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# Experimental Study on Performance of Green Complex Binder of Low-grade Fly Ash and Limestone Powder

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**Abstract.** In this article, the effects of different content and compound ratio of low-grade fly ash and limestone powder on the strength, water requirement and adaptability with admixture of green complex binder were studied, and the influence of particle size distribution and particle morphology on its performance was analyzed. The results indicated that the strength decreased obviously with the increase of mineral content. There was an optimum ratio of fly ash and limestone powder (6:4) at a certain mineral content. Water requirement decreased, and the saturated content of admixture points became small with the increasing of limestone powder. The effects of content on the strength were much more than that of particle size distribution for composite cement with high volume of mineral admixtures.

## Introduction

The biggest disadvantage of traditional Portland cement is that it has high early hydration heat and poor durability, is easy to crack [1], which brings a huge pollution problem and makes a waste of resources and energy. At present, fly ash is widely used as mineral admixture, while 95% of them is Ⅲ-grade or off-grade ash because there is not enough excellent fly ash produced by power plants[2]. Furthermore, it's bad for performance to use it directly as admixture. In addition, limestone powder can be got after machining, is fine powder particles with the size of smaller than 0.16mm, and it's easily available and inexpensive. Therefore, it is significant to produce green complex binder by using limestone powder and low-grade fly ash as the replacement of cement clinker.

## Primary material and test method

**Primary material.** The 45μm sieve residue of cement clinker is 11.9%. The fineness of Low-grade fly ash is 68.9%, its water demanding ratio is 105%, loss on ignition is 8.58%. The 45μm sieve residue of limestone powder is 2.2%, its water demanding ratio is 94%.The admixture is naphthalene series water reducer. The main chemical composition of cement clinker, fly ash and limestone powder are showed on the Table 1.

Table1 The main chemical composition of primary material

| Sample | $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | CaO | MgO | $SO_3$ |
|---|---|---|---|---|---|---|
| Clinker | 21.69 | 2.97 | 4.89 | 64.29 | 2.18 | 1.09 |
| Fly ash | 38.4 | 15.26 | 27.26 | 5.61 | 0.98 | 1.72 |
| Limestone powder | 6.48 | 0.73 | 1.85 | 43.57 | 5.39 | - |

**Test method.** Cement clinker, gypsum, fly ash and limestone powder were mixed in proportion, and mixed evenly with a mortar mixer, then the physical properties were tested according to "Water Requirement of Normal Consistency, Setting Time, Stability Test Method of Cement" (GB/T1346-2001). And the mechanical property was tested according to "Strength Test Method of

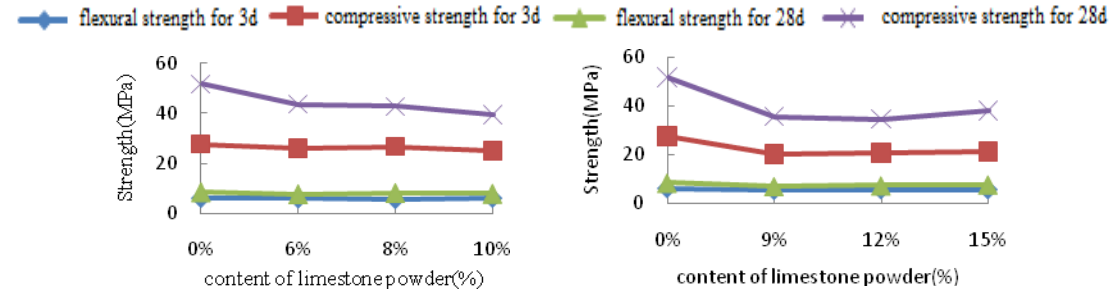
Cement Mortar (ISO Method)" (GB/T 17671-1999).Cement paste fluidity test was carried according to Appendix A of "Technical Specifications of Concrete Admixtures" (GB 501 19-2003).Particle size distribution was tested by Using BT-9300H Laser.

## Results and discussion

**Strength test of complex binder.** The green complex binder was produced by using limestone powder and low-grade fly ash as the replacement of cement clinker, and the total content of mineral admixtures was 20%, 30%, 40% and 50%. The composition and properties of complex binder was shown in Table 2.

Table 2 The composition and properties of complex binder

| Sample | Clinker and gypsum | Content of mineral admixtures | Content of LP | FA: LP | Water Requirement | Flexural strength (MPa) | | Compressive strength (MPa) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | 3d | 28d | 3d | 28d |
| S1 | 100% | 0% | 0% | 0:0 | - | 6.1 | 8.5 | 27.7 | 51.7 |
| B1 | 80% | 20% | 10% | 5:5 | 26.0 | 6.1 | 7.9 | 27.1 | 39.4 |
| B2 | 80% | 20% | 8% | 6:4 | 26.4 | 5.6 | 8.2 | 26.7 | 42.7 |
| B3 | 80% | 20% | 6% | 7:3 | 26.8 | 5.9 | 7.7 | 26 | 44.6 |
| B4 | 70% | 30% | 15% | 5:5 | - | 5.6 | 7.8 | 21.3 | 38.1 |
| B5 | 70% | 30% | 12% | 6:4 | - | 5.6 | 7.4 | 20.8 | 34.6 |
| B6 | 70% | 30% | 9% | 7:3 | - | 5.3 | 7.1 | 20.3 | 35.6 |
| B7 | 60% | 40% | 20% | 5:5 | 27.2 | 4.4 | 7.2 | 16.6 | 29.8 |
| B8 | 60% | 40% | 16% | 6:4 | 28.2 | 4.7 | 7.0 | 17.1 | 31.4 |
| B9 | 60% | 40% | 12% | 7:3 | 28.6 | 4.5 | 7.0 | 15.7 | 32.6 |
| B10 | 50% | 50% | 25% | 5:5 | - | 3.5 | 6.1 | 12.9 | 24.0 |
| B11 | 50% | 50% | 20% | 6:4 | - | 3.3 | 6.3 | 12.1 | 26.3 |
| B12 | 50% | 50% | 15% | 7:3 | - | 3.5 | 6.4 | 11.3 | 26.6 |




**(a) 20% of total content of mineral admixtures**

**(b) 30% of total content of mineral admixtures**

**(c) 40% of total content of mineral admixtures**

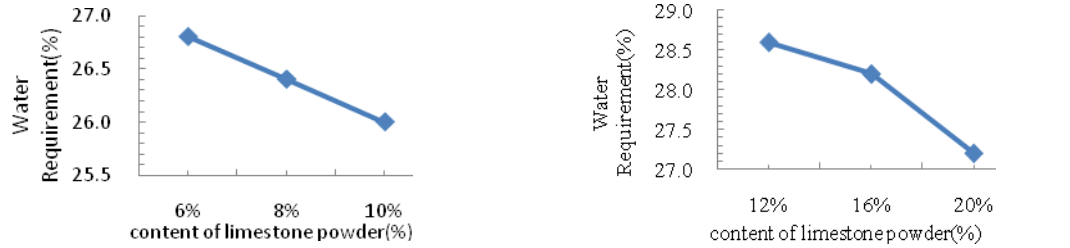
**(d) 50% of total content of mineral admixtures**

Fig. 1 The mechanical property with different content of mineral admixtures

Fig.1 presented that the strength would decrease obviously when adding limestone powder and grade-Ⅲ fly ash into the cement clinker. Both the flexural strength for 3d, 28d decreased, the compressive strength for 28d decreased with the increase of limestone content,but the compressive strength for 3d increased slightly. At 20% of admixture, the average compressive strength for 3d decreased less than 2MPa, but decreased by 9.5MPa for 28d, it could be up to 42.7MPa and 44.6MPa when the ratio of fly ash and limestone was 6:4 and 7:3, which met the strength requirements of P.O 42.5 cement.At 40% of admixture, compressive strength for 3d decreased by 11.2MPa, decreased by

20.4MPa for 28d,B9 was the highest of all when the ratio was 7:3 whose strength was 32.6MPa, and it could be satisfied with the requirements of P.C 32.5. At 50% of admixture, compressive strength for 3d decreased by 15.9MPa, 28d decreased by 26.1MPa, was only 50% of pure clinker sample. Above all, the better ratio of fly ash and limestone powder were 7:3 and 6:4 at a certain mineral content.

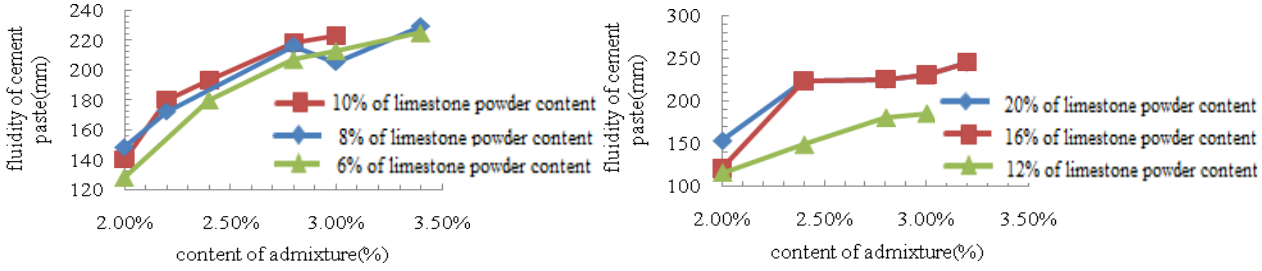
**Water requirement test.** The effect of limestone powder on water requirement of normal consistency was presented in Fig.2. It was found that the water requirement decreased with the increase of limestone powder at a certain mineral content. The reason might be that fly ash had bigger water demand(water demand ratio of fly ash was 105%, while limestone powder was 94%). In addition, limestone powder, as an inert material, didn't participate in the early cement hydration basically[3], and it had much more fine particles which could fill the gap between cement clinker and fly ash particles to reduce the water of the gap, so the water requirement decreased.




**(a) 20% of total content of mineral admixtures** **(b) 40% of total content of mineral admixtures**

Fig. 2 The effect of limestone powder content on water requirement

**The adaptability with admixture test.** When the total content of mineral admixtures was 20%and 40%, the fluidity of cement paste sample in different content of naphthalene series water reducer was shown in Fig.3. It can be seen from Fig.3 that the sample whose limestone powder content was 10% was first up to the saturated content of admixture points when the total content of mineral admixtures was 20%, so did that of 40%.Hence, the more limestone powder, the better fluidity of cement paste at a certain mineral content. The reason may be that limestone powder has low surface energy and good dispersity and excellent water demand behavior. Secondly, mineral admixtures couldn't adsorb or little water reducing agent due to its poor activity compared to cement clinker, so the free water reducing agent would be greater with the increase of mineral admixtures. Thirdly, the fine particles of limestone powder reduced the packing void of complex binder, leading to less water reducing agent.




**(a) 20% of total content of mineral admixtures** **(b) 40% of total content of mineral admixtures**

Fig.3 The effect of content of admixture on fluidity of cement paste

**Particle size distribution and performance.** Cumulative percentages of particle size and range of percentage content were shown in Table 3. Table 3indicated that fly ash had more coarse particles, on the contrary, the limestone had more fine particles, and the cement clinker was between two parties. Actually, the main role of fly ash and limestone powder was filling effect due to its low activity. It could get compact structure by mixing them with appropriate ratio, which had good particle size distribution. As shown in Fig.4, the hydrated product of B2 and B9 sample overlapped each other to promote the densification of set cement. Particles of 3~32μm played a major role on the strength of growth in cement clinker[4,5].It was found that both B2 and B9 had the same cement of 3~32μm in general, but the compressive strength reduced by a difference of about 10MPa.Because B9 had 20% content of mineral admixture more than B2, lead to the decreasing of clinker(3~32μm), and the

strength decreased obviously. In hence, the effects of content on the strength were much more than that of particle size distribution for composite cement with high volume of mineral admixtures.

Table 3 Particle size distribution

| Sample | range of particle size | | | | |
|---|---|---|---|---|---|
| | 1μm | <3μm | 3~32μm | 32~65μm | >65μm |
| Clinker | 3.00% | 17.16% | 59.24% | 16.46% | 7.73% |
| Limestone powder | 1.40% | 20.00% | 79.70% | 0.30% | 0.00% |
| Fly ash | 2.00% | 11.40% | 47.60% | 17.00% | 25.00% |
| B2 | 3.76% | 18.28% | 56.92% | 15.45% | 9.35% |
| B9 | 3.35% | 16.23% | 54.48% | 14.98% | 14.31% |

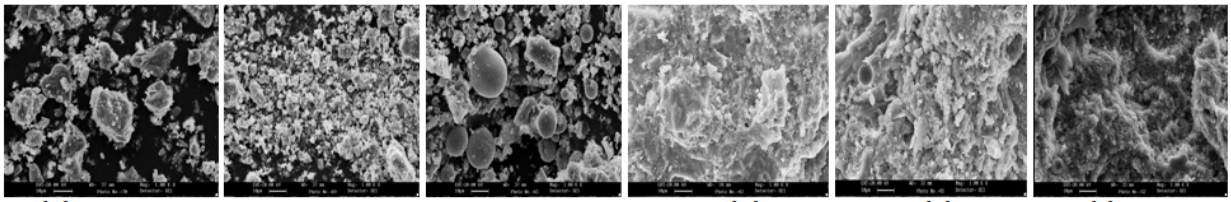



Fig. 4 SEM of granule morphology and hydration for 28d

## Conclusions

1. The strength would decrease obviously when adding limestone powder and grade-III fly ash into the cement clinker, decreased obviously with the increase of mineral content.
2. Both the flexural strength for 3d and 28d decreased slightly, the compressive strength for 3d increased, but it for 28d decreased with the increase of limestone content at a certain mineral content. The strength was roughly equal when FA:LP was 7:3 and 6:4, while it decreased when it was 5:5.
3. Water requirement of normal consistency decreased, and saturated content of admixture points became small with the increasing of limestone powder, which showed a good adaptability with admixture.
4. There was an optimum ratio of fly ash and limestone powder (6:4). It could meet the strength requirements of P.O 42.5 cement when fly ash was 12%, limestone powder was 8%, and the strength for 28d could be up to over 30MPa when fly ash was 24%, limestone powder was16%.
5. The effects of content on the strength were much more than that of particle size distribution for composite cement with high volume of mineral admixtures.

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