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In-situ investigation of superplasticizers: From fluorescence microscopy to concrete rheology

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ABSTRACT

Concretes with advanced strength and durability necessitates organic polymers to receive a homogeneous concrete mixture due to a low amount of mixing water and a high content of fine fillers with large inner surface. The basic working mechanisms of those so-called superplasticizers are widely understood in theory, but still there are unclear phenomena like incompatibilities with certain additives. This study presents a novel method to investigate the interaction of superplasticizers with mineral particles. With the application of fluorescence microscopy, it is possible for the first time to localize and quantify the adsorption of superplasticizers to particles and to vary experimental parameters during the measurement. The presented results prove this method, which enables first time to investigate the superplasticizer interaction with mineral surfaces in situ. The important role of calcium ions for the necessary adsorption of those polymers to mineral particle surfaces is obvious in the shown fluorescence microscopic experiment. Furthermore, the detected amount of adsorbed polymers depending in the concentration of calcium ions present in the used suspension correlates with the development of the zeta potential of various minerals. Finally, a correlation between the microscopically measured adsorption of two different superplasticizers to rheological properties of a test mortar succeeded.

1. Introduction

Concrete is the world's most important building material and with about 15 billion m³, calculated with an annual cement production of 4.2 billion tons in 2016 [1], by far the most human made product on earth. In the last decades, special concretes have been developed comprising enhanced compressive strength and durability. With the reduction of mixing water and the use of micro fillers like silica fume a very dense concrete matrix can be achieved, resulting in compressive strength of > 150 MPa. Concretes of this character are called ultra-high performance concretes (UHPC) [2–4]. Without this progress in material science, modern buildings like the Burj Khalifa in Dubai cannot be realised [5–7]. One very important aspect of UHPC is the application of superplasticizers. These admixtures are organic polymers, which enable sufficient plasticity of fresh concrete despite of low water/binder ratio (w/b-ratio) and high inner surface of very fine powder mixtures. The required workability is achieved by the interaction of superplasticizer molecules with the surface of cement and filler particles [8]. Without plasticizing admixtures, concretes like UHPC with low w/b-ratio and high amounts of micro fillers are not applicable, because the particles are not dispersed sufficiently in the mixing water and no homogeneous and workable mixture can be obtained. Superplasticizers enhance the

workability in concrete by shielding attractive forces between the particles, like Van-der-Waals- and electrostatic forces. Today, the most efficient superplasticizers for UHPC and self-compacting concrete (SCC) are polycarboxylate ethers (PCE), invented by Dr. Hirata in 1981 [9]. These *comb*-shaped polymers consist of a backbone carrying carboxyl groups and polyethylene glycol sidechains (Fig. 1).

In alkaline conditions, typically for cementitious systems, the carboxyl groups are deprotonated and thus negatively charged. This negative charge is the main reason for the interaction of PCE-molecules with mineral particles, because particles in aqueous suspension show surface charge caused by dissociation of functional groups and adsorption of dissolved ions [10]. By the electrostatic adsorption to those surfaces, the superplasticizer prohibits the agglomeration of the mineral particles by shielding attractive electrostatic forces and the steric hindrance of the sidechains (Fig. 2), resulting in a homogeneous dispersion of all particles and in this manner a concrete with good workability. In general, good adsorption induces good plasticity, but a lot of other effects are still under investigation [11–19].

The surface charge, characterised by the zeta potential, depends on the chemical composition of the particle material, the pH-value of the suspension and the concentration of different dissolved ions [20]. Beside the chemical structure of the polymer, the interaction of

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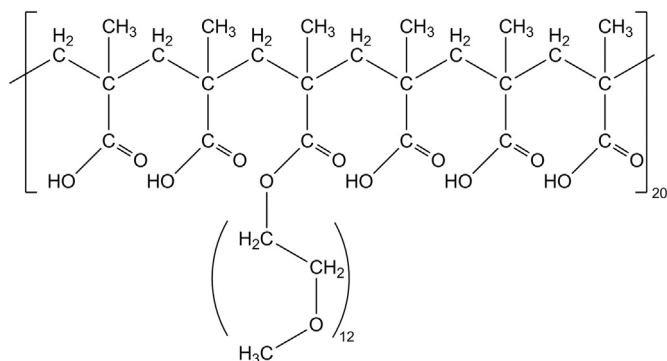


Fig. 1. Chemical structure of PCE 12PC5.

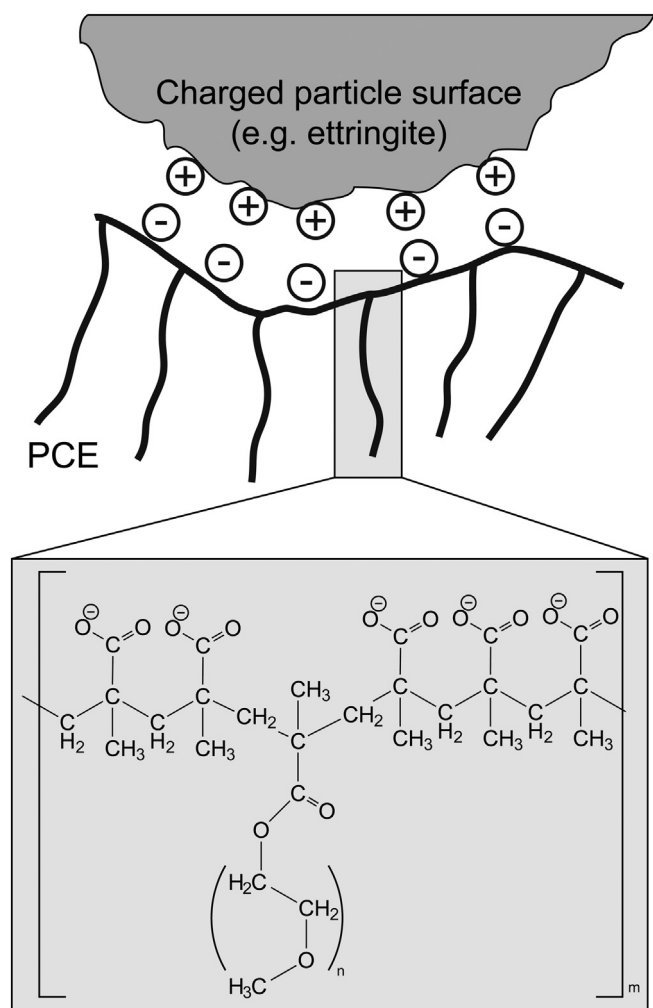


Fig. 2. Schematic illustration of the interaction of PCE with charged particle surface.

superplasticizer and particle as well as the plasticizing effect depends on various parameters. Caused by the hydration of cement, the chemical condition of a concrete mixture is changing over time. That means the interaction of superplasticizer and particle is influenced from the moment of the addition until the beginning of the hardening. The continuous change of surface composition and morphology (intermediate and hydration products) and the varying amount of dissolved ions like calcium cations or sulphate anions influences the adsorption of polymers on short time scales (seconds to hours). Hence, a method to analyse these processes in situ complements the prevalent methods of

superplasticizer investigation like TOC (total organic carbon method) and the measurement of the zeta potential during polymer solution titration. Both indirect methods allow the determination of the amount of adsorbed superplasticizer, but are not able to provide localization and quantification. This information is very important to enhance the understanding of the working mechanisms of superplasticizers and for purposeful development of new admixtures. To provide in situ analysis, a fluorescence-microscopic approach is presented in this study. Fluorescence microscopy is an established tool in biology, but rarely used in concrete science. The basic idea is to mark organic components with fluorescent dyes to locate them in specially prepared samples [21–23] or to generate a contrast to not fluorescent material [24,25]. Wetzel [26] applied this technique the first time to localize superplasticizer in hardened concrete samples. Based on this work, fluorescence-microscopic in situ experiments in fresh particle suspensions are carried out to investigate superplasticizers in the period, when adsorption occurs and they deploy their benefit. As mentioned above, many parameters influence the adsorption, so the observed systems are kept as simple as possible at first to validate the use and the reliability of this method. The influence of calcium ions is detectable by the fluorescence microscopic approach and the obtained data corresponds to measured development of zeta potentials, proving the method to be consistent to prevalent techniques of superplasticizer-investigation. The potential of this method to deliver useful information for the application of superplasticizers is shown by the comparison of the amount of adsorbed polymer to rheological measurements of corresponding concrete pasts.

2. Materials and methods

For this study, three different types of PCE were used: 12PC5 (Fig. 1), 45PC2 (Fig. 3) and 45PC6 (Fig. 4). The first number in the sample label represents the average length of the sidechains in the number of ethylene glycol units, the second number stands for the rate of charge carrying carboxyl groups to sidechain carrying ester groups. These representatives differ in the charge density of the molecule (45PC6 > 12PC5 > 45PC2), chain length and molecular weight. 12PC5 with a molar weight of about 18.000 g/mol was obtained from MC Bauchemie and 45PC2 (~25.000 g/mol) and 45PC6 (~16.000 g/mol) were synthesised by the group of Prof. Plank at the Department of Chemistry at TU Munich. All superplasticizers were obtained in aqueous solution with a polymer content of about 40 wt%.

To make PCE-molecules detectable for optical microscopy,

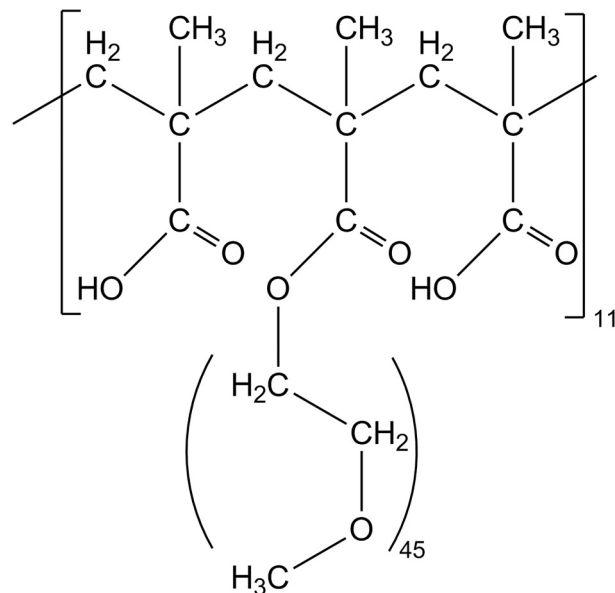


Fig. 3. Chemical structure of PCE 45PC2.

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