

Scientific paper

Effectiveness of Polycarboxylate Superplasticizers in Ultra-High Strength Concrete: The Importance of PCE Compatibility with Silica Fume

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Abstract

Methacrylate ester as well as allylether based polycarboxylates (PCEs) were synthesized to plasticize pastes of cement and silica fume having a water/cement ratio of 0.22. Methacrylate ester copolymers were found to disperse cement well, whereas allylether copolymers are more effective with silica fume. Mechanistic investigations revealed that in cement pore solution, the surface charge of silica fume becomes positive by adsorption of Ca^{2+} onto negatively charged silanolate groups present on the silica surface. This way, polycarboxylate copolymers adsorb to and disperse silica fume grains. Thus, mixtures of both copolymers were tested in cement-silica fume pastes. These blends provide significantly better dispersion than using only one polymer. Apparently, the surfaces of hydrating cement (here mainly ettringite) and silica fume are quite different with respect to their chemical composition. Therefore, PCEs with different molecular architectures are required to provide maximum coordination with calcium atoms present on these surfaces.

1. Introduction

To ensure good workability of concrete at low w/c ratios, plasticizers and superplasticizers are used (Collepari 2006). These chemical admixtures reduce the water demand of concrete at comparable workability. For this reason, and depending on their effectiveness, they are known as water-reducing agents (plasticizers) and high-range water-reducers (superplasticizers). Some of them also introduce air because of their amphiphilic nature. Among the most effective superplasticizers are comb-type copolymers which consist of an anionic backbone and uncharged side chains (Sakai *et al.* 2003; Plank 2004).

Recently, ultra-high strength concretes possessing very low w/c ratios (< 0.25) and a high content of fines were developed. Particles finer than cement are introduced to fill the intergranular space and to achieve a denser packing. Thus, the space no longer needs to be filled by water. This greatly reduces the water demand. The result is a significant increase in compressive strength and a decrease in capillary pore volume. Usually, the ultra-fine particles are silica materials, commonly known as silica fume, microsilica or nanosilica

(approx. 10 to a few 100 nm particle size) (Schmidt *et al.* 2003).

Both low w/c ratio and high packing density demand highly effective superplasticizers to ensure adequate workability (Kodama and Okazawa 1992; Vikan and Justnes 2007; Schröfl *et al.* 2008). However, the search for superplasticizers suitable for these concretes has been mainly conducted by empirical testing (Artelt and Garcia 2008). So far, mechanistic investigations have been focused on the interaction between superplasticizer and cement or some kind of model powder like limestone or MgO (Ohta *et al.* 2000; Banfill *et al.* 2007), while other components have been regarded as inert (Yamada *et al.* 2000; Banjad Pecur and Stirmer 2006). These approaches ignored that in cement pore solution, components other than cement such as silica fume, can develop a positive surface charge and may interact with anionic admixture molecules.

In this work, the interaction between various superplasticizers and cement as well as silica fume was investigated. Understanding the interactions is crucial to determine optimized molecules with improved performance in ultra-high performance concrete possessing a w/c ratio of 0.22. For this purpose, approximately 50 different polycarboxylate molecules were synthesized. Their dispersing power and interaction (adsorption) with cement and silica fume alone and the combination cement/silica were studied. Both cement and silica fume were characterized with respect to their specific surface area (BET) and their surface charge developed in cement pore solution. The goal was to ascertain whether methacrylate ester and allylether based polycarboxylates show different dispersion effectiveness with cement and silica fume, respectively, and whether combinations of different types of polycarboxylate molecules were better suited to disperse the blend of cement and silica fume.

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2. Experimental

Copolymers from methacrylic acid, (ω -methoxypolyethyleneglycol) methacrylate and methallylsulfonic acid, in the following referred to as “MA-based PCEs”, and copolymers containing maleic anhydride and α -allyl-(ω -methoxypolyalkylene oxide) ether (“allylether PCEs”), were synthesized by aqueous radical polymerization following procedures described before (Plank and Sachsenhauser 2006; Plank *et al.* 2008). After copolymerization, the aqueous polymer solutions were neutralized with NaOH, producing a solution of the sodium salts of the PCEs. Their chemical compositions are shown in **Fig. 1**. The MA-based PCEs are statistic copolymers in which the comonomers are arbitrarily incorporated into the polymer backbone (Yamada *et al.* 2000), while the AE-based PCEs are strictly alternating copolymers. Thus, it is obvious that both types of PCEs possess distinctly different molecular architectures.

For MA-based PCEs, the trunk chain length (degree of polymerization) and the molar ratio of comonomers (a/b/c) were varied, while the side chain length was kept constant at 45 ethylene oxide units. For allylether PCEs, the ratio of comonomers was kept constant at 1/1, whereas the degree of polymerization (length of main chain) and the number of ethylene oxide units present in the side chains varied. Additionally, one polymer contained vinyl phosphonic acid as a further comonomer (PCE 22, molar ratio vinyl phosphonic acid/maleic anhydride = 3/1) and one contained mixed ethylene/propylene oxide side chains (PCE 23, molar ratio EO/PO = 4/1). Both modifications had no significant effect on the molecular structure of the PCE molecules.

Polymer characterization was done by size exclusion chromatography (manufacturer: Waters, PCE concentration 30 mg/mL, solvent 0.1 mol/L NaNO₃ solution at pH 12) and subsequent static and dynamic light scattering experiments (Wyatt Technologies) and measurement of the refractive index (Waters). The anionic charge amount of the polymers was measured in a particle charge detector (manufacturer: Müttek, Herrsching, Germany; PCE concentration 0.2 mg/mL, solvent NaOH at pH 12.8 with 0.5 g Ca²⁺/L in the form of

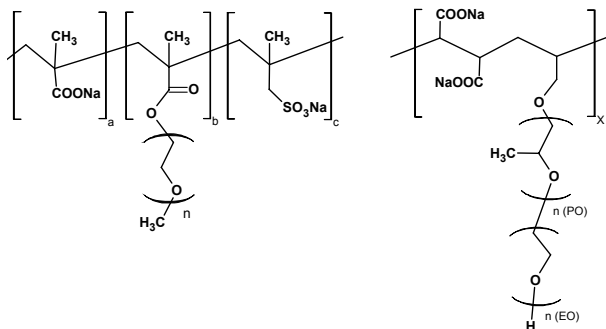


Fig. 1 Chemical composition of methacrylate ester- (left) and allylether-based PCE (right).

CaCl₂·6H₂O to mimic the ionic content of cement pore solution). The anionic PCEs are titrated with a standard solution of 0.001 mol/L cationic poly-DADMAC (poly diallyl dimethyl ammonium chloride) until charge neutralization is achieved. From the consumption of poly-DADMAC solution, the anionic charge amount of the PCE can be calculated.

Approx. 50 PCEs possessing different backbone lengths, side chain lengths, and different types of comonomers and comonomer ratios were synthesized and tested. From this pool, a total of six PCEs was selected to be presented in this study because of their superior performance.

The characteristic properties of the superplasticizers which produced the best results in the mini slump test are shown in **Tables 1** and **2**, respectively. In **Fig. 2**, schematic representations of the comb-type copolymers are given. It is obvious that PCE molecules which are particularly effective in UHPC possess a relatively short trunk chain. According to the concept of GAY and RAPHAEL (2001), the MA-based PCEs 11 to 13 show the molecular architecture of a “flexible backbone worm” molecule whereas all allylether PCEs are “stretched backbone star” molecules. Thus, the molecular architecture of the two PCE types differs.

The dispersing power of the PCEs was tested with a mini-slump test using a VICAT cone. For this purpose, the complete UHPC recipe containing water, superplasticizer, steel fibers, crushed basalt, quartz powder, cement and silica fume (Schmidt *et al.* 2003) was reduced to silica fume, cement, water and superplasticizer only (**Table 3**). The w/c ratio was 0.22. As cement, a high sulfate resistant, low alkali, low heat Portland cement was chosen. Its chemical composition is given in **Table 4** and its phase composition (determined by XRD with RIETVELD refinement) is presented in **Table 5**. In **Ta-**

Table 1 Properties of synthesized methacrylate ester-based PCEs.

	PCE 11	PCE 12	PCE 13
Molar mass M_n [g/mol]	12,000	25,000	49,000
Monomer ratio a/b/c	12/1.0/ 3.00	12/1.0/ 1.40	12/1.2/ 0.48
Trunk chain length [nm]	13	27	48
Side chain [n_{EO}]	45	45	45
Anionic charge density [$\mu\text{eq/g}$]	2,800	2,500	2,400

Table 2 Properties of synthesized allylether-based PCEs.

	PCE 21	PCE 22	PCE 23
Molar mass M_n [g/mol]	8,000	7,000	10,000
Trunk chain length [nm]	2.3	2.2	2.2
Molar ratio n_{EO}/n_{PO}	1/0	1/0	4/1
Side chain [$n_{EO} + n_{PO}$]	34	34	52
Anionic charge density [$\mu\text{eq/g}$]	65	90	60

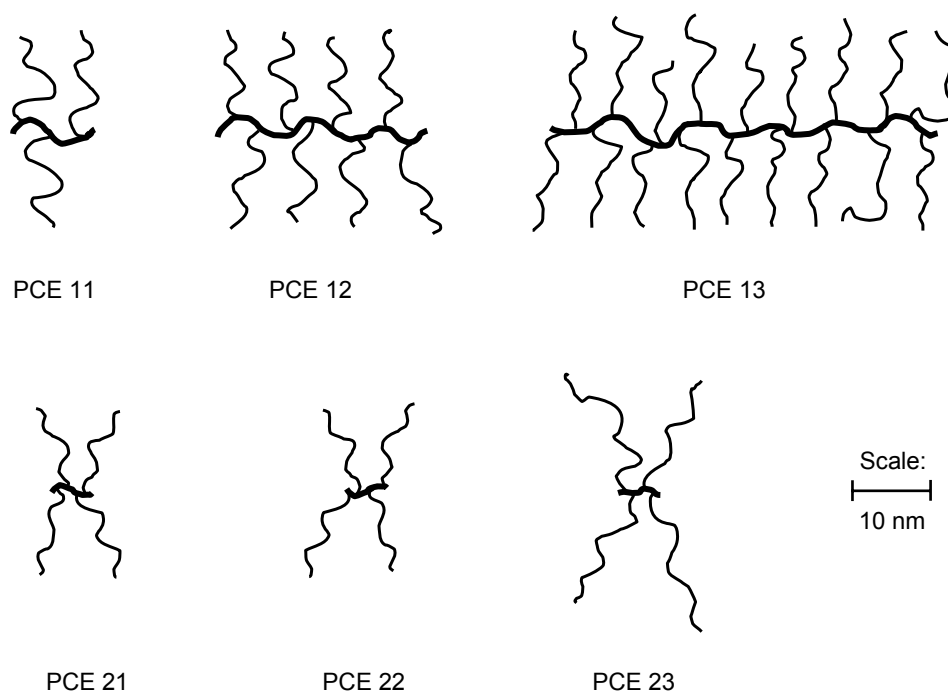


Fig. 2 Schematic representation to scale of the molecular architectures of methacrylate ester PCEs 11 to 13 and allylether-based PCEs 21 to 23.

ble 6, some characteristic properties of the cement and silica fumes are shown. Both silica fumes contain measurable amounts of carbon, presumably with very low particle sizes (< 10 nm).

Figures 3 and **4** show SEM pictures of the two types of silica fumes, SF 1 and SF 2, respectively. As can be seen, the silica particles possess a spherical shape. Particle sizes determined by acoustic attenuation spectroscopy (**Table 5**, d_{50}) are in accordance with visually determined diameters measured from the SEM pictures. Because of their small particle sizes, the silica fumes possess large surface areas. For the UHPC mixture shown in **Table 3**, the surface area of SF 2 measured by nitrogen adsorption is three times larger than that of cement. This way, the surface of silica fume can play a dominant role regarding the interaction with superplasticizers.

Before performing the mini-slump test, the pastes were mixed in a WARING blender, a high-shear mixer commonly used in oil well cementing. This blender was chosen because its shear force best simulates the mixing conditions and friction forces occurring when concrete is prepared in a compulsory mixer (Farrington 2007). Cement and silica fume were preblended in dry form while the superplasticizer was dissolved in the mixing water. Within 30 seconds, the dry blend was poured into the water containing the superplasticizer while the mixer was stirring at 18,000 rpm. After this, mixing was continued for 30 seconds at 22,000 rpm. Next, the paste was filled into a VICAT cone (height 40 mm, upper di-

Table 3 Reduced UHPC formulation.

Component	Content [kg/m^3]
Cement CEM I 52.5 HSR-LH	832
Silica fume (16 % bwoc)	135
Water	184
w/c	0.22
w/silica fume	1.35

Table 4 Chemical composition of OPC used in the study.

Component	Content [wt.-%]
SiO ₂	21.3
CaO	64.5
Al ₂ O ₃	3.4
Fe ₂ O ₃	5.2
MgO	0.7
SO ₃	2.2
Na ₂ O	0.1
K ₂ O	0.3
Loss of ignition	1.3

iameter 70 mm, bottom diameter 80 mm) which had been placed on a glass plate. Lifting the VICAT cone allowed the paste to spread. The dosage of superplasticizer necessary to obtain a paste flow of 26.0 ± 0.5 cm was used to assess the dispersing effectiveness of PCE.

To investigate the interaction occurring between PCE and silica fume in cement pore solution, zeta potential measurements were performed using the electroacoustic

Table 5 Phase composition of the OPC.

Phase	Content [wt.-%]
C ₃ S monoclinic	60
C ₂ S monoclinic	21
C ₃ A	0.7
C ₄ AF	14
CaO free	1.2
CaSO ₄ ·0.5H ₂ O	0.5
CaSO ₄ ·2H ₂ O	1.8
Methods	XRD (C ₃ S, C ₂ S, C ₃ A, C ₄ AF); acid titration according to FRANKE (CaO free); DSC/TG (CaSO ₄ ·0.5H ₂ O, CaSO ₄ ·2H ₂ O)

Table 6 Characteristic properties of cement and silica fume samples.

Property	Cement	SF 1	SF 2
Specific surface area, BET [m ² /g]	1.3	16	24
d ₅₀ [μm]	6.80	0.24	0.08
SiO ₂ [wt.-%]	-	98	97
C [wt.-%]	-	0.41	0.47

apparatus DT 1200 from Dispersion Technology. Silica fume was suspended in water possessing a pH value of 12.2 adjusted with KOH. A solution of calcium nitrate tetrahydrate was gradually added while the zeta potential was recorded. At the same time, the pH was kept constant by simultaneous addition of 6 mol/L KOH. To obtain liquid suspensions, a w/sf ratio of 5 had to be applied. For the mechanistic investigations later on, a model suspension based on a typical UHPC pore solution, but free of sulfate, was used (Table 7).

To study the dispersing power of PCE on silica fume, the following procedure was employed. Superplasticizer and calcium nitrate were dissolved in 0.1 mol/L KOH solution (w/sf 1.35). Silica fume was added within 1 minute, and then the slurry rested for another minute. Next, it was mixed by hand with a spoon for 3 minutes. Afterwards, the mini-slump test was performed as described above. PCE adsorption was determined by the depletion method. After the mini-slump test, the paste was centrifuged (10 minutes, 8500 rpm). The amount of nonadsorbed superplasticizer present in the supernatant fluid was detected by the TOC (total organic carbon) method. From this, adsorbed amounts of PCE were calculated.

3. Results and discussion

3.1 Dispersion of cement/silica fume paste

Previous work has shown that only few superplasticizers can liquefy UHPC effectively (Schröfl *et al.* 2008). In this study, three MA-based and three allylether-based PCEs proved to be effective in cement/silica fume pastes. The dosages required to obtain a spread of 26.0 ± 0.5 cm for the UHPC paste are shown in Figs 5 and 6, respectively.

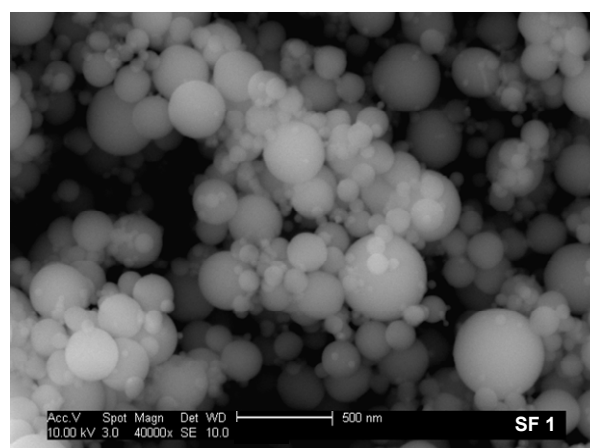


Fig. 3 SEM picture of silica fume SF 1 (magnification: 40,000x)

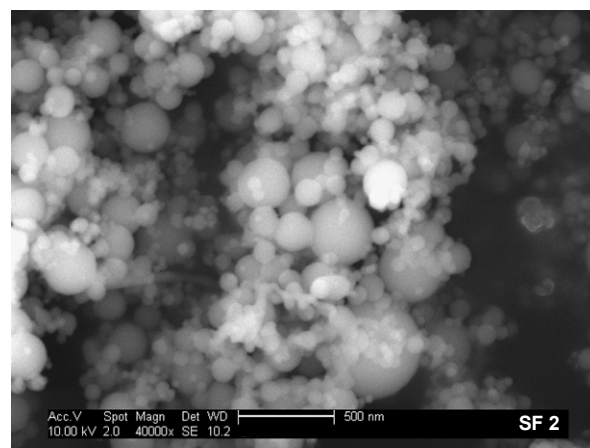


Fig. 4 SEM picture of silica fume SF 2 (magnification: 40,000x).

Table 7 Composition of silica fume slurries used in mini-slump tests and adsorption measurements.

Component	Amount [g]
Silica fume	110.0
KOH (0.1 mol/L)	148.5
Ca(NO ₃) ₂ · 4H ₂ O	9.72
w/ms ratio	1.35
pH	12.2

With cement only, all MA-based PCEs show quite similar performance (Fig. 5). Introducing silica fume SF 1, however, results in significantly higher dosages for all PCEs. The effect is most significant with PCE 13 (dosage 2.45 wt.-% bwoc). Among the PCEs tested, PCE 11 is the most effective one when silica fume SF 1 is used (dosage: 0.6 wt.-% bwoc). None of the MA-based PCEs was able to disperse a paste of cement and silica fume SF 2. This effect is attributed to the higher surface area and carbon content of SF 2 (see Table 6), compared to SF 1. Another potential factor is the less regular shape of the SF 2 particles (see Fig. 4). Recently, it has been demonstrated that such type of particle shape

can significantly increase the dosage of PCE (Kakinuma *et al.* 2008). It can be concluded that MA-based PCEs disperse cement particles quite well while their effectiveness is limited in the presence of silica fume.

In cement paste, allylether-based PCEs (PCE 21 to 23) require slightly higher dosages than MA-based PCEs (Fig. 6). However, they are much more effective when silica fume is present. They even disperse UHPC containing silica fume SF 2 quite well. Thus, allylether-based PCEs effectively disperse different types of silica fumes. PCEs 21 and 22 are particularly effective. Introducing fine silica powder to the cement paste significantly increases the dosage of superplasticizer required for good workability. Obviously, not only is the very low w/c ratio in UHPC a challenge, but also the presence of silica fume. With respect to interaction with superplasticizers, silica fume cannot be regarded as an “inert” component. Consequently, the dispersing performance of PCEs was studied by using pure silica fume suspensions.

3.2 Dispersion of silica fume

The dispersing effectiveness of the PCEs on silica fumes was investigated by mini-slump tests. Silica fume was suspended in a solution of potassium hydroxide and

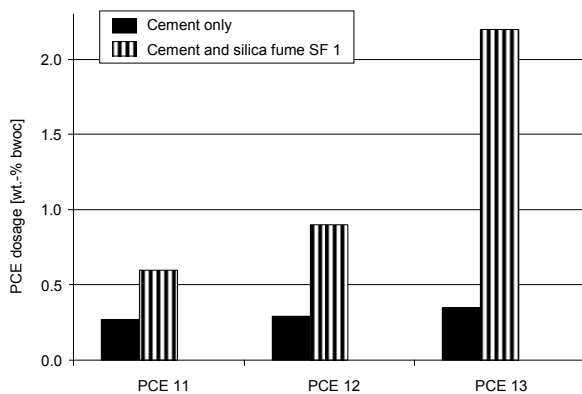


Fig. 5 Dosages of MA-based PCEs required for a paste flow of 26.0 ± 0.5 cm.

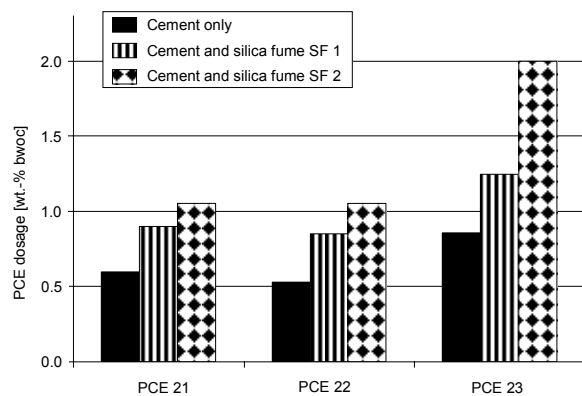


Fig. 6 Dosages of allylether-based PCEs required for a paste flow of 26.0 ± 0.5 cm.

calcium nitrate (pH 12.2, c(Ca²⁺) = 11 g/L), simulating the composition of an UHPC pore solution except for sulfate. The PCE dosages necessary for a paste flow of 26.0 ± 0.5 cm at a w/ms ratio of 1.35 are shown in Figs. 7 and 8, respectively.

The MA-based PCEs 11 to 13 disperse SF 1 slurries well. In line with the results from mixes of cement and SF 1, PCE 11 is most effective. Compared to the allylether-based PCEs 21 to 23, it is slightly less effective when SF 1 is used. However, in presence of SF 2, all the MA-based PCEs 11 to 13 are completely ineffective. Thus, the failure of these polymers in the cement/SF 2 blend is reflected in the results from a pure SF 2 suspension (Fig. 7).

In contrast, the allylether-based PCEs 21 and 22 disperse pastes of both SF 1 and SF 2. These polymers have also been most effective in blends of cement and SF 2 (Fig. 6). PCE 23 which required a significantly higher dosage than PCEs 21 and 22 in the cement/SF 2 blend (Fig. 6) consequently failed completely with SF 2 alone.

It is demonstrated that for the successful dispersion of silica fume, PCEs possessing very specific chemical structures and molecular architectures are required whereas for cement, a broader variety of PCEs can be used. Generally, allylether-based PCEs are better suited to disperse silica fume than MA-based PCEs. This is due to their different molecular structure. Not only their chemistry is different, but also their molecular shape. One can conclude that for effective dispersion of silica fume, polymers need to possess the shape of “star polymers”. As a next step, we tried to discover the causes for the differences in the interaction between PCEs and silica fume.

3.3 Adsorption of PCEs on silica fume

The plasticizing effect of superplasticizers on cement is commonly explained by an adsorptive working mechanism. According to this concept, differences in superplasticizer effectiveness are attributed to different amounts of polymer mass adsorbed per unit mass of solid (mg/g). This concept turned out to be not applica-

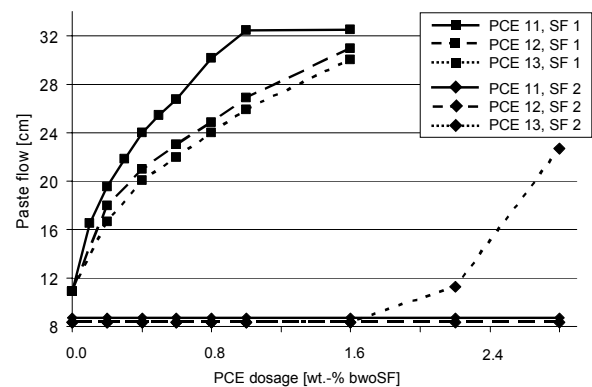


Fig. 7 Dosages of MA-based PCEs required for silica fume paste flow of 26.0 ± 0.5 cm (w/sf ratio 1.35).

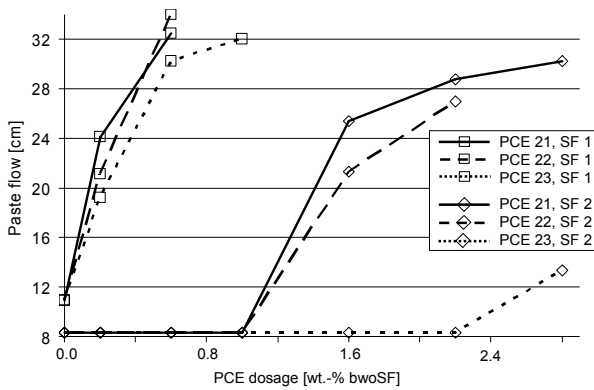


Fig. 8 Dosages of allylether-based PCEs for a silica fume paste flow of 26.0 ± 0.5 cm (w/sf ratio 1.35).

ble for silica fume slurries. **Figures 9 and 10** show that MA-based PCEs generally adsorb to a much higher extent on silica fume SF 2 than allylether-based PCEs. In spite of this, they do not disperse SF 2 effectively.

Additionally, methacrylate-based PCEs 11-13 show similar adsorbed amounts on SF 1 and SF 2, respectively. Therefore, in **Fig. 9** only data with SF 2 is presented. Similarly, allylether-type PCEs produced comparable adsorbed amounts on both SF 1 and SF 2. Thus, only adsorption data on SF 2 is shown in **Fig. 10**.

It is concluded that for silica fume slurries, the adsorbed amount of PCE is not indicative of the dispersion effectiveness of this polymer. Instead, the type of bonding between the PCE and the atoms/ions present on the silica fume surface appears to determine the dispersing effect. This result needs further investigation. Hence, we next investigated the mode of interaction between PCE and the silica fume surface.

3.4 Adsorption of Ca^{2+} and PCE on silica fume surface

It is commonly known that silica surfaces are negatively charged in alkaline solution. The effect is due to deprotonation of silanol groups present on the surface of silica fume (Foissy and Persello 1998). In a saline medium such as the cement pore solution, cations present may adsorb. In UHPC pore solution, a Ca^{2+} equilibrium concentration of 30 to 62 mmol/L is present. Thus, it is possible that the initially negatively charged silica fume surface adsorbs Ca^{2+} ions. To investigate this, increasing dosages of Ca^{2+} (in the form of $\text{Ca}(\text{NO}_3)_2$) were added to an aqueous alkaline suspension (pH 12.2) of the silica fumes and the resulting zeta potential was measured (**Fig. 11**).

The surface charge of silica turns from negative to positive due to surface adsorption of Ca^{2+} . Thus, silica fume can compete with cement for PCE. Adsorption of Ca^{2+} was also confirmed by elemental analysis, showing a decrease of Ca^{2+} in the aqueous phase versus the initial concentration.

The uptake of Ca^{2+} was found to be even higher for SF 2 than for SF 1. The reason is that its initial zeta po-

tential is more negative (-20 mV) than for SF 1 (-17 mV). The saturated adsorption for Ca^{2+} lies at higher Ca^{2+} concentrations than for SF 1. Consequently, it develops an even higher positive surface charge than SF 1. This explains why SF 2 requires higher PCE dosages and is more difficult to disperse than SF 1. Additionally,

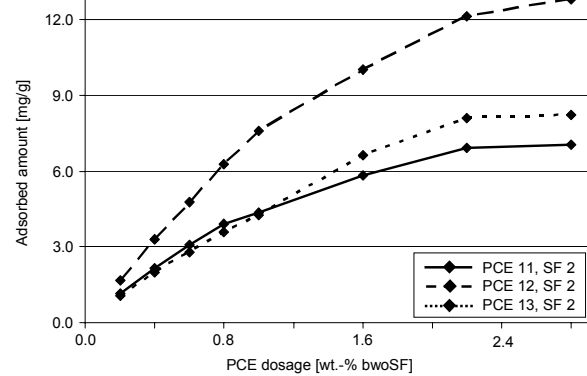


Fig. 9 Adsorbed amount of MA-based PCEs on silica fume SF 2 as a function of dosage (w/sf ratio 1.35).

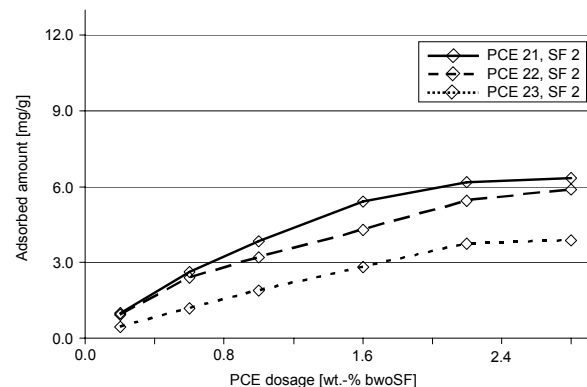


Fig. 10 Adsorbed amount of allylether-based PCEs on silica fume SF 2 as a function of dosage (w/sf ratio 1.35).

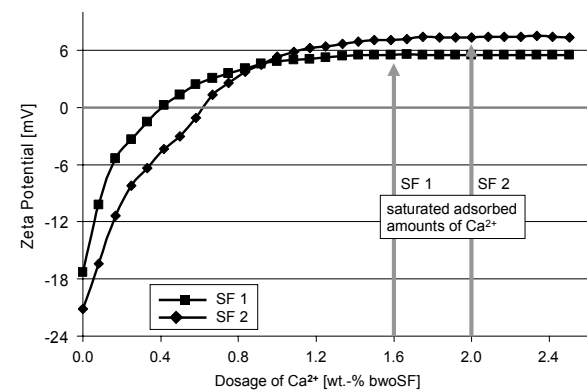


Fig. 11 Zeta potential of silica fume (SF 1 and SF 2) suspensions as a function of Ca^{2+} addition at w/sf ratio 5.0 (pH 12.2).

the specific surface area of SF 2 is larger than that of SF 1. This effect also benefits adsorption of Ca^{2+} . The saturated adsorbed amount of Ca^{2+} , indicated by a flat zeta potential, appears at approx. 1.6 wt.-% Ca^{2+} for SF 1 and at approx. 2.0 wt.-% Ca^{2+} for SF 2 at a w/sf ratio of 5 (Fig. 11).

In cement pastes, Ca^{2+} is continuously dissolved from the clinker phases. Thus, Ca^{2+} adsorbed on the silica surface is immediately replenished. The processes involved in the adsorption of superplasticizers onto the positively charged surface of silica fume are illustrated in Fig.12.

3.5 Dispersing effectiveness of PCE blends

The uptake of superplasticizer by the silica fume surface is an important fact to be considered in UHPC pastes. Both cement and silica fume surfaces have to be covered effectively by superplasticizers to obtain good workability. As shown above (Figs 5-8), cement pastes are dispersed more effectively by MA-based PCEs whereas allylether PCEs are more effective with silica fume. Thus, blends of PCEs from both groups possessing different chemistries were tested for their dispersing power in the cement/silica fume blends used in UHPC. From the group of MA-based PCEs, PCE 11 was selected because of its superior performance with cement. Allylether-based PCE 21 was chosen because it worked best with silica fume. Different blending ratios of PCE 11 and PCE 21 were used. The result is shown in Fig. 13.

Blends of PCE 11 and 21 at different mass ratios (1/3 to 6/1) generally produce better dispersion of the UHPC paste than the individual polymers. The blend consisting of 3 to 6 parts by weight of PCE 11 and 1 part of PCE 21 turned out to perform best. When SF 1 is applied, superplasticizer dosage could be decreased from 0.60 wt.-% bwoc (PCE 11) or 0.90 wt.-% bwoc (PCE 21) to 0.53 wt.-% bwoc when the optimized blend was used. With SF 2, the decrease in PCE dosages is even more

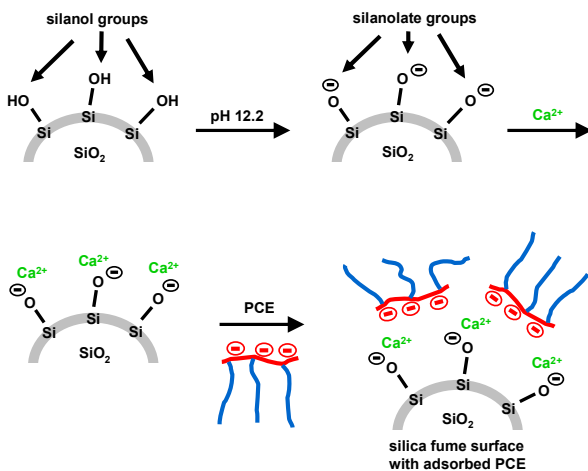


Fig. 12 Illustration of processes involved in the adsorption of PCE on silica surface.

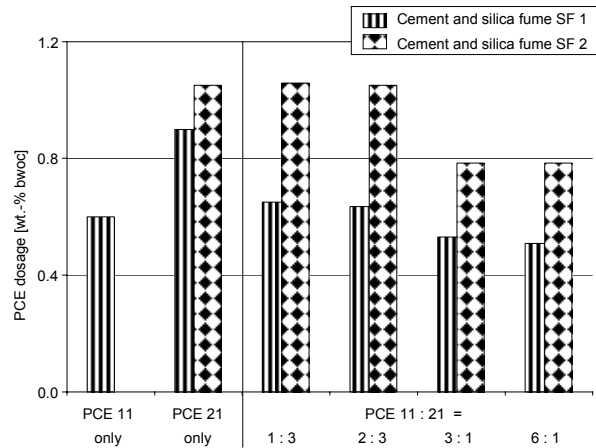


Fig. 13 Dosages of blends from PCE 11 and 21 to reach a paste flow of 26.0 ± 0.5 cm.

significant. PCE 11 was not able to liquefy the paste, and PCE 21 had to be applied with 1.05 wt.-% bwoc (Figs 5 and 6, resp.). The blend of PCE 11/21 = 3-6/1 needs only 0.79 wt.-% bwoc dosage. Thus, surprisingly, the weight ratio between cement and silica fume, and not their respective specific surface areas, determines the optimum mix proportion of these two different PCEs.

4. Conclusion

In cement pore solution, not only cement hydrates, but also silica fume possess a positive surface charge. Thus, silica fume competes with cement for the adsorption of PCE molecules onto its surfaces. While the amount of silica fume present in our UHPC formulation is only 16 wt.-% based on cement, its surface area exceeds the surface area of cement. Based on the BET data shown in Table 5, the specific surface area of SF 1 is twice as much as that of cement. The surface area of SF 2 is even three times greater than that of cement. Hence, a PCE molecule dissolved in this UHPC mix predominantly recognizes silica fume surface for adsorption while cement presents a minor constituent. In other words, effective dispersion of silica fume, and not cement, is necessary to achieve a highly flowable UHPC paste.

Methacrylate-based PCEs primarily disperse cement, whereas allylether-based PCEs are more effective with silica fume present in a UHPC. For this reason, a blend consisting of a methacrylate-based PCE and an allylether-based PCE is best performing in UHPC. Thus, when different mineral surfaces are present in a concrete mix, combinations of superplasticizers possessing different molecular architectures should be considered. Optimized interaction with different types of surfaces is achieved with PCE molecules possessing a specific stereochemistry which provides maximum coordination with the atoms or ions present on the mineral surface. This concept may generally apply to blended cements containing fly ash, blast furnace slag, limestone powder

or other secondary cementitious materials. The absolute value of their positive surface charge and their specific surface area will determine their impact on flowability of the concrete and how much they compete with cement for superplasticizer adsorption.

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