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Synthesis of phosphonated comb-like copolymers and evaluation of their dispersion efficiency on $CaCO_3$ suspensions part II: Effect of macromolecular structure and ionic strength

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ABSTRACT

The aim of this paper is to investigate effects of macromolecular structure and ionic competition phenomena induced by an increase of ionic strength on the dispersive action of new superplasticizers. These superplasticizers were synthesized and their structure is based on that of polycarboxylates. These superplasticizers are comb-like copolymers with phosphonic acids. Macromolecular parameters studied are the monomer repartition along the carbon backbone and the chain length. Ionic strength is increased either by adding sulfate or nitrate ions. The effects of these factors are then investigated using adsorption, stability and rheology results. It appears that statistical copolymers with phosphonic acids having the shortest chain length are the most efficient in terms of fluidity improvement even in the presence of sulfate or nitrate ions.

1. Introduction

The incorporation of additional components (admixtures and mineral additions) to cementitious materials aims to control the reactivity of the material, as well as its fresh and hardened behavior [1,2]. This incorporation made it possible to formulate concretes that were previously impossible to produce, such as high-performance concretes (HPC) and self-compacting concretes (SCC) [3,4]. Superplasticizers or High Range Water Reducers (HRWR) are among the admixtures commonly added to the cementitious materials. These admixtures allow reducing the water content and thus improving the mechanical properties and durability of the hardened concrete while maintaining workability, or without changing the water content, they allow improving the workability of the fresh concrete by increasing its fluidity.

The most efficient superplasticizers are polycarboxylates PCEs, which allow reducing the water content by 40% [5]. These admixtures are a class of synthetic *comb*-like copolymers possessing poly(ethylene oxide) (PEO) side chains and anionic moieties [6]. In addition to their high efficiency, PCEs also have a good compatibility with different type of cements. In fact, the dispersive action of superplasticizers, such as PCEs, can be influenced by on the chemical composition of the pore solution of cement paste. This chemical composition can vary depending on the type of cement, which can cause incompatibilities with superplasticizers leading to a loss of fluidity [2,3,7]. It is then possible to modify the macromolecular structures of PCEs to avoid these incompatibilities phenomena by adapting their structural parameters (molecular mass, side chain length and ratio, nature and distribution of anionic moieties) to the type of cement [8].

It is well known that sulfate concentration in the pore solution of cement paste significantly affects the action of superplasticizers [9–11]. Superplasticizers can be consumed to form organo-mineral phases (OMP) in the early stages of hydration at low sulfate concentration [12] [13]. Furthermore, ionic competition at high sulfate concentration can occur [14]. The adsorption of superplasticizer on cement particles can be hindered, resulting in loss of the dispersive action.

In the context of nuclear wastes storage, one of the main concerns is the behavior of fresh concrete in the presence of high concentration of nitrates [15]. At such concentration, the phenomenon of ionic competition could potentially take place. Recent studies have been conducted to develop new superplasticizers more resistant to ionic competition [16,17]. These new superplasticizers, based on the PCEs structure, were designed by changing the nature of anionic moieties, with dicarboxylate function [18], or phosphonic acid functions instead of carboxylic acids [19,20]. Pourchet et al. have modified the monomer distribution along the macromolecule backbone, resulting in a gradient

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copolymer [17]. These new PCEs revealed a good dispersive action and an improved sulfate resistance.

In our previous work [21], the synthesis of several comb-like copolymers with phosphonic acid moieties and PEG side chains was described. These copolymers were tested on calcite suspensions in alkaline conditions through adsorption measurement, stability with Turbiscan MA2000, and rheology. Calcite suspensions are commonly used as a model material to overcome the complexity of cementitious materials [22,23] . In fact, physical properties of calcite suspensions are close to that of cement pastes. It has to be kept in mind that the use of calcite suspensions cannot account for the effects of early stages of hydration that occur in the case of cementitious materials. In our previous study, we found that dispersive action is improved when phosphonic acid content in macromolecular structures increased.

The aim of this paper, which is the second part of the previous work, is to investigate the effects of macromolecular structure (monomer repartition along carbon backbone and macromolecular chain length) and ionic competition phenomena on the dispersive action of new synthesized superplasticizers. These effects were studied through adsorption measurement by total organic carbon (TOC), stability by turbiscan, and rheology. The ionic competition phenomena were investigated by increasing the ionic strength of solution by adding sodium sulfate or sodium nitrate.

2. Experimental

2.1. Materials

The new synthesized superplasticizers were tested on calcite suspensions in different ionic media by adding sodium sulfate or sodium nitrate. The calcite BL was supplied by OMYA France. Sodium nitrate and calcium hydroxide were provided by Panreax AppliChem, and sodium sulfate was purchased from Prolabo. The granular and physicochemical characteristics of calcite powder were determined in a previous work [21]. Measured density was of about 2.75 g/cm^3 and specific surface area was 1.25 m^2/g. Calcite particles are of monomorphic angular shape. The particle size distribution was determined by a laser granulometer S13320 from Beckman Coulter Company. Calcite exhibited particle size distribution ranging from 0.1 to 30 μm, with a main mode of about 8 μm. Pourchet et al. [24] found that the zeta potential of calcite clearly depends on the sulfate concentration. In limewater, the zeta potential of calcite is of about 20 mV and decreases with increasing sulfate concentration. For sulfate concentrations higher than 20 mmol/l, Pourchet et al. [24] found that the zeta potential becomes negative. It would have been interesting to measure the zeta potential to understand the effect of ionic strength [25]. However, this measurement was not made, due to the difficulty of performing it at high ionic strength using electrophoresis, and it should be done in a future work.

2.2. Sample preparation

Calcite suspensions were prepared using limewater to ensure alkaline conditions (pH ≈ 12.8) close to cement pore solution. Ionic strength was evaluated using the freeware Phreeqc [26] (Table 1). Ionic salts were added to a milk of lime obtained with an excess of lime $Ca(OH)_2$ in deionized water. Then, the milk of lime containing ions is filtered through a Büchner funnel with a sintered glass disc, resulting in a totally clear limewater containing ions. Note that the formation of gypsum is taken into account by Phreeqc calculations. The solution is re-filtered if precipitated solid particles due to carbonation and/or formation of gypsum are detected.

Calcite suspensions were mixed in a beaker using a magnetic stirrer according to the following sequence: (1) aqueous solution of superplasticizer is added to the freshly prepared ionic solution according to the amount of liquid required, (2) calcite is added with the respect of liquid to solid ratio (L/S) of 0.5, which corresponds to mass fraction ϕ_m of 66.7% and volume fraction ϕ_v of 43%, (3) the suspension is kept under magnetic stirring for at least 10 min before being diluted. Superplasticizer dosage corresponds to the mass of polymer added by the mass of calcite.

2.3. Methods

2.3.1. Total organic carbon (TOC)

The concentration of free polymer in the pore solution extracted from calcite suspensions was measured with the total organic carbon (TOC) analysis. The TOC analysis was performed using a Vario TOC Cube from Elementar. Calcite suspensions were prepared with superplasticizer dosage of 0.5%. This dosage is chosen for different reasons. As described in our previous work [21], there is no marked adsorption difference between superplasticizers for dosages lower than 0.5%. Moreover, limited amounts of polymers have been synthesized. The 0.5% dosage therefore seems to be a good compromise to limit the amount of polymer used for the TOC analysis and to observe adsorption differences between superplasticizers. It should be noted that this dosage is at the plateau for some molecules (statistical PCE-30P and PCE-15P), whereas for others (statistical PCE and Block PCE), this dosage is not yet at the plateau.

Calcite suspension is centrifuged (at 7000 rpm during 7 min) after 10 min of magnetic stirring. Supernatant liquid is filtered with 0.45 μm PTFE filter. Part of this solution (4 mL) is diluted with deionized water with a factor of 5, and then acidified with some drops of concentrated sulfuric acid to prevent carbonation. Different concentrations of ethanol are used to calibrate the device. All the tests were performed in triplicate. The TOC analyzer is calibrated with unadmixtured calcite suspension to take into account the amount of organic carbon in calcite. The standard deviation of TOC measurement is of about ±2.3%.

2.3.2. Stability measurement

Stability measurements were performed by using an optical analyzer Turbiscan MA2000 from Formulaction. This device is an optical analyzer well suited for the study of concentrated suspensions. It is composed by a light source ($\lambda = 860$ nm) moving along a glass tube with a step of 40 μm. The light transmitted across the sample is collected by a transmission detector (0° from incident beam) whereas backscattered light is analyzed by a backscattering detector (135° from incident beam). Evolutions of transmitted and backscattered lights are plotted as a function of column height and time, and are linked to the mean diameter of particles and solid volume fraction from the Lorentz and Mie theory [27]. From sedimentation studies, it is possible to access information about mesostructural organization of suspensions and dispersion/agglomeration phenomena.

Table 1

Quantities of salts to add in order to reach ionic strength targeted. Ionic strength and molar concentrations computed by Phreeqc.

Ionic strength mmol/L	$NaNO_3$					Na_2SO_4				
	Mass to add g/L	$[Na^+]$ mmol/L	$[NO_3^-]$ mmol/L	$pH_{measured}$	$\sigma_{measured}$ mS/cm	Mass to add g/L	$[Na^+]$ mmol/L	$[SO_4^{2-}]$ mmol/L	$pH_{measured}$	$\sigma_{measured}$ mS/cm
66	Limewater: 4 g of $Ca(OH)_2$/L (excess)								12.8	11.4
171	9.4	110	110	13	17.05	7.1	95.3	37.37	13.3	16.75
855	65	760	760	13.1	54.3	48,3	595	225	13.3	65