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Chemical Adsorption Characteristics of Auxiliary Cementitious Materials

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In the mixing process of concrete, the addition of auxiliary cementitious building materials can improve the performance of concrete while saving resources, but due to the compatibility problem of raw materials, there shall occur poor fluidity and abnormal setting etc. for the early-period concrete. For this, based on the adsorption mechanism of water reducer on auxiliary cementitious building materials, this paper carries out the study on the adsorption characteristics of three kinds of polycarboxylate superplasticizer (PCS) on the surface of fly ash, and solves the problem of relationship between the PC dosage/adsorption capacity and particle size of fly ash. The results show that the PC structure has a significant influence on the adsorption capacity, and its adsorption capacity on the surface of fly ash gradually increases and becomes saturated with the increase of its dosage. This study is of great significance for the selection of water reducer and the dosage application.

1. Introduction

The rapid advancement of urbanization has led to the fast development of cement concrete technology, and a wide variety of auxiliary gel materials have been widely used in concrete (Zhu et al., 2017). The addition of admixtures and auxiliary gel materials has greatly improved the mechanical and chemical properties of cement concrete and expanded its application fields (Zhang et al., 2015), which plays an important role in promoting the economic development and urbanization (Zhang et al., 2014). The commonly used admixtures include water reducer, quick-setting agents, and rust inhibitors; commonly used auxiliary gel materials include fly ash, and slag, etc. (Fang et al., 2012). Water reducer can significantly reduce the amount of water used in concrete mixing, as the most used agent in various admixtures (Zhu et al., 2015). Fly ash, as the waste discharged from coal-fired power plants, can be re-used for waste utilization in concrete, which is of great significance for resource conservation and environmental protection.

Superplasticizers (High-range water reducer) can improve concrete setting time, pore structure and compressive strength (Harada et al., 2017), which is the key to improving concrete strength (Walker et al., 2014). Commonly used superplasticizers include: lignosulfonate series, naphthalene sulfonate series, and poly-carboxylic acid series, etc. (Zhang et al., 2016; Li and Ren Y., 2018). Among them, polycarboxylate PCS has the advantages of low dosage and high-water reduction rate. Therefore, many research institutes have carried out research on polycarboxylate superplasticizer (PCS). As early as 1986, the Japanese Nippon Shokubai developed a polycarboxylate water-reducing agent with a hydrophilic function and also applied it in reality (Wei et al., 2016). In 1997, developed countries in Europe and the United States etc. published related papers on PCS (Zhang et al., 2010). However, domestic research on PCS mainly focuses on the influence of preparation process and type on performance, and there has been no research on its action mechanism and microstructure (Jassam, 2015). For this, this paper conducts study on the adsorption characteristics of three different types of PCS on the surface of fly ash.

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2. Research background

2.1 Polycarboxylate superplasticizers

The PCS mainly comprises the types of methacrylic acid, methyl acrylate PC copolymer, allyl ether PC and copolymer. Its main synthesis methods include direct copolymerization of polymerizable monomers, functionalization after polymerization, and the like.

2.2 Action mechanism of polycarboxylate superplasticizer

(1) The DLVO theory proposed by Derjgauln, Lnadua, Verway, and Ovehteek in the 1940s believed that the gelling system maintains its dispersion stability by electrostatic repulsion between particles, and the addition of water reducer can improve the dispersibility of the gelling system. This theory has been widely used in the study of system dispersion stability. It’s the theoretical basis for the action mechanism of water reducer.
(2) The traditional DLVO theory can well reveal the mechanism of action for the naphthalene sulfonate series water-reducer, but not enough for that of the PCS. The subsequent studies have shown that the PCS has adsorption and dispersion function on the cementitious particles, and it is usually adsorbed on the surface of the cementitious material in the form of ring adsorption, which has the function of steric hindrance. Meanwhile, the branched group of PCS has a reactive group capable of forming a hydrated film when the cementitious material is combined, with a lubricating effect.

3. Experimental materials and research methods

3.1 Experimental materials

(1) Class II fly ash produced by a power plant was used with a density of 2.6 g/cm^3 in the experiment. Table 1 lists its chemical composition.

Table 1: Chemical content of fly ash

Mat.	Chemical content/%										
	SiO_2	Al_2O_3	CaO	Fe_2O_3	LOI	MgO	TiO_2	K_2O	SO_3	Na_2O	Others
Fly ash	50.01	23.98	12.35	4.26	3.93	1.71	1.14	0.94	0.92	0.23	0.53

Note: LOI indicates the rate of incineration.

(2) Water reducer
In this paper, three kinds of PCS with different molecular structures were used, and the solid contents were 41%, 42%, and 25%, respectively, represented by No. 1, 2, and 3.

3.2 Experimental methods

3.2.1 Raw material handling

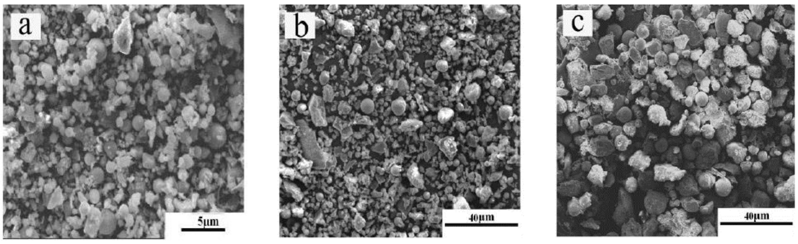
The fly ash was ground to a specific surface area of 370±10m^2/Kg using a φ500×500mm ball mill, and then classified by a gas classifier. Particle distribution, surface morphology and chemical composition analysis were tested using a Mastersizer laser particle size analyser, a scanning electron microscope (SEM), and an X-ray fluorescence analyser.
(1) The particle distribution of fly ash after grinding is shown in Table 2, and coarse, medium and fine fly ash are represented by F1, F2 and F3, respectively.

Table 2: Particle size distribution parameters of fly ash

Fraction	F1	F2	F3
D_{10}/μm	19.87	7.61	0.30
D_{50}/μm	26.93	10.39	1.52
D_{90}/μm	32.16	13.33	0.78
SSA/(m^2/kg)	481	1175	4802

Note: D10, D50, and D90 indicate the maximum particle sizes when the cumulative volume reaches 10%, 50%, and 90%, respectively.

(2) It can be seen from the SEM images of the fly ash in Figure 1 that the fine fly ash is mainly composed of spherical particles; the medium fly ash has relatively poor sphericity and contains a large number of needle-like particles; the coarse fly ash is mainly composed of spherical particles and porous particles.



D_{50}=1.52μm D_{50}=10.39μm D_{50}=26.93μm

Figure 1: SEM images of fly ash

(3) Table 3 shows the chemical composition of fly ash with different particle sizes: the content of SiO_2 and Fe_2O_3 decreases with the decrease of fly ash particle size; CaO, SO_3, K_2O, Na_2O and carbon content increase, indicating that there is certain phase separation phenomenon in the process of grinding fly ash.

Table 3: Chemical content of grinded fly ash

D_{50}/μm	Chemical content/%									
	SiO_2	Al_2O_3	CaO	Fe_2O_3	LOI	MgO	TiO_2	K_2O	SO_3	Na_2O	Others
26.93	50.62	24.25	11.87	5.62	2.93	1.7	1.14	0.58	0.62	0.17	0.5
10.39	49.83	24.21	12.37	4.35	3.89	1.58	1.14	1.03	0.88	0.2	0.52
1.52	40.88	23.98	15.36	3.41	10.2	1.53	1.14	1.34	1.69	0.22	0.25

3.2.2 Adsorption test

The fly ash was mixed with the water reducer solution at room temperature at the water-to-binder ratio of 3. After the admixture was magnetically stirred for 5 min, it was shaken again for 5min, 15min, 30min, 60min, 90min, and 120min, respectively. With the centrifugation at 4500 rpm for 10min, the supernatant was taken out for microfiltration, and diluted 10 times. Then, the TOC instrument manufactured by Elementar, Germany was used to measure the difference in concentration of the PCS before and after adsorption.

3.2.3 Rheological property test

The admixture of fly ash, water and PCS solution was stirred for 5 minutes, and then the shear stress and viscosity values of the admixture were measured using a Brookfield R/S-SST rheometer.

3.2.4 Infrared (IR) spectroscopy test

After the PCS sample was dried at 60°C and grinded, it's analysed by an IR spectrometer to determine the group type of the PCS.

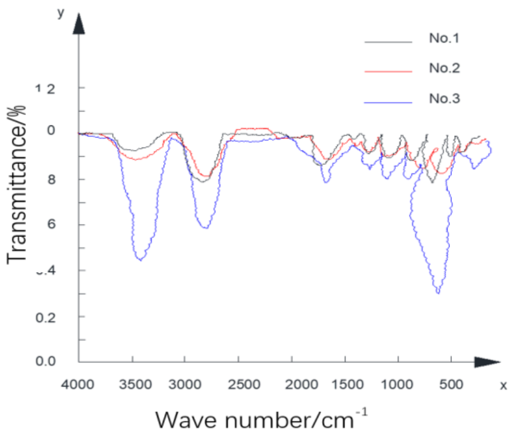


Figure 2: IR spectrums of 3 kinds of PCs

Figure 2 shows the IR spectrum analysis results for the three kinds of PCSs. It can be seen that the three PCSs have characteristic absorption peaks of C=O and -OH and -COOH at about 1700cm^{-1} and 3500cm^{-1}, respectively. Therefore, the three have similar functional groups, but the carboxyl group and the hydroxyl group content are different.

3.2.5 Gel Permeation Chromatography (GPC) Test

Through the analysis of gel permeation chromatography (GPC), it's found that for the polydispersity index (PID), No.2 water-reducer is the largest and No.3 is the smallest, and according to the Mw/Mn distribution between 1.5 and 2.0, it is judged that the water-reducer is formed by the chain polymerization.

Table 4: GPC data of PCs

Parameters	No.1	No.2	No.3
Peak RV/ml	8.39	8.91	8.73
Mn/daltons	60158	21897	41209
Mw/daltons	100897	38032	63587
Mw/Mn	1.683	1.741	1.532

According to the IR spectrum and GPC analysis results, the structure of the PCSs is obtained as shown in Table 5.

Table 5: Molecular structural characteristics of PCs

Sample	Molecular structural characteristics
No.1	With largest molecular weight, longest main chain, longest branching chain and smallest carboxyl content.
No.2	With smallest molecular weight, shortest main chain, short branching chain and largest carboxyl content.
No.3	With meadium molecular weight, meadium main chain, short branching chain and small carboxyl content.

4. Study on adsorption characteristics of PCS on fly ash surface

Through the adsorption of the PCS and the cementitious building material, the surface properties of the cementitious material are changed to make it stable.

4.1 Adsorption isotherm curve

Figure 3 shows the adsorption isotherm curve of the PCS on the surface of the fly ash. It can be seen from the figure that as the dosage of PCS increases, its adsorption capacity on the surface of fly ash gradually increases and tends to be saturated. This is because the high negative charge of the PCS is rapidly adsorbed on the surface of the cementitious particles and the early hydration product, and an electrostatic repulsion is generated, so that the gel particle flocculation structure is disintegrated. Also, the critical amounts of PCS No. 1, 2 and 3 are 0.6%, 0.4%, and 0.4%, respectively, and the adsorption capacity are 4.5 mg/g, 2.5 mg/g, and 1.5 mg/g, respectively.

4.2 Effect of particle size of fly ash on adsorption capacity

It is generally considered that the smaller the particle size, the greater the system free energy and the larger the adsorption capacity. However, Figure 4 shows that the particle size does not significantly affect the adsorption amount of the PCS on the surface of the fly ash except that with the fine particle size, the adsorption capacity of the No.2 PCS is obviously coarser and the medium particle size is larger. The structure of the PCS has a significant influence on the adsorption capacity. The adsorption capacity of No. 2 and 3 PCSs on the surface of fly ash is smaller than No. 1. With the coarse and medium particle size, the amount of PCS No. 2 is smaller than that of No. 3, but in the case of fine particle size, the adsorption of the two is not much different.

4.3 Effect of specific surface area

It can be seen from Figure 5 that as the specific surface area of the fly ash increases, the saturated adsorption of the PCS on the surface also increases. With the increase of the specific surface area for fly ash particles, the saturated adsorption capacity of No.1 increases uniformly; that of No.2 and No.3 in the medium and small particle size distribution range has relatively small changes, but significantly higher than that with the coarse particle size.

4.4 Effect of Surface morphology

The unit specific surface area saturated adsorption capacity of the PCS on the surface of the fly ash decreases as the particle size of the fly ash decreases. The reason is that the increase rate of the saturated fly ash adsorption capacity with the increase of the specific surface area is much smaller than the increase rate of the specific surface area; in addition, the repulsion may be caused by overcrowding between the PCSs, making the adsorbed PCSs on the surface of cementitious particles to be desorbed.

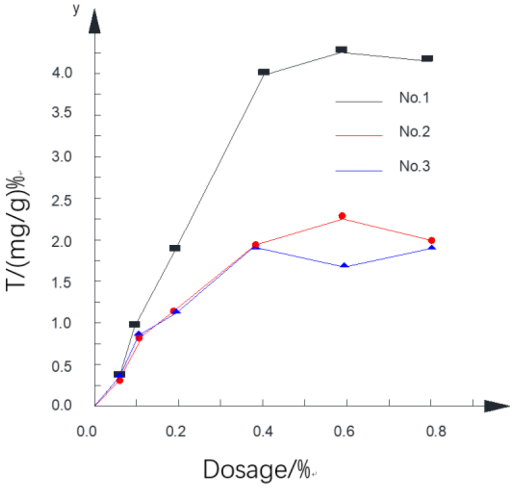


Figure 3: Adsorption isotherms curves of PC on the surface of fly ash particles

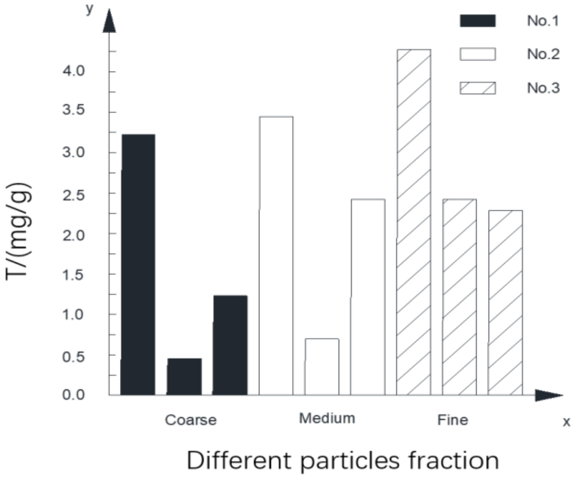


Figure 4: Adsorption capacity of PC on the surface of fly ash with different particle sizes

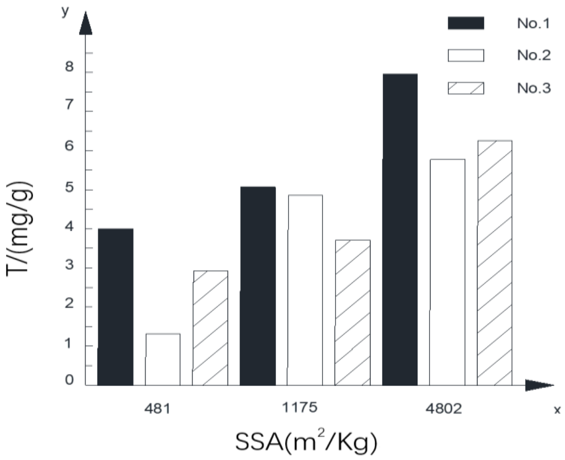


Figure 5: Saturated adsorption capacity of PC on fly ash with different specific surface area

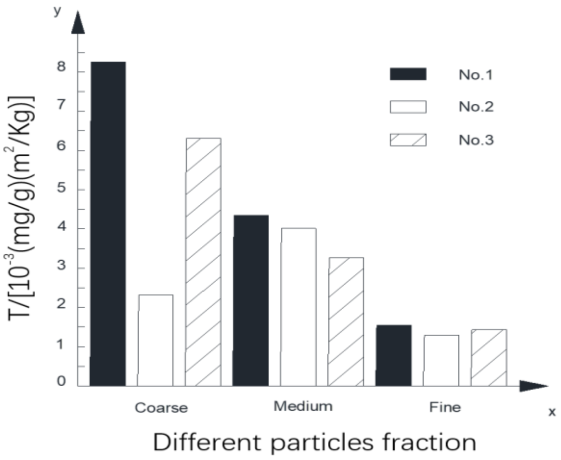


Figure 6: Adsorption capacity of PC on fly ash surface under different particle sizes

4.5 Coverage of PCS at critical dosage on the fly ash surface

The dispersion effect becomes better as the surface coverage increases. When the coverage exceeds 70%, the flocculation structure of the gelling system will be broken. Table 6 shows that the surface coverage of fly ash is mostly distributed between 40% and 50%, except that that of No.1 PCS in the coarse-grained range is higher than 70%.

Table 6: Coverage of different PC on the surface of fly ash under different particle sizes

Sample Parameters	No.1	No.2	No.3
F1	0.821	0.539	0.409
F2	0.683	0.162	0.634
F3	0.542	0.418	0.382

5. Conclusions

In the concrete mixing process, the addition of the high-range water reducer can effectively save water and improve the concrete’s setting and flow characteristics. In this paper, the adsorption characteristics of PCS (water reducer) on the surface of supplementary cementitious building materials (fly ash) were studied, drawing the following conclusions:
(1) With the increase of the water reducer dosage, the adsorption capacity of the water reducer on the surface of the fly ash gradually increases and tends to be saturated. The critical dosages of water reducer No. 1, 2 and 3 are 0.6%, 0.4%, and 0.4%, respectively, and the adsorption capacities are about 4.5mg/g, 2.5mg/g, and 1.5mg/g, respectively.
(2) The chemical structure of the water reducer has a significant effect on the adsorption capacity, while the particle size of the fly ash does not significantly affect the adsorption capacity of the water reducer on the surface.
(3) The saturated adsorption capacity of the water reducer on the surface of the fly ash increases as the specific surface area of the particles increases. The surface coverage is mostly distributed between 40% and 50%.

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