Multi-method approach to study influence of superplasticizers on cement suspensions

L. Ferrari [a,b,*], J. Kaufmann [a], F. Winnefeld [a], J. Plank [b]

[a] Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Concrete/Construction Chemistry, Ueberlandstr. 129, 8600 Duebendorf, Switzerland
[b] Technische Universität München, Department of Chemistry, Lichtenbergstr. 4, 85747 Garching, Germany

ABSTRACT

Superplasticizers are widely used in concrete processing to increase the rheological properties of hardening pastes. In this study, different techniques (rheology, adsorption, atomic force microscopy—AFM, and ζ-potential) are used to characterize the impact of polycarboxylate-ether based superplasticizer (PCE) on particle suspensions. Results obtained with two cements and two inert powders (MgO and calcite) show that superplasticizer efficiency is strongly influenced by polymer architecture and by the ionic species present in solution. Additionally, experiments performed with AFM and ζ-potential contributed to characterize dispersion forces exerted by superplasticizers at the solid–liquid interface. The application of plateau AFM-tips coated with platinum reveals that dispersion forces depends on the presence of ions in solution, and that multilayer formation occurs with certain superplasticizer types. A further conclusion includes the idea that the PCE has a lubricating effect between adjacent particles and PCE increases surface wettability.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Polycarboxylate-ether based superplasticizers (PCEs) are widely used in different industrial fields to improve the rheological properties of particle suspensions. Especially in cement application, their addition allows a reduction of the water-to-cement (w/c) ratio, thus strongly increasing the workability of the fresh mixtures and the performances of the hardened pastes, mortars or concretes. Despite their widespread utilization, these polymers are currently still the subject of many studies, because details about their working principles lack of a full understanding. Indeed, sometimes unpredictable incompatibility with certain cements was observed [1–3].

A multi-method approach is required to understand different aspects of superplasticizer behavior in fresh cementitious suspensions. The workability of a particulate mixture is usually characterized by detecting its rheological properties [4,5]. Apparent yield stress and viscosity, which describe the fluid's internal resistance to flow, are the two main macroscopic parameters which are used to quantify the effects of PCE addition to the suspensions. A further key factor, to quantify the efficiency of a superplasticizer, is to investigate how much polymer is really interacting and remaining on the particle surfaces. The adsorption behavior on colloid surface may be determined by means of total organic carbon (TOC) measurements [6,7]. Moreover, the detection of the ζ-potential enables to study the influence of superplasticizers on particle charges and to analyze the effect of electrostatic dispersion forces acting between them [8].

Houst et al. [9] recently collected results, obtained with many techniques, to asses the adsorption behavior and the rheological properties of different systems, and to model superplasticizer action at the solid–liquid interface. Studies from Plank et al. [10–12] highlighted the influence of different polymer architectures and their interaction with cementitious systems. They showed that short side chains, resulting in a high polymer charge, perform strong adsorption especially on positively charged particles. Other studies by Zingg et al. on pure cement phases confirmed that ettringite is the cement phase which most adsorbs superplasticizers [13].

Additionally to this variety of techniques, atomic force microscopy (AFM) was applied in the past to measure in liquid the dispersion forces due to PCE [14]. In order to obtain reliable results with this technique, substrates that are smooth, flat and non-reacting are a prerequisite. Since these characteristics can not be provided by cement, the use of inert model systems is necessary to enable these kinds of force measurements. Spherical probes of magnesium oxide approaching MgO substrates were used to simulate a cement-like colloidal particle [15]. It was proposed that, for a more complete understanding of the measured force–distance curves, additional studies on the polymer adsorption and the ζ-potential are required [16]. This investigation revealed that the standard AFM tips, composed of silicon nitride, are positively charged, and so they adsorb PCE.

In the present study, a multi-method approach involving all these experimental techniques (rheology, adsorption, ζ-potential, and AFM) is reported, in order to contribute to a more general

* Corresponding author at: Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Concrete/Construction Chemistry, Ueberlandstr. 129, 8600 Duebendorf, Switzerland. Tel.: +41 58 765 43 60; fax: +41 58 765 40 35.
E-mail address: lucia.ferrari@empa.ch (L. Ferrari).