Consequences of competitive adsorption between polymers on the rheological behaviour of cement pastes

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ABSTRACT

Self Compacting Concretes (SCC) are characterized by their high fluidity so they can be placed in sections with congested reinforcements and in restricted areas without vibration. Furthermore, SCC cement paste has to be viscous enough to avoid segregation and to maintain the stability of the suspension until the onset of hardening. To fulfil these rheological requirements, mix design engineers combine use of superplasticizers and viscosity agents. The mechanism of action of these chemical admixtures is very sensitive to their adsorption. The blending of these polymers generates a competitive adsorption on surface sites of cement particles, which influences their performances. For a better understanding of competitive adsorption, we measure here both the amount of adsorbed polymers and its consequences on the rheological behaviour of the system in terms of yield stress and plastic viscosity. Our results suggest that the competitive adsorption prevents some of the polymer molecules from adsorbing, thereby moderating the performances of adsorbing polymers and enhancing the effects of polymers potentially in solution on the rheological properties of cement paste.

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1. Introduction

Polymers are fundamental ingredients for formulating a self-compacting concrete. Understanding the mechanism of action of these polymers is a key in selecting effective admixtures for various practical applications. A vast literature has studied the effect of these macromolecules on the rheology of cement pastes. These polymers either stay in the interstitial fluid, modifying its rheological behaviour, or adsorb at the surface of cement grains, modifying their colloidal interactions [1,2]. Most of these studies, however, have focused on individual polymers. In order to reach the rheological target requirements for self-compacting concretes, mix design engineers have to mix various organic molecules. When the polymers added to the system are both adsorbing species, a competitive adsorption may occur. The outcome of this adsorption competition between molecules shall dictate the rheological behaviour of the SCC. In this work, we studied the competitive adsorption of a so-called viscosity agent and of a plasticizer molecule. We measured both the amount of adsorbed polymers and its consequences on the rheological behaviour of the system in terms of yield stress and plastic viscosity.

Our results show that competitive adsorption prevents some of the polymer molecules from adsorbing. This process moderates the performances of adsorbing polymers and enhances the effects of polymers remaining in solution on the rheological behaviour of cement pastes.

2. Materials and procedures

2.1. Materials and mixing procedures

The cement used in this study is a Portland cement CEM I 52 PMES CP2 (SAINT VIGOR LAFARGE). The polymers investigated here belong to two different families of polymers: a superplasticizer (polycarboxylate) referred as PCE and a cellulose derived viscosity enhancing agent (methyl-hydroxy-ethyl cellulose) referred as CE. They were used in liquid form. The preparation procedures of cement pastes for both rheological and adsorption measurements were identical. Water and cement were first homogenized by hand before a one minute high speed mixing phase using Turbo test Rayneri VMI mixer at 840 rpm. The cement paste was left at rest for 18 min before polymer addition in order to allow for the nucleation of the first hydration products without any interference with the organic molecules [3]. Polymer addition was followed by a 1 min high speed mixing phase. The mixture was then finally mixed at low speed for 18 min.

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2.2. Adsorption measurements

After the mixing protocol described above, the cement pastes were centrifuged at 1000 g during 10 min in order to extract the interstitial fluid.

The carbon content was determined using a Total Organic Carbon analyser (TOC) manufactured by Shimadzu. The results were corrected for the carbon contained in cement powder mostly because of the presence of grinding aids. The quantity of polymer adsorbed was then computed from the difference between the carbon content in the interstitial solution extracted by centrifugation solution before and after contact with cement [4].

2.3. Rheological measurements

Rheological experiments were conducted using a Bohlin C-VOR shear rheometer equipped with a Vane geometry [5]. The Vane tool diameter is 25 mm, the outer cup diameter is 50 mm whereas its depth is 60 mm. The cup of the rheometer was filled with the tested cement paste and the measurement sequence was started. In order to bring the cement paste to a reference structural state, it was first pre-sheared at a shear stress equal to 90 Pa during 120 s. A decreasing shear rate was then directly applied from $100 \, s^{-1}$ to $1 \, s^{-1}$ (with a logarithmic distribution of shear rates) during 200 s.

3. Experimental results

3.1. Single adsorption isotherms of CE and PCE on cement

The measured adsorption isotherms for both polymers are reported in Fig. 1. Both adsorption equilibrium data are well fitted by the Langmuir representation.

$$\Gamma = \frac{\Gamma_m K_L C_e}{1 + K_L C_e}$$

where Γ (g/kg of cement) is the adsorbed polymer amount per mass of cement, Γ_m is the maximum adsorbed, K_L (L/g) is the Langmuir constant and C_e (g/L) is the concentration of polymer remaining in the suspending fluid.

Determination of the maximum adsorbed amount Γ_m and the Langmuir constant K_L for these polymers on cement particles is carried out for comparison purpose. These fitting parameters are given in Table 1. The plateau value for PCE is around three times
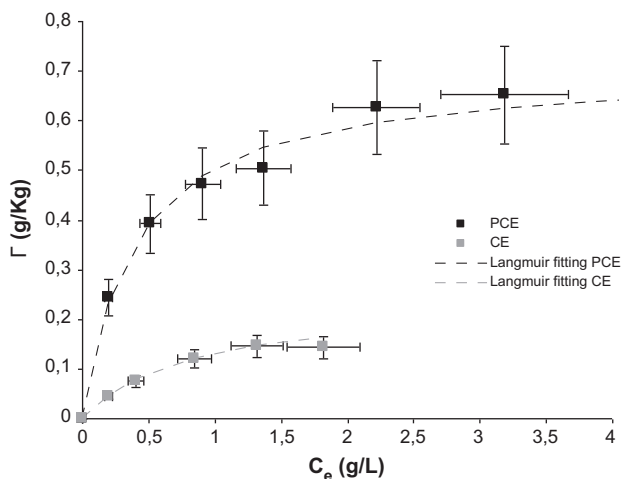
Table 1
Langmuir parameters for adsorption of PCE and CE.

Polymer	K_L (L/g)	Γ_m (g/kg)
PCE	2.5	0.7
CE	1.24	0.24

higher than CE. The Langmuir constant of CE is around two times lower than the Langmuir constant of PCE.

3.2. Competitive adsorption between CE and PCE

Adsorption of PCE and CE when simultaneously added to the cementitious system are measured and compared to their individual adsorptions in Fig. 2, in which the ratio between dosage of PCE and CE is constant (PCE/CE = 0.3). As the TOC technique does not allow for a distinction between the two polymers, the total amounts of adsorbed polymer and polymer remaining in solution are expressed in Carbon/kg of cement and Carbon/L respectively. We also plot in Fig. 2 the resulting sum of the polymers individual adsorption. The abscissa or ordinate of this curve, for a given amount of PCE and CE, are respectively computed by simply summing the abscissa or ordinate of both PCE and CE single adsorption.

It can be noted that the measured total adsorption is systematically lower than the sum of the individual adsorptions, indicating that competitive adsorption seems to prevent some of the polymer molecules from adsorbing. This reduction in adsorption seems to increase when the amount of adsorbed species becomes closer to the saturation plateau.

3.3. Rheological consequences

In order to get additional information on the competitive adsorption between the two polymers, we now measure the rheological changes in the system due to a change in polymer proportions.

The apparent viscosity is plotted as a function of shear rate for some of the tested cement pastes (W/C = 0.4) in Fig. 3. Each flow curve is fitted with a Bingham model in order to compute the value of yield stress and plastic viscosity. The dependence of yield stress and plastic viscosity on dosage and type of admixture is shown in Figs. 4a and 4b. We observe, as expected, a decrease in plastic viscosity and yield stress with the dosage of PCE. The addition of CE, however, increases both yield stress and plastic viscosity.

The effects of these two polymers on cement paste rheology can be explained by their mechanism of action from literature. On one
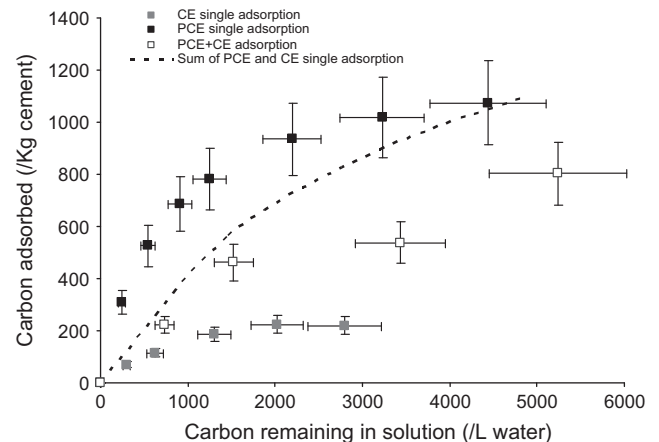

Fig. 1. Adsorption isotherms of PCE and CE on cement paste.

Fig. 2. Measured and computed adsorption of PCE and CE.