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Fly ash effects
III. The microaggregate effect of fly ash

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Abstract

In this paper, the microaggregate effect of fly ash is studied systematically by micromechanics, the hypothesis of center particle and pore size distribution. It is pointed out that the microaggregate effect is an important effect of fly ash. It is strengthened with the increase of content of fly ash, but weakened with age. At early age, fly ash cannot fine the pore structure. At late age, fly ash may fine the pore structure. However, in general, the fining role is only a relative fining role.
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1. Introduction

Although fly ash has pozzolanic activity, it does not fully react with $Ca(OH)_2$. Can unreacted fly ash contribute to the properties of cement stone or not? Yes, unreacted fly ash particle can still contribute to the properties of cement stone very well. This is the microaggregate effect—a very important effect—of fly ash.

The good microaggregate properties of fly ash particles are reflected in three aspects [1]: (1) The self-strength of the glass microbeads in fly ash particles is very high, over 700 Mpa. (2) Fly ash particles have excellent interfacial property. For ordinary microconcrete, the weakest place in the structure of hardened cement stone is the interfacial zone between microaggregate and cement stone. However, results in microhardness tests show that the microhardness of the interfacial zone between fly ash particle and cement stone is higher than that of cement gel. A lot of research shows that the destruction of cement stone does not occur in the interfacial zone between fly ash and cement gel, but in cement gel. (3) Fly ash has good dispersibility. It is advantageous to improve the uniformity of fresh and hardened concrete, and to fill and fine the pores and capillary pores in hardened concrete as well. Present research work has recognized the three aspects of microaggregate effect and its important role for the properties of materials. However, it is not thorough and systematic.

This paper tries to systematically analyze the three aspects of the microaggregate effect of fly ash. The influence of the self-strength and the amount of fly ash on the properties of cement stone is studied by micromechanics method; the influence of the properties of microaggregate on the strength of cement stone is studied by the hypothesis of center particle; and the fining role of the microparticles of fly ash to pore cement stone is studied by pore-size distribution. The object is to understand comprehensively the microaggregate effect of fly ash.

2. Micromechanics analysis of the microaggregate effect of fly ash

2.1. Theoretical deduction [2]

Fly ash cement stone is a type of multiphase composite material. For the sake of convenience, it may be considered a binary system, composed of the microaggregate, the

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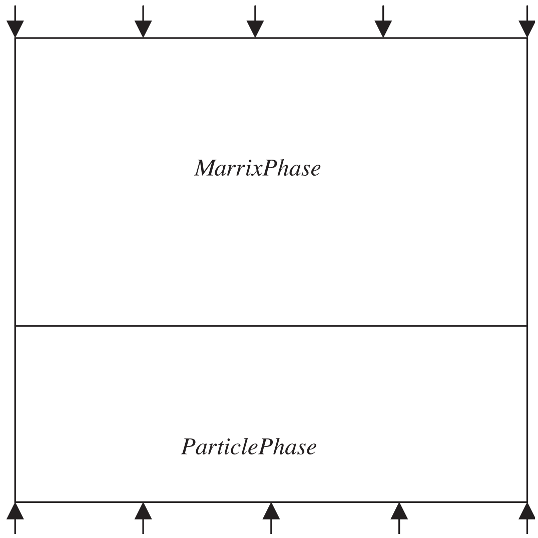

Fig. 1. Series model.

particle phase, and the matrix phase. According to the series model (see Fig. 1), the following equation can be obtained:

$$\sigma_c = \sigma_p = \sigma_m \tag{1}$$

where σ_c is the compressive stress on the composite materials, σ_p is the compressive stress on the particle phase and σ_m is the compressive stress on the matrix phase.

Because the strength of the microaggregate is higher than that of the matrix, the compressive strength of composite materials depends on one of the matrix phase. Thus,

$$R_c = R_m \tag{2}$$

where R_c is the compressive strength of composite materials and R_m is the compressive strength of the matrix phase.

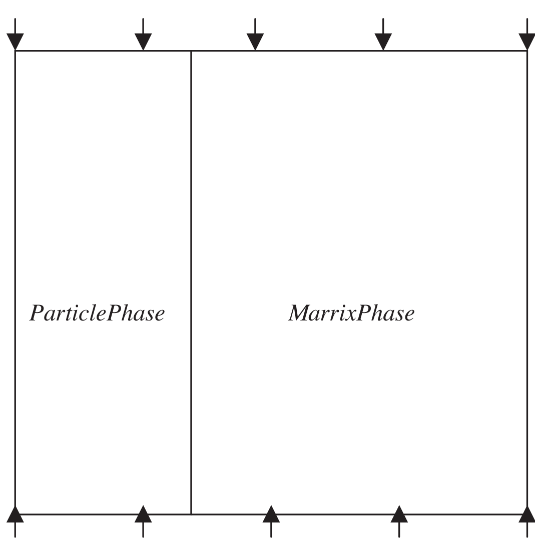

Fig. 2. Parallel model.

According to the parallel model (see Fig. 2), the following equation can be obtained:

$$R_c = R_m \frac{\frac{V_a}{V_m}\frac{E_a}{E_m} + 1}{\frac{V_a}{V_m} + 1} \tag{3}$$

where V_a is the portion of the microaggregate in volume, V_m is the portion of the matrix phase in volume, E_a is the elasticity modulus of the microaggregate and E_m is the elasticity modulus of the matrix phase.

Because E_a is larger than E_m, R_c is larger than R_m. This reflects the strengthening role of the microaggregate in cement stone. In fact, the result obtained by Eq. (2) is the lowest limit, and that obtained by Eq. (3) is the highest limit. Thus,

$$R_m < R_c < R_m \frac{\frac{V_a}{V_m}\frac{E_a}{E_m} + 1}{\frac{V_a}{V_m} + 1} \tag{4}$$

To analyze more rationally the role of microaggregate, the combined model may be produced (see Fig. 3). By this model, Eq. (5) can be obtained:

$$R_c = R_m \left[(1 - x)\left(V_m + V_a \frac{E_a}{E_m} \right) + \frac{x}{V_a \frac{E_m}{E_a} + V_m} \right] \tag{5}$$

where x is the weighted factor. When $x = 1$, it is equal to the series model. When $x = 0$, it is equal to the

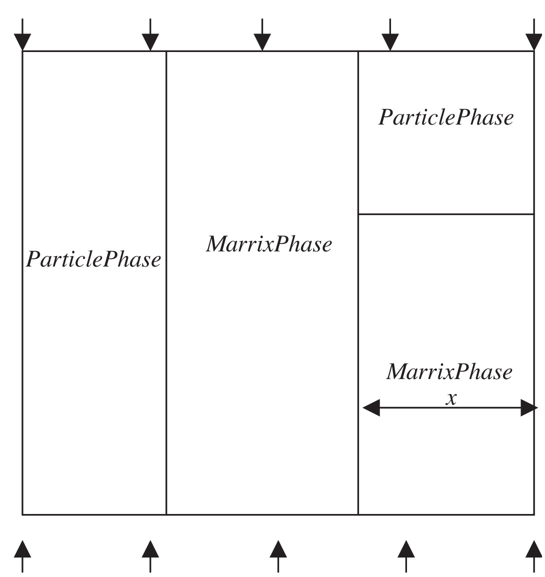

Fig. 3. Combined model.

Table 1
Results calculated by Eq. (8)

Age (days)	Fly ash (%)						
	0	10	20	30	40	50	60
7	1	1.0892	1.1990	1.2909	1.4337	1.6014	1.8322
28	1	1.0492	1.1198	1.1858	1.2670	1.3493	1.4693
90	1	1.0355	1.0804	1.1208	1.1647	1.2185	1.3181
365	1	1.0277	1.0676	1.1057	1.1477	1.1969	1.2987

parallel model. If x is taken as 0.5, Eq. (5) is changed into:

$$R_c = \frac{R_m}{2}\left(V_m + V_a\frac{E_a}{E_m} + \frac{1}{V_a\frac{E_m}{E_a} + V_m}\right) \quad (6)$$

2.2. Analysis of the microaggregate effect of fly ash

To analyze the microaggregate effect of fly ash, Eq. (3) may be changed into:

$$\frac{R_c}{R_m} - 1 = \frac{\frac{E_a}{E_m} - 1}{1 + \frac{V_m}{V_a}} \quad (7)$$

$(R_c)/(R_m) - 1$ means the portion that the strength of cement stone is raised by the microaggregate of fly ash. It may be termed as the index of the microaggregate effect, I. Thus,

$$I = \frac{\frac{E_a}{E_m} - 1}{1 + \frac{V_m}{V_a}} = V_a\left(\frac{E_a}{E_m} - 1\right) \quad (8)$$

because $E_a > E_m$, $I > 0$. Thus, the microaggregate effect is a positive effect. It may also be seen from Eq. (8) that the microaggregate effect rises with the content of fly ash because V_a increases with the content of fly ash. With age, V_a decreases and E_m increases because of the pozzolanic reaction of fly ash and the hydration of cement. Thus, the microaggregate effect reduces.

Table 2
Results calculated by Eq. (9)

Age (days)	Fly ash (%)						
	0	10	20	30	40	50	60
7	1	1.0654	1.1445	1.2115	1.3126	1.4332	1.5850
28	1	1.0378	1.0914	1.1421	1.2035	1.2668	1.3556
90	1	1.0282	1.0642	1.0971	1.1327	1.1760	1.2518
365	1	1.0227	1.0549	1.0860	1.1202	1.1602	1.2378

Similarly, Eq. (6) may be changed into:

$$I = \frac{R_c}{R_m} - 1$$

$$= \frac{V_a}{2}\left(\frac{E_a}{E_m} - 1\right)\left[1 + \frac{1}{\frac{E_a}{E_m} - V_a\left(\frac{E_a}{E_m} - 1\right)}\right] \quad (9)$$

from this equation, the same conclusion can be obtained.

According to the hydration degree of cement and the pozzolanic reaction degree of fly ash, I can be estimated by Eqs. (8) and (9). The results are given in Table 1 and Table 2, respectively. It may be seen that I obtained by Eq. (8) is larger than that obtained by Eq. (9), but their regularities are consistent.

3. Analysis of the effect of center particle on the microaggregate effect of fly ash

In the 1950s, Wu Zhongwei [3] put forward the hypothesis of the big center particle. He defined the aggregate as a big center particle. He considered that there is an effect radius, x_0, around the big center particle. The big center particle can influence the behavior of the medium within the range. However, it weakens with the increase of distance. The big center particle does not influence the behavior of the medium without effect range. The effect of different center particles may be superimposed. The superimposed role depends on the effect radius, x_0, and the space of center

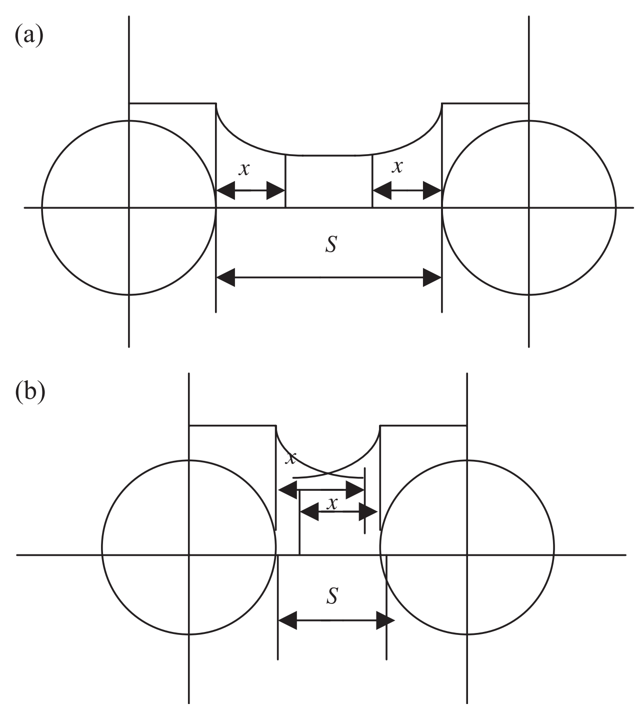

Fig. 4. Diagram of the superimposed role of center particle effect.

particles, S (see Fig. 4). When $S \geq 2x_0$, there is no superimposed role. When $S < 2x_0$, there is superimposed role. The less S becomes and the larger x_0 is, the stronger the superimposed role. Particles of unreacted fly ash may be considered as center particles that can influence the behavior of the medium. Thus, analysis of the superimposed role of center particle effect conduces to deepening the understanding of the microaggregate effect of fly ash.

The fly ash content influences not only the amount of center particle, but also S. The larger the fly ash content, the less S is, and the stronger the superimposed role. Thus, the microaggregate effect of fly ash is strengthened with the increase of its content.

x_0 is closely related to the difference between the properties of the center particle and that of the medium. It decreases with the decrease of the difference. With the hydration of cement and the pozzolanic reaction of fly ash, the properties of the medium are improved, and x_0 decreases. At the same time, the unreacted fly ash particles become smaller, and S increases. Thus, the superimposed role weakens with age. In other words, the microaggregate effect of fly ash weakens with age.

4. Fining role of the microparticles of fly ash on the pores in cement stone

The properties of cement stone are relative with respect to the porosity and to pore size distribution. Research results have proved that under the same porosity, increasing the amount of smaller pores and decreasing the amount of bigger pores may improve the properties of cement stone. Some high-quality fly ash just has the function of fining pore structure.

Fig. 5 shows the accumulation curve of pore volume. Fig. 6 shows the accumulation curve of the percentage of pore size distribution. As seen from Fig. 5, at early age, the curve moves toward the right with the content of fly ash. With age, these curves are progressively close. As seen from Fig. 6, at 7 days, the curve moves toward the right with the content of fly ash. However, after 28 days, the curve moves toward the left with the content of fly ash.

The influence of fly ash on the pore size distribution may be analyzed from two aspects. One is the influence of fly ash on initial pore size distribution, and the other is the influence of fly ash on the pore size distribution in the process of hydration.

The initial pore size distribution of cement stone depends on the particle size distribution of cement and its water retentivity. If cement is fine, mixed water may be distributed uniformly in the system. Thus, smaller pores will be formed. The water retentivity of cement influences the gathering process of water. If the water retentivity of cement is worse, even if the water is dispersed uniformly in the mixing process, it still can gather together to form bigger pores because of subsidence. Thus, the water retentivity of cement may influence markedly the initial pore size distribution of cement stone. Addition of finer fly ash may decrease the average size of cement. Thus, addition of high-quality fly ash may fine the initial pores by dispersing the water and improving the water retentivity of cement.

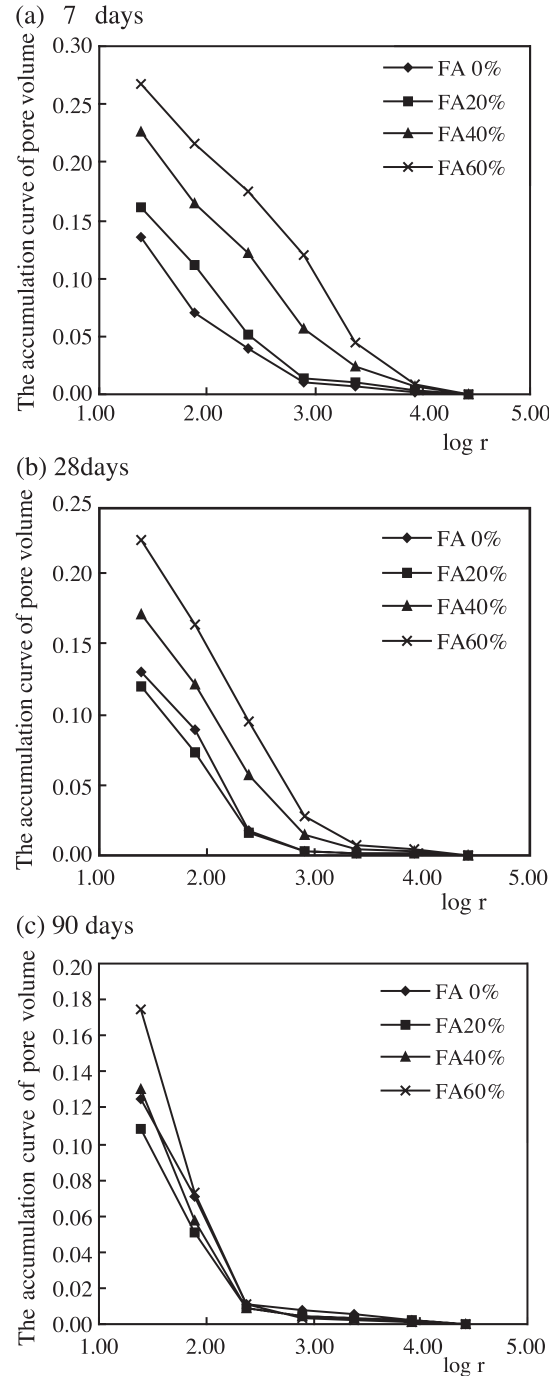

Fig. 5. The accumulation curve of pore volume.

A large quantity of hydrated product is formed in the hydration. The hydrated product fills in the pores. This not only reduces the porosity, but also changes bigger pores into smaller pores. Thus, the pores in cement stone trend toward

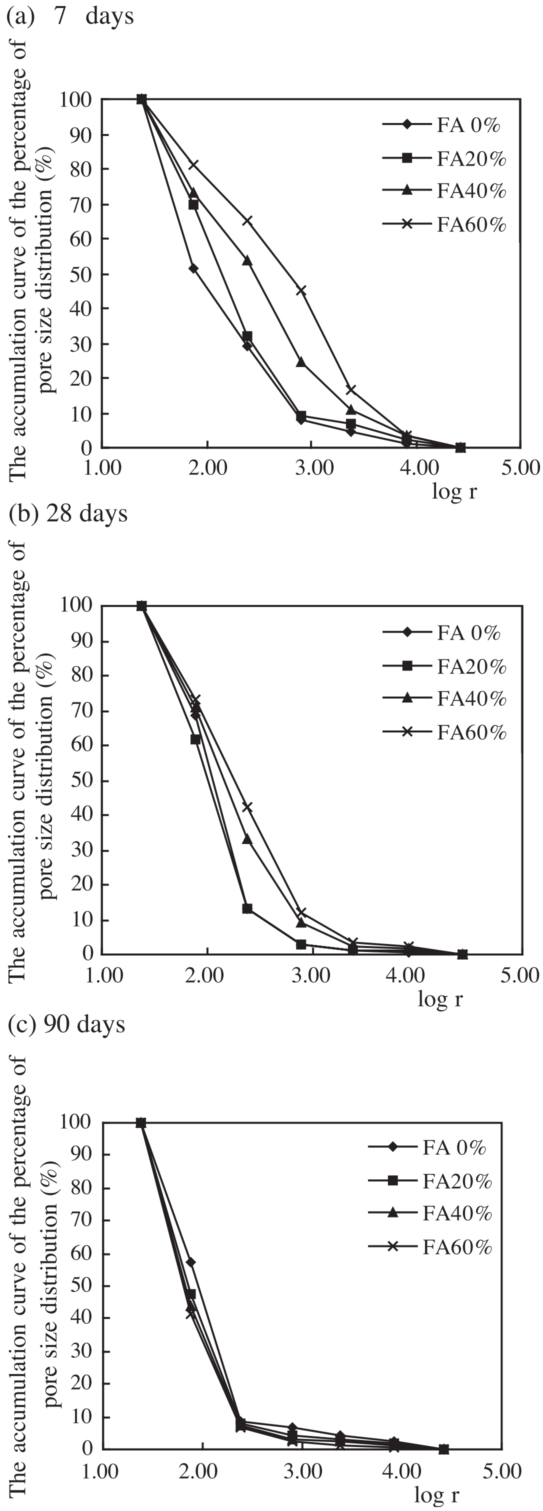

Fig. 6. The accumulation curve of the percentage of pore size distribution.

fining. It is obvious that the higher the degree of hydration, the stronger the fining role is. It makes the accumulation curve of pore size distribution move toward the left. That cement is partly replaced by fly ash influences the amount of reacted product, thus influencing the fining role too. At 7 days, fly ash does not react with $Ca(OH)_2$, and its role in promoting the hydration of cement is weaker. Thus, that cement is partly replaced by fly ash causes the reduction of the degree of hydration. The fining role of reacted product on the pores weakens. With age, the degree of pozzolanic reaction of fly ash rises and its role in promoting the hydration of cement strengthens. Although the degree of pozzolanic reaction of fly ash is lower than the hydration degree of cement, the difference of the total reaction degree decreases because the hydration of cement is promoted. The influence of the fly ash content on the fining role weakens too.

It may be seen from the above analysis that the influence of the fly ash content on the initial pore size distribution is not changed with age, but the influence of the hydration process on the pore size distribution is changed with age. At early age, the influence of the fly ash content on the reaction degree of the system is larger. The positive effect caused by its influence on initial pore size distribution is not enough to compensate for the negative effect caused by its influence on the reaction degree of the system. For cement stone without fly ash, even if its initial pore size distribution is coarser, these bigger pores will be changed into smaller pores because a large quantity of hydrated product fills in the initial pore system. The volume of bigger pores decreases and that of the smaller pores increases. The pore size distribution of cement stone is fined. For cement stone with fly ash, even if its initial pore size distribution is finer than that of the cement stone without fly ash, it only has little change in the initial term of the hydration process because the hydration degree of system reduces markedly when fly ash is added. As a result, the pore size distribution of cement stone with fly ash is coarser than that without fly ash. Thus, at 7 days, the pore is not fined but is coarsened with the increase of the fly ash content. The coarsening role is not only in the absolute amount of pores but also in the relative amount of pores. With increasing age, the influence of fly ash on the initial pore size distribution is greater than its influence on the hydration because of the reaction between fly ash and $Ca(OH)_2$ and the promoting role of fly ash in the hydration of cement. Under this condition, addition of fly ash makes the pore fine. Because the total hydration degree reduces with the increase of the fly ash content, the total porosity of cement stone increases. Thus, from the absolute amount of pores, the fining role is not clearly seen, but from the relative amount of pores, the fining role may be seen clearly. Thus, in general, the fining role of fly ash is only a type of relative fining role. Only when the fly ash content is lower and at late age is it possible to see the absolute fining role of fly ash.

5. Conclusions

In this paper, the microaggregate effect of fly ash is studied systematically from micromechanics, center particle effect and pore size distribution. By the above research, the following conclusions can be obtained:

(1) The microaggregate effect of fly ash is strengthened with the increase of the fly ash content. From the micromechanics viewpoint, it is because of the increase of the amount of microaggregate. In the center particle hypothesis, increase in the fly ash content means increase in the amount of center particles and decrease of the space of center particles. This strengthens the superimposed role of the center particle effect. Thus, the microaggregate effect of fly ash is strengthened with the fly ash content. Although the analytical method is different, the same conclusion is obtained.

(2) The microaggregate effect of fly ash weakens with age. From the micromechanics viewpoint, the volume fraction of microaggregate decreases with age because of the pozzolanic reaction of fly ash. Thus, the microaggregate of fly ash weakens. In the center particle hypothesis, the center particle becomes smaller because of the pozzolanic reaction of fly ash and the space of center particle increases. At the same time, the properties of medium are improved because of the hydration of cement and the pozzolanic reaction of fly ash. The effect radius of the center particle decreases. By these two reasons, the superimposed role of center particle effect weakens. Thus, the microaggregate effect of fly ash weakens with age. It is obvious that the same conclusion is obtained by a different method.

(3) Analyzing the microaggregate effect of the influence of fly ash on pore size distribution, fly ash has no fining role at early age and has fining role at later age. In general, the fining role is only the relative fining role. Absolute fining role is not seen.

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