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Adsorption characteristics of water-reducing agents on gypsum surface and its effect on the rheology of gypsum plaster

Jiahui Peng*, Jindong Qu, Jianxin Zhang, Mingfeng Chen, Tizhi Wan

Department of Building Materials, Chongqing University, Chongqing, 400045, PR China

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Abstract

In this study, by using UV-visible adsorption spectrophotometer, Zeta potential analyzer and X-ray photo spectroscopy, the adsorption characteristics and surface electrochemical properties of two types of superplasticizer-β-naphthalene sulfonic acid type (BNS) and polycarboxylate type (PC) and their effects on the fluidity of gypsum plaster were studied. The results show that the adsorption of BNS and PC on gypsum surface approximately conforms to Langmuir's adsorption isotherm. The adsorption of BNS belongs to physical adsorption, its adsorption heat being 14.71 kJ/mol and the thickness of adsorption layer 120 Å; while the adsorption of PC belongs to chemical adsorption, with an adsorption heat of 20.85 kJ/mol and a thickness of adsorption layer of 120 Å. The adsorption conformation of BNS is lying on the flat of gypsum surface, generating weak steric hindrance to inhibit agglomerate of gypsum particles. Its dispersion effect mainly depends on electrostatic repulsive force caused by ζ-potential, which is determined by the adsorbed amount of BNS at the first adsorption layer on gypsum surface. The adsorption conformation of PC is comb-shaped, generating strong steric hindrance by side chains of adsorption layer, thus, its dispersion ability mainly comes from a combination effect of steric hindrance and electrostatic repulsive force. The dispersion by steric hindrance is less affected by the rapid hydration of gypsum, thus, its stability is much better than that of electrostatic repulsive force, resulting in little flow loss of fresh gypsum plaster.

Keywords: Gypsum; Superplasticizer; Adsorption; Steric hindrance effect; Zeta potential

1. Introduction

Adding water-reducing admixture is one of most efficient ways to improve the fluidity of bonding materials. Past researches on water reducer mainly focused on concrete system. It is broadly accepted that water-reducing agents produce dispersion effect through adsorption on cement surface [1–3], and the interface structure and electrochemical properties of cement particles depend on the molecule structure and adsorption conformation of the admixture [4,5]. In case of traditional superplasticizer, such as β-naphthalene sulfonic (BNS) acid type and sulfonated melamine formaldehyde, their adsorption conformation is in the form of lying on gypsum surface, and their dispersion capacity depends on the electrostatic repulsive force produced by the adsorption double-electrical layer [6]. On the other hand, the adsorption conformation of polycarboxylate (PC)-type superplasticizer is comb-shaped, and their dispersion ability comes from a combination effect of steric hindrance and electrostatic repulsive force [7,8].

With respect to concrete superplasticizers, the researches on gypsums are largely lagged behind. Present reports only limit to effects of plasticizer on the fluidity of gypsum plaster and the strength of the hardened paste [9–11]. Because of the lack of theoretical research on gypsum admixture, concrete superplasticizer is blindly used in gypsum systems. Gypsum-based materials are very different from cement for many aspects, such as phase composition, crystal morphology, rheology, hydration and stiffening; thus, there is compatibility between concrete admixtures and gypsum. Therefore, an admixture theory especially for gypsum is required to provide direction for the application of admixture in gypsum-based materials.

In this study, the adsorption characteristics of two typical types of superplasticizer -BNS acid type and PC type on gypsum surface was systemically investigated, and their saturated adsorbed amount and adsorption heat, as well as adsorption layer thickness, were also investigated. Further-

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* Corresponding author. Tel./fax: +86-23-65120781.
E-mail address: pengjh@cqu.edu.cn (J. Peng).

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more, the relationship between adsorption and surface electrochemical properties, solid–liquid interface structure of gypsum particles and their effects on fluidity of gypsum paste were discussed.

2. Experimental

2.1. Materials

Building gypsum came from Bishan Gypsum in China. Its chemical composition and performance index were as follows: SO_3 and crystallization water contents were 41.9% and 16.5%, respectively; the water/gypsum ratio at standard consistency was 0.63; and the specific surface area of gypsum was 4122 cm^2/g. The BNS acid and PC types superplasticizers used in this study were both commercial products.

2.2. Adsorbed amount measurement

First, a series of BNS and PC solutions with different concentrations were prepared. Then, gypsum was added according to a water/gypsum ratio of 0.8. After 4 min, the plaster was vacuum filtered, and the extracted solution was then centrifuged by ultracentrifugation to separate the fine particle suspended in solution. Superplasticizer concentration in the liquid phase was measured by UV adsorption spectrophotometer (Shimadzu UV-260, Japan). The quantities adsorbed were calculated from the differences in the concentration of admixtures in the liquid phase before and after adsorption.

2.3. Adsorption layer structure analysis

The thickness of the adsorbed layer of the admixtures on the surface of gypsum particles was determined by X-ray photo spectroscopy technology. The instrument employed XSAM × 800 multifunctional electrics energy spectrum analyzer (Kratos, England). A sample gypsum was dipped for 4 min in an aqueous solution of admixture, with the same concentration as that used for adsorption amount measurement in distilled water, and then dipped in methyl alcohol to stop hydration. By using XPS aid of Ar-ion etching analyzer, the bonding energy and spectrum strength of the characteristic element on gypsum surface at different etched depths, before and after adsorption, were measured to determine adsorption property and thickness of adsorbed layer of admixture.

2.4. Fluidity test

The fluidity of gypsum paste was evaluated by pullout spread of gypsum paste from a pipe of 50-mm inner diameter and 100-mm height, according to GB9776-88 (China building gypsum national standard). The spread was the average of two perpendicularly crossing diameters.

For ζ-potential measurements, the JS94F microelectrophoresis analyzer was used.

3. Results and discussions

3.1. Adsorption characteristics of water-reducing agent on gypsum surface

The relationship between the adsorbed amounts of plasticizer on gypsum surface and its dosage, concentration, as well as temperature, and the effect of gypsum particle fineness on adsorption were measured. By using X-ray photo spectroscopy, the adsorption layer thickness of the superplasticizers on gypsum particles was also analyzed. The results are given in Figs. 1–5.

From Fig. 1, it can be seen that at low dosage (< 0.5%), the adsorbed amount of two superplasticizers increases linearly as a function of dosage. At higher dosages, the adsorbed amount reached equilibrated gradually. Fig. 2 shows the relationship between the adsorption amount of superplasticizer on gypsum surface and its concentration in the aqueous phase. Similar with that between the adsorbed amount and dosage (as shown in Fig. 1), the adsorption of superplasticizer on gypsum surface approximately conformed to Langmuir's adsorption isotherm equation [1] as follows:

$$\Gamma = \Gamma_{\infty}\frac{kc}{1+kc} \quad (1)$$

where Γ is the adsorbed amount, in mg/g; Γ_{∞} is the saturated adsorbed amount, in mg/g; c is the superplasticizer concentration, in g/l; and k is the adsorption constant. The above formula can be converted into Eq. (2):

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_{\infty}} + \frac{1}{\Gamma_{\infty}kc} \quad (2)$$

The Γ_{∞} can be assessed through Eq. (2) by the linear relationship of $1/\Gamma$ versus $1/c$ and then calculating the cut length at the $1/\Gamma$ axis. The saturated adsorbed amount of BNS and PC calculated by this way is 12.67 and 4.42 mg/g, respectively.

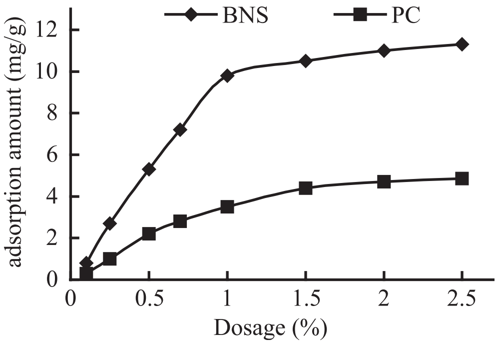

Fig. 1. Relationship between superplasticizers dosage by weight of gypsum and adsorption amount.

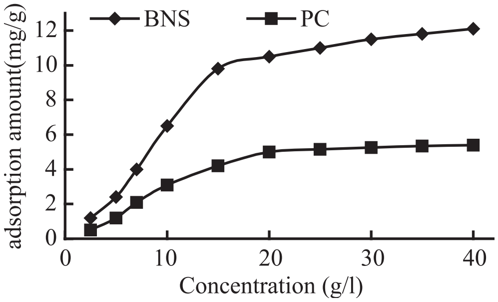

Fig. 2. Relationship between superplasticizers concentration and adsorbed amount.

As shown in Fig. 3, the adsorbed amount of admixture on gypsum surface increased with the fineness of gypsum particles, which was especially evident at low dosage. The higher the specific surface area of gypsum particles, the higher the saturated adsorption amount of admixture was. When the specific surface area of gypsum particle exceeded 8000 cm^2/g, fineness had a minor effect on the adsorbed amount. Therefore, an appropriate increase in gypsum fineness is helpful to improve the action efficiency of admixtures.

Adsorption is a process that develops heat. The adsorbed amount usually decreases by increasing temperature (as shown in Fig. 4), according to the Clausius–Clapeyron formula as follows:

$$\frac{\Delta H}{R} = \frac{\mathrm{d}\ln\Gamma}{\mathrm{d}(l/T)} \tag{3}$$

where ΔH is the adsorption heat, in kJ/mol; Γ is the adsorbed amount, in mg/g; T is the absolute temperature, K; and R is the gas constant, 8.314 J/mol·k. ΔH could be attained by making a link of $\ln\Gamma$ versus $1/T$ and then calculating its slope. According to the previous formula, the adsorption heat of BNS and PC was 14.71 and 20.85 kJ/mol, respectively.

Carbon is a characteristic element that can distinct gypsum surface from admixtures. Hence, by analyzing its concentration at different depths of gypsum etched surface region, the thickness of adsorbed layer can be induced. From Fig. 5, it was found that with the increase of etched depth, the adsorption peak strength of C_{1s} decreased slowly. When peak strength was equal to that of plain gypsum (without admixture), the etched depth was considered to be the thickness of the adsorption layer. According to this method, the thickness of the adsorption layer of BNS and PC was 120 and 75 Å, respectively. For BNS, the bonding energy of Ca_{2P} did not cause any chemical shift before and after adsorption, which indicated that the adsorption of BNS belonged to physical adsorption and that its adsorbed amount and thickness of adsorption layer were large. On the contrary, in the presence of PC, the bonding energy of Ca_{2P} on gypsum surface causes a chemical shift at a certain level, which proved that PC was chemically adsorbed on gypsum surface in form of monolayer, with a small amount adsorbed.

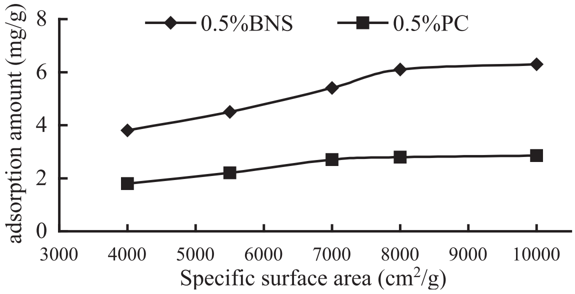

Fig. 3. Influence of the specific surface area of gypsum on adsorption amount.

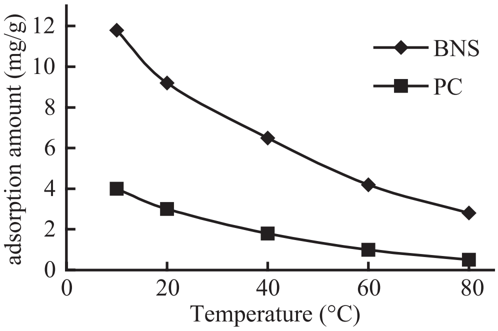

Fig. 4. Influence of temperature on adsorption amount.

3.2. Effect of superplasticizer adsorption on the ζ-potential of solid–liquid interface

Fig. 6 shows the Zeta potential of the gypsum particle surface with the addition of 1% of superplasticizer. In the absence of the admixtures, the ζ-potential of gypsum particles was 19 mv. After adding BNS and PC, the ζ-potential was -38.7 and -30.4 mv, respectively. Both BNS and PC were anionic surfactants. Their adsorption changed the charge distribution of double-electrical layer of gypsum surface, leading to ζ-potential changing from positive to negative, but with a higher absolute value, to an increase of repulsive force between gypsum particles and improvement of dispersion. BNS had a lot of anionic groups, and its adsorbed amount on gypsum particle surface

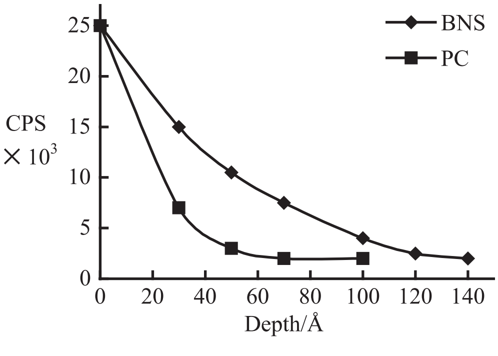

Fig. 5. Change of XPS peak strength of C_{1S} with etched depth.

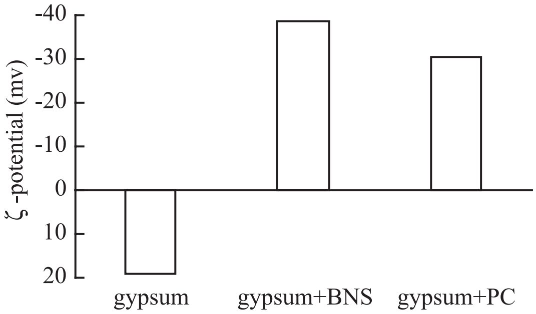

Fig. 6. ζ-potential on the surface of gypsum particle.

was large, thus, gypsum plaster with BNS had a relatively high ζ-potential absolute value.

As shown in Fig. 7, when the addition of BNS was lower than 1%, its adsorbed amount and ζ-potential increased with the admixture dosage. Whereas after the dosage reached up to 1%, despite the adsorbed amount continually increased, ζ-potential did not increase anymore and even had a light trendy to reduction. By taking into account the molecule structure of BNS, it could be induced that, when it occurs a monolayer adsorption, its adsorbed amount and ζ-potential were positively related with its concentration. After gypsum surface was fully covered with BNS monolayer, with further increase of BNS concentration, the adsorbed amount also increases due to multilayer adsorption, but ζ-potential does not increase with the BNS dosage. This indicates that ζ-potential mainly depends on the adsorbed amount of monolayer and that the BNS of the subsequent layer had a shelter effect on the electrostatic repulsive force effect generated by the first layer BNS, and this can be responsible for the lower increase, and even the decrease, of the ζ-potential.

PC had a small adsorbed amount, its ζ-potential absolute value was much lower than that of BNS, whereas its dispersion capacity was much stronger than that of BNS, which showed that its dispersion mechanism was quite different from that of BNS (Fig. 8).

3.3. Effect of superplasticizer on the fluidity of gypsum paste

The effects of the superplasticizer dosage on the fluidity and time dependency of fluidity of fresh gypsum plaster were examined. The results are presented in Figs. 9 and 10.

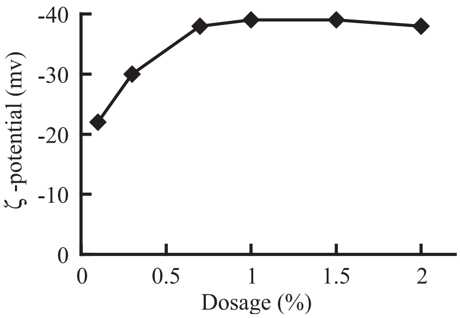

Fig. 7. ζ-potential as a function of BNS dosage.

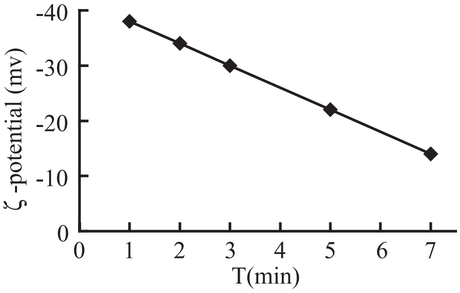

Fig. 8. ζ-potential of gypsum paste with BNS as a function of hydration time.

As can be seen in Fig. 9, the superplasticizer can significantly improve the fluidity of gypsum plaster. The dispersion capacity of PC was stronger than that of BNS. By increasing the PC dosage, the fluidity of gypsum plaster also increases, while for BNS, when the dosage exceeds 1%, the fluidity does not increase any more. During hydration, fluidity loss of gypsum plaster with BNS is very large, while fluidity loss of gypsum plaster with PC is very little, which shows that the dispersion stability of PC is superior to that of BNS.

The adsorbed amount and ζ-potential of PC is lower than that of BNS, but its dispersion capacity is more strong than that of BNS. These differences between PC and BNS showed that their dispersion mechanisms are quite different. The dispersion effect of BNS depends on electrostatic repulsion force produced by adsorption double-electrical layer, while the dispersion ability of PC comes from a combination of steric hindrance and electrostatic repulsion. The dispersion effect generated by electrostatic repulsion is not stable. The reason is interpreted as follows: Because the hydration of gypsum is very quick, with progress of hydration, new hydration products would coagulate on the surface of hemihydrates. Consequently, the adsorbed layer of BNS is sheltered, resulting in a reduction of ζ-potential and of electrostatic repulsive force and in a rapid flow loss of gypsum plaster as a function of time.

PC is polycarboxylate-based polymer by graft with polyoxyethylene chain and has many polyoxyethylene side chains. During adsorption, main chains “anchor” on the gypsum surface by the complex action between the carbox-

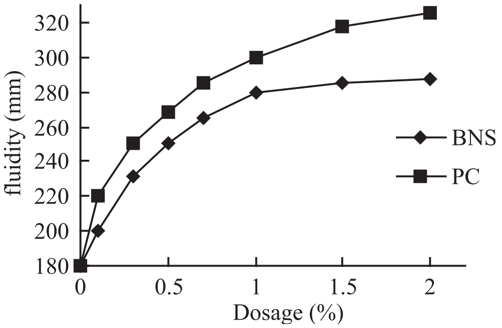

Fig. 9. Effect of BNS addition on the fluidity of gypsum paste.

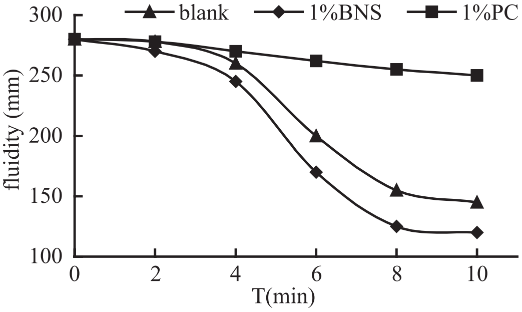

Fig. 10. Time dependency of the fluidity of gypsum paste.

ylic group and Ca^{2+}, whereas side chains protrude in the liquid phase. The superplasticizer molecules appear to be in a spatial distribution at the solid–liquid interface, impeding the agglomeration of gypsum particles. In other words, the dispersion effect of PC is ascribed to a combination effect of the steric hindrance, generated by side chains, and the electrostatic repulsive force caused by anion groups on the main chain. Steric hindrance is less affected by gypsum hydration and can keep the dispersion capacity for relatively long times.

4. Conclusions

1. The adsorption of BNS and PC on gypsum surface approximately conforms to Langmuir's adsorption isotherm. The adsorption of BNS belongs to physical adsorption. Its adsorbed amount is large, and its saturated adsorbed amount can reach up to 12.67 mg/g; however, its adsorption is not stable. On the other hand, PC is adsorbed on gypsum surface in the form of chemisorption, with small adsorption amount and good dispersion stability.
2. The adsorption conformation of BNS is lying on the flat surface of gypsum, generating weak steric hindrance to inhibit agglomerate of gypsum particles. Its dispersion effect mainly depends on electrostatic repulsive force caused by the ζ-potential, which is determined by the adsorbed amount of BNS at the first adsorption layer on gypsum surface. Shelter effects on electrostatic repulsive force from bihydrate gypsum crystals generated during rapid hydration of gypsum and the desorption of the adsorption molecule make its dispersion capacity reduce rapidly with the progress of gypsum hydration.
3. The adsorption conformation of PC is comb-shaped, generating strong steric hindrance by side chains of adsorption layer, thus, its dispersion ability is mainly related with the steric hindrance effect, rather than with the electrostatic repulsive force mechanism. The dispersion of steric hindrance is less affected by the rapid hydration of gypsum, thus, its stability is much better than that of electrostatic repulsive force, resulting in little flow loss of fresh gypsum plaster.

Acknowledgements

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