



Organic admixtures and cement particles: Competitive adsorption and its macroscopic rheological consequences



Hela Bessaies-Bey^a, Robert Baumann^b, Marc Schmitz^b, Michael Radler^b, Nicolas Roussel^{a,*}

^a IFSTTAR, Laboratoire Navier, Université Paris Est, France

^b Dow Construction Chemicals, Horgen, Switzerland

ARTICLE INFO

Article history:

Received 21 July 2015

Accepted 22 October 2015

Available online 4 December 2015

Editor: Keith Baldie

Keywords:

Adsorption (C)

Admixtures (D)

Polymers (D)

Rheology (A)

Cement paste (D)

ABSTRACT

In this work, we study the competitive adsorption in cement paste between a superplasticizer and a so-called viscosity agent along with the competitive adsorption between the same superplasticizer and a retarder. We develop a new protocol using dynamic light scattering, which allows for distinguishing the relative adsorption of different fractions of admixtures when introduced simultaneously in cement paste. Our results show that the result of competitive adsorption is not only a matter of admixture chemical structures or physical properties but is also very dependent on surface coverage. We identify from our results, similarly to other authors in polymer literature, three main competitive adsorption regimes. We finally show that the outcome of competitive adsorption measured at the microscopic scale can explain the measured macroscopic variations in rheology in terms of yield stress and viscosity.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Admixtures are fundamental components of cementitious materials in the fresh state. In the construction materials industry, these admixtures can be chosen among an impressive variety of molecules with very different chemical structures and physical properties. Some of them, called plasticizers or superplasticizers, allow, for instance, for a decrease in the yield stress [1] and viscosity [2] of the material, in which they are introduced. Some others, called viscosity agents or stabilizers, allow for a decrease in bleeding and segregation [3] or an enhancement of water retention capability [4–6]. Retarders can also be used to postpone cement hydration [7,8] and therefore increase flowability retention and what is often called the “open time” of the product [9,10]. When targeting specific rheology requirements, mix design of cementitious materials is generally achieved through the blending of these different admixtures.

A major source of difficulty in the simultaneous integration of various admixtures in a cement paste lies in the competitive adsorption between these molecules at the surface of cement particles [11–20]. From a more general point of view, this issue relates to the adsorption competitions between all adsorbing species (i.e. including ions) in the system. As the outcome of this competition dictates the rheological behavior of the cement paste by dictating the nature and intensity of cement particles interactions, the understanding and prediction of this competition

has become of utter importance for the mix design engineer [21]. An example that has been extensively studied in the literature of cementitious materials is the competition between sulfate ions and superplasticizers [22,23]. By adsorbing on the surface of cement particles, these ions restrict the adsorption of polycarboxylate-type superplasticizer and therefore affect their dispersion efficiency from a macroscopic point of view.

In this work, we focus on the competitive adsorption between a superplasticizer molecule and a so-called viscosity agent along with the competitive adsorption between the same superplasticizer and a retarder. We develop a new protocol using dynamic light scattering, which allows for distinguishing the relative adsorption of different admixtures added to a cement paste. We identify from our results, similarly to other authors, three main competitive adsorption regimes. We finally measure the macroscopic changes in rheology in terms of yield stress and residual viscosity and correlate them to the outcome of the competitive adsorption observed at the microscopic scale.

2. Materials

2.1. Cement

The cement used in this study is an ordinary Portland cement equivalent to ASTM Type I cement. Its chemical composition obtained through ICP-AES and ATD-ATG is given in Table 1. Its Bogue composition is also given in Table 1. The free lime content was determined by extraction with hot ethylene glycol [24]. The cement powder maximum

* Corresponding author.

E-mail address: nicolas.roussel@ifsttar.fr (N. Roussel).

Table 1

Main document only. Chemical and Bogue compositions of the cement studied here.

C ₃ S	C ₂ S	C ₃ A	C ₄ AF	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	CaO free	L.O.I.
64%	14%	2.50%	14%	21%	3.34%	4.14%	65.43%	0.83%	0.22%	0.35%	0.69%	1.53%

packing fraction was estimated to be around 60% in [25] and its Blaine specific surface is $3650 \pm 100 \text{ cm}^2/\text{g}$.

2.2. Polymers and molecules

We study here a comb co-polymer (PCE) in the flexible backbone worm regime as defined in [26]. It is a poly-carboxylate with methacrylic acid backbone and polyethylene oxide side chains prepared specifically for this study by the Dow Chemical Company® through an esterification process. Its molecular structure is shown in Fig. 1a. The number of monomers in the backbone is in average 60 whereas each side chain contains in average 23 monomers. The grafting ratio is 1/3 and the polymer molar mass, computed from its molecular structure, is approximately 20,000 g/mol. Grafting density was determined from stoichiometry of reactants.

We also study here a sodium gluconate (NG). Its chemical structure is shown in Fig. 1b. It is an organic molecule mostly used as a retarder in cement pastes [7,8]. In some cases, it can also be used as a plasticizer [9, 10]. It was purchased from Sigma Aldrich and provided in powder form. Its molecular weight is around 200 g/mol.

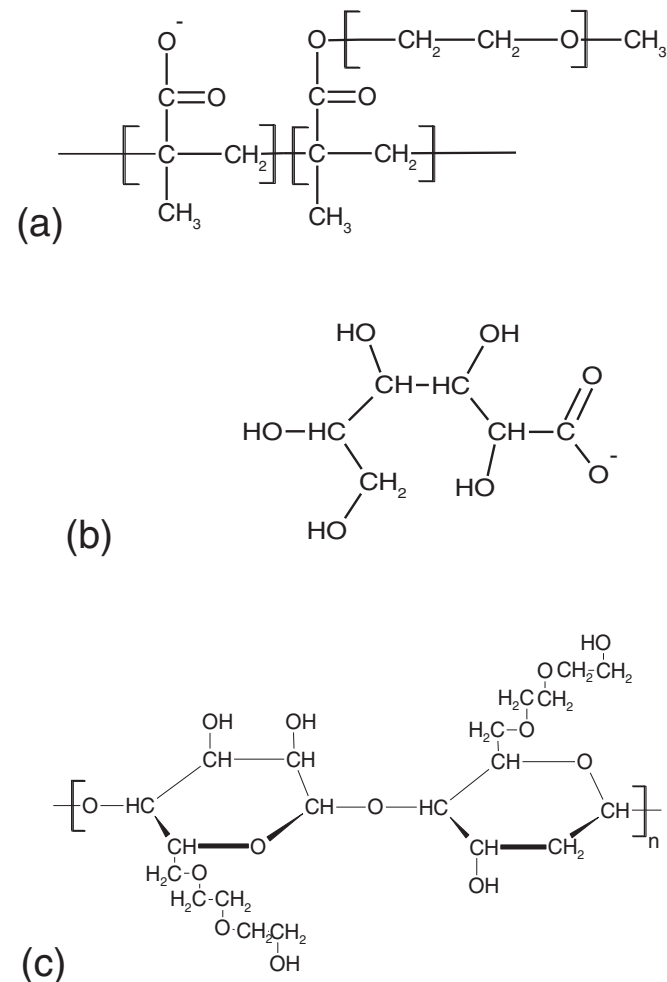


Fig. 1. Molecular structures of (a) polycarboxylate, (b) sodium gluconate and (c) hydroxyethyl cellulose.

We finally test here a hydroxyethyl cellulose derivative (HEC). The hydroxyl groups of the initial glucose units were partially replaced by hydroxyethyl groups (cf. Fig. 1c). The resulting molecule is a linear copolymer defined by its molar mass and the degree of substitution [29]. This degree of substitution (DS) is the average number of substituted hydroxyl groups per glucose unit. The molar substitution (MS) is the average level of hydroxyethyl substitution on the cellulose chain. For the HEC studied here, $\text{DS} = 1.0$ and $\text{MS} = 1.9$. Average molar mass by weight was estimated by viscosimetry as being around 6.10^5 g/mol . This cellulose ether was washed with hot water during the production process. The Dow Chemical Company® provided this macromolecule.

3. Experimental protocols

3.1. Mixing protocol

All cement pastes were prepared with the same mass ratio $\text{W/C} = 0.4$. Only dosage and nature of organic admixtures varied from one sample to another. All sample preparations were carried out at 20°C . We used, in this work, a mixing protocol, which was shown to limit the consequences of any early chemical interactions such as polymer intercalation or co-precipitation [30]. This is crucial, for instance, in the case of polymers such as PCE, for which the measured polymer depletion in the solution can partially find its origin in other modes of polymer fixation in the paste than surface adsorption [31,32]. The cement paste preparation was carried out in several steps. The first step was common to all cement pastes studied in the following. The cement powder and 80% of the amount of water were first homogenized by hand and then mixed during 1 min using a Turbo test Rayneri VMI mixer at 840 rpm. In a second step, the dosage of organic admixtures and the order of addition depended on the studied competitive adsorption as described below.

To prepare the samples for competitive adsorption between PCE and NG, the PCE dissolved in 10% of the amount of water was added to the system 15 min after the first contact between the cement powder and water (*i.e.* we expect that most of the initial aluminates have already nucleated). The cement paste was then mixed in the turbo test Rayneri mixer for 1 min. After 15 min of rest, the NG dissolved in the remaining 10% of the water amount was added to the cement paste. After 15 min of rest, the cement paste was mixed again for 1 min. To study the competitive adsorption between PCE and HEC, we followed the same previous mixing protocol but we replaced PCE and NG by HEC and PCE respectively.

The last step was common to all cement pastes studied here. To carry out adsorption measurements, the liquid phase of the paste was extracted by 10 min centrifugation at an acceleration of 1000 g. As shown in [33] for large polyethylene oxides chains, such a centrifugation protocol is able to extract from the paste non-adsorbed polymer coils as large as several tens of nano meters. To carry out rheological measurements, the cement paste was placed directly in the cup of the rheometer.

It can finally be stated once again that the above delayed mixing protocols were chosen to allow for the assumption that the specific surface or number of adsorption sites in the system did not change much while we measured organic admixtures adsorption and that aluminates did not co-precipitate with the studied admixtures [1,30]. This is obviously never the case in fresh cement paste but this protocol was shown to strongly decrease the variations of the system with time [2,13].

3.2. Total organic carbon measurements

A total organic carbon (TOC) analyzer manufactured by Shimadzu was used in this work. The analysis technique used here involved a

Download English Version:

<https://daneshyari.com/en/article/1456013>

Download Persian Version:

<https://daneshyari.com/article/1456013>

[Daneshyari.com](https://daneshyari.com)