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STUDY OF THE INFLUENCE OF THE PARTICLE SIZE DISTRIBUTION ON THE PROPERTIES OF CEMENT

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ABSTRACT

In the paper, the influence of the particle size distribution in binary system on the packing density and the rate of hydration is analysed. On the basis of the analysis, the relationship between the porosity and the particle size distribution is calculated and discussed. The result indicates that: (1) The influence of the particle size distribution on the porosity is dependent on both the packing density and the rate of hydration. When the depth of hydration is less, the packing density is the main factor, thus the wide distribution can obtain the low porosity; when the depth of hydration is greater, the influence of both must be considered comprehensively. There is the best distribution, and the best value of d_1/d_2 is about 0.3 for binary system. (2) The relative ratio between two components depends mainly on the packing density. The mixture ratio when the porosity is the lowest equals to one when the packing density is the highest. © *1997 Elsevier Science Ltd*

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Introduction

In recent years, the problem about the particle size distribution of cement has attracted the attention of a lot of researchers because it affects some properties of cement. The research includes mainly two aspects:

(1) In packing of particles. R. Feret published the first treatise about the packing of particles in concrete in 1892, and put forward the possibility of selecting appropriate aggregate types for high quality concrete and the relationship between the porosity of hardened mortar and the compression strength of concrete.

In the theory, some models have been put forward(1,2,3). For example, Furnas, Aim and Goff, Toufar, Klose and Born put forward some models about the binary system, and some researchers treated the ternary system by triangular diagram, and so on. These methods provide a tool to calculate the packing density of particle material.

(2) In the hydration of cement Since G. Frigione and S. Marya first began the research in the influence of the particle size distribution on the rate of hydration of cement (4), some researchers did a lot of highly effective work (5,6). Their conclusion was that the more narrow the particle size distribution of cement, the faster the rate of the hydration of cement is.

It is known to all that the properties of cement are closely related to the porosity, and the porosity depends on the packing density of the cement particles and the degree of hydration of cement. Higher packing density results in lower porosity, and higher degree of hydration results in lower porosity too. But the influence of particle size distribution on the packing density and the degree of hydration is inconsistent. For a wider particle size distribution, the packing density is higher, but the degree of hydration is lower. For a more narrow particle size distribution, the packing density is lower, but the degree of hydration is higher. The purpose of this paper is that on the basis of the binary modal, both the packing density and the rate of hydration are considered comprehensively; the influence of particle size distribution is discussed; and the best particle size distribution is sought.

The Theoretical Deduction of the Relationship Between Particle Size Distribution and Porosity

1. Basic hypotheses

In the deduction, the model of the spherical particle is used, and the basic hypotheses are as follows:

(1) The particle of cement is spherical;
(2) The process of hydration is homogeneous and from outside to inside;
(3) The hydration depth is independent of the particle size, and only depends on the rate that water passes through the layer of hydration product. It may be expressed by Fick's second law;
(4) The specific weight of both bigger and smaller particles is same, the packing density of one-size particle is the same too.

2. Basic concept and symbol

For convenience' sake, some basic concepts and symbols are as follows:

(1) d_1 the diameter of the smaller particle, cm;
(2) d_2 the diameter of the bigger particle, cm;
(3) y_1 the volume fraction of the smaller particle;
(4) y_2 the volume fraction of the bigger particle;
(5) ε_0 the voidage of one-size particle;
(6) ρ the specific weight of cement;
(7) ϕ the packing density;
(8) h the depth of hydration, cm;
(9) δ the thickness of water film,cm. It influences directly the fluidity of paste, and the larger δ, the better the fluidity is.
(10) P the porosity;
(11) α the hydration degree.

3. The deduction of the relationship between porosity and particle size distribution

3.1 The relationship between packing density and particle size distribution

According to Aim and Goff's model(1), for two kinds of particle whose diameter are d_1 and d_2 respectively, y*, which is the volume fraction of smaller particle for the mixture with the maximum packing density, can be calculated by following equation:

$$y^* = \frac{1(10.9d_1/d_2)(1\varepsilon_o)}{2(10.9d_1/d_2)(1\varepsilon_o)} \tag{1}$$

For $y_1 y^*$,

$$\phi = \frac{1-\varepsilon_0}{1-y_1} \tag{2}$$

For $y_1 y^*$,

$$\phi = \frac{1-\varepsilon_0}{y_1(1y_1)(10.9d_1/d_2)(1\varepsilon_0)} \tag{3}$$

3.2 The volume concentration of solid and the ratio of water to cement for fresh paste

In order to achieve certain fluidity, the water film with certain thickness must be formed on the surface of particle. The added water includes both the water filling the void between the particles and the water forming the film on the surface of particle.

If the volume fraction of solid in fresh paste is r, for unit volume paste,

the volume of solid $V_v = r$

the volume of water filling void $V_f = 1 - \phi$

the volume of water on surface $V_s = \rho V_v S\delta = \rho S\delta r$

where, S is the specific surface of solid particle.

Thus, $r + (1 - \phi) + \rho S\delta r = 1$

$$r = \frac{\phi}{1+\rho S\delta} \tag{4}$$

In unit volume paste, the mass of cement $C = \rho r$

the mass of water $w = 1 - r$

$$w/C = \frac{1-r}{\rho r} = \frac{1}{\rho}\left(\frac{1+\rho S\delta}{\phi} - 1\right) \tag{5}$$

3.3 The porosity of hardened cement paste

In unit volume paste, the total volume of the smaller particle $V_1 = y_1 r = \dfrac{y_1\phi}{1+\rho S\delta}$

the number of the smaller particle $N_1 = \dfrac{6V_1}{\pi d_1^3} = \dfrac{6y_1\phi}{\pi d_1^3(1+\rho S\delta)}$

the total volume of the bigger particle $V_2 = y_2 r = \dfrac{y_2\phi}{1+\rho S\delta}$

the number of the bigger particle $N_2 = \frac{6V_2}{\pi d_2^3} = \frac{6y_2\phi}{\pi d_2^3(1+\rho S\delta)}$

When $h\frac{1}{2}d_1$, the volume of hydration solid is:

$$V_h = N_1[\frac{\pi}{6}d_1^3 - \frac{\pi}{6}(d_1-2h)^3] + N_2[\frac{\pi}{6}d_2^3 - \frac{\pi}{6}(d_2-2h)^3]$$
$$= \frac{\phi}{1+\rho S\delta}\{y_1[1-(\frac{d_1-2h}{d_1})^3] + y_2[1-(\frac{d_2-2h}{d_2})^3]\}$$

Since $y_1 + y_2 = 1$, $V_h = \frac{\phi}{1+\rho S\delta}\{1-[y_1(\frac{d_1-2h}{d_1})^3 + y_2(\frac{d_2-2h}{d_2})^3]\}$

According to Power's model, the volume of hydrated product is about 2.2 times as large as original volume. Thus, the incease of solid volume by hydration is:

$$\Delta V_s = 1.2V_h = \frac{1.2\phi}{1+\rho S\delta}\{1-[y_1(\frac{d_1-2h}{d_1})^3 + y_2(\frac{d_2-2h}{d_2})^3]\}$$

$$P = 1 - r - \Delta V_s = 1 - \frac{\phi}{1+\rho S\delta}\{2.2 - 1.2[y_1(\frac{d_1-2h}{d_1})^3 + y_2(\frac{d_2-2h}{d_2})^3]\} \qquad (6)$$

$$\alpha = \frac{V_h}{r} = 1 - [y_1(\frac{d_1-2h}{d_1})^3 + y_2(\frac{d_2-2h}{d_2})^3] \qquad (7)$$

When $\frac{1}{2}d_1 h \frac{1}{2}d_2$, all smaller particles have been hydrated. Thus,

$$V_h = N_1\frac{\pi}{6}d_1^3 + N_2[\frac{\pi}{6}d_2^3 - \frac{\pi}{6}(d_2-2h)^3] = \frac{\phi}{1+\rho S\delta}[1-[y_2(\frac{d_2-2h}{d_2})^3]$$

$$P = 1 - \frac{\phi}{1+\rho S\delta}[2.2 - 1.2y_2(\frac{d_2-2h}{d_2})^3] \qquad (8)$$

$$\alpha = 1 - y_2\,(\frac{d_2-2h}{d_2})^3 \qquad (9)$$

3.4 The calculation of the specific surface

$$S = \frac{1}{\rho r}(N_1\pi d_1^2 + N_2\pi d_2^2) = \frac{6}{\rho}(\frac{y_1}{d_1} + \frac{y_2}{d_2}) = \frac{6}{\rho d_1}(y_1 + y_2\frac{d_1}{d_2}) \qquad (10)$$

Analysis and Discussion

1. Influence of particle size distribution on packing density and water demand

When $y_1 y^*$, $\phi = \frac{1-\varepsilon_0}{1-y_1}$. ϕ has nothing to do with particle size, and the higher y_1, the higher ϕ is. When $y_1 = 0$ (there is only one-size particle), ϕ has minimum, $\phi_{min} = 1 - \varepsilon_0$.

When $y_1 y^*$, $\phi = \dfrac{1-\varepsilon_0}{y_1 + (1-y_1)(1+0.9\frac{d_1}{d_2})(1-\varepsilon_0)}$

Obviously, the smaller d_1/d_2, the higher ϕ is. When d_1/d_2 0, ϕ has maximum

$$\frac{1-\varepsilon_0}{y_1 + (1-y_1)(1-\varepsilon_0)}$$

For the mixture with maximum packing density y^*, according to equations (1) and (2),

$$\phi = \frac{1-\varepsilon_0}{1-y^*} = (1-\varepsilon_0)[2-(1+0.9d_1/d_2)(1-\varepsilon_0)]$$

ϕ is linear with d_1/d_2, and the smaller d_1/d_2, the higher ϕ is. When d_1/d_2 0, ϕ has maximum, $\phi max = 1 - \varepsilon_0^2$

It is seen from above analysis that under any circumstance, the greater the difference between the particles' size, the higher the packing density. In other words, the more inhomogeneous the particle size distribution, the higher the packing density is.

According to equation (5), w/C $= \frac{1}{\rho}(\frac{1+\rho S\delta}{\phi} - 1)$. When S, the specific surface, is constant, the higher ϕ, the lower the demand water under the same fluidity is. Because the more inhomogeneous the particle size distribution, the higher the packing density, it is considered that under same specific surface, the more inhomogeneous the particle size distribution, the lower the demand water under same fluidity is.

2. Influence of particle size distribution on degree of hydration

2.1 $h\frac{d_1}{2}$

According to equation (7), $\alpha = 1 - [y_1(\frac{d_1-2h}{d_1})^3 + y_2(\frac{d_2-2h}{d_2})^3]$. Under the constant $S(= \frac{6}{\rho}(\frac{y_1}{d_1} + \frac{y_2}{d_2}))$, the maximum of α is found as follows:

Given: $\Phi(d_1,d_2) = \frac{y_1}{d_1} + \frac{y_2}{d_2} - \frac{S\rho}{6}$

$$F(d_1,d_2) = 1 - [y_1(\frac{d_1-2h}{d_1})^3 + y_2(\frac{d_2-2h}{d_2})^3] - \lambda(\frac{y_1}{d_1} + \frac{y_2}{d_2} - \frac{S\rho}{6})$$

$$\frac{\partial F}{\partial d_1} = 3y_1(\frac{d_1-2h}{d_1})^2\frac{2h}{d_1^2} + \frac{\lambda y_1}{d_1^2} = 0$$

$$\frac{\partial F}{\partial d_2} = 3y_2(\frac{d_2-2h}{d_2})^2\frac{2h}{d_2^2} + \frac{\lambda y_2}{d_2^2} = 0$$

Simplified above two equations:

$$\lambda = 6h(\frac{d_1 - 2h}{d_1})^2$$

$$\lambda = 6h(\frac{d_2 - 2h}{d_2})^2$$

Thus, $$(\frac{d_1 - 2h}{d_1})^2 = (\frac{d_2 - 2h}{d_2})^2, d_1 = d_2 .$$

2.2 $d_1/2hd_2/2$

According to equation (9), $\alpha = 1\ y_2(\frac{d_2 - 2h}{d_2})^3$

Given: $F(d_1,d_2) = 1\ y_2(\frac{d_2 - 2h}{d_2})^3\ \lambda(\frac{y_1}{d_1} + \frac{y_2}{d_2} - \frac{S\rho}{6})$

$$\frac{\partial F}{\partial d_1} = \frac{\lambda y_1}{d_1^2} = 0$$

$$\frac{\partial F}{\partial d_2} = 3y_2(\frac{d_2 - 2h}{d_2})^2\frac{2h}{d_2^2} + \frac{\lambda y_2}{d_2^2} = 0$$

Simplified above two equations:

$$\lambda y_1 = 0$$

$$\lambda = 6h(\frac{d_2 - 2h}{d_2})^2$$

It is obtained from $\lambda y_1 = 0$ that:

(1) $\lambda = 0$. It can be given by this result that $6h(\frac{d_2 - 2h}{d_2})^2 = 0$. Thus, $d_2 = 2h$, or $h = d_2/2$. Obviously, it is inconsistent with the condition that $d_1/2\ hd_2/2$.

(2) $y_1 = 0$. It shows that there is not a smaller particle than diameter d_1 in system. In other words, there is only one-size particle in the system.

It is seen from the above analysis that under same specific surface, the hydration degree is higher in the homogeneous system than the inhomogeneous system. It is consistent with some results of former research (4).

3. Influence of particle size distribution on porosity under different depth of hydration

3.1 Influence of d_1/d_2 on porosity under same specific surface and constant y_1

It is known from above analysis that homogeneous distribution is in demand for the packing state of particle, but inhomogeneous distribution is in demand for the rate of hydration. The two effects are just the opposite. For the properties of materials, these effects should be considered at the same time. On the one hand, higher packing density is demanded; on the other hand, higher degreed hydration is demanded. The synthetic result should be that the material has the porosity as low as possible.

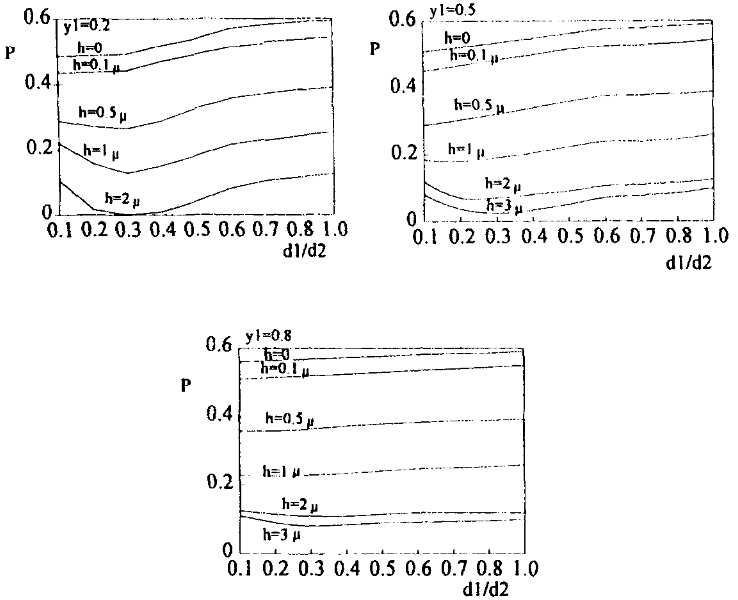

FIG. 1.
The calculated relationship between porosity and d_1/d_2.

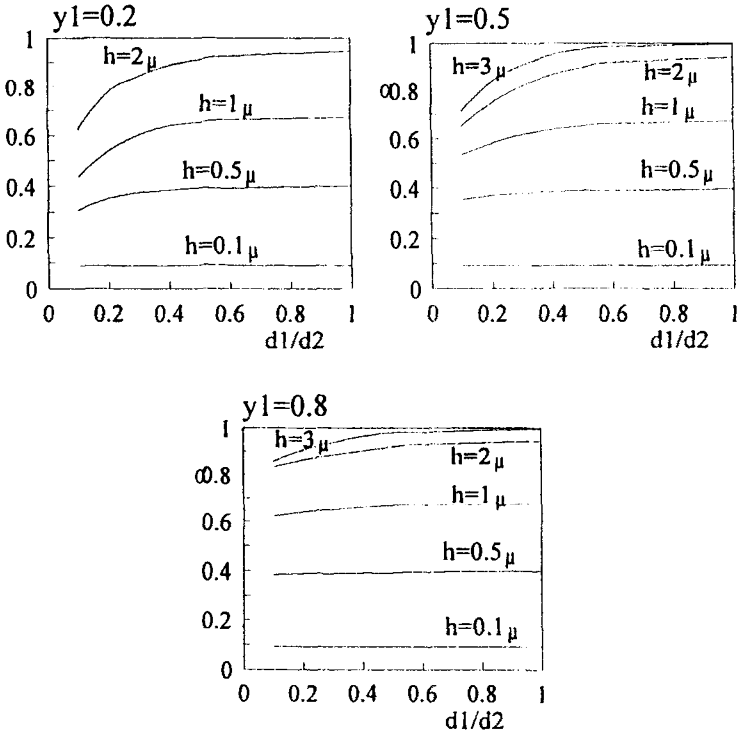

FIG. 2.
The calculated relationship between the hydration degree and d_1/d_2.

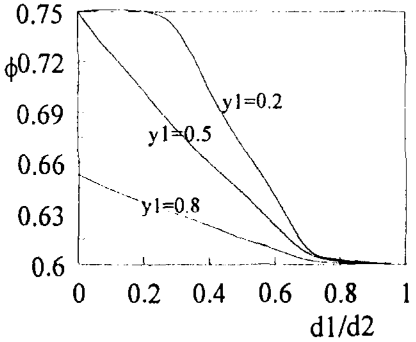

FIG. 3.
The relationship between packing density and d_1/d_2.

The calculated results by equation (6) and (8) are shown in Fig. 1. It may be seen from the figure that:

(1) When the depth of hydration is smaller, i.e. at early age, the smaller d_1/d_2, the lower the porosity is.
(2) When the depth of hydration is greater, i.e. at late age, d_1/d_2 is about 0.3 at which the porosity is minimum.

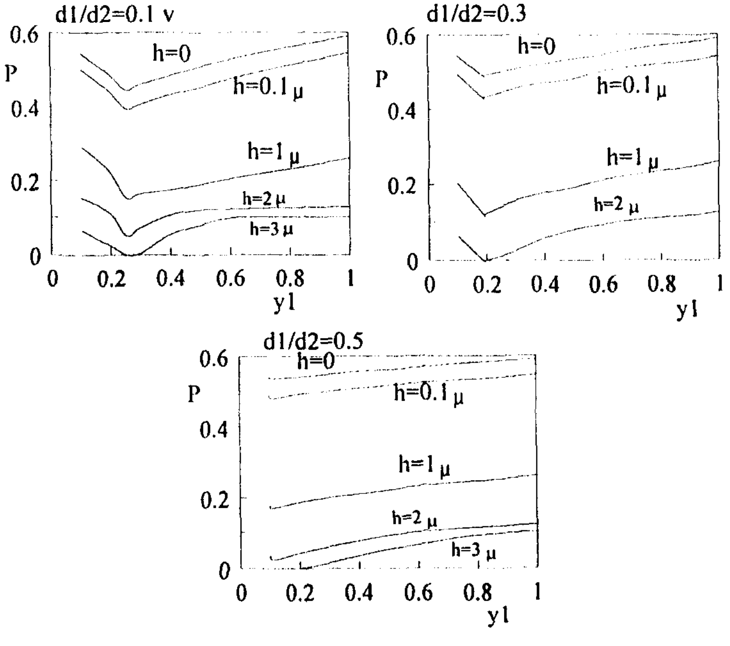

FIG. 4.
The relationship between porosity and mix ratio.

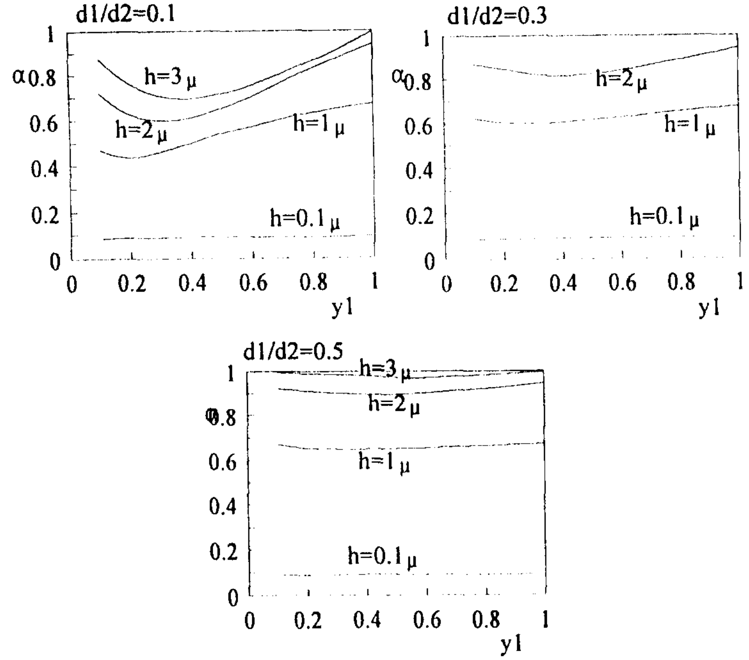

FIG. 5.
The relationship between the hydration degree and mix ratio.

(3) The influence of d_1/d_2 on porosity is the more and more unnoticeable with the increase in the number of smaller particles.

In order to understand further the phenomenon, the influence of d_1/d_2 on the hydration degree and packing density is shown in Fig. 2 and Fig. 3 respectively. It is seen from Fig. 2 that the influence of d_1/d_2 on the hydration degree is more noticeable with the increase of the depth of hydration. The influence is noticeable when $d_1/d_2 0.6$, but is unnoticeable when $d_1/d_2 0.6$. In other way, the influence of d_1/d_2 on α is weakened with the increase in the number of smaller particle.

It is seen from Fig. 3 that when d_1/d_2 0.7; packing density, ϕ, decreases with the increase of d_1/d_2, and its rate is reduced with the increase of y_1; but when d_1/d_2 0.7, the influence of d_1/d_2 on ϕ is unnoticeable. In another way, it should de noticed that for $y_1 = 0.2$, ϕ is basically constant when $d_1/d_2 0.3$. This may be explained geometrically. When the smaller particle is very much smaller, the smaller particle within certain limitation of particle size may fill in the void of the greater particle. Thus, within this limitation, the change of smaller particle size does not influence the packing density. Hypothesized that the void of the greater particle is a tetrahedron, the limitation may be calculated geometrically;

$$(d_1/d_2)^* = \frac{\sqrt{6}}{2}1 = 0.2247$$

It is very closely with the result in Fig. 3.

For $y_1 = 0.2$, when $d_1/d_2 0.3$, ϕ is contant, whereas the change of hydration degree is greater within the range. The hydration degree is increased markedly with the increase of d_1/d_2, thus

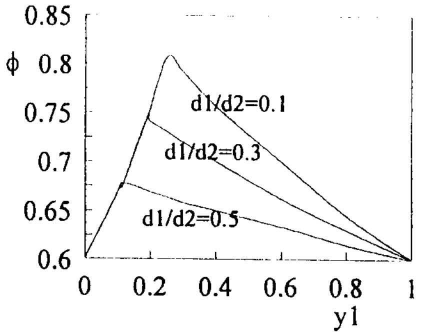

FIG. 6
The relationship between the packing density and mix ratio.

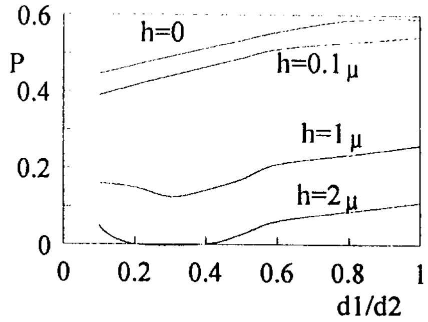

FIG. 7.
The relationship between porosity and d_1/d_2 at optimum mix ratio.

the porosity drops markedly. When $0.3d_1/d_20.7$, the change of hydration degree is smaller, whereas packing density drops suddenly with d_1/d_2. This results in the increase of porosity. When d_1/d_2 0.7, the changes of both hydration degree and packing density are smaller with d_1/d_2, thus the change of porosity is smaller too.

For y_l = 0.3, there is not a level on ϕ curve, and ϕ is reduced with d_1/d_2 when d_1/d_2 0.7. Thus only when the increase of hydration degree is greater than the decrease of packing density, porosity shows the trend decreased with d_1/d_2. When h1μ, the effect of increased hydration degree is not enough to counteract the effect of decreased packing density, thus the porosity is raised with d_1/d_2 at early-age.

For y_1 = 0.8, the changes of hydration degree and packing density are smaller than that of the above two conditions, thus the change of porosity with d_1/d_2 is unnoticeable.

3.2 The influence of mix ratio, y_1, on porosity at same specific surface

Fig. 4 shows the relationship between P and y_1 under different d_1/d_2 and the depth of hydration. Fig. 5 and Fig. 6 show the relationships between hydration degree, packing density and y_1 respectively. It is seen that the mix ratio at the lowest porosity is coincident with that at the maximum packing density, where hydration degree is generally lower. This shows that the effect of packing density is the more important factor.

Fig. 7 gives the relationship between the lowest porosity and d_1/d_2. It may be seen from the figure that porosity is decreased with d_1/d_2 at early-age (h is smaller), and is the lowest when d_1/d_2 is about 0.3.

Conclusion

1. The influence of particle size distribution on the properties of hardened cement stone is mainly in packing density and degree of hydration.
2. Wider particle size distribution is advantageous to the increase of packing density, and homogeneous distribution is advantageous to the increase of hydration degree.
3. From the standpoint of porosity, both should be considered cooperatively. At early-age, the effect of packing density is primary, and the effect of hydration degree is secondary. At late age, the effects of packing density and hydration degree cannot be neglected. Considered these factors cooperatively, there should be the suitable distribution of cement particle. For binary system, it is more suitable that d_1/d_2 is about 0.3.

4. The mix ratio mainly depends on packing density. The optimum mix equals that at the densest packing state.
5. If the property of hardened cement stone at early-age is stressed, a wider particle size distribution should be considered. If the property of hardened cement stone at late age is stressed, a suitable distribution should be considered.

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