Force modeling of interparticle pair interaction of spheroid in composite cement

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Abstract. The paper discusses the modeling of the forces of interparticle pair interaction of spheroidal agglomerate in composite cement. Based on the calculation of the autohesion forces that make up the spheroidal agglomerate, i.e. the Portland cement (“carrier particles”) and silica fume (“guest particles”), it was found that for uncharged particles the magnitude of the electric interaction forces is negligible in comparison with molecular van der Waals and capillary forces. The bipolar charging of particles in the corona discharge field at a corona electrode potential of +18 and –18 kV sharply increases the electric component of the autohesion force, which in value approaches the value of capillary forces. In this case, the Coulomb attractive forces between oppositely charged particles begin to act before the direct contact of the particles, which contributes to the agglomeration of particles. These calculations are confirmed by the results of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) of composite cement samples containing Portland cement (75 %) and dry gas purification silica fume (25 %), the number of angular particles of irregular shape decreases for a mixture of these materials processed in the device for surface modification.

1. Introduction

As the fineness of grinding of composite cement increases, the water demand increases, i.e. the normal density of cement paste increases by 5–7 % when the specific surface area changes from 320 to 500 m²/kg. To reduce water demand and, consequently, improve workability of concrete mixtures and concrete quality, optimization of particle size distribution of dispersed mineral components is needed. Particle shape, as well as the quantitative content of fine fractions, have an important effect on the water demand of the mineral components of concrete. In [1], it was shown that with an increase in the content of fly ash from TPPs, instead of Portland cement, the fluidity of the cement paste increases. This is explained from the standpoint of interparticle interactions in colloidal systems: for particles of fly ash, the value of the electrokinetic potential is \( \xi = -12 \ldots -14 \text{ mV} \), and for particles of Portland cement it is \( \xi = +2.17 \text{ mV} \). With a small amount of ash in the composition of the cement paste, the particles of ash and cement flocculate due to electrostatic attraction. When the ash consumption is high (more than 50 % cement replacement), the negative integrated charge of the particles prevails in the system, and their electrostatic repulsion occurs, which increases the mobility of the paste. In addition, the adhesion of smaller particles of ash on oppositely charged particles of the clinker phases causes repulsion of the latter with the release of water immobilized in the floccules. An increase in mobility is
also due to a decrease in friction between particles, since they take the form of spheroids [2, 3]. The spherical shape also minimizes the specific surface of the particles [4].

Currently, in various industries where highly dispersed powders are used, the research on the so-called dry particle coating is being intensively developed. The essence of the method consists in the fixation of finely dispersed particles with the size of 0.1–50 microns (guest particles – “guest” particles) on the surface of larger ones, i.e. 1–500 microns (host particles – “carrier particles”) in the process of intensive mixing.

The percentage of “guest” particles required for the experiment is calculated based on the assumption of 100% surface coverage of the carrier particles with a monolayer of “guest” particles. It is assumed that the “carrier particles” and the “guest’ particles are spherical with an appropriate size and density that do not change their shape during the coating process. Based on these assumptions, the mass fraction of “guest” particles for 100 % coverage can be determined [5] by the following formula:

\[
W, \% = \frac{(Nd_{\text{guest}} \cdot \rho_{\text{guest}})}{(D_{\text{host}} \cdot \rho_{\text{host}}) + (Nd_{\text{guest}} \cdot \rho_{\text{guest}})} \cdot 100
\]

where

- \( W \) is a mass fraction of guest particles, \( \% \);
- \( d_{\text{guest}} \) is the diameter of guest particles, microns;
- \( \rho_{\text{guest}} \) is the density of guest particles, kg/m3;
- \( D_{\text{host}} \) is the diameter of the carrier particles, microns;
- \( \rho_{\text{host}} \) is the density of carrier particles, kg / m3.

With the ratio \( D_{\text{host}} \gg d_{\text{guest}} \) (especially, \( D_{\text{host}} / d_{\text{guest}} = 10 \)):

\[
N = \frac{4(D_{\text{host}} + d_{\text{guest}})^2}{d_{\text{guest}}^2}
\]

Higher efficiency of surface modification is achieved in the installations where the mixing of the particles is accompanied by their intense collision with each other (High energy impact blending coater “Nara Hybridizer”, High shear mixer “Cyclomix”). As a result of surface modification of powders, an increase in their rheological characteristics, a decrease (increase) in wettability, a change in granulometry and other properties are achieved [1, 5–7].

![Figure 1. Drawing of the mixer – hybridizer (triboactivator): 1 – rotor; 2 – mixer; 3 – output channel; 4 – input channel; 5 – circular circulation; 6 – outer shell [12].](image-url)
In this context, it is worth highlighting a promising direction that is being developed in the research of Japanese scientists, i.e. the technology for the formation of “spheroidal” cement (Spherical cement) [8–11]. The technology for producing such cement consists in processing Portland cement together with mineral additives in a special device, i.e. a mixer-hybridizer (Figure 1). In the process of high-speed mixing, an intense friction and collision of particles occur, which leads to the formation of surface charges. As a result, adhesion of small particles of gypsum, mineral additives and an intermediate phase to the surface of larger angular particles of silicate phases is ensured. Capillary forces also promote particle fixation since in the spaces between hydrophilic particles pressed against each other, water molecules are adsorbed by the condensation surface and liquid menisci are formed. During processing, the particles coarsen, reducing the total specific surface, and acquire a shape close to spherical ($k_d=0.85$).

As a result of reduction in the number of “free” fine particles (diameter less than 3 microns), reduction in the surface roughness of “spheroids”, and a slowdown of the early stages of cement hydration, the mobility of concrete mixtures prepared on the basis of “spheroidal” cement increases ($W/C$ decreases by 6–8 %). When using superplasticizers in the concrete mixtures, a decrease in their adsorption per unit surface of cement was also noted (up to 20 %).

2. Methods and materials

Modeling the forces of interparticle pair interaction in a spheroidal agglomerate.

The efficiency of the formation of spheroidal agglomerates can be increased when using Portland cement compositions with highly dispersed mineral additives (silica fume, metakaolin).

Surface modification of composite cement by particles of silica fume was carried out on a special installation (Figure 2).

![Figure 2](image-url)

**Figure 2.** Installation drawing for surface modification of mineral dispersed concrete components: I – particle electrification chamber (bipolar charging) in the corona discharge field; II – agglomerator

At first, the initial dispersed mineral components can be charged in a high-voltage field of a corona discharge, while a sample of finely dispersed component (“guest” particles) is poured through an electrification chamber – (1) with a negative corona electrode, and a sample of coarse component (“carrier particles”) through the chamber electrification – (2) with a positive corona electrode. The unit
of electrification chamber consists of a corona electrode located in the center of the pipe, which is made of copper wire with the diameter of 0.6 mm. The current-voltage characteristics of the electrification chamber are as follows: electric field strength \( E = 18–20 \text{ kV/cm} \), current strength \( I = 30–50 \mu \text{A} \).

As a result of the electric field impact created between the corona and external electrodes, the initial mineral components adsorb ions from the interelectrode space and acquire a negative (positive) charge.

After that, the bipolar charged mineral dispersed components enter the agglomerator, where under the impact of a high-voltage alternating electric field, the vibrations with different amplitudes and frequencies are carried out. Large particles oscillate with bigger amplitude and frequency than small particles, the gradient of the frequency and amplitude of oscillations causes an increase in the frequency of collisions of particles, which leads to the formation of spheroidal agglomerates.

Since the autogenesis of many particles that make up bulk material is composed of forces (molecular, electric, capillary) that manifest themselves in the individual contacts between particles, it is possible to calculate these forces by simulating the pairwise interaction of two particles that make up a spheroidal agglomerate – Portland cement ("carrier particles") and silica fume ("guest" particles). We assume that the average particle size of silica fume is 2 \( \mu \text{m} \), and that of Portland cement is 20 \( \mu \text{m} \), then the mass fraction of "guest" particles according to formula (1) will be 25.5 %.

Electric forces.

According to [10], the electric charge density for the particles of Portland cement and silica fume is as follows, respectively:

\[
q_1 = 9 \cdot 10^{-9} \text{ C/m}^3 \\
q_2 = -8 \cdot 10^{-11} \text{ C/m}^3
\]

Then, some particles:

\[
q = Q \cdot S = Q \cdot 4\pi r^2
\]

\[
q_1 = 9 \cdot 10^{-9} \cdot 4 \cdot 3.14 \left(10 \cdot 10^{-6}\right)^2 = 113.04 \cdot 10^{-19} \text{ C}
\]

\[
q_2 = -8 \cdot 10^{-11} \cdot 4 \cdot 3.14 \left(1 \cdot 10^{-6}\right)^2 = -100.48 \cdot 10^{-23} \text{ C}
\]

Particle electric capacity:

\[
C = 4 \pi \varepsilon_0 \varepsilon_r r
\]

\[
C_1 = 4 \cdot 3.14 \cdot 4.5 \cdot 8.85 \cdot 10^{-12} \cdot 10^{-16} = 50 \cdot 10^{-16} \Phi_f; C_2 = 4 \cdot 3.14 \cdot 3.9 \cdot 8.85 \cdot 10^{-12} \cdot 1 \cdot 10^{-6} = 43.3 \cdot 10^{-17} \Phi_f
\]

where \( \varepsilon_r \) is the dielectric constant of the particle substance, \( \varepsilon_0 \) is the electric constant (F/m), \( r \) is the particle radius, m.

The potential of particle surface:

\[
\varphi = \frac{q}{C}
\]

\[
\varphi_1 = \frac{113.04 \cdot 10^{-19}}{50.02 \cdot 10^{-15}} = 2.25 \cdot 10^{-4} \text{ V}; \quad \varphi_2 = \frac{-100.48 \cdot 10^{-23}}{43.35 \cdot 10^{-17}} = -2.32 \cdot 10^{-4} \text{ V}.
\]

The electric field strength at the surface of a cement particle is calculated by the following formula:

\[
E = \frac{1}{4\pi \varepsilon_0 \varepsilon_r} \cdot \frac{q}{r^2}
\]

where \( \varepsilon \) is the dielectric constant of the medium in which the particle is placed (air \( \varepsilon = 1 \)).

\[
E = \frac{113.04 \cdot 10^{-19}}{4 \cdot 3.14 \cdot 1 \cdot 8.85 \cdot 10^{-12} \cdot 10^{-6}} = 102.7 \text{ V/m}.
\]

The force acting on a silica particle at the surface of a cement particle is determined by the following formula:

\[
F_{el} = Eq_2
\]

\[
F_{el} = 102.7 \left(-100.48 \cdot 10^{-23}\right) = 10.3 \cdot 10^{-20} \text{ N}
\]

Molecular forces.
Since \(d_2 << d_1\), we can assume that a convex surface of radius \(r_2\) is in contact with a flat surface. The strength of the molecular interaction according to Hamaker has the following form:

\[
F_m = \frac{A r_2}{12 H^2}
\]

where \(A=(0.01…3.2) \cdot 10^{-18}\), \(J\) is the constant of molecular interaction, depending on the heterogeneity of solid surfaces; \(H=0.5 \cdot 10^{-9} m\) is the width of the gap between the contacting bodies.

\[
F_m = (0.01…3.2) \cdot 10^{-18} \cdot \frac{10^{-9}}{12 \cdot 0.25 \cdot 10^{-18}} = (3…1060) \cdot 10^{-3} N
\]

Capillary forces.

If the shape of the formed menisci of the liquid is concave, then according to the Kelvin equation, the saturated vapor pressure above them is calculated by the following formula:

\[
p = p_0 \exp \left( \frac{2 \sigma v}{aRT} \right),
\]

where \(p_0\) is the saturated vapor pressure above a flat surface, \(\sigma\) is the surface tension coefficient of water, \(v\) is the molar volume of water, \(r\) is the meniscus curvature radius (negative for a concave surface), \(T\) is the absolute temperature, \(R = 8.31 J/(mol \cdot K)\) is the universal gas constant. At a temperature of \(T =293 K\), we have \(p_0=2.33 kPa\), \(\sigma=73 mN/m\), \(v=18 \cdot 10^6 m^3/mol\).

Saturated vapor pressure over a concave surface is lower than over a flat surface. Thus, capillary condensation occurs at pressures lower than \(p_0\), i.e., at lower air humidity:

\[
\phi = \frac{p}{p_0} = \exp \left( \frac{4 \sigma v}{aRT} \right),
\]

where \(a \sim 1 nm\) is the size characteristic of atomic-molecular roughness. It follows that capillary condensation occurs already at a relative humidity of \(\sim 10 \%\).

According to the Laplace equation, the fluid pressure under the concave surface is reduced by:

\[
\Delta p = 2a/r
\]

which leads to the appearance of the capillary component of forces of autohesion. Substituting \(r=a/2=0.5 \text{ nm}\) into the equation, we obtain \(\Delta p \approx 300 \text{ MPa}\). Since \(d_2<<d_1\), we can assume that a convex surface of radius \(r_2\) is in contact with a flat surface. Then the capillary force will be equal to:

\[
F = 4 \pi \sigma r_2,
\]

Thus, the calculations show that the main role in the formation of spheroidal aggregates is played by capillary and molecular van der Waals forces. The electrical component of the forces of autohesion is significantly inferior to these forces.

Let us consider the case when particles of Portland cement and silica fume are pre-bipolar charged in the corona discharge field. According to the data given in [12], fly ash particles with the size of 0.1 \(\mu m\), processed at a corona electrode potential of 8 kV, acquire about ten elementary charges, and 1 \(\mu m\) in size acquire one hundred elementary charges. With increasing particle size and electric field strength, the particle charge increases significantly [13, 14].

For particles of Portland cement and silica fume treated accordingly with the potential of the corona electrode +18 and –18 kV, we take their charge value:

\[
q_1 = 2 \cdot 10^3 \cdot 1.6 \cdot 10^{-19} = 3.2 \cdot 10^{-16} C;
q_2 = 2 \cdot 10^3 \cdot 1.6 \cdot 10^{-19} = 0.32 \cdot 10^{-16} C
\]

Let us find the potential for particles in the corona discharge field:

\[
\phi_1 = 3.2 \cdot 10^{-16} \cdot 0.5 \cdot 10^{-19} = 6.4 \cdot 10^{-4}; \quad \phi_2 = 0.32 \cdot 10^{-16} \cdot 0.43 \cdot 10^{-19} = 0.74 \cdot 10^{-4}
\]

Let us repeat the calculation of electric forces based on this potential value. Electric field strength at the surface of a cement particle:

\[
E = \frac{3.2 \cdot 10^{-16}}{4 \cdot 3.14 \cdot 1 \cdot 8.85 \cdot 10^{-12} \cdot (10 \cdot 10^{-6})^2} = 3200 V/m
\]
The force acting on a charged silica particle at the surface of a cement particle:

\[ F = 32 \times 10^{-2} \cdot 0.32 \times 10^{-10} = 10.2 \times 10^{-14} \text{ N}. \]

3. Results

Obviously, the charging of particles in the field of the corona discharge sharply increases the electric component of the forces of autohesion, which approaches the magnitude of the capillary forces in value. In this case, the Coulomb attractive forces between oppositely charged particles begin to act even before the direct contact of the particles, which contributes to the agglomeration of particles. These assumptions are confirmed by the results of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

After the mixing of a mixture of materials that contain Portland cement (75%) and dry silica fume silica (25%), the number of angular particles of irregular shape decreases (Figure 3, c), this is true for a mixture of these materials processed in a device for surface modification (Figure 3, d). At the same time, larger aggregates up to 50-100 microns in size are found (Figure 3, a).

![Figure 3. SEM of dispersed materials: a – Portland cement; b – silica fume; c – mechanical mixture of Portland cement and silica fume; d – a mixture of Portland cement with silica fume after surface modification.](image)

According to the energy dispersive spectroscopy, the surface of such “spheroids” (point 1, Figure 4. b) is represented by the following oxides, %: SiO\(_2\) (84.93); SO\(_3\) (11.91); Al\(_2\)O\(_3\) (1.85); MgO (0.84); K\(_2\)O (0.45), which is a characteristic of the chemical composition of silica fume. For the purpose of comparison, a particle on the surface of a “spheroid” (point 2) is represented by such a set of oxides, %: CaO (51.44); SiO\(_2\) (37.31); Fe\(_2\)O\(_3\) (4.21) SO\(_3\) (2.24 %); Al\(_2\)O\(_3\) (1.43); K\(_2\)O (3.07), which is very close to the chemical composition of Portland cement.
The mobility of cement pastes of the composition “Portland cement – silica fume – superplasticizer” C-3 (1 %) was evaluated by the yield index G, which is determined by the formula 
\[ G = \frac{F^2}{502-1} \]
where F is the average diameter of the mixture according to Suttard. It was found that for a cement paste of the composition PC (210 g) – SF (70 g) – S-3 (2.8 g), B/B = 0.32, the index G is 1.1, while for a cement paste based on modified cement, the value of G = 1.1 is achieved with a water-binding ratio B/B=0.285 (11 % less in comparison with the control composition). This provides an increase in compressive strength of cement stone at the age of 28 days of normal hardening by 37 %. It should also be noted the high stability of spheroidal agglomerates obtained during the modification of composite cement, which, according to scanning electron microscopy, were found in the structure of a cement stone at the age of three days of normal hardening (Figure 5).

The results obtained are consistent with the data provided by Japanese scientists [8–11], who identified spheroidal agglomerates in the structure of modified cement hydrated for 28 days.

**4. Conclusion**

Based on the simulation of forces of interparticle pair interaction, the calculation of the autohesion forces that make up the spheroidal agglomerate, i.e. particles of Portland cement \(d_1 = 20 \, \mu m\) and particles of silica fume \(d_2 = 2 \, \mu m\) was performed. It is shown that, for uncharged particles, the magnitude of the electric interaction forces is negligible in comparison with the molecular van der Waals and capillary forces. The bipolar charging of particles in the corona discharge field at a corona electrode potential of +18 and −18 kV sharply increases the electric component of the autohesion force, which approaches the magnitude of molecular forces in value.

In this case, the Coulomb forces of attraction between oppositely charged particles begin to act before the direct contact of the particles, which contributes to the agglomeration of particles. These calculations are confirmed by the results of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) of samples of composite cement, which contains Portland cement (75 %) and silica fume of dry gas cleaning (25 %), the number of angular particles of irregular shape is reduced for a mixture of these materials processed in a surface modification device.
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