

Predicting the efficacy of superplasticizers by fluorescence

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INTRODUCTION

Microscopic methods are widely used in inorganic material science either to characterize raw materials or to investigate hardened specimens for instance in terms of hydrations products, interfacial transition zone or micro cracking. The samples in these investigations are usually solid and static. The following work presents a light microscopic approach to observe the interaction of superplasticizers with mineral particles in suspensions and pastes in situ. Superplasticizers are admixtures added to concrete to provide good workability despite of low water/cement values (w/c) and high amounts of micro fillers like silica fume. Especially for high and ultra-high performance concretes, these admixtures are indispensable. The plasticizing effect of modern superplasticizers mostly based on polycarboxylate ethers (PCE), results from an electrostatic repulsion and steric hindrance when the comb-shaped polymers adsorb to charged particle surfaces as they are in aqueous suspensions of oxide based materials. Thus, the superplasticizer molecules shield interparticular attractive forces prohibiting the agglomeration of particles in the mixture [1]. The result is a homogeneous mixture with well-dispersed solids even in low amounts of mixing water (down to w/c of ~0.2) enabling workable concrete consistency [2]. The adsorption of the superplasticizer is very important for the effectiveness of the admixture. It depends on the chemical structure of the polymers, the composition of the liquid phase (in case of cement based mixtures the pore solution) and the phases of the present particles. If the PCE is chemically coupled to a fluorescence dye before it is used in the experiment, in-situ-investigation of the adsorption of PCE on particles is possible with fluorescence microscopy. The amount of adsorbed superplasticizer relates to the detected fluorescence intensity of the particles in the fluorescence image. The correlation of adsorption and plasticizing capacity of certain PCEs is generally assumed and can be shown by the presented experiments. Furthermore, time resolved measurements are possible to investigate superplasticizers for example during the hydration of cement, which changes the particle surface and chemical environment of the liquid phase by the formation of hydration phases and thus the conditions for the

adsorption of the polymers. During these experiments it was noticed, that the dissolution of gypsum grains in Ordinary Portland cement (OPC) depends on the presence and character of PCEs. The given examples in this contribution show the high potential of the fluorescence microscopic approach for superplasticizer research because the microscopic findings seem to correlate quite well to results of macroscopic experiments in the concrete laboratory and application.

MATERIALS AND METHODS

The fluorescence microscopy was conducted with a *M 205 FA* by *Leica Microsystems GmbH*. This stereomicroscope was used to investigate cement suspensions in a measurement cell made of two microscope slides with a thin spacer foil (60 μm) between, fixed in an aluminium holder [3]. *Sulfo CEM I 52,5 R-HS/NA* by *Holcim* was used as Portland cement. As dyes for the PCE labelling *Fluorescein* and *Rhodamin B* (both purchased from *Merck*) were used. For detailed chemical staining procedure see *Arend et al* [3]. The superplasticizers PC2, PC6 and Phos3 (Figure 1) were provided by the *Department of Chemistry* at TU Munich (Prof. Plank). All polymers consist of a polycarboxylate backbone and contain polyglycol sidechains with an average length of 45 units as well as carboxyl groups as charge carrier. The charge carrying units are in case of PC2 and PC6 deprotonated carboxyl and in case of Phos3 phosphate groups.

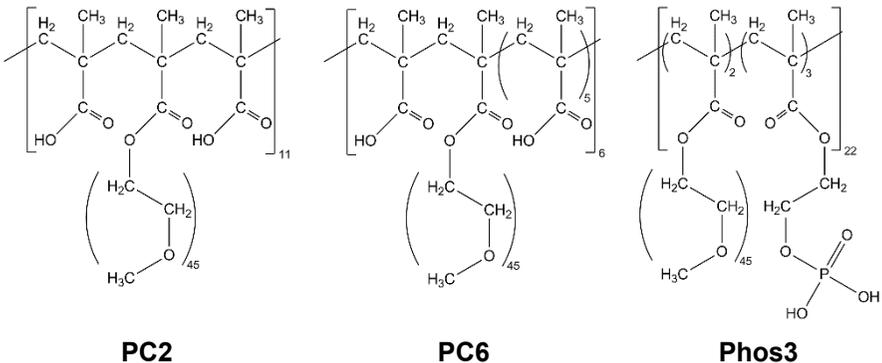


Figure 1: Chemical structure of used PCEs

For the microscopic experiments 0.01 molar potassium hydroxide and synthetic pore solution [4] were used as solvent for the PCE solutions. The PCE concentration was 1 mg/ml. 10 mg cement were dispersed in 50 μl solution with stained PCE (w/c = 5).

The fluorescence intensity of the images was digitally analyzed with the open source software *ImageJ*. The slump of a paste made of Portland cement and an UHPC mortar with the same cement is measured depending on the used PCE (PC2 or PC6). The composition of the mixtures is given in Table 1.

Table 1: Composition of tested paste (**bold**) and mortar (*all*)

Material	Mass [g/L]
CEM I 52,5 R Sulfo	775
Silica fume	164
Quartz powder	193
Quartz sand	946
Water	183
Superplasticizer (40 w% PCE)	23.5
w/c	0.25
PCE by weight of cement	1.2%

RESULTS AND DISCUSSION

In order to present the correlation between the amount of adsorbed PCE determined via fluorescence microscopy and the rheology of pastes and mortars PC2 and PC6 were chosen. PC6 has a higher charge density because of a higher ratio of carboxyl groups to sidechains. Higher charge density causes stronger interaction with the particle surface causing faster and stronger adsorption of the PCE. For this experiment, potassium hydroxide solution was used to provide an alkaline environment (pH ~12) and thus the deprotonation of the carboxyl groups of the PCEs. In applied cement based mortars and concretes the pH value increases very fast when water is added due to the dissolution of alkalis. To compensate the high dilution of the test suspension (high w/c value in comparison to mortars and concretes), the hydroxide solution is used a priori. The fluorescence images (in false color) in Figure 2 show the signals of PC2 (a) and PC6 (b). It is obvious that the detected fluorescence and in the same manner the adsorption to the cement grains of PC6 is higher than of PC2. The digital analysis shows about 25% more fluorescence and thus adsorption in case of PC6.

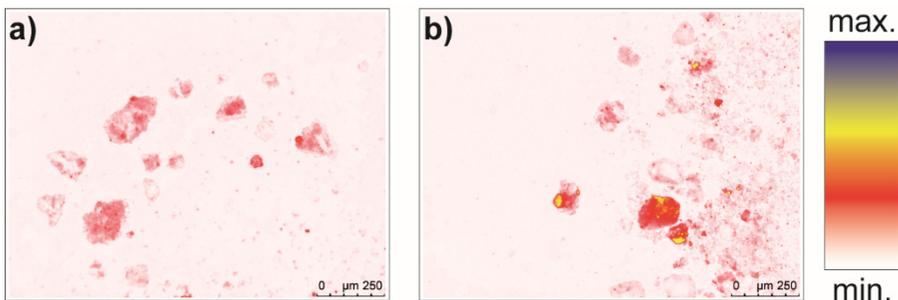


Figure 2: False color fluorescence images of stained PC2 (a) and PC6 (b) with Portland cement

A slump test using the *Haegermann* method (EN DIN 1015-3) was conducted to validate the plasticizing effect of both PCEs. With both PCEs, it is possible to mix a

homogeneous UHPC mortar, but in case of PC2 the mixture is very stiff and shows almost no slump (11 cm, starting from 10 cm). In contrast, PC6 liquefies the mixture strongly to a slump of almost 30 cm. For pure cement pastes, the effect is similar, shifted to higher values due to the lack of aggregates (PC2: 20 cm, PC6: 55 cm). These results show the possibility to predict the plasticizing capacity of superplasticizers by fluorescence microscopic experiments. Up to this point, the correlation is of qualitative character but will be quantified in continuative work.

In another experiment, the time dependency of PCE adsorption to hydrating cement particles was investigated. Here, white particles attract attention, because they disappear within several minutes depending on the used superplasticizer. EDX analysis proved those particles to be gypsum. Interestingly the dissolution of this setting regulator is affected by PCEs. Further investigation showed, that if no PCE is present in alkali conditions the white gypsum grains (1a) and b) in Figure 3) seem to solvate over time, but do not dissolve completely. This is the case, when PCEs are present (2a) and b) Figure 3) whereupon the speed is depending on the superplasticizer (Figure 4).

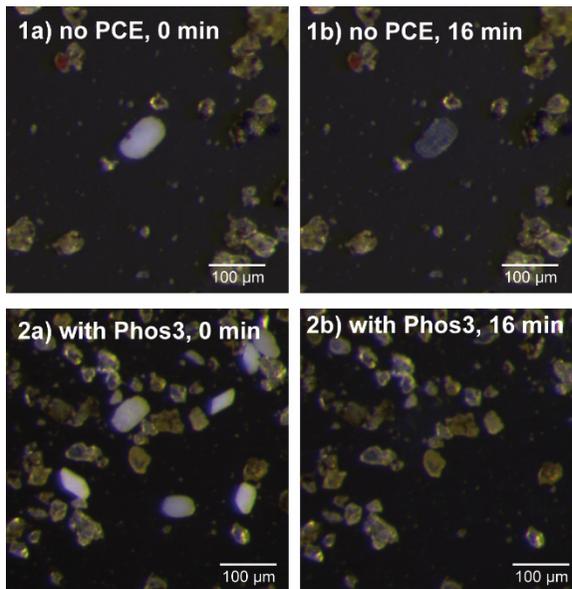


Figure 3: Gypsum grains in CEM I in pore solution without (1) and with Phos3 (2) at 0 and 16 min

The reason for this phenomenon might be the complexation of the dicationic calcium ions by the negatively charged groups of the PCEs to a chelate-like structure [5]. Concerning the high concentration of calcium in the synthetic pore solution, it is

saturated and the gypsum usually cannot be dissolved. If the presence of PCEs allows a complexation of additional calcium ions, gypsum dissolved completely.

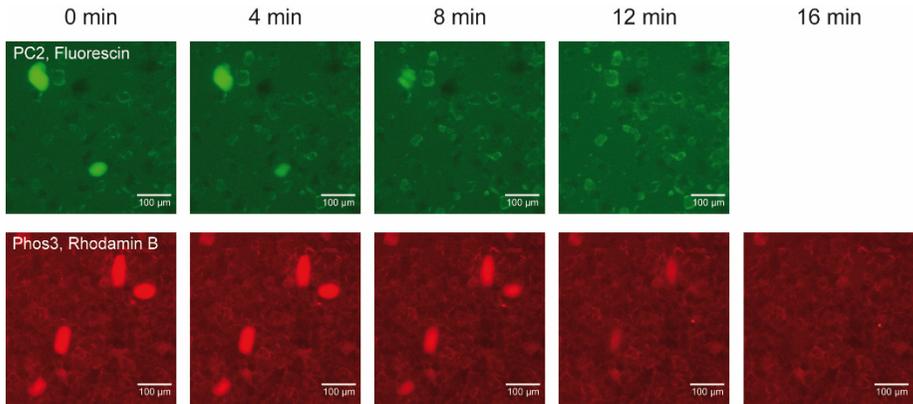


Figure 4: Fluorescence images illustrating different speed of gypsum dissolution of CEM I in pore solution with PC2 (green, Fluorescein) and Phos3 (red, Rhodamin B)

Indicated by the high fluorescence intensity, PCEs adsorb very well to the gypsum particles (Figure 4). The gypsum grains dissolve within 12 min, if PC2 is used. The dissolution process with Phos3 seems to be retarded or slowed down. An explanation for this finding is the different chemical structure and charge density of both PCEs. Phos3 is carrying highly charged phosphate groups so a strong adsorption to the gypsums forms a dense layer, protecting the particle against dissolution for a while. PC2 with lower charge density does not adsorb to a comparably dense layer and the complexing effect of the PCE comes faster into account. If this phenomenon is not caused only by the chosen experimental conditions, an influence of different superplasticizers to the setting of concrete might be recognized because of the affected dissolution of the setting regulator gypsum.

CONCLUSION

The shown experiment indicate the fluorescence microscopic approach as a very powerful tool to investigate superplasticizers and other organic admixtures in model suspensions and fresh mortars. Beside the rheology, further effects of PCEs may be explained with results obtained with this method. For example, the hydration of C_3A and with it the setting of PCE containing concretes could be affected by the interaction of PCE and gypsum. Further work will show how precise the prediction of superplasticizer effects by microscopic experiments can be executed.

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