



Tailoring the anionic function and the side chains of comb-like superplasticizers to improve their adsorption



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ABSTRACT

Nowadays admixtures and especially superplasticizers are unavoidable components of the concrete formulation. The high fluidizing efficiency of the comb-like superplasticizers must not overshadow their high costs. This study aims to determine the PCE structure parameters which influence their adsorption in order to enhance their resistance to sulfate competitive adsorption and thus minimize their dosage. The PCE adsorption has been studied on calcite and ettringite which are both surfaces representative of early hydrating cement. The effect of the POE side chain length and density and also of the PCE anionic function i.e. carboxylate, dicarboxylate or phosphate on the adsorption has been analyzed. As main result, the modification of the anionic is a good technological way to improve the resistance to sulfate competition. At equivalent charge density, the dicarboxylate polymer is less sensitive to sulfate ion concentrations than the monocarboxylate one, while the phosphate PCE is quite insensitive for the concentrations studied.

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1. Introduction

Since their invention in 1981 by Hirata et al. in Japan, the comb-like superplasticizers or polycarboxylate ethers (PCEs) never stop revolutionizing the civil engineering by increasing continually the mechanical and environmental performances of the admixed concrete. At long term, the concrete is more durable because it is less porous. At short term, superplasticizers ensure a high water reduction or a high initial fluidity and also a long slump life. The pumpability is increased enabling to make buildings higher and higher. The fluidizing effect is due to the poly(ethylene oxide) side chains ensuring a steric repulsion. The side chains are grafted on a carboxylate anionic backbone which promotes the adsorption on positively charged surfaces of cement [1]. As demonstrated by numerous studies [2–6], the fluidity is well correlated with the amount of PCE adsorbed by square meter of solid, then a good adsorption ability is unavoidable to attain a high fluidity. A way to improve the workability of future concrete formulation (e.g. cement substitution by secondary cementitious materials, lower water-to-binder ratio, etc.) passes through a better understanding of the adsorption and the parameters able to control it.

The adsorption depends on three entities: a solid interface, a pore solution containing different ions, and a polymer. In the case of portland cement, the main solid interfaces result from the hydration of calcium silicate and aluminate phases. Due to partial dissolution of anhydrous phases, the solution becomes supersaturated according

to some hydrates which can thus precipitate. To study the adsorption, a key point is to know the surface proportion of the various solid interfaces. At long term of hydration (several months or years), a cement paste is mainly composed of calcium silicate hydrates (C-S-H) which have a high specific surface area and are potentially able to adsorb a huge amount of superplasticizers, and also of portlandite and hydrated calcium aluminate phases. The scheme of surface proportion is completely different during the workability period (0–3 h) when PCE superplasticizers must play their fluidizing role. While the hydration of aluminate phases is very fast compared to the silicate phase hydration, a high surface proportion consists of aluminate phases in the early age. The main phases found at this stage are: ettringite, gypsum, a little of C-S-H and of course anhydrous phases. According to previous adsorption studies [7–12], ettringite belongs to the phases that have the highest adsorption capacity of superplasticizer. Ettringite is thus a key phase to understand the rheology and the adsorption of admixed systems as shown by several studies highlighting the effect of tricalcium aluminate [11,13]. As mentioned before, even if C-S-H precipitated in a low amount, their presence can infer a high surface fraction. However in the conditions tested in the literature, superplasticizers do not show a good affinity for C-S-H. By considering a specific surface area of 10–20 m²/g for ettringite and 100–200 m²/g for C-S-H, the adsorption isotherm plateau expressed in mg/m² has been compared on both hydrates [7,9–11]: ettringite adsorbs at least 3–10 times more than C-S-H. The anhydrous phases also induce a significant surface fraction. But the difficulty in studying anhydrous phases lies in their fast hydration as soon as they are in contact with water.

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To simplify the understanding and avoid hydration effects, the adsorption will be studied on inert mineral systems representative of an early hydrating cement system. In contact with a pore solution, the surface of the silicate phases that are preponderant in cement, is seen slightly positive due to calcium ions adsorption. A suspension of calcite in a solution saturated with respect to $\text{Ca}(\text{OH})_2$ is a reliable inert model for these phases and has often been used to study the interactions between anionic polyelectrolytes i.e. superplasticizers and cement [6,14,15]: indeed calcite exhibits surface and colloidal properties very similar to that of silicate phases at early stages of hydration [16,17]. Furthermore to faithfully duplicate cement suspension the chosen calcite has similar specific area and particle size distribution as those of cement particles. We briefly describe the surface of both calcite and ettringite. The structure of ettringite is composed of columns of aluminium and calcium coordination polyhedra lying parallel to the *c*-axis surrounded by six channels filled with sulfate ions and water molecules. The columns bear a positive structural charge. This gives rise to a surface charge density $\sigma_0 = 1.25$ electron/nm² estimated from stoichiometric/structural consideration [18]. In the bulk of the crystal, this structural charge is balanced by the sulfate ions present in the channels. The estimation of the calcite charge is more difficult because of the number of non-equivalent crystal faces in a powder grain.

The second entity is the pore solution containing mainly Ca^{2+} , SO_4^{2-} , K^+ , Na^+ and also OH^- ions giving pH values higher than 12.6 in the case of portland cement. The surface charge and the so-called counter-ions and co-ions form the electrical double layer and induce the apparent charge of the mineral phase seen by the polyelectrolyte in pore solution. Some zeta potential studies can be found in the literature to compare electrokinetic properties of both calcite and ettringite/pore solution interfaces. According to previous results [11,17,18], ettringite and calcite surfaces are positively charged at high pH and in the presence of calcium ions. Considering the zeta potential values of 40 ± 10 mV and 18 ± 2 mV respectively measured for ettringite and calcite suspensions in a 15 mM $\text{Ca}(\text{OH})_2$ solution, the apparent surface charge of ettringite is higher than that of calcite. This behavior reflects the chemistry of the interface previously mentioned. As soon as there are sulfate ions in the pore solution, one can notice an inversion of the apparent surface charge. From 6 mM of sulfate ions, ettringite has an apparent negatively charged surface, sulfate ions overcompensate the positive charge of the columns [11,18]. The ζ -potential of calcite becomes almost negligible when the sulfate concentration exceeds 15 mM due to calcium–sulfate ion pairing. In presence of PCE, there is a competition between anionic PCE and OH^- [19] or SO_4^{2-} [20–22] to charge balance the positive surfaces.

The last entity in the adsorption process is of course the polymer. The adsorption process is a dynamic equilibrium, i.e. a certain polymer equilibrium concentration is reached near the interface. The added polyelectrolyte is thus shared between the pore solution where it interacts with calcium ions according to an electrostatic/non-electrostatic or "specific" way, and, adsorbed onto the surface as a consequence of electrostatic/specific interaction (enthalpic contribution) and release of ions and water molecules from the interface into the bulk solution (positive entropic contribution). Basically an anion (hydroxide or sulfate) is then exchanged by one or two carboxylate, or other anchoring functions, in the double layer. This phenomenon is often reported as a competitive adsorption between anions and polyelectrolyte. It is commonly accepted that the PCE adsorption is sensitive to the sulfate ions. Particularly it is possible to correlate the sulfate/hydroxide sensitivity and the molecular structure as established by Flatt et al. [20,22] for carboxylate polymers. Numerous studies, mainly on cement [2,23–25] or on inert system [6–8,26–28], reported the effect of the length and density of side chains on the adsorption: increasing the PCE grafting ratio is then known to increase its sulfate sensitivity. Most of the PCEs synthesized up to now are derived from polymethacrylate and have an anchoring function carboxylate. A few studies report

the effect of the anionic function on the adsorption such as dicarboxylate, phosphonate or biphosphonate [29], sulfonate [24] and also trialkoxysilane [30]. The sulfonate PCE does not show an improvement whereas silane and phosphonate based polymers enhance the sulfate resistance.

The main objective of this work is to study the adsorption of comb-like polymers on both surfaces, calcite and ettringite, representative of the early age of hydrating cement. These interfaces will be studied in both ionic conditions: an ideal case with only calcium and hydroxide ions and a more realistic case with calcium, hydroxide and sulfate ions. The originality lies in the range of PCE chosen: we analyze the effect of the POE side chain length and density and also the modification of the anionic function. We select the following anionic functions: carboxylate as reference, dicarboxylate and phosphate. From this point of view, we aim to determine the PCE structure parameters which influence the adsorption and can enhance their resistance to competitive adsorption. The high fluidizing efficiency of the comb-like superplasticizers must not overshadow their high costs. The ultimate goal is thus to understand how to minimize the added dosage by an optimization of the adsorption.

2. Materials and methods

2.1. Materials

2.1.1. The mineral interface

The first mineral studied is a natural crushed calcite supplied by OMYA (France). The BET specific surface area with N_2 has been determined after an outgassing at 200 °C during 5 h: $S_{\text{BET}} = 0.7 \pm 0.1$ m²/g.

The second mineral is a synthetic ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$. Ettringite was obtained by precipitation from solutions containing quasi-stoichiometric contents of burned CaO (for 12 h at 1000 °C) and $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ in excess of deionized water (mass of water/mass of ettringite = 20). The suspension was continuously stirred for 3 days at 23 °C. The BET specific surface area with N_2 has been determined after an outgassing at 40 °C during 20 h: $S_{\text{BET}} = 9.9 \pm 0.3$ m²/g.

2.1.2. The solution

The adsorption measurements have been done in various solutions simulating the pore solution in a cement paste to test the sulfate competitive adsorption. In the case of calcite, the solutions were saturated with respect to calcium hydroxide and contained various sulfate concentrations: a known amount of Na_2SO_4 and 1.8 g of CaO was added to 1 L of deionized water. After stirring, the solution was then filtered and mixed with calcite to attain a liquid-to-solid ratio of 0.34.

In the case of ettringite, the pore solution is directly the solution in which ettringite was prepared. It initially contained a slight excess of CaO as initial reagent to reach a final calcium concentration of about 3 mmol/L. In other words ettringite was not filtered and dispersed in a new solution. It allows having a well dispersed suspension of ettringite with a liquid-to-solid ratio of 20. The sulfate ions were added by dissolving a known amount of Na_2SO_4 . The ionic conditions were then determined by atomic emission spectroscopy (ICP OES, Varian Vista Pro) and were given in Table 1.

2.1.3. Comb-like superplasticizers

In order to study the effect of the PCE structure (i.e. side chains density and length), four carboxylate PCEs were synthesized by a living/controlled radical polymerization technique (RAFT) of PEO methacrylate and methacrylic acid with the same polymerization degree ($\text{DP} = 50$) [32]. According to Ref. [32] the reaction conditions used induce a random reactivity between the two monomers. The length of the side chains was set at values of 1100 g/mol (coded s, $z = 25$) and 2000 g/mol (coded m, $z = 45$). Then the chosen grafting degrees ($y/(x + y) = \text{XX} \%$ mol) were 20%, 33% and 40%. Codes for

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