The Composite Effect of Mineral Additives to the Performances of Concrete

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Abstract: In this study, silica fume, fly ash, slag and metakaolin were used as mineral additives to make concrete by the means of adding one, two, or three minerals into the admixture. Through comparing mechanical properties, anti-corrosion performance, and microstructure of the parallel samples, the composite effect of mineral additives were discussed in detail. The results show that, active minerals replace cement of 40% by the method of equivalent substitute, the mechanical properties and anti-corrosion performances of the concrete were observably enhanced. When mixing slag and metakaolin, the 28-day compressive strength of the samples had reached 91.1 MPa, mixing slag and silica fume, the 28-day compressive strength of the samples had reached 96.0 MPa. This suggests that the mineral additives can contribute actively to the properties of the concrete, and adding two or three kinds of the mineral additives can bring the result of superiority supplementary.

Key Words: mineral additives, composite effect, concrete

1 Introduction

In the 20th century, one of the most prominent achievements of the concrete materials science was the development and application of the active minerals. Addition of the mineral additives can not only significantly reduce the cost, and benefit environmental protection, but also can enhance the compressive strength and durability of the concrete. In addition, durability performance of the additive bearing concrete also caught more and more attention of the concrete researchers.

In recent years, there are many literature reports and projects about active minerals to replace cement by the method of excessive substitutions. For researches in equivalent substitutes is relatively less. In the current study, silica fume, fly ash, slag, and metakaolin were selected as mineral additives to make concrete by adding one, two, or three kinds of minerals. Through comparison of mechanical properties, anti-corrosion performance, and microstructure of the samples, the composite effect of mineral additives were discussed at the equivalent substitute level of 40%.

2 Experiment

2.1 Materials of the Experiment

Cement: Ordinary Portland cement, strength grade 42.5;
Fine aggregate: sand, fineness modulus is 2.9, silt content is 2.48%;
Coarse aggregate: gravel grain size between 5-25 mm, rate of crushing 8%;
Fly ash: class F, with a specific surface area of 465 m^2/kg;
Slag: Alkalinity modulus is 1.0, mass modulus is 1.9, and specific surface area is 420 m^2/kg;
Silica Fume: grain size 0.08 μm, apparent density 250 kg/m^3;
Metakaolin: specific surface area 1272 m^2/kg, containing over 90% SiO_2 and Al_2O_3 ;
Water reducing agent of high efficiency: UNF-5 naphthalene type;
Water: ordinary freshwater.

2.2 Proportioning of cement concrete

Researches indicate that, using excessive active minerals to replace a part of the cement can result in high-performance concrete with grade better than C80 [1].

In this study, equivalent substitute method has been taken. Concrete design was defined according to the materials selected, and the main objective was to guarantee the four requirements of execution of works, strength, durability, and economical efficiency. The water requirement was 160 kg per cubic meter concrete and W/C was 0.25. To ensure a good working performance, the slump constant was controlled greater than or equal to 180 mm, and divergence was kept between 400 mm to 600 mm. the addition quantity was 40% weight of the gross mixture. Substitution coefficient was 1.0. The concrete design is showed in Table 1.

Table1. Proportioning of the cement concrete

Items	A	B	C	D	E	F	G	H
W/C %	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Sand Ratio %	38	38	38	38	38	38	38	38
Water kg	157	157	157	157	157	157	157	157
Cement kg	629	377	377	377	377	377	377	377
Fly Ash kg	0	252	0	126	0	0	94.5	94.5
Slag(kg)	0	0	252	126	126	126	94.5	94.5
Silica Fume(kg)	0	0	0	0	126	0	63	0
Metakaolin(kg)	0	0	0	0	0	126	0	63
Fine Aggregate(kg)	606	606	606	606	606	606	606	606
Coarse Aggregate (kg)	989	989	989	989	989	989	989	989
UNF-5 Water Reducing Agent %	1.0	1.2	1.0	1.0	1.0	1.1	1.0	1.2
Slump constant mm	228	232	220	235	210	180	220	220
divergence mm	595	565	600	54.5	463	400	498	400

3. Performance Testing

3.1 Mechanical Property Testing

The cube compressive strength testing was carried out according to GB-T50081-2002, the mechanical property testing method of normal concrete. The 3-day, 7-day, and 28-day compressive strength data are shown in Table 2.

Table2. The result of mechanic strength of the concrete MPa

Number	3-day	7-day	28-day
A	41.1	64.7	74.8
B	38.3	49.4	73.5
C	40.2	58.0	73.0
D	43.2	57.5	78.5
E	48.0	57.8	96.0
F	50.1	64.6	91.1
G	46.5	58.8	84.5
H	46.2	68.1	84.0

It is seen that, the 28-day strength of the samples B or C was just the same as reference sample A. Samples D, E, and F, which contained two kinds of minerals, and the samples G and H, which contained three kinds of minerals, had exceeded the reference sample. Specially, when mixed with slag and silica fume (sample E) or mixed slag and metakaolin (sample F), the samples' 28-day-age compressive strength was above 90.0 MPa.

3.2 The anti-corrosion experiment of the concrete

Experiment scheme: Being soaked in saturated Na_2SO_4 solution for 20h, and then the 28-day-age samples were dried for 4h in an oven at 105±5^{o}C. This was one cycle. The operation was repeated for 25 cycles. The anti-corrosion property was tested by the loss of mass and strength of the samples. The testing result is in Table 3.

Table 3. The mass loss and strength loss of the samples

Number	A	B	C	D	E	F	G	H
Mass Loss %	1.0	0.5	0.6	0.6	0.3	0.5	0.4	0.3
Strength Loss %	26.8	21.2	16.4	18.3	4.4	14.8	11.1	9.7

4. Discussion

4.1 Enhancement Effect of the Mineral Additives

Secondary hydration reaction can take place between SiO_2 or Al_2O_3 in the mineral additives and $Ca(OH)_2$ generated from the cement hydration products, low alkalinity C-S-H gel, and hydrous calcium aluminates. It can improve the constitution of the cement stone and reduce $Ca(OH)_2$. The reduction of the amount of $Ca(OH)_2$ can accelerate the hydration reaction speed[2]. The 28-day-age XRD analysis of hydrated samples is displayed in Fig.1.

In sample A (reference sample), $Ca(OH)_2$ can be obviously seen. $Ca(OH)_2$ can't be found in sample E (containing slag and silica fume) and sample F (containing slag and metakaolin). This indicates that adding active minerals into the concrete can reduce the content of $Ca(OH)_2$ in cement stone and can produce more C-S-H and hydrous calcium aluminates.

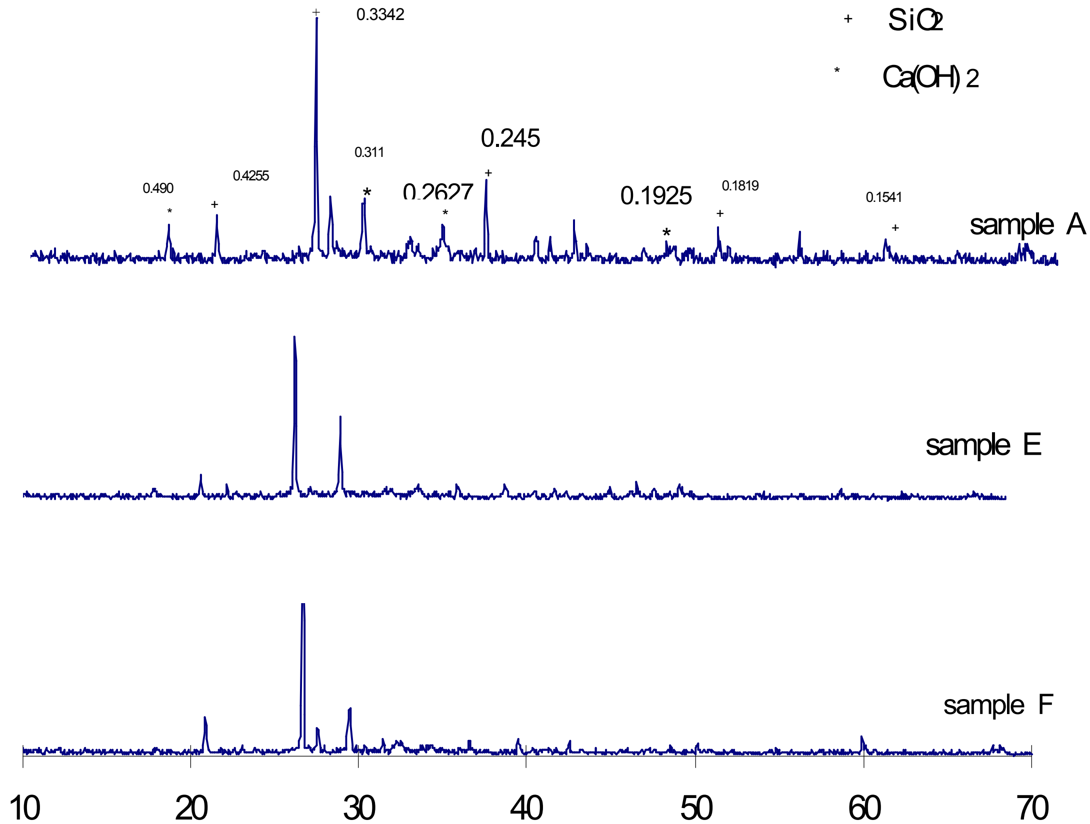


Fig.1 XRD analysis of hydrated samples

This has also been confirmed by the mechanical strength testing results. The growth ratio of 7d/3d and 28d/7d is showed in Fig. 2.

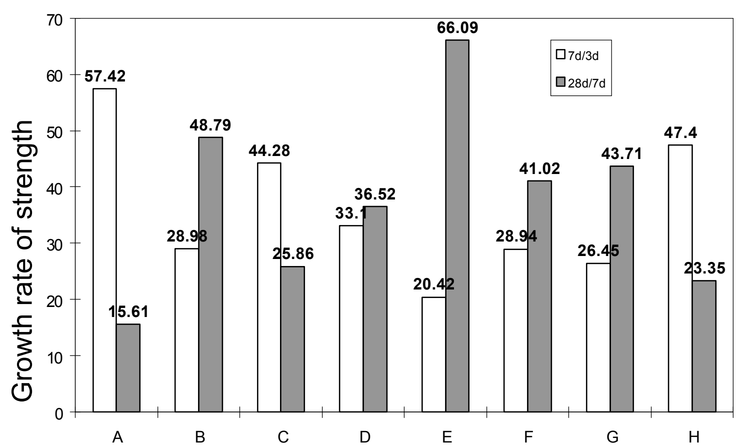
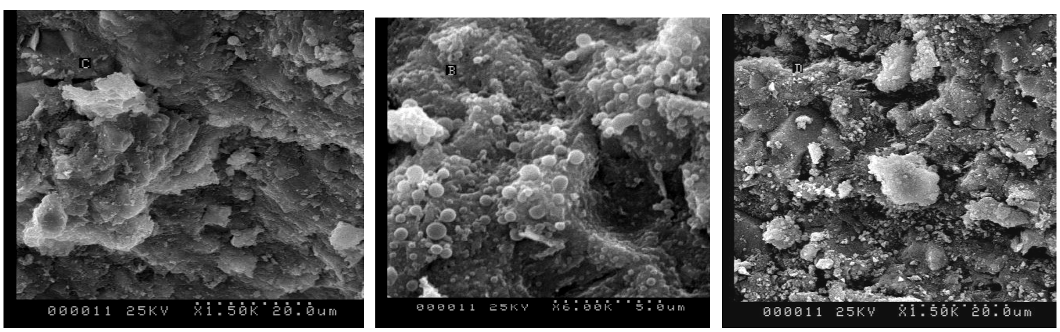


Fig. 2. Comparison of strength decreasing rate

It is seen that the growth ratio of strength on 7d/3d of the reference sample A is the highest (57.42%), while its 28d/7d ratio is lowest (15.61%). Though other samples with additive minerals are in the shade of the reference sample in the growth ratio of strength of 7d/3d, they had got much improvement in ratio of 28d/7d. Especially, the growth ratio of strength on 28d/7d of sample E had reached 66.09%.

4.2 Micro-Packing Effect

The structure of concrete is a very complex multiphase system. It is difficult to homogenize all the compositions and materials. Adding active materials can improve the gradation of the concrete effectively. In the system, the cement grains fill in the framework formed by the aggregates (the first filling action); then fly ash, fine flag fill in the smaller cavities (the second filling action); and metakaolin and silica fume particles fill in the even smaller cavities (the third filling action). This leads to the high compactness of the hiddenites. The micro-packing effect phenomena can be obviously seen in Figs.3 (a), (b) and (c).



(a) Sample D (b) Sample E (c) Sample F

Fig.3 SEM photographs of samples

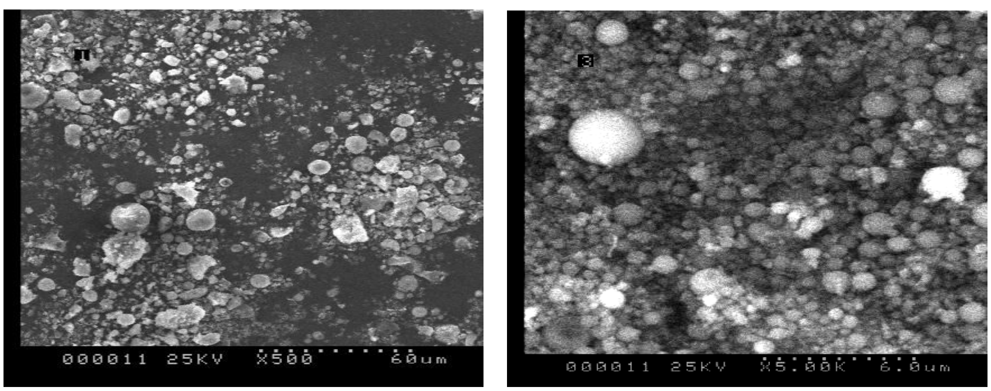
The micro-packing effect also reflected in the fashion of adding mineral particles filling in the suspended structures and occupying the space taken by water. Then the water is released to destruct the concrete paste [3].
This also be illustrated by the data in Table 2. The 28-day strength of samples D (with slag and fly ash) is 78.5 MPa that of sample E (slag and silica fume added) and that F (slag and metakaolin added) is 96.0 MPa, and 91.1MPa, respectively. Different mass and strength loss of the samples in anti-corrosion experiments has proved the viewpoint in another aspect. According the foregoing micro-packed standpoint of view, there are just the first and second filling action taking place in sample D, while all the three

level filling actions exist in sample E and sample F. It is clear that the structure of the latter is correspondingly denser than the former. The difference in packing style is reflected indirectly by the difference in the strength and durability.

4.3 Morphology Effect

The shape, surface flatness, and texture of additive minerals have great influence on the performances of the concrete, especially the fresh concrete. This is called the additive's "morphology effect".

Usually, the smaller the powder particle is, the larger the surface area is and the greater the admixture's water requirement to satisfy given workability. But the results of the experiment show that the slump constant of the mineral-containing samples have not reduced obviously compared to the reference samples. Some sample's slump constant is even superior to the reference samples. This is attributed to the active influence of the superfine mineral additive's "morphology effect".



(a) Fly ash (b) Silica fume

Fig.4 The SEM photographs of fly ash and silica fume

It can be seen that the fly ash particle (Fig.4 (a)) and silica fume particle (Fig.4 (b)) are round and slippery, so they can act as balls when mixed in the cement to improve the workability and service behavior.

4.4 Pozzolana Effect

The additive mineral's pozzolana effect is also one of the improvement causes of the concrete's intensity grade and durability. The additive minerals do not haven absolute hydration reaction. Its contribution to the strength of the concrete is based on the secondary hydration reaction taking place between the $Ca(OH)_2$ generated from the hydration of cement and the high alkalinity silicate. Fly ash partials have compact vitreous outer layer, so their secondary hydration action takes place relatively late. The documents [4] prove that superfine fly ash participates in the secondary hydration action after 14 days. The 28d testing strength of sample B shows that the fly ash's pozzolana activity was functioning then. The compressive strength of the concrete samples will increase for quite a long time. In sample D, fly ash was partially replaced with slag. As a result, the compressive strength was higher than that of sample B at the same ages. This was attributed to the larger amount of active CaO and Al_2O_3 existing in the slag that could produce more gel of hydrous calcium silicate and hydrous calcium aluminates at the early age.

Metakaolin is a kind of sintered clay materials with a strong hydration activity and it is called super pozzolana [5]. It is showed that the 7d compressive strength of sample F was higher, and their 28d strength was also relatively higher.

4.5 Durability Improving Effect of the Additive Minerals

It is seen in Fig.4 and Fig.5 that the mass loss and strength loss of sample E is the least. Many investigations indicate that superfine flag and silica fume are beneficial to gelatinization mineral to confect HPC. They can form ternary composite gelatinization mineral with cement and enhance the

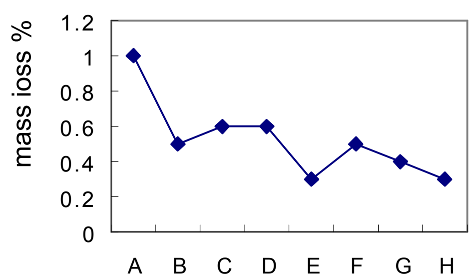


Fig.4 Mass loss of the samples

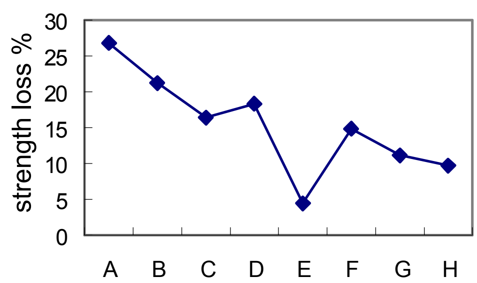


Fig.5 Strength loss of the samples

strength and performances of the concrete. Samples G and H (containing three kinds of additive minerals) has high conservation rate of mass and strength. It incarnates the superiority of adding more than one kind of mineral into the concrete.

5. Conclusions

1 When the mixture of slag and silica fume or mixture of slag and metakaolin were used as active minerals additives replace cement, the resultant 28-day compressive strength of the sample was above 90.0 MPa at the equivalent substitute level of 40%.

2 Adding complex additive minerals increased the amount of hydrated gel, improved its quality, and reduced the amount of the $Ca(OH)_2$ produced from the hydrated cement. As a result, this enhanced the compactness of the concrete and improved the anti-corrosion property of the concrete.

(3) Adding two or three mineral additives could bring about a supplementary effect in their superiority. The integrated functions of enhancement effect, micro-packing effect, morphology effect, and pozzolana effect of the mineral additives lead to a significant improvement in the performance of the concrete.

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