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Evaluation of the wettability of spherical cement particle surfaces using penetration rate method

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Abstract

The wettability of cement particles is related to the fluidity of cement paste. This paper describes the mechanism of the higher fluidity imparted by the spherical cement particles in light of their wettability. In addition, the effects of gypsum on the wettability were also studied. This study has shown the following: (1) The weight of water and water-reducing agent solution penetrating the spherical cement powder bed is 24–150% higher than that for the ordinary Portland cement powder bed. This results in the improvement of the wettability of the particle surfaces of spherical cement. The high wettability of spherical cement contributes to its high fluidity. (2) The presence of many fine gypsum particles on the spherical cement particle surface reduces the wettability. (3) To prepare spherical cement, the optimum amount of gypsum added is determined by the acceleration of the formation of spherical particles and the wettability of particle surfaces.

Keywords: Workability; Characterization; Permeability; Gypsum; High-performance concrete

1. Introduction

Spherical cement is characterized by round particles and is prepared by a dry impact blending method (microhybridization technology) [1–5]. Owing to its round shape, spherical cement powder provides excellent packing characteristics. Concrete containing spherical cement exhibits high fluidity, thereby improving the workability. Moreover, spherical cement requires less mixing water, facilitating the fabrication of concrete with higher strength and durability [1–5]. Currently, there are demands within the construction industry for the improvement of concrete fluidity, the enhancement of concrete strength and an increase in concrete durability. In this respect, spherical cement is spotlighted as a new cement that has the potential to fulfill such requirements.

The physical properties of mortar and concrete made of spherical cement have been investigated [1–5]. These investigations have shown that spherical cement contributes in the significant increase in the fluidity, strength and durability of mortar and concrete compared to ordinary Portland cement. With the same fluidity and workability, spherical cement requires 1/3 times high-performance water-reducing agent in comparison with ordinary Portland cement. Furthermore, for the same strength, cement usage can be reduced by 20%. This will decrease heat generation in the initial state of hardening. In addition, to explain the mechanism of higher-fluidity implementation and the mechanism of spherical cement formation, the surfaces of cement particles were studied using an electronic microscope, and the element distribution was analyzed. The zeta potential, and various powder characteristics and electric charges were also measured during the processing of cement particles into a round shape [3,5,6]. The results have shown that the higher fluidity peculiar for spherical cement is imparted

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particularly by round particles, less fine powder, less specific surface area and less hydration in the very early phase, as well as gypsum stacking on the particle surfaces. Spherical cement is produced by initial crush, fine particle generation, the adhesion of fine particles to the surface of larger core particles and fixing [2,5,6]. That is to say, the processes for the formation of spherical cement include the following: (1) grinding and shaving off the sharp-pointed edges of large particles in the initial stage; (2) an increase in very fine particles; (3) an attachment of fine particles to the surfaces of larger core particles; and (4) fixing and embedding of fine particles. Moreover, it was observed that gypsum plays the role of an electrostatic binder in the process of fine particle adhesion and that the addition of finely ground gypsum accelerates the process of spherical cement formation [6].

In this paper, the mechanism of the higher fluidity imparted by the spherical cement was studied in light of the wettability of cement particles by measuring the weight of water and the high-performance water-reducing agent solution that penetrate the layer filled with cement powder (cement bed). The rate of penetration was measured to investigate the wettability of water and water-reducing agent solution on the surfaces of spherical cement and ordinary Portland cement particles. In addition to this, the effects of gypsum on the wettability were studied in order to find out the optimum conditions for adding gypsum, which accelerates spherical cement formation.

Table 1
Characteristics properties of ordinary Portland cement and spherical cement

	Ordinary Portland cement	Spherical cement
Mean diameter (μm)	13.9	10.8
Specific surface area		
Blaine (cm^2/g)	3250	2700
BET (m^2/g)	0.94	0.58
Density (g/cm^3)	3.16	3.16
Chemical compositions (%)		
SiO_2	21.6	21.1
Al_2O_3	5.1	5.0
Fe_2O_3	3.0	2.9
CaO	63.7	64.4
MgO	1.7	1.4
SO_3	2.0	2.0
Na_2O	0.29	0.22
K_2O	0.47	0.42

2. Experimental details

2.1. Materials

2.1.1. Cement

Commercially available ordinary Portland cement (SO_3: 2.0%, BET specific surface area: 0.94 m^2/g) and spherical cement (SO_3: 2.0%, BET specific surface area: 0.58 m^2/g) were used. Table 1 shows the characteristics properties of the cement. Spherical cement was prepared by processing commercial ordinary Portland cement as the raw material for 20 min using a dry impact blending method (microhybridization technology) [2,5]. This is the method used to form microparticles into spherical shapes by causing rotary impact as a result of high-speed air flow in a ring-shaped impact chamber [7,8]. The equipment used was a Nara Hybridization System (Model NHS-1; Nara Machinery, Tokyo, Japan). It was operated at a rotation speed of 8000 rpm at temperatures from 45 to 75 °C. Raw cement was put into the equipment in 150-g batches.

2.1.2. Clinker powder, mixture of clinker powder and gypsum powder

Clinker powder was prepared by crushing ordinary Portland cement clinker. The BET specific surface area of the clinker powder was 0.79 m^2/g. For the treatment method of forming the clinker powder particles into a spherical shape, the same dry impact blending method as that for the cement was used. Crushed natural gypsum powder ($CaSO_4{\cdot}2H_2O$, BET specific surface area: 0.80 m^2/g) was used like in a cement plant. The clinker powder and the gypsum powder in a weight ratio of 100 to 10.75 (SO_3: 4.2%) was mixed. For the treatment method of forming this powder particle mixture into a spherical shape, the same dry impact blending method as that for the cement was used.

2.1.3. Water

Distilled water was used for the penetration experiment and for diluting the water-reducing agent. For making mortar, tap water was used.

2.1.4. Water-reducing agents

Naphthalene sulfonic acid-based superplasticizer and polycarboxylic acid-based superplasticizer (MT-150 manufactured by Kao, Tokyo, Japan and SP-8S manufactured by NMB, Tokyo, Japan, respectively) were used.

2.1.5. Aggregate

As the fine aggregate for mortar, standard sand from Toyoura (JIS R 5201-1987, maximum grain diameter: 0.3 mm) was used.

2.2. Experimental method and apparatus

2.2.1. Preparing the cement

Ordinary Portland cement, spherical cement, the clinker powder and the mixture of clinker powder and gypsum powder were left for 24 h in an experimental room (maintained at temperatures of 20–25 °C) before being tested.

2.2.2. Preparing the water-reducing agent solution

Commercially available water-reducing agents were diluted with water to obtain a water solution of 3.3%. The

3.3% naphthalene sulfonic acid-based water-reducing agent solution had a density of 1.005 (at a temperature of 25 °C) and viscosity of 1.085 mPa·s (at a temperature of 25 °C). The 3.3% polycarboxylic acid-based water-reducing agent solution had a density of 1.002 (at a temperature of 25 °C) and viscosity of 1.7 mPa·s (at a temperature of 25 °C). Assuming that 0.9 g of water solution (water to powder ratio = 0.3) penetrates the powder bed, a concentration of 3.3% corresponds to 1% (by weight to cement). The solution was prepared in the experimental room. The water had a density of 0.997 (at a temperature of 25 °C) and viscosity of 0.89 mPa·s (at a temperature of 25 °C).

2.2.3. Evaluating the wettability of the water and water-reducing agent solution on the cement

2.2.3.1. Measuring the amount of water and water-reducing agent solution penetrating the cement powder bed. The weight of the liquid, which penetrated the powder bed, was measured using an automatic penetration rate gauge (model WET-6100 manufactured by RHESCA, Tokyo, Japan). Fig. 1 illustrates the automatic penetration rate gauge [7]. A glass tube with an inside diameter of 11.4 mm, a height of 50 mm, with the bottom covered in a nylon mesh, was filled with 3 g cement powder, and tapping was carried out 100 times. After tapping, the porosity was 0.5–0.6. The glass tube filled with powder was hung from the electronic balance of the testing apparatus. Then, the glass tube bottom was dipped in water or the water-reducing agent with a dipping rate of 2 mm/s and depth of 0.5 mm, respectively. The liquid entered in the spaces of the powder bed, and the weight of the penetration liquid was measured. The penetration rate was determined from the changes in weight of the penetration liquid with the time after dipping.

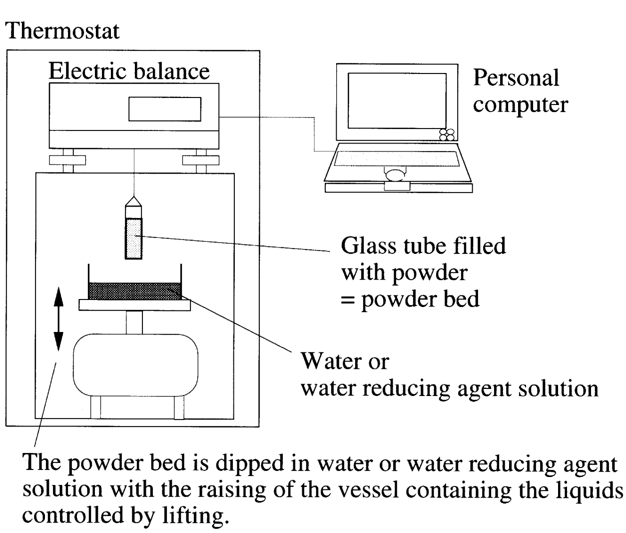

Fig. 1. Schematic outline of automatic penetration rate gauge [7].

2.2.3.2. Analyzing the penetration rate and evaluating the wettability [9]. For liquid flowing through a capillary tube with a radius of r, the penetration rate can be given by the following Poiseuille equation (Eq. (1)):

$$u = (r^2/8\eta)(P - P_t)/h_t, \tag{1}$$

where u stands for the penetration rate, η for the viscosity of the liquid, P for capillary pressure, P_t for the hydraulic pressure at time t and h_t for the distance of liquid penetration at time t. Capillary pressure P is expressed equivalently by $(2\gamma_1\cos\theta)/r$, while hydraulic pressure P_t by $g\rho_1 h_t$, where ρ_1 stands for liquid density, g for the gravitational acceleration and γ_1 for the surface tension of liquid. The penetration rate can, therefore, be expressed as follows:

$$u = \mathrm{d}h_t/\mathrm{d}t = (r^2/8\eta h_t)\{(2\gamma_1\cos\theta)/r - g\rho_1 h_t\}, \tag{2}$$

Using the relationship of $P = g\rho_1 h_\infty$, Eq. (2) can be rewritten as follows:

$$u = \mathrm{d}h_t/\mathrm{d}t = (r^2 g\rho_1/8\eta)\{(h_\infty/h_t) - 1\}, \tag{3}$$

where h_∞ stands for the distance of liquid penetration under balance.

The weight of the penetrating liquid after time t, W_t, is given by the following equation, where S stands for the cross-sectional area of the powder bed and ε for the porosity of the powder bed, W_t replaces $\varepsilon S\rho_1 h_t$ and W_∞ stands for the weight of penetrating liquid under balance (Eq. (4)):

$$\mathrm{d}h_t/\mathrm{d}t = (1/\varepsilon S\rho_1)(\mathrm{d}W_t/\mathrm{d}t), \quad h_\infty/h_t = W_\infty/W_t. \tag{4}$$

Thus, the following equation for the penetration rate corresponding to the penetration weight from Eq. (3) is obtained:

$$u = \mathrm{d}W_t/\mathrm{d}t = K\{(W_\infty/W_t) - 1\} \tag{5}$$

$$K = (r^2\varepsilon S g\rho_1^2/8\eta). \tag{6}$$

Now, in plotting $1/W_t$ and $\mathrm{d}W_t/\mathrm{d}t$ (the gradient of the recorded penetration curve), W_∞ and K from that curve are obtained. Thus, the mean capillary radius (r) and the adhesion can be calculated from Eq. (7):

$$r = (8\eta K/\varepsilon S\rho_1^2 g)^{1/2}. \tag{7}$$

Next, from the equations, $W_\infty = \varepsilon S\rho_1 h_\infty$, $P = g\rho_1 h_\infty$ and $P = (2\gamma_1\cos\theta)/r$, the adhesion $\gamma_1\cos\theta$ is determined as (Eq. (8)):

$$\gamma_1\cos\theta = (rgW_\infty)/2\varepsilon S. \tag{8}$$

2.2.4. Evaluating the fluidity

According to JIS R 5201-1987, the mortar flow value under conditions of cement/fine aggregate = 0.5 and water/cement = 0.55 was measured.

3. Results and discussion

3.1. Amount of liquid penetrating the cement bed

Figs. 2–4 show temporary changes in the weight of water and the water-reducing agent solution that penetrated the powder bed filled with the ordinary Portland cement and the powder bed filled with spherical cement. Spherical cement has a higher curve gradient than the ordinary Portland cement. After 100 s, the weight of the penetrating water was shown to be 24% higher, and the weight of the penetrating water-reducing agent solution was higher by 30–150%. This means that the spherical cement bed provides higher liquid wettability than the ordinary Portland cement bed. The highest increase rate was shown in water, followed by naphthalene sulfonic acid and the polycarboxylic acid-based water-reducing agent solution.

It is to be noted that only a small amount of polycarboxylic acid-based water-reducing agent solution penetrated the ordinary Portland cement bed. This is possibly because the viscosity of this admixture, which is higher than that of water and the naphthalene sulfonic acid-based water-reducing agent, significantly affected the initial penetration into the cement bed. Furthermore, it was predicted that the ordinary Portland cement would be accompanied by differences in wettability depending on the type of water-reducing agent. On the contrary, spherical cement did not exhibit significant differences in the penetration weight between the naphthalene sulfonic acid- and polycarboxylic acid-based water-reducing agents, as illustrated in Figs. 3 and 4. Spherical cement can therefore, without fail, effectively induce the water reduction effects of various water-reducing agents.

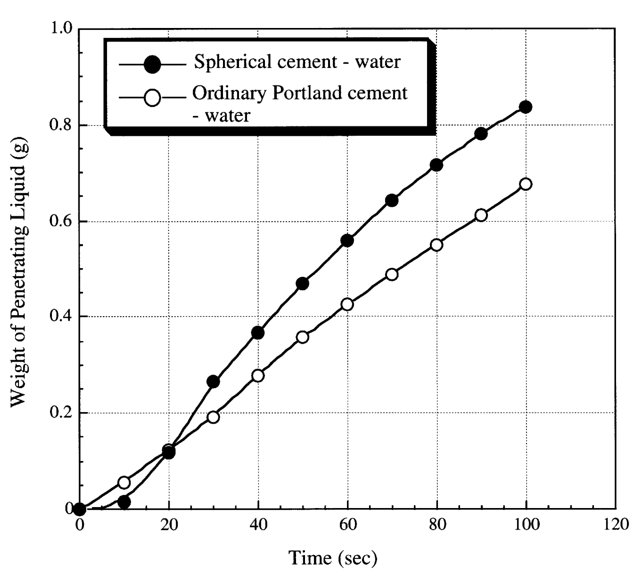

Fig. 2. Changes in the weight of water penetrating the cement bed with time after dipping the cement bed in water.

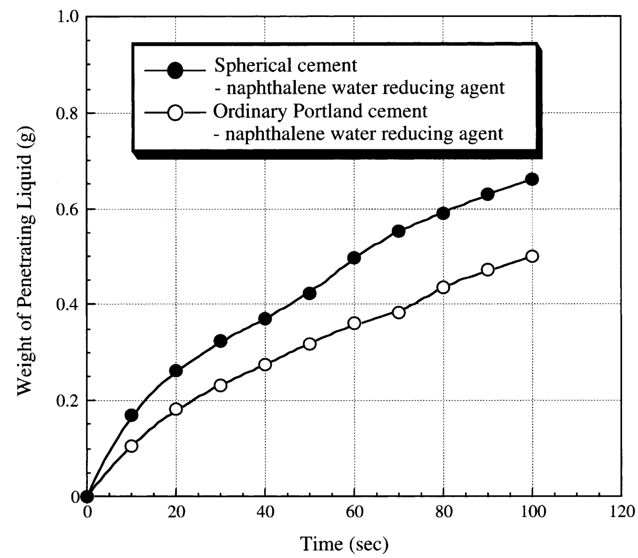

Fig. 3. Changes in the weight of the naphthalene sulfonic acid-based water-reducing agent penetrating the cement bed with time after dipping the cement bed in the water-reducing agent solution.

3.2. Evaluating the wettability of liquid on cement particle surfaces

Based on the results obtained above, the wettability of various liquids on cement particle surfaces was evaluated. Figs. 5 and 6 show the relationships between $1/W_t$ and

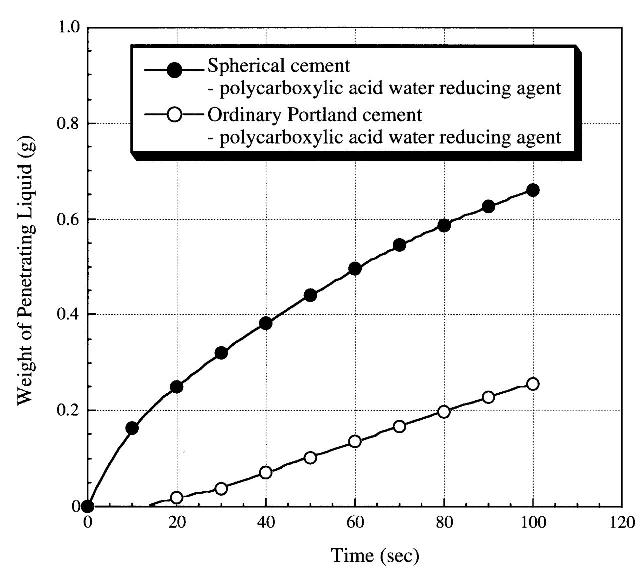

Fig. 4. Changes in the weight of the polycarboxylic acid-based water-reducing agent penetrating the cement bed with time after dipping the cement bed in the water-reducing agent solution.

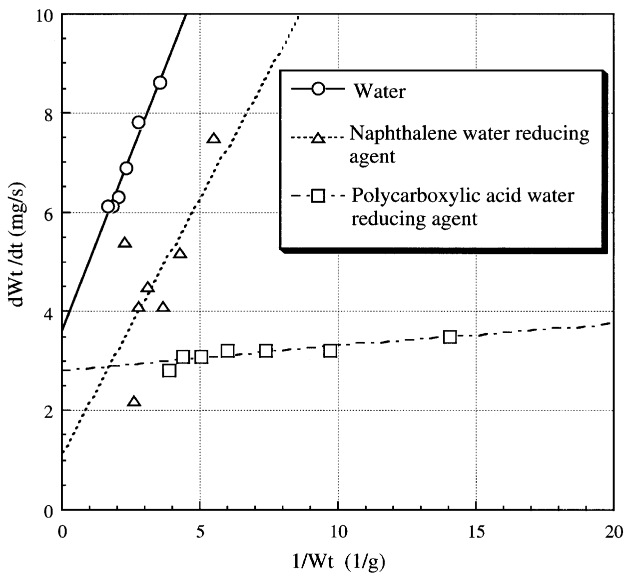

Fig. 5. Weight of liquids penetrating the ordinary Portland cement ($1/W_t$ against dW_t/dt plotted).

dW_t/dt plotted according to Eq. (5). Table 2 lists the values of the adhesion force $\gamma\cos\theta$ of liquid to the cement particle surface fixed from the values of K and W_∞ determined from figures. The porosity ε ranged from 0.5 to 0.6 for the powder beds. In Table 2, the value of $\gamma\cos\theta_{SC}/\gamma\cos\theta_{OPC}$ indicates the degree of improvement of the wettability on the spherical cement particle surface in comparison with the wettability on the ordinary Portland cement particle surface. While spherical cement has a BET specific surface area 40% smaller than the ordinary Portland cement and provides lower powder bed porosity (0.52 and 0.59, respectively), the value of $\gamma\cos\theta_{SC}/\gamma\cos\theta_{OPC}$ was calculated, including differences in the specific surface area and the porosity.

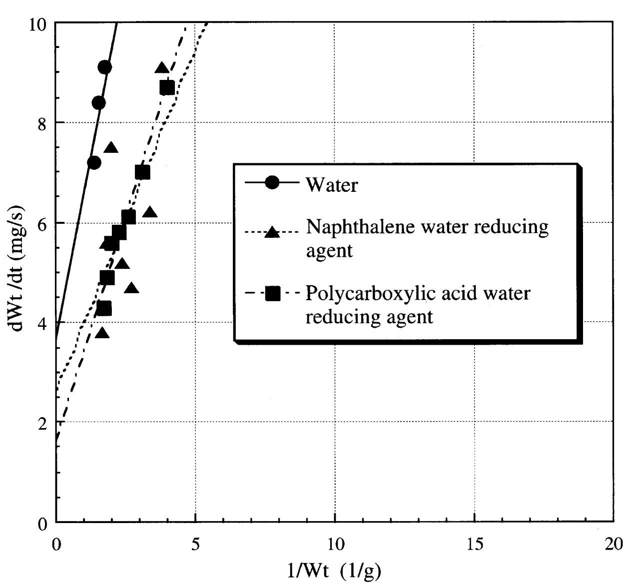

Fig. 6. Weight of liquids penetrating the spherical cement ($1/W_t$ against dW_t/dt plotted).

Table 2
Differences in the adhesion force of liquids to cement

	Penetrating liquid		
	Water	Naphthalene water-reducing agent	Polycarboxylic acid water-reducing agent
$\gamma\cos\theta_{OPC}$ Adhesion force of liquid to ordinary Portland cement	0.21	0.32	0.01
$\gamma\cos\theta_{SC}$ Adhesion force of liquid to spherical cement	0.50	0.59	0.64
$\gamma\cos\theta_{SC}/\gamma\cos\theta_{OPC}$	2.37	1.85	52.4

In all cases of water, the naphthalene sulfonic acid-based water-reducing agent and the polycarboxylic acid-based water-reducing agent, the values of $\gamma\cos\theta_{SC}/\gamma\cos\theta_{OPC}$ were over 1 as shown in Table 2; namely, they were about 2–50. Therefore, it is thought that spherical cement provides higher wettability on the cement particle surface than the ordinary Portland cement possibly owing to its particle surface structure. Unlike the ordinary Portland cement particle, the spherical cement particle has a sponge-like surface structure on which very fine particles of approximately 1–3 μm are stacked as shown in Fig. 7. Water and the water-reducing agent solution, therefore, can easily penetrate the sponge-like structure. Assuming that water and the naphthalene sulfonic acid-based water-reducing agent have a surface tension of 72 dyn and that the polycarboxylic acid-based water-reducing agent has a surface tension of 40 dyn, the contact angles at which those liquids contact the cement particle surface were calculated. Consequently, the spherical cement particle provides an angle about 0.2° smaller for water and the naphthalene sulfonic acid water-reducing agent solution and an angle for the polycarboxylic acid water-reducing agent about 1° smaller than the ordinary Portland cement particle. Thus, it is believed that the wettability is improved and that this high wettability of spherical cement contributes to the high fluidity.

3.3. Effects of gypsum on wettability on cement particle surface

It has been reported that gypsum plays the role of a binder for binding cement fine particles in the process for forming spherical cement and contributes significantly to shortening the spherical cement formation process [6]. The effects of gypsum on the wettability of cement particle surfaces were determined. For this, clinker powder particles and a mixture of clinker powder and gypsum powder (addition of 4.2% as SO_3) were treated using the dry impact blending method. The aforementioned glass tubes were packed with the powder samples, then the weight of the penetration water, naphthalene sulfonic acid-based water-

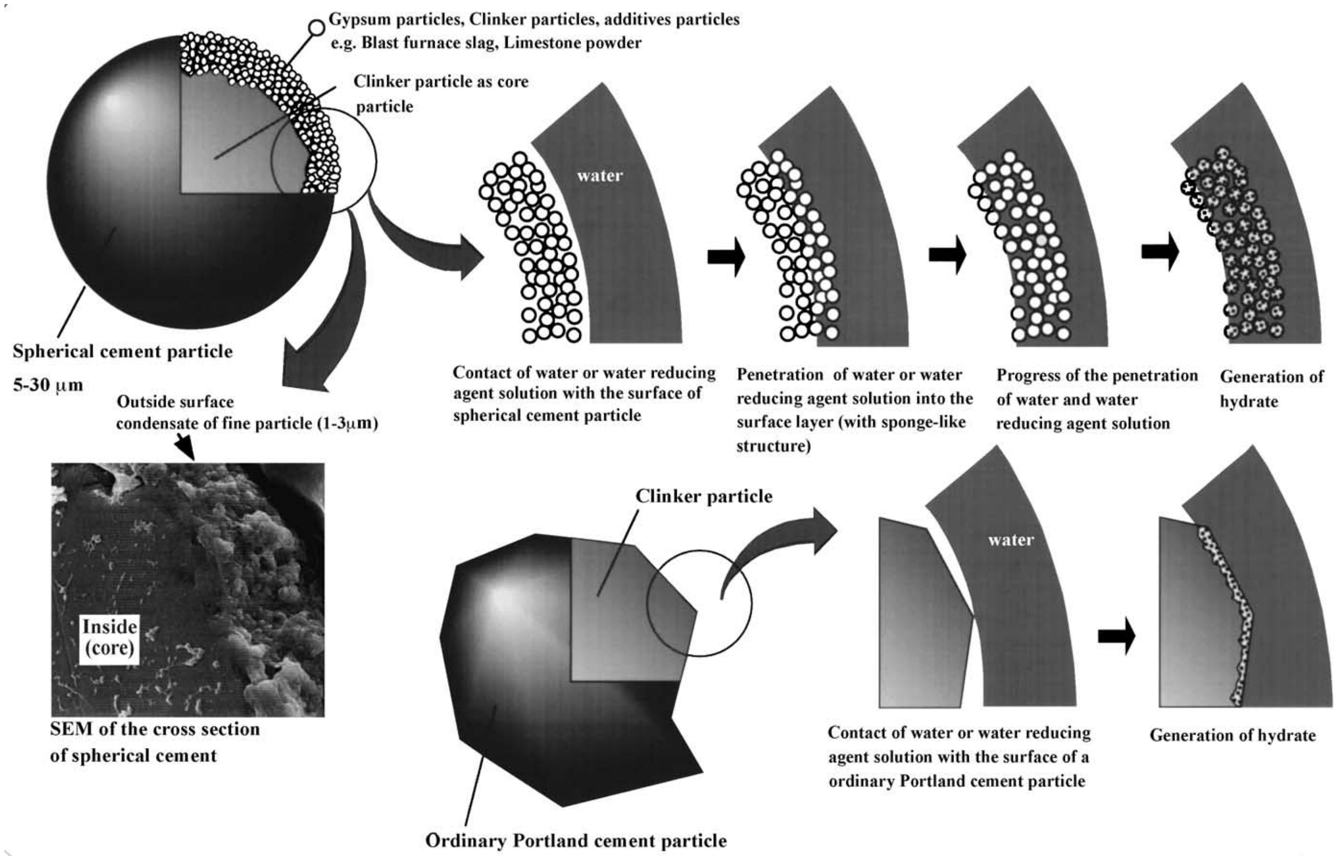

Fig. 7. Structure of the cross section of the cement particle, and image of the penetration of water and water-reducing agent solution into the particle surface.

reducing agent and polycarboxylic acid-based water-reducing agent were measured, respectively.

The results are presented in Figs. 8–10. The plotted gradient indicates significant differences, especially for

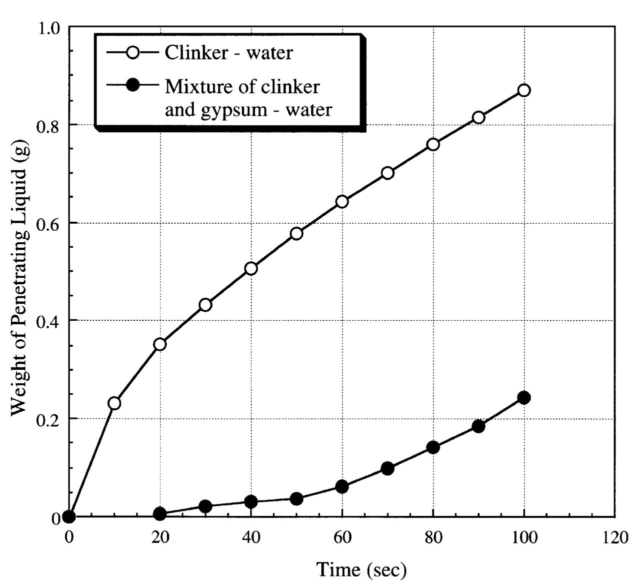

Fig. 8. Changes in the weight of the water penetrating the sphered clinker powder bed, and a mixture of clinker and gypsum bed with time after dipping the powder bed in water.

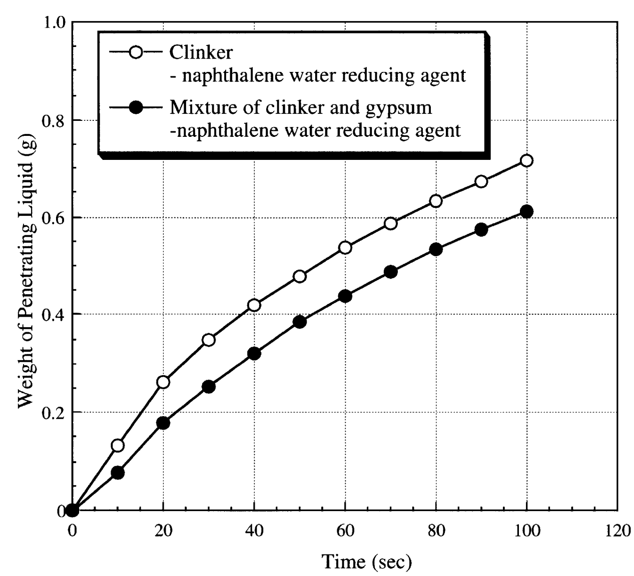

Fig. 9. Changes in the weight of the naphthalene sulfonic acid-based water-reducing agent penetrating the sphered clinker powder bed, and a mixture of clinker and gypsum bed with time after dipping the powder bed in the water-reducing agent solution.

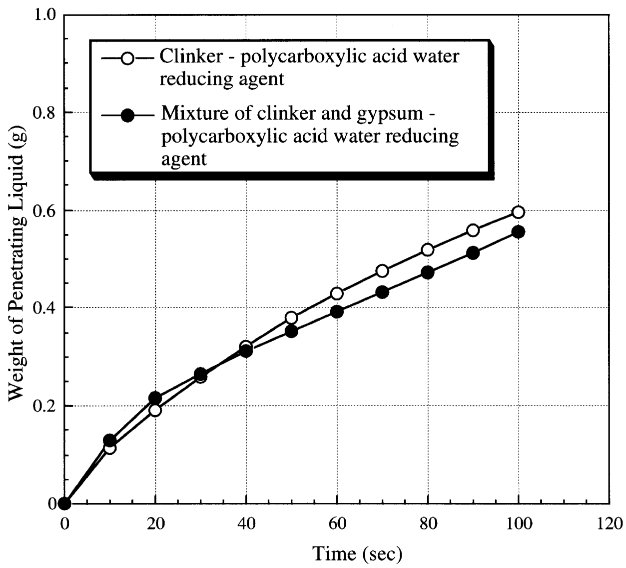

Fig. 10. Changes in the weight of the polycarboxylic acid-based water-reducing agent penetrating the sphered clinker powder bed, and a mixture of clinker and gypsum bed with time after dipping the powder bed in the water-reducing agent solution.

water. With gypsum powder added, the weight of penetration was decreased considerably. This is possibly because many fine gypsum particles presenting on the spherical cement particle surface reacted with water together with the neighboring clinker, and, consequently, the hydration products filled the empty spaces and water penetration was decreased. This reaction was considered to have occurred very quickly because the gypsum particles were very fine. On the contrary, the water-reducing agent did not show significant differences when compared with water. Small differences originating from the gypsum are possibly due to the suppression of the reaction of gypsum and clinker with water by the water-reducing agent. It was previously reported that the amount of the naphthalene sulfonic acid-based water-reducing agent adhering to the spherical cement particle surface was reduced in comparison with the same amount adhering to the ordinary Portland cement particle surface [3]. This is because the adhesion of the water-reducing agent to the spherical cement particle surface, particularly in the interstitial phase, is accompanied by competitive adhesion between SO_4^{2-} ions from the gypsum particles existing locally on the spherical cement surface and the water-reducing agent [10]. Some investigators have reported that the polycarboxylic acid-based water-reducing agent, as well as the naphthalene sulfonic acid-based water-reducing agent, is affected by the gypsum and SO_4^{2-} in the adhesion process to the cement particle surface with the amount of decreased adhesion [11,12]. Therefore, it is considered that the competitive adhesion between gypsum and the water-reducing agent suppressed the reaction of gypsum and clinker with water.

3.4. Optimum amount of gypsum added to prepare spherical cement

The above observation implies that existing gypsum may reduce the wettability of water on cement. A reduction in wettability results in a reduction in the dispersibility of cement particles and, thus, in a reduction in fluidity. Therefore, the fluidity of the clinker powder and gypsum mixtures, which were treated by the dry impact blending method at various treatment times with differing amounts of gypsum addition, were investigated.

Fig. 11 shows the relationships between the treatment time for the formation of spherical particles and the mortar flow value of the powder mixture after the treatment. If no gypsum is added, or if 3.33% or more of gypsum is added, the flow value is not significantly increased with an increase in the treatment time. This result suggests that the optimum amount of gypsum added, which is determined by the acceleration of the formation of spherical particles and the wettability of particle surfaces, exists to reveal the high fluidity of cement after the treatment. According to this experiment, the optimum amount is 0.65–2.65% relative to clinker powder. However, the amount of SO_3 converted from 2.65% of added gypsum is 1.2%, being lower than the approximately 2.0% of SO_3 in ordinary Portland cement. Since this value may cause abnormal condensation and

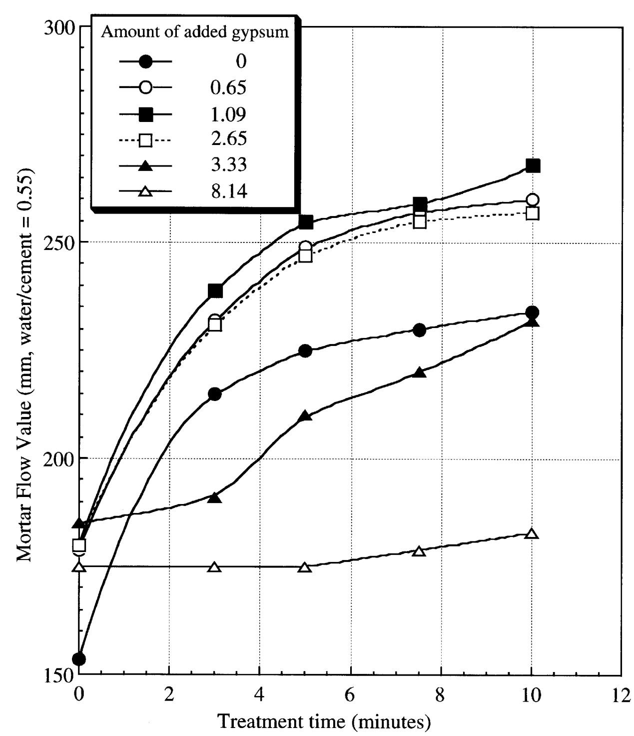

Fig. 11. Relationships between the treatment time for the formation of spherical particles and the mortar flow value of the powder mixture after treatment with differing amounts of gypsum addition ($CaSO_4{\cdot}2H_2O$ wt.% vs. clinker powder).

lower durability, further investigations are required to fix the optimum amount of gypsum.

4. Conclusion

The mechanism of spherical cement's high fluidity implementation in light of the wettability of cement particles was studied. In addition, the effects of gypsum on the wettability were observed. As a result, the following conclusions were reached.

(1) The weight of water and the water-reducing agent solutions penetrating the spherical cement powder bed is 24–150% higher than that for the ordinary Portland cement powder bed. This results from the improvement of the wettability of the particle surfaces of spherical cement. It is believed that this high wettability of spherical cement contributes to the high fluidity.

(2) The presence of many fine gypsum particles on the spherical cement particle surface reduces the wettability of water on the particle surface.

(3) To prepare spherical cement, it is necessary to add the optimum amount of gypsum, which is determined by the acceleration of the treatment time for the formation of spherical particles and by the increase in the wettability of particle surfaces, to the clinker powder. According to this experiment, the optimum amount was 0.65–2.65% relative to clinker powder.

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