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Interaction mechanisms between Na montmorillonite clay and MPEG-based polycarboxylate superplasticizers

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ABSTRACT

Sodium montmorillonite clay is shown to negatively impact the dispersion force of two methacrylate based polycarboxylates (PCEs) in cement paste. The PCEs tested consist of methacrylic acid/MPEG methacrylate-ester with molar ratios of 6:1 and 1.5:1. It was found that the PCEs sorb both chemically and physically onto clay. The sorbed amounts are ~100 times more than on cement. Chemisorption occurs via intercalation of the poly(ethylene oxide) side chains into the interlayer region between the alumosilicate layers, while physisorption occurs on clay surfaces which are positively charged through uptake of Ca^{2+}. PCEs possessing high grafting density predominantly intercalate and show less surface adsorption, and vice versa. Also, the type of sorption is dosage dependent, whereby side chain intercalation dominates at higher PCE dosages, while electrostatic attraction via the anionic backbone prevails at lower dosages. Polyglycols can be utilised as sacrificial agents when highly grafted PCEs are employed at high dosages.

1. Introduction

Montmorillonite is a 2:1 smectite clay mineral, consisting of stacked octahedral aluminate layers sandwiched between two tetrahedral silicate layers (Fig. 1). The resulting alumosilicate layers measure about 1 nm in thickness [1]. The general composition of montmorillonite can be expressed as $M_x(Mg,Al,Fe)_2(OH)_2[Si_4O_{10}]\cdot nH_2O$, with $M^+ = Na^+$, K^+, 0.5 Mg^{2+} or 0.5 Ca^{2+}. Partial substitution of Si^{4+} by Al^{3+} generates an overall negative charge of the basal surfaces. This charge is balanced by intercalation of cations (M^+; hydrated or non-hydrated) in between the alumosilicate layers [2].

When clay is dispersed in electrolyte containing fluids such as cement pore solution, cations can also adsorb onto the permanently negatively charged basal surfaces of the clay platelets. Other anchoring sites for cations are the crystal edges where terminal –OH groups from aluminates and silicates are present [3,4]. Under high pH conditions, these terminal –OH groups are deprotonated and develop a negative charge (Fig. 2).

Montmorillonite is among the most researched clay minerals because of its natural abundance and its viscosifying property. Over the last two decades, novel nanocomposites comprising of polymer layered silicates (PLS) were developed whereby a wide range of monomers and polymers including glycols and polyimides intercalates into the galleries of montmorillonite clay. Such PLS nanocomposites, when compared to conventional materials based on glass or mineral fibre enforced polymers showed enhanced mechanical stiffness, strength and barrier properties [5–9]. Specifically, PLS nanocomposites provide enhanced thermal stability to the materials. In the construction field, applicators have observed that presence of certain clays may affect and can be detrimental to the initial workability of concrete [10–12]. Montmorillonite was found to be more harmful than other clays due to its expanding lattices which promote intercalation, swelling and cation exchange [13,14]. The extent of these interactions is dependent on many factors including pH and the type of polyelectrolyte present in the medium. The ability of this clay to sorb water and swell causes an increase in viscosity of the cement paste (a loss in workability) or a higher water demand to produce the same workability as before. This is detrimental for the mechanical properties and durability of concretes [15].

Some studies have shown that polymers can sorb on clay particles [16]. The impact of this process in the construction field is dependent on the type of admixtures used. For superplasticizers, polycondensates were shown to be less affected by the presence of clay than polycarboxylates [10,11,17,18]. This indicates that when concrete is contaminated by a significant quantity of montmorillonite, competing demands by different components (cement and clay) for the polycarboxylate can occur, thus reducing its availability for dispersion. In contrast to PCEs, polycondensates do not show this effect.

In the present study, the effect of clay addition to cement (dosage: 1% by weight of cement) on the behaviour of two polycarboxylate based superplasticizers was investigated. A naturally occurring sodium montmorillonite clay was employed. First, the influence of clay on the workability of cement pastes containing two different

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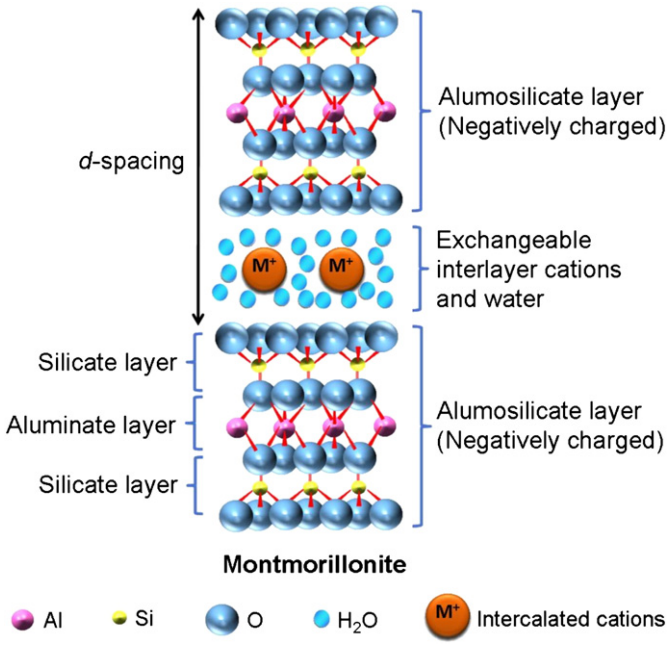

Fig. 1. Schematic illustration of the layer structure present in montmorillonite clay.

methacrylic acid–methacrylate ester based PCEs was determined by 'mini slump' test. The two PCEs varied by their grafting densities and correspondently anionic charge amounts. To ascertain the interaction of these PCEs with clay, their adsorption on the cement/clay mixture was measured via total organic carbon (TOC) method. A simplified system comprising only clay, PCE and synthetic cement pore solution was subsequently utilised to identify the sole effect of clay on PCE. First, the amount of PCE sorbed by clay was determined. XRD analysis was performed to probe a potential chemisorption of PCE by clay. For clarification of the specific interaction of individual PCE building blocks with clay, adsorption of the polymethacrylate backbone and of the poly(ethylene oxide) side chain were studied separately. This investigation was performed by using poly(methacrylic acid) (PMA) and polyethylene glycol (PEG). The individual amounts of side chain or backbone sorbed were used to calculate the idealised amount of PCE sorbed by clay. This way, the mechanism of interaction between PCE and clay in the cementitious system was sought to be clarified.

2. Materials and methods

2.1. Cement

A CEM I 52.5 R HS/NA (Holcim, Lägerdorf/Germany) was used. Its phase composition as obtained by quantitative X-ray diffraction (Bruker D8 advance instrument, software Topas 4.0) is presented in Table 1. The

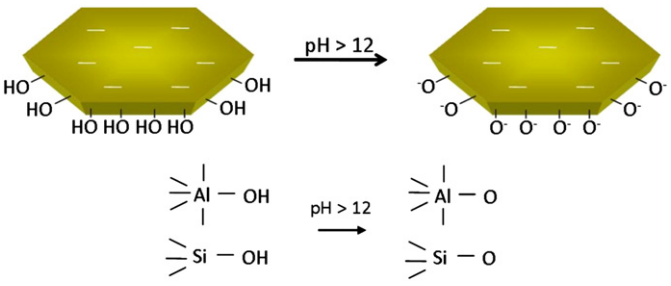

Fig. 2. Schematic illustration of charge distribution and deprotonation of terminal –OH groups present along crystal edges of a montmorillonite particle at high pH.

Table 1
Phase composition of CEM I 52.5 R HS/NA sample as determined by XRD using *Rietveld* refinement.

Phase	[wt.%]
C_3S, monoclinic	60.1
C_2S, monoclinic	19.0
C_3A, cubic	1.2
C_3A, orthorhombic	0.4
C_4AF, orthorhombic	14.5
Calcite	1.3
$CaSO_4 \cdot 1/2\ H_2O$[a]	2.2
$CaSO_4 \cdot 2\ H_2O$[a]	1.0
$CaSO_4$	0.4

[a] Determined by thermogravimetry.

specific surface area of 4300 cm^2/g was measured using a *Blaine* instrument (Toni Technik, Berlin/Germany). The particle size (d_{50} value) of 8.33 μm was obtained on a laser granulometer CILAS 1064 (Cilas, Marseille/France), while the density was 3.22 g/cm^2 measured by ultrapycnometry (Quantachrome, Odelzhausen/Germany).

2.2. Sodium montmorillonite clay

A commercial sodium montmorillonite clay sample (RXM 6020 supplied by Rockwood, Moosburg/Germany) was used as per obtained. This clay is a naturally occurring sodium montmorillonite clay. Its oxide composition is presented in Table 2. It develops a pH of ~9 when prepared as a 2 wt.% aqueous suspension. The XRD pattern of the dry clay reveals a *d*-spacing of 1.07 nm (Fig. 3).

2.3. Polycarboxylate samples

Two PCE superplasticizers and two polymers representing the poly(methacrylic acid) backbone and poly(ethylene oxide) side chain of the PCEs were utilised. The PCEs were synthesized according to a literature description by aqueous free radical copolymerization of methacrylic acid (MAA) and methoxy terminated poly(ethylene oxide) methacrylate (MPEG-MA) ester at molar ratios of 1.5 and 6 respectively [19]. Methallylsulfonic acid was used as chain transfer agent. Both copolymers have side chains made up of 45 ethylene oxide units (EOUs). They are denoted by 45PCx, where 45 refers to the number of EOUs in the side chain, and x corresponds to the molar ratio of MAA:MPEG-MA. The chemical formula of the PCEs is presented in Fig. 4. PMA was synthesized by aqueous free radical polymerization of MAA [20], while PEG-2000 was used as per obtained (Clariant, Frankfurt am Main/Germany).

For polymer characterisation, size exclusion chromatography (Waters Alliance 2695 from Waters, Eschborn/Germany) equipped with RI detector 2414 (Waters, Eschborn/Germany) and a 3 angle dynamic light scattering detector (mini Dawn from Wyatt Technologies, Santa Barbara, CA/USA) was used. Prior to application on the columns, the polymer solutions were filtered through a 0.2 μm filter. The polymers were separated on an Ultrahydrogel™ precolumn and three Ultrahydrogel™ (120, 250 and 500) columns (Waters, Eschborn/Germany) using 0.1 M aqueous $NaNO_3$ solution (adjusted to pH 12.0 with NaOH) as an eluant at a flow rate of 1.0 mL/min. From this separation, the molar masses (M_w and M_n), the polydispersity index (PDI) and the hydrodynamic radius ($R_{h(z)}$) of the polymers were

Table 2
Oxide composition of sodium montmorillonite clay sample, RXM 6020 as determined by X-ray fluorescence.

Oxide	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	K_2O	TiO_2	LOI	Total
[wt.%]	59.7	18.4	0.8	2.3	4.0	2.3	0.1	0.1	12.1	99.8