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Fundamental mechanisms for polycarboxylate intercalation into C_3A hydrate phases and the role of sulfate present in cement

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ABSTRACT

The fundamental reactions leading to the intercalation of polycarboxylate (PC) superplasticizers into calcium aluminum hydrates were studied by hydration of pure C_3A in the presence of PC at 75 °C. It was found that the amount of dissolved sulfate present in cement pore solution determines whether organo-mineral phases are formed or not. In the absence of sulfate, PCs easily intercalate during C_3A hydration in alkaline solution. Under these conditions, only excessive steric size of the PC will prevent intercalation. At low sulfate concentrations (SO_4^{2-}/C_3A molar ratios of 0.1–0.35), PC intercalates with intersalated alkali sulfate, are formed. At high sulfate concentrations (SO_4^{2-}/C_3A molar ratios of 0.7–2), PC can no longer intercalate. Instead, sulfate, because of its higher negative charge density, fills the interlayer space and monosulfoaluminates with different water contents are formed.

Anion exchange experiments confirm that from the initially formed C_4AH_{13}, PC will exchange the interlayer OH^- anion whereas with monosulfoaluminates, no replacement of sulfate by PC was found. Consequently, in alkaline solution, PC intercalates will not exchange their PC against OH^- anions whereas sulfate will gradually replace the PC.

Generally, intercalation of PC is an unwanted process because it consumes superplasticizer which is effective only when it adsorbs onto the cationic surfaces of AF_m and AF_t phases. Our experiments demonstrate that intercalation can be avoided by using PCs with long side chains or highly sulfated cements (SO_4^{2-}/C_3A molar ratio ≥ 0.75) containing alkali or calcium sulfates which dissolve fast. In undersulfated cements, however, PC intercalates can be formed, either directly during the stacking process of the $[Ca_2Al(OH)_6]^+$ main layer, with PC acting as the template which determines the interlayer distance, or by anion exchange between initially formed aluminate hydrates (e.g. C_4AH_{13} or C_2AH_8) and the PC anion.

1. Introduction

Polycarboxylate-based superplasticizers (PCs) are recognized as important admixtures for use in modern concrete technology [1]. They allow the production of a highly flowable concrete or to reduce the water to cement ratio of concrete, resulting in higher compressive strength. For optimum use, it is essential to profoundly understand all potential ways of interaction between PCs and the mineral compounds formed during cement hydration. It has been generally accepted that the high range water reduction and the high fluidity of concrete containing PC is attributed to the PCs adsorbing onto the surface of cement hydrate phases [2]. Thus, a layer exercising a steric effect is formed which leads to the dispersion of the cement particles [3–6]. The hydration of tricalcium aluminate (C_3A) and tetracalcium alumoferrite (C_4AF) present in cement can produce hydrocalumite-type layered double hydroxides (LDHs) which have the potential to intercalate various anions between the cationic main layers.

C_3A accounts for approx. 5–10% of the clinker mass of ordinary Portland cement (OPC). During its hydration, the layered phases C_2AH_8 and C_4AH_{13} which belong to the family of calcium aluminum layered double hydroxides (Ca–Al–LDHs), are initially formed as metastable compounds [7,8]. They contain hydroxide as interlayer anion. Depending on temperature, they convert within minutes or hours to the cubic katoite phase C_3AH_6 which is the most stable calcium aluminate hydrate at room temperature. Sulfate, e.g. in the form of gypsum which is commonly present in any OPC to control its setting behavior, can intercalate into the layered calcium aluminate hydrates as well, resulting in $[Ca_4Al_2(OH)_{12}](SO_4)\cdot 6\ H_2O$, or monosulfoaluminate which is also called AF_m phase [9]. Its interlayer is occupied by sulfate anions and water molecules. β-Naphthalene sulfonate (BNS) formaldehyde condensate, a linear unbranched polymer commonly used as superplasticizer, was the first concrete admixture for which intercalation into calcium aluminate hydrate phases has been experimentally confirmed [10]. Also, novel hybrid LDH materials incorporating arene sulfonates such as nitrobenzoic acid, naphthalene-2,6-disulfonic acid

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and naphthalene-2 sulfonic acid have been reported [11]. Recently, we described the intercalation of comb-type PC superplasticizers into calcium aluminum layered double hydroxides formed during the hydration of C_3A in the absence of sulfate [12,13].

Generally, LDHs are host–guest materials consisting of positively charged metal oxide/hydroxide sheets with intercalated anions and water molecules. Their general composition can be expressed by the formula $[M^{II}_{1-x} M^{III}_{x} (OH)_2]^{x+} [A^{n-}_{x/n}] \cdot z\ H_2O$, where M^{II} and M^{III} represent metal cations and A^{n-} the interlayer anion. Allmann and Brown et al. were the first to elucidate the structure of LDHs [14,15]. A schematic illustration of the lamellar structure of Ca–Al–A–LDH is shown in Fig. 1. The steric size and orientation of the anions intercalated between the main layers determine the interlayer distance. The *001* reflection shown in the X-ray powder diffractograms of these compounds allows one to calculate the basal spacing d between the main layers.

Owing to the highly tunable LDH main layer and interlayer composition coupled with a wide possible choice of organic anions, a large variety of LDH hybrid materials has been reported. Various kinds of polymers such as linear polymers, poly(ethylene oxide) derivatives [16], poly(α,β-aspartate) [17], poly(acrylic acid), poly(vinyl sulfonate), poly(styrene sulfonate) [18] and bimolecular DNA [19] have been intercalated between double hydroxide layers. The formation of these hybrid materials may proceed via different pathways such as coprecipitation, anion exchange, surfactant-mediated incorporation, rehydration, or restacking.

In this study, we investigated potential mechanisms of PC incorporation into calcium aluminate hydrates formed during early cement hydration. It is important to understand these potential processes because intercalation reduces the amount of PC available for adsorption and thus decreases its dispersing power. Out of all potential formation processes for LDH compounds mentioned above, rehydration of C_3A and anion exchange between AF_m phases and PC may occur during early cement hydration. Therefore, these two processes were chosen for the study. Coprecipitation was not investigated because of the low concentration of Al^{3+} commonly present in cement pore solution (0.2–0.3 µm/L). Thus, it was concluded that in industrial cements, this potential route of PC intercalation will not be significant. First, the ability of PC to intercalate as a function of its steric size (side chain length) was investigated. Then, C_3A (re)hydration experiments were carried out in presence and absence of PC and with varying amounts of sulfate, representing cements with different ratios between C_3A and sulfate. Finally, anion exchange reactions between PC intercalates and OH^- and SO_4^{2-}, resp., as well as between monosulfoaluminate and C_4AH_{13}, resp. and PC were performed. Our goal was to gain an understanding of conditions favorable for PC intercalation and to develop a scheme of potential reaction patterns involved in the intercalation of PCs into cement hydrate phases.

2. Experimental

2.1. Materials and methods

Pure tricalcium aluminate (C_3A) was synthesized via a sol–gel process followed by calcination of the gel for 14 h at 1260 °C with intermediate grindings [20]. Analysis by X-ray powder diffraction confirmed the resulting product to be pure tricalcium aluminate.

The Ca–Al–A–LDH-phases ($A = SO_4^{2-}$ or OH^-) described in the following were synthesized from freshly prepared calcium oxide obtained by calcination of calcium carbonate for 12 h at 950 °C (p.a., Merck). Additional raw materials were aluminum hydroxide (p.a., Merck), gypsum (p.a., Merck) and C_3A.

Monosulfoaluminate, $[Ca_4Al_2(OH)_{12}](SO_4) \cdot 12\ H_2O$ was synthesized according to a patent [21]. 13.46 g calcium oxide (0.24 mol), 12.48 g aluminum hydroxide (0.16 mol) and 13.77 g gypsum (0.08 mol) were suspended in 27.2 g water and stirred vigorously for 30 min. Next, 15 mL of the resulting suspension were hydrothermally treated in a 20 mL autoclave for 3 h at 180 °C. After cooling to ambient temperature, the paste obtained was removed from the autoclave and air-dried at 50 °C. X-ray powder diffraction confirmed that the product was pure $[Ca_4Al_2(OH)_{12}](SO_4) \cdot 12\ H_2O$ (see Fig. 6).

C_4AH_{13}, $[Ca_2Al(OH)_6](OH) \cdot 3\ H_2O$ was synthesized following the method described by Buttler et al. [22]. We modified their process by using C_3A and lime in water instead of anhydrous $CaO \cdot 2Al_2O_3$ (CA_2) in slightly undersaturated lime solution. Thus, 10.43 g C_3A (0.039 mol) and 2.80 g lime (0.05 mol) were suspended in 200 mL water and were left to react at 5 °C for at least 14 days in a closed bottle under careful exclusion of carbon dioxide. After centrifugation the precipitate was dried at ambient temperature under a nitrogen atmosphere in a desiccator over silica gel and pure C_4AH_{13} was obtained. Note that pure C_3A, suspended at room temperature in water, will react quantitatively within less than an hour to katoite (C_3AH_6), the thermodynamically stable hydration product of C_3A.

The comb structured PC superplasticizers of the methacrylic acid–*co*–ω-methoxy poly(ethylene glycole) methacrylate type were synthesized following a patent instruction [23]. The chemical structure of the PCs is presented in Fig. 2. Gel permeation chromatography (GPC) analysis of the synthesized polymers was performed using Waters 2695 Separation Module, Waters Ultrahydrogel™ 120, 250 and 500 separation columns, Waters 2787 Dual λ UV Absorbance Detector and Waters 2414 Refractive Index Detector. The eluent was 0.1 mol/L $NaNO_3$ at pH 12 (adjusted with NaOH). PC samples were measured in 1 wt.% aqueous solution and filtered through a 0.2 mm filter before the measurement. From GPC analysis, molar masses (M_w, M_n), polydispersity index and size of the dissolved polymers expressed by their hydrodynamic radius were obtained. The results are shown in Table 1.

The specific architecture of the synthesized polycarboxylate macromolecules was determined as well. Based on M_n obtained from GPC data and applying the procedure described in [4], the main chain length (MCL) of the PCs was calculated. The side chain length (SCL) of the PCs is known from the ester macromonomer used in the synthesis. Our PCs with side chains possessing 8.5 and 17 ethylene oxide units (EOUs)

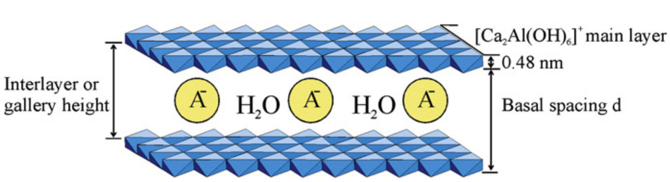

Fig. 1. Schematic illustration of the lamellar Ca–Al–A–LDH structure ($A^- =$ anion).

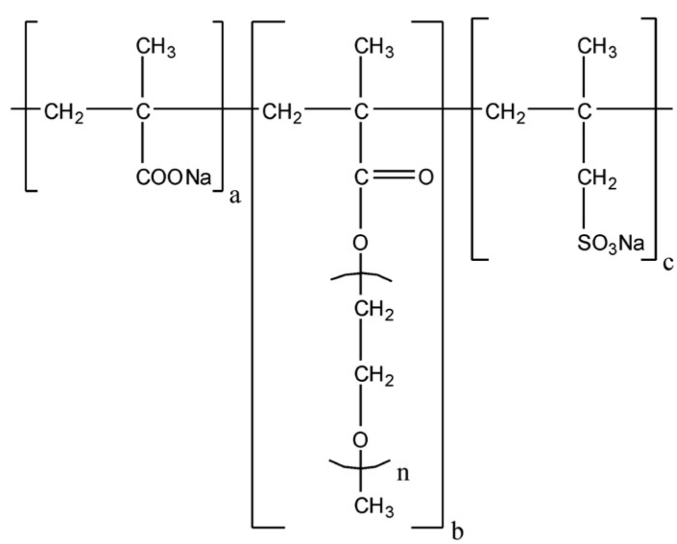

Fig. 2. Chemical composition of the synthesized PCs (a:b:c = 6:1:0.2); n = number of ethylene oxide units.