Study on properties and pore structure characteristics of cement-based materials with limestone powder

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Abstract: In order to study the effect of limestone powder as an auxiliary cementing material replacing part of cement on the properties and pore structure of cement mortar, the working performance, mechanical properties and pore structure characteristics of cement mortar with 0%, 10%, 20% and 40% substitutions of limestone powder were tested. The experimental results show that with the increase of the amount of limestone powder, the fluidity of mortar increases continuously and the water retention also becomes better. The addition of limestone powder improves the workability of mortar, but with the increase of limestone powder, the compressive strength of mortar decreases continuously. The results of low field NMR show that the porosity of cement mortar increases firstly and then decreases with the increase of limestone powder content. Compared with the reference mortar, its porosity is improved to some extent, however the pore throat distribution indicates that the increase of porosity is caused by the increase of small pores between 0.01μm and 0.16μm. The harmful macropores between 0.16μm and 0.63μm in mortar are reduced, which indicate that the addition of limestone powder can effectively improve the pore diameter distribution of mortar.

1. Introduction
Cement concrete is one of the largest civil engineering materials, and cement is the main material of concrete. Its production consumes large amounts of natural resources and emits carbon dioxide[1], in order to reduce resource consumption and CO₂ emission, the auxiliary cementitious materials, such as fly ash and granulated blast furnace slag powder, are commonly used to partially replace cement[2]. Along with the rapid construction of infrastructure, the growing demand of mortar and concrete, so the demand for auxiliary cementitious materials also will increase, but uneven distribution of resources and fly ash in our country, especially high quality fly ash supply of sichuan and other southwes t provinces is insufficient. Using III level or false fly ash has happened repeatedly[3]. On the other hand, because about 15% of limestone powder is inevitably produced in the production of limestone mechanized sand[4], secondary pollution will result if it is not utilized. Limestone powder, as a
by-product of mechanized sand, can be used as an auxiliary cementitious material for mortar and concrete, which can not only reduce carbon dioxide emissions and environmental pollution, but also save cement[1,5]. In addition, because the main component of limestone powder is calcium carbonate, it can have hydration reaction with C₃A in cement to form hydrated calcium carboaluminate, thus improving the strength of mortar or concrete.

Scholars at home and abroad on the application of the limestone powder in cement mortar and concrete research, the current way of limestone powder mixed with cement mortar or concrete has two kinds, One is adulteration, the limestone powder replacing part of the cement as cementing material, another kind is the additive, which do not change the quality of cement and the limestone powder is added into the extra[3]. The research results of Ma Pengfei et al.[6] show that a certain amount of limestone powder could improve the working properties of concrete, such as water retention and slump. The addition of limestone powder has a great effect on the early strength of concrete. The compressive strength of concrete increases first and then decreases with the increase of the content of limestone powder. When the content of limestone powder is 15%, the compressive strength reaches the maximum. The test results of Li Jing et al.[7] show that with the increase of dosage of lime stone powder, the concrete slump gradually become smaller, the water retention and adhesiveness have improved, with the increase of limestone powder content, concrete compressive strength first increases then decreases, when the dosage is 20%, the compressive strength is the largest.

Zhu Ke [9], Cao[10], Mei Songqi[11] et al. carried out the study on the mixing of limestone powder and analyzed the content within the maximum is 30% when the influence of the performance of concrete, the studies show that limestone powder to replace cement can effectively improve the working performance of concrete, but also can reduce the compressive strength, especially when the content is higher, lower compressive strength is more obvious. The study of Zhang Feng et al.[11] shows that the addition of 10% limestone powder will increase the capillary pore and total porosity in cement stone, the double mixing of 2% nano-CaCO₃ and limestone powder could refine the pore size and reduce the porosity. Xiao Jia et al.[12] used mercury injection method to study the influence of limestone powder dosage on the pore structure of cement slurry, the test results show that limestone powder transforms small holes into large holes in the slurry, resulting in a coarsening effect. The study of Liu Shuhua et al.[13] shows that limestone powder could effectively improve the pore structure of mortar and reduce its porosity.

In view of the limestone powder content of mortar, concrete pore structure effect in conclusion differences and now more than 30% of the high content study is less. In this paper, an experimental study on the working performance, mechanical properties and pore structure characteristics of cement mortar with 0%, 10%, 20% and 40% of cement replaced by limestone powder was carried out by mixing limestone powder into cement mortar. The effect of the content of limestone powder on the properties of cement-based materials was obtained to further perfect the limestone powder used in mortar and concrete theory, so as to provide guidance for practical engineering application.

2. Raw materials and test methods

2.1 Raw materials

In this study, Type P·O 42.5 cement was produced by Tianshui Zhongcai Cement Co., Ltd. Its basic properties and chemical composition are shown in table 1 and table 2. The high purity calcium carbonate produced in Yangzhou was selected as the limestone powder, in which the content of CaCO₃ is more than 98%, the fineness of 325 mesh sieve allowance is less than 0.02%, and the specific surface area is 1468 m²/kg. According to the provisions of "Limestone Powder Used in Cement, Mortar and Concrete" (GB/T 35164-2017), the jumping table method was used to conduct the fluidity ratio test of Limestone Powder, as shown in figure 1. The measured comparison of the fluidity of mortar was 192 mm, and the fluidity of test mortar was 205 mm. According to formula (1), the fluidity ratio of limestone powder was calculated to be 106.8%. The fine aggregate adopts machine-made sand with fineness modulus of 3.0, which meets the requirements of second zone. The high performance of
polycarboxylic acid was adopted as the water-reducing admixture, water reduction rate is 30%, and the
dosage is 0.3% of cementitious material. In order to ensure the accuracy of the test results, the stone
powder and muddy debris in the machine sand were cleaned before the test. The XRD analysis
patterns of cement and limestone powder are shown in figure 2 and figure 3.

Table 1. Basic properties of cement

| Water consumption for standard consistency (%) | Specific surface area (m²/kg) | Setting time (min) | Compressive strength (MPa) | Rupture strength (MPa) | Ignition loss (%) | stability |
|-----------------------------------------------|-------------------------------|-------------------|---------------------------|-----------------------|------------------|-----------|
|                                               |                               | initial set       | 3d 28d                    | 3d 28d                |                  |           |
| 27.6                                          | 352                           | 260               | 330                       | 21.3                  | 49.2             | 4.8       | 7.4       | 2.43 qualified |

Table 2. Chemical composition of cement

| w(%)          | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | SO₃ | MgO | K₂O | Na₂O | TiO₂ | P₂O₅ |
|---------------|-----|------|-------|-------|-----|-----|-----|------|------|------|
| w(%)          | 59.61 | 22.64 | 7.35  | 3.78  | 3.02 | 1.45 | 0.846 | 0.648 | 0.334 | 0.114 |

(a) The fluidity of contrast mortar  (b) The fluidity of test mortar

Figure 1. fluidity of mortar

\[ F = \frac{L}{L_m} \times 100\% = \frac{205}{192} \times 100\% = 106.8\% \]

Where: \( L \) is the fluidity of test mortar, mm; \( L_m \) is the fluidity of contrast mortar, mm; \( F \) is limestone powder fluidity ratio, %.

Figure 2. XRD pattern of cement  Figure 3. XRD pattern of limestone powder

2.2 Test mix ratio

In the light of the cement mortar strength testing method (ISO) law (GB/T 17671-1999) specified in the material dosage of cement mortar configuration. Water/cement ratio is 0.5, limestone powder to replace cement quantity was 0%, 10%, 20% and 40% respectively. The corresponding specimens were
numbered as S-0, S-10, S-20 and S-40. The specific material dosage is shown in table 3.

| Number of samples | Cement | Water | Sand | Limestone powder | Water reducer |
|-------------------|--------|-------|------|------------------|---------------|
| S-0               | 450    | 225   | 1350 | 0                | 1.35          |
| S-10              | 405    | 225   | 1350 | 45               | 1.35          |
| S-20              | 360    | 225   | 1350 | 90               | 1.35          |
| S-40              | 270    | 225   | 1350 | 180              | 1.35          |

### 2.3 Test methods

#### 2.3.1 Work performance

Cement mortar fluidity test was carried out by jumping table method stipulated in "Cement mortar fluidity measurement method" (GB/T 2419-2005).

#### 2.3.2 Mechanical property

According to the requirements in the Standard of Test Methods for Basic Properties of Building Mortar (JGJ/T 70-2009), each group made 3 cube specimens of 70.7mm×70.7mm×70.7mm, which were cured for 28d under the standard curing conditions, and the compressive strength of cement mortar was tested.

#### 2.3.3 Pore structure testing

According to "building mortar basic performance test method standards" (JGJ/T 70-2009) requirements, each group made 3 cube specimens of 70.7mm×70.7mm×70.7mm, after standard curing 28 d. After filling the specimen with water in vacuum for 18h, the excess water on the surface was wiped dry, using the new mai MacroMR12-150-H-I large-diameter magnetic resonance imaging analyzer for porosity, pore diameter and pore distribution test, magnet type for permanent magnets, magnetic field intensity was 0.3±0.05T, probe diameter is 150 mm. The test equipment is shown in figure 4.

![Large diameter NMR analyzer](image)

#### Figure 4. Large diameter NMR analyzer

### 3. Test results and analysis

#### 3.1 Work performance

The test results of fluidity of cement mortar with different cement quality replaced by limestone powder are shown in table 4 and figure 5. It can be seen from table 4 and figure 5, mortar fluidity gradually improve along with the increase of the limestone powder to replace cement quality. Limestone powder instead of cement was 10%, 20%, 40%, the fluidity of limestone powder-cement mortar, compared with the pure cement mortar fluidity increased by 15.1%, 19.8% and 31.3% respectively. This is mainly because the specific surface area of limestone powder used in the test is larger than that of cement, but it requires less water than cement. It is because the limestone powder surface is smooth and belongs to the hydrophobic material, the adsorption capacity of water is less...
than that of cement and the particles are small, so it can be well filled in the cement slurry and improve the grading of cementing materials, and thus increased the fluidity. With the increase of the content of limestone powder, the van der Waals force between fine particles and molecules was greater than the effect of gravity, so the mortar mixture is not easy to appear the phenomenon of segregation and bleeding. Therefore, when the fluidity of limestone powder-cement mortar was increased, the water retention and cohesion will also be improved[10,14-16].

![Images](a) 0% (b) 10% (c) 20% (d) 40%

Figure 5. Fluidity of cement mortar with different amounts of limestone powder

| Number of samples | Fluidity (mm) | Compressive strength of cement mortar (MPa) |
|-------------------|---------------|---------------------------------------------|
| S-0               | 192           | 41.2                                        |
| S-10              | 221           | 38.3                                        |
| S-20              | 230           | 34.3                                        |
| S-40              | 252           | 23.8                                        |

### 3.2 Mechanical property

The compressive strength of cement mortar with different dosage of limestone powder is shown in Table 4. It can be seen from table 4 that the compressive strength of cement mortar decreased with the increase of the content of limestone powder. When the dosage of limestone powder replacing cement was 10%, 20% and 40%, the compressive strength of mortar decreased by 6.9%, 16.7% and 42.3% respectively compared with pure cement mortar. It can be seen that when the content of cement mortar was relatively low, the compressive strength of cement mortar decreased slightly, however, when more cement was replaced by limestone powder, its compressive strength decreases obviously. The main reason is that although limestone powder also has a certain activity effect and can promote cement hydration, these effects are far less than those of the replaced cement[17,18], so the strength of cement mortar will be reduced. When the amount of limestone powder replacing cement was small, although the fine particles of limestone powder can fill the larger gap between fine aggregate and cement and improve the overall grading of mortar, the filling effect was not very significant, therefore, the hydration of cement was greater than the filling effect of limestone powder, showing a decrease in compressive strength. When the mixing amount of limestone powder was too large, the interaction force between fine particles and molecules of limestone powder was greater than the effect of gravity. After the limestone powder was turned into suspension by adding water, the electrostatic repulsion between particles played a major role, as a result, the gap of cementitious material increased and the compression strength of mortar decreased[19]. According to the test results, the content of limestone powder should be controlled at about 10%.
Figure 6. Properties of cement mortar with different amounts of limestone powder

3.3 Pore structure testing
Nuclear magnetic resonance imaging (NMR) was used to test the pore structure of limestone powder-cement mortar. Pore characteristics of cement mortar mixed with different limestone powder are shown in figure 7, it was also known from the analysis of figure 7(a), with the increase of the content of limestone powder, the porosity of limestone powder-cement mortar increased first and then decreased. And when the dosage was 10%, the porosity was the largest, which was 8.7% higher than that of pure cement mortar. The main reason is that the activity of limestone powder is not as good as that of cement, after limestone powder replaced cement, less cementitious materials was involved in the reaction making effective water cement ratio increased, some of the free water was not involved in hydration reaction, the free water evaporated. As a result, the internal porosity of cement hydrate increased and the porosity increased[19]. When the dosage of limestone powder increased to 20% and 40%, the number of smaller particles in limestone powder also increased, and part of the pores in mortar were filled, which reduced the porosity. With the increase of the content of limestone powder, the proportion of fine pores increased was also known from the analysis of figure 7(b). And in order to further analyze the variation rule of pore structure of limestone powder-cement mortar with different dosage, the pore throat test was carried out. Figure 7(c) for the different dosage of limestone powder cement mortar distribution of pore throat, it can be seen that the pure cement mortar were mainly concentrated in the pore size of 0.1 μm and 0.63 μm, and after adding limestone powder, the pore size of limestone powder-cement mortar mainly concentrated between 0.1 μm and 0.16 μm. It can be seen that the addition of limestone powder effectively full part of the pores in the cementing material, refined the pore size, reduced the large-size pores, increased the small-size pores and optimized the pore structure inside the mortar.

Figure 7. Pore structure of cement mortar with different amounts limestone powder

4.Conclusion
Through the analysis of the test results, the following conclusions were drawn:

(1) With the increase of the content of limestone powder, the fluidity of mortar increased gradually, and the compressive strength of mortar decreased gradually. When the content of limestone powder
exceeded 20%, the decline range of the compressive strength increased. Therefore, it is suggested that the amount of limestone powder to replace cement should not exceed 20%.

(2) Due to the micro-aggregate filling effect of limestone powder, the large pore size of limestone powder-cement mortar can be obviously reduced, and the pore structure characteristics of limestone powder-cement mortar can be refined and optimized.

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