

Adsorption of PCE in alkali-activated materials analysed by fluorescence microscopy

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Abstract

The realisation of high-performance concrete mixtures requires the use of superplasticizers to achieve a low water/binder ratio and thus high strengths. Polycarboxylate ethers (PCE) are mostly used as superplasticizers. The effectiveness of these superplasticizers depends on their chemical structure, the binders' alkaline environment and the ions present in the pore solution of the binder. In high alkaline systems like some alkali-activated materials no effective superplasticizer have been found yet. To unravel the compatibility of certain PCE to such a highly alkaline system a fluorescence microscopy approach was used. In first experiments, the adsorption of APEG (allyl ether) and MPEG (methacrylate) PCE on ground granulated blast furnace slag and fly ash was investigated varying the concentration of the activators. At a certain concentration, a complexation of the PCE can be recognised in fluorescence microscope. APEG shows a better stability compared to MPEG; this correlates with rheological investigations.

KEYWORDS

fluorochrome, fly ash, ground granulated blast furnace slag, polycarboxylate ether, staining

1 | INTRODUCTION

For the application of high-performance concrete, the mixture needs to come with both flowability and high strengths. To achieve the high strength, it is necessary to decrease the water/binder ratio. Without superplasticizers, these mixtures would not be applicable due to their high viscosity.

By adsorption of superplasticizer molecules to the surfaces of fine particles, a shielding of the interparticular forces results in an effective dispersion of the particles and thus a liquefying effect in the suspension. The adsorption of these polymers itself is due to electrostatic attractive forces, too.¹ Currently, polycarboxylate ethers (PCE)

are used almost exclusively due to their high performance and are therefore considered central in this investigations. The PCE copolymers have a variety of molecular structures and chemical characteristics. This results in variations in their effectiveness as superplasticizers for different concrete compositions.^{2–6} In the deprotonated state, which is due to the alkaline environment of cement-containing binders, the carboxyl groups of the PCEs bound in the backbone carry negative charges. Due to this negatively charged backbone, PCEs attach to positively charged surface areas of the cement grains and, in addition to electrostatic repulsion, prevent agglomeration through steric shielding, thus promoting the dispersion of the fine particles in the cement paste.²

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The chemical structure of the polymers, that is the length and structure of the backbone and side chains, functional groups and charge density, is decisive for their effect as superplasticizers has been intensively investigated and proven.^{2,3,5,6} The composition of the cement paste itself in terms of different mineral phases of varying morphology, surface charge reactivity with water and type and concentration of interaction-relevant ions fundamentally determines the performance of the respective superplasticizer.^{8–11} The charges of mineral surfaces, described by their zeta potential, play a special role for the adsorption of dissolved polymers in mineral-bound systems. Therefore, the zeta potential is considered for the prediction of electrostatic interactions in suspensions. Anionic PCE superplasticizer molecules bind electrostatically on surfaces with positive zeta potential. In Portland cement systems, sodium and potassium are present as cations in addition to calcium. Compared to this, the proportion of sodium and potassium to calcium in alkali-activated binders is significantly higher, depending on the type of the activator. Here, on the one hand, the zeta potential can influence the adsorption of the molecules on mineral surfaces.² On the other hand, the attachment of alkali ions to carboxylate groups can influence the attachment of the molecules.⁷ In addition to the high alkali levels, the high pH value affects the system in general and the effectiveness of superplasticizers in particular. Due to this high pH value of >13, the side chains of the superplasticizers decompose.¹² This leads to a reduced effectiveness of the steric repulsion and thus to a lower dispersion.

Alkali-activated binders are based on alumino-silicate precursors, which are ideally available in a fine-grained and reactive form. Fly ash and ground granulated blast furnace slag as well as burnt clays and in particular mainly metakaolin are used here. Between these three groups, as well as within them, there are great differences in granulometric, chemical and mineralogical characteristics. As a result, on the one hand, different types of activators and concentrations can and partly must be used and on the other hand, the solid properties of the set system vary. The most commonly used activators are alkali waterglasses and alkali hydroxides; alkali carbonates and alkali sulphates are used less frequently but are also applicable.¹³

Regardless of the variation of the precursors and the activators, the process for alkali-activated binders in general can be described in a simplified way as follows: the alumino-silicate network of the precursor is dissolved in the alkaline environment and Si and Al tetrahedra initially reorganise into gel-like structures which subsequently form a three-dimensional network. Depending on the chemical composition of the precursors and in par-

ticular the Calcium content, different reaction products are formed. Since AAM precursors in combination with the alkali activators have a lower CO₂ footprint compared to Ordinary Portland Cement (OPC), they represent a promising, ecological alternative.¹⁴

By coupling admixtures with fluorochromes, admixtures in mineral-bound systems can be localised by fluorescence microscopy.^{15–17} An analytical method has been developed in the past few years which, based on fluorescence microscopy, enables the observation of the adsorption behaviour of organic concrete admixtures on solid surfaces.^{18–20} In particular, in situ investigations limit the possible analysis methods to light microscopy for preparative reasons, the resolution is not sufficient to detect the admixtures. This problem can be solved by means of fluorescence microscopy, in which dyes previously bound to the additives are excited to fluorescence, which serves the actual imaging. Depending on the additive, different approaches are used to bind the dye and polymer: All of the superplasticizers investigated in the above-mentioned project have carboxyl groups that can serve as anchor groups for chemical coupling with dyes. In the present investigations, the adsorption of APEG and MPEG superplasticizers could be shown in solutions of potassium waterglass and potassium hydroxides.

2 | METHODS

Two different PCE were used: 7APEG2 and 45PC2 (MPEG) (for further description please see^{18,19} The superplasticizers were synthesized by the department of chemistry at the TU Munich. The superplasticizers were stained with aminofluorescein as described in Arend et al.^{18,19}

For the alkali-activation potassium, waterglass and potassium hydroxide solutions were used. As particles, a Si-rich fly ash and a ground granulated blast furnace slag were used. A sample of particles was infused with deionised water and then transfused. This procedure separates only the coarse particles, which are optimum for microscopic investigations.

For the experiments in the fluorescence microscope, 1 mg of stained superplasticizer was mixed with 1 ml of the activator. Then 10 mg of particles was dispersed in 50 μ l of this solution. To investigate the adsorption behaviour, 2.5 μ l of the suspension was placed onto a microscope slide. With a spacer of 60 μ m, another microscope slide was placed on top (Figure 1). The potassium waterglass, which has a modulus (molar ratio of SiO₂:K₂O) of 1, was diluted by deionised water to gain a solution containing 10, 15, 20 and 30 vol.% of waterglass.

Reflected-light images and fluorescence images were taken with the fluorescence stereoscope Leica M 205 FA.

FIGURE 1 Setup of in situ measurements of PCE-adsorption in fluorescence microscope

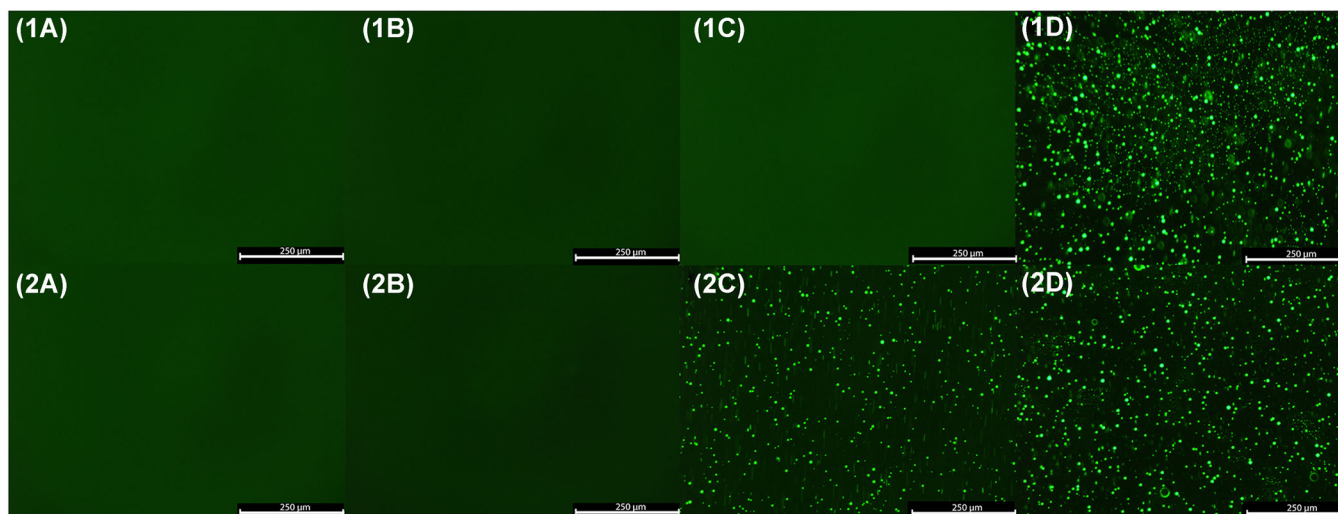
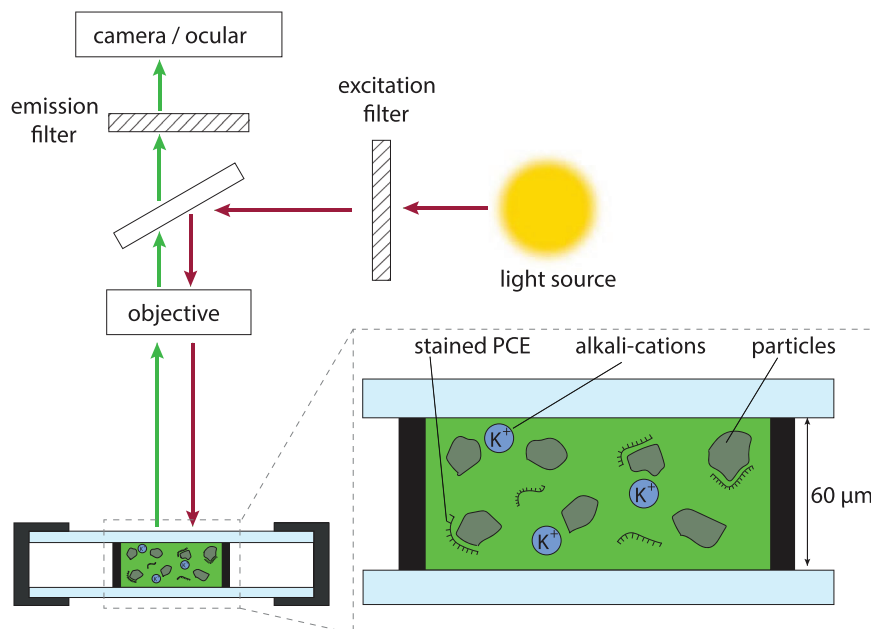


FIGURE 2 Fluorescence images of APEG (1) and MPEG (2) at 10% (A), 15% (B), 20% (C) and 30% (D) of waterglass dissolved in water

For detection of the green fluorescence signal of the stained superplasticizers, a GFP filter with an excitation wavelength of 450–490 nm and an emission wavelength of 500–550 nm were used. The illumination time was kept constant at 500 ms for the reflected-light images and 2 s for the fluorescence images. To process the images the software tool ImageJ was used. The fluorescent background of the images was subtracted.

3 | RESULTS

In the first tests, only the stability of both superplasticizers in alkaline solutions with different concentra-

tions of potassium waterglass was investigated. It becomes clear that already at a concentration of 15% of waterglass, the MPEG superplasticizer forms spherical agglomerates, while APEG still shows a uniform distribution at 20% waterglass solution (Figure 2). Similar observations could also be found for the stability of these superplasticizers in potassium hydroxide solution. Thus, the APEG superplasticizers were still stable in a 2-molar solution, while agglomerates were again formed by MPEG superplasticizers.

Figures 3 and 4 show the reflected-light and the fluorescence images of fly ash dispersed in a waterglass solution combined with APEG and MPEG, respectively. The used PCE show good adsorption on fly ash and

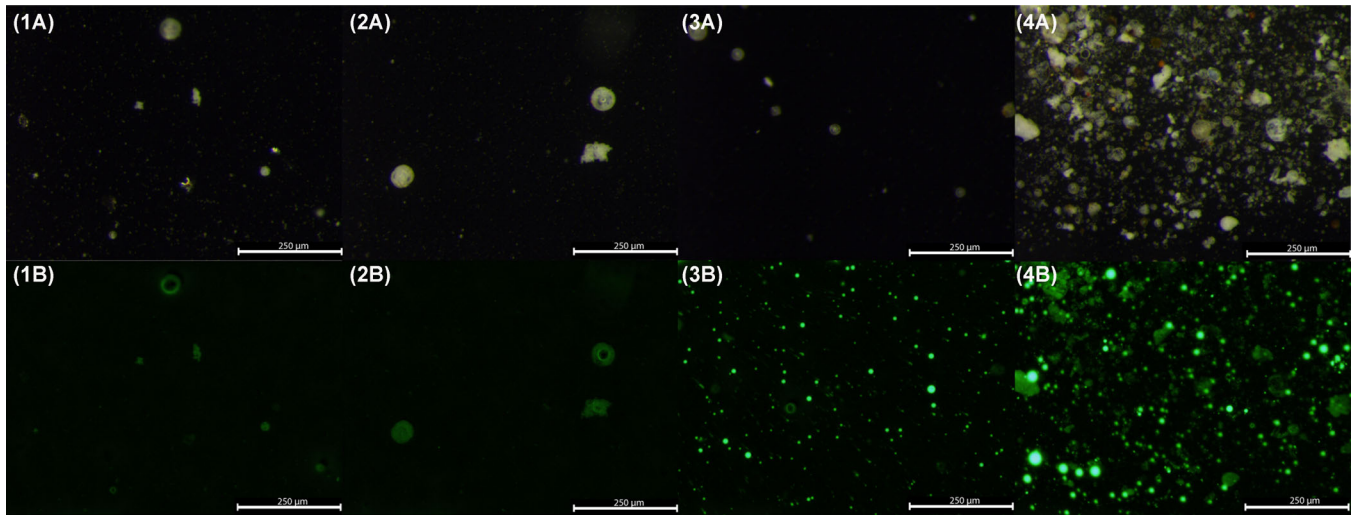


FIGURE 3 Fly ash particles in reflected light (A) and fluorescence signal of stained APEG (B) at 10% (1), 15% (2), 20% (3) and 30% (4) of waterglass dissolved in water

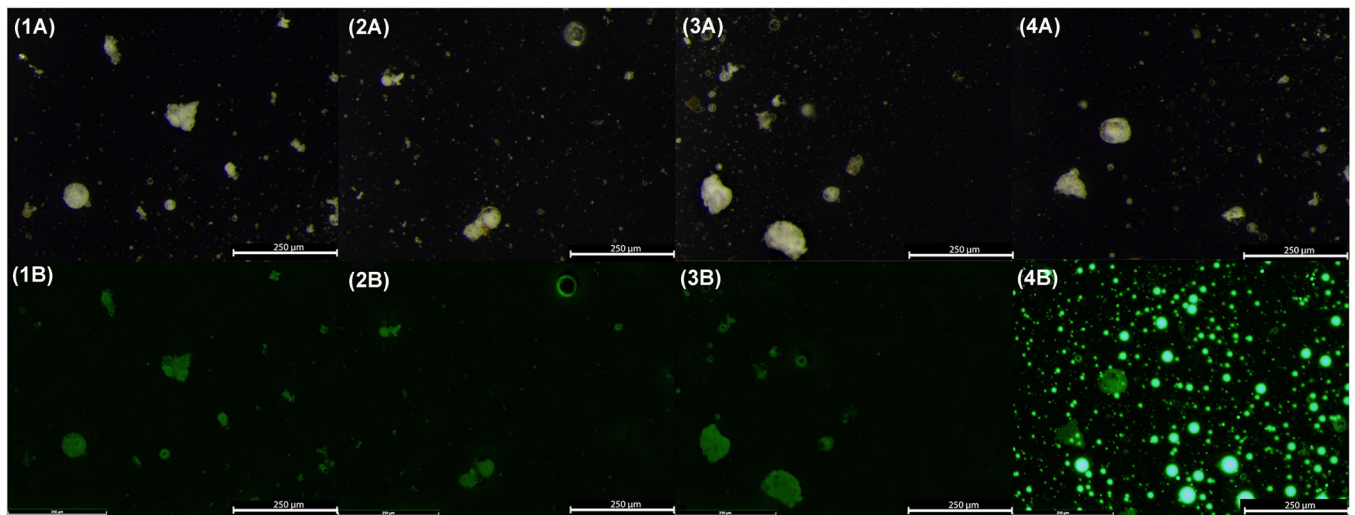


FIGURE 4 Fly ash particles in reflected light (a) and fluorescence signal of stained MPEG (b) at 10% (1), 15% (2), 20% (3) and 30% (4) of waterglass dissolved in water

slag up to 20% potassium waterglass solution and up to a 2-molar-solution of potassium hydroxide – the results of the experiments with potassium hydroxide instead of waterglass, and the results of slags are not shown here. Again agglomerations, even bigger compared to solutions without any particles (Figure 2), could be recognised at higher concentrations of waterglass. APEG (Figure 3) holds a better stability up to 20% compared to MPEG (Figure 4) in both potassium waterglass and potassium hydroxide.

4 | DISCUSSION

The stability of superplasticizers in alkaline solution might be correlated to their performance in real binder systems. The better performance of APEG compared to MPEG in alkali activated binder system was shown elsewhere.^{21,22} Thus, these experiments confirm rheological investigations and bring new insights into the processes in the very first seconds to minutes of a fresh mixture. On higher waterglass concentrations the PCE form agglomerates,

which can be detected as high-fluorescent spheric spots. For experiments with reactive particles, these spots are even bigger. The processes leading to these agglomeration are not understood yet. For higher concentrations of Ca^{2+} cations, the formation of complexes was reported,⁶ while K^+ cations did not show a big impact on complex formation. Due to the high pH value a degradation of the side chains going along with a possible agglomeration might be possible, too.¹² In order to get more information about the formation of these agglomerates, they will be analysed via FTIR after precipitation.


5 | CONCLUSION

An approach using fluorescence microscopy was presented, providing a more detailed insight into adsorption processes and interactions of superplasticizer molecules with mineralic surfaces and with other superplasticizer molecules in different environment. For alkaline environment based on potassium, waterglass and hydroxide experiments were conducted using fly ash and slag as mineralic surfaces. A good adsorption of both and a slightly better stability in alkaline solution were found for APEG-PCE compared to MPEG-PCE. This method might bring more information about the performance optimisation of alkali-activated materials, which is important for the future establishment of AAM as a possible alternative to OPC.

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