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A study on the process for formation of spherical cement through an examination of the changes of powder properties and electrical charges of the cement and its constituent materials during surface modification

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Abstract

In the initial stage of surface modification treatment to form cement particles into a spherical shape, the fine cement particles below 3 μm increased and the specific surface area also increased. However, in the final stage of treatment, both the fine particles and the specific surface area decreased when compared to raw cement. These results seem to endorse a process for formation of spherical cement, namely grinding of the particles in the initial stage and then adhering and fixing the fine particles to the surfaces of larger core particles in the next stage. Clinker powder had a positive charge, whereas gypsum powder had a negative charge. The difference observed in the electrical charge proved that the attachment of gypsum particles to clinker particles was caused by the attraction of opposite charges in addition to the van der Waals interaction. Therefore, gypsum played an important role as an adhesive agent. The fluidity of clinker powder after it was treated with finely ground gypsum improved. This was because the fine gypsum particles quickly attached to the surfaces of the larger particles of clinker, and consequently, the final process for formation was accelerated. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Spherical cement; Particle size distribution; Specific surface area; Electrical charge; Gypsum

1. Introduction

Spherical cement is characterized by round particles and prepared by a dry impact blending method (microhybridization technology). The packing ratio of spherical cement increases, and the fluidity and workability of concrete using spherical cement also increase as compared to those of normal Portland cement [1–5]. Furthermore, the strength and durability of spherical cement concrete are improved because less water is required for mixing. The adiabatic temperature rise of spherical cement is smaller than normal cement due to a reduction of the unit weight of cement for the same strength appearance [4,5]. The authors believe that spherical cement is a new type of cement that can be used for several high-quality concrete types including high-fluidity concrete mixtures, high-strength concrete and high-durability concrete. In previous papers [2,3,5], both an observation of a cross-section of a cement particle by scanning electron microscopy (SEM) and an analysis of the element distribution of the surface of a spherical cement particle were shown to clarify the mechanism for formation of spherical cement. We have reported that very fine particles condense to the surface of spherical cement and that the elements Al and S, which are constituent elements, were found surrounding the surface of the spherical cement particle. From these results, we [2,5] have presumed that the processes for formation are: (1) grinding and shaving off the sharp-pointed edges of large particles in the initial stage; (2) an increase of very

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fine particles; (3) an attachment of fine particles to the surfaces of larger core particles; and (4) fixing and embedding. It was considered that the attachment of fine particles to larger core particles mainly occurs in the first 10 min, and strong fixation of fine particles mainly occurs after 10 min during the surface modification process [5]. However, it is not yet clear what the driving force is for adhesion among particles. Koishi [6] and Honda et al. [7] have reported that the adhesion forces between particles were due to the van der Waals interaction and electrostatic interaction. They considered fine organic polymer particles using surface modification technology (dry impact blending method). Generally, it is expected that inorganic compounds in cement particles have a smaller electrical charge than particles consisting of organic polymers [8,9]. Regardless of the compound type, it is important to make clear the electrical charge and electrostatic interaction of cement and its constituent materials for determination of the mechanism of adhesion, fixing and embedding of fine particles to the surfaces of larger core particles.

In this paper, an examination was conducted of particle size distribution and the specific surface area of cement and cement constituent materials treated at several treatment times (0–20 min). The results seem to endorse our presumption of the process for formation of spherical cement. Moreover, electrical charges of cement and cement constituent materials were investigated to clarify the driving force for adhesion among particles.

2. Experimental details

2.1. Measurement of the changes of the particle size distribution and specific surface area during surface modification for preparation of spherical cement

2.1.1. Material

The cement used for raw material was a commercial normal Portland cement. Table 1 shows the fundamental characteristics of the cement.

Table 1
Characteristics of normal Portland cement used as row cement for modification

Characteristics	
Mean diameter (μm)	13.9
Fine particles under 3 μm	18.0
Specific surface area	
Blaine (cm^2/g)	3250
BET (m^2/g)	0.94
Density (g/cm^3)	3.16
Mineralogical composition (%)	
C_3S	51.3
C_2S	22.2
C_3A	8.3
C_4AF	9.4
SO_3	1.9

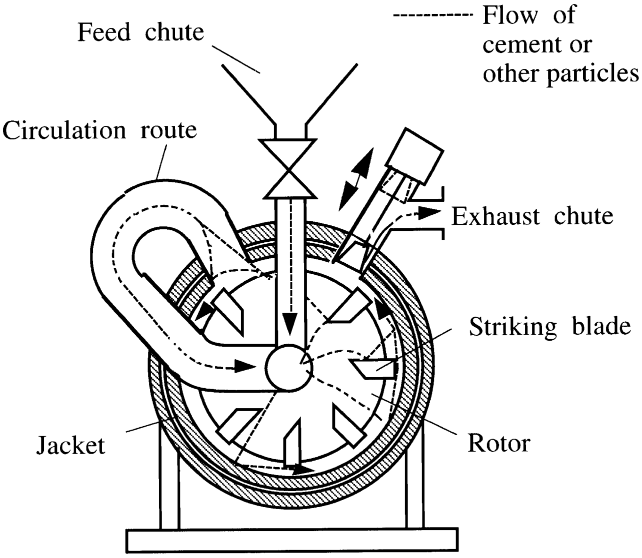


Fig. 1. Schematic outline of surface modification apparatus.

2.1.2. Apparatus and technique

2.1.2.1. Surface modification. The method used was a dry impact blending method (microhybridization technology), which is the method used to form microparticles into spherical shapes by causing rotary impact as a result of a high-speed air flow in a ring-shaped impact chamber [6,7]. The equipment used was a Nara Hybridization System (model NHS-1; Nara Machinery, Tokyo, Japan). Fig. 1 presents its schematic outline [6,7]. It was operated at a rotation speed of 8000 rpm at temperatures from 45 °C to 75 °C. Raw cement was put into the equipment in 150 g batches. The treatment time was 0–20 min, since it is understood that the properties of treated cement remain unchanged after more than 20 min of treatment [5].

2.1.2.2. Particle size distribution and specific surface area. Particle size distributions were measured by a laser scattering particle size distribution analyzer (model Cilas; New Metals and Chemicals, Tokyo, Japan). An amount of 0.1 g of sample powder was put in 100 ml of ethanol and underwent dispersion treatment by an ultrasonic dispersion unit for 60 s.

Specific surface areas were measured by the Blaine method utilizing the procedure specified in JIS R 5201.

2.2. Measurement of both initial and changed electrical charges of the cement and cement constituent materials during the surface modification

2.2.1. Material

The materials used in the experiment were commercial normal Portland cement, clinker powder for normal Portland cement, tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF) and gypsum ($CaSO_4 \cdot 2H_2O$; natural type and byproduct type = gypsum from sulfur dioxide removal in flue gas).

C_3S, C_2S, C_3A and C_4AF were synthesized in the laboratory. The preparation was based on a report already published [10,11]. The special grade reagent for the following substance was used as the raw material: $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3, MgO and Na_2CO_3. An electric furnace was used to sinter the samples—C_3S: at 1500 °C for 18 h; C_2S: at 1400 °C for 2.5 h; C_3A: at 1400 °C for 3 h; and C_4AF: at 1350 °C for 8 h. Fly ash (a byproduct from solid fuel power plants), blast furnace slag and lime stone powder, which were ground into fine particles for practical use in cement, were used as additives for the cement. The mixture of clinker powder and the natural type gypsum powder (95:5 in weight) was used to directly examine their electrical charge interaction. Table 2 shows the characteristics of these materials.

2.2.2. Apparatus and technique

2.2.2.1. Surface modification. Surface modification treatment was conducted in a similar method as described in Section 2.1.2.

2.2.2.2. Measurement of electrical charge. As shown in Fig. 2, both a Faraday cage and an electrostatic voltmeter with vibration and focus indication (model Statiron DZ3; Shishido Electric, Tokyo, Japan) were used. The specimens, which were powders before and after being treated within various time frames (0–20 min), were carefully set into the inner vessel of the Faraday cage, and the electrical charge was measured with an electrostatic voltmeter and determined by using the Eqs. (1) and (2) below [12]. The measurement was carried out in 16–18 °C, 30% RH.

$$Q = C \cdot E \tag{1}$$

Here, Q is electrical charge (C), C is electrostatic capacity between inner and outer vessels (F) and E is potential of inner vessel (V).

Table 2
Characteristics of cement and cement constituent materials

Materials	BET specific surface area (m^2/g) or particle size (μm)
Normal Portland cement	0.94
Clinker powder for normal Portland cement	0.79
C_3S	0.73
C_2S	0.77
C_3A	0.89
C_4AF	0.55
Gypsum (natural type)	0.80
Gypsum (byproduct type)	0.79
Fly ash-1, -2	below 72 μm
Blast furnace slag	below 72 μm
Lime stone powder	below 72 μm

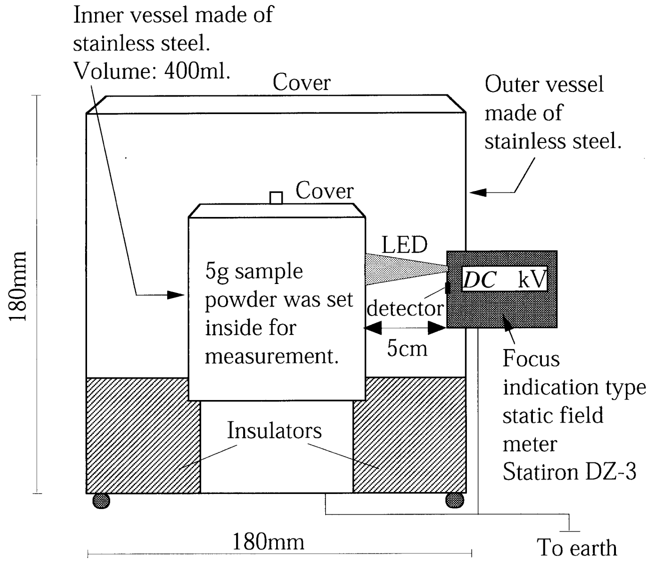


Fig. 2. Schematic outline of the apparatus for measurement of electrical charge (Faraday cage).

Now, C is previously set at 10 pF. Therefore, Eq. (1) is transferred to Eq. (2):

$$Q = 10^{-12} \cdot E \tag{2}$$

2.2.2.3. Specific surface area. In this experiment, the Brunauer–Emmett–Teller (BET) method was adopted in order to determine the surface area in consideration for the electrical charge. The apparatus was a type of single-point determination using nitrogen gas (model FLOWSORB-2-2300; Shimadzu, Kyoto, Japan).

2.2.2.4. Shape. The shapes of the cement particles were observed with a scanning electron microscope (model JXA-8600S; JEOL, Tokyo, Japan). The degree of roundness of the cement particles was evaluated using the following equation (Eq. (3)):

$$\text{The degree of roundness} = 4\pi S/L. \tag{3}$$

Here, S = the project area of the particle, L = the perimeter of the particle's project. Thirty larger-than-5-μm particles that exhibited remarkable changes in shape were measured.

2.3. Measurement of fluidity for the purpose of evaluation of the effect of adding fine gypsum particles on surface modification

2.3.1. Materials

Natural type gypsum powders, which were ground to 2.8, 3.3 and 8.7 μm in mean diameter by means of an impact fine grinding mill (model Cosmomizer and Micros; Nara Machinery), were added to normal Portland cement clinker (Blaine: about 3000 cm^2/g) in a condition where the SO_3 content was about 2 wt.%. These mixtures were treated by a dry impact blending method and then mixed with Toyoura standard sand and tap water for mortar preparation. The properties of the sand were as follows: maximum size: 0.3 mm, specific gravity: 2.63, water absorption: 0.29%. The mortar was mixed with ratios of water/cement = 0.55 and cement/sand = 0.5.

2.3.2. Apparatus and technique

The mixing for mortar was performed according to JIS R 5201-1987 through the use of a mixer conforming to the standard in the following order. Two hundred eighty-six grams of water was poured in a mixing bowl. Next, the mixer was started. With the paddle rotating, 520 g of powder samples, such as cement, was poured in a 30-s period. While continuing to mix, 1040 g of standard sand was poured in the second 30-s period. Sixty seconds of mixing was followed by a 20-s pause. During the pause, mortar deposited on the bowl and paddle was scraped off using a spoon. In addition, to scrape up the mortar on the bottom of the bowl, two or three stirring actions were performed. The mixer was started again to perform mixing for 120 s. After this, the sample was stirred 10 times with a spoon. The fluidity of the fresh cement mortar was measured according to the procedure specified in JIS R 5201-1989. This method was similar to ASTM-C109 (determination of flow), but it differed in that the flow table used had a 300-mm diameter and the casting mold had a 60-mm height. In addition, the process of dropping the flow table after lifting the mold was carried out 15 times in 15 s. Weighing, mixing and measurement of the fluidity were carried out at room temperature at 20 °C, 85% RH.

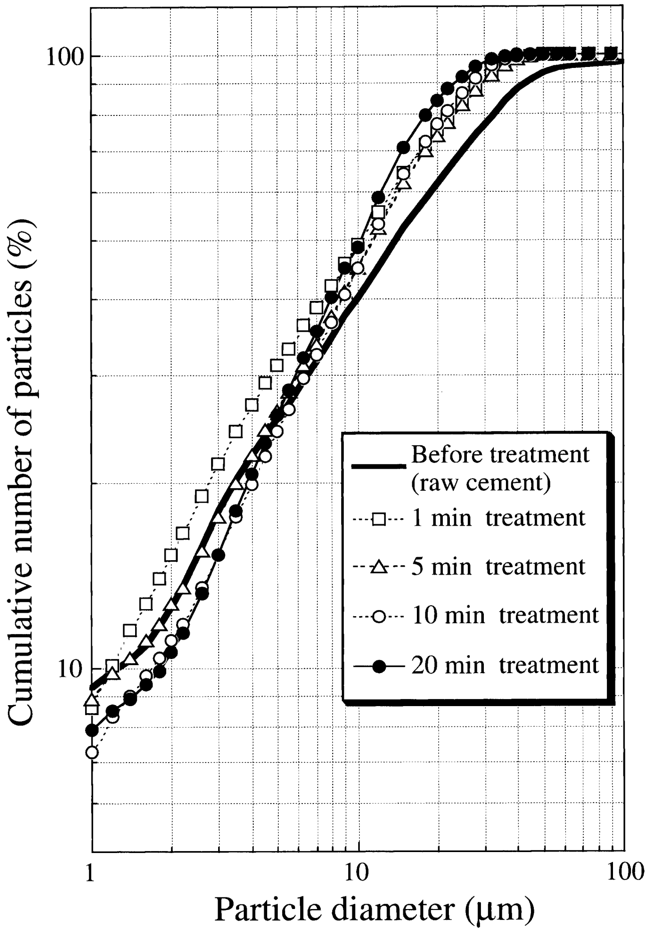


Fig. 3. Particle size distribution curves of cement prepared in various treatment times.

3. Results and discussion

3.1. Changes of the particle size distribution and specific surface area during surface modification for preparation of spherical cement

3.1.1. Particle size distribution

Fig. 3 shows the particle size distribution curves of cement prepared within various treatment times. Fig. 4 shows the relationship between the treatment time (0–20 min), the mean particle diameter and the number (%) of fine particles below 3 μm in the modification of the cement. The change of the number of fine particles below 3 μm, which is very condensable without dispersant and suppresses increases of fluidity [13], was noted in this experiment. The particle size distribution was changed with an increase in length of the treatment time. In the initial 1-min period, large particles over 40 μm decreased. Meanwhile, smaller particles, such as 1–10 μm particles especially fine particles below 3 μm, increased as compared to raw cement. As a result of the grinding, the mean diameter of the cement was smaller than that of raw cement. In the next stage, a decrease in the number of fine particles occurred, in particular, the number of particles below 3 μm was less than that found in raw cement with treatment for 5 min or more. In the final stage of treatment at 20 min, the number of particles over 40 μm and below 3 μm decreased, and as a result, the width of the particle size distribution became narrower. It is believed that these results suggest that the processes for formation of spherical cement are: (1) grinding and shaving off the sharp-pointed edges of large particles in the initial stage; (2) an increase of very fine particles; (3) an attachment of fine particles to the surfaces of larger core particles; and (4) fixing and embedding of fine particles.

3.1.2. Blaine specific surface area

Fig. 5 shows the relationship between the treatment time (0–20 min) and the specific surface area measured by the Blaine method. In the initial 1-min period, specific surface area also increased with increases of the fine particles below 3 μm and decreases of large particles over 40 μm. However, the specific surface area of particles treated over 3 min was smaller than that of raw cement. The value of cement treated over 20 min was 16% smaller than that of raw cement, and this converged to about 2700 cm^2/g. Though the particle size became smaller with this surface

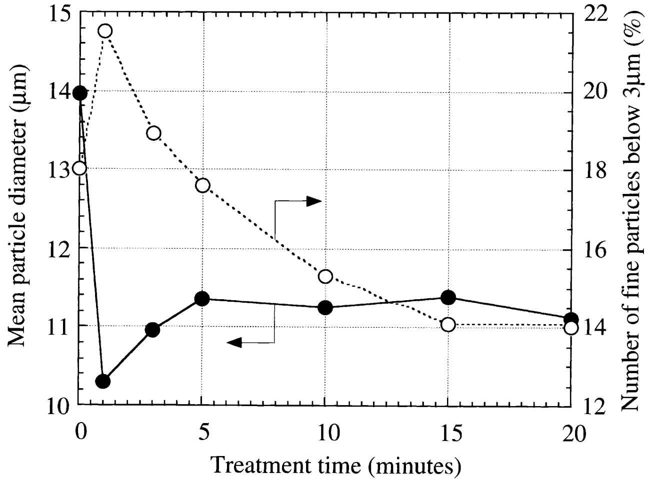


Fig. 4. Change of mean particle diameter and number of fine particles below 3 μm with treatment time (0–20 min) for modification of cement.

modification, as previously shown in Figs. 3 and 4, the specific surface area did not increase. This result supports the notion that the particles became rounder through this surface modification.

Furthermore, after a 10-min treatment, the specific surface area changed only slightly. It is considered that this phenomenon was due to the progress of surface modification, namely fixing and embedding of fine particles to the surfaces of the larger particles. That is to say, it is the process by which fine particles, which were faintly attached to the surfaces of larger core particles with a porous layer structure, were tightly fixed and embedded to the surfaces of larger particles by being hit with the striking blade on the rotor or through collision with other particles. It is believed that these results endorse our presumption that the attachment of fine particles to larger core particles mainly occurred in the first 10 min, and strong fixation of fine particles mainly occurred after 10 min as mentioned in the previous report [5].

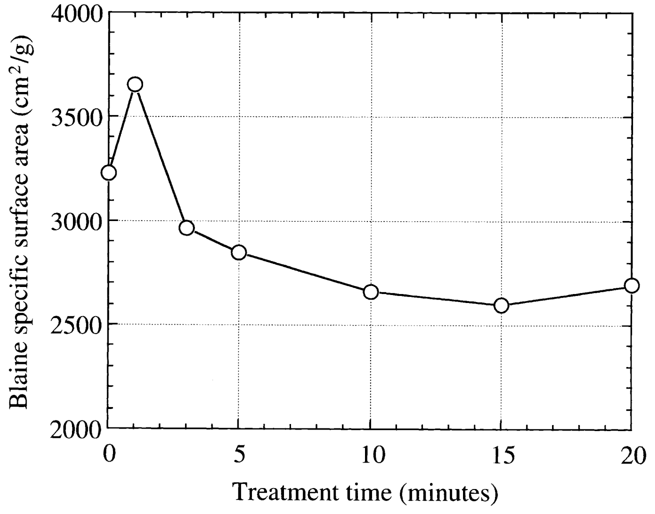


Fig. 5. Change of Blaine specific surface area with treatment time (0–20 min) for modification of cement.

3.2. Electrical charge of cement and cement constituent materials and consideration of the process for formation of spherical cement through examination of electrical charge

3.2.1. Electrical charge of cement and cement constituent materials

Fig. 6 shows the electrical charge of normal Portland cement, spherical cement, clinker powder, C_3S, C_2S, C_3A, C_4AF and additives for cement, namely gypsum (natural and byproduct type), fly ash, blast furnace slag and lime stone powder. Though it is difficult to simply compare the absolute values of these electrical charges because of various particle sizes and surface areas of each sample, the different positive and negative charges in each material were recognized. Both normal Portland cement and spherical cement were positively charged. Clinker powder was also positive, while gypsum powder was negatively charged. It is expected that this difference of electrical charge affects the attachment of particles in the process for formation of spherical cement. Moreover, fly ash was shown to be negative and blast furnace slag powder and lime stone powder were shown to be positive. Therefore, it is assumed that these additives also electrically affect the formation of spherical cement. The changes of the electrical charge of cement and cement constituent materials during the surface modification treatment were examined in the following.

3.2.2. The change of electrical charge of cement and cement constituent materials during the surface modification treatment

Normal Portland cement, clinker powder, mixture of clinker powder and gypsum powder (natural type, 5 wt.%) and gypsum powder (natural type) were treated by the Hybridization System for surface modification, and the specific surface areas and electrical charges of each sample

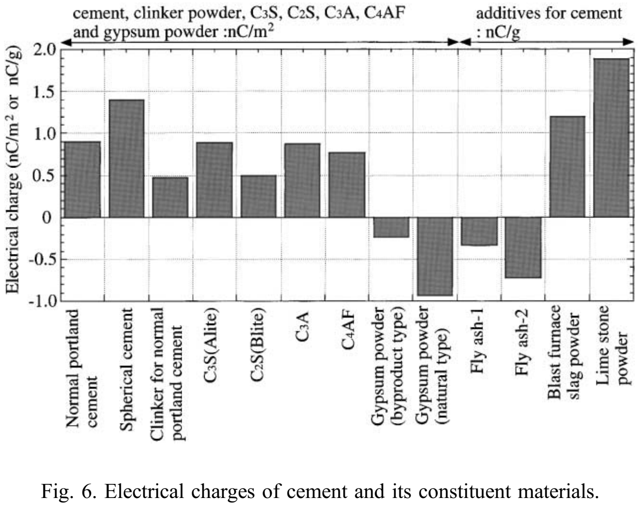


Fig. 6. Electrical charges of cement and its constituent materials.

during various treatment times were measured. In this experiment, the specific surface area was measured by means of the BET method to determine the surface area in consideration of the electrical charge.

Fig. 7 shows the changes of the specific surface area over various treatment times. When treated for 20 min, the specific surface area of cement, clinker powder and the clinker–gypsum mixture was reduced by 30–40% when compared to the specific surface area before treatment, and these surface areas converged to about 0.56 m^2/g. These results were due to the modification from sharp-cornered particles to spherical particles. It was observed that the surface modification to the spherical shape based on the fixing and embedding of fine particles proceeded in every sample, though there was some difference in the degree of roundness as shown in Fig. 8. Incidentally, the BET specific surface areas of samples treated for 1 min, especially cement and clinker powder, increased as described in Section 3.1.2. On the other hand, gypsum powder was ground up easily, and its specific surface area was 5.64 m^2/g after a 1-min treatment and 9.54 m^2/g after a 20-min treatment; therefore, the values were about 10–17 times those of cement or clinker powder.

Fig. 9 shows the relationship between the treatment time (0–20 min) and the electrical charge. Clinker powder was positively charged and gypsum powder was negatively charged before treatment. With the surface modification treatment, the electrical charge of clinker powder increased slightly from +0.2 to +0.5 nC/m^2. There was little change in the electrical charge of gypsum powder after a 1-min treatment, and the values were from −0.2 to −0.3 nC/m^2. In the previous paper, we reported that gypsum is specifically located on the surface of spherical cement [2,3,5]. It is believed that the difference in the electrical charge between clinker powder and gypsum powder proves that the attachment of gypsum particles to clinker particles is caused by attraction of the opposite charge in addition to the van der Waals interaction.

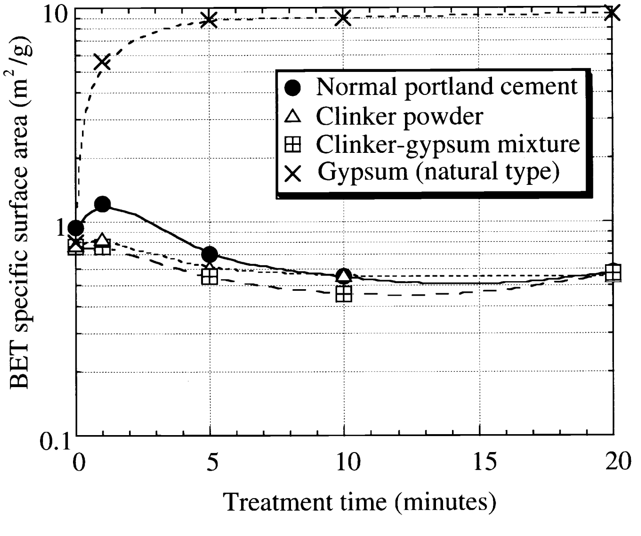
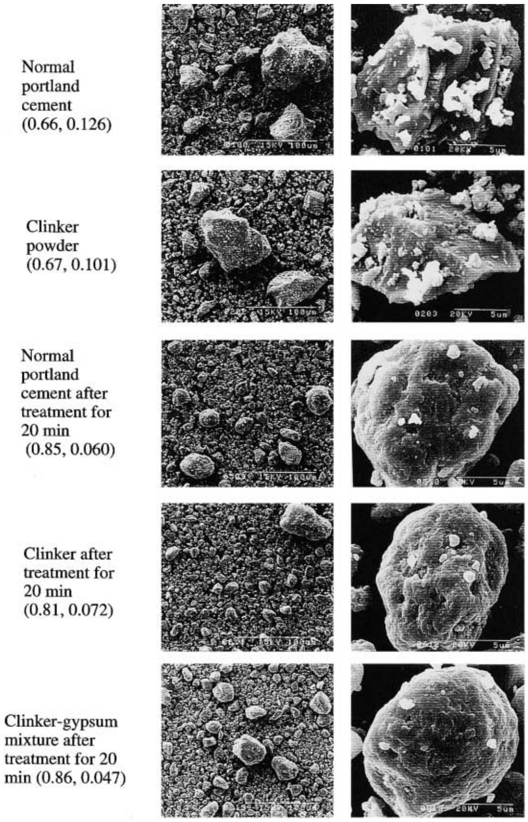


Fig. 7. Change of the specific surface area with various treatment times.



(): (The degree of roundness, Standard deviation)

The degree of roundness was evaluated using the following equation.

The degree of roundness = 4 πS/L .

Here, S = project area of the particle, L= perimeter of project area of the particle

Fig. 8. Scanning electron microphotograph of particles of cement, clinker powder and clinker–gypsum mixture before and after treatment.

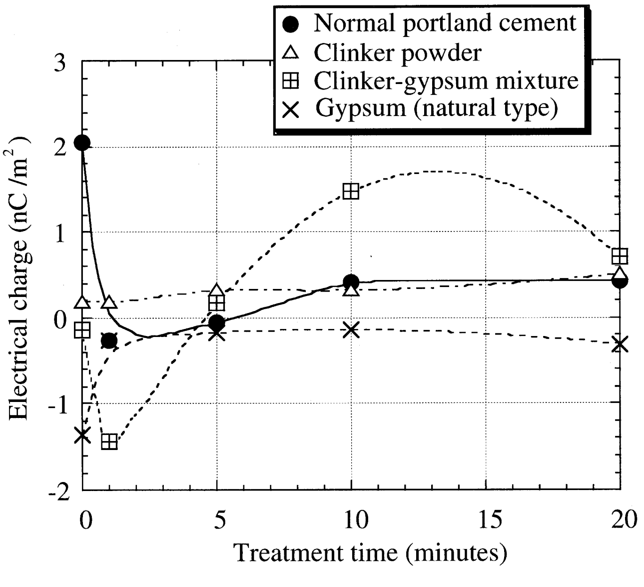


Fig. 9. Change of electrical charge in various treatment times.

On the other hand, the electrical charge of cement was +2 nC/m^2 before treatment, and it showed a negative charge

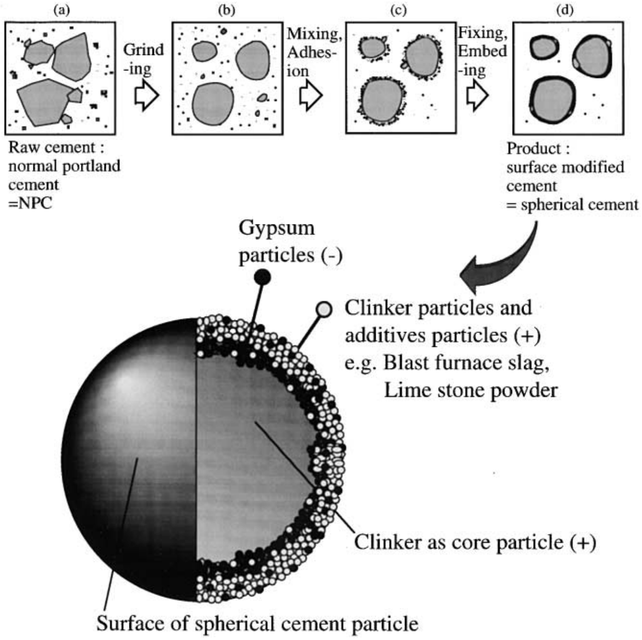


Fig. 10. Image of the structure of cross-sectional view of spherical cement and the process for the formation of spherical cement.

during a 1- to 5-min treatment and showed a positive charge again after a 5-min treatment. The electrical charge of the mixture of clinker and gypsum (5%) was slightly negative (-0.1 nC/m^2) before treatment, and it showed a large negative value (-1.5 nC/m^2) following a 1-min treatment. It returned to positive after being treated for 5 min, and then it showed $+0.5$ to $+0.7$ nC/m^2 following a 20-min treatment. This was similar to the results of cement and clinker powder. Both cement and the clinker–gypsum mixture showed a change to negative charges in the initial stage of treatment, especially the clinker–gypsum mixture which showed a high negative charge. It is believed that the negative charges were due to the increased surface area of gypsum, which is easily ground, and due to the neutralization and reversal in the electrical charge (changed to negative) as a result of the attachment of gypsum particles to clinker particle surfaces (positively charged) in this modification treatment. However, as shown in Fig. 7, the specific surface area of the mixture did not increase remarkably. Therefore, it is thought that the production of ultrafine particles of gypsum and the attachment of these ultrafine particles to clinker particle surfaces would take place at the same time in this treatment.

Furthermore, the phenomenon of the electrical charges changing back to positive again with the progress of treatment is thought to be due to the following. The surface area of gypsum decreased with the progress of attachment of gypsum to clinker particle surfaces. As a result, the negative charge based on the surface area of gypsum also decreased. Conversely, fine grinding of clinker or additives, which were positively charged, proceeded and these positively charged fine particles adhered to and surrounded the surfaces of negatively charged particles consisting of clinker that have an outside layer of gypsum. Moreover, it was observed that the positive value of the clinker–gypsum mixture following a 10-min treatment was larger than that of cement. This may be because of the effect of the kind and the amount of additives for cement. That is to say, though the components of clinker (C_3S, C_2S, C_3A, C_4AF) were positively charged, some of the additives showed a positive charge and others showed a negative charge as shown in Fig. 6. Because the clinker–gypsum mixture and cement had such different positive values following 10 min of treatment, it is presumed that the cement used in this experiment contained additives that showed a negative charge.

From the above, it is reasonable to conclude that the processes for the formation of spherical cement are: (1) the attachment of ultrafine particles of gypsum to the surfaces of larger core particles of clinker; (2) the adherence of fine particles of clinker and additives to the surfaces of negatively charged particles that have outer layers of gypsum; (3) the formation of a multiple-layer structure; and (4) the fixing of these layers. Therefore, it is believed that gypsum played an important role in the formation of spherical cement as an adhesive agent. Fig. 10 shows the image of a cross-sectional view of the spherical cement and the process for the formation of spherical cement.

Fig. 8 presents the SEM photograph of the cement particles treated for 20 min and the degree of roundness of their particles. The degree of roundness of cement or the clinker–gypsum mixture was larger than that of clinker particles. The degrees were 0.85, 0.86 and 0.81, respectively. This is probably because the result revealed that the function of gypsum is as an adhesive, accelerating the attachment of particles for the formation of spherical cement.

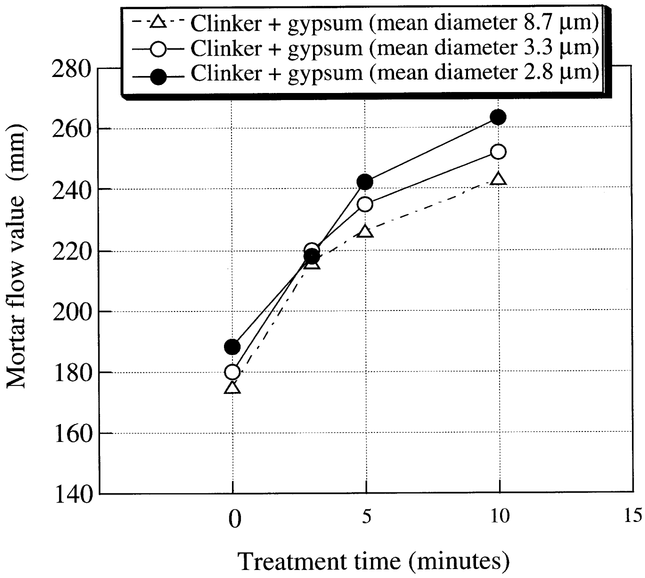


Fig. 11. Relationship between the treatment time (0–10 minutes) for modification and flow of clinker-gypsum mixtures which contain various sizes (2.8, 3.3, 8.7 μm) of gypsum particles.

3.3. Improvement of fluidity of cement through treatment with finely ground gypsum particles in surface modification

Fig. 11 shows the relationship between the treatment time (0–10 min) for modification and the flow value of the mortar for the clinker–gypsum mixture that contained various sizes of gypsum particles. We have reported that the fluidity of cement is increased with the process for the formation of spherical cement [1–5]. The fluidity of clinker powder treated with finely ground gypsum (2.8 or 3.3 μm) increased as compared to clinker powder treated with gypsum (8.7 μm) that was not finely ground. As a result, adding finely ground gypsum made it possible to shorten the time required for the formation of a spherical shape. For this reason, it is considered that the large amount of fine particles of gypsum that were negatively charged quickly attached to the surfaces of larger particles of clinker powder, and consequently, the final process of formation, namely fixing and embedding of the particles, was accelerated.

4. Conclusions

Measurements were taken of the distribution of particle size, the specific surface area and the electrical charge of the cement and cement constituent materials treated at various treatment times. These results were discussed and it was determined that they endorse our presumption of the process for formation of spherical cement, and that they help to clarify the driving force for adhesion between particles. The following conclusions were reached.

(1) The particle size distribution and specific surface area of cement changed with an increase in the length of the treatment time. In the initial period, the fine particles below 3 μm increased as a result of the grinding, and consequently, the specific surface area also increased as compared to raw cement. However, in the final stage of treatment, the width of the particle size distribution became narrower because of a decrease in the number of particles below 3 μm and over 40 μm, and the specific surface area decreased by 16%, converging to about 2700 cm^2/g (Blaine value). It is believed that these results endorse the following processes for formation of spherical cement: (a) grinding and shaving off the particles in the initial stage; and (b) adhering, fixing and embedding of fine particles to surfaces of larger core particles in the next stage.

(2) Clinker powder and its constituent parts, namely C_3S, C_2S, C_3A, C_4AF, were positively charged and gypsum powder had a negative charge. The difference in the electrical charge between clinker and gypsum proved that the attachment of gypsum particles to clinker particles is caused by attraction of the opposite charges in addition to the van der Waals interaction. Therefore, it is believed that gypsum played an important role in the formation of spherical cement as an adhesive agent and that the processes for the formation of spherical cement are: (1) the attachment of ultrafine particles of gypsum to the surfaces of larger core particles of clinker; (2) the adherence of fine particles of clinker and additives to the surfaces of negatively charged clinker particles that have outer layers of gypsum; (3) the formation of a multiple-layer structure; and (4) the fixing of these layers.

(3) The fluidity of clinker powder treated with finely ground gypsum (2.8 or 3.3 μm) increased as compared to the clinker powder treated with gypsum, which was not very finely ground, and as a result, adding finely ground gypsum made it possible to shorten the time required for the formation of spherical cement. The reason must be because the fine particles of gypsum, which were negatively charged, quickly attached to the surfaces of the larger particles of clinker, and consequently, the final process of formation, namely fixing and embedding of particles, was accelerated.

Acknowledgments

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