Characterization of the mesostructural organization of cement particles in fresh cement paste

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Abstract: Comparative study on the mesostructures of fresh cement paste (FCP) in different dispersion mediums was carried out aiming at characterizing the structural organization of cement particles in FCP at a mesoscopic scale and establishing the correlation of mesostructure with rheological properties. For the first time, Morphologi G3 was adopted to *in-situ* characterize the mesostructure of FCP. Several dispersion mediums including air, deionized water, ethanol and an aqueous solution of ethanol were chosen to study the dispersion of cement particles in the selected mediums. Superplasticizers, as dispersing aids for cement particles, were added to change the dispersion of cement particles. Results show that Morphologi G3 with the high sensitivity and the high resolution is a powerful tool for *in-situ* characterization of the mesostructure of FCP by providing high-quality images associated with structural parameters. The structural parameters including particle size, circularity and fractal dimension of particle spatial distribution (Dpd) allow to quantitatively characterize the organization of cement particles in FCP at a mesoscopic scale, through which the relationship between the mesostructure and the rheological behavior of FCP was established. Higher fluidity signifies larger Dpd and circularity but a lower mean particle size. Moreover, the mean particle size and Dpd are more sensitive to indicate the fluidity change.

Key words: Characterization; Mesostructure; Fresh cement paste; Superplasticizers; Rheology

1. Introduction

Workability of cementitious materials has drawn considerable attentions due to its essential role in the construction process as well as the important impacts on the mechanical properties and even the durability of hardened concrete. Extensive research has been carried out on the workability by measuring the rheological properties, viscoelastic properties and thixotropy of fresh cementitious materials [1–3]. From the microscopic point of view, all these macroscopic properties of fresh cementitious mixtures are primarily determined by the microscopic structures, e.g. the packing or dispersion state of cement particles in the suspension systems [4–6]. It has been widely realized that agglomeration of cement particles immediately takes places upon the contact of cement to water, which originates from the minimization of the interfacial energy between cement and the dispersion medium, usually water, and from the basically electrostatic interaction between cement particles [7, 8]. Superplasticizers are practically used to achieve higher fluidity of fresh cement paste (FCP). The working mechanism of superplasticizers is to facilitate the dispersion of cement particles by generating the so-called steric and/or electrostatic repulsion between cement particles [6, 9–11]. Thus, the desired fluidity could be achieved by properly modifying the microstructure of the paste, namely by the enhanced dispersion of cement particles. This stimulated the interest of many researchers to investigate the microstructure of FCP as well as its correlation with the macroscopic rheological properties.

The observation of FCP by microscopes is a direct way to analyze the microstructure of the FCP. Much research has been dedicated to studying the structural organization of cement particles in FCP as well as its time dependent evolution based on microscopy and granulometry techniques [12–19]. Optical and scanning electron microscopes have been frequently used to observe the mesostructure of a diluted FCP focusing on the granular shape and surface as well as the flocculation [12–15]. Analysis of the microscopic images by image processing software enables us to obtain the quantitative information of different granular populations like the shape index, size distribution and so on [15–18]. However, the obtained information is far from being satisfied due to the low resolution and the limited measuring area of a regular microscope. Furthermore, laser granulometry has also been applied in the quantitative analysis of the mesostructure of cement paste [15, 19]. Autier [15] characterized the dispersion state of cement particles by using a morpho-granulometric approach based on the complementarity of scanning electron microscopy and laser granulometry, in which dispersion indices were introduced to characterize the mesostructural variation caused by the inclusion of superplasticizers. However, it was found that the particle size results provided by laser granulometry do not well correspond to the images presented in SEM, i.e., some agglomerates appeared in the particle size distribution curve were not observed in microscopy. Meanwhile, the dispersion indices could be used to identify the influence of the superplasticizers but not the influence of molecular structure. The different influences of the molecular structure were distinguished by an indirect characterization approach of mesostructural organization in term of behavior settling (Phase separation Index) [20]. Wang [21] considered cement paste as a Menger sponge with fractal structure and figured out the fractal dimension of particle size distribution to quantitatively characterize the flocculated structures. But it did not present evident variations when different dosages of superplasticizers were added into the paste. It is supposed that there must miss some vital information in the case of characterizing the microstructure using dispersion indices or particle size fractal dimension.

In spite of some efforts put on this topic, quantitative characterization on the mesostructure of FCP remains a challenge and accordingly the clear correlation of mesostructure with rheological behaviors of FCP has not been established. In this study, Morphologi G3 with high sensitivity and resolution was employed to systematically explore the mesostructure of diluted FCPs with the aim of quantitatively characterizing the structural organization of cement particles in FCP at a mesoscopic scale and establishing the correlation of mesostructure with macroscopic rheological properties.

As the first step, different structural organization of cement particles were identified in reference cement pastes with different dispersion mediums like air, deionized water, ethanol and an aqueous solution of ethanol. Structural parameters including particle size distribution, shape index and fractal dimension of particle spatial distribution were obtained on the basis of tens to hundreds of thousands of particles to characterize the mesostructure of FCP. In addition, two types of superplasticizers were added into the cement pastes to investigate the sensitivity of the selected structural parameters to the change of the dispersion states of the cement particles that is caused by the addition of the superplasticizers. Relying on the three structural parameters, we established the relationship between the mesostructural organization of cement particles in a fresh cement paste and its rheological behavior. This research allows us to have a better understanding of the influence of superplasticizers (amount, type i.e. PCE and NSF) on the rheological behavior of a cement pastes and may provide theoretical guidance for adjusting workability of FCP.

2. Experimental

2.1. Materials and sample preparation

2.1.1. Materials

Reference cement P·I 42.5 with the fineness of 2.3% and the density of 3.10 $g \cdot cm^{-3}$ was used in this study, which was provided by China Building Materials Academy and complies with the Chinese standard GB8076-2008. The composition of the cement is listed in Table 1.

Table 1 Chemical and mineral composition of cement

Chemical composition (wt %)										Mineral composition (wt %)			
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2Oeq	f-CaO	Loss	Cl^-	C_3S	C_2S	C_4AF	C_3A
21.58	4.03	3.46	61.49	2.60	2.83	0.51	0.67	1.97	0.010	57.34	18.90	11.25	6.47

A self-synthesized polycarboxylate (PCE) type superplasticizer with solid content of 40 *wt.*% was employed, which is an aqueous solution of copolymer of acrylic acid, methyl polyethylene glycol methacrylate and 2-acrylamido-2-methylpropane sulfonic acid with number average molecular weight M_n of 3.662×10^4 and polydispersity index M_w/M_n of 2.48. A commercial naphthalene sulfonate formaldehyde (NSF) type superplasticizer was provided by Huadi Synthetic Material Co. Ltd.

Analytical grade of ethanol absolute (>99.7% purity) and deionized water were employed.

2.1.2. Sample preparation and measurements

2.1.2.1. Mesostructure characterization of fresh cement pastes

Microfabric of rock and soil materials usually consists of morphological characteristics, geometric characteristics and energy characteristics, and could be described by some structural factors such as granular morphology, contact relation, orientation and porosity etc [22–24]. Furthermore, a structural feature could be characterized quantitatively by one or several structural parameters. Fresh cement paste is generally considered as a suspension system and its mesostructure may also be characterized by this approach based on several structural parameters. In this study, special attentions were paid to the structural factors including granular morphology, granular agglomerates and the spatial distribution of particles. Three corresponding structural parameters, particle size, granular shape and fractal dimension of particle spatial distribution (Dpd), were extracted from the image analysis to quantitatively characterize the mesostructure of diluted fresh cement paste.

A high sensitivity and high resolution analytical tool Morphologi G3 (Malvern Instruments Limited, Malvern, UK) was employed to characterize the mesostructure of diluted FCP. The instrument captures the image of each particle by scanning the sample underneath the microscope optics, while keeping the particles in focus. Advanced graphing and data classification options in the software ensure that the extracted relevant data concerning the morphological properties for each particle from the measurement is as straightforward as possible, via an intuitive visual interface.

Table 2 Formulation of the diluted cement suspension samples

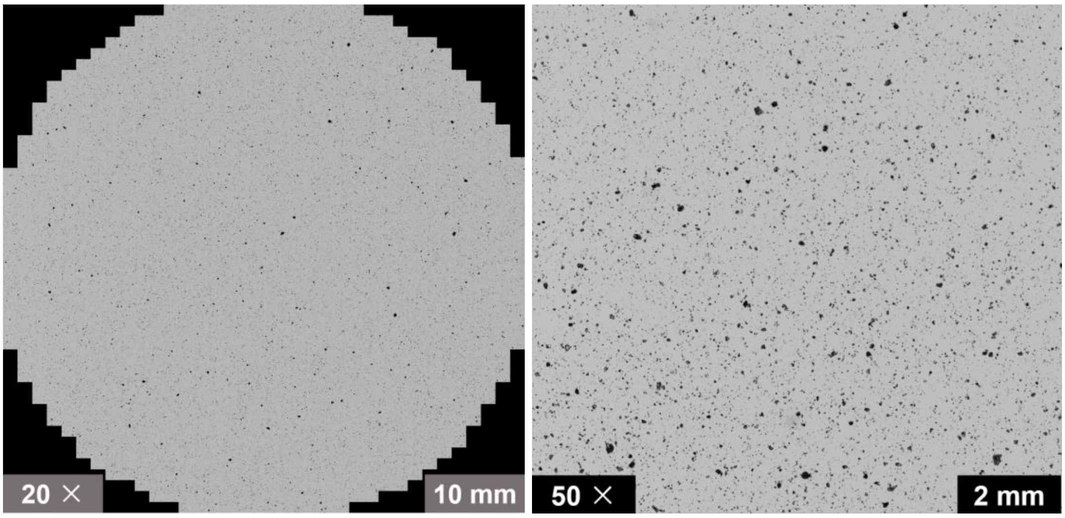
Sample No.	Dispersed phase	Dispersion medium	E/C[a]	W/C[b]	Superplasticizer concentration
C-A	Cement	Air	0	0	0
C-E	Cement	Ethanol	200	0	0
C-W	Cement	Water	0	200	0
C-EW	Cement	Ethanol solution	100	100	0
C-E+C-W	Cement	Ethanol and water	200	200	0
C-W-P0.1	Cement	Water+ PCE superplasticizer	0	200	0.1%
C-W-P0.3	Cement	Water+ PCE superplasticizer	0	200	0.3%
C-W-P0.5	Cement	Water+ PCE superplasticizer	0	200	0.5%
C-W-N0.5	Cement	Water+ NSF superplasticizer	0	200	0.5%

[a] denotes the mass ratio of ethanol to cement.

[b] means the mass ratio of water to cement in C-W, C-EW and C-E+C-W system while indicates the mass ratio of superplasticizer solution to cement in the C-W-P and C-W-N system.

The cement suspension samples with different dispersion mediums were prepared according to the formulations shown in Table 2. 1) C-A system: a small amount of cement powder was dispersed on a stage using an integrated dry powder disperser with an air pressure of 200 and 500 kPa. 2) C-E system or C-W system: cement powder was introduced into deionized water or ethanol with the mass ratio of 1:200, and then was mixed at a speed of 125 rpm for 2 minutes. After a 10 sec interval, mixing was resumed for an additional 2 min at 125 rpm. 3) C-EW system: an aqueous solution of ethanol was prepared with mass ratio of ethanol to water of 1:1 and then cement powder was introduced into the solution with mass ratio of 1:200. They were mixed according to the above procedure. 4) C-E+C-W system: equal mass of C-E mixture and C-W mixture were taken and mixed well. 5) C-W-P system: three aqueous solutions with PCE mass concentration of 0.1%, 0.3% and 0.5% as well as an aqueous solution with NSF mass concentration of 0.5% were prepared, and then cement powder was introduced to the solutions with mass ratio of 1:200 and mixed well.

The well-mixed cement suspension of 2 mL was taken and injected into a wet cell. The dispersed cement powder on the stage as well as the suspension in the wet cell was instantly subjected to observation by Morphologi G3. In the meantime of scanning the particles, the high-quality image of each particle was captured and a 2-dimensional projection using geometrical calculations was performed on these collected images. Finally, apart from a global picture containing all the scanned particles as shown in Fig. 1, the structural parameters, particle size and shape as well as fractal dimension of spatial distribution, were constructed on the basis of the tens to hundreds of thousands of particles. The whole process including sample preparation and analysis by Morphologi G3 lasted for 15 min. That is to say that the effect of cement hydration within such a short period can be neglected in the case of cement and water mixtures.



(a) (b)

Fig. 1 Global images of samples by Morphologi G3

(a) C-A system; (b) C-W-P0.3 system

Cement particles are 3-dimensional objects with irregular shapes, thus they cannot be fully described by a single dimension such as a radius or diameter. In order to simplify the measurement process, the particle size is defined by the diameter of an equivalent circle (CE diameter) having an area the same as the particle image, which is different from the volume diameter measured by a laser granulometry. The particle shape is described by circularity, which is the ratio of the circumference of a circle equal to the projected area to the perimeter of the particle, and is calculated as:

$$\mathrm{C} = \frac{2\times\sqrt{\pi\times Area}}{Perimeter} \quad (1)$$

where Area is the projected area of the particle and perimeter is the perimeter of the particle.

Fractal dimension of particle distribution (Dpd) provides necessary information about the distribution of particles in a 2-dimension image, i.e. the dispersion degree of particles, which is defined based on the statistical analysis theory about mesh simplification on a 2-dimension image.

$$\mathrm{D_{pd}} = -\lim_{\varepsilon \to 0} \frac{\ln N(\varepsilon)}{\ln \epsilon} \quad (2)$$

in which, ε and $N(\varepsilon)$ are respectively the side length of the mesh and the amount of mesh with side length of ε on the particle image. In this case, higher Dpd reflects larger dispersion degree and vice versa.

2.1.2.2. Rheological tests

Mini-cone test is a simple and effective method to get a rough view on the rheological properties of cementitious materials, which is represented by spread diameter. The spread diameter result has been proved to be able to classify different materials in terms of their ability to fill a formwork and is inversely proportional to the yield stress that is one of key rheological parameters of FCP. In this study, a copper cone with top diameter of 36 mm, bottom diameter of 60 mm and height of 60 mm was used.

The samples were prepared in accordance with the formulations in Table 3. The mass solid/solid ratios of superplasticizers to cement varied from 0 to 0.5%. The mass ratio of water to cement in all the cement pastes was fixed at 0.4, in which the water contained in the superplasticizers was included. In the case of ethanol included as dispersion medium, the total mass of water and ethanol was fixed at half of the mass of cement. Dispersion mediums were firstly added into a mixer, and then cement powder was gradually introduced over a time span of 2 min into the mixer at 62 rpm. After a 10 sec interval, mixing was resumed for an additional 2 min at 125 rpm. The well-mixed fresh paste was poured into the cone right away and then, the cone was quickly lifted up. The average value of spread diameters of the FCP in varied dispersion mediums was recorded after the paste stopped flowing. It is noted that a slight bleeding phenomenon happened at Sp/C of 0.5% and hence the bleeding water ring surrounding the paste was excluded in the measurement of spread diameter.

Table 3 Formulation of the cement suspension samples

Sample No.	Dispersed phase	Dispersion Medium	E/C[a]	W/C[b]	Sp/C[c]
C-A	Cement	Air	0	0	0
C-E	Cement	Ethanol	0.4	0	0
C-W	Cement	Water	0	0.4	0
C-EW	Cement	Ethanol solution	0.2	0.2	0
C-E+C-W	Cement	Ethanol and water	0.4	0.4	0
C-W-P0.1	Cement	Water+ PCE superplasticizer	0	0.4	0.1%
C-W-P0.3	Cement	Water+ PCE superplasticizer	0	0.4	0.3%
C-W-P0.5	Cement	Water+ PCE superplasticizer	0	0.4	0.5%
C-W-N0.5	Cement	Water+ NSF superplasticizer	0	0.4	0.5%

[a] The mass ratio of ethanol to cement.

[b] The mass ratio of water to cement.

[c] The mass solid/solid ratios of superplasticizers to cement.

3. Results and discussion

3.1. Characteristics of cement particles in varied dispersion mediums without superplasticizer

3.1.1. C-A system

The cement particles dispersed in air fluid are observed by Morphologi G3 as shown in Fig. 2, in which small particles (S) are the particles with size of 1-10 μm, medium particles (M) indicate the particles of 10-30 μm and large particles (L) denote the particles with size of larger than 30 μm. Separated cement particles with spinous edge as well as a large quantity of loosely agglomerated cement particles are observed. The agglomerations of cement particles are present in two modes: the association of small particles and the adhesion of small particles on large particles, as circled in Fig. 2(a)-2(c). We define the structure of the association of the small particles as S-S structure and the structure of the small particles sticking to the larger ones as L-S structure. It is believed that the intrinsic charges on the cement surface originating from the fracture of valence bond during the grinding procedure of cement clinker are majorly responsible for the existence of agglomerates [25]. Moreover, small particles usually present strong adhesive force (Van der Waals force) because of their huge surface energy, and hence tend to form agglomerates more easily by associating with each other or adhering on the surface of large particle. If the dispersion pressure is increased to 500 kPa, the total amount of agglomerates significantly reduce as shown in Fig. 2(d)-2(f). The particle size distribution of cement particles in air fluid from 1 to 100 μm is shown in Fig. 3, with a mean size of 4.98 μm. The circularity and Dpd of C-A system is 0.91 and 1.84, respectively.

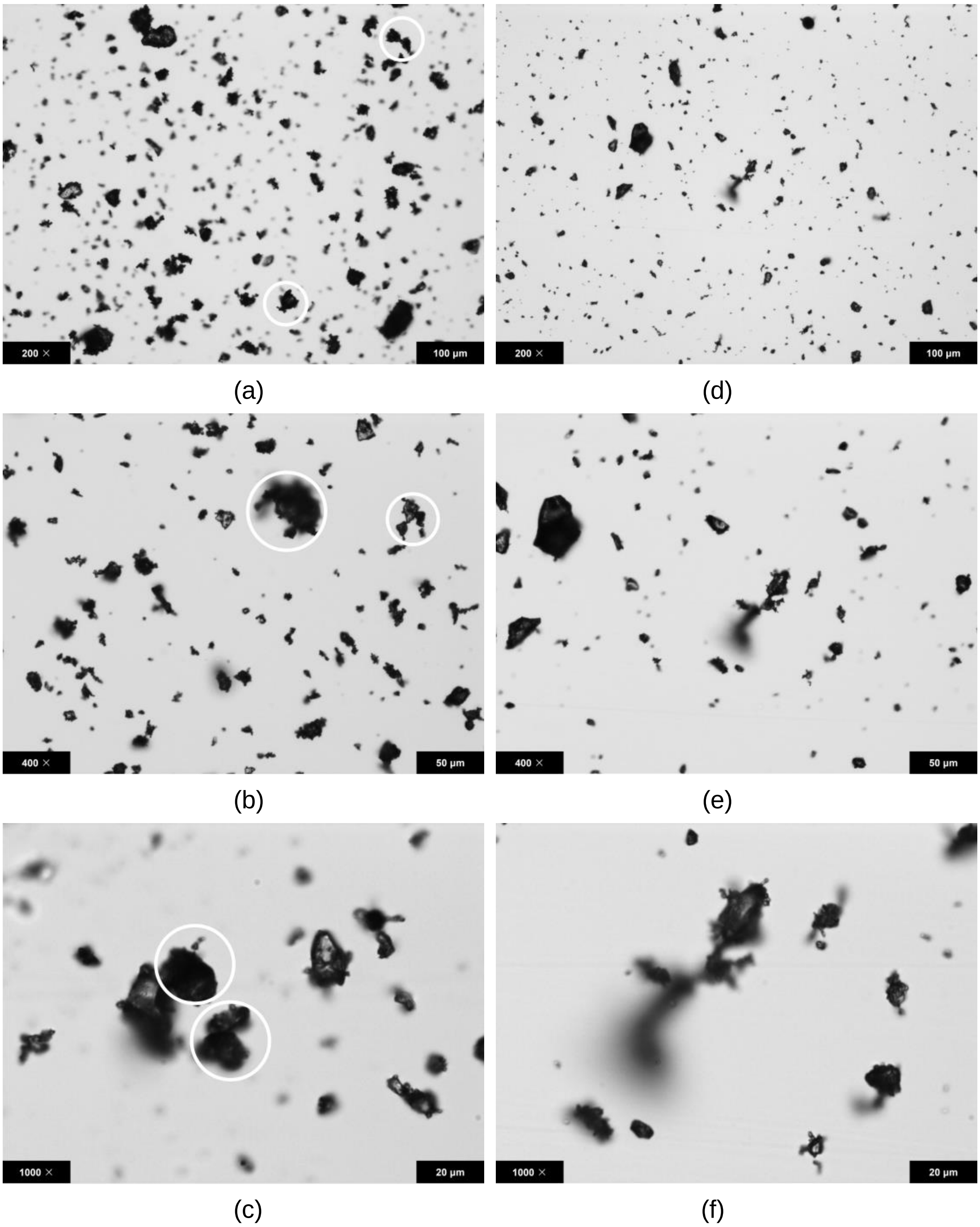


Fig. 2 Images of organization structure of cement particles in C-A system at different dispersed pressures (a)(b)(c) 200 kPa; (d)(e)(f) 500 kPa

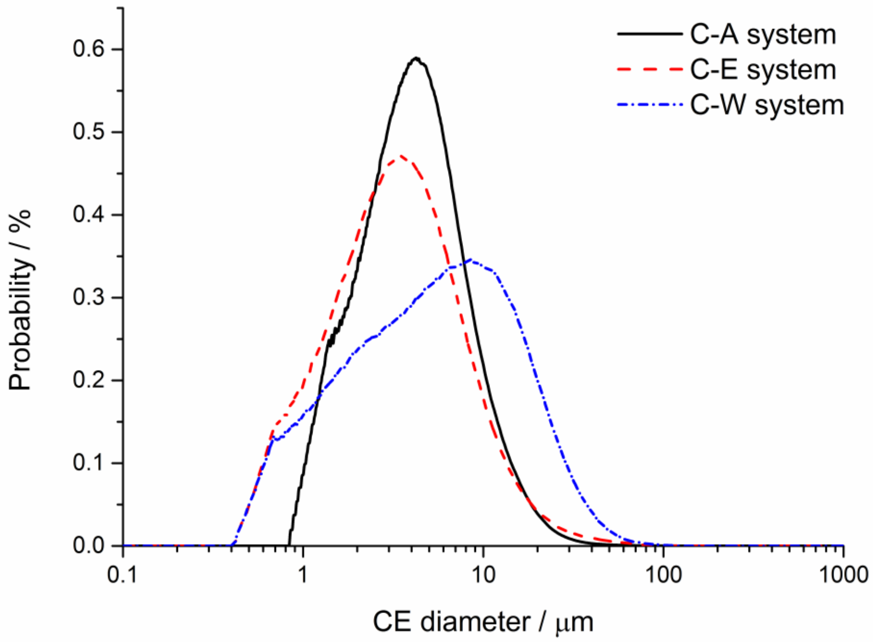


Fig. 3 Particle size distribution of C-A, C-E and C-W systems

3.1.2. C-E and C-W systems

When cement powder is dispersed in ethanol, it has been well-understood that neither dissolution of the mineral phases in cement nor any reaction between cement and ethanol takes place in a short time range [15]. Thus, it can be assumed that the charges properties of cement particles presenting in ethanol should be similar to those of cement dispersed in air. The organization of cement particles in C-E system should be similar to that of C-A system, i.e. the association of small particles (S-S structure) and the adhesion of small particles on large particles (L-S structure). Surprisingly, it is found from Fig. 4(a)-4(c) that the cement particles present majorly individual particles together with a small amount of association structure of L-S structures. That is to say, S-S structures, which abound in C-A system, are rarely observed in C-E system. From this finding, we may propose that the formation of S-S structure is mainly driven by the minimization of surface energy rather than by the electrostatic interaction among particles. This driving force in C-E system is weaker than that in C-A system because the interfacial energy between cement surface and ethanol is lower than that between cement surface and air [26]. As a consequence, the cement particles exhibit better dispersion in ethanol medium than in air. The mean particle size of C-E system is 4.59 μm, which is slightly lower than that of C-A system due to the increased amount of small particles as seen in Fig. 3. The circularity and Dpd of C-E system are 0.83 and 1.87, respectively. These evidence the hypothesis that ethanol behaves as an inert and good dispersion medium for cement particles [15].

On the contrary, once cement comes into contact with water, quick dissolution of mineral phases as well as hydration starts immediately, which produces numerous positive and negative charges on cement surface and hence strong electrostatic interactions among cement particles that is believed to be much stronger than that in C-A or C-E system. The strong electrostatic interaction may cause more intensive association of cement particles. It is noted from Fig. 4(d)-4(f), cement particles of different sizes aggregate together and enwrap much water, as circled in Fig. 4(d) and 4(e). The whole structure with blurry and spinous edge exhibits irregular shape of vesicle and is called flocculated structure, which contains agglomeration of cement particles with full range of size. The association of large particles, L-L structure, which is absent in C-A and C-E systems, is produced mainly by the strong electrostatic interactions among cement particles. That is to say, the dispersion of cement particles in water is much worse than in the mediums of air and ethanol.

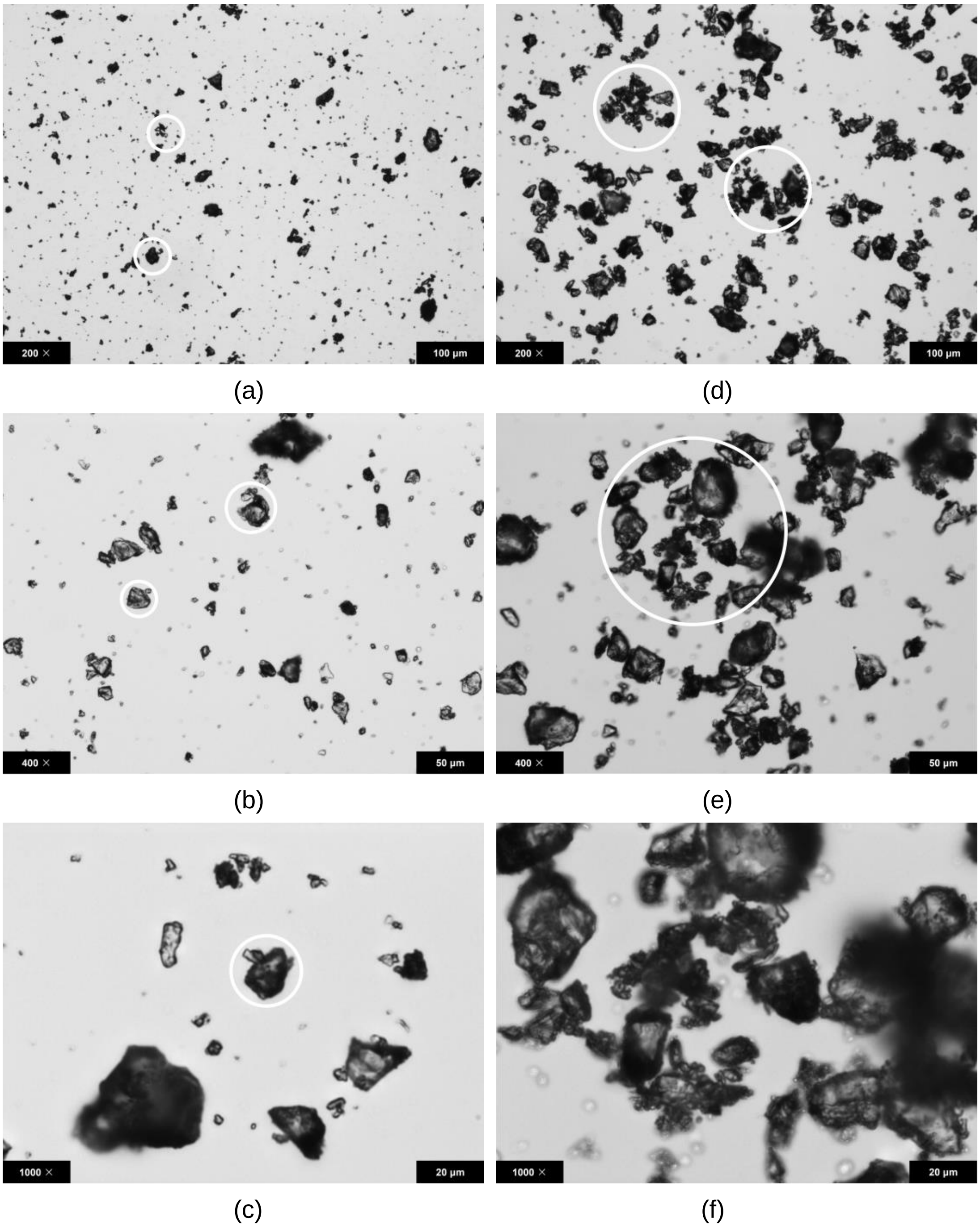
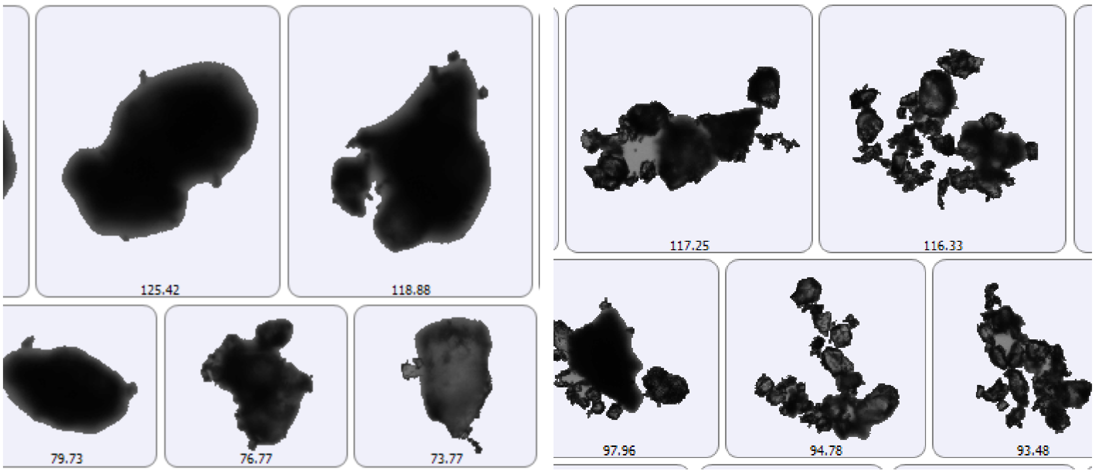


Fig. 4 Images of organization structure of cement particles in C-E system (a)(b)(c)and C-W system (d)(e)(f)

As seen from Fig. 3, the particle size distribution of C-W system evidently differs from those of C-A and C-E systems, in which the amount of the particles with size of larger than 20 μm sharply rises. As a result, the mean particle size of C-W system increases to 8.09 μm. In addition, the Dpd descends to 1.68, which demonstrates the dispersion degree of cement particles in deionized water is very low.

A part of images of large particles captured by Morphologi G3 is exhibited in Fig. 5. The abovementioned differences between C-E and C-W systems in term of granular morphology could be distinctly noticed.

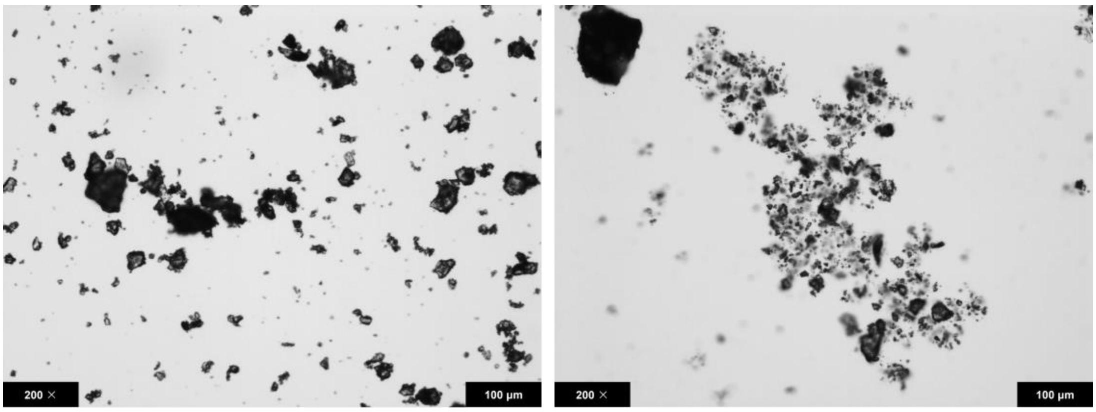


(a) (b)

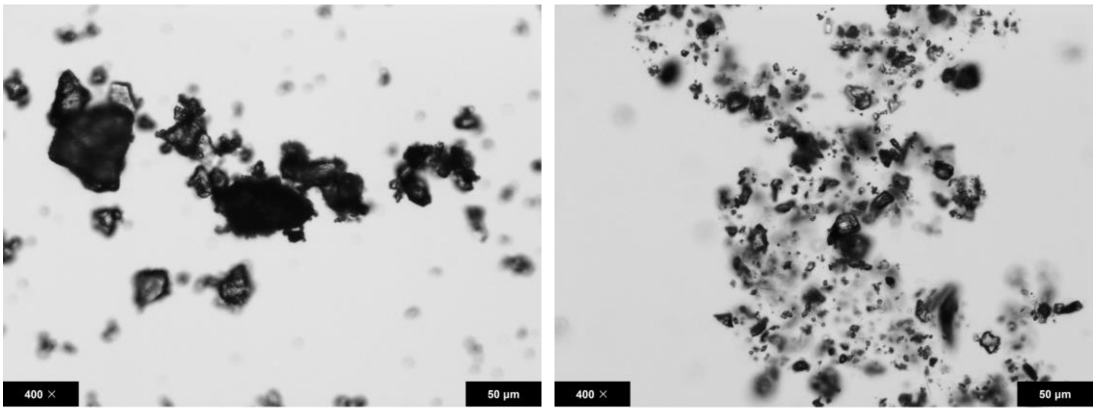
Fig. 5 Typical morphology and CE diameter of particles in C-E system (a) and C-W system (b) (μm)

3.1.3. C-EW and C-E+C-W systems

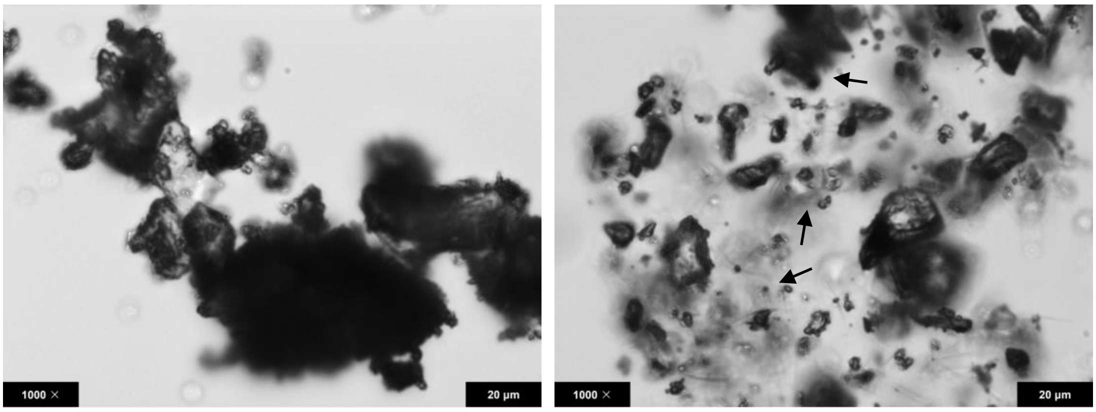
Compared to the case of ethanol as the dispersion medium, when the aqueous solution of ethanol is used as the dispersion medium for cement, it is expected that the water in solution may facilitate the dissolution of mineral phases and hydration of cement, and hence influences the agglomeration of cement particles. The structural organization of cement particles in C-EW system is presented in Fig. 6(a)-6(c). Flocculated structures with larger size than that in both C-W and C-E systems are observed in C-EW system. The severer flocculation in C-EW system than that in C-E system should be caused by the enhanced dissolution of mineral phases and production of hydrates, which certainly produces more charges on surface of cement particles. On the other hand, when we compare the C-EW system with C-W system, the ion strength of the medium in C-EW system must be lower than that in C-W system, because of the less dissolution of mineral phases in C-EW system than in C-W system. We believe that the lowered ion strength of the medium in C-EW system should be responsible for the larger flocculated structures than in C-W system. The mean particle size of C-EW system ascends to 9.40 μm from the 8.09 μm of C-W system and 4.59 μm of C-E system. Meantime, the decreases of circularity and Dpd to 0.80 and 1.51 indicate that the dispersion degree of particles is lowest in the mixture medium.



(a) (d)



(b) (e)



(c) (f)

Fig. 6 Images of organization structure of cement particles in C-EW system (a)(b)(c) and C-E+C-W system (d)(e)(f)

Different from being dispersed in the new type dispersion medium of ethanol solution (C-EW system), cement particles may form a distinctive structural organization if C-W system containing flocculated structures is mixed with C-E system with large amount of individual particles. By mixing the C-W system and C-E system with the mass ratio of 1:1, C-E+C-W system was obtained, whose mesostructure is displayed in Fig. 6(d)-6(f). A unique woolly cloudlike aggregation is observed in C-E+C-W system. Specifically, the aggregation structure contains two parts, the main body that is formed by a variety of flocculated particles and a covering layer of individual tiny particles, respectively corresponding to the typical structures in C-W system and C-E system. That is to say, the organization of cement particles in C-E+C-W system is simply a mixture of that in C-E system and C-W system whereas cement particles in ethanol solution (C-EW system) form flocculated structures with larger size than that in both C-W and C-E systems. The difference between the morphologies of C-EW and C-E+C-W systems may be associated with the changes in the zeta potential of cement particles in different dispersion mediums. In the particle size distribution curve of C-E+C-W system (Fig. 7), large particles with size of 30~300 μm are found. Consequently, the mean particle size increases to 10.12 μm and Dpd decreases to 1.51 due to the appearance of aggregations, indicating a bad dispersion state of cement particles in C-E+C-W system.

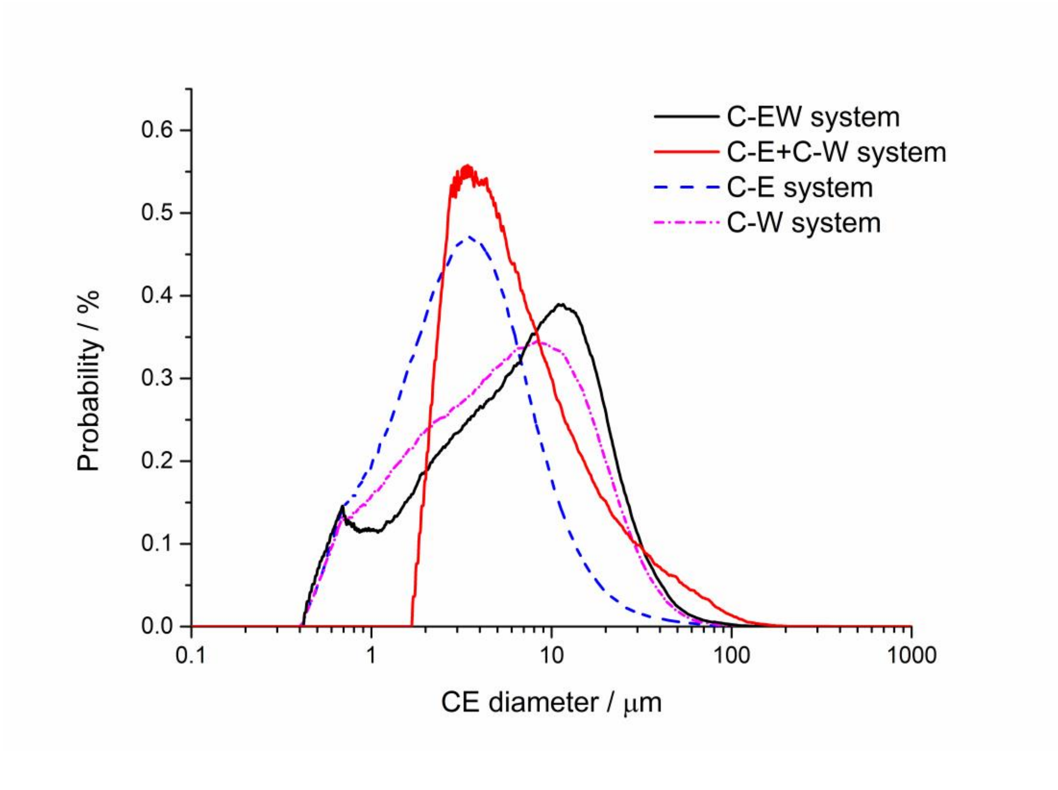
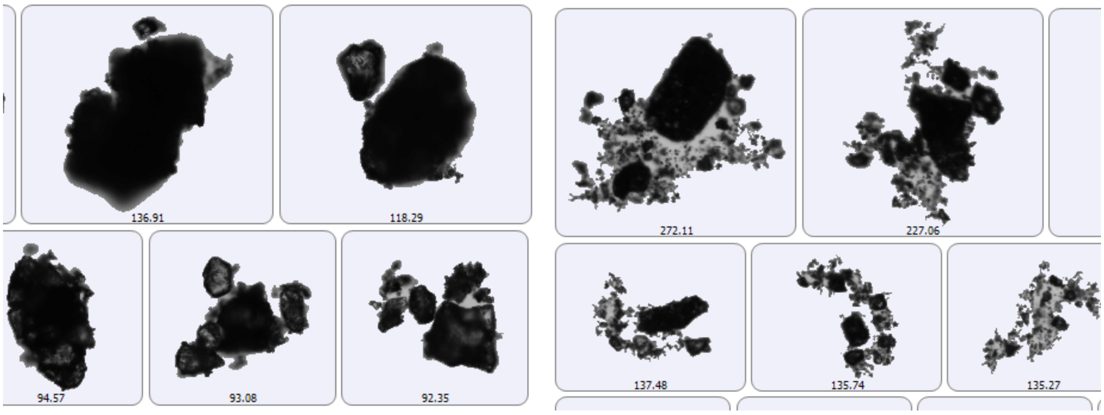


Fig. 7 Comparisons of particle size distribution of C-EW, C-E+C-W, C-E and C-W systems

Figure 8 provides some typical images of large particles in C-EW and C-E+C-W systems extracted by the image analytical software, in which the grey particles are supposed to be the adsorbed water and the entrapped water while the black ones are the cement particles. The significant variations on the granular morphology of the two systems could be clearly seen.



(a) (b)

Fig. 8 Typical morphology and CE diameter of particles in C-EW system (a) and C-E+C-W system (b) (μm)

In summary, the results presented above indicate that this analytical approach using Morphologi G3 is a suitable technique to identify and differentiate the varied mesostructural organization of cement particles in different dispersion mediums in term of particle size, granular shape and fractal dimension of spatial distribution. It has been observed that S-S structure and L-S structure are the main dispersed phases in C-A system due to the huge surface energy of small particles and the existence of instinct charges on cement surface. Ethanol, an inert and good dispersion medium, enables cement particles to present majorly individual particles and a small amount of L-S structures. There is a large quantity of flocculated structures in C-W system caused by the strong electrostatic interactions among cement particles stemming from the dissolution of mineral phases and initial hydration of cement. Flocculated structures with larger size are observed in C-EW system, while in the case of C-E+C-W system, a unique woolly cloudlike association agglomeration structure is observed. Based on the three structural parameters, it is found that the dispersion degree of cement particles in these mediums is in the order of C-E > C-A > C-W > C-EW > C-E+C-W.

3.2. Influences of superplasticizers on mesostructure of FCP

It has been well accepted that the addition of superplasticizers in cement pastes destroys the flocculated structure of cement particles in cement pastes and thus leads to enhanced dispersion of cement particles, due to the generation of electrostatic repulsion and/or steric hindrance between cement particles [9, 10]. It is possible to visualize and quantify the influences of the superplasticizer on the mesostructure of cement pastes by comparing the granular images and the structural parameters of the cement pastes containing superplasticizer with those of the reference cement paste, in which a great number of flocculated structures are observed with the mean particle size of 8.09 μm and the Dpd of 1.68 as water is used as the dispersion medium. Indeed, the incorporation of superplasticizer causes a significant change on the granular morphology, agglomerates and the spatial distribution as shown in Fig. 9-10.

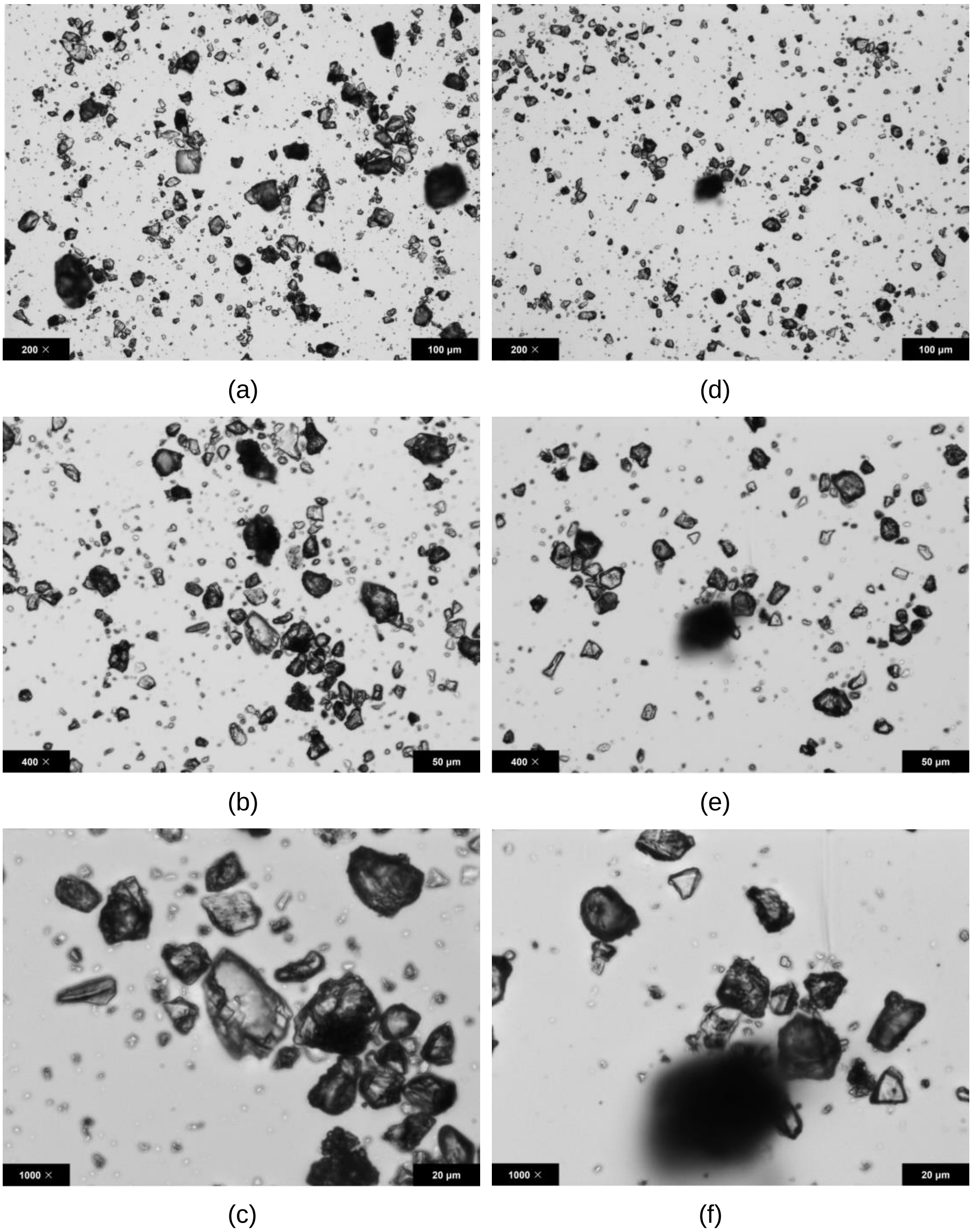


Fig. 9 Images of organization structure of cement particles in C-W-P0.1 system (a)(b)(c) and C-W-P0.3 system (d)(e)(f)

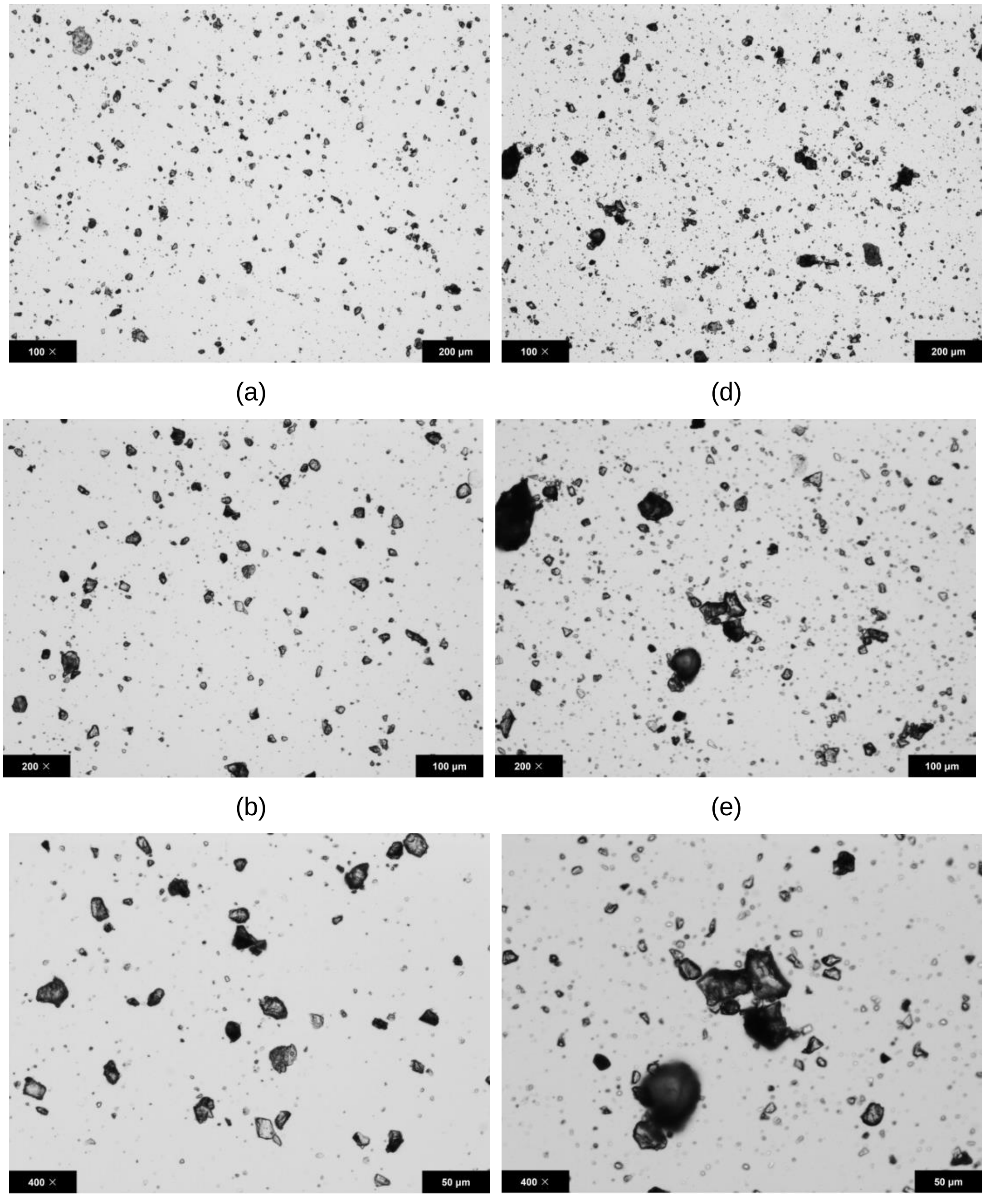


Fig. 10 Images of organization structure of cement particles in C-W-P0.5 system (a)(b)(c) and C-W-N0.5 system (d)(e)(f)

Most of the cement particles with clear edges and hard corners, associated with some flocculated structures, are well dispersed under the influence of the superplasticizer. The structural organization of cement particles depends on the superplasticizer amount and type. Higher superplasticizer dosage brings about flocculated structures with smaller size and evidently reduces their amounts in the meantime. In the dispersion medium of aqueous solution with PCE mass concentration of 0.5%, polygon crystals are present in greater numbers and small flocculated structures almost disappear, as shown in Fig. 10(a)-10(c). On the other hand, in the aqueous solution with NSF mass concentration of 0.5%, small flocculated structures are always visible regardless of the dosage of NSF, which may stem from the different dispersion capability of PCE and NSF. It has been well documented that the dispersing capability of PCE is stronger than that of NSF, and hence PCE allows much better dispersion of cement particles in aqueous medium [1, 27] at the same dosage. Limited by the dispersion capability, NSF is less effective to disassemble the strongly bonded flocculated structures.

On the basis of the granular characteristics shown in Fig. 9-10, the flocculated structures could be roughly sorted into three groups (classes) according to the level of difficulty to be disassembled, which are denoted cluster I, II, and III from small to large order. Factually, the division of the flocculated structures is closely dependent on the bonding forces between particles. It is seen from the micrograph that the cement particles are mainly composed by small particles of 1-10 μm (S), medium particles of 10-30 μm (M) and large particles of 30-100 μm (L), in which small particles tend to agglomerate together to form S-S structure due to their huge specific surface energy and could be broken apart easily in the presence of a low dosage of superplasticizer, namely cluster I structure. On the contrary, large particles with strong electrostatic interactions form L-L structure and are hard to be dispersed, i.e., cluster III structure. The rest of particles constitutes S-M-L structure corresponding to cluster II structure, as shown in Fig. 11. Obviously, the interaction forces between the particles are in the order of $F_{S\text{-}S} < F_{S\text{-}M\text{-}L} < F_{L\text{-}L}$. Thus, superplasticizers are able to disassemble different flocculated structures depending on their types and dosages, thereby presenting distinct plasticizing effects. Superplasticizers with stronger dispersing capability facilitate the disassembly of more strongly bonded flocculated structures, thereby increasing the flowability of FCP more significantly.

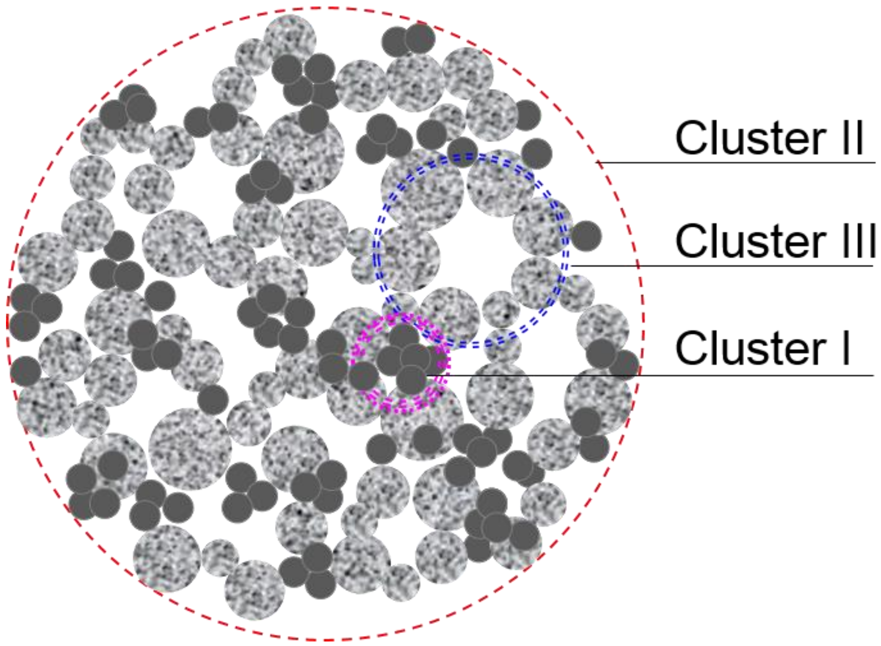


Fig. 11 Schematic illustration of flocculated structure of cement particles

From a quantitative point of view, the variations of the three structural parameters reflect the influence of superplasticizers on the mesostructure of fresh cement paste. The particle size distribution curves of the cement pastes containing different superplasticizers are presented in Fig. 12. It is noticed that the incorporation of superplasticizers leads to a notable left shifting of particle size distribution due to the decrease in the amount of large particles and the marked increase in small particles content. In such way, with the increase of superplasticizer concentration, the mean particle size decreases to 2.99 μm in C-W-P0.5 system from the 8.09 μm of C-W system while the circularity and Dpd rise to 0.89 and 1.94 from the original 0.83 and 1.68 in C-W system respectively, suggesting the superior dispersion state of cement particles in the aqueous medium with PCE superplasticizer. In comparison, C-W-N0.5 system displays a relatively inferior dispersion state indicated by the mean particle size of 3.71 μm and the Dpd of 1.86.

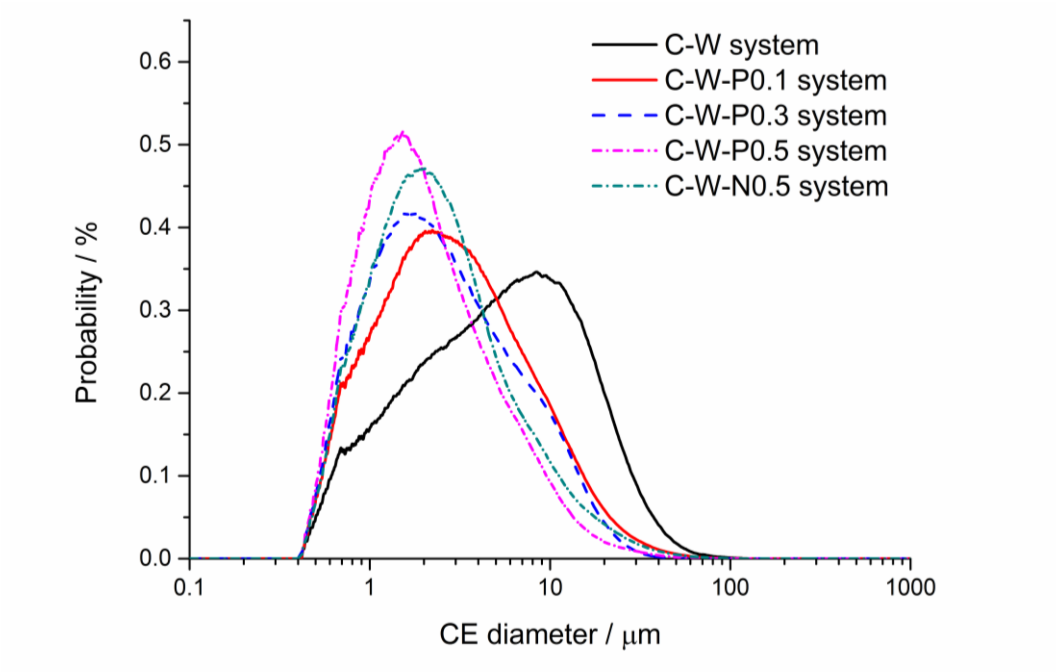
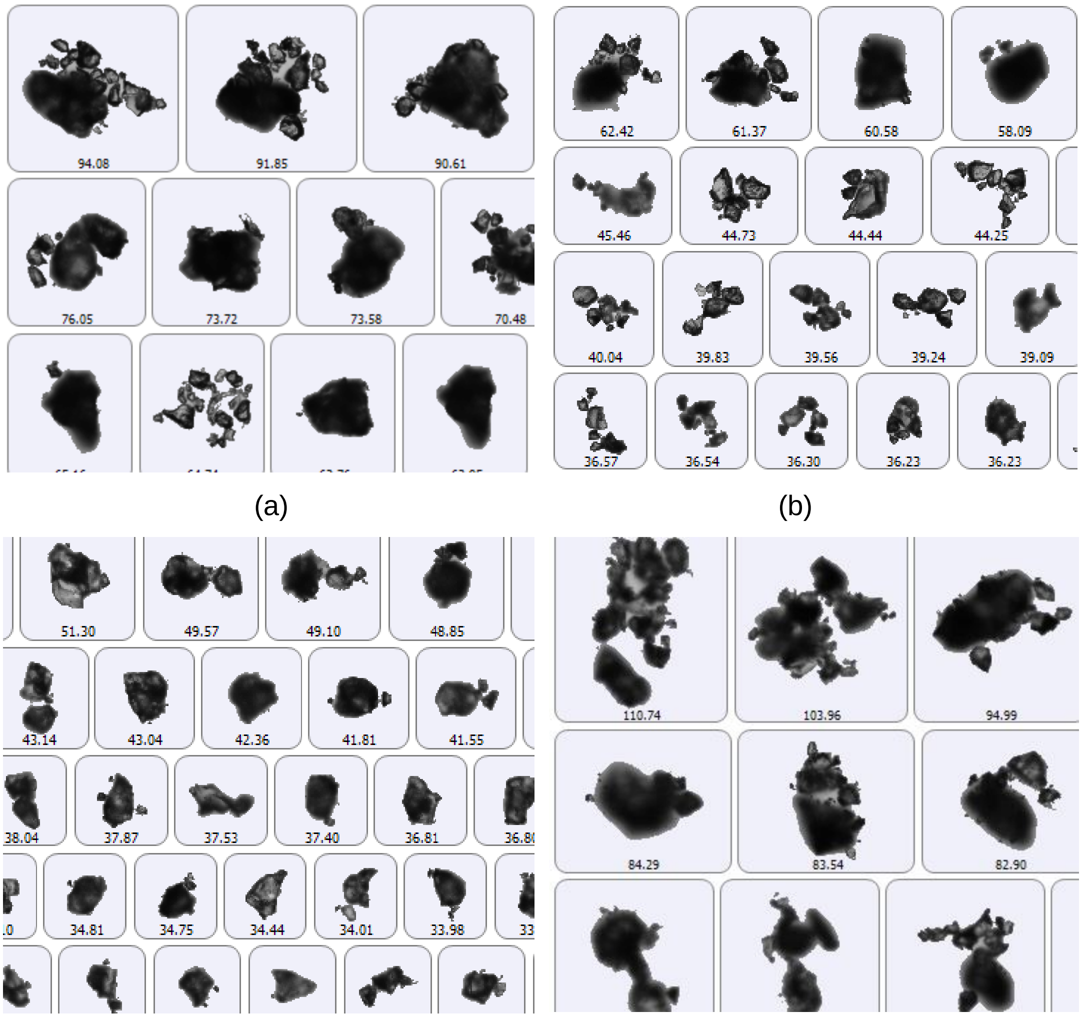


Fig. 12 The influence of superplasticizers on the particle size distribution of fresh cement pastes

Similarly, some typical images of large particles in C-W-P and C-W-N systems are presented in Fig. 13, where the significant variations of the structural organization depending on the types and concentrations of superplasticizers could be apparently observed. The high-quality images associated with the variations in particle size and shape as well as spatial distribution provide straightforward information on the mesostructure of FCP, which is essential for understanding the working mechanism of superplasticizers.



(a) (b)

(c) (d)

Fig. 13 Typical morphology and CE diameter of particles in C-W-P and C-W-N systems (μm) (a) C-W-P0.1 system; (b) C-W-P0.3 system; (c) C-W-P0.5 system; (d) C-W-N0.5 system

3.3. Correlation of mesostructure with rheological behavior

The rheological behaviors of fresh cement pastes are usually characterized by the spread diameter according to the fluidity test [27, 28]. By comparing the fluidity curve of FCPs with the curves of the three structural parameters corresponding to different suspension systems, (Fig. 14), it is interesting to see that the curves of Dpd and circularity behave in much the same way as the fluidity curve. Contrary to them, the mean particle size curve shows an inverted variation trend to the fluidity curve. That is to say, higher fluidity corresponds to larger Dpd and circularity as well as a lower mean particle size. Moreover, mean particle size and Dpd are more sensitive to indicate the change of the fluidity of FCP.

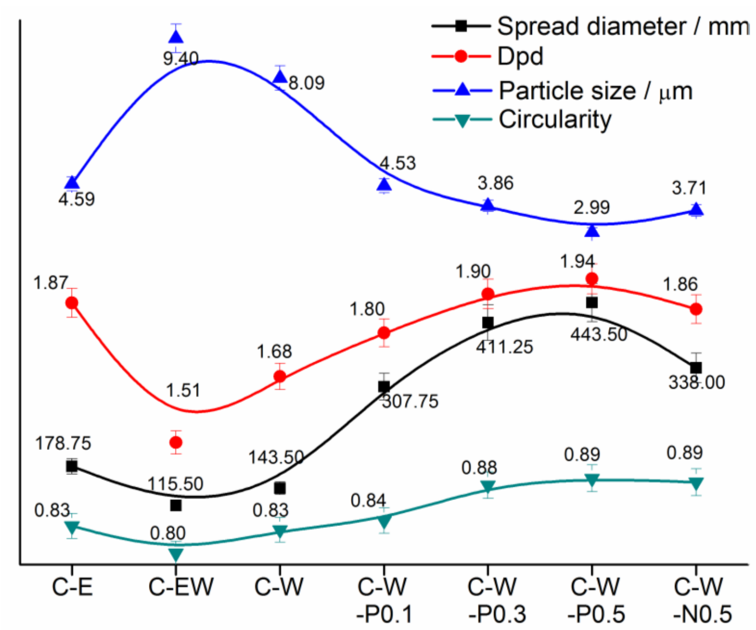


Fig. 14 The variations of fluidity and structural parameters of fresh cement paste in different dispersion mediums

The comparison between the structural parameters and the fluidity of the FCP in varied mediums allows a better understanding of the real granular morphology in varied dispersion mediums and the influences of superplasticizers on the dispersion state of cement particles, and thus the mesostructural organization of cement particles in the pastes. In this way, the connection between the mesostructure and the macroscopic rheological properties is established through the structural parameters.

4. Conclusions

In this paper, for the first time, comparative study on the mesostructure of diluted FCPs with different dispersion mediums was carried out using Morphologi G3 with the aim of characterizing the organization of cement particles in the FCP at a mesoscopic scale and establishing the correlation of mesostructure with macroscopic rheological properties. On the basis of the results above, the following conclusions can be drawn:

(1) Morphologi G3 with high sensitivity and high resolution is a powerful tool to identify and differentiate the structural organization of cement particles dispersed in different mediums by providing high-quality images associated with structural parameters. Three structural parameters including particle size, granular shape and fractal dimension of particle spatial distribution (Dpd) allow to quantitatively characterize the organization of cement particles in fresh cement pastes at a mesoscopic scale.

(2) The association of the small particles (S-S structure) and the agglomeration of the small particles sticking to the larger ones (L-S structure) are the main dispersed phases in C-A system. Cement particles present majorly individual particles and a small amount of L-S structures in C-E system. There is a large quantity of flocculated structures in C-W

system caused by the quick dissolution of mineral phases as well as hydration. Flocculated structures with larger size are observed in C-EW system while in the case of C-E+C-W system, a unique woolly cloudlike association agglomeration structure is observed. Based on the three structural parameters, it is found that the dispersion degree of cement particles in these mediums is in the order of C-E > C-A > C-W > C-EW > C-E+C-W.

(3) In the presence of superplasticizer, most of the cement particles with clear edges and hard corners, associated with some flocculated structures, are well dispersed. With the increase of superplasticizer concentration, the mean particle size decreases while both of the circularity and Dpd rise. According to the level of difficulty to be disassembled, the flocculated structures were roughly sorted into three classes from small to large order, i.e., cluster I, II, and III, corresponding to S-S structure, L-M-S structure and L-L structure respectively.

(4) The relationship between the mesostructural organization of cement particles in a fresh cement paste and its rheological behavior is established by employment of the three structural parameters. Higher fluidity corresponds to larger Dpd and circularity as well as a lower mean particle size. Moreover, the mean particle size and Dpd are more sensitive to indicate the change of the fluidity of fresh cement paste.

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