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Cement and Concrete Research 34 (2004) 1017–1024

CEMENT AND CONCRETE RESEARCH

The fluidity of fly ash–cement paste containing naphthalene sulfonate superplasticizer

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Received 16 July 2003; accepted 17 November 2003

Abstract

The zeta potential measurement indicated that the surface potential of fly ash was different from ordinary Portland cement (OPC) in both sign and value. Hence, the Derjaguin–Landau–Verway–Overbeek (DLVO) theory for dispersion–flocculation of heterogeneous particles with different surface potentials was applied to explain the influence of fly ash on the rheology of cement paste containing naphthalene sulfonate superplasticizer. For the fly ash–cement paste without superplasticizer, the sign of zeta potential of fly ash was different from OPC. Thus, the extent of the potential energy barrier between particles was small or even showed negative value, and the change in the rheology of the fly ash–cement paste was mainly dependent on the bulk solid volume of fly ash, which was related to available free water for fluidizing paste. For the fly ash–cement paste with naphthalene sulfonate superplasticizer, fly ash and cement had the same sign and dispersed well due to higher potential barrier. The extent of potential energy barrier depended on the absolute value of surface potential, which was represented by a function of the amount of adsorbed superplasticizer. The bulk solid volume of fly ash also affected the change in flow ability, but the effect of potential energy barrier between particles was superior to that of the bulk solid volume of fly ash.

Keywords: Fly ash; Rheology; Adsorption; Admixture; Potential energy

1. Introduction

Superplasticizer is commonly used to disperse cement particles. When superplasticizer is added, the yield value of the paste decreases close to zero, but the plasticity does not decrease significantly. Thus, the paste and concrete will obtain good flow ability without ingredient segregation. Naphthalene sulfonate superplasticizer is often used to improve the rheology of fresh concrete [1]. It was reported that in cement paste, the mechanism of this kind of superplasticizer could be explained well by the Derjaguin–Landau–Verway–Overbeek (DLVO) theory [2–6]. Many researchers studied about cement paste added with naphthalene sulfonate superplasticizer [7–9]. When naphthalene sulfonate superplasticizer is adsorbed to the surface of cement particles, it changes the sign of the zeta potential of particle surface to negative and increases the absolute value [10,11]. Then, cement particles having the same sign of zeta potential cannot approach each other closely due to the electrostatic repulsion.

However, there are few studies reported on the fly ash–cement paste. In the fly ash–cement paste with superplasticizer, the improvement of the rheology of paste does not only come from the increase in the amount of adsorption but from the properties of fly ash, namely, bulk solid volume as well [12]. Even when the fly ash with poor bulk solid volume is used, and the amount of adsorption of superplasticizer does not increase, the flow value increases as the replacement ratio of fly ash increases. The purpose of this study is to investigate the application of the DLVO theory on fly ash–cement paste, taking into account the effect of the properties of fly ash.

In this study, we measured the zeta potential of powder particles. The amount of adsorption of superplasticizer and the flow value were evaluated. Then, by considering the effect of the properties of fly ash, the flow behavior was

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doi:10.1016/j.cemconres.2003.11.017

analyzed and compared with the potential energy barrier calculated via the DLVO theory. The rheology of paste containing 100% fly ash was also studied and compared with fly ash–cement paste.

2. Theoretical background

In general, the dispersion action of cement particles by naphthalene sulfonate superplasticizer has been explained by the DLVO theory. According to the DLVO theory, the dispersion stability of particles is determined based on the shape of the total potential energy curve, which is the sum of the electrostatic repulsion potential energy and Van der Waals attraction potential energy. The flocculation–dispersion of particles is determined by the extent of the potential energy barrier (V_{max}) on the total potential energy [13]. As the extent of potential energy barrier increases, the particle disperses well, and then the flow ability of suspensions, such as cement paste, is improved.

Meanwhile, the model reported previously was based on a simple interaction between two particles, both having the same surface potential. However, cement particles actually have different values or signs of surface potential. Thus, in this study, we attempt to theoretically understand the effect and role of fly ash quality on the rheology from a point of view of the DLVO theory for the heterogeneous particles with different diameters and zeta potentials. The total potential energy between heterogeneous particles can be described as

$$V_{\mathrm{DLVO}} = V_{\mathrm{VDW}} + V_{\mathrm{elect}} \quad (1)$$

Where V_{DLVO} is the sum of the Van der Waals potential energy (V_{VDW}) and the electrostatic repulsion (V_{elect}).

The Van der Waals interparticle potential energy (V_{VDW}) can be presented as follows:

$$V_{\mathrm{VDW}} = -\frac{Aa_1a_2}{6(a_1+a_2)H_0} \quad (2)$$

In which A is the Hamaker constant, H_0 is the minimal distance of surface separation for two particles, and a_1 and a_2 are the radius of Particles 1 and 2, respectively. The negative sign means the attractive force.

For the electrostatic repulsion (V_{elect}), the equations are described below:

$$V_{\mathrm{elect}} = \frac{4\pi\varepsilon\varepsilon_0 a_1 a_2(\Psi_1^2+\Psi_2^2)}{4(a_1+a_2)} \times \left[\frac{2\Psi_1\Psi_2}{(\Psi_1^2+\Psi_2^2)}\ln\frac{1+\exp(-\kappa H_0)}{1-\exp(-\kappa H_0)} + \ln\langle 1-\exp(-2\kappa H_0)\rangle\right] \quad (3)$$

$$\kappa = \sqrt{\frac{2AC_\mathrm{i}e^2}{\varepsilon\varepsilon_0 kT}} \quad (4)$$

$$C_\mathrm{i} = \frac{1}{2}\times\sum_i c_\mathrm{i}Z^2 \quad (5)$$

Here, ε and ε_0 are the dielectric constants of the medium and the vacuum, respectively; ψ_1 and ψ_2 are the surface zeta potentials of Particles 1 and 2, respectively; κ is the Debye–Hückel parameter; C_i is the ionic strength; c_i is the ion concentration; Z is the electric charge; e is the elementary electronic charge; k is the Boltzmann constant, and T is the absolute temperature.

3. Experiment

Ordinary Portland cement (OPC) was used. The fly ash used here was produced by Hokkaido Electric Power Plant. It is well known that unburned carbon affects to the amount of adsorption of superplasticizers. Thus, to neglect the effect of unburned carbon, the ignition loss of fly ash was kept under 5%. The bulk specific density of fly ash was measured according to the method that was proposed by Nagataki et al. [14]. Fly ash was put into the cylindrical container. Then it was compacted by thumping through the drop of the flow table. The top surface was levelled off. The concentration of powder by volume was defined as the bulk solid volume, and the mass of contents per unit volume was defined as the bulk specific density. Table 1 shows the chemical and physical properties of OPC and fly ash. The superplasticizer was a commercial naphthalene sulfonate superplasticizer.

Table 1
Physical and chemical properties of OPC and fly ash

Kind of powder	Density (g/cm^3)	Bulk solid volume (%)	Bulk specific density	Blaine surface area (cm^2/g)	Ignition loss (%)	SiO_2 (%)	CaO (%)	Al_2O_3 (%)	Fe_2O_3 (%)
OPC	3.16	57.10	1.804	3350	1.88	20.97	63.23	4.69	2.69
MS/BA	2.32	64.00	1.485	2560	1.00	54.00	5.72	23.64	6.26
UL/BA	2.14	54.30	1.162	2960	2.10	68.40	0.27	21.59	4.03

The water–powder ratio of paste was 1.0 by volume. The specified temperature of paste was adjusted within 20 ± 2 °C. The dosage of superplasticizer varied from 0.05 to 1.80 wt.% of powder, whereas the replacement ratio of fly ash varied from 0 to 100 vol.%. Cement and fly ash powder were mixed together and were kept in the controlled temperature room for 24 h. After that, all ingredients were mixed for 3 min by using a handy-type mixer.

The rheology of cement paste was measured by the flow test according to JASS15 M-103. First, sample paste was poured into the cylindrical cone, 50 mm in diameter and 51 mm in height. Then, 10 min after mixing, the cone was slowly pulled up vertically. The flow value was the averaging value of the two crossing diameters of the spreading paste. In the mean time, the amount of superplasticizer absorbed was measured by using the following method. The amount of superplasticizer molecules adsorbed onto the powder surface was measured by using total organic carbon (TOC) equipment (Shimadzu TOC-5000). The liquid phase was separated from the cement paste by using the centrifugal separator at 6000 rpm for 3 min. After that, the liquid phase was filtered through the microfilter. Then the amount of organic carbon that remained in the solution was examined by TOC equipment. The difference of the total carbon in liquid phase before and after adsorption was defined as the amount of adsorbed superplasticizer.

The zeta potential of the cement surface was measured by using an electrophoretic technique. An amount of 0.15 g of powder was used in suspension with 50 ml of deionic water at room temperature. For the superplasticizer, 0.30 wt.% of powder was used.

4. Results and discussions

4.1. Paste without superplasticizer

4.1.1. Paste with individual powder

Table 2 shows the zeta potential and flow value of paste for each powder when superplasticizer was not added. The sign of the average zeta potential of the cement particle was positive, while that of the fly ash particle was negative. Fig. 1 shows the potential energy curves of two particles calculated by the DLVO theory when the radius of both particles (a_1 and a_2) are 1 μm, the absolute temperature is 293 K, and the ionic strength, C_i, is 500 mol/m^3. The Hamaker constant, A, is 1.7×10^{-21} J based on the results of Hattori [4].

Table 2
The comparison of average zeta potential and flow value in the system without superplasticizer

Kind of powder	Average zeta potential (mV)	Flow value (mm)
OPC	2.17	65
MS/BA	− 14.6	168
UL/BA	− 21.1	115

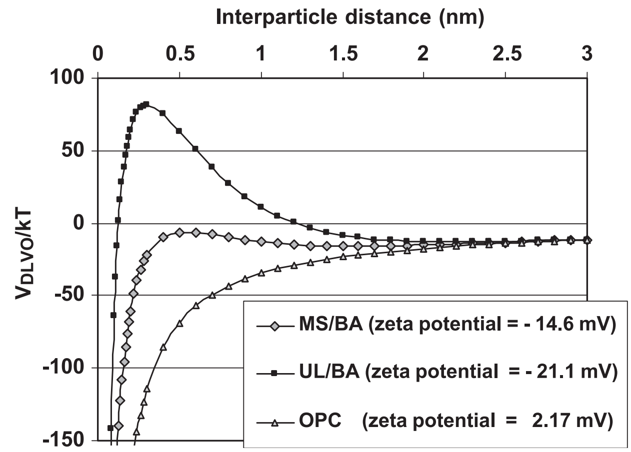

Fig. 1. The potential energy between the same kinds of particles in solution without superplasticizer. The relations were calculated base on the DLVO theory when the radius of both particles (a_1 and a_2) are 1 μm, the absolute temperature is 293 K, and the ionic strength, C_i, is 500 mol/m^3. The Hamaker constant, A, is 1.7×10^{-21} J based on the results of Hattori [4].

In Fig. 1, the potential energy of both fly ash MS/BA and OPC were below zero. It means that the particles flocculated each other. This figure also shows that the potential energy of OPC was lower than fly ash MS/BA; thus, the degree of flocculation of OPC was higher than fly ash MS/BA. From Table 2, the flow value decreased in the following order: fly ash MS/BA, fly ash UL/BA, and OPC.

For fly ash UL/BA, on the other hand, the value of potential energy barrier was about 80 V/kT, which is higher than fly ash MS/BA and OPC. The flow ability of fly ash UL/BA was better than OPC but worse than MS/BA. This means that the DLVO theory for homogeneous system cannot explain the flow ability of paste in the case of a homogeneous particle system.

Some researchers [14,15] pointed out that the rheology of paste was affected strongly by the bulk solid volume. When the bulk solid volume was high, the restricted water on the surface of particles became smaller, and thus, available free water for fluidizing paste increased. Accordingly, the flow value of paste increased as the bulk solid volume increased. In the case of fly ash MS/BA, the bulk solid volume was quite higher than that of OPC. Moreover, the potential energy barrier of fly ash MS/BA, as shown in Fig. 1, was higher than that of OPC. In this case, the degree of flocculation of fly ash MS/BA was lower than that of OPC. Therefore, the flow ability of fly ash MS/BA paste was better than OPC paste due to the effect of both the potential energy barrier and the solid volume fraction.

On the other hand, the bulk solid volume of OPC was slightly higher than that of fly ash UL/BA. However, the potential energy barrier of fly ash UL/BA particles was significantly higher compared with that from OPC. In this case, the effect of potential energy barrier might be superior to the effect of solid volume fraction. Thus, fly ash UL/BA paste showed better flow ability than OPC paste.

The potential energy barrier of fly ash UL/BA was higher than that of fly ash MS/BA, which was near zero. This might imply that both fly ash particles hardly flocculated. In this case, it was therefore possible that the bulk solid volume was the major effect to determine the rheology of paste; consequently, the flow value of fly ash MS/BA was higher than that of fly ash UL/BA.

4.1.2. Fly ash–cement paste

Fig. 2 illustrates the relationship between the flow value and the replacement ratio of fly ash in the paste without superplasticizer. For fly ash MS/BA + OPC paste, the flow value increased with increasing replacement ratio. However, for fly ash UL/BA + OPC paste, the rheology did not increase at any extent of replacement. The potential energy curves between cement particle and fly ash particle are shown in Fig. 3. The total potential energy of cement particle and fly ash particle became lower than those between OPC particles and showed a negative value at all interparticle distance; thus, the flocculation should occur.

However, for fly ash MS/BA, it was found that although the flocculation occurred, the flow value still increased as the replacement ratio of fly ash increased (Fig. 2).

This improvement due to replacement of fly ash can be related to the effect of physical properties of fly ash, namely, bulk solid volume. The change in bulk solid volume with the replacement ratio of fly ash is shown in Fig. 4. For fly ash MS/BA, the bulk solid volume increased as the replacement ratio increased; thus, the flow value increased as the replacement of fly ash MS/BA increased.

For fly ash UL/BA, on the other hand, the bulk solid volume decreased as the replacement ratio increased. Thus, it was expected that the flow value should decrease. However, due to the minimum limit of the measurement of rheology (cylindrical cone diameter is 50 mm; hence, the minimum limit may be 60–65 mm), the reduction of flow value cannot be detected.

In addition, the flow value increased slightly when the replacement ratio of fly ash UL/BA changed from 75% to 100%. This was because a large amount of fly ash particles contained in the system increased the probable existence of fly ash particles around a fly ash particle, increasing the potential energy barrier.

In the paste without superplasticizer, it could be concluded that when the potential energy barrier was not so high a positive value or showed a negative value (flocculation system), the change in the rheology of fly ash–cement paste was mainly influenced by the physical property of fly ash, namely, the bulk solid volume.

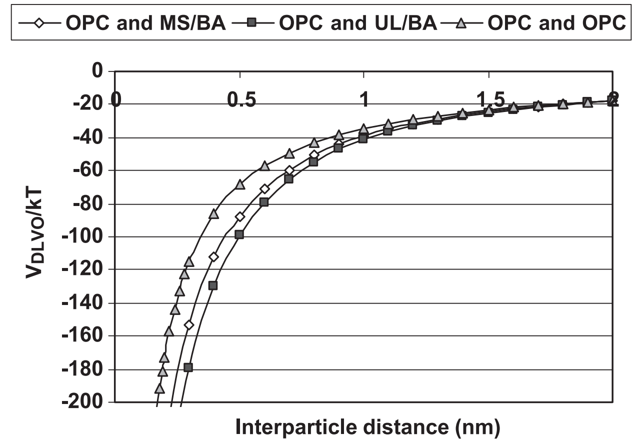

Fig. 3. The potential energy between different kinds of particles in solution without superplasticizer became lower than those between OPC particles and showed a negative value at all interparticle distances.

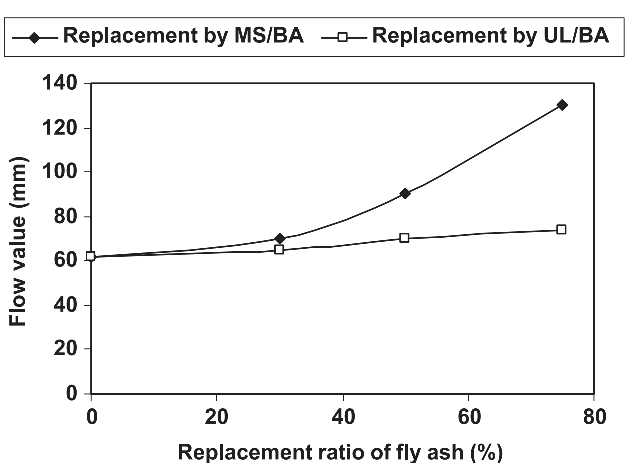

Fig. 2. Change in flow value with replacement ratio of fly ash in the case without superplasticizer. For fly ash MS/BA + OPC paste, the flow value increased with increasing replacement ratio. However, for fly ash UL/BA + OPC paste, the rheology did not increase at any extent of replacement.

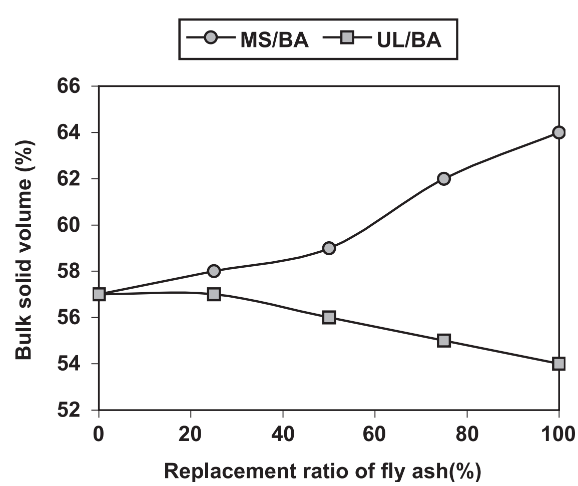

Fig. 4. Change in bulk solid volume with replacement ratio of fly ash. For fly ash MS/BA, the bulk solid volume increased as the replacement ratio increased. For fly ash UL/BA, however, the bulk solid volume decreased as the replacement ratio increased.

4.2. Paste with superplasticizer

4.2.1. Paste with individual powder

Fig. 5 shows the flow value of individual powder at different dosages of superplasticizer. The flow ability of paste with superplasticizer was not consistent with the result of the paste without superplasticizer, as shown in Table 2.

In the case of paste without superplasticizer, the flow value reduced in the following order: fly ash MS/BA>fly ash UL/BA>OPC. On the other hand, the flow value of paste with superplasticizer reduced in the following order: fly ash UL/BA>fly ash MS/BA>OPC.

Table 3 shows the zeta potential of powder in the solution with naphthalene sulfonate superplasticizer. When naphthalene sulfonate superplasticizer was adsorbed to the particle surface, it changed the zeta potential of the particle. From Table 3, the zeta potential value of all powder showed a high negative value, especially fly ash UL/BA (− 63.3 mV). The potential energy between particles having the same surface potential was calculated. The results are shown in Fig. 6. When the superplasticizer was added at 0.30 wt.%, the potential barrier of fly ash UL/BA increased significantly to more than 2000 kT, while that of fly ash MS/BA was about 1000 kT. In this case, the effect from potential energy barrier may become superior to that of bulk solid volume. In other words, dispersing ability of naphthalene sulfonate superplasticizer may become superior to the influence of fly ash properties on the rheology of paste. Consequently, the rheology of fly ash UL/BA paste became better than that of fly ash MS/BA paste.

4.2.2. Fly ash–cement paste

Figs. 7 and 8 show the flow value as a function of replacement ratio of fly ash when superplasticizer was added in the cases of fly ash MS/BA and UL/BA, respectively. From the results, as shown in the figures, the flow value of the paste with fly ash MS/BA improved as the replacement ratio increased at all dosages of superplasticizer. The flow value also improved when the dosage of superplasticizer increased. The relationships between the rheology of paste and the replacement ratio of fly ash at different dosages of superplasticizer are quite parallel.

In Fig. 8, fly ash UL/BA has no effect on the rheology of fly ash–cement paste without superplasticizer. However, it improved flow ability as the replacement ratio increased when superplasticizer was added.

It is recognized that the absolute value of zeta potential enhances as the amount of adsorbed superplasticizer on the surfaces of cementitious particles increases. Figs. 9 and 10 illustrate the amount of adsorption of superplasticizer as a function of the replacement ratio of fly ash. It is expected that the surface area of powder affects the adsorption of superplasticizer as increasing surface area enhances the adsorption of superplasticizer. In this study, to get rid of the effect of surface area on the adsorption of superplasticizer, we normalized the amount of adsorption of superplasticizer by dividing it by the surface area of mixtures of OPC and fly ash. The results show that the amount of adsorption per unit area of fly ash–cement mixture had no significant change even when the replacement ratio of fly ash increased. This can mean that the improvement of rheology of paste when the replacement ratio of fly ash

Table 3
The comparison of average zeta potential in the system with superplasticizer

Kind of powder	Average zeta potential (mV)
OPC	− 28.4
MS/BA	− 48.6
UL/BA	− 63.3

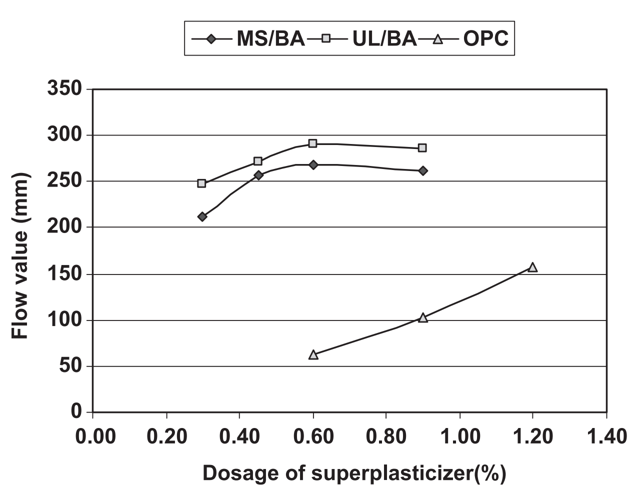

Fig. 5. The flow value of fly ash and OPC paste. The flow value of paste with superplasticizer reduced in the following order: fly ash UL/BA>fly ash MS/BA>OPC.

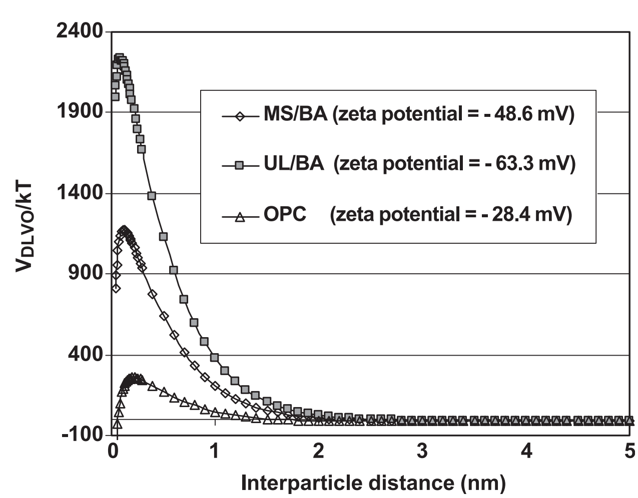

Fig. 6. The potential energy between the same kinds of particles in solution with superplasticizer.

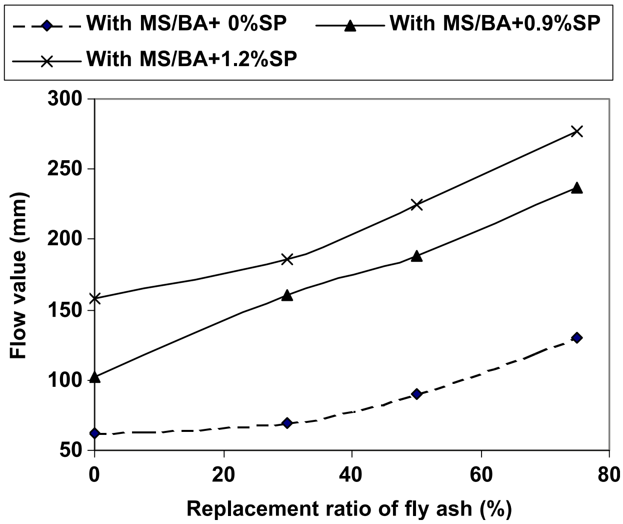

Fig. 7. Change in flow value with replacement ratio of fly ash MS/BA in the case of paste with superplasticizer. The flow value of paste with fly ash MS/BA improved as the replacement ratio increased at all dosages of superplasticizer.

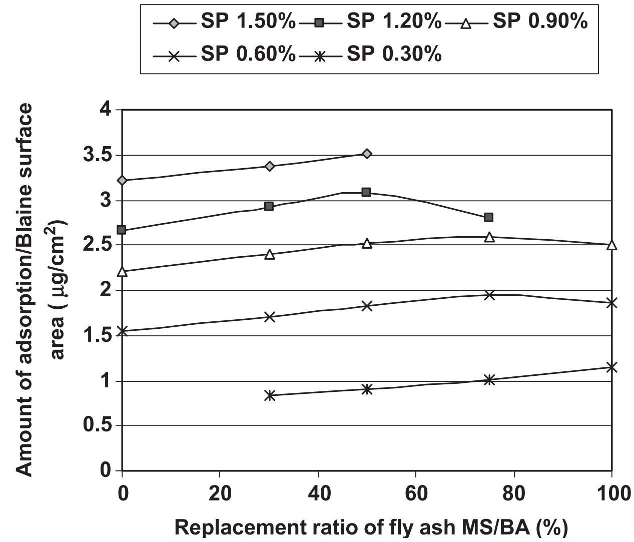

Fig. 9. Change in the amount of adsorption with replacement ratio of fly ash MS/BA.

increased was not due to the increase in the amount of adsorption of superplasticizer. Especially in the case of fly ash UL/BA, even when the bulk solid volume became lower and the amount of adsorption did not increase, the flow value still increased as the replacement ratio of fly ash increased. This leads us to consider the other effects, such as the potential energy barrier caused by the surface potential of particles.

The potential energy curves between cement particle and fly ash particle with the presence of naphthalene sulfonate superplasticizer calculated by the DLVO theory is shown in Fig. 11. This figure indicated that the total potential energy between fly ash and OPC showed the maximum value for both fly ash MS/BA and UL/BA, about 500 and 600 kT, respectively. When the replacement ratio of fly ash increased, the particle with high negative zeta potential also increased. Consequently, the total potential energy of all particles increased, enhancing the flow ability.

With the presence of superplasticizer, fly ash particle and OPC particle have the same sign of surface potential, but the absolute value of zeta potential of OPC particle was lower than that of fly ash particle. Hence, the extent of potential energy barrier between particles in fly ash–cement paste became lower than that of the 100% fly ash paste. However, the extent of potential barrier was still high enough to recognize the paste as a good dispersed system.

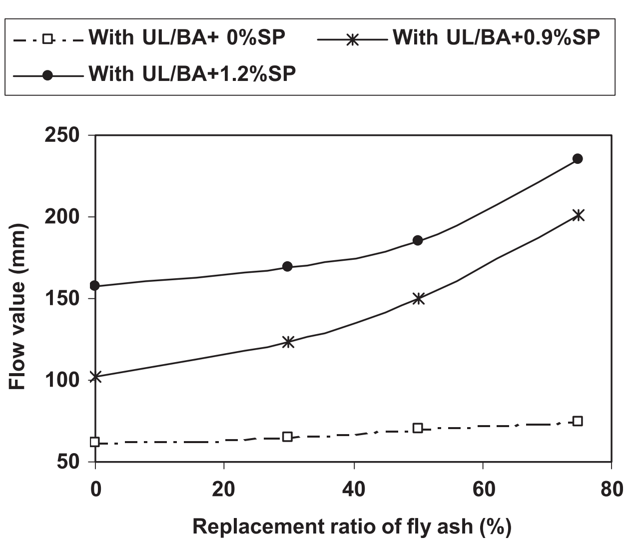

Fig. 8. Change in flow value with replacement ratio of fly ash UL/BA in the case of paste with superplasticizer. Fly ash UL/BA improved flow ability as the replacement ratio increased when superplasticizer was added.

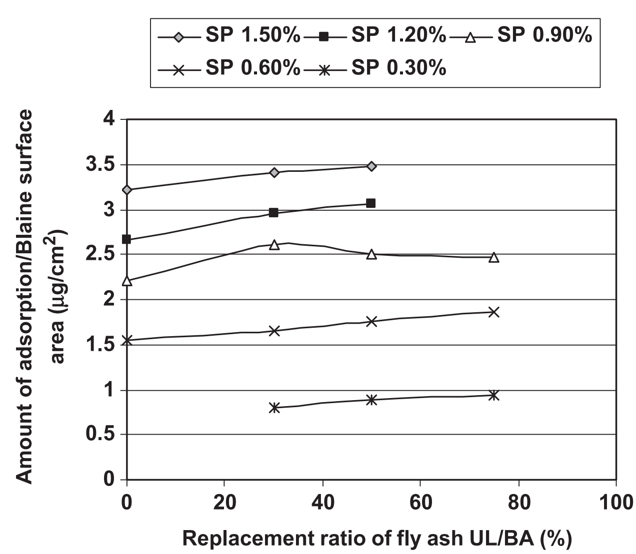

Fig. 10. Change in the amount of adsorption with replacement ratio of fly ash UL/BA.

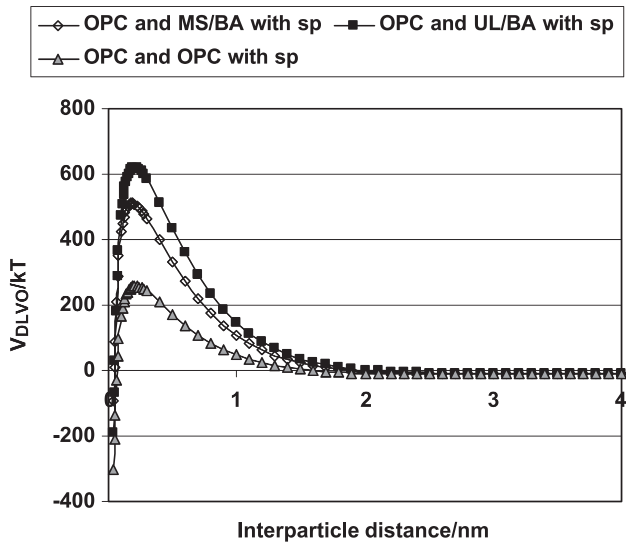

Fig. 11. The potential energy between different kinds of particle in the case with superplasticizer. The total potential energy between fly ash and OPC showed the maximum value for both fly ash MS/BA and UL/BA—about 500 and 600 kT, respectively.

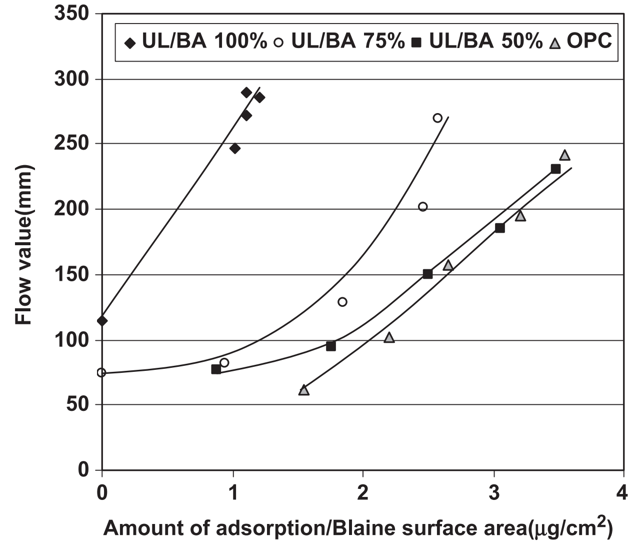

Fig.13. The relation between the amount of adsorption of superplasticizer per Blaine surface area and the flow value at different replacement ratios of fly ash UL/BA. The shift of relationships between the rheology of paste and the amount of adsorption per unit surface area was not proportional to the replacement ratio of fly ash.

Figs. 12 and 13 show the relationship between the flow value and the amount of adsorption per unit area incorporating with fly ash MS/BA and UL/BA, respectively. For fly ash MS/BA + cement paste, the relationships between the rheology of paste and the amount of adsorption per unit surface area at different replacement ratios were quite parallel to each other. In this case, it seems that at least two factors contributed to the improvement of flow ability. One was the increase of bulk solid volume due to an increase in replacement ratio of fly ash; the other was the increase of potential energy due to the increased replacement ratio of fly ash MS/BA and the amount of adsorption of superplasticizer.

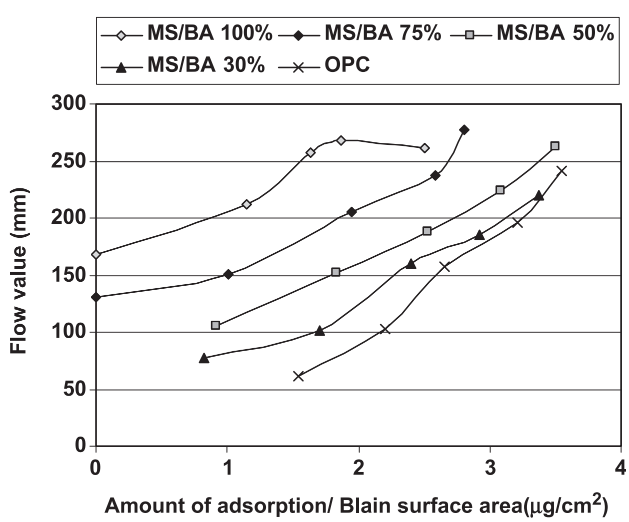

Fig. 12. The relation between the amount of adsorption of superplasticizer per Blaine surface area and the flow value at different replacement ratios of fly ash MS/BA. The relationships between the rheology of paste and the amount of adsorption per unit surface area at different replacement ratios were quite parallel to each other.

In the case of fly ash UL/BA + cement paste, however, the shift of relationships between the rheology of paste and the amount of adsorption per unit surface area was not proportional to the replacement ratio of fly ash. The bulk solid volume of fly ash US/BA was lower than OPC. From these results, it seems that when the replacement ratio was low, the particles in paste tended to flocculate, and the flow ability of paste still depended on the bulk solid volume. On the contrary, when the replacement ratio was higher, the particles in paste might disperse, and the flow ability of paste hardly depended on the bulk solid volume.

From the above discussion, it could be concluded that for paste added with superplasticizer, the change in the rheology of fly ash–cement paste was mainly influenced by the potential energy barrier between particles.

5. Conclusions

Based on the results of this research, we can conclude that the DLVO theory can be used to estimate the flow behavior of the fly ash–cement paste with and without naphthalene sulfonate superplasticizer.

In the fly ash–cement paste without superplasticizer, when the potential energy barrier was not so high a positive value or showed negative value (flocculation system), the change in the rheology of fly ash–cement paste was mainly influenced by the physical property of fly ash, namely, the bulk solid volume.

In the fly ash–cement paste with naphthalene sulfonate superplasticizer, the particles dispersed well due to the electrostatic repulsion. The bulk solid volume of fly ash also affected the change in flow ability, but the flow ability of paste is mainly governed by the potential energy barrier between particles.

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