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Correlations of the dispersing capability of NSF and PCE types of superplasticizer and their impacts on cement hydration with the adsorption in fresh cement pastes

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ABSTRACT

Comparative study of NSF and PCE superplasticizers was carried out aiming at correlating the adsorption in fresh cement pastes (fcps) with their dispersing capability and the impacts on cement hydration. Results show that the adsorption of NSF follows a typical Langmuir monolayer adsorption model while PCE exhibits a multi-layer adsorption. The fluidity of fcps containing NSF and the retardation effect of NSF on hydration are directly proportional to the surface coverage of NSF on cement grains. As full coverage is achieved, the fluidity enhancement and the retardation effect reach maximum by addition of NSF. By contrast, the fluidity of fcps with PCE is related to the coverage of the first adsorbed layer and the secondary adsorbed layer does not contribute to the enhancement of fluidity. Both the adsorbed PCE and the PCE remaining in aqueous phase participate in retarding cement hydration because of the complexation effect of $-COO^-$ with Ca^{2+}.

1. Introduction

Fluidity has been considered as one of the essential properties of fresh cement-based materials due to its importance in determining the construction workability and various properties of hardened ones. Generally, adequate fluidity could be achieved by adding superplasticizers in concrete mixtures [1], which are working as dispersing agents for the flocculated cement grains through their adsorption on cement surface [2]. Various types of superplasticizer with different dispersing capabilities have been developed and applied in cement-based materials in the last decades such as lignosulfate, polycondensates and the latest generation of comb-like polycarboxylate (PCE) superplasticizers, among which naphtalene sulfonate formaldehyde polycondensate (NSF) and PCE are the main types popularly used in most of the cement-based materials nowadays. Their impacts on the properties of fresh cement pastes (fcps) including the rheological properties and hydration kinetics as well as on the strength development and pore structure of hardened cement pastes, have been intensively investigated for many years, and remain an ongoing field of research today [3–10].

Extensive research has been carried out for understanding the plasticizing effects of NSF and PCE in the context of investigating the interactions between the superplasticizer molecules and cement grains. The superplasticizers added to a cement paste suspension can be divided into three parts: integrated in the hydration products such as Afm and C–S–H, adsorbed onto the surface of cement grains as well as hydration products and remaining in the aqueous phase [4]. It has been widely accepted that the dispersing capability of superplasticizers is closely linked to their adsorption behaviors on the surface of cement grains [4]. This stimulated the interest of many researchers in the investigation of the adsorption behaviors of superplasticizers on cement surface, including the adsorption isotherms, the driving force of adsorption and even the conformation of the adsorbed superplasticizer molecules, etc. It has been found that the driving force of adsorption and the adsorption capability greatly differ from the varied types of superplasticizer [11–15]. NSF superplasticizer is physically adsorbed on the surface of cement grains via electrostatic forces while PCE bearing $-COO^-$ groups interacts with cement grains through both electrostatic forces and the complexation bonding between $-COO^-$ and Ca^{2+} [16,17]. PCE with the higher molecular weight, lower side chain density and shorter side chains is favorable to achieve a higher adsorption amount on cement surface [13]. Similarly, the conformation of the adsorbed polymers also depends on their molecular architecture and dosages [11,18,19]. So far, it has been accepted that the adsorption isotherms of both NSF and PCE superplasticizers generally conform to Langmuir monolayer adsorption [15,20–24]. The dispersing forces between cement grains are immediately introduced by the adsorbed superplasticizer molecules. Due to large adsorption amounts and high anionic charge density in the molecules, the adsorption of NSF homogenizes the surface charges of hydrating cement grains and creates electrostatic repulsive forces between cement grains [16]. PCE presents

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a higher dispersing capability because of the introduction of an additional steric by the adsorbed molecules, although its adsorption amount and charge density are lower than NSF [17]. It is qualitatively believed that for a certain superplasticizer, the larger adsorption amount on cement grains usually brings about higher fluidity of fcps, and the fluidity reaches maximum after the adsorption is saturated [4, 15].

On the other hand, the addition of superplasticizers has strong influences on the hydration kinetics of cement, generally observed as a retardation effect [8,13]. Mollah et al. [14] proposed that the influences of superplasticizers on cement hydration might originate from three aspects: 1) the adsorbed superplasticizer layers hindered the diffusion of water and ions at the cement–solution interface; 2) the Ca^{2+} ions in aqueous solution might be chelated by the $-COO^-$ groups in PCE molecules and thus the nucleation and precipitation of hydrates were inhibited; 3) better dispersion of cement grains caused by superplasticizers changed the growth kinetics and the morphology of hydrate phases. It has been well accepted that the retardation effects of superplasticizers are related to the adsorption amounts of superplasticizers on cement surface. A higher adsorption amount usually results in a stronger retardation effect on cement hydration. By contrast, Yamada et al. [25] reported that higher concentrations of the carboxylic and sulfonic groups remaining in the aqueous phase could more effectively delay the setting of cement paste. That is to say, those non-adsorbed PCE molecules play an important role in the retardation effects. What the mechanism is behind remains unanswered.

In spite of mounting efforts put on the topic, there are still open questions concerning detailed mechanism through which superplasticizers affect the fluidity of fcps and cement hydration. For example, what are the adsorption behaviors on cement surface for different types of superplasticizer, such like NSF and PCE? How are the enhancement of the fluidity of fcps and the retardation effects dependent on the dosages of superplasticizers? Can the enhancement of the fluidity and the retardation infinitely grow with the dosages? In this paper, the adsorption behaviors of two selected typical superplasticizers, NSF and PCE as model superplasticizers, were comparatively investigated by means of total organic carbon (TOC) measurement. Fluidity test and calorimetry were conducted in the cement pastes with varied dosages of superplasticizers. The correlations of the dispersing capability and the impacts of NSF and PCE superplasticizers on cement hydration with their adsorption on the surface of cement grains were then ascertained. The identification on the correlations may lend the theoretical support to the development of new superplasticizers with more efficient and robust performance.

2. Experimental

2.1. Materials and sample preparation

Commercial reference cement P·I 42.5 complying with the Chinese standard GB8076-2008 was used and its composition is listed in Table 1. The content of $CaSO_4$ in the cement is 4.9%. The fineness of the cement is 2.3% and the density is $3.10\ g\cdot cm^{-3}$.

Two types of superplasticizer were used in this study including a self-synthesized polycarboxylate (PCE) type superplasticizer and a commercial polycondensate type superplasticizer of β-naphthalene sulfonate formaldehyde (NSF). The PCE superplasticizer was a comb-shaped co-polymer of acrylic acid (AA), methyl polyethylene glycol methacrylate (MPEGMA) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) with a monomer molar ratio of 2.12:1.00:0.29 prepared via free radical polymerization by using ammonium persulfate (APS) as initiator at 80 °C. The weight average molecular weight (Mw) of MPEGMA was about 1300 and the average polymerization degree of the poly (ethylene oxide) was about 28. AMPS monomer was used to introduce a certain amount of $-SO_3^-$ groups into the polymer chains of PCE, which is popular in many PCE structures [20,25]. By such amount of $-SO_3^-$ groups in PCE chains, it is believed that the adsorption of PCE on cement surface could be enhanced to some extent and the electrostatic repulsion among cement grains with PCE adsorption layers can also be strengthened.

A general description of the preparation procedure of the PCE superplasticizer is summarized as following. 70.0 g of water was pre-charged into a flask vessel equipped with two feeding pipes. The flask was firstly washed by using nitrogen gas for 3 times and heated up to 80 °C in an oil bath. 196.0 g of the mixture of monomers, together with 1.3 g of the chain transfer agent, was dissolved in 170.0 g of deionized water. Initiator solution was prepared by dissolving 1.0 g of APS in 40.0 g of deionized water. Then the initiator solution and the monomer solution were separately fed into the vessel dropwise over 2.5 h and 2.0 h respectively. The inside temperature was kept constant at 80 ± 2 °C during polymerization. After completion of dosing, the whole reactant mixture was kept at 80 °C for an additional post-polymerization time of 30 min under stirring to complete the polymerization and then was allowed to cool down to a room temperature at 25 °C. An aqueous solution of PCE superplasticizer with a solid content of ca. 40 wt.% was obtained. The number average molecular weight (Mn) of the synthesized PCE was 3.66×10^4 and the polydispersity index (Mw/Mn) was 2.48.

The commercial NSF superplasticizer was provided by the Huadi Synthetic Material Co. Ltd.

The mass solid/solid ratios of superplasticizers to cement (P/C) varied from 0 to 2.0% in the preparation of the cement pastes. 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.

All the specimens were prepared in accordance with the Chinese standard GB/T8077. Water and superplasticizers were firstly added into a mixer, and then the cement was gradually introduced over a time span of 2 min into the mixer at 62 rpm. After a 10 s interval, mixing was resumed for an additional 2 min at 125 rpm. The freshly mixed cement pastes were instantly subjected to the following measurements.

2.2. Test methods

2.2.1. Fluidity

In this study, a fluidity test of fcps was carried out to investigate the dispersing performance of NSF and PCE. The fluidity of the fcps was characterized by spread diameter in a mini-cone test, in which a copper cone with a top diameter of 36 mm, bottom diameter of 60 mm and height of 60 mm was used. After well mixed, the fresh paste was poured into the cone right away and then, the cone was quickly lifted up. After the paste stopped flowing, the average value of four crossing spread diameters of the cement paste was recorded.

2.2.2. Adsorption amount

The adsorption amounts of superplasticizers on cement grains were measured by a TOC analyzer (Shimadzu, TOC-VCPH, Japan), the

Table 1
Chemical and mineral composition of cement.

Chemical composition (*mass* %)									Mineral composition (*mass* %)			
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2Oeq	f-CaO	SiO_2	C_3S	C_2S	C_4AF	C_3A
21.68	4.80	3.70	64.90	2.76	0.29	0.56	0.93	21.68	57.34	18.90	11.25	6.47