Pergamon

CEMENT AND CONCRETE RESEARCH

Cement and Concrete Research 29 (1999) 1721–1726

The theoretic analysis of the influence of the particle size distribution of cement system on the property of cement

Wang Aiqin[a,*], Zhang Chengzhi[a], Zhang Ningsheng[b]

[a]*China Institute of Water Resources and Hydropower Research, Department of Structures & Materials, A1 Fuxing Road, Beijing 100038, China*
[b]*Constructional Engineering Cost Management Centre, Fushan Construction Committee, Fushan 528000, China*

Received 15 September 1998; accepted 23 June 1999

Abstract

According to the Rosin-Ramler-Benuet equation, the influences of continuous particle size distribution on water demand, degree of hydration, packing density, and porosity are deduced. On this basis, the influences of the particle size distribution on the properties of cement are analyzed under different conditions. The optimum distribution of cement particles is proposed.

Keywords: Continuous distribution; Water demand; Degree of hydration; Packing density; Porosity

1. Introduction

It is well known that the particle size distribution of cement influences not only the energy consumption in the milling process, but also the properties of fresh cement paste and hardened cement stone [1–4]. Thus, many researchers approached this subject from different angles. In [5] Feret studied the influence of particle size distribution on the properties of concrete from particle packing, and determined that to obtain high quality concrete, there should be suitable distribution of different size particles to attain the maximum packing density. Frigione and Marra [3] studied the problem vis-à-vis the hydration of cement, and put forth the viewpoint that the more narrow the particle size distribution of cement, the faster the hydration of cement.

It should be noted that the porosity is a very important parameter for the properties of material. It is the bridge that links both the particle size distribution and the properties of materials. From the properties of materials, both the packing states of the particles and their hydration rates should be evaluated relative to their effect on the porosity. We previously inquired into this problem by the model of binary system [4], and determined that there are suitable ratios of particle size and mix ratio between different size particles.

Although the research has warned people not to pursue the distribution as widely as possible to obtain only the maximum packing density or the distribution as narrowly as possible to obtain only the fastest hydration [4], the model of the binary system is different than the actual situation of the particle size distribution of cement. Thus, this paper will inquire into the most suitable particle size distribution for continuous distribution from the Rosin-Ramler-Benuet equation.

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

2.1. Basic hypotheses

For convenience' sake, some hypotheses are taken as following:

1. The particle size distribution of cement system obeys Rosin-Ramler-Benuet equation [i.e., Eq. (1)]

$$R = 100\exp\left[-\left(\frac{x}{\bar{x}}\right)^n\right] \qquad (1)$$

where R is the percentage of residue by weight (%), $\bar{x}$ is the characteristic particle size of the distribution (corresponding to the particle size that the residue is 36.79%), and n is the distribution index. If turned it into the function of distribution $F(x)$ and the function of distributing density $\Phi(x)$, they are [see Eqs. (2) and (3)]:

$$F(x) = 1 - \exp\left[-\left(\frac{x}{\bar{x}}\right)^n\right] \qquad (2)$$

* Corresponding author. Tel.: +86-010-68-515-511; fax: +86-010-68-529-680.

E-mail address: zczhw@publica.bj.cninfo.net (A. Wang)

0008-8846/99/$ – see front matter
PII: S0008-8846(99)00148-9

$$\Phi(x) = \frac{n}{\bar{x}}\left(\frac{x}{\bar{x}}\right)^{n-1}\exp\left[-\left(\frac{x}{\bar{x}}\right)\right] \quad (3)$$

2. The particle of cement is spherical.
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 is independent of the particle size. The packing density of one size particle is independent of the particle size also.

2.2. Theoretic deduction

1. The relationship between the specific surface, S, and particle size distribution [see Eq. (4)]:

$$S = \frac{3}{\rho}\int_0^\infty \frac{\Phi(x)}{x}dx = \frac{3n}{\rho\bar{x}}A(n) \quad (4)$$

where ρ is the specific weight of cement (g/cm^3) [see Eq. (5)]:

$$A(n) = \int_0^\infty \left(\frac{x}{\bar{x}}\right)^{n-2}\exp\left[-\left(\frac{x}{\bar{x}}\right)^n\right]d\left(\frac{x}{\bar{x}}\right) \quad (5)$$

it may be obtained by numerical integral. For shown specific surface, S, can be obtained by Eq. (6):

$$\bar{x} = \frac{3n}{\rho S}A(n) \quad (6)$$

2. The relationship between packing density and particle size distribution. According to the model of linear packing density [6,7], packing density can be calculated by Eq. (7):

$$\phi = \inf_{0 \leq t < \infty}\left[\frac{\phi_0}{1-(1-\phi_0)\int_t^\infty g(t,x)\Phi(x)dx - \int_0^t f(t,x)\Phi(x)dx}\right] \quad (7)$$

where: ϕ_0 is the packing density of one size particle [see Eq. (8) and Eq. (9)];

$$g(t,x) = (1-t/x)^{1.6} \quad (8)$$

$$f(t,x) = (1-x/t)^{3.1} + 3.1\frac{x}{t}(1-x/t)^{2.9} \quad (9)$$

3. The calculation of the volume concentration of solid and the water-cement ratio for fresh paste. The volume concentration of solid is shown in Eq. (10):

$$V_g = \frac{\phi}{1+\rho S\delta} \quad (10)$$

and the water-cement ratio can be seen in Eq. (11):

$$w/c = \frac{1}{\rho}\left(\frac{1+\rho S\delta}{\phi} - 1\right) \quad (11)$$

where δ is the thickness of water film layer.

4. The calculation of hydration degree. When the hydration depth is h, the particles that have radius less than h have hydrated completely. For per unit volume, the volume of the particles that the radius is within $x \rightarrow x + dx$ ($x \geqslant h$) is $dV = \Phi(x)dx$. The number of the particles is seen in Eq. (12):

$$dN = \frac{dV}{\frac{4}{3}\pi x^3} = \frac{\Phi(x)}{\frac{4}{3}\pi x^3}dx \quad (12)$$

The volume of unhydrated cement is seen in Eq. (13) and Eq. (14):

$$dV_u = \frac{4}{3}\pi(x-h)^3 dN = \left(1-\frac{h}{x}\right)^3\Phi(x)dx \quad (13)$$

$$V_u = \int_h^\infty \left(1-\frac{h}{x}\right)^3\Phi(x)dx \quad (14)$$

Hydration degree is seen in Eq. (15):

$$\alpha = 1 - V_u = 1 - \int_h^\infty \left(1-\frac{h}{x}\right)^3\Phi(x)dx \quad (15)$$

5. The calculation of porosity. When the hydration depth is h, the porosity of cement stone is seen in Eq. (16):

$$P = 1 - V_g - 1.2V_g\alpha = 1 - \frac{\phi}{1+\rho S\delta}\left[2.2 - 1.2\int_h^\infty \left(1-\frac{h}{x}\right)^3\Phi(x)dx\right] \quad (16)$$

3. Analysis and discussion

3.1. Packing density

According to Eq. (7), if taken $y = x/\bar{x}$, and $T = t/\bar{x}$, Eq. (17) may be obtained:

$$\phi = \inf_{0 \leq T < \infty}\left[\phi_0/1-(1-\phi_0)\int_T^\infty\left(1-\frac{T}{y}\right)^{1.6}ny^{n-1}\exp(-y^n)dy - \int_0^T\left[\left(1-\frac{y}{T}\right)^{3.1} + 3.1\frac{y}{T}\left(1-\frac{y}{T}\right)^{2.9}\right]ny^{n-1}\exp(-y^n)dy\right] \quad (17)$$

It is seen from Eq. (17) ,that ϕ is independent of $\bar{x}$ and only depends on n.

Because of the transcendence of the function, it is difficult to obtain its analytic solution. However, its numerical solution may be found. Fig. 1 shows the calculated results. It can be seen from the figure that ϕ decreases with the increase of n. In other words, the more narrow the distribution, the less the packing density is.

3.2. Water demand

It may be known from Eq. (11) that the water demand is related to specific surface and packing density. The larger the specific surface, the more the water demand is.

The packing density is related to the distribution index closely. The more n, the less the packing density is. It can be

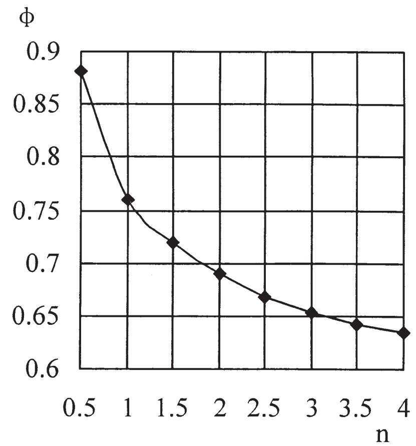

Fig. 1. The estimated relationship between the packing density and the distribution index.

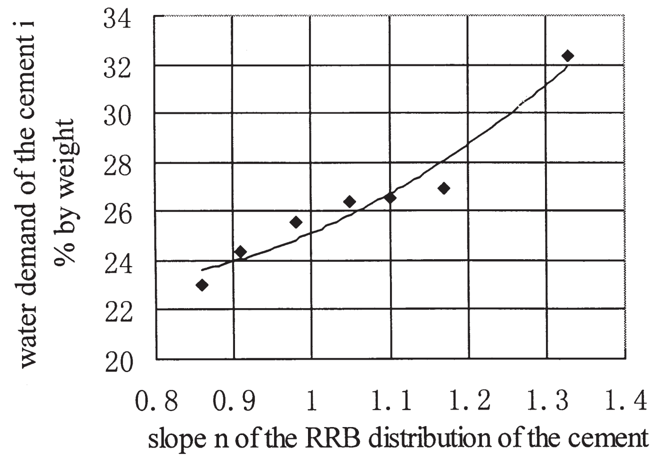

Fig. 3. Sprung's experimental result.

seen from Eq. (11) that the less the packing density, the more the water demand is. A concept may be obtained from these (i.e., under the circumstance of same specific surface, the narrower the particle size distribution and the more the water demand is). Fig. 2 shows the relationship between the water demand and the distribution index. Fig. 3 shows Sprung's experimental result. It is identical with the above analysis.

Turning Eq. (11) into Eq. (18):

$$S = \frac{1}{\rho\delta}[\phi(\rho w/c + 1) - 1] \tag{18}$$

It may be seen that if water-cement ratio is constant, S increases with the increase of ϕ. That is to say, the specific surface may be increased without increasing the water demand by adjusting the particle size distribution. However, it should be noted that this effect is very limited. Because $\phi < 1$, it may be deduced that [see Eq. (19)]

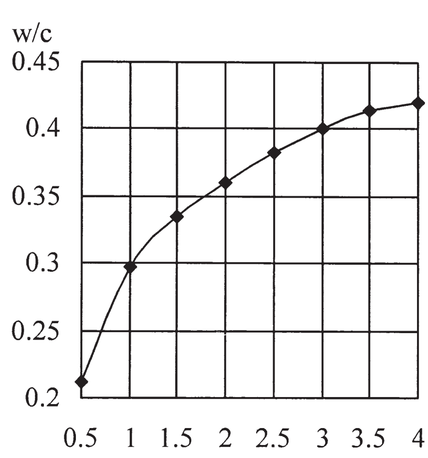

Fig. 2. The estimated relationship between the water demand and the distribution index.

$$S_{max} = \frac{w/c}{\delta} \tag{19}$$

When $S > S_{max}$, it is always the case that the increase of the specific surface will accompany the increase of the water demand.

3.3. Hydration degree

Fig. 4 shows the results calculated by Eq. (15). It may be seen that for same specific surface and incident hydration depth, the hydration degree rises with the increase of the distribution index. That is to say, under the condition of same specific surface, the more narrow the particle size distribution, the higher the hydration degree is. This fact has been proved by many researchers.

3.4. Porosity

The porosity influences directly many properties of cement stone, and is one of the important factors to consider when evaluating the influences on materials' properties. To analyze the influence of particle size distribution on the properties of cement stone, the packing density and the hydration degree are both indirect. The direct relation can be established only by the porosity.

The influence of particle size distribution on the porosity of cement stone is complex. Different researchers reached different conclusions from different perspectives. To understand this problem more clearly, it is analyzed from following three aspects:

1. Under the same water-cement ratio, the influence of particle size distribution on the porosity of cement stone. It can be deduced from Eq. (11) that [see Eq. (20) and Eq. (21)]:

$$\frac{\phi}{1 + \rho S\delta} = \frac{1}{\rho w/c + 1} \tag{20}$$

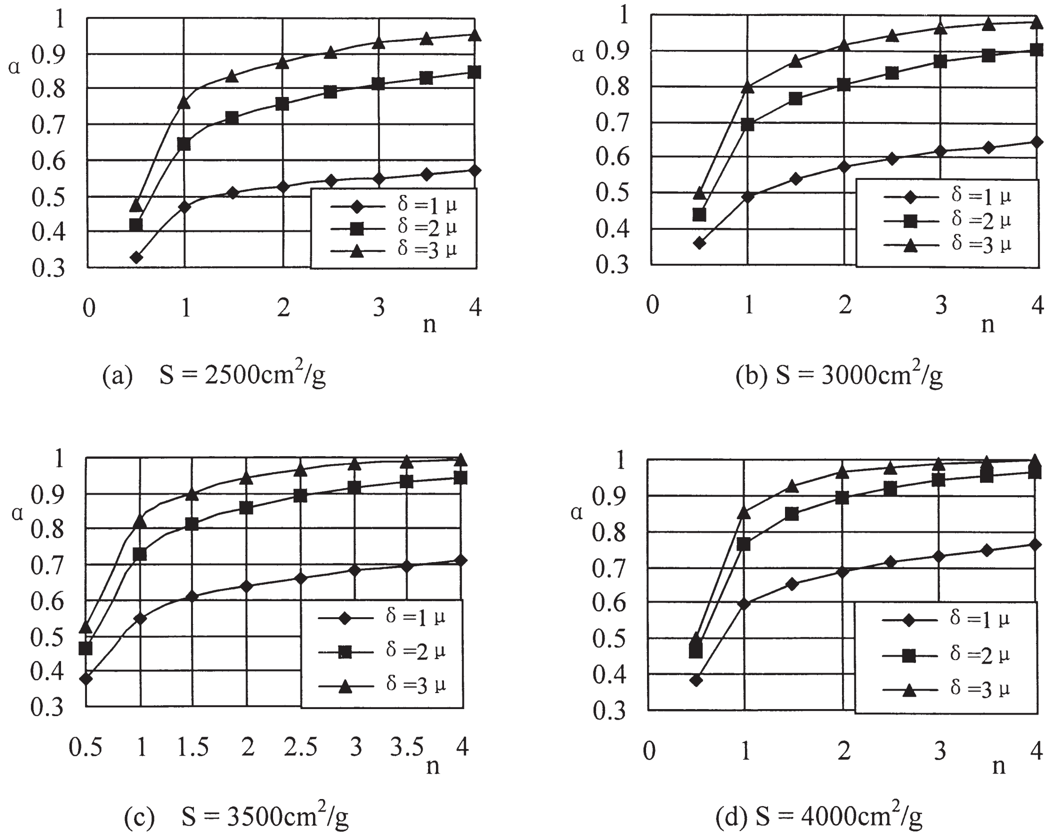

Fig. 4. The estimated influence of the distribution index on the hydration degree.

$$P = 1 - \frac{\phi}{1+\rho S\delta}\left[2.2 - 1.2\int_h^\infty \left(1-\frac{h}{x}\right)^3 \Phi(x)dx\right.$$

$$= 1 - \frac{1}{\rho w/c + 1}\left\{1 + 1.2\left[1 - \int_h^\infty \left(1-\frac{h}{x}\right)^3 \Phi(x)dx\right]\right\}$$

$$= 1 - \frac{1+1.2\alpha}{1+\rho w/c} \tag{21}$$

It can be seen from Eq. (21) that under same water-cement ratio, the porosity only depends on the hydration degree. The higher the hydration degree, the lower the porosity is. The relationship between the hydration degree and particle size distribution has been discussed above. At same hydration depth (or at same age), the more narrow the particle size distribution, the higher the hydration degree is, and the lower the porosity is. Thus, some researchers claimed that cement particle distribution should be as narrow as possible.

2. At same hydration degree, the influence of particle size distribution on the porosity. It may be obtained from Eq. (16) that [see Eq. (22)]:

$$P = 1 - \phi\frac{1+1.2\alpha}{1+\rho S\delta} \tag{22}$$

It may be seen that at same hydration degree, the porosity is linear with the packing density. The higher some researchers considered that to get the cement stone with higher performance, cement particles should have the distribution as wide as possible to attain a packing density as high as possible.

3. Under same workability, the influence of the particle size distribution on the porosity. Workability is a very important property of fresh cement paste. Except to provide the reactant of cement hydration, the water mixed with cement is to make fresh paste that has certain workability to satisfy the necessity of mixing and molding.

It is necessary to emphasize that same water-cement ratio doesn’t mean the same workability, and the same hydration degree doesn’t mean the same time. The above two circumstances represent the influence of particle size distribution only from different aspects. From practice, two concepts of “same workability” and “same time” must be stressed to understand still better the influence of the particle size distribution on the porosity. It can be seen from Eq. (22) that the porosity depends on both the packing density and the hydration degree. But the influence of particle size distribution on them is just opposite. Thus, the two aspects should be considered at the same time, and their comprehensive effect should be noted.

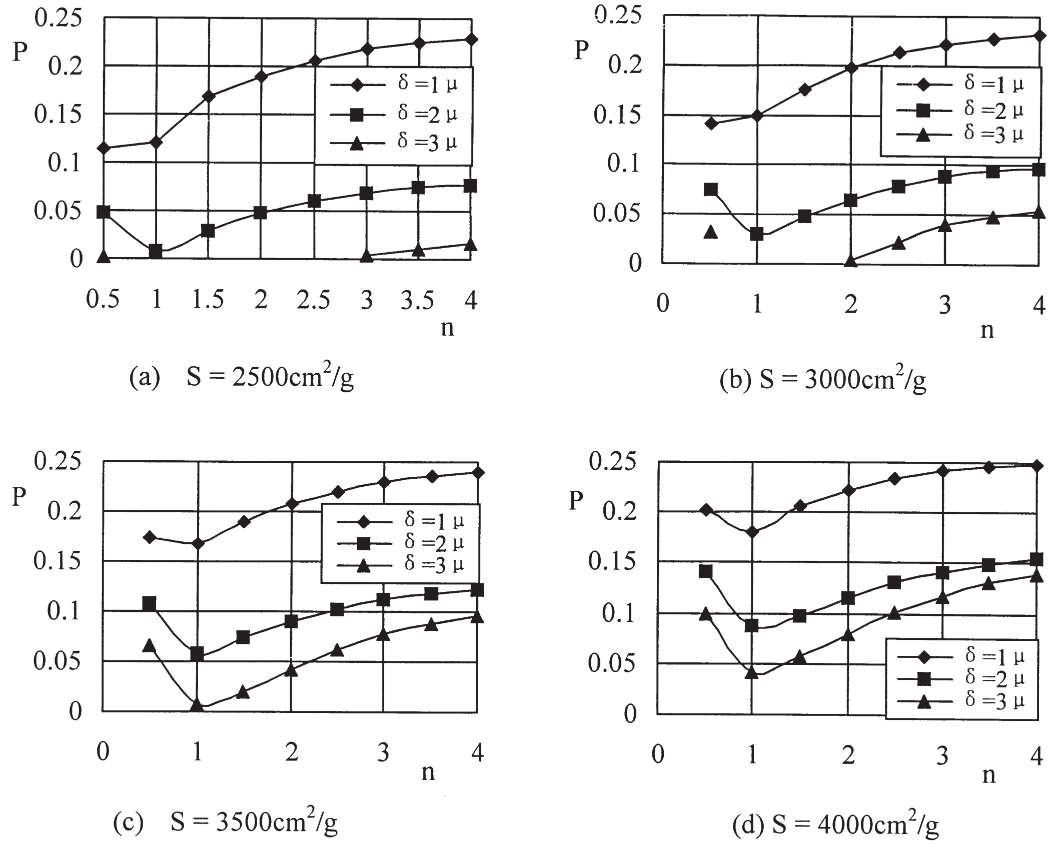

Fig. 5. The estimated influence of the distribution index on the porosity.

Fig. 5 shows the results calculated according to Eq. (16). When the hydration depth is less (at earlier age), the influence of the packing density is primary, and the influence of the hydration degree is secondary. Their comprehensive effect is that the porosity increases with the increase of distribution index. That is, the wider the particle size distribution, the lower the porosity is. This is concordant with the influence of the particle size distribution on the packing density.

When the hydration depth is larger (at later age), P attains the minimum where $n = 1$. Under this circumstance, both the packing density and the hydration degree effect the porosity at same time. When n is less, although the packing density is higher, the porosity is still higher because the hydration degree is very low. When n is larger, although the hydration degree is higher, the porosity is higher also because the packing density is lower. When n is about 1, the system has not only higher packing density but higher hydration degree; thus the porosity is lower. This shows that the very narrow particle size distribution is disadvantageous for improving the properties of cement. Kuhlmann et al. [1] even pointed out that “In view of the requirements that the functional properties of cement have to satisfy, efforts to grind cements with narrow particle size distribution are therefore likely to come up against limits.” The reason lies in aforementioned.

It may be seen from above analysis and calculation that the suitable distribution of cement particle is when n is about 1. For the characteristic particle size, $\bar{x}$, it is not an independent variable. When the specific surface is certain, and can be obtained by Eq. (6). When $n = 1$, $A(n) = 2.352$ [see Eq. (23)].

$$\bar{x}S = 2.276 \quad \text{or} \quad \bar{x} = \frac{2.276}{S} \tag{23}$$

It is necessary to point out that:

1. It is not necessary that the method attaining the narrow distribution is sought to overemphasize high hydration rate. On the one hand, it is difficult to attain more narrow distribution in industrial-scale production. It entails a very complex process and much equipment and increases costs. On the other hand, if more narrow distribution is attained, it is advantageous to accelerate the hydration of cement, but the water demand is raised because the packing density is decreased. It not only cannot improve the performance of cement stone, but can even make it drop.
2. It is also unsuitable that to overemphasize high packing density requires wider particle size distribution. If n is too small, although the system has higher packing

density, the performance of the material is still diminished because the hydration rate is reduced.

4. Conclusions

By analysis and calculation, the following conclusions can be obtained:

1. Wider particle size distribution is advantageous for increasing the packing density of the system and decreasing the water demand. The less the distribution index, the higher is the packing density and the lower the water demand is.
2. Narrower particle size distribution is advantageous to raise the hydration rate. The larger the distribution index, the higher is the hydration rate.
3. Under the condition of the same water-cement ratio, narrow distribution is advantageous to reduce the porosity of cement stone. Under the condition of the same hydration degree, wide distribution is advantageous to reduce the porosity of cement stone. In the more practical sense, there should be an optimum particle size distribution. It occurs when n equals 1.

References

[1] K. Kuhlmann, H.-G. Ellerbrock, S. Sprung, Particle size distribution and properties of cement, Part I: Strength of Portland cement, Cement-Lime-Gypsum 6 (1985) 136–144.
[2] S. Sprung, K. Kuhlmann, H.-G. Ellerbrock, Particle size distribution and properties of cement, Part II: Water demand of Portland cement, Cement-Lime-Gypsum 11 (1985) 275–281.
[3] G. Frigione, S. Marra, Relationship between particle size distribution and compressive strength in Portland cement, Cem Concr Res 6 (1976) 113–128.
[4] A. Wang, C. Zhang, N. Zhang, Study of the particle size distribution on the properties of cement, Cem Concr Res 27 (5) (1997) 685–695.
[5] V. Johansen, P.J. Andersen, Particle packing and concrete properties, Materials Science of Concrete 1., The American Ceramic Society, USA (1991) 111–147.
[6] T. Stovall, F. DeLarrard, M. Buil, Linear packing density model of grain mixtures, Powder Technology 48 (1986) 1–12.
[7] N. Standish, D.E. Borger, The porosity of particulate mixture, Powder Technology 22 (1979) 121–125.