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Analysis of mechanism on water-reducing effect of fine ground slag, high-calcium fly ash, and low-calcium fly ash

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Abstract

The addition of ultrafine powder (UFP) to concrete can improve the fluidity of concrete, showing a water-reducing effect. The aim of this article was to analyze the water-reducing mechanism of UFP both experimentally and theoretically. Three UFPs—fine ground slag, high-calcium fly ash, and low-calcium fly ash—were chosen for the study. The contrastive experiments were done to investigate the fluidity of mortars with 30%, 45%, 60%, and 75% equivalent cement replaced by fine ground slag, high-calcium fly ash, and low-calcium fly ash, respectively. The results showed the physical and chemical characteristic of the powders, such as their grain morphology, glass phase activities, densities, specific areas, and their grain cumulating conditions, can strongly affect their water-reducing effect.

Keywords: Workability; Admixture; Cement paste; Fly ash; Granulated blast-furnace slag

1. Introduction

The environmental protection and cost-effective considerations bring about the era of using the industrial by-products such as fly ash and blast furnace slag in concrete. In recent years, ultrafine powders (UFPs) of fly ash and slag even become necessary ingredients of high-performance concrete. The main reason for this is that the properties of concrete can be greatly improved by incorporating these UFPs in concrete. Because of this, more and more investigations have been made in the area of studying their effects on concrete.

Most investigators reported that adding UFPs to concrete could effectively improve the properties of hardened concrete. Investigations also show that the addition of fly ash can increase the fluidity of fresh concrete, representing the water-reducing effect [1–3]. Fine ground slag, when used together with superplasticizer, can also represent the water-reducing effect, which is termed as *aided water-reducing effect* [4–7].

Previous studies concentrated on the effects of UFPs on the fluidity of concrete. Although many studies have been performed, little analysis has been made concerning the mechanism of the effects.

The purpose of this study was to analyze the mechanism of water-reducing effect of UFPs on fresh concrete. The water-reducing effect of three UFPs—ground slag powder, high-calcium fly ash, and ultrafine low-calcium fly ash—has been systematically investigated in this article. Their different water-reducing mechanisms were analyzed based on their characteristics such as grain morphology, activity of volcanic glass, density, specific area, and grain cumulating condition.

2. Experimental materials and methods

2.1. Materials

The materials used in this investigation were a 42.5R grade Portland cement, a fine ground blast furnace slag, a high low-calcium fly ash, and a high-calcium fly ash. Their physical properties are listed in Table 1. An XP-2-type water-reducing agency with 20% water-reducing ratio was applied. A natural river sand with fineness modulus of 2.72 and apparent density of 2.63 g/cm^3 was selected.

2.2. Experimental methods

A JSM-6300 model of scanning microscope was used to observe the grain morphology of materials. A JL-1155 model

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Table 1
Characteristics of cement and UFPs

Characteristics	Cement	Fine ground slag	High-calcium fly ash	Low-calcium fly ash
Density (g/cm^3)	3.18	2.91	2.66	2.55
Specific area (cm^3/g)	4168	4620	5860	6910
Bulb density (g/cm^3)	1.101	0.932	0.9	0.741
Ratio of water requirement (%)	–	100	89.1	84.8
Specific surface mean diameter (μm)	15.32	14.81	12.88	12.33

of laser granulometer was applied to determine the distribution of grain size. The specific surface mean diameter of particles was calculated according to the methods given in Ref. [8]. The glassy structure of fine ground slag, high-calcium fly ash, and low-calcium fly ash is determined by the XRD.

Two methods were used to determine the water-reducing effects of different UFPs. One was to measure the water requirement of standard pastes with UFP [5]. The lesser the water requirement, the better the water-reducing effect. The other was to measure the required superplasticizer dosage of mortars with the same water-to-binder ratio and similar flow [4]. The lesser the dosage, the higher the water-reducing effect. In this study, the mortars were prepared at a water-to-binder ratio of 0.26 and sand-to-binder ratio of 1.5, with 30%, 45%, 60%, and 75% equivalent replacement of cement by fine ground slag, high-calcium fly ash, and low-calcium fly ash, respectively. The required dosage of superplasticizer was determined by testing mortars with similar water-to-binder ratio to obtain similar flows.

3. Experimental result

3.1. Water requirement of standard pastes

Fig. 1 shows the water requirements of standard pastes of the UFPs. It can be seen that without superplasticizer, only low-calcium fly ash progressively decreases in water requirement with increased percentages of replacement. High-calcium fly ash can reduce some water under 35% replacement. However, if the replacement surpasses 35%, the water requirement increases. Fine ground slag has no water-reducing ability in the absence of superplasticizer, which is consistent with the previous experimental result showed in Ref. [4].

3.2. The dosage of superplasticizer required in mortars

It is shown in Fig. 2 that compared with mortars without the powders, the dosage of superplasticizer required in mortars with the UFPs decreased to some extent. The decreasing rate is related to what kind of UFP is added and how much it is added. When the replacement is under 30%, as the rates increase, there is a great decrease in the dosage of superplasticizer. When the replacement is between 30% and 45%, the dosage can be decreased continuously for high- and low-calcium fly ash, and the reduction of low-calcium fly ash is less than high-calcium fly ash. However, the dosage of fine ground slag increased a little. When the replacement is increased from 45% to 60%, the dosage can still be reduced for high-calcium fly ash, with a slower degree. However, there is a great increase in the dosage for low-calcium fly ash since the 45% of replacement, and the dosage of fine ground slag continuously increases slowly. When the replacement is increased from 60% to 75%, the dosage can still be decreased for high-calcium fly ash, but increased tremendously for low-calcium fly ash, and cannot be increased anymore for fine ground slag.

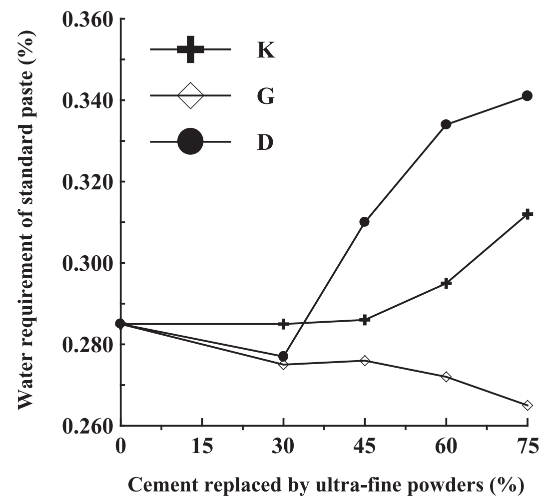

Fig. 1. Relation between the water requirement of standard paste and cement replacement.

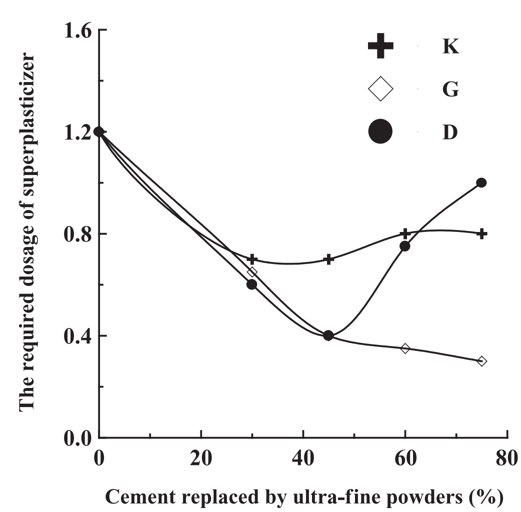

Fig. 2. Relation between the required dosage of superplasticizer in mortars and cement replacement.

It was found out in the experiment that mortars with more than 60% of low-calcium fly ash replacement are very dry and hard to mold. After vibration, the fluidity of mortars can be obtained, but the mortars are sticky and their setting times are prolonged. Mortars with fine ground slag replacement of more than 60% is also dry and not so sticky after vibration, but obvious bleeding and air entrainment occurred, even at a lower percentage of replacement. As for high- and low-calcium fly ash, no similar cases occurred.

4. Analyses

4.1. Influence of particle morphology and volcanic glass activity of the UFPs on water-reducing effect

Fig. 3 illustrates the particle morphology of high-calcium fly ash, low-calcium fly ash, and fine ground slag. It can be seen that the particles of high- and low-calcium fly ash are spherical and will roll in fresh paste, which can reduce the fraction resistance of cement particles and improve the fluidity of the mixture. However, the water-reducing effect of high-calcium fly ash is better than low-calcium fly ash because of their different volcanic glass activity. It is shown from the XRD results (Fig. 4) that high-calcium fly ash and fine ground slag have similar glass structure, which has a higher activity and accordingly a faster surface protonization and a weaker ability to absorb water [6]. It is not easy for this structure to disperse itself and make a lower filling and deflocculating effect. The effect means ground powder, whose particles are smaller than those of cement, can fill in the voids between cement particles and in the flocculated structure to release water restrained on the structure and improve the fluidity. The glass structure of fine ground slag is similar to high-calcium fly ash, but because its particles are not spherical, they are easy to agglomerate after being mixed with water but not easy to fill in the space in cement paste, so it is difficult for the filling and deflocculating effect to take place. Only when proper superplasticizer is used to make the powder particles absorb molecules of superplasticizer and form the electrical double layer in its surface can the effect occurred.

4.2. Influence of density difference of UFPs on water-reducing effect

It is shown from Table 1 that the density of both fly ash and fine ground slag is smaller than that of cement. When

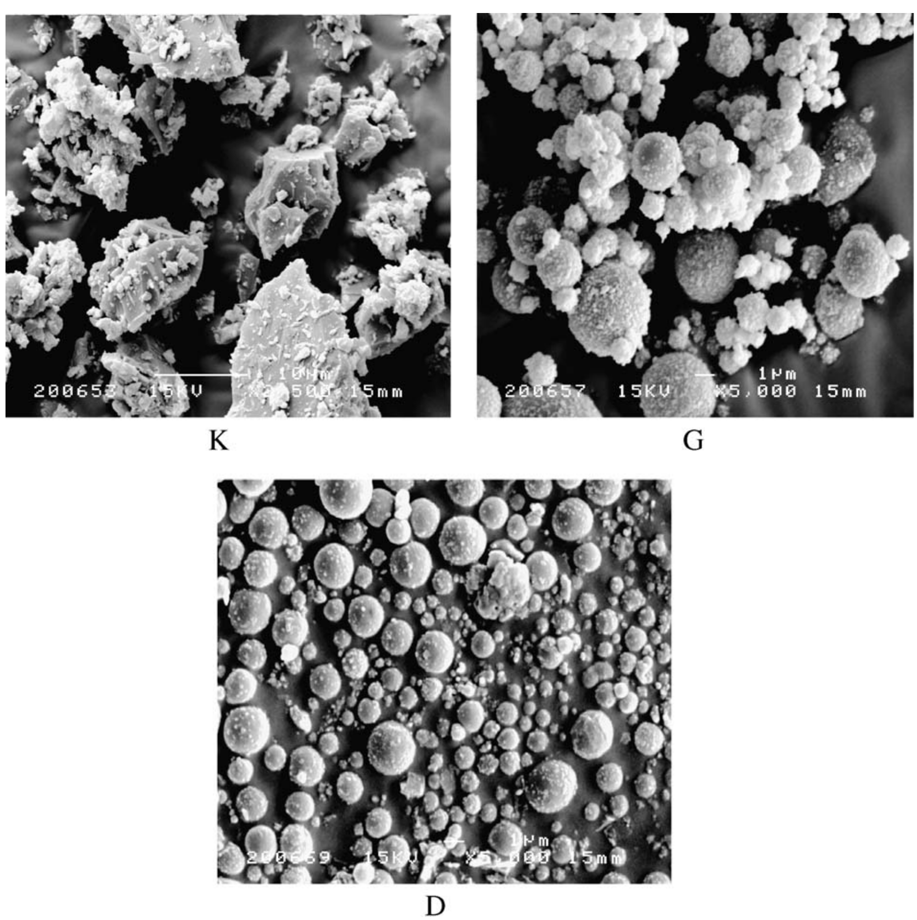

Fig. 3. The grain morphology of the UFPs shown by S.E.M.

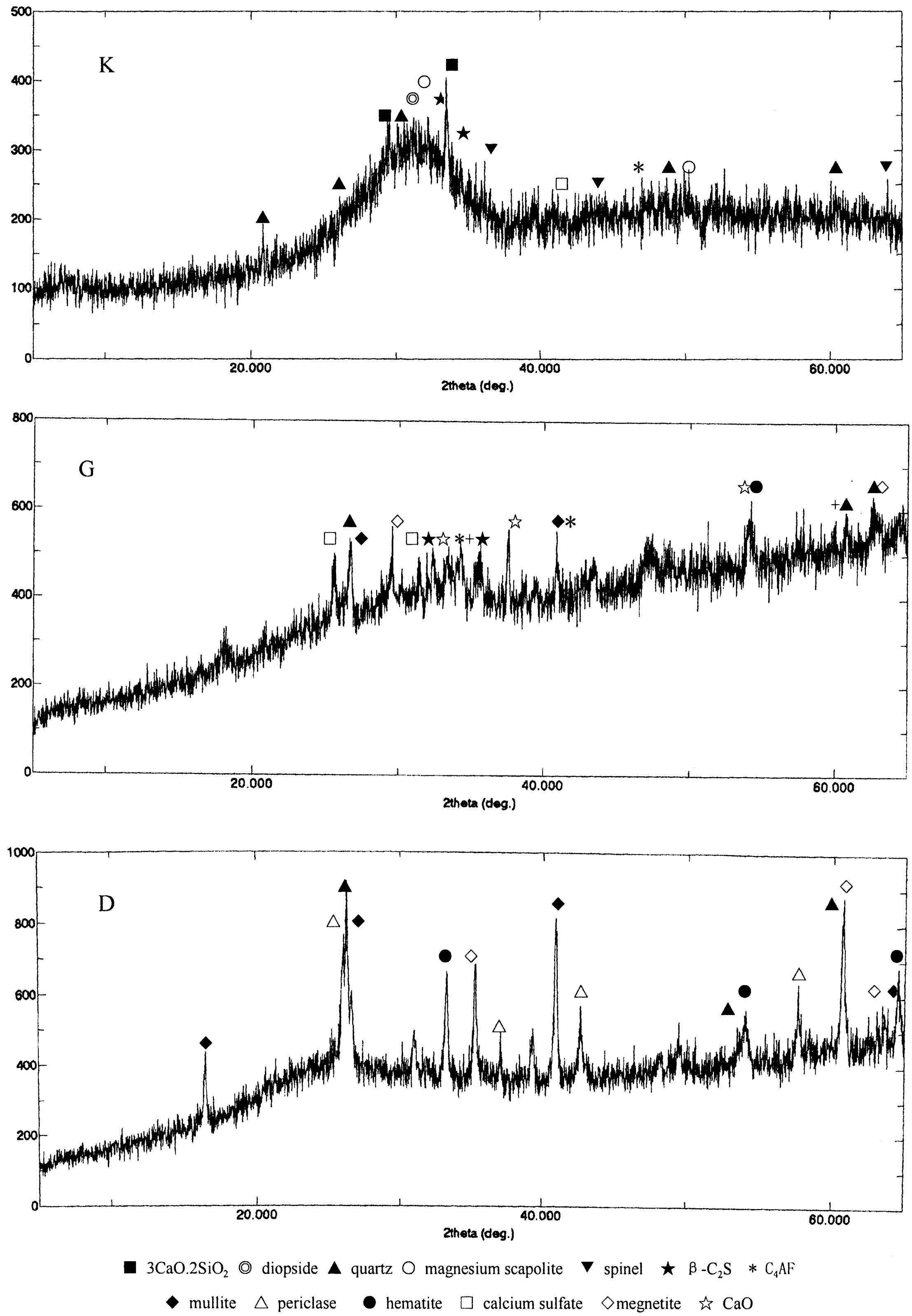

Fig. 4. The XRD spectrogram of the UFPs.

cement is equivalently replaced by UFP, the volume of solid phase with the same mass will be increased, and the water content will be decreased in fresh mortar with similar volume. In terms of Refs. [9,10], water in fresh paste is divided into two parts. One is filling water existing in the space between solid particles, which is a fraction of fresh paste and has little effect on the fluidity of fresh paste. The other is the surface water lying around the particles, which is divided into the absorbed water on the surface of particles and the film water outside the surface. Only the film water influences the fluidity of the mortar, and the thicker the film, the more fluid the mortar will be. In our opinion, when the content of solids and water in the mortar with fly ash or fine ground slag replacement of cement is kept constant, there will be additional film water in the mix, which is termed *free water*. Under the effect of free water, the cohesiveness of the paste was improved, the fluidity increased, and the dosage of superplasticizer decreased.

Take 1 m^3 fresh paste with water-to-cement of 0.3 as an example to explain the existence of the free water (the water-to-cement ratio is selected so as to be able to mix well without the addition of superplasticizer). The wet apparent density of the paste is 2115 kg/m^3, so the 1-m^3 paste contains 1627 kg of cement and 488 kg of water. When some cement is replaced by UFP, the volume of the paste will be more than 1 m^3. The difference in the volume before and after the replacement is the volume of free water. Fig. 5 shows a theoretically calculated result of the free water caused by density variation among the powders and cement. It is shown that the volume of free water is increased as the replacement increased. The increase of free water of low-calcium fly ash is maximal because of its least density, next to it are high-calcium fly ash and fine ground slag in turns. The fluidity increases are in the same order. But it is observed that when the replacement is more than 60%, mortars with low-calcium fly ash and fine ground slag replacement are dry, and they become sticky after vibration, especially that with low-calcium fly ash. It shows that in this case the free water calculated theoretically does not exist anymore. It has been changed because of other negative influences.

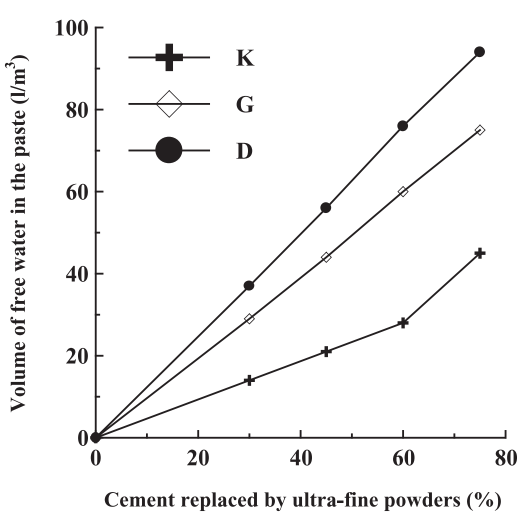

Fig. 5. Relation between the volume of the free water and cement replacement.

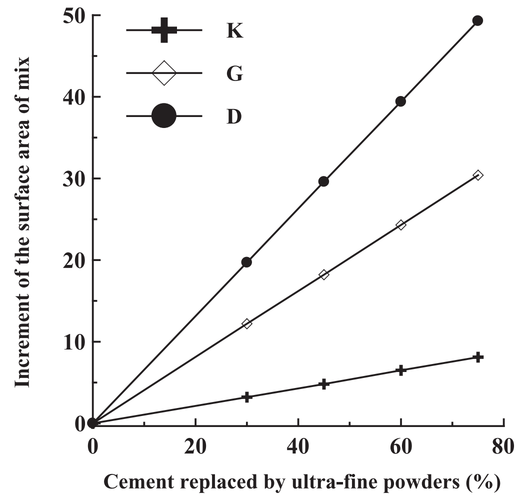

Fig. 6. Relation between the increment of the surface areas of the mixes and cement replacement.

4.3. Influence of specific areas of UFPs on water-reducing effect

The specific areas of fine ground slag, high-calcium fly ash, and especially low-calcium fly ash are larger than that of cement. With UFPs substituting for some cement, the specific areas of the mix will be increased. This means the increase of the surface absorbed water. In the case of a fixed water content in the mortar, the free water will turn into surface water, which will reduce the fluidity of the paste. The increment of surface areas of the mix can be calculated in terms of the following formulation:

$$\Delta s = \frac{(s_f - s_c)x}{s_c} \qquad (1)$$

where Δs is the increment of surface areas of the mix, s_f and s_c are the specific areas of the powder and cement, respectively, and x is the powder replacement (%). The calculations are shown in Fig. 6. It can be seen that with the UFP replacing some cement, the specific areas of the mixes increased to some extent. The increment of low-calcium fly ash is the highest, so that free water in the mortar is changed into absorbed water and the fluidity of the paste is decreased. The increment of high-calcium fly ash is next to that of low-calcium fly ash, but the water-reducing effect of high-calcium fly ash is not so evident because of its weak ability of absorbing water. The effect of the specific area of fine ground slag on the fluidity is not stronger because of its lowest increment of specific area as well as its weak ability in absorbing water.

4.4. Influence of heap density of the UFPs on water-reducing effect

Free water can also be changed into filling water. This depends on the void variation of the mix after the cement being replaced by UFP. If the void is increased, the free water will turn into filling water, which is an ingredient of the fresh paste and has no influence on fluidity.

The void ratio ε of a mix can be calculated as follows:

$$\varepsilon = \left(1 - \frac{\varphi}{\rho}\right)100\% \quad (2)$$

where φ represents the bulb density of a mix of two-phase system, which can be calculated by Eq. (3) in terms of Toufar model [11] as the model is applied to the mix with average diameter ratio larger than 0.22, which is the case in our study (see Table 1).

$$\varphi = \frac{1}{\frac{r_1}{\varphi_1} + \frac{r_2}{\varphi_2} - r_2\left[\frac{1}{\varphi_2} - 1\right]\frac{d_2 - d_1}{d_1 + d_2}\left\{1 - \frac{1 + 4\frac{r_1}{r_2}\frac{\varphi_2}{\varphi_1(1-\varphi_2)}}{\left[1 + \frac{r_1}{r_2}\frac{\varphi_2}{\varphi_1(1-\varphi_2)}\right]}\right\}} \quad (3)$$

In Eq. (3), r_1 and r_2 are the volume fractions, d_1 and d_2 are the diameters, φ_1 and φ_2 are the bulb densities of the larger and smaller particles of the mix, respectively.

The density of the mix ρ can be calculated as follows:

$$\rho = r_1\rho_1 + r_2\rho_2 \quad (4)$$

where ρ_1 and ρ_2 are the densities of the larger and smaller particles, respectively, and r_1 and r_2 are similar to those in Eq. (3).

Fig. 7 shows the calculating results of the bulb density of the mix at different rate of replacement. It is shown that the bulb density decreased to some extent as the replacement increased, which corresponds to the actual case quite well.

Fig. 8 shows the calculation result of the void of the mixes with UFP replacement of cement. It is shown that the void ratio of the mix increased as the replacement increased, except for high-calcium fly ash at a replacement smaller than 30%. The increased magnitude of void ratio is different, which is smaller for high-calcium fly ash, not so much for fine ground slag and amplified for low-calcium fly ash. The increasing void ratio means that more filling water and more superplasticizer are needed to obtain the same fluidity of paste with a constant water content. This coincides with the experimental result. It is also shown that the Toufar model can be used to calculate the void ratio of a mix and determine the effect of the powder replacement on the fluidity of fresh cementitious materials.

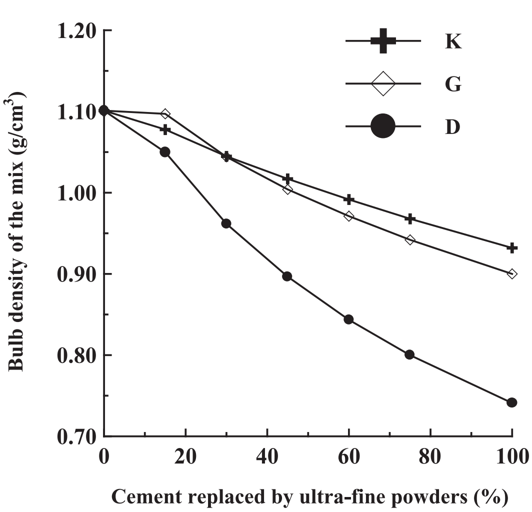

Fig. 7. Relation between the bulb density of the mixes and cement replacement.

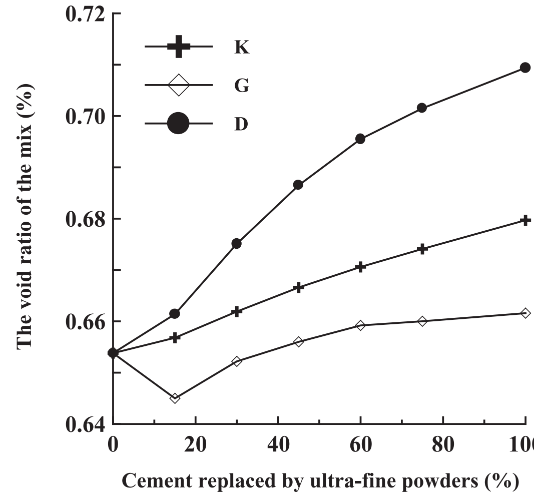

Fig. 8. Relation between the voids ratio of the mixes and cement replacement by UFPs.

5. Conclusions

1. The physical and chemical characteristics of the UFPs, such as the grain morphology, volcanic glass structure, density, specific area, and grain diameter, have great influence on the water-reducing effect of mixes. They affect the existing conditions of water in the mixes.
2. The water-reducing effect of high-calcium fly ash is increased with its increased replacement. Its effect is superior to other powders even without the addition of admixtures. The lubricating effect of its spherical particles is the main reason. The lower absorption of its high active particles also plays a part, which makes free water caused by the density variation between high-calcium fly ash and cement turn into surface absorbing water as its specific area is larger than that of cement. The little increase of void ratio before and after the replacement assured that the free water could not change into filling water.
3. The water-reducing effect of low-calcium fly ash is obvious at the lower replacement. Again, the lubricating effect of its spherical particles plays an important role. However, because of its lower activity of volcanic glass, its particles absorb water strongly. The specific areas of the system will be increased at the higher replacement, and the void ratio of the system will also be increased. In this case, the free water caused by the density difference

of low-calcium fly ash and cement will change into the surface absorbing water and filling water. The water-reducing effect is decreased consequently.

4. The water-reducing effect of high-calcium fly ash is less in the absence of admixtures, although its activity of volcanic glass is high enough to absorb water. Unlike fly ash whose particles are spherical, high-calcium fly ash's particles are with edges and corners and are not easy to disperse. However, when it is used together with admixtures, the water-reducing effect occurs. This is because its particles absorb the molecules of admixture to form double electrical layer and keep their particles apart. Since the specific area, void rate, and free water content change little before and after the replacement, the effect decreases slowly with the increase of its replacement.

Acknowledgements

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