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Using settling behaviour to study mesostructural organization of cement pastes and superplasticizer efficiency

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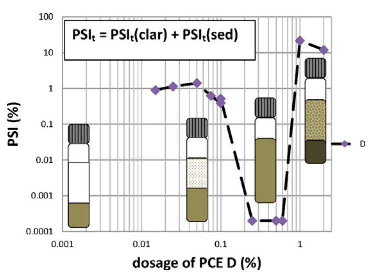
HIGHLIGHTS

- Highlighting influence of organo-mineral interactions on dispersion state of cement suspension.
- Characterization of different polycarboxylate efficiency by settling behaviour study.
- Quantification of stability ranges in function of molecular structure of PCE by a Phase Separation Index (PSI).

GRAPHICAL ABSTRACT



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ABSTRACT

Superplasticizers are polymer admixtures which have been used for decades in the building industry. Their role is to increase the workability of fresh concrete by dispersing cement particles through an electrostatic or steric repulsion mechanism. Their efficiency is generally related to their adsorption ability and intrinsic rheological behaviour of mineral materials. However, at an intermediate scale, mesostructural organization is a major parameter that controls not only the fluidity but also the homogeneity and the stability of a suspension. The aim of this paper is to highlight the relationship between mesostructure and organo-mineral interactions occurring between superplasticizers and mineral particles. The influence of the molecular structure of polycarboxylates (PCEs) on the destabilization phenomena was characterized. Stability ranges were assessed using Turbiscan MA 2000 and quantified by a Phase Separation Index (PSI) inspired by previous works. A relationship with mesostructural organization was established by correlation with the dispersion state characterized by laser granulometry. The affinity of PCEs with cement particles as a function of molecular structure was characterized by Total Organic Carbon (TOC) measurements.

1. Introduction

Superplasticizers have been developed for decades in order to increase the workability of fresh concretes by dispersion of mineral particles composing concrete pastes. Many studies deal with the influence of the molecular structure of superplasticizers on their efficiency [1–5]. The influence of the cement characteristics like chemical composition or specific surface as well as mixing procedure was also studied [6,7]. Most studies in this field focus on adsorption property of superplasticizers and rheological behaviour of the materials in which they are incorporated [8–11]. In this way, fluidity is directly related to the affinity of the polymer for cement surfaces.

However, at an intermediate scale, mesostructural organization is a major parameter that controls not only the fluidity but also the homogeneity and the stability of a suspension.

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Table 1
Characteristics of the cement used.

Chemical characteristics		Value
Na_2O equivalent		0.35%
Oxides	%	
Al_2O_3	4.7	
Fe_2O_3	2.8	
SiO_2	19.4	
CaO	65.8	
SO_3	5.1	
Surface characteristics		Value
B.E.T. specific surface area		1.1 m^2/g
Blaine specific surface		0.4 m^2/g
Specific surface area by granulometry		
• Deionized water		0.3 m^2/g
• Dry way		0.4 m^2/g
Dormant period		
• By conductivity (25 °C)		3 h45

Mesostructural organization can be defined as the organization resulting of interactions between unit or agglomerated particles in an intermediate scale between unit particle one and the suspension. This relationship was studied by some authors with various mineral suspensions like kaolins or alumina. While some studies focused on the influence of the addition of dispersants or surface treatments on particles, others focused on the influence of the suspension solid volume fraction [12–20]. For this reason, the Turbiscan MA2000 from the Formulaction Company was used. This device was indeed developed to study nascent instability phenomena in concentrated suspensions allowing to take into account interparticle interactions present in the suspension [21,22]. The coupling of this technique with other ones such as SEM or laser granulometry allows to provide information about mesostructural organization and hence interparticle interactions.

The aim of this paper is to highlight the influence of mesostructural organization, in connection with organo-mineral interactions (occurring between the superplasticizer and cement particles) on the homogeneity and the stability of fresh cement pastes. This study is focused on Ordinary Portland Cement (OPC) pastes during the dormant period when the chemical reactivity slows down. In these conditions, the physicochemical phenomena are favoured over hydration reactions.

The stability and homogeneity of cement pastes over time as a function of the dosage of several PCE-based superplasticizers (PCE) were characterized using Turbiscan MA 2000 and laser granulometry. The influence of the molecular structure of the PCE on the destabilization phenomena and the stability range was highlighted. A Phase Separation Index (PSI) inspired by the works of Vié [12] was defined to characterize the stability of the suspensions. The relationship with mesostructural organization was established through the correlation with the dispersion state characterized by laser granulometry.

The correlation with adsorption by Total Organic Carbon (TOC) measurements allowed showing the influence of organo-mineral interactions on larger scales. Indeed, the affinity of a PCE with the cement particles as a function its molecular structure was highlighted.

2. Materials and methods

2.1. Materials

A commercial Ordinary Portland Cement provided by Calcia, the characteristics of which are presented in Table 1, was chosen for the preparation of the paste. The cement composition was determined using X-ray fluorescence. The Na_2O equiv. is low, so competitive adsorption with sulphate ion is low [5]. The dormant period, determined by conductivity and calcium concentration measurement, lasts 3 h45 at 25 °C [23]. The Blaine fineness and specific surface areas by laser granulometry show similar low values and slightly higher values than the B.E.T. specific surface area (factor 3), which characterizes the absence of porosity and few agglomeration phenomena on the dry powder.

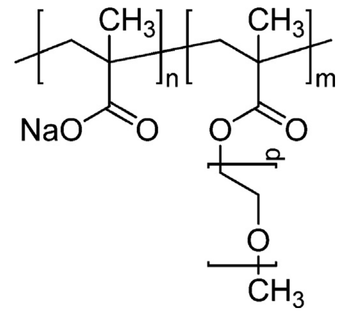

Fig. 1. Molecular structure of the PCEs tested.

Four PCEs provided by the CHRYSO Company (France) were studied and called A, B, C and D later in this paper. They are composed of a poly(methacrylic acid) backbone, responsible for adsorption, partially esterified with methoxy-terminated polyoxyethylene side-chains (PEO) responsible for steric repulsion. The chemical structure is shown in Fig. 1. The ester grafting ratio ($m/n+m$) increases from 10 to 40% through polymers A to D with a fixed PEO length (p) of 45 monomers. This series of polymers was chosen in order to study the influence of grafting ratio on the efficiency of PCE.

2.2. Pastes preparation

Cement suspensions were prepared by adding 200 g of cement powder to admixture solutions in deionized water (liquid chosen to control the water quality: pH, ionic conductivity, etc.) with water to cement ratio of 0.5 (including the amount of water provided by the admixture). Each polycarboxylate was tested through a dosage range up to 1% of dry active matter with respect to cement weight. The mixing equipment consisted in a twisted mixing anchor blade adapted to a Stuart, SS 30 mixer and a stainless steel beaker. The suspension was mixed at a speed of 185 rpm during 20 min before analysis that must be done during the 2 h of the dormant period (checked by conductivity and calcium concentration measurements).

For granulometric, suspension stability and Total Organic Carbon measurements, paste samples were first diluted in deionized water. This perturbation should modify ionic strength and solid-solution equilibrium of studied system, but it was neglected in a first approximation. As far as possible the dilution was the same (30% weight) for suspension stability and TOC analysis.

2.3. Characterization of the cement pastes by TOC and laser granulometry

The particle size distributions of the cement pastes were measured in deionized water using a LS 230 laser granulometer (Beckman Coulter). The optical model used was computed with a refractive index with a real part of 1.7 and an imaginary part of 1. The analysis time was fixed to 1 min. The particle size distributions obtained were expressed in a percent by volume and were normalized to 100%. The particle size distributions as a function of