time elapsed until the first time the steel needle was inserted into the slurry to a depth of no more than 1 mm was the end Setting time. The 40mm × 40mm × 160mm prism samples were hydrated and hardened in an indoor environment for 3 days, then dried in a 40 ± 4 °C oven to constant weight, and finally the strength value was measured using a DYE-10A testing machine; TEDCAN VEGA2 variable vacuum scanning electron microscope was used. The samples were dried in a vacuum oven at 40°C to a constant weight, and then subjected to a scanning electron microscope test. The mercury intrusion method MIP (Mercury Intrusion Porosity) was used to determine the pore structure using an AUTOPORE IV9500 V1.09 mercury intrusion meter manufactured by Micromeritics and the test pore size range was 3nm~350μm.

3. Results and discussion

3.1. Standard consistency water requirement
The standard consistency water consumption of gypsum-based cementitious materials is an important indicator of its working performance, and it also has an important influence on the physical and mechanical properties of the later hardened matrix. The effect of LP on the water requirement of standard consistency for phosphogypsum is shown in Figure 2.

![Figure 2. Effect of LP on water requirement of standard consistency for phosphogypsum.](image)

It can be known from Figure 2 that the water requirement of standard consistency of phosphogypsum decreases first and then increases with the increase of LP content. Specifically, when the amount of LP is increased from 0 to 10%, the water consumption of gypsum standard is gradually reduced from 0.62 to 0.58, a decrease of 6.5%. However, the amount of LP added continued to increase, and the water consumption of phosphogypsum was increasing, especially as high as 0.65 at 20% dosage. The main reason is that: a small amount of LP can effectively fill the gaps in the gypsum slurry, improve the compactness, and reduce the water demand; while continuing to increase the amount of addition, the increased specific surface area of the powder plays a major role, thereby increasing water demand.

3.2. Setting time
Figure 3 shows the effect of LP on the setting time of phosphogypsum. We can find that LP has the effect of shortening the setting time of phosphogypsum. Specifically, the initial setting of the blank phosphogypsum is 12 minutes, and the final setting is 18 minutes. However, the initial setting time of phosphogypsum with 20% LP was greatly reduced to 6 minutes, and the final setting time was shortened to 13 minutes.

The main reasons can be summarized as follows: on the one hand, the dilution effect of LP reduces the total amount of gypsum in the mixture, thereby accelerating the hydration process; on the other hand, the LP has a surface effect of heterogeneous nucleation, that is, part of the gypsum in the liquid phase crystal nucleus is formed on the surface of stone powder, which reduces the nucleation barrier, thereby increasing the nucleation probability and speeding up the hydration process.

![Figure 3. Effect of LP on setting time of phosphogypsum.](image)

### 3.3. Setting time

The effects of limestone powder on the bulk density and water absorption of the phosphogypsum-based cementitious materials were measured, and the results are shown in Figure 4.

![Figure 4. Effect of LP on water absorption and absolute dry bulk density of phosphogypsum.](image)

It can be found from Figure 4 that the limestone powder has a certain effect of increasing the bulk density of the phosphogypsum-based hardened matrix and reducing the 24-hour water absorption. In particular, when the amount of limestone powder was 20%, the bulk density of the phosphogypsum-
based composite material increased significantly from 1256 kg/m$^3$ of the blank sample to 1326 kg/m$^3$; the 24-hour water absorption rate decreased significantly from 31.5% of the blank sample to 25.7%. The results show that the limestone powder particles can play the role of micro-aggregate filling in the gypsum matrix, thereby compacting the hardened body, reducing the porosity, and weakening the pore connectivity, which is consistent with the increase in density and the decrease in water absorption in the macroscopic view. The results further show that an appropriate amount of limestone powder is beneficial to improve the strength and water resistance of gypsum.

The dry strength of phosphogypsum-based composites was measured at different dosages of limestone powder and the results are shown in Figure 5. We can see from Figure 5 that as the amount of limestone powder gradually increases, the dry strength of the gypsum-based composite material increases first and then decreases and the critical dosage range is 5%-15%. Specifically, when the limestone powder content is 10%, the dry compressive strength of the gypsum-based composite material is increased from 11.7 MPa of the blank sample to a maximum value of 12.9 MPa, an increase of up to 10.3%; the dry flexural strength is increased from 5.8 MPa in the blank sample to a maximum of 6.5 MPa, an increase of 12.1%.

The main reasons are: when the limestone powder is less than the critical content, the effective filling effect of the fine aggregate in the gypsum basic is prominent, and the dense hardened body structure is conducive to increasing the strength; when the limestone powder is greater than the critical content, a large amount of inert powders can weaken the bonding force between gypsum crystals and have a significant negative impact on the strength of the hardened body. Therefore, the strength of gypsum-based composites depends on the combined result of the positive and negative effects caused by the two aspects of limestone powder. According to the test results, the recommended amount of limestone powder in the gypsum matrix is 5%-10%.

![Figure 5. Effect of LP on dry strength of phosphogypsum.](image)

### 3.4. Microstructure of hardened matrix

This section mainly uses the micro-morphology and pore distribution characteristics of the hardened matrix to determine the action mechanism of LP on the physical and mechanical properties of phosphogypsum.

The pore structure distribution results of hardened matrix of phosphogypsum mixed LP are shown in Figure 6. It is interesting to find that when the amount of LP is gradually increased to 10%, the hardened matrix shows a decrease in porosity and refinement of pore size; however, when the amount of LP is further increased to 15%, the pore structure of the hardened matrix does not change significantly. The microscopic pore structure results can reasonably explain the inherent reasons for the effect of LP on the physical and mechanical properties of phosphogypsum. When the amount of LP is less than 10%, it can effectively reduce the porosity, refine the pore size, and play a role of dense hardened matrix. Therefore, when the amount of LP is within 10%, the strength of the composite matrix gradually
increases. However, when the amount of LP is increased to 15%, the hardened matrix pore structure has not continued to be improved, which is almost equivalent to that of the hardened matrix with a content of 10%. At this stage, the negative effects of larger amounts of inert filler LP play a major role, so the macroscopic strength of the composite matrix begins to gradually decrease (Figure 5).

![Graph](image)

**Figure 6.** Pore structure distribution of hardened matrix of phosphogypsum mixed LP.

![Images](image)

**Figure 7.** Effect of LP on microstructure of phosphogypsum hardened matrix: (a) blank sample, (b) gypsum+10% LP, and (c) gypsum+20% LP.

The influence of the LP on the microstructure of the hardened matrix of the gypsum-based composite was measured and the results are shown in Figure 7. The overlap state between the dihydrate gypsum crystals has an important effect on the strength of the hardened body. Tight and effective overlap can increase the bonding force between the crystals and compact the hardened body structure, which is conducive to the increase of the matrix strength. We can find from Figure 6a that there are some defects in the overlap between dihydrate crystals in the blank gypsum and there is a certain gap between the crystals, which has a certain negative impact on the strength of the matrix. However, what is surprising is that when 10% LP is added, a layer of limestone particles is adsorbed on the surface of the dihydrate crystals in the gypsum-based composite, which increases the contact area between the crystals and increases the bonding force between the crystals. In addition, it also plays a role of compacting the hardened matrix structure, reducing the porosity and refining the pore size. Therefore, the matrix shows an increase in bulk density and strength at the macro level, a decrease in water absorption for 24 hours. Micro and macro test results remain highly consistent.

In addition, we can see from Figure 6c that when the amount of LP is increased to 20%, the adsorption of inert LP particles by the dihydrate crystals increases, causing the spacing between the crystals to increase and weakening the bonding force between the crystals, which has a negative impact on macro strength. Therefore, phosphogypsum-based composites mixed with 5%-10% amount of LP will have superior physical and mechanical properties.
4. Conclusions
This paper mainly studies the effect of LP on the physical and mechanical properties of phosphogypsum-based composites. Based on the results, the conclusions were as follows:

1. LP has the effect of reducing the standard consistency water requirement and shortening the setting time of fresh phosphogypsum-based composites slurry.

2. LP can increase the bulk density and reduce 24-hour water absorption of hardened phosphogypsum-based composites. In addition, the strength of the matrix increases first and then decreases with the increase in the amount of LP and the recommended amount of LP is 5%-10%.

3. Microscopic tests have shown that when the amount of LP is less than 10%, it can effectively reduce the porosity, refine the pore size, and play the role of a dense hardened matrix. In addition, the appropriate amount of LP particles can be adsorbed on the surface of dihydrate crystals, increasing the bonding force between the crystals, compacting the hardened matrix structure, and increasing the strength.

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