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Study on Microstructure Characteristics of Fresh Cement Paste

Yijie Zhang[1,2], Yanfeng Zuo[2,3*], Chongzhi Li[1], Hao Sun[1], Guolin Ye[1]

[1]Beijing University of Civil Engineering and Architecture, School of Civil and Traffic Engineering, 10261 Beijing, China

[2]Key Laboratory of Building Damage Mechanism and Defense, China Earthquake Administration,065201 Langfang,China

[3]Institute of Disaster Prevention, School of Civil Engineering, 065201 Langfang, China

*Corresponding author: 34014713@qq.com

Abstract: In this paper, RST rheometer is used to test the rheological characteristics of fresh cement paste under different water-cement ratio and different shear rate, and quantitatively calculate the area of hysteresis loop and the destruction energy of flocculation structure.The microstructure of cement paste with different water-cement ratio was observed by Ultra depth of field optical microscope, and the microstructure pictures were processed by Image-J software,then quantify the quantity and size of cement congeries.It is found that the destruction energy of flocculation structure can quantitatively characterize the destruction degree of flocculation structure.Under the condition of the same shear rate, the larger the water-cement ratio, the smaller the hysteresis loop area, the smaller the destruction energy of flocculation structure, the increase of the number of aggregates in cement paste, the enhancement of dispersion and the reduction of aggregate size.The attachment strength of aggregates in cement paste is weakened, and the flocculation structure is more easily damaged.Under the same water-cement ratio, the smaller the shear rate, the smaller the destruction energy and the lower the destruction degree of flocculation structure.With the increase of shear rate, the destruction energy of flocculation structure increases.

1. Introduction

Concrete materials are widely used in industrial and civil buildings, bridges, underground tunnels and other construction fields.With the continuous improvement of social demand, higher demands are put forward for the workability, mechanical properties, durability, production efficiency, environmental protection and economy of concrete.The fluidity of concrete with large flow state is good, which can effectively improve the constructability and filling performance of concrete.It has good mechanical properties and durability after hardening of concrete with large flow state.In concrete, cement paste plays a role in lubrication and bonding, which directly affects the workability of concrete.During construction, water reducing agent is usually used to improve the fluidity of concrete.It is generally believed that water reducing agent molecules destroy the flocculation structure of cement paste through adsorption-dispersion mechanism.Free water wrapped in the flocculation structure is released, thereby improving the fluidity of concrete.It can be seen that the flocculation structure of fresh cement paste is the receptor of water reducing agent's dispersing power.Therefore, the structural characteristics of fresh cement paste are of great significance to the workability of concrete, and are also of positive significance to deeply understand the dispersion mechanism of water reducing agent.People have also studied the structural characteristics of fresh cement paste.

Fresh cement paste is a solid-liquid suspension dispersion system with plasticity, fluidity and thixotropy.At the initial stage of cement hydration, cement particles and cement hydration particles have larger surface energy, and the bonding force between cement particles is mainly van der Waals force, supplemented by electrostatic attraction of positive and negative charges on the surfaces of C_3A, C_3S and C_2S particles.A flocculating structure[1]enclosing part of the free water is formed.Power[2]thinks that the flocculation structure and size in cement paste are single, but after a lot of tests, Zuo Yanfeng, Zhang Weili[3-4]and others think that the cement paste is composed of multi-stage flocculation structure, and the aggregates in cement paste have different sizes and irregular shapes.The change of flocculation structure in fresh cement paste can be measured by the macroscopic properties of cement paste, but the macroscopic properties are determined by the internal structure.Therefore, it is necessary to study flocculation structure from microscopic level or even microscopic level.

Helmuth[5]established a model of freshly mixed cement slurry.He thought that water adsorbed on the surface of cement particles formed a water film, and the thickness of the water film tended to be uniform when the cement slurry was stirred or water reducing agent was added into the cement slurry.Tattersall[6]thinks that after mixing cement with water.The resultant hydrate film coats cement particle aggregates.In the rheological research of cement paste, the influence of external factors on the destruction difficulty of flocculation structure is usually represented by the area of hysteresis loop.The smaller the area of hysteresis loop, the easier it is to destroy flocculation structure[7], but the hysteresis loop has some arbitrariness.The change of shear rate and shear time will change the area of hysteresis loop[8-9]The area of hysteresis loop will change with the change of shear time and shear rate, which has certain randomness.Therefore, the destruction energy of flocculation structure can be obtained by calculating the work done by shear friction on cement paste,The destruction degree of flocculation structure can be characterized more accurately by the destruction of flocculation structure.

In this paper, RST rheometer is used to test the rheological parameters of cement paste with different water-cement ratio, including shear rate, shear stress, viscosity and shear action time.By calculating the area of "hysteresis loop" and the destruction of flocculation structure under different water-cement ratios, the destruction degree of flocculation structure of cement paste can be characterized.Ultra-depth-of-field optical microscope was used to observe the internal microstructure of fresh cement paste with different water-cement ratios[10]ImageJ software was used to quantitatively analyze the number of aggregates and projection area[11]It is found that with the increase of water-cement ratio, the dispersion of flocculation structure in fresh cement paste increases and its stability decreases.At the same rotating speed,The energy needed to destroy the flocculation structure is reduced, the connection strength of the flocculation structure in cement paste is weakened, and the flocculation structure is more easily destroyed.Through this study, the change law of internal flocculation structure of fresh cement paste with the change of water cement ratio was revealed.

2. Raw materials and test methods

2.1. Raw materials

The cement adopts the special reference cement for testing the performance of concrete admixture, and its chemical composition and mineral composition are shown in Table 1, and the physical properties of cement are shown in Table 2,Figure 1 shows the particle size distribution of cement particles.

Table 1 Chemical composition and mineral composition of cement clinker.

SiO_2	Fe_2O_3	Al_2O_3	SO_3	MgO	CaO	Na_2O_{eq}	f-CaO	Cl^-	IL	C_3S	C_2S	C_4AF	C_3A
21.56	2.78	4.44	3.14	2.32	62.83	0.60	0.79	0.007	2.04	46.00	27.14	8.45	7.05

Table 2 Physical Properties of Benchmark Cement.

Fineness/(0.08/%)	Specific surface area /(m^2/kg)	Density /(g/cm^3)	Standard consistency/(%)	Average particle size/(μm)
0.4	350	3.12	24.40	24

2.2. Sample preparation

According to the method specified in 13.3 of Test Methods for Uniformity of Concrete Admixtures (GB8077-2012), the fresh cement paste is prepared with water-cement ratio of 0.35, 0.45 and 0.55 respectively.

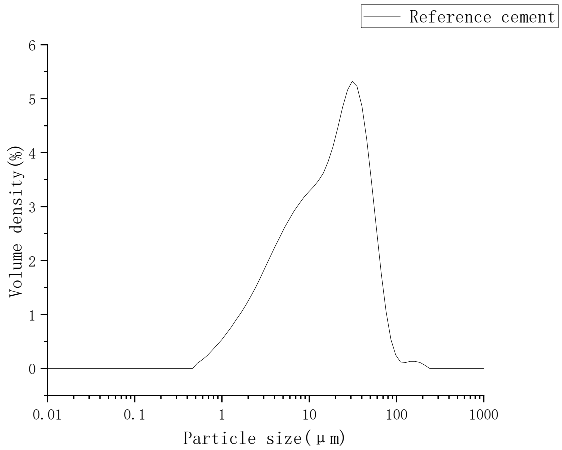


Figure 1 Distribution of cement particle size.

2.3. Test method

2.3.1 Rheological experiment

(1) Area of hysteresis loop

Weigh 60ml of fresh cement paste into a sample cup (provided with RST rheometer), and use RST rheometer (Bolefei Company, USA) and CC3-40 rotor to carry out rheological test on the cement paste.When testing the rising curve of hysteresis loop, set the initial shear rate as 0s-1, the end shear rate as 150s-1, and the test time as 150sWhen testing the falling curve of hysteresis loop, set the initial shear rate to 150s-1.The end shear rate is 0-1and the test time is 150s .The hysteresis loop is drawn with X axis as shear rate and Y axis as shear stress plot function in Matlab software is used to fit up curve L_{up} and down curve L_{down}, and formula (1) is used to calculate the area S of hysteresis loop in Pa·s.

$$S=\int_0^{150}(L_{up}-L_{down})\mathrm{dx} \tag{1}$$

(2) Destruction energy of flocculation structure

In the constant shear rate rheological test, the rotor exerts shear friction on the cement paste, and the flocculation structure in the cement paste is destroyed due to the continuous action of shear friction.Therefore, in the process of destruction of flocculation structure in cement paste, the work done by the shear friction force of the rotor due to shear action can be indirectly expressed as flocculation structure destruction energy E.

Weigh 60ml of fresh cement paste into FTK-RST sample cup of RST rheometer, and use CC3-40 rotor to carry out rheological test on cement paste.Test the work done by shear friction on fresh cement paste, and set the shear rate to be 40s-1, 60s-1, 80s-1, and the test time to be 150s.

Using formulas (2)-(5),the power of shear friction is calculated.

$$F_f=\tau\cdot 2\pi R\cdot L \tag{2}$$

In formula (2), F_f is the shear friction force (N) caused by the rotor's shearing action on cement paste, τ is the shear stress (Pa),R is the radius of the inner barrel of FTK-RST sample cup, R is 2.5cm, and L is the height of cement paste after pouring into FTK-RST sample cup, L is 13cm.

$$M=\tau\cdot 2\pi R\cdot L\cdot R \tag{3}$$

In formula (3), M is torque (N/m).

$$P=M\cdot\omega=2\pi R2\cdot L\cdot\tau\cdot\omega \tag{4}$$

$$\omega=(2\pi\cdot n)/60 \tag{5}$$

In formulas (4)-(5), P is power (W),ω is angular velocity (1/rad), and n is rotational speed (rad/min).

The work curve of shear friction is drawn with time as x axis and power as y axis the plot function in Matlab is used to fit the nonlinear curve of shear friction curve, and the area enclosed by the curve and x coordinate axis is calculated, which is the work done by shear friction.Calculate the change rate of shear friction work every 5s.When the absolute value of the change rate of shear friction work is less than 1% for 30s,The point where the absolute value of the first change rate is less than 1% is regarded as the collapse pointThe difference between the total shear friction work and the corresponding shear friction work at the collapse point is flocculation structure destruction energy E.

2.3.2 Observation of microstructure

Ultra-depth-of-field microscope (Model VH-100R, KENSHIS, Japan) was used to observe the microstructure of fresh cement paste.Dilute the slurry to 400 times, drop it onto the glass slide, and observe the change of the number and size of microstructure under a microscope, with a magnification of 300 times.

ImageJ (version ImageJ Fiji) software is used to gray-scale the microstructure picture of fresh cement paste and quantitatively analyze the number and projection area of aggregates in the picture.Considering that there are independent cement particles in the picture of analyzing the microstructure of cement paste.Therefore, when using ImageJ software to count aggregates.Particles with projected area larger than that of cement average particle size should be selected for counting.

2.3.3 Particle size analysis

The particle size and distribution of cement particles were measured by laser particle sizer (Panaco Company, malvin, Model 3000).

3. Results and discussion

3.1. Hysteresis loop area

The area of hysteresis loop can qualitatively characterize the thixotropic destruction performance of fresh cement paste and the difficulty of destruction of flocculation structure in cement pasteIn this study, rheological tests were carried out on cement pastes with water cement ratios of 0.35, 0.45 and 0.55.See Figure 2 for hysteresis loop area and Table 3 for hysteresis loop area results.

It can be seen from Figure 2 that the smaller the water-cement ratio, the greater the shear stress and the larger the hysteresis area.According to Table 3, we can quantitatively compare the size of hysteresis loop, which is $S_{0.35}> S_{0.45}>S_{0.55}$.With the decrease of water-cement ratio, the attraction between cement particles is greater, the bonding degree between cement particles is stronger, and the flocculation structure is less likely to be destroyed.

3.2. Destruction energy of flocculation structure

See Table 4 for shear friction power curve fitting and flocculation structure destruction energy.It can be seen from Figure 3-5 that the work done by shear friction in unit time increases with the decrease of water-cement ratio and decreases with the decrease of shear rate.It gradually decreases with the extension of shearing time.According to the analysis in Table 4, the destruction energy of flocculation structure under shear action decreases with the increase of water-cement ratio and the decrease of shear rate.Under different shear rates, the destruction of flocculation structure is different.The higher the shear rate, the more complete the destruction of flocculation structure, as shown in Figure 6.

Different cement particles have different hydration rates, and the bonding forces between the particles are different, so the internal flocculation structure of cement paste is a multi-stage flocculation structure with irregular shape and different sizes.Under the same water-cement ratio, when the shear rate is low, the shear stress produced by the rotor is small,Shear action can only destroy the flocculation particles with weak binding force and the outer cement particles with large size in cement paste, while the flocculation structure with strong binding force and large size needs larger shear stress.Therefore, under the same water-cement ratio, the higher the shear rate, the higher the destruction energy of flocculation structure, and the more complete the destruction of flocculation structure.

Table 3 Area of hysteresis ring with different water-cement ratios.

W/C	Upward curve equation	The relation coefficient R^2	Downward curve equation	The relation coefficient R^2	The area of hysteresis loop s/(pa s)
0.35	$2.9e^{-5}x^3-0.012x^2+1.7x+13$	0.98466	$2.1e^{-5}x^3-0.0069x^2+1.1x+3.5$	0.9989	2555.6
0.45	$2.01e^{-5}x^3-0.006x^2+0.62x+4$	0.97871	$1.4e^{-5}x^3-0.0038x^2+0.44x+3.2$	0.98582	508.5
0.55	$3.5e^{-9}x^5-1.5e^{-6}x^4+0.00025x^3-0.018x^2+0.61x+1.37$	0.94386	$4.3e^{-6}x^3-0.0011x^2+0.13x+1.4$	0.97838	376.1

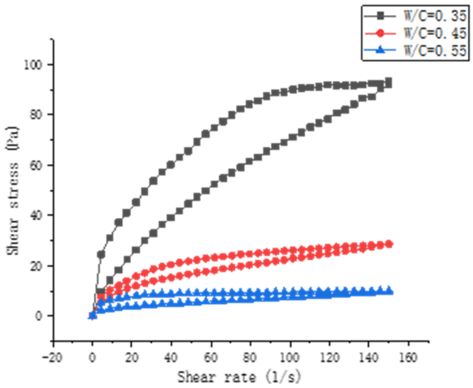


Figure 2 Comparison of hysteresis circles with different water-cement ratios.

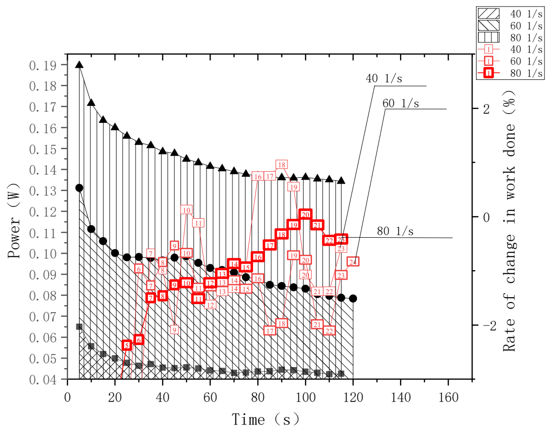


Figure 3 Work done by shear friction at different shear rates and the rate of change of work done (W/C=0.35).

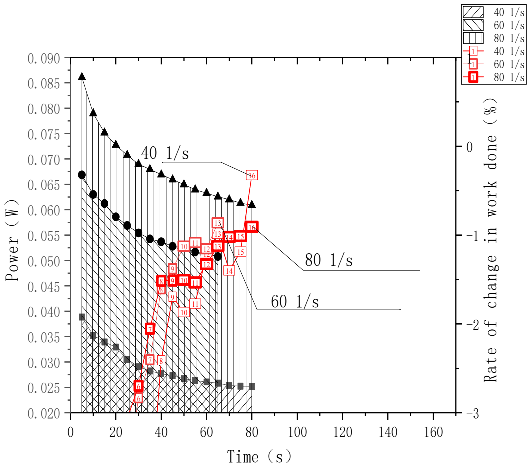


Figure 4 Work done by shear friction at different shear rates and the rate of change of work done (W/C =0.45).

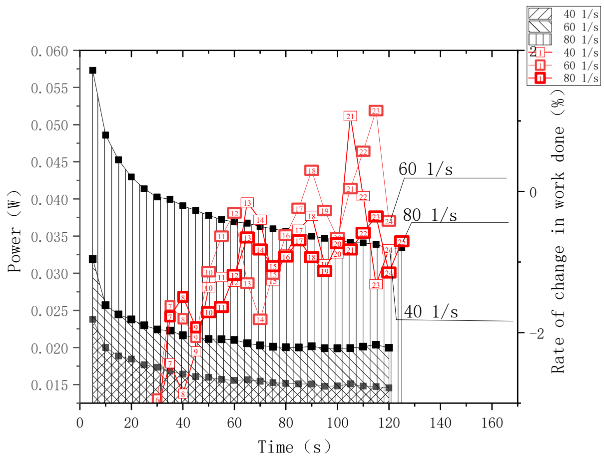


Figure 5 Work done by shear friction at different shear rates and the rate of change of work done (W/C =0.55).

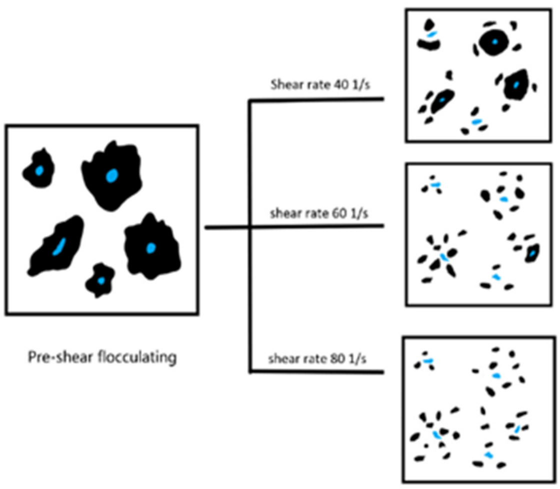


Figure 6 Destruction model of flocculated structure at different shear rates.

Table 4 Shear friction power curve fitting and destruction energy of flocculating structure.

W/C	Shear rate /(1/s)	equation of a curve	The destruction energy E/(J) of flocculation structure
0.35	40	$1.32e^{-13}x^6-6.90e^{-11}x^5+1.43e^{-08}x^4-1.49e^{-06}x^3+8.35e^{-05}x^2-0.0024x+0.074$	5.1
	60	$4.29e^{-13}x^6-2.24e^{-10}x^5+4.62e^{-08}x^4-4.69e^{-06}x^3+0.00024x^2-0.0059x+0.15$	9.8
	80	$3.47e^{-13}x^6-1.75e^{-10}x^5+3.45e^{-08}x^4-3.38e^{-06}x^3+0.00017x^2-0.0048x+0.21$	16.1
0.45	40	$-4.21e^{-14}x^6-6.81e^{-13}x^5+8.06e^{-09}x^4-2.28e^{-06}x^3+0.00027x^2-0.016x+1.04$	2.2
	60	$1.86e^{-14}x^6-3.07e^{-11}x^5+1.23e^{-08}x^4-2.19e^{-06}x^3+0.00020x^2-0.01x+0.79$	3.4
	80	$6.52e^{-13}x^6-3.35e^{-10}x^5+6.81e^{-08}x^4-6.99e^{-06}x^3+0.00038x^2-0.012x+0.59$	5.1
0.55	40	$5.10e^{-14}x^6-2.61e^{-11}x^5+5.28e^{-09}x^4-5.37e^{-07}x^3+2.91e^{-05}x^2-0.00084x+0.027$	1.9
	60	$1.17e^{-13}x^6-5.91e^{-11}x^5+1.17e^{-08}x^4-1.14e^{-06}x^3+5.76e^{-05}x^2-0.0014x+0.037$	2.6
	80	$1.29e^{-13}x^6-6.75e^{-11}x^5+1.39e^{-08}x^4-1.45e^{-06}x^3+7.96e^{-05}x^2-0.0023x+0.066$	4.6

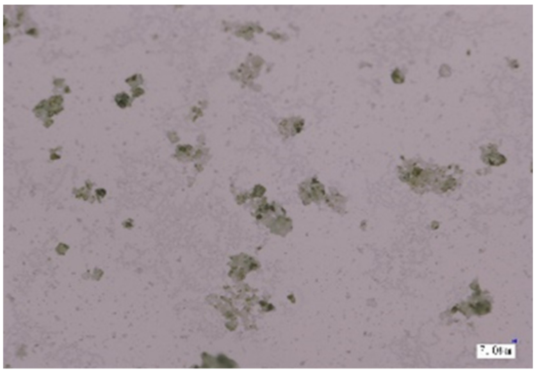
3.3. The quantity and size of aggregates

The particle size of cement particles is micron, and the influence of different water-cement ratio on the microstructure quantity, size and dispersion of cement paste can be directly observed by using ultra-depth-of-field optical microscope.

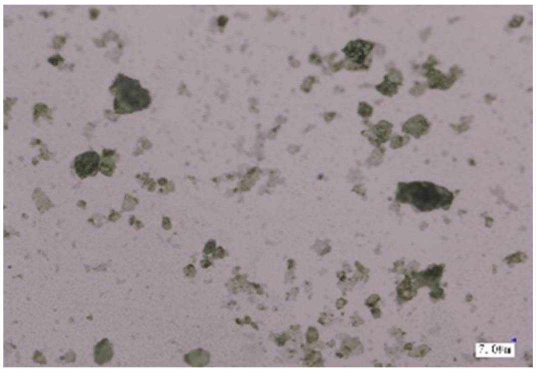
The microstructure of fresh cement pastes with water cement ratios of 0.35, 0.45 and 0.55 when hydrated for 5 minutes is shown in Figure 7.It can be seen from Figure 7 that cement particles overlap with each other to form aggregates, which are irregular in shape.When the water content in cement paste increases, the distance between cement particles is far away, the repulsion between cement particles is large, and the number of aggregates increases but the size decreases.When the water content in cement paste decreases, the distance between cement particles is closer, the attraction between cement particles is larger, and the number of aggregates decreases but the size increases.In order to show the influence of water-cement ratio on aggregates more clearly, ImageJ software should be used to process the microstructure pictures and count the number of aggregates in the pictures.See Figure 8 after gray processing.It can be seen quantitatively from the figure that with the increase of water-cement ratio, the projected area of aggregates decreases and the number increases.

It can be seen from Table 2 that the average particle size of cement particles is 24μm.In order to reduce the influence of single cement particle on the number of aggregates in the picture, cement particles are regarded as spheres with a radius of 12μm and an average projection area of 452μm^2.ImageJ was used to count aggregates with projection area above 452μm^2.The aggregate number, average projected area and flocculation structure destruction energy with different water-cement ratios are shown in Table 5.

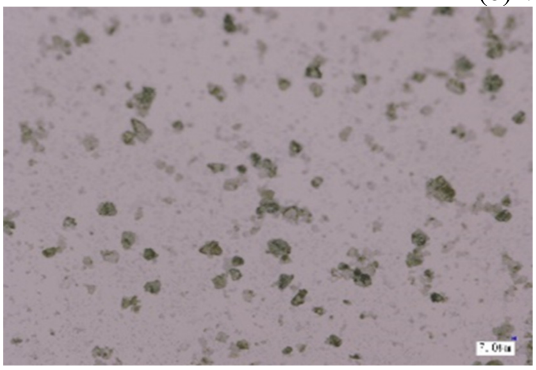
In the process of cement hydration, cement particles are connected with each other to form aggregates that wrap free water, so the size of aggregates should be larger than that of single cement particles.The unit area of ultra-depth-of-field pictures is 530μm*400μm.It can be seen from Table 5 that the average projection area of aggregates in unit area is larger than that of cement particles.With the increase of water-cement ratio,With the increase of the number of aggregates per unit area, the average projected area decreases, and the destruction energy of flocculation structure increases with the increase of the average projected area of aggregates.Therefore, with the increase of water-cement ratio, the size of aggregates decreases, the dispersion of cement particles increases, and the mutual attraction between cement particles weakens.



(a) W/C=0.35,5min



(b) W/C=0.45,5min

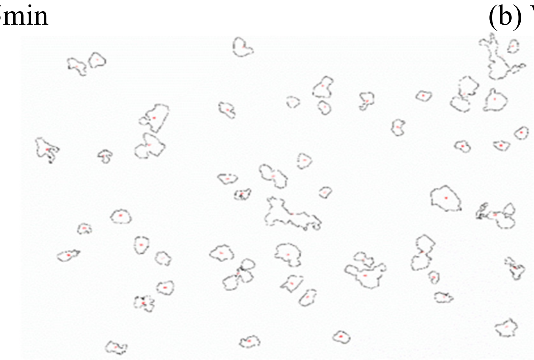


(c)W/C=0.55,5min

Figure 7 Microstructure and morphology of freshly mixed cement paste observed by light microscope.

(a) W/C=0.35,5min

(b) W/C=0.45,5min



(c)W/C=0.55,5min

Figure 8 Microstructure and morphology of freshly mixed cement paste observed by light microscope after treatment.

Table 5 The number, size and work done by shear force of flocculating structures with different water-cement ratios.

W/C	Number of aggregates/(one /530μm*400μm)	Average projected area /(μm^2)
0.35	22	2176.8
0.45	34	2083.3
0.55	51	1336.9

4. Conclusion

（1）When the shear rate is the same, with the increase of water-cement ratio, the hysteresis loop area increases, the destruction energy of flocculation structure increases, the aggregate size decreases, and the flocculation structure is easy to be destroyed.

（2）Through the calculation and analysis of the destruction energy of fresh cement paste, it is known that under the same water-cement ratio, with the increase of shear rate, the destruction energy of flocculation structure increases, and the destruction degree of flocculation structure in cement paste increases The size of aggregates in cement paste gradually decreases and the number gradually increases.

（3）Through microscopic observation and quantitative analysis of aggregate quantity, it is found that with the increase of water-cement ratio, the aggregate quantity in cement slurry increases, the average projection area decreases, and the aggregate distribution is small and dense.

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