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THE ROLE OF STERIC REPULSIVE FORCE IN THE DISPERSION OF CEMENT PARTICLES IN FRESH PASTE PREPARED WITH ORGANIC ADMIXTURE

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ABSTRACT

The existence of the steric repulsive force has never yet been determined, though the improved dispersibility of solid particles in concrete by adding the organic admixture is considered to be primarily caused by the dispersion of solid particles by the electrostatic repulsive force based on the formation of an electric double layer made of the admixture adsorbing to the surface of solid particles and the increase of the surface potential, and by the steric repulsive force based on the interaction between the adsorption layers of admixture. The authors proved for the first time the existence of the steric repulsive force acting on the surface of cement particles adsorbing the organic admixture by measuring the interactive force between surface of cement clinker adsorbing the admixture with an atomic force microscope, and measuring the zeta potential of fresh cement paste under actual water-to-cement ratio by electrokinetic sonic amplitude method. It is also clarified that the rate of contribution of electrostatic and steric repulsive force to the dispersion of cement and hydrated cement particles differs by the kind of organic admixture. *Copyright © 1997 Elsevier Science Ltd*

Introduction

An organic admixture for concrete is called a fluidizing agent, a water-reducing agent or an air-entraining-water-reducing agent. Since the organic admixture gives fluidity required for preparing concrete to it by dispersing cement, a blending component (mineral admixture) and hydration products with a small quantity of water and entrained air if necessary, it is an indispensable additive for preparing high-performance concrete with high-workability, high-strength and good-durability.

Examples of high-performance concrete prepared by putting the organic admixture to practical use for improving the physical properties of concrete include self-placable concrete endowed with excellent fluidity, high-strength concrete prepared by sharply reducing the mixing water and good-durability concrete created by changing the pore and void structure and the interfacial structure between aggregate and paste by reducing the mixing water and entraining air bubbles.

The improved fluidity of concrete by adding the organic admixture is considered to be caused mainly by the dispersion of solid particles by the electrostatic repulsive force due to the increase of the surface potential caused by the admixture adsorbed to the surface of solid particles and by the steric repulsive force based on the interaction between the adsorption layers of admixture (1). The electrostatic repulsive force has been proved by measuring the zeta potential of diluted suspension of cement, while the steric repulsive force is, at present, only estimated from the current knowledge of surface and organic chemistries, and the existence of the steric repulsive force has never been evidenced by experimental determination.

This paper studies the relationship between the electrostatic and steric repulsive forces by measuring the interactive force (force acting between surfaces) of cement clinker adsorbing the admixture with an atomic force microscope and measuring the zeta potental of low W/C cement paste by electrokinetic sonic amplitude method, aiming at acquisition of the basic data for the material design and appropriate application of the organic admixture by proving the existence of the steric repulsive force in the dispersion of solid particles in concrete prepared by adding the organic admixture, and determining the contribution of it according to the types of admixture, and relationship of the contribution with the physical properties.

Interactive Force Between Cement Particles Coexisting with Organic Admixture

The fluidity of concrete is strongly affected by that of cement paste, which correlates with the repulsive force between the cement particles. The force acting between the cement particles comprises van der Waals force (FA) and the electrostatic repulsive force (FRE) generated by the electric charge on the surface of particles. It is considered, however, that adding the organic admixture to the cement paste, in addition to those forces, the electrostatic repulsive force is increased by the organic admixture adsorbed to the surface of the cement particles and the steric repulsive force (FRS) is generated from the osmotic pressure for relieving the local increase of density caused by overlapping of the adsorption layers of admixture. According to this idea, the force acting between the cement particles (F) in the coexistence of the organic admixture is represented as follows:

$$F = FA + FRE + FRS \tag{1}$$

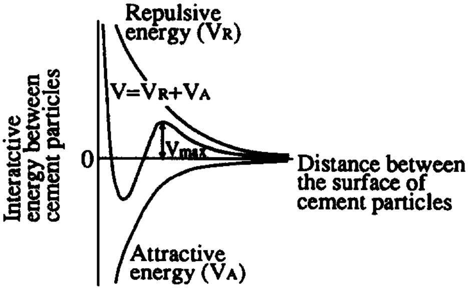


FIG. 1.

Relationship between distance and interactive energy of cement particles.

It is known that the force acting between the cement particles depends upon the distance between them, which is related to the interactive energy as illustrated in FIG. 1 (2). Let the maximum repulsive energy on the potential curve equal to Vmax, then the minimum Vmax required for keeping dispersion is considered to be 15kT (2). Taking Boltzmann constant, k, as 1.381×10^{-23}J/K and the absolute temperature, T, as 297K, the minimum Vmax required for keeping dispersion is 10^{-20}J.

Assuming that the diameter of a cement particle is 2μm, the repulsive energy corresponding to 15kT will correspond to repulsive force of 10 nN. Assuming that all of this energy is caused by the electrostatic repulsive force, the surface potential of the particle will be -15 mV (1).

Since the working region of van der Waals force is within 1 nm from the surface of particles and the magnitude of it is approximately 0.5 nN (3), it is negligible small compared with the force corresponding to Vmax and the compensated interactive force described later.

Selection of Measuring Methods

Force Acting Between Surfaces. The direct measurement of the force acting between the solid surfaces has been investigated since the 1950s in such a way that the distance, which is controlled within a range of an order of magnitude of nm between the surface of a solid suspended with a spring and that of another fixed solid is varied, and the interactive force (F) is determined from the displacement of the spring according to the following formula:

$$|F| = k|\Delta H| \qquad (2)$$

where k = spring constant and ΔH = displacement of spring (3). A surface force apparatus (SFA) (4) representive of that method is operated in such a way that two solid samples fixed to respective springs are brought close to a distance of 0.1 nm or less and interactive force is obtained by multiplying the displacement of the samples caused by the interactive force by the spring constant. Minimum measureable value in this method is 10nN. The distance between the solid surfaces is measured at the accuracy of 0.2 nm by the interference caused by white incident light from the bottom of the apparatus transmitting those solids. Although the distance between the solid surfaces can be measured accurately, since the contact position of a solid with another one can be accurately determined, the solid samples must be transparent and the surfaces of them must be smooth at the molecular level. The sample applied to the method is, therefore, limited to a few kinds of solid such as a plane of cleavage of mica.

The measurements of the surface force apparatus are only a few examples including hydration force acting between two pieces of mica in an aqueous solution of KCl (5), force of hydrophobic mutual action of a cationic surface active agent (6) and interactive force between surfaces covered with macromolecular adsorption film (7).

The atomic force microscope (AFM) placing few limitations on the sample is, therefore, used for measuring the force acting between the solid surfaces in this study. The atomic force microscope is used for measuring very little force acting between the sample and the probe brought close to it to approximately 1 nm (8). The distance between the probe and the sample can be controlled at the accuracy of 0.05 nm with a piezo-electric element. The displacement of a cantilever caused by the force acting between the surfaces is determined at an accuracy of 0.1 nm at least by measuring the intensity of laser beams reflected from the back side of the lever with a position-sensitive photo-detector. The force acting between the surfaces is calculated by multiplying the displacement of the cantilever by the spring constant of the lever and the lower limit of the measurement is 10^{-3} nN. The atomic force microscope cannot so accurately determine the contact position of the probe with the sample as the surface force apparatus. The measurements of the distance in the curve of the distance between the surfaces versus the force acting between the surfaces (F-D curve) with the atomic force microscope are not so accurate as those with the surface force apparatus. The former is, however, more easily operated than the latter and does not require so much smooth surface of the sample as the latter because the measuring region is as small as an order of μm^2 as well as can use an opaque sample.

In this study, therefore, AFM was used for measuring the force acting between the solid surfaces.

Researches on the measurements of the force acting between the surfaces with the atomic force microscope include; verification of the DLVO theory from the measurements of F-D curve of aqueous solutions with various concentrations of NaCl (9); estimation of adsorption state of a nonionic surface active agent (10); determination of isoelectric points of the probe from the measurements of force of action in aqueous solutions with various pH values (11); and measurement of very small interactive force between biomolecules (12).

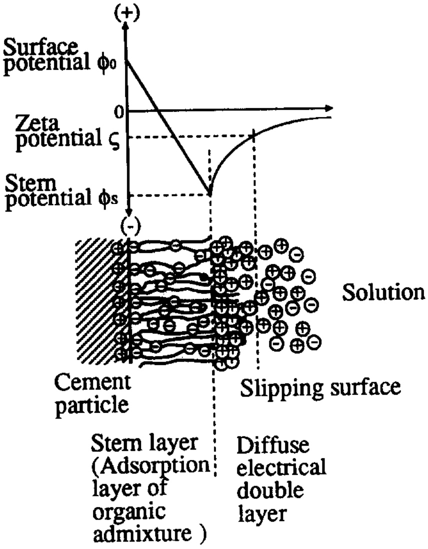


FIG. 2.

Schematic explanation of interfacial electric double layer formed on the cement particle absorbing organic admixture.

TABLE 1

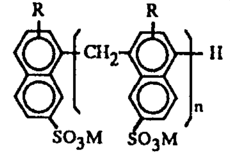
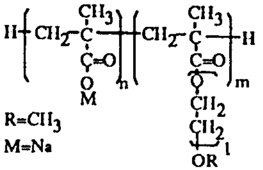
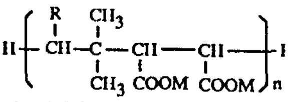
Character of Normal Portland Cement

Chemical composition (%)								Free lime (%)	Blaine specific surface area (cm^2/g)
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O		
22.1	5.3	3.1	65.2	1.2	2.1	0.43	0.23	0.5	3,350

Zeta Potential. As mentioned before, one of the dispersion forces of cement particles in fresh cement paste is the electrostatic repulsive force which is related to the surface potential of cement particle. As illustrated in Fig. 2, cement particles suspended in water containing the organic admixture form a Stern layer (a) made of dissolved ions, hydrate ions and molecules of organic admixture and a diffuse electric double layer (b) outside of it in which the concentration of ions with the opposite charge to the Stern layer gradually decreases with going away from cement particle. A slipping surface (c) between the particles and the liquid is generally contained in the diffuse electric double layer. Since the surface potential (ϕ_0) of bare particles and the Stern potential (ϕ_s) outside of the Stern layer cannot be measured, the potential on the slipping surface or zeta potential is substituted for the surface potential of the solid in solid-liquid suspension. Zeta potential is generated from the ions with opposite charge to that of the Stern surface and that of cement particles in fresh cement paste is generally higher than the surface potential of the adsorption layer of organic admixture (Stern potential) and lower than the surface potential.

TABLE 2

Character of Organic Admixture

Kind	Main component	Structural formula of main component	Solid content (%)	Mean molecular weight	Sodium content (mol/l)
NS	Condensate of β-naphthalene sulfonate with formalin	 R=H, CH_3, C_2H_5, M=Na	41	1,400	1.3
PC-A	Copolymer of acrylic acid with acrylic ester	 $H{-}\left[CH_2{-}\underset{\underset{\underset{M}{O}}{C=O}}{\overset{CH_3}{C}}\right]_n{-}\left[CH_2{-}\underset{\underset{\underset{\underset{\underset{OR}{\left[CH_2\right]_l}}{CH_2}}{O}}{C=O}}{\overset{CH_3}{C}}\right]_m{-}H$ R=CH_3 M=Na	30	88,000	0.8
PC-B	Copolymer of olefin with maleic acid	 $H{-}\left[\overset{R}{CH}{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{COOM}{CH}{-}\underset{COOM}{CH}\right]_n{-}H$ R=H, CH_3	34	59,000	3.0

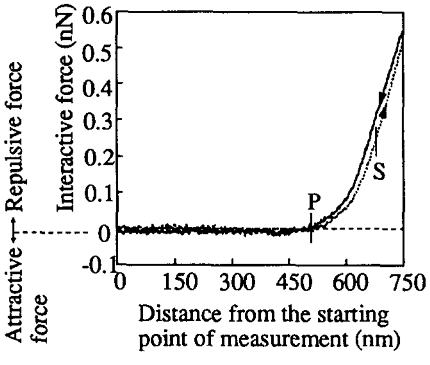


FIG. 3.

Interactive force-distance curve of silicon wafer surface immersed in the 10% solution of NS measured by AFM.

The electrophoretic method which has been used so far as a measuring method of zeta potential requires diluted concentration of particles in suspension because the migration speed of dispersed particles to which voltage is applied is directly observed. The streaming potential method is not only unsuitable for practical cement paste with a W/C of 0.5 or less because it requires the concentration of particles of 1vol% or less but also it has shortcomings including poor reproducibility and low accuracy. The zeta potential measured with conventional methods does not necessarily correspond to the fluidities of cement paste and concrete (13).

In this study, therefore, the electrokinetic sonic amplitude (ESA) method (14) which has recently been developed for measuring zeta potential of cement paste with a practical W/C as low as 0.3 is used. This method is applied to the measurement of zeta potential in such a way that the electrokinetic sonic amplitude value (E) caused by the particles moving between both electrodes by applying alternating voltage with higher frequency than 1MHz to the charged

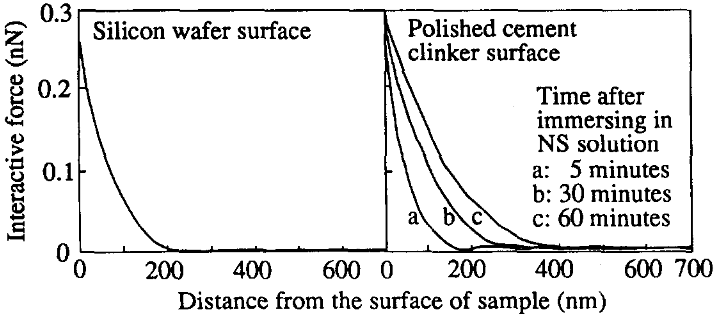


FIG. 4.

Influence of the time elapsed after immersing the cement clinker sample in organic admixture solution on the force-distance curve of it measured by AFM.

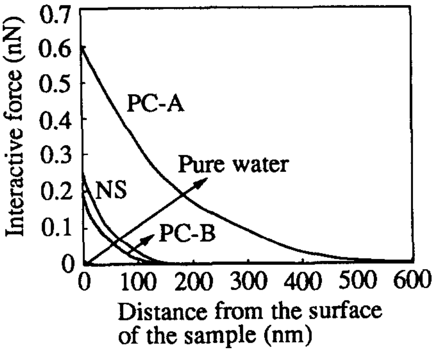


FIG. 5.
Relationship between interactive force and distance of polished cement clinker immersed in pure water and the 10% solutions of organic admixtures measured by AFM.

particles is measured, and calculated according to the following formulas representing the relationship of E with dynamic mobility (μd) and zeta potential (ζ) of particle:

$$E = C \cdot V \cdot (\Delta\rho/\rho) \cdot \mu d \cdot (Zs / Zs + Zg) \quad (3)$$

$$\mu d = (\epsilon\, \zeta\, G(\alpha)) / \eta \quad (4)$$

where C = apparatus constant, V = volume fraction of particles, $\Delta\rho$ = difference of density between particle and disperse medium, ρ = density of disperse medium, Zs = acoustic impedance of solution, Zg = acoustic impedance of glass rod, ϵ = permittivity of disperse medium, η = viscosity of disperse medium, and $G(\alpha)$ = correction term of inertia force.

The ESA method is applicable to the sample with the volume concentration of the dispersoid in the suspension as high as 30 to 50% or cement paste with a W/C of approximately 0.3.

Sample and Experimental Method

Cement and Admixture. Normal portland cement shown in Table 1 was used. Polished surfaces of cement clinker produced at the time when the cement shown in Table 1 was manufactured were used for measuring the force acting between the surfaces of cement particles.

TABLE 3

Zeta Potential of Cement Particle in Fresh Cement Paste Prepared by Adding Organic Admixtures Measured by Electrokinetic Sonic Amplitude Method

Admixture	Zeta potential (mV)
NS	-11.0
PC-A	-1.5
PC-B	-9.1
No added	-1.8

Three types of organic admixtures in total-a type of sulfonate-based and two types of polycarbonate-based admixtures-were used. Assuming that polycarbonate-based admixture, PC-A, has 40 branches of ethylene oxide in a molecule, it is inferred from the bond length of C-C and mean molecular weight that the lengths of the main chain and side chain will be approximately 30 and 20 nm, respectively. It is also inferred from the mean degree of condensation of 256 obtained from the mean molecular weight and the length of C-C bond of polycarbonate based-admixture, PC-B, that the molecular length of it will be approximately 154 nm.

Ten percent (10%)-aqueous solutions of NS, PC-A and PC-B and 10^{-2} mol/l-aqueous solution of sodium sulfate similar to the concentration of ion in the liquid phase of cement paste were used as admixture or immersing solution.

The characters of the organic admixtures used for the experiment are listed in Table 2.

Analysis of Admixture. Solid content, mean molecular weight and sodium content were determined according to the procedures described in the previous paper (15). The solid content was determined from the weight after drying the liquid admixture sample for an hour at 110°C. The mean molecular weight was determined by gel permeation chromatography. The sodium content was determined by high-frequency inductively coupled plasma emission spectrometry.

Measurement of Force Acting Between Surfaces of Cement Particles Adsorbing Admixture. Force acting between the surfaces of cement particles adsorbing the admixture was measured by immersing a polished surface of cement clinker sample or a silicon wafer in the admixture solution and determining the F-D curve of the adsorption surface of the admixture with the AFM. Auto Probe CP manufactured by Nikon/Park Scientific Instruments Co. was used as the AFM which uses a quadrangular silicon nitride probe of approximately 100nm base length and a cantilever with the spring constant of 0.05 N/m. The dimensions of the polished sample of cement clinker are 5 mm × 5 mm × 3 mm and the surface is finished with aluminum oxide of 0.05 μm in diameter. The silicon wafer covered with silicon dioxide (SiO2) supplied by Nikon was used. Prior to the measurement, the surface of the sample was washed by UV ozone cleaning to remove the contaminants including organic matter. The surface was carefully washed until it was evenly wetted by water. The working range and speed of the cantilever were zero to 750 nm and 1,500 nm/sec, respectively.

Measurement of Zeta Potential of the Surface of Cement Particle Adsorbing Admixture. Cement paste with the W/C of 0.3 was prepared by adding the admixture to it so as to make the weight ratio of the solid content of admixture to cement 0.6%. The zeta potential of the cement paste was determined with an electrokinetic sonic amplitude type zeta potential measuring apparatus (Acoustosizer made by Matec Applied Sciences Co.) five minutes after adding the mixing water.

Measurement of Flow of Cement Paste. The value of flow of the same cement paste as used for measuring zeta potential was measured with the flow cone for mortar test specified by JIS R 5201 five minutes after the addition of water. The flow cone is 70 mm in top diameter, 100 mm in bottom diameter and 60 mm high.

Results and Discussion

Force Acting Between Surfaces. A F-D curve of silicon wafer surface immersed in 10% aqueous solution of naphthalenesulfonate based-admixture (NS) is illustrated in Fig. 3. The probe was brought close to the surface of sample at the speed of 1,500 nm/sec. The moving distance of the probe from the starting point and the interactive force calculated from the deflection of the cantilever are put on the X- and Y-axes, respectively. The point S at which the interactive force begins linearly increasing shows the point where the probe is brought into contact with the surface of sample. The force acting between the solid surfaces is determined as the difference of the interactive force between points S and P, and the range of the interactive force acting is determined from the moving time of probe. Fig. 3 reveals that there is a difference between the F-D curve of the probe approaching the sample and that of the probe going away from it. In this study, however, the force acting between the surfaces was evaluated using the former force curve.

The left side figure of Fig. 4 is a figure drawn anew by transferring the point S in Fig. 3 showing the actual measurements to the point of origin of distance. Since that figure is convenient for understanding the change of the interactive force perpendicular to the surface of cement particle, F-D curve will be illustrated such as this hereafter.

The relationship between the distance of the probe from the surface of the adsorption layer of admixture and the interactive force on the polished surface of cement clinker immersed in a 10%-NS aqueous solution is illustrated in the figure on the right side of Fig. 4. The F-D curve varied according to the passage of time from the immersion in the aqueous solution of admixture. Maybe this is because the distance between the probe and the polished surface of clinker varied with time by the dissolution of component elements and the deposition of hydrates on the surface. It is, therefore, important to choose the measuring time in such a highly accurate study of a material progressing reaction during the measurement as in this particular case. The F-D curve obtained in five minutes after the immersion was not so different from that of silicon wafer.

The relationships between the distances from the surfaces of the adsorption layer of admixtures determined from the F-D curves obtained in five minutes after immersing the polished surface of cement clinker in various organic admixtures and the interactive force are illustrated in Fig. 5. The repulsive force on the polished surface of cement clinker immersed in pure water was 0.004 nN, while the maximum repulsive forces on the polished surface of cement clinker immersed in such aqueous solutions of admixtures as NS, PC-A and PC-B were 0.24, 0.60 and 0.19 nN, respectively. The distance beginning to work the repulsive force increased with increasing the repulsive force given from the admixture. It was approximately 10 nm for pure water, while approximately 160, 560 and 120 nm for the NS, PC-A and PC-B aqueous solutions, respectively. The interactive force logarithmically fell off in inverse proportion to the distance from the surface of the adsorption layer of admixture.

Zeta Potential of Cement Particle in Fresh Cement Paste. The result of measurements of zeta potential of cement particle in fresh cement pastes with the W/C of 0.3 prepared by adding and without adding the organic admixture are listed in Table 3.

NS contains 64 mmol/l of $SO4^{2-}$ (15) which is dissociated into anions. The zeta potential of cement particle in fresh cement paste prepared by adding NS was high. The PC-A contains as little as approximately 3% of carboxyl group and the hydrophobic group may enclose carboxyl group dissociated, so the zeta potential of cement particle in fresh cement paste prepared by adding PC-A was low. Meanwhile PC-B contains as high as approximately 60% of carboxyl group according to the calculation based on the molecular structure and maleic acid as a component is easily dissociated, therefore the zeta potential of cement particle in fresh cement paste prepared by adding PC-B was high.

In this experiment, even the zeta potential of well-dispersed cement particles in the fresh cement paste containing NS was -10mV. Maybe this is because the zeta potential is higher (lower in absolute value) than the surface potential.

Conversion of Measured Zeta Potential to Electrostatic Repulsive Force. It is necessary to convert electric potential to force for determining the electrostatic repulsive force from the measurements of zeta potential of cement particles in fresh cement paste. To the relationship in two spherical particles between the surface charge density (σ), Debye parameter (κ) and the electrostatic repulsive force (FRE), the following formula applies (16):

$$\mathrm{FRE} = [(2\pi\ \sigma^2 R) / (\epsilon_r \epsilon_0 \kappa)]\ \exp(-\kappa\ D) \qquad (5)$$

where R = radius of spherical particle, ϵ_r = relative permittivity of water, ϵ_0 = vacuum permittivity, and D = distance between surfaces of particles.

The reciprocal number of Debye parameter (κ^{-1}) represents the thickness of an electric double layer. The following relationship exists between the concentration of electrolyte and κ^{-1}:

$$\kappa^{-1} = 0.304/C^{1/2} \qquad (6)$$

where C = concentration of electrolyte. Since the concentration of electrolyte in the liquid phase of fresh cement paste is approximately 0.1mol/l, the thickness of diffuse electric double layer formed on the surface of cement particle adsorbing the admixture will be approximately 1 nm.

The surface charge density of the cement particle in cement paste can be calculated using the zeta potential instead of the surface potential from the following formula:

$$\sigma = (8n\ \epsilon_r \epsilon_0 kT)^{1/2}\ \sinh\ (Ze\phi_0/2kT) \qquad (7)$$

where n = concentration of electrolyte, k = Boltzmann constant, T = absolute temperature, Z = ionic charge number, e = elementary electric charge, and ϕ_0 = surface potential.

Values 1μm, 78.3 and $8.854 \times 10^{-12}\ C^2/J\ m$ were used as the radius of cement particle, the relative permittivity of pure water and vacuum permittivity, respectively. Although the thickness of the adsorption layer of admixture corresponding to the Stern layer varies according to the types and concentrations of admixture (17), 100 nm was used as the mean value of it in this study.

Taking the concentration of electrolyte as 0.1 mol/l, the temperature as 20°C, the ionic charge number as 1 and the elementary electric charge as 1.602×10^{-19}C, the electrostatic repulsive force of -15mV equivalent to the minimum value of Vmax (=15kT) required for keeping the dispersion of cement particles 2μm in diameter in fresh cement paste is approximately 10 nN at the distance between the particles of 1 nm.

Factors Affecting Fluidity of Fresh Cement Paste. The results of measurements of flow of cement paste with the W/C of 0.3 prepared with and without adding the organic admixture are

TABLE 4

Flow of Fresh Cement Paste Prepared by Adding Organic Admixtures

Admixture	Flow (mm)
NS	248
PC-A	476
PC-B	182
No added	113

illustrated in Table 4. The table reveals that the flow value is sharply increased by the addition of the admixture in such a manner that the fluidity is remarkably increased by adding PC-A, but the flow value is less increased by adding PC-B than by adding NS.

The relationship between the measured value of force acting between the polished surfaces of cement clinker immersed in an aqueous solution of organic admixture and the flow of fresh cement paste, and that between the zeta potential of the cement particle in cement paste containing the admixture and the flow of fresh cement paste are illustrated in Fig. 6. The force acting between the surfaces is linearly related to the flow of fresh cement paste independently of what type of admixture is added and whether the admixture is added or not. The flow value increased with increasing the force acting between the surfaces. Meanwhile, the zeta potential is not necessarily linearly related to the fresh cement paste flow, especially the relation was remarkably separated from the linear relation by adding PC-A. This suggests that force other than the zeta potential or electrostatic repulsive force contributes to the dispersion of cement particles; namely, the fluidity of fresh cement paste containing PC-A.

Effects of Electrostatic and Steric Repulsive Forces on Fluidity. The steric repulsive force is considered to be one of the most important forces contributing to the fluidity of cement paste. The value of it can be calculated by subtracting the electrostatic repulsive force converted from the zeta potential from the force acting between the surfaces of cement particles in cement paste. Since no steric repulsive force acts in fresh cement paste without admixture, the electrostatic repulsive force converted from the zeta potential of it should be equal to the

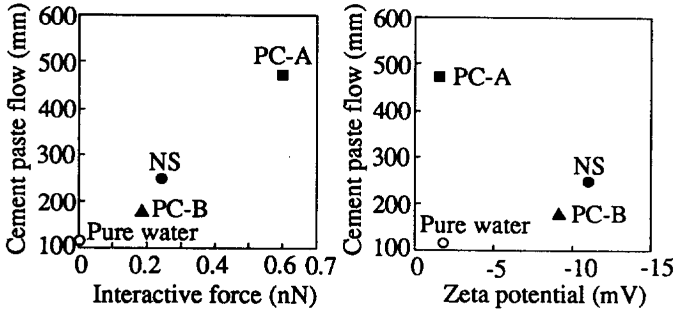


FIG. 6.
Relationships between fresh cement paste flow and interactive force, and zeta potential.

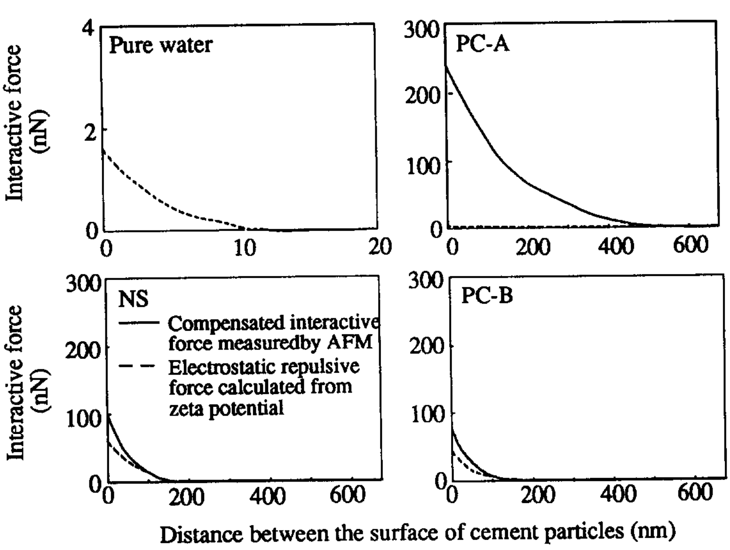


FIG. 7.
The rate of contribution of electrostatic repulsive force to total repulsive force.

repulsive force measured with the AFM. The former value is, however, 1.5 nN, while the latter value is 0.004 nN. The former is, therefore, 375 times as much as the latter.

The repulsive force measured with the AFM is the force acting between the probe and the solid surface and the tip of probe is quadrangular with a side of 100 nm. Since the interactive force is proportional to the area, assuming that the tip of probe is a cement particle 2μm in diameter, it will be 400 times [(2000 nm/100 nm)^2] as much as the force acting between the probe and the solid (cement clinker), which is nearly equal to the above-mentioned value of 375 times.

The relationship between the compensated interactive force of the surface of the adsorption layer of admixture on polished surface of cement clinker opposite to the cement particle 2μm in diameter obtained by multiplying the value measured with the AFM by 400 and the distance is illustrated in Fig. 7. A curve drawn by plotting the electrostatic repulsive force converted from the measured value of zeta potential versus the distance is included in the figure.

Fig. 7 reveals that though the electrostatic repulsive force contributing to the dispersion of cement particles in fresh cement paste without admixture is extremely small and the working region is also narrow, the force acting on the surface of cement particle is increased by adding the admixture. The steric repulsive force predominates in the large repulsive force acting between the cement particles in fresh cement paste containing PC-A. Meanwhile, the steric repulsive force contributes only to the regions in the vicinity of cement particles in fresh cement paste containing PC-B and NS, but it disappears in the region exceeding 90 nm from cement particle and accordingly the mean contributions in the former and latter cases to total repulsive force are estimated to be 30 and 20%, respectively. Maybe this is because each molecule of PC-A with a long straight chain and side chains branched from it is adsorbed overlapping each other to the surface of cement particles and the adsorption layer containing many high-density regions is formed, thereby generating large steric repulsive force.

The results mentioned above prove for the first time that the steric repulsive force of the organic admixture, which has been a matter of speculation, acts on the dispersion of cement particles, and that the magnitude of the steric repulsive force is closely related to the molecular structure of the admixture. Most of the action dispersing the particles is attributed to the steric repulsive force in fresh cement paste containing a polycarbonate based-admixture mainly composed of acrylic acid-acrylic acid ester copolymer.

Conclusions

The conclusions obtained by investigating the function dispersing the particles of cement in concrete by the organic admixture are as follows:

(1) The force acting the polished surface of cement clinker adsorbing the admixture can be measured with good reproduciblity as a function of the distance from the adsorption surface of admixture with the atomic force microscope.

The zeta potential of cement particles in fresh cement paste with low W/C can be reliably determined by measuring the magnitude of a pressure wave or an electrokinetic sonic amplitude value caused by the dynamic mobility of cement particles to which high-frequency alternating voltage is applied.

(2) Although the fluidity of fresh cement paste containing the organic admixture correlates with the repulsive force of cement particles, there is no constant relationship between the fluidity and the zeta potential. This suggests that a force other than the electrostatic repulsive force acts on the dispersion of cement particles.

(3) Considering that van der Waals force is a negligibly small attractive force, it has been proved for the first time in this study that the cement particles adsorbing the organic admixture have the steric repulsive force besides the electrostatic repulsive force by determining the difference between the compensated interactive force obtained from measured value of force acting between the surfaces and the force converted from the measured value of zeta potential.

(4) The repulsive force of the cement particles in fresh cement paste is increased by adding the organic admixture, and the magnitude and working region of it depend upon the types of the admixture. The action dispersing the particles of a polycarbonate based-admixture mainly composed of an acrylic acid-acrylic acid ester copolymer is mainly attributed in the steric repulsive force, while that of naphthalene sulfonate based-admixture is attributed in considerable part to the electrostatic repulsive force.

(5) Steric repulsive force contributes predominantly to the dispersion of cement and cement hydrate particles in the addition of admixture composed of acrylic acid-acrylic acid ester because its molecular structure is composed of a long straight chain of carbon atoms and the side chains branched from it. It forms an adsorption layer containing many high-density regions overlapping each other to the surface of cement particles. Less content of carboxyl group with electric charge ionized in water and the enclosure of carboxyl group with electric charge by hydrophobic groups may also be responsible to reduce the contribution of electrostatic repulsive force for the dispersion of particles.

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