



Research paper

Effect of polyacrylic acid emulsion on fluidity of cement paste

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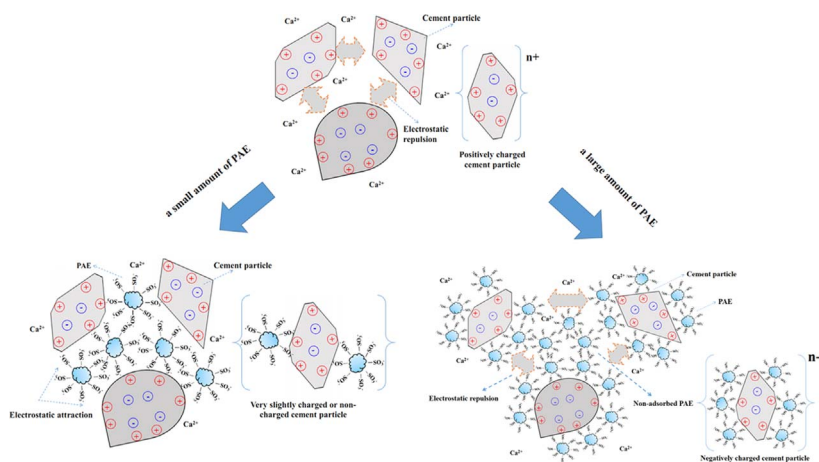


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GRAPHICAL ABSTRACT



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ABSTRACT

Polymer-modified cement-based materials (PMC) have been widely applied in civil construction and municipal projects. In order to obtain deeper insight into the workability of PMC, the effect of polyacrylic acid emulsion (PAE) on fluidity of cement paste was investigated in this study. The fluidity was assessed with mini slump, and the change of Ca^{2+} concentration in pore solution was tested with inductive coupled plasma emission spectrometer. Zeta potential and adsorption behavior were characterized to reveal the mechanism behind the fluidity results. The results show that the effect of PAE on fluidity depends on the added dosage: dosage less than 5.0% reduces the fluidity, while the opposite is true with dosage more than 5%, which can also be indicated from the change of Ca^{2+} concentration in pore solution. Conductivity and X-ray photoelectron spectrometer (XPS) results demonstrate the chemical adsorption of PAE on the surface of cement particles. Dynamic light scattering (DLS) results strongly prove that the surface group of the PAE used is SO_3^- rather than COO^- . Finally, the dispersion model was proposed to illustrate mechanism behind: with a small amount of PAE, the decline in zeta potential caused by adsorption of negatively charged PAE and the agglomeration of cement particles caused by electrostatic attraction of PAE are responsible for the reduced fluidity; while with a great amount of PAE, the negatively increased zeta potential, lubrication effect provided by non-adsorbed PAE, and filling effect of PAE are the main

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reason for the increased fluidity. Such results would give deeper understanding about the effect of polymer emulsion on rheology of cement paste.

1. Introduction

In recent years, polymer-modified cement-based materials (PMC) have been widely applied in civil construction and municipal projects, and increasingly attracting the attention in research area and industrial area in civil engineering [1]. The main reason for this is due to its excellent performance, such as impermeability, workability, adhesive strength, and toughness [2–4].

Many attempts have been made in the literatures to clarify the mechanism behind the improvement of polymers in performance of cement-based material [5]. Three-step model, proposed by Ohama, has been accepted as the most popular one in these reported studies [6]. As illustrated in this model, first of all, polymer particles would be dispersed in cement suspension; and then in the process of cement hydration, a continuous close-packed layer, mainly composed of polymer particles, should be formed on the surface of cement particles; finally, all these layers would coalesce into a continuous film, and more importance is that this film should be uninterrupted in order to interpenetrate throughout the cement hydrates. It is inferred that the first step, namely dispersing polymer particles in cement suspension, is of great importance, and it would further affect the following two steps. These results would help us understand the interaction between polymer particles and cement particles in PMC [7].

In order to achieve the aim of the first step in Ohama model, these nano polymer particles should be efficiently dispersed. However, cement hydrates may exert negative effect on dispersing the polymer particles. As reported, polyacrylate latex could chemically react with Ca^{2+} in cement hydration process, and this interaction could provide crosslinking, namely the combination between Ca^{2+} and COO^- , to enhance the basic performance of PMC [8]. Even though this phenomenon was found in hardened paste, cement hydrates formed at the very beginning may negatively affect the dispersion process of polymer particles [9,10], with negative influence on the achievement of the first step in Ohama model. It is worth noting that polymer particles can quickly adsorb onto the surface of the cement particles, and the adsorption may significantly affect the rheology of the cement paste [11,12]. To be more precise, these polymer particles adsorbed can alter the structure of interface between liquid and these particles, thereby affecting the interface performance, such as zeta potential and surficial structure. The interface performance would significantly influence the rheology of the cement paste, and further determine the pumpability, self-compacting, and self-leveling [13], being similar to that in cement paste plasticized by superplasticizer [14]. Taking superplasticizer for example, superplasticizer adsorbed on the surface of cement particles can change zeta potential to improve the fluidity [15]. Actually, in real engineering practice, workability is one of the most important performances for cement-based materials, which determines the application in some sense. Therefore, to obtain deeper insight into the effect of polymer particles on rheological properties of the cementitious materials is of both scientific and practical importance.

Polyacrylic acid emulsion (PAE) is one of the most popular polymers used for PMC. With addition of PAE, on the one hand, the carboxyl group would be combined with Ca^{2+} in pore solution and Ca^{2+} on the surface of cement particles; on the other hand, PAE would adsorb on the surface of cement particle. Both these processes most likely affect the dispersion of polymers, and also influence the rheology performance of PMC. In this study, the effect of PAE on fluidity of cement paste was investigated. The fluidity of the paste was assessed with mini slump. Ca^{2+} in pore solution was tested with inductive coupled plasma (ICP) emission as supplementary evidence to further clarify the fluidity

results. Zeta potential was measured to characterize the interface performance of cement particles. Adsorption behavior was discussed with total organic carbon analyzer (TOC), X-ray photoelectron spectrometer (XPS), dynamic light scattering (DLS) and conductivity; and then the surface structure of PAE was deduced. Finally, a dispersion model was proposed to illustrate the mechanism behind. Such results would show deeper understanding about the interaction between polymers and cement particles.

2. Experimental

2.1. Materials

2.1.1. Cement

An ordinary Portland cement (P.I 42.5, supplied by China United Cement Co., Ltd., China), in according with Chinese standard GB175-2007, was used in this study. The chemical compositions obtained with X-ray fluorescence spectrometer (Axios advanced) is shown in Table 1, and the basic information obtained from the company is shown in Table 2.

2.1.2. Polyacrylic acid emulsion

Commercially available polyacrylic acid emulsion (PAE), a white and milky liquid, was used in this study. The physical properties of PAE are shown in Table 3. The pH value of PAE was tested with a pH meter. PAE (1.0 g/L) was obtained from the raw PAE, and then the particle size was characterized with Dynamic light scattering (DLS, Zetasizer Nano, made by Malvern instrument Ltd., UK). The solid content was tested in accordance with the Chinese standard GB 8077-2012. Additionally, raw PAE (0.5 g) was added into deionized water (49.5 g) and mixed, and the zeta potential was then tested with a zeta potential analyzer (Zetasizer Nano ZS, made by Malvern instrument Ltd., UK). PAE used in the experiment was marked as solid content.

2.2. Test methods

2.2.1. Fluidity of the cement paste

PAE modified cement pastes were prepared with a water/cement ratio ($w/c = 0.50$) and addition of various dosages of PAE (0%, 2.5%, 5.0%, 7.5%, 10.0%, 20.0% of cement). The initial fluidity (within 5 min) was measured with a truncated cone mold (height: 60 mm; top diameter: 36 mm; bottom diameter: 60 mm) in accordance with the Chinese standard of GB/T 8077-2012. The truncated cone was filled with the paste on a glass plate, and then removed slowly. The maximum diameter of the spread sample and the maximum width perpendicular to that diameter were measured. The average of these two results was defined as the fluidity value.

2.2.2. Adsorption amount

PAE (0–12.0 g/L), diluted by deionized water from raw PAE, was prepared in advance. Cement (1.0 g) was then mixed these emulsions (10.0 g) by magnetic stirrer. After stirred for 5 min, the mixture was separated by centrifugation at 3500 r/min for 5 min. The upper solution was prepared for the TOC measurement.

Table 1
Chemical composition of cement (wt%).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Loss
21.402	5.277	3.017	61.917	2.459	2.689	0.758	0.056	1.913

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