Effect of Limestone Micro-powder on Hydration Properties of Composite Cement Grout

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Abstract. The effect of limestone micro-powder on the basic properties of composite cement grout, including fluidity, compressive strength, temperature rise, were studied by taking cement, slag, fly ash, zeolite as initial cementitious material. The methods of XRD, SEM and TG-DSC were carried out to analyze hydration products and mechanism of composite cement grout. The experiment results showed adding 10% limestone micro-powder can reduce grout internal shearing stress, improve grout fluidity, promote hydration reaction, raise reaction rate and hydration temperature, and make the exothermic peak forward; limestone micro-powder can fill the pores of cement paste, increase the density and the compressive strength. The XRD and TG-DSC pattern showed limestone micro-powder was not involved in hydration reaction of composite cement grout.

1. Introduction
Cementitious materials or concrete are often prepared with some mineral admixtures to improve the performances. Admixtures can reduce the cement usage of cement-based materials, improve the workability, reduce the hydration temperature rise and increase the strength. Common admixtures include fly ash, slag, silicon powder, and natural ash materials. Fly ash and slag have hydration activity and are commonly used as cement or concrete admixtures, but their content must be determined by experiments. Jiang Linhua's research showed too many fly ash content can easily cause the cement grout segregation and bleeding, and the excessive amount of slag can cause the viscosity of the grout to become larger and the early strength to decrease[1]. The addition of limestone powder can reduce segregation and bleeding, decrease viscosity, and increase mobility of cement grout[2-4]. Celik et al.[5] prepared high workability self-compacted concrete by adding fly ash and limestone powder. Liu Shuhua's test results showed limestone powder finer than cement can fill the pores in the cement grout, improve the pore structure, make the grout stone more dense, and in the final hydration stage, limestone powder can be hydrated as hydrated calcium aluminate[6-7]. Yin Geng's studies showed limestone powder with certain fineness can increase the early strength of cement-based materials, reduce the strength if excessive addition[8]. Xu Caiyun's results showed that limestone powder decrease the fluidity of cement paste and increase the fluidity of cement mortar. The early strength of hardened cement paste and mortar increased then decreased with increasingly limestone powder usage. When limestone powder content was 10 %, the strength reached the maximum[9]. Xiao Jia's studies showed limestone powder can promote the early hydration of cement, hinder its later hydration, and produce new phase calcium aluminate hydrate. With the increase of hydration age, limestone powder causes the pore structure of cement grout to change from small holes to large holes, resulting in pore roughening effect[10]. Tydlitat et al.[11] studied the limestone silicate cement made of 80 % silicate cement and 20 % limestone powder, monitored the early hydration heats of the grout under conditions...
of 20 °C and 35 °C with a water-binder ratio of 0.35 and 0.50. The studies showed limestone powder have an important effect on the early release of hydration heat. Tsivilis et al.\[12\] studied thermal comparison test using pure cement and cement containing 5% limestone powder, the results showed limestone powder can advance cement hydration exothermic peak, increase the total heat release in 24 hours by 1.25%. The single addition of the limestone or slag powder can inhibit the autogenous shrinkage of the paste for 0-1 d, and the double addition can make the inhibitory effect more obvious. For 1-180d, the autogenous shrinkage of the hardened pastes increased first and decreased later with the limestone content, and which reached the maximum when the limestone content was 10%\[13\]. Dong Yun et al.\[14\] believed that the hydration products of the cement-fly ash-limestone powder ternary cementitious system were C-S-H gel, Ca(OH)$_2$ and AFt, which were not significantly different from pure cement grout. The addition of limestone powder can promote the early hydration of cementitious material. When the amount of limestone powder was small, its influence on the hydration mechanism was also small. Although it can promote hydration, the process hydration reaction was longer; When the amount of limestone powder was large(50%), the hydration reaction of the cementitious material was intense and the control mechanism was changed\[15\]. At present, there are more researches on the hydration reaction characteristics of pure cement mixed limestone powder, and less researches on the hydration reaction of composite cementitious materials mixed limestone powder. In this paper, cement, slag, fly ash, zeolite powder, etc. were used as the initial cementitious material to study the effects of the basic properties of the cement grout mixed limestone powder, such as the fluidity, compressive strength and hydration temperature rise. XRD, SEM, TG-DSC and other test methods were used to analyze the hydration products and hydration mechanism of composite cement grout.

2. Experiment

2.1 Raw materials and mix proportion

Cement(C): 42.5 portland cement, median diameter is 13.11 μm, specific surface area is 610 m$^2$/kg. Its basic performance is shown in table 1. Slag(S): the median diameter is 11.88 μm, specific surface area is 620 m$^2$/kg. Fly ash(F): Class II fly ash, the median diameter is 14 μm, specific surface area is 640 m$^2$/kg. Zeolite powder(Z): the median diameter is 56 μm, specific surface area is 640 m$^2$/kg. Expansion agent(U): UEA-H type, the median diameter is 34.3 μm, specific surface area is 400 m$^2$/kg. Limestone powder(L): 1250 meshes, median diameter is 2.79 μm, specific surface area is 1370 m$^2$/kg, specific particle size distribution is shown in Figure 1, and the main chemical composition is shown in Table 2. Water-reducing agent(J): polycarboxylate superplasticizer with water reduction efficiency greater than 28%. Water(W): running water. The composite cement grout mix proportions is shown in table 3.

| Setting time /h | Compressive strength /MPa | Flexural strength /MPa | Soundness |
|----------------|--------------------------|-----------------------|-----------|
| Initial        | Final                    | 3d                   | 28d       | 3d       | 28d       |           |
| 4.5            | 7.5                      | 18                   | 46        | 3.6      | 9.8       | Good     |

Note: The distribution of particle size and grading curve of the limestone is given in Figure 1.
Table 2. Chemical compositions of the limestone (\%)  

|      | CaO   | MgO   | SiO\textsubscript{2} | Fe\textsubscript{2}O\textsubscript{3} | Al\textsubscript{2}O\textsubscript{3} | SO\textsubscript{3} | Loss |
|------|-------|-------|------------------------|--------------------------------------|------------------------|------------------|------|
|      | 52.4  | 2.56  | 0.12                   | 0.3                                  | 0.45                   | 0.01             | 43.6 |

Table 3. Mix proportions of the composite cement grout (g)  

| Sample | C   | S   | F   | Z   | U   | L   | J   | W   |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|
| M1     | 20  | 30  | 40  | 1.9 | 10  | 0   | 1.5 | 25  |
| M2     | 18  | 27  | 36  | 1.71| 9   | 10  | 1.5 | 25  |

2.2 Experimental methods  
The use of cement paste mixer mixing materials, first mix the powder evenly, then add water reducer and water, continue to mix well. All experiments use the same mixing method and mixing time. First measure the fluidity and setting time of the mixed grout, then pour some grout into the temperature test device shown in Figure 2 to measure the hydration temperature rise. The remaining grout is poured into cement mortar triple steel mold, and placed in a concrete standard maintenance box. Finally, measure the corresponding age strength. The core portion of the cement hardened body after 28 days is used as samples for TG-DSC, SEM and XRD experiments.

Fig 2. Schematic diagram of temperature test device

3. Results and discussion

3.1 Effect of limestone micro-powder on the liquidity of composite cement grout  
The trend of fluidity on composite cement grout with time is shown in Figure 3. The initial fluidity of M2 added limestone micro-powder is 300 mm, but the fluidity loss is large, about 40 % in 60 minutes, later loses liquidity. The initial fluidity of M1 without limestone micro-powder is 280 mm, the fluidity loss in the first 20 minutes is smaller, in the next 20 minutes becomes larger, and the change in the last 20 minutes is smaller. The results show that adding limestone powder can improve the fluidity of composite grout\textsuperscript{[16]}. Limestone powder is hydrophilic, can break the cement particle masses when cement hydration, release water, thereby increase the mobility of concrete mixer\textsuperscript{[4]}. The linear decline of fluidity with time shows that limestone micro-powder can promote early hydration of cement\textsuperscript{[15]}.

Fig 3. The curves of fluidity on cement grout with time

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3.2 Effect of limestone micro-powder on the strength of composite cement grout

The changes about compressive strength of the composite cement grout at 7-day, 15-day and 28-day are shown in Figure 4. It can be seen that the compressive strength of each age of M2 added limestone micro-powder is significantly higher than that of M1 without limestone micro-powder. At 28-day, the compressive strength of M2 can reach 50 MPa, which is 44 % higher than that of sample M1.

Fig 4. The curves of compressive strength on cement grout with time

The samples of the composite cement grout were tested using SEM at 28-day as shown in Figure 5. There are obvious holes in the sample M1, fewer holes in the sample M2, and the cement stone of M2 is relatively dense. Combining the analysis of Figure 4 and Figure 5, it is concluded that limestone micro-powder promotes the hydration reaction of cement, fills the micro-holes in the cement stone structure for its fine particles, causes the cement stone dense, and the strength of each age period is higher than that of the sample M1 without limestone micro-powder.

Fig 5. SEM photographs of sample M1/M2 (The left image is M1, right is M2)

3.3 Effect of limestone micro-powder on temperature rise of composite cement grout

Figure 6 shows that the initial temperature of the sample M1 without limestone micro-powder is 21.5 °C, the maximum temperature of the center is 62.4 °C, and the temperature rise is 40.9 °C. The initial temperature of the sample M2 with limestone micro-powder is 20 °C, the maximum temperature of the center is 64.6 °C, and the temperature rise is 44.6 °C. The maximum temperature of the sample M2 is higher than the sample M1, and the arrival time is earlier, indicating that limestone powder promotes the hydration reaction of composite cement. Yang Huashan et al. [17] believes that the appropriately adding limestone powder acts as the nucleation base of CSH, reduces the nucleation barrier, and accelerates the hydration of the cement.
Fig 6. Test curves of hydration temperature rise

3.4 Effect of limestone micro-powder on hydration products of composite cement grout

The hydrated products of composite cement grout at 28-day were examined by XRD and TG-DSC, as shown in Figures 7 and 8.

![XRD Patterns of Hydration Products](image)

**Fig 7. XRD patterns of hydration products**

![TG-DSC Curves of Hydration Products](image)

**Fig 8. TG-DSC curves of hydration products (The thin curve is M1, thick curve is M2)**

Figure 7 shows, comparing to the M1, the characteristic peaks of the XRD on CaCO$_3$ of the sample M2 are obvious. In the hydration products of M2, there is no new characteristic peak, no C3S or CaSO$_4$·2H$_2$O, furthermore, the mass of Ca(OH)$_2$ and SiO$_2$ decline significantly. The results show that the limestone micro-powder does not participate in the hydration reaction of the composite cement grout, but can promote hydration reaction more completely.

Figure 8 shows that M1 has an obvious thermal weight loss step and heat absorption peak. Before 100 °C, free water evaporate, and about 130 °C, crystal water of AFt evaporate. There are two relatively significant thermal weight loss steps and heat absorption peaks in M2. Before 100 °C, free water evaporate, about 150 °C, crystal water of AFt and other hydration products evaporate, and...
limestone decomposition reaction occurs at 650〜850 ℃. The TG-DSC curves of M1 and M2 are basically same before 650 ℃, and the weight loss is about 18 %, then the decomposition of carbonate occurs in M2. This also shows the hydration products of M1 and M2 are basically same, confirm the results of XRD analysis.

4. Conclusions
(1) The addition of 10 % limestone micro-powder in the composite cement grout can reduce the internal shear stress, and increase the fluidity of the grout, but shorten the setting time.
(2) The addition of limestone micro-powder can promote the hydration reaction of the grout, increase the reaction rate and hydration temperature rise, and advance the heat release peak.
(3) The addition of limestone powder can fill the micro-holes in the cement stone structure, increase the compactness and the compressive strength.
(4) The addition of 10 % limestone micro-powder does not participate in the hydration reaction of the composite cement grout, but can promote hydration reaction more completely.

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