



Impact of particle size on interaction forces between ettringite and dispersing comb-polymers in various electrolyte solutions



Lucia Ferrari^{a,b,*}, Josef Kaufmann^{b,*}, Frank Winnefeld^b, Johann Plank^c

^a Chryso, 7 rue de l'Europe, 45300 Sermaises, France

^b Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Concrete/Construction Chemistry, Ueberlandstr. 129, 8600 Dübendorf, Switzerland

^c Technische Universität München, Department of Chemistry, Lichtenbergstr. 4, 85747 Garching, Germany

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ABSTRACT

The inter-particle forces play a fundamental role for the flow properties of a particle suspension in response to shear stresses. In concrete applications, cement admixtures based on comb-polymers like polycarboxylate-ether-based superplasticizer (PCE) are used to control the rheological behavior of the fresh mixtures, as it is negatively impacted by certain early hydration products, like the mineral ettringite.

In this work, dispersion forces due to PCE were measured directly at the surface of ettringite crystals in different electrolyte solutions by the means of atomic force microscopy (AFM) applying spherical and sharp silicon dioxide tips.

Results show an effective repulsion between ettringite surface and AFM tips for solutions above the IEP of ettringite (pH~12) and significant attraction in solution at lower pH. The addition of polyelectrolytes in solution provides dispersion forces exclusively between the sharp tips (radius ≈ 10 nm) and the ettringite surface, whereas the polymer layer at the ettringite surface results to be unable to disperse large colloidal probes (radius ≈ 10 μ m).

A simple modeling of the inter-particle forces explains that, for large particles, the steric hindrance of the studied PCE molecules is not high enough to compensate for the Van der Waals and the attractive electrostatic contributions. Therefore, in cement suspensions the impact of ettringite on rheology is probably not only related to the particle charge, but also related to the involved particle sizes.

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1. Introduction

In the last years, rheology modifying agents became continuously more relevant to adapt the flow properties of granular mixtures to specific industrial applications, like food production, drugs preparation, cosmetic formulation, and concrete mix-design in construction. The rheology of particle suspensions results however from a combination of different physical–chemical phenomena [1,2]. Particle size distributions and shapes, inter-particle forces and solvent properties play a significant role in the fluidity of such complex systems [3,4].

The workability of cement pastes, which are highly heterogeneous and concentrated particle suspensions, is fundamental for concrete and mortar production [5]. The rheological behavior is influenced by a complex system of differently charged particles, cement clinker phases and early hydration products of a wide

range of sizes, which are dispersed in a pore solution containing different electrolytes. Some early hydration products, in particular ettringite, which forms in the first few minutes after the addition of water to the dry cement, were shown to distinguishably alter the flow properties of the fresh paste [6]. Possible explanations of this effect are reconnected to the needle-shape size or to its positive surface charge which attracts oppositely charged particles forming agglomerates [7,8]. Fine particles impact on rheology for different reasons: at equivalent mass, fine particles provide more surface area than large grains and they significantly influence the packing density of a granular system.

To improve the rheological properties of cement pastes the use of dispersing agents is a widely applied method. The most recent generation of superplasticizers is represented by polycarboxylate ether-based superplasticizer (PCE), which are comb-shaped polymers composed by an acrylic or a meth-acrylic acid chain that serves as backbone with grafted poly-ethylene oxides as side chains [9]. Zeta-potential and adsorption measurements revealed that the PCE adsorption is preferential on positively charged particles [10–12]. Thus superplasticizers are assumed to preferentially

* Corresponding authors. Fax: +41 58 765 69 35 (J. Kaufmann).

E-mail addresses: lucia.ferrari@chryso.com (L. Ferrari), josef.kaufmann@empa.ch (J. Kaufmann).

act on the positively charged ettringite phase [13], providing repulsive forces, steric or electrostatic, that enable the dispersion of oppositely charged particles within the cement paste [14].

In order to understand the correlation between dispersion forces of superplasticizers and rheological properties, several studies were carried out on the dispersive action of superplasticizers at the particle surfaces by performing force measurements in liquid using atomic force microscopy (AFM). However, due to the reactivity and heterogeneity of cement clinker surfaces, most of the experimental setups are limited to the application of model mineral substrates supposed to imitate the inter-particle interactions of cement [17–20]. Furthermore, few studies showed the application of spherical AFM tips, which are suitable to simulate a colloidal particle and to model the effective tip–surface interaction [21,22]. On the other side, regarding the size of the AFM tips, spherical probes of few micrometers in diameter represent a cement grain better than the usually applied sharp tips, typically possessing a radius of few nanometers.

In this study, a special focus was put on the investigations of inter-particles forces at ettringite surfaces by means of AFM technique. The application of negatively charged SiO₂-probes (sharp tips and colloidal probes) of two different sizes is supposed to simulate the ability of superplasticizers to disperse ettringite particles small (10 nm) or large (10 μm), negatively charged clinker or quartz grains in their vicinity. The detection of the particles charge via zeta potential measurements is combined with the AFM force measurements and provides information about the adsorption of ions and PCE on the involved particle surfaces. The goal of this work is to reproduce in an experimental setup the interaction forces effectively occurring at the surface of ettringite crystals in solutions containing different concentrations and types of electrolytes and polyelectrolytes. This allows a comprehensive understanding of the parameters playing a role in PCE adsorption at ettringite surfaces and its influence on inter-particle forces. Furthermore, modeling of the force equations as function of the distance clarifies the different effects of particle size and of the polymer layer on the dispersion forces of superplasticizers in cement suspensions.

2. Experimental

2.1. Ettringite and its preparation

Ettringite is a naturally occurring calcium aluminosulfate mineral (CaO)₃(Al₂O₃)(CaSO₄)₃·32H₂O mineral. Its single crystal structure was first described by Moore and Taylor [23]. The structure is composed of columns of aluminum and calcium surrounded by channels filled with sulfate ions and water molecules. Within each column, [Al(OH)₆]³⁻ octahedral alternate with triples of calcium ions disposed around a triad axis. The columns are nearly cylindrical in cross-section, and their net positive charge is probably distributed among the hydrogen atoms of the water molecules of which their surfaces are composed. The locations of O and H atomic position influence the hydrogen bonding network which stabilize the ettringite structure [24]. From stoichiometric estimation a surface charge density of 1.25 e/nm² was calculated, and it is independent on the pH [25]. Indeed the surface charge of ettringite is generally positive, and becomes negative only depending on the concentration of sulfate ions in solution.

In a first attempt ettringite crystals were synthesized applying different synthesis methods according to [26] in order to obtain relatively large needles which should serve as substrates in the AFM experiments. Despite the different synthesis methods, it was not possible to obtain the required size (nearly 1 × 100 μm²) that is necessary to be handled on a sample holder and a surface

that can be scanned by AFM with a reasonable resolution. For this reason, some natural crystals of ettringite (see Fig. 1), found inside a nodule of leucitic lava in the quarry of Vallerano, Rome, were used as AFM-substrates for the force measurements.

Few needle-shaped crystals were extracted by means of sharp glass tweezers and attached on a properly cut microscopy slide. The long hardening time (~90 min) of the used commercial glue (Adhesive Araldit, Huntsman Advanced Materials (Switzerland) GmbH) composed of 2 parts, the epoxy and hardener, allowed the correct placement of the minerals on the glass substrate. Fig. 2 reports an AFM image (contact mode in air) of such prepared ettringite surface.

Ettringite and quartz powders (Quarzmehl K8, Carlo Bernasconi AG) were used for the zeta-potential measurements to verify the behavior of these two minerals in correlation to the ions in solution. For this purpose, ettringite powder was synthesized according to [12] by precipitation from solutions containing stoichiometric contents of burned CaO and Al₂(SO₄)₃·16H₂O (Fluka) in excess of deionized water. Once the precipitated content was separated from the solution by filtration, the ettringite was gently grained in an open mortar and then the finer particles were separated with a 63 μm sieve. XRD tests determined the purity of ettringite around 95% with some gypsum traces. Particle size distribution and density of both synthetic ettringite and quartz samples are reported in Table 1. Particle size distributions were obtained by laser diffraction measurements (Mastersizer X, Malvern, UK), and surface areas were derived from nitrogen sorption applying BET theory (SA 3100, Beckman Coulter, Fullerton, CA).

2.2. Dispersive polymers

Two types of polycarboxylate ether-based dispersive polymers were used in this study. Their chemical composition (Fig. 3) is represented by a main chain holding carboxylic groups (*n*). The polymer is organized in a comb structure with ethylene oxide (EO) units (*p*) along the side chains (*m*).

In Table 2 the chemical characteristics of the polymers studied in this work are reported. 8.5PC3 was synthesized according to [9], while 45C12 was synthesized as described in [27]. These two particular structures were chosen because of their corresponding relatively high charge densities (CD), calculated as the ratio between the moles of anionic charge and the molar mass of each PCE unit, which was shown to afford a good compatibility with cement pastes, form the adsorption and from a rheological point of view [8]. All the dosages reported in this article refer to the pure polymer concentration of PCE in solution. A concentration of 1 g/l was used to perform the tests, as it was shown that higher

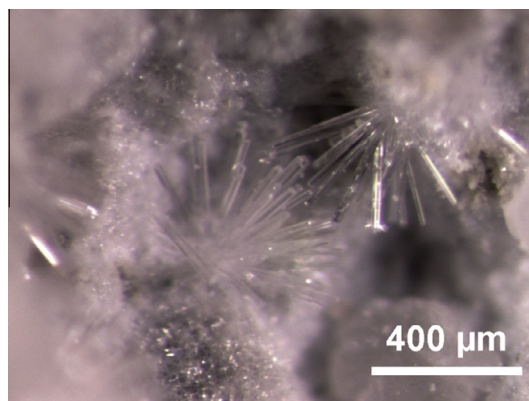


Fig. 1. Optical microscopy image of natural ettringite crystals.

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