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Fly ash effects: I. The morphological effect of fly ash

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Abstract

The morphological effect is an important part of fly ash effects. The paper analyzes emphatically this effect and points out that it is composed of the filling role, surface role and lubricating role. For different fly ash, these roles are different. They must be considered synthetically when the morphological effect is analyzed. Analyzing result shows that the filling role is relative to the particle size, the surface role is relative to the specific surface area and the water affinity and the lubricating role is relative to the shape of particle. The morphological effect of fly ash is the synthetical embodiment of these roles.

Keywords: Fly ash; Cement; Workability

1. Introduction

It has been above 70 years to research and use fly ash. With its application, the action mechanism of fly ash had been recognized. During the initial stage, only its pozzolanic activity is paid attention [1,2]. Many researchers devoted themselves to the research of the potential activity of fly ash and the hydration process of fly ash cement. With the deepening of the cognition for fly ash properties, some people found that the particles of fly ash have the morphology that is different to other pozzolanic materials. It is the unique particle morphology to make it have the ability reducing water, which other pozzolanic materials do not have [3–6]. It influences not only the rheological property of fresh mortar but also the initial structure of hardened cement stone. In the end of 1970s, Jan de Zeeuw and Abersch [7] put forward that the role of fly ash, which its particle size is less than 30 μm, may be similar to that of the microparticle of unhydrated cement in cement stone. In 1981, Danshen and Yinji [8] and Danshen [9] summarized the previous research results and put forward the hypothesis of "fly ash effects." They considered that fly ash has three effects in concrete, i.e., morphological, activated and microaggregate effects. The three effects are relative each other. This shows that the morphological effect is the important aspect of fly ash effects. In this paper, it will be discussed emphatically. The activated and microaggregate effects will be analyzed in other papers.

The morphological effect means that in concrete, mineral-powdered materials produce the effect due to the morphology, structure and surface property of the particle and the particle size distribution. From the influence of fly ash on the properties of cement-based materials, the morphology effect includes three aspects: filling, lubricating and well distributing. These roles depend on the shape, size distribution, etc., of fly ash and influence many properties of concrete.

2. Theoretical analysis

Before water is added, however close the solid particles are, there is always some space in the system. After water is added, a part of water is filled into these spaces, which is called as filling water. Other water forms the layer of water on the surface of the solid particle, which is called as the layer water. Because of the adsorption of the solid surface to water molecule, the part of water that is closer to the surface of solid will be restrained by solid particle and is not able to move freely. The water may be called as the

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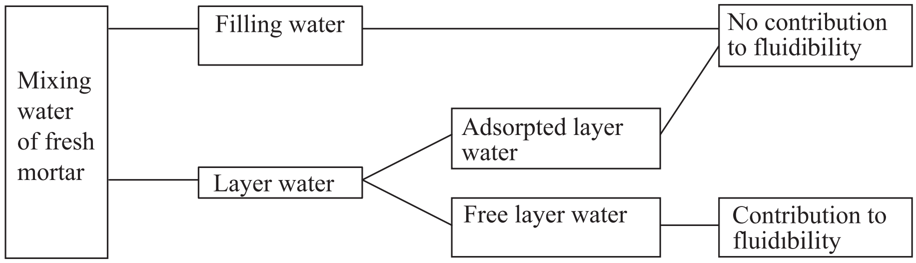

Fig. 1. The model of water action and their contribution to fluidibility.

adsorpted layer water. The layer water that is not restrained by solid particle is called as the free layer water. Mixing water is the sum of filling water, adsorpted layer water and free layer water.

In the flow process of fresh mortar, filling water does not contribute to the fluidibility because it only fills in the space and cannot make the particles separate to decrease the moving resistance of particle. Of course, the filling water is able to move freely, but the fluidity of fresh paste means that cement particles move with water under the action of water. If only the water moves but the cement particle does not, it is not the fluidity of cement paste but the separation. When fresh mortar flows, adsorpted layer water moves with solid particle. It shows the property that a solid has. Thus, it does not contribute to the fluidibility too. In fact, this water can be exchanged with other in cement paste. This is a dynamic balance. As a part, the adsorbed layer water does not contribute to fluidity. But for any molecule of water, it is uncertain because it may be in the adsorbed layer or the free layer. It can be seen from these that only free layer water contributes to the fluidibility. In the flow process, free layer water makes the particles separate each other. The effort between particles decreases. Thus, if the shape of solid particles is not considered, in a certain degree, the thicker the free water layer, the better the fluidibility is. Fig. 1 shows the model of water action and their contribution to the fluidibility.

In fresh mortar, the amount of filling water depends on the packing density of system. The higher the packing density, the less the filling water is. The amount of adsorpted layer water depends on the specific surface area and surface property of solid particles. It is the product of the specific surface area and the thickness of the adsorpted layer. The thickness of adsorpted layer depends on the water affinity of solid particles. The thickness of free water layer depends on the amount of free layer water and the specific surface of solid particles. Under the condition of same amount of free layer water, the larger the specific surface of solid particles, the thinner the free water layer is. Of course, the increase of the amount of free layer water will increase the thickness free water layer.

The particle of fly ash is different from one of cement in particle size, specific surface and particle shape. They will influence the distribution of various of water in fresh mortar. This is the essential reason of the influence of the morphological effect on the fluidibility of fresh mortar.

3. Experiment and results

3.1. Experiment

To research the morphological effect, four sorts of fly ash are used. Fly ash A comes from Pingwei power plant, fly ash B comes from Nanjing power plant and fly ash C and D come from Zhenjiang power plant. Fly ash C is separated by air classification, but fly ash D is obtained by milling. They have the same specific surface and average size. For fly ash A, B and C, SEM results are similar. The particle is mainly spherical shape. In the experiment, Portland cement is used. Table 1 gives the specific surface and the average size of the cement and fly ash. The specific surface is measured by Blaine apparatus. The average particle size of cement and fly ash is calculated by the particle size distribution. It can be

Table 1
The specific surface and the average size of cement and fly ash

Name	Specific surface (cm^2/g)	Average size (μm)	Loss on ignition (%)	Percentage of < 80 μm (%)
Portland cement	3837	14.38	1.18	1.53
Fly ash A	5450	7.22	3.04	0.86
Fly ash B	4220	9.14	0.72	0.75
Fly ash C	4152	10.85	3.46	1.37
Fly ash D	4056	11.13	3.73	1.44

Table 2
Without superplasticizer, the influence of the content of fly ash on water demand of mortar

The content of fly ash (%)	0	10	20	30	40	50	60
Fly ash A	0.460	0.417	0.400	0.387	0.377	0.370	0.363
Fly ash B	0.460	0.433	0.427	0.420	0.413	0.407	0.400
Fly ash C	0.460	0.443	0.433	–	0.440	–	0.450

The content of fly ash means the percentage replacing cement. The number in the table is water/binder.

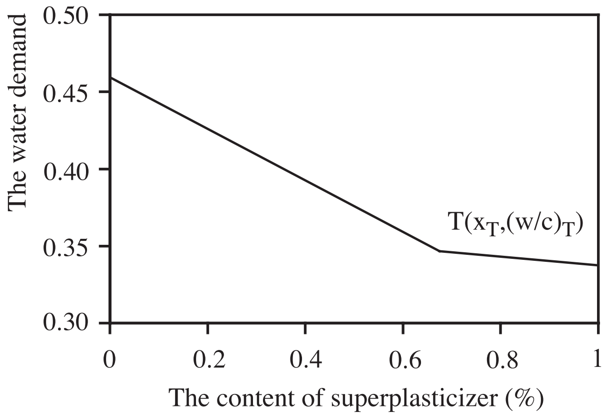

Fig. 2. The diagram of the relationship between the water demand and the content of superplasticizer.

seen from Table 1 that fly ash A is finer and fly ash C is coarser.

The ratio of cementing material (cement + fly ash) and sand is 1:2.5. The workability of mortar is controlled within 130 ± 5 mm. The method for measuring the workability is the spreading on the table.

The research includes three aspects: (1) without superplasticizer, the influence of the content of fly ash on the water demand of mortar; (2) under the action of superplasticizer, the influence of the content of fly ash on the water demand of mortar; and (3) the difference between separating fly ash and milling fly ash in the influence on the water demand of mortar.

3.2. Results

3.2.1. Without superplasticizer, the influence of the content of fly ash on the water demand of mortar

Table 2 shows the experimental results of the workability of mortar. It may be seen that the influence of different fly ash on the water demand of mortar is different. Fly ash A has stronger ability reducing water. The ability reducing water of fly ash B is weaker than that of fly ash A. For fly ash B, it has a very weak ability reducing water only when the content of fly ash is less and has not the ability reducing water when the content of fly ash is more.

Table 3
The relationship between the optimum content of superplasticizer and the content of fly ash

The content of fly ash (%)	Fly ash A	Fly ash C
0	0.65	0.65
10	0.74	0.70
20	0.84	0.78
30	0.90	0.80
40	0.97	0.84
50	1.03	–
60	1.10	0.90

Table 4
The relationship between the lowest water demand and the content of fly ash

The content of fly ash (%)	Fly ash A	Fly ash C
0	0.350	0.350
10	0.313	0.330
20	0.300	0.330
30	0.293	0.340
40	0.290	0.340
50	0.267	–
60	0.263	0.340

3.2.2. Under the action of superplasticizer, the influence of the content of fly ash on the water demand of mortar

It is known well that to add superplasticizer may reduce markedly the water demand of mortar, but the influence is different for with or without fly ash. To explain clearly the difference, the diagram of the relationship between the water demand and the content of superplasticizer is given in Fig. 2. Normally, there is a turning point T on the relation curve. When the content of superplasticizer is less than X_T, the water demand of mortar will decrease markedly with the increase of the content of superplasticizer. When the content of superplasticizer is larger than X_T, the change of the water demand with the increase of the content of superplasticizer is very little. In other words, if the content of superplasticizer is over X_T, to increase superplasticizer cannot reduce further the water demand of mortar. X_T is called as the optimum content of superplasticizer, and $(w/c)_T$ is called as the lowest water/cementing ratio. The sort and content of fly ash will influence both X_T and $(w/c)_T$.

Table 3 shows the relationship between the optimum content of superplasticizer (X_T) and the content of fly ash. Obviously, the optimum content of superplasticizer (X_T) increases with the increase of the content of fly ash. This influence is more marked for fly ash A than fly ash C.

Table 4 is the relationship between the lowest $(w/c)_T$ and the content of fly ash. For fly ash A, $(w/c)_T$ reduces markedly with the increase of fly ash, but it is not marked for fly ash C.

3.2.3. The difference between separating fly ash and milling fly ash in the influence on the water demand of mortar

Table 5 shows the comparison between milling fly ash and separating fly ash. Although their average particle size and specific surface are very close, they are different in the influence on the water demand of mortar. Milling fly ash cannot decrease markedly the water demand. Reversely, the water demand will increase when its content is larger.

Table 5
The comparison of water demand between milling fly ash and separating fly ash

The content of fly ash (%)	0	10	20	40	60
Milling fly ash	0.460	0.450	0.450	0.460	0.490
Separating fly ash	0.460	0.443	0.433	0.440	0.450

4. Analysis and discussion

It has been seen clearly from experimental results that the influence of fly ash on the water demand is different for different fly ash and the different content of fly ash. Why is there so large difference? It is due to the difference in particle size, specific surface and particle shape. It may be seen from Table 1 that the average particle size of fly ash is smaller than one of cement, and the specific surface of fly ash is large than one of cement. The smaller particles of fly ash may fill in the space of bigger cement particles. Thus, it may decrease the filling water. Because the specific surface of fly ash is larger than that of cement, to add fly ash will increase the layer water. Some researches have shown that the particles of fly ash are spherical. They correspond to some small ball and play a lubricating role in the flow process of mortar. Because different fly ash has different particle size, surface properties and shape, they have different effect on different part of water. It is the essential reason to cause the difference in the water demand.

To explain quantitatively this question, mixing water may be expressed as following equation:

$$w_{\mathrm{m}} = w_{\mathrm{f}} + w_{\mathrm{i}} - w_{\mathrm{l}} \tag{1}$$

Where w_{m}—the amount of mixing water; w_{f}—the amount of filling water; w_{i}—the amount of layer water; w_{l}—the amount of the water decrease by lubricating role.

The amount of filling water depends on the packing density of system. According to Aïm and Goff's model [10], for a binary system, there is a maximum packing density. The volume fraction (y_{f}*) of fly ash particles that furnishes the mixture with the maximum packing density may be calculated from the following equation:

$$y_{\mathrm{f}}^* = \frac{1-(1+0.9d_{\mathrm{f}}/d_{\mathrm{c}})(1-\varepsilon_0)}{2-(1+0.9d_{\mathrm{f}}/d_{\mathrm{c}})(1-\varepsilon_0)} \tag{2}$$

When $y_{\mathrm{f}} < y_{\mathrm{f}}^*$, ϕ, the packing density of system may be calculated from the following equation:

$$\phi = \frac{1-\varepsilon_0}{1-y_{\mathrm{f}}} \tag{3}$$

When $y_{\mathrm{f}} > y_{\mathrm{f}}^*$, ϕ may be calculated from the following equation:

$$\phi = \frac{1-\varepsilon_0}{y_{\mathrm{f}} + (1-y_{\mathrm{f}})(1+0.9d_{\mathrm{f}}/d_{\mathrm{c}})(1-\varepsilon_0)} \tag{4}$$

Where d_{f}—average diameter of fly ash particle; d_{c}—average diameter of cement particle; y_{f}—volume fraction of fly ash particle; ε_0—void ratio when there is only one kind of particle.

According to the packing density, filling water may be calculated. For 1 g cementing material, the amount of filling water is:

$$w_{\mathrm{f}} = \left(\frac{1-x}{\rho_{\mathrm{c}}} + \frac{x}{\rho_{\mathrm{f}}}\right)\frac{1-\phi}{\phi}\rho_{\mathrm{w}} \tag{5}$$

Where x—the content of fly ash (%); ρ_{c}—the density of cement (g/cm^3); ρ_{f}—the density of fly ash (g/cm^3); ρ_{w}—the density of water (g/cm^3).

Fig. 3 shows the influence of the content of fly ash on the amount of filling water. It can be seen from the figure that to add fly ash A may decrease the amount of filling water when its content is less than 45% but may increase the amount of filling water when its content is more than 45%. To add fly ash B may decrease the amount of filling water when its content is less than 30% but may increase the amount of filling water when its content is more than 30%. To add fly ash C and fly ash D cannot decrease the amount of filling water.

The amount of layer water depends on the surface area of cementing material and the thickness of water film layer. Thus,

$$w_{\mathrm{i}} = [(1-x)S_{\mathrm{c}} + xS_{\mathrm{f}}]\delta\rho_{\mathrm{w}} \tag{6}$$

Where S_{c}—the specific surface of cement (cm^2/g); S_{f}—the specific surface of fly ash, (cm^2/g); δ—the thickness of water film layer (cm).

w_{l} depends on the content of fly ash, It may be expressed as:

$$w_{\mathrm{l}} = kx \tag{7}$$

Where: k—the coefficient of lubricating role.

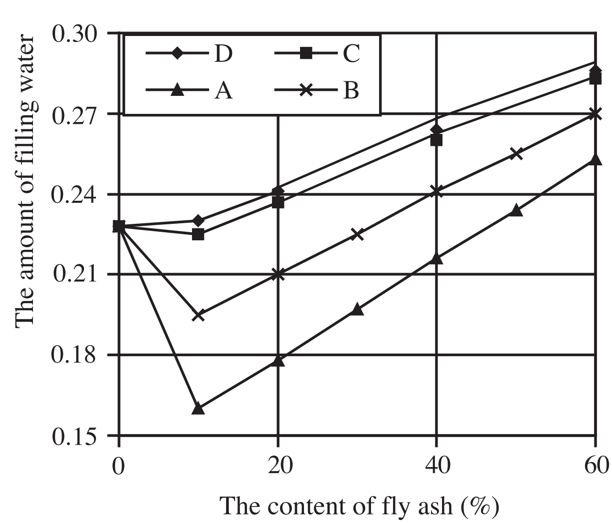

Fig. 3. The influence of the content of fly ash on the amount of filling water.

Thus, following equation can be obtained:

$$w_m = w_f + [(1-x)S_c + xS_f]\delta\rho_w - kx$$

$$\text{or } w_m - w_f = S_c\rho_w\delta + [(S_f - S_c)\rho_w\delta - k]x \tag{8}$$

It may be seen from Eq. (8) that the relationship between $w_m - w_f$ and x is linear, i.e.,

$$w_m - w_f = a + bx \tag{9}$$

Where:

$$a = S_c\rho_w\delta \tag{10}$$

$$b = (S_f - S_c)\rho_w\delta - k \tag{11}$$

Fig. 4 gives the results that are obtained by regression analysis. It may be seen that the linear relationship between $w_m - w_f$ and x is true. All related coefficients are more than .9. According to the regression coefficients, δ and k can be solved by Eqs. (10) and (11). The calculated results are given in Table 6. It can be seen that the difference between different fly ash is less for δ but larger for k. This shows that these fly ash have similar surface property, but they are different in the shape and size of the particle. The lubrication role of fly ash depends on not only the shape of particle but also the number of particle. The number of particle for per gram fly ash can be calculated by the average size of particle. It is about 2.31×10^9 for fly ash A, 1.14×10^9 for fly ash B and 0.68×10^9 for fly ash C. Fly ash A has more and smaller spherical particle. They disperse around cement particle and make cement particle be easy to move. Thus, the lubrication role of fly ash A is stronger. Reversely, the lubrication role of fly ash C is weaker. For milling fly ash, the particles are broken in milling process and change into irregular particles. These particles do not have lubrication role. Thus, k closes to 0.

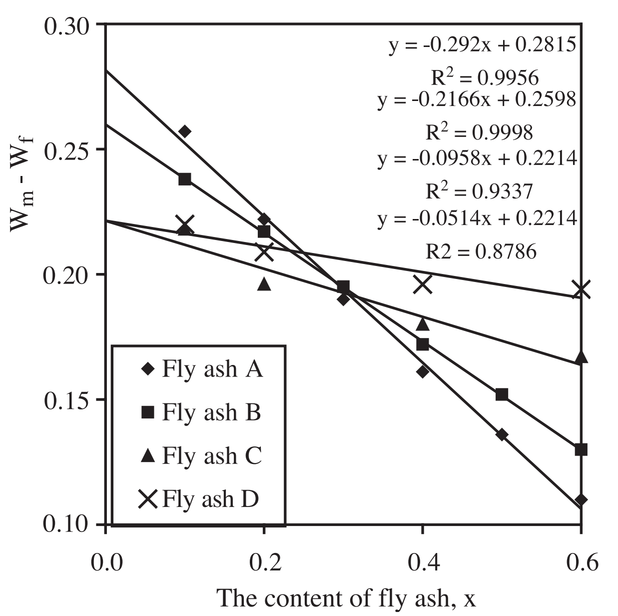

Fig. 4. The results that are obtained by regression analysis for different fly ash.

Table 6
δ and k of different fly ash

Name of fly ash	δ (μm)	k
Fly ash A	0.7336	0.4103
Fly ash B	0.6771	0.2425
Fly ash C	0.5770	0.1140
Fly ash D	0.5770	0.0640

Fig. 5 shows the results of regression analysis with or without superplasticizer. Fly ash A is used. δ and k are given in Table 7. The results show that the influence of superplasticizer on k is less but its influence on δ is very more. The molecule of superplasticizer adsorbs on the surface of solid particles. It makes the surface change from water affinity into water repellency to decrease adsorpted layer water. The optimum content of superplasticizer means the minimum amount of superplasticizer that the molecule of superplasticizer can cover all surfaces of the particles of cementing material. Because the specific surface area of fly ash is larger than one of cement, the total surface area of the system is increased when cement is replaced by fly ash. Thus, the optimum content of superplasticizer will increase too. Because the surfaces of solid particles have been water repelled after superplasticizer is added, it does not adsorptive water. Under this condition, the layer water is free layer and δ is the thickness of free water layer. For fly ash A, if the workability of the mortar with 1:2.5 cementing/sand ratio is 130 ± 5 mm, the total thickness of layer water is about 0.7336 μm and the thickness of free water layer is about 0.4673 μm. Thus, the thickness of adsorbed water layer is about 0.2663 μm.

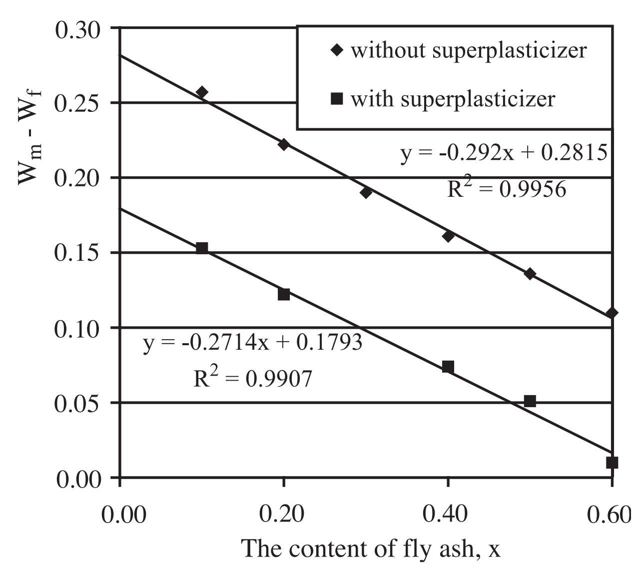

Fig. 5. The results of regression analysis with or without superplasticizer.

Table 7
δ and k without and with superplasticizer

	δ (μm)	k
Without superplasticizer	0.7336	0.4103
With superplasticizer	0.4673	0.3468

Table 8 gives the analyzed results of various water. For fly ash A and B, they have stronger filling role and weaker lubricating role when the content is less. When the content of fly ash is larger, they have no filling role but have stronger lubricating role. Although the layer water increases with the increase of the content of fly ash because the specific surface of fly ash, the water decreased by filling role and lubricating role can offset the influence. Silica fume is a very special pozzolanic material. It has very little particle size (about 0.1 ~ 0.2 μm) and very large specific surface area (about 100,000 ~ 200,000 cm^2/g). Its filling and lubricating roles are very strong, but its layer water is very more too. In general, the water decreased by its filling and lubricating roles is not enough to offset increased water due to the increase of surface area. Thus, to add silica fume will increase the water demand. If superplasticizer is added, it will decrease the water demand when cement is replaced partly by silica fume, but the content of superplasticizer must be larger [10].

It may be seen from the above analysis that the filling, lubricating and surface roles are three parts of the morphological effect. They are inseparable. They must be considered synthetically when the morphological of fly ash is analyzed. The fly ash with bigger particle, although it does not increase surface layer water, cannot reduce the water demand because its filling and lubricating roles are very weak. The fly ash with smaller particle may reduce the filling water and has stronger lubricating role, but it will increase the surface layer water too. To increase the content of superplasticizer may reduce effectively the surface layer water. It makes the morphological effect reflect fully.

The water demand will influence the initial structure of cement stone. Thus, it will influence the mechanics properties and durability. In view of this, the mechanics properties and durability of hardened cement stone are relative to the morphological effect of fly ash. However, the mechanics properties and durability are relative to its active effect and microaggregate effect too. Thus, they are not analyzed in the paper.

5. Conclusions

The morphological effect of fly ash is an important part of fly ash effects. It includes three aspects: filling role, surface role and lubricating role. By above analysis, the following conclusions can be obtained:

1. The filling role depends on the particle size of fly ash. Smaller fly ash particle can fill on the space between the particles of cement. Thus, it can reduce the filling water.
2. The surface role depends on the specific surface of fly ash and its water affinity. The finer the fly ash, the larger the specific surface area is, thus the more their surfaces layer water demand is. Superplasticizer can reduce effectively the surface layer water, but the content of superplasticizer

Table 8
The analyzed results of various of water

Name of fly ash	Name of water	The content of fly ash (%)						
		0	10	20	30	40	50	60
Fly ash A	Filling water	0.228	0.160	0.178	0.197	0.216	0.234	0.253
	Surface layer water	0.281	0.293	0.305	0.317	0.329	0.340	0.352
	The water reduced by lubrication role	0	0.041	0.082	0.123	0.164	0.205	0.246
	Total	0.509	0.412	0.401	0.391	0.381	0.369	0.359
Fly ash B	Filling water	0.228	0.195	0.210	0.225	0.241	0.255	0.270
	Surface layer water	0.260	0.262	0.265	0.268	0.270	0.273	0.275
	The water reduced by lubrication role	0	0.024	0.049	0.073	0.097	0.121	0.146
	Total	0.488	0.433	0.426	0.420	0.414	0.407	0.399
Fly ash C	Filling water	0.228	0.225	0.237	–	0.260	–	0.283
	Surface layer water	0.221	0.223	0.225	–	0.229	–	0.232
	The water reduced by lubrication role	0	0.011	0.023	–	0.046	–	0.068
	Total	0.449	0.437	0.439	–	0.443	–	0.447
Fly ash D	Filling water	0.228	0.230	0.241	–	0.264	–	0.229
	Surface layer water	0.221	0.223	0.224	–	0.226	–	0.229
	The water reduced by lubrication role	0	0.0064	0.0128	–	0.0256	–	0.0384
	Total	0.449	0.447	0.452	–	0.464	–	0.477

should be increased with the content of fly ash for the fly ash with larger specific surface area.

3. The lubrication role of fly ash depends on the shape of fly ash particles. Smaller spherical particle has stronger lubrication role. The spherical particle can be broken in milling process. Thus, the lubrication role of milling fly ash is very weak.
4. The morphological effect of fly ash is the synthetical embodiment of the filling, surface and lubrication roles. Coarser fly ash does not show good morphological effect although its surface role is not strong. It is because it has a not so good filling role and lubrication role. Superplasticizer cannot improve the morphological effect of coarse fly ash. Very fine fly ash does not show good morphological effect although its filling and lubrication roles are stronger. It is because its surface role is too strong to offset its filling and lubrication roles, but to add superplasticizer may weaken the surface role. The good morphological effect may be shown by the way. Milling fly ash does not show good morphological effect. It is because it has a not so good lubrication role, and the filling role is offset by the surface role.
5. The fly ash that its filling role is stronger is suit to less content of fly ash. When the content of fly ash is larger, its filling role is often offset by its surface role. The fly ash that its lubrication role is stronger is suit to large content of fly ash.

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